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Simulation of biomass gasification

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Dissertação apresentada à

Escola Superior de Tecnologia e Gestão

Instituto Politécnico de Bragança

no âmbito do mestrado em

Engenharia Química

October, 2016

Abstract

Biomass is used since ancient times as combustion fuel for cooking, keeping houses warm, etc. Biomass is cheap and available abundantly and it can be converted into energy and/or products using the suitable processes. So, biomass is considered a potential energy source which can be converted by gasification processes into a gas mixture known as synthetic gas (syngas). A gasification process is a thermo-chemical process which converts carbon material into syngas gas streams, mainly constituted by mixtures of hydrogen and carbon monoxide. Typically, hydrogen gas is chemically produced from natural gas reforming; the use of renewable energy sources such as biomass to produce hydrogen offers a promising alternative.

This study is focused on the modelling, simulation and performance analysis of biomass gasification processes using UniSim software. UniSim Design is a process simulator especially suited for the design and simulation of chemical processes. The performance of the gasification processes was studied varying the reaction temperature, and the gasifying agents' flows (air and steam) in order to obtain realistic hydrogen/carbon monoxide productions in the syngas stream. Almond shell was chosen as the biomass source.

Two models were constructed and tested using different conditions of temperature, biomass mass flow, air mass flow, and steam mass flow. For the first model, the best result was obtained when steam was used as gasifying agent producing syngas streams with mole compositions of 0.34 and 0.5 H_2 and CO, respectively. Using the second model, there were observed small deviations in hydrogen and carbon monoxide compositions in the synthesis gas stream. However, the best result was obtained using steam as gasifying agent producing syngas streams with mole compositions of 0.45 and 0.5 for H_2 and CO, respectively.

Resumo

Há milénios que a biomassa é usada como combustível para cozinhar, aquecimento, etc. A biomassa é barata e abundantemente disponível, podendo ser convertida em energia e/ou produtos através de processos de conversão adequados. Assim, a biomassa é considerada uma fonte de energia potencial que pode ser convertida por processos de gaseificação numa mistura gasosa conhecida como gás de síntese (syngas). Um processo de gaseificação é um processo termoquímico que converte material condensado de carbono em gás de síntese, constituído principalmente por misturas de hidrogénio e monóxido de carbono. Normalmente, o hidrogénio é produzido a partir de reforming de gás natural; a utilização de fontes de energia renováveis como a biomassa, para a produção de hidrogénio oferece uma alternativa promissora.

Este estudo centra-se na modelação, simulação e análise de desempenho de processos de gaseificação de biomassa utilizando o software UniSim. O UniSim Design é um simulador especialmente vocacionado para a conceção e simulação de processos químicos. O desempenho dos processos de gaseificação foi estudado, variando a temperatura de reação e os fluxos dos agentes gasificadores (ar e vapor), a fim de obter produções viáveis e significativas de hidrogénio e monóxido de carbono na corrente de gás de síntese. A casca de amêndoa foi escolhida como fonte de biomassa.

Dois modelos foram construídos e testados, utilizando diferentes condições de temperatura, caudal mássico de biomassa, de ar e de vapor. Para o primeiro modelo, o melhor resultado foi obtido quando o vapor foi usado como agente de gaseificação produzindo fluxos de gás de síntese com composições molares de 0.34 e 0.5 para o H_2 e CO, respetivamente. Usando o segundo modelo, foram observados pequenas variações das composições de hidrogénio e monóxido de carbono na corrente de gás de síntese. No entanto, o melhor resultado foi obtido utilizando o vapor como agente de gaseificação, produzindo fluxos de gás de síntese com composições molares de 0.45 e 0.5 para H_2 e CO, respetivamente.

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Chapter 1 - Introduction

1.1 - Motivation

Due to the increasing awareness of the limited nature of oil and gas energetic resources, which inevitably introduce serious economic and social issues for the actual and specially for the next generations, the developed societies are driving their effort on the recovery of energy from renewable chemical sources. The recovery of energy from biomass using gasification technologies is particularly envisaged, since it meets one of the major needs of environmental sustainability, by producing near zero emissions.

Biomass gasification is not a new technology. In fact, thermochemical processing of carbon materials (from fresh or fossil biological sources) for energy recovery represents a large variety of technologies already developed and commercially explored since the beginning of the XXth century (and specifically until the post second world war period), when the cheap fossil energy sources became definitely the main resources for energetic applications at a world scale.

Biomass gasification is a possibility to explore important renewable chemical resources from which it can be extracted energy, power or moment. For this purpose, the main focus of this work is the simulation of the gasification processing of specific sources of biomass, using the UniSim Design simulator, and exploring the different available numerical tools to replicate a specific type of gasifier (namely a fixed bed gasifier or other types), and the several physical and chemical steps that constitute a typical gasifying process. Using thermodynamic and kinetic data, available in the simulator database and found in the literature, it is intended the design of the optimal configurations of gasifying processes (including raw-material treatment, gasification steps, and synthesis gas conditioning), for energetic recovery from selected biomass sources.

The simulator UniSim Design is similar to the well-known packages Aspen Plus and Hysys. Unisim Design is used to simulate a wide range of chemical processes including those involving solid processing. The solid processing applications in UniSim Design include processes such as: Bayer process, cement kiln, coal/biomass gasification, hazardous waste incineration, iron ore reduction and zinc smelting roasting.

Therefore, the main motivation of this work is the assessment for the possibility of valorization and energetic recycling of agricultural wastes, abundant in Trás-os-Montes region (for example, almond shells), by the modelling and simulation of gasification processes which use biomass sources with the typical elemental content of those biological wastes.

1.2 - Biomass

Biomass can be converted to solid, liquid and gaseous fuels by different methods which are broadly classified as thermal, chemical and biochemical methods (Twidell, 1998). The definition of biomass refers to essentially all organic matter that originates from plants including all land and water-based vegetation such as algae, trees and crop residues. Goyal et al. also define biomass as any living matter on earth. More precisely, biomass can be defined as material derived from growing plants or from animal manure which mainly consists of carbon, hydrogen, oxygen, nitrogen and smaller portions of inorganic species (Goyal et al., 2008). In the scope of biomass for energy generation, it can be either used directly via plants or indirectly from plant-derived industrial, commercial or urban wastes, or agricultural and forestry residues (Jahirul et al., 2012).

1.2.1 - Types of Biomass

Biomass may be divided into two broad groups: (a) virgin biomass and (b) waste. Primary or virgin biomass is extracted from plants and/or animals. Waste biomass is extracted from different biomass-derived products. Table 1 gives a list of biomass types, grouping them as virgin or waste. In Table 1 are shown the major groups of biomass and their sub classification (Bhavanam and Sastry, 2011).

Virgin biomass grown especially for the purpose of producing energy is also known as energy crops. This type encompasses short-rotation or energy plantations, including herbaceous energy crops, woody energy crops, industrial crops, agricultural crops and aquatic crops. Typical examples are eucalyptus, willows, poplars, sorghum, sugar cane, soy beans, sunflowers, cotton, among others. These crops are intended to be used in combustion, pyrolysis and gasification for the production of biofuels, synthesis gas and hydrogen, in addition to biological and chemical conversion methods for the production of bioethanol and biodiesel. Large quantities of agricultural plant residues are produced annually worldwide and are vastly underutilized. The most common agricultural residue is the rice husk, which makes up to 25% of rice by mass (Bhavanam and Sastry, 2011).

TABLE 1 - BIOMASS CLASSIFICATION

Virgin biomass	Terrestrial biomass	Forest biomass, grasses, energy crops, cultivated crops
	Aquatic biomass	Algae, water plant
Waste	Municipal waste	Municipal solid waste, bio solids, sewage, landfill gas
	Agricultural solid waste	Livestock and manures, agricultural crop residue
	Forestry residues	Bark, leaves, floor residues
	Industrial wastes	Black liquor, demolition wood, waste oil or fat

1.2.2 - Components of Biomass

Biomass consists of three major types of biomass materials from which bioenergy feedstock derived: lipids, sugar/starches and cellulose/lignocellulose, where the lipids are energy-rich water-insoluble molecules such as fats, oils and waxes. Lipids are found in nonwoody plants and algae, such as in oil palm soybean and various seed crops as sunflower, which are common agriculture sources of oils for biodiesel. The second type is sugar and starches, carbohydrates found in edible portions of food crops such as crops grains (e.g. Zea mays). The last types of biomass, cellulosic/lignocellulosic, consist of complex carbohydrates and no carbohydrates that are actually found in stems and leaves of plants. The cellulosic/lignocellulosic biomass is chemically accessible by only a rarely range of organisms because it has little or no food value to humans. In this sense, the advanced biofuel production technologies, such as gasification, introduced an opportunity to use these relatively low value materials for the production of high value energy products (Jose and Bhaskar, 2015).

The cellulosic/lignocellulosic feedstock is further derived in two categories: woody and nonwoody. Cellulose is defined as a fibrous glucose polymer found in the plant cell walls where the cellulose assists the physical strength of the plant cell. Cellulose can break into simple sugars by biological conversion and can be converted into ethanol and other fuels.

Lignocellulose represent is composed by hemicellulose, cellulose and lignin. Hemicelluloses are heteropolymers (i.e. very large, complex carbohydrate molecules) that helps to cross-link cellulose fibers in plant cell walls. Lignin is defined as a no carbohydrate polymer that fills spaces between cellulose and hemicellulose. Hemicellulose can break down into fermentable sugars, which convert into ethanol and other fuels, while it's difficult to convert lignin into other usable forms. Accordingly, lignin is classified as a by-product (i.e. waste) and sometimes it's burned for recovery of heat.

For biological conversion, the pretreatment of lignocellulosic biomass is required to break down the cellulose and hemicellulose into sugars and separate the lignin and other plant constituent from fermentable materials (Jose and Bhaskar, 2015).

1.2.3 - Composition of Biomass

All types of biomass have carbon, hydrogen and oxygen as basic chemical constitutive elements. These element fractions can be measured by ultimate analysis, reported using the CxHyOz formula, where x, y and z represents the elemental proportions of C, H and O respectively. To debate the biomass characteristics, it's usually necessary to provide the proximate analysis, defined as the composition of biomass in terms of gross components, such as moisture (M), volatile matter (VM), ash (ASH) and fixed carbon (FC). It is a relative simple and inexpensive process when compared with ultimate analysis (Bhavanam and Sastry 2011). The proximate analysis of various biomass feed is given in Table 2 and the ultimate analysis of a diverse variety of biomass compositions are reported in Table 3, where the WT% is (wet basis) (Bhavanam and Sastry 2011).

TABLE 2 - ANALYSIS OF BIOMASS TYPES

Biomass	VM (WT %)	ASH (WT %)	FC (WT %)
Bagasse	84.2	2.6	15.8
Coconut shell	80.2	0.7	19.8
Corn stalks	80.1	6.8	19.9
Groundnut shell	83.0	5.9	17.0
Rice husk	81.6	23.5	18.4
Subabul	85.6	0.9	14.4
Wheat straw	83.6	11.2	16.1

TABLE 3 - DIFFERENT TYPES OF BIOMASS COMPOSITIONS

	Rice straw/husk	Sawdust	Sewage sludge	MSW (Municipal Solid Waste)	Animal Waste
C (%)	39.2/38.5	47.2	29.2	47.6	42.7
H (%)	5.1/5.7	6.5	3.8	6.0	5.5
N (%)	0.6/0.5	0	4.1	1.2	2.4
O (%)	35.8/39.8	45.4	19.9	32.9	31.3
S (%)	0.1/0	0	0.7	0.3	0.3
Ash%	19.2/15.5	1.0	42.1	12.0	17.8

1.2.4 - Biomass Conversion Processes

Conversion of biomass into energy is undertaken using three main process technologies: Thermochemical, biochemical/biological and mechanical extraction (with esterification/ transesterification) for biodiesel production, within thermochemical conversion four process options are available: combustion, pyrolysis, gasification and liquefaction. Bio-chemical conversion encompasses two process options: digestion (production of biogas, a mixture of mainly methane and carbon dioxide) and fermentation (production of ethanol). The flowchart is explaining, the intermediate energy carriers and the final energy products to each type of thermo-chemical conversion.

1.3 - Gasification of Biomass

Gasification is the biomass conversion process that has been mostly studied as an alternative solution to environmental issues associated with energy production (Abuadala et al., 2012). Gasification is one of the technologies mostly used due to its economy and efficiency. The properties of the biomass feedstock and its preparation are key design parameters when selecting the gasifier system. In the third world countries, the use of a simple and robust technology represented by gasification can improve the development of rural economies by providing electricity extracted from gasification from local sources of biomass. (McKendry, 2002c).

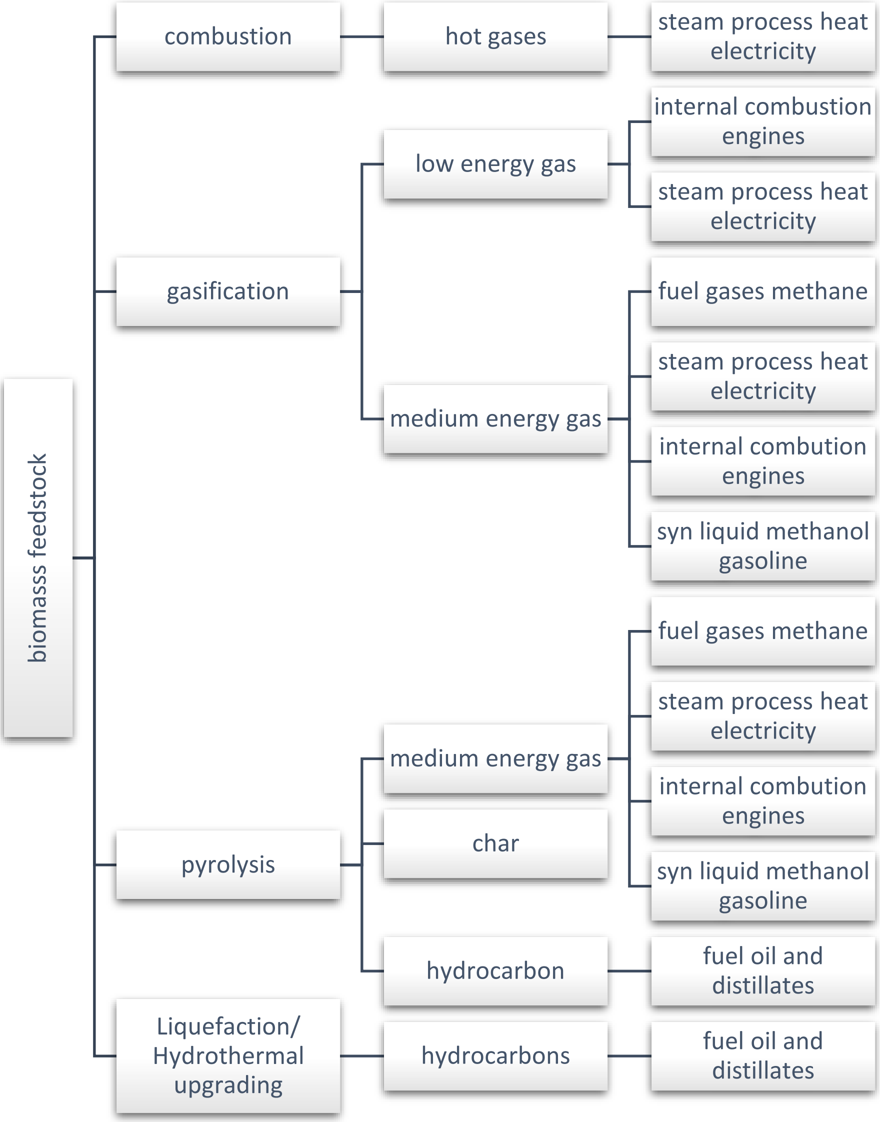


FIGURE 1. MAIN PROCESSES, INTERMEDIATE ENERGY CARRIERS AND FINAL ENERGY PRODUCTS FROM THE THERMO-CHEMICAL CONVERSION OF BIOMASS (MCKENDRY, 2002B).

Gasification is a thermochemical process that converts a carbonaceous feedstock, such as biomass or coal, through partial oxidation at elevated temperature, into a gaseous energy carrier (Bridgwater, 1995), a gaseous mixture of syngas consisting of hydrogen (H_2), carbon monoxide (CO), methane (CH_4) and carbon dioxide (CO_2) (Wang et al 2008). The final gas composition of the gasification process is the result of the combination of a series of complex and competing reactions, given in Table 4, occurring to a varying degree (Franco et al., 2003).

TABLE 4 - GASIFICATION REACTIONS (LIU ET AL, 2009)

Incomplete Oxidation	$\mathbf{C + 0.5O_2 \rightarrow CO}$	Equation (1)
Boudouard	$C + CO_2 \rightarrow 2CO$	Equation (2)
Heterogeneous shift	$C + H_2O \rightarrow CO + H_2$	Equation (3)
Hydrogasification	$C + 2H_2 \rightarrow CH_4$	Equation (4)
Partial combustion of carbon monoxide	$CO + 0.5O_2 \rightarrow CO_2$	Equation (5)
Partial combustion of H_2	$H_2 + 0.5O_2 \rightarrow H_2O$	Equation (6)
Water-gas shift	$CO + H_2O \rightarrow CO_2 + H_2$	Equation (7)
Steam-methane reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	Equation (8)

1.3.1 - Historical Development

1.3.1.1- Early Development of Gasification

The gasification method was discovered in 1798 in France and England. In 1850 this technology was developed to light much of London with manufactured gas (or town gas) from coal. Later, manufactured gas technology reached the United States and, in 1920, most American towns and cities supplied gas to the residents for cooking and lighting through the local "gasworks". In Texas, in 1930, the first natural gas pipeline was created to transport the natural gas to Denver from the oil field of Texas. When the pipelines crisscrossed in the country, the cheap cost of natural gas supplanted that of manufactured gas and the once widespread industry soon was forgotten. "Town gas" continued to be used in England until the 1970s, but the plants were dismantled following the discovery of North Sea oil.

1.3.1.2- Vehicle gasifiers

In the First World War, a small gasifier was developed around charcoal and biomass feedstock to operate vehicles, boats, trains and small electric generators. In the period between the first and second wars, the pursuit to develop gasification was mostly due to amateur enthusiasts since gasoline was cheap and of easier use than biomass. In 1939, the German blockade halted all oil transport to Europe. Military use of gasoline received top priority and the civilian populations had to fend for themselves for transport fuels. During the period of war there was about one million gasifiers used to operate vehicles. The alternative fuels had the greatest deal of interest by 1943, with almost 90% of the vehicles powered by gasifiers. After the end of war there were more than 700000 wood-gas generators.

1.3.2 - Design of gasifier

Depending on the mode of biomass–air (or oxygen) contact, biomass gasifiers are classified into two main types, fixed-bed and fluidized bed. In turn, fixed-bed is sub-classified as updraft, downdraft and cross-draft gasifiers, depending on the relative directions of biomass and air flows. Fluidized bed is sub-classified as bubbling bed and circulating fluidized bed gasifiers, depending on the mode of fluidization. In addition, for the two types, entrained bed gasifiers (used for coal gasification) were also developed for biomass, but they proved unsuitable since fibrous biomass, such as wood, could not be easily ground to the particle size range (100–400 μm) required for these gasifiers (McKendry, 2002c), making the process largely unsuitable for most biomass materials (Huber et al., 2006). Pre-treatment of biomass and their properties also influence the performance of gasifiers. In addition, proper cleaning and conditioning of gas is of utmost importance for proper functioning of the generator sets, in terms of both stability and efficiency (McKendry, 2002c).

In the last two decades the fixed bed lost a part of their industrial market appeal for large scale production (higher than 10 MW) (Dhepe and Fukuoka, 2008). But on the small scale (lower than 10 MW) the fixed-bed gasifier has kept on commercial interest especially for locally based power generation, due to the high thermal efficiency and minimal pretreatment needs of the provided biomass (Klimantos et al., 2009).

1.3.2.1- Fixed-bed gasifiers

Fixed-bed gasifiers are significantly studied due to their simplicity in design and operation. Depending on airflow direction, the gasifiers are classified in the modes previously mentioned. Updraft and downdraft gasifiers are represented in Figures 2 and 3. The cross-flow gasifier is represented in Figure 4. In updraft and downdraft gasifiers, the gas composition (by volume) leaving the gasifier is usually in the following ranges: CO (20-30%), H_2 (5-15%), CH_4 (1-3%) and CO_2 (5-15%) (Gordillo et al., 2009). The distribution of the reaction regions in a fixed-bed reactor are different depending on the type of gasifier design.

1.3.2.1.1- Updraft gasifier

In the updraft mode, biomass is fed from the top and air is supplied at the bottom via the grate of the gasifier. When the biomass is in the top section of the gasifier it is dried and moving downward to reach the devolatilization zone (pyrolysis zone, as marked in Figure 2). In the devolatilization zone biomass is decomposed into volatiles and considerable quantities of tars are formed. Following this, in the reduction zone, the volatiles evolve and produce the permanent gas. After that, the residuals of biomass reach to the grate where the solid char is formed and the remaining of biomass is combusted at approximately 1000 ºC.

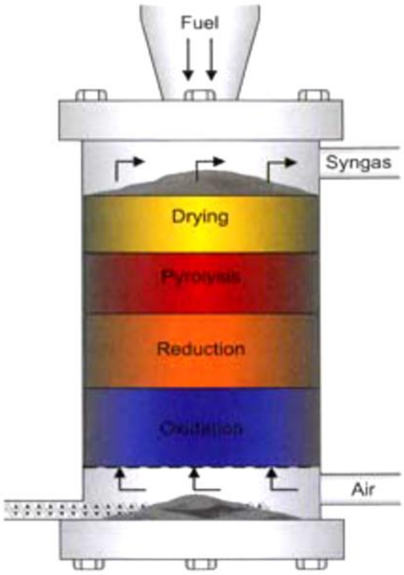


FIGURE 2. UPDRAFT (PUIG-ARNAVAT, 2011)

The hot gases formed in the combustion zone (oxidation zone) start moving in the upward direction into the reduction step. Tar condenses partially on the descending biomass, also leaving the gasifier with the product gas. Thus, in the updraft gasifier, biomass may have a favorable filtering effect producing a gas with low tar content. The temperature in the gasification zone can also be controlled by co-feeding steam and air or by humidifying the air. Because of the low temperature of the gas leaving the gasifier the formed gases are cooled down to 200-300 ºC. The overall energy efficiency is high in the updraft gasifier (Nagel et al., 2009).

1.3.2.1.2- Downdraft gasifier

The design of the downdraft gasifier is basically the same as the updraft, the major difference being that in the downdraft design, biomass and air move concurrently downward from the top to the bottom (as illustrated in Figure 3). The downdraft gasifier has four distinct zones: (1) upper - drying zone, (2) upper medium - pyrolysis zone, (3) lower medium - oxidation zone and (4) lower - reduction zone. The synthesis gas gets out from the upper medium section, after passing the lower medium zone, where partial cracking of the formed tars occurs, thus resulting in a synthesis gas with low amount of tar. In the oxidation zone, the temperature is about 1000-1400 °C and the tars produced are almost exclusively tertiary tars. Particulates and tars in the synthesis gas have low concentration (about 1 g/Nm^3), as the majority of the tar are combusted in the gasifier. The downdraft gasifier is thus ideal when clean gas is desired (Sheth et al., 2009). Negative aspects in this design are the low thermal relatively efficiency and the difficulty to process the moisture and ash contents of the biomass.

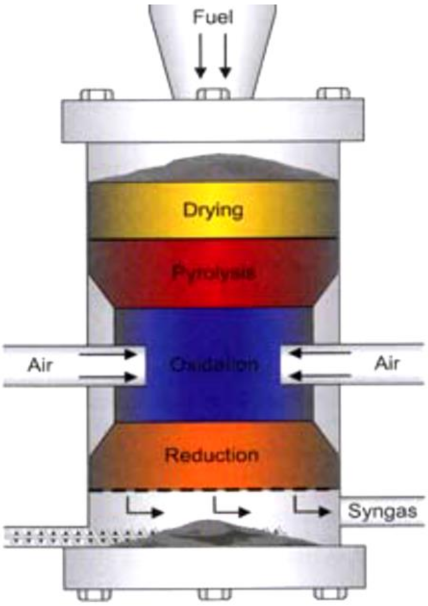


FIGURE 3. DOWNDRAFT GASIFIER (PUIG-ARNAVAT, 2011)

1.3.2.1.3- Cross-flow gasifier

The cross-flow gasifier is designed with the biomass introduced in the top and the air fed in a lateral side. The synthesis gas exits in the opposite lateral side, more or less at the same level. Biomass moves downwards and it gets dried, devolatilized, pyrolyzed and finally gasified. Figure 4 shows a schematic of a cross-flow gasifier. A hot combustion/gasification zone is formed around the air entrance, with both pyrolysis and drying zones being formed higher up in the vessel. Due to the design of this gasifier, the residence time of the gases in the high temperature zone is small (as the gas enters and leaves from the opposite sides). As a consequence, the temperature of gasification (around 800-900 ºC) is almost the same of the leaving synthesis gas, resulting in less tar cracking, higher contents of tar and lower thermal efficiency than the other designs presented (Buragohain et al., 2010).

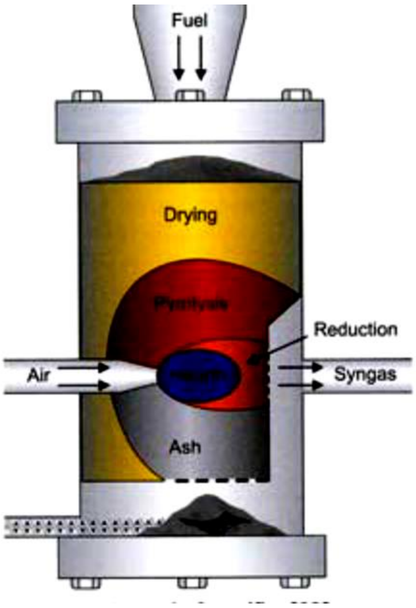


FIGURE 4. CROSS-FLOW GASIFIER (PUIG-ARNAVAT, 2011)

1.3.2.2- Fluidized bed gasification

Among all the gasifiers used for biomass combustion, fluidized bed gasifiers began to appear as the best given their flexibility and high efficiency. Fluidized bed gasification has been widely used for coal gasification over the years. Its advantage over fixed bed gasifiers is the uniform temperature distribution that took place in the reduction zone. This temperature consistency is done by using a bed of fine granular material (e.g. sand) into which air is circulated, fluidizing the bed. Intense bed fluidization promoting solid circulation favors the mixing of the hot bed material, hot combustion gases and biomass feed. Fluidized beds are used for a broad variety of fuels. This flexibility is actually another important advantage of fluidized beds (Bartels et al., 2008). Loss of adequate fluidization or defluidization due to bed agglomeration is a major problem in fluidized bed gasifiers. The most common problem found in fluidized beds as a preamble to defluidization in commercial-scale installations is the “coating-induced” agglomeration of the fine granular material forming the bed. During reactor operation, a coating is formed on the bed sand particle surface. At certain critical coating thicknesses and/or temperature levels, the sintering of the bed particles is promoted by biomass sodium content. Sodium lowers the melting point of the silicates and aluminosilicates of the bed particles. Agglomeration associated with fluidized bed gasifiers is still a major issue when used to gasify certain herbaceous biofuels. However, there are successful solutions that have been reported for other biomass feedstock’s (Khan et al., 2009). These solutions are mainly based on lowering and controlling the bed temperature. Two main types of fluidized bed gasifiers are in current use: a) bubbling bed and b) circulating fluidized bed. The third type of fluidized bed gasifier, an internally circulating bed, which combines the design features of the other two types, is currently being investigated at the pilot plant scale.

1.3.2.2.1- Bubbling bed

This gasifier design looks like a vessel with a grate in the bottom and the air introduced through it, as shown in Figure 5. Above the grate, biomass is fed during the moving bed of fine-grained material. Typically, the temperature in this type of gasifier is around 700-900 ºC, maintained by controlling the air/biomass ratio. After gasification, biomass is pyrolzed to form char, gaseous compounds and tar. In this hot bed, the high molecular weight tar is cracked by contact with the hot bed material, giving a synthesis gas with lower tar content (< 1–3 g/Nm^3). For steam gasification without a catalyst, the tar produced in the gasifier is about 12 WT % (wet basis) of the cellulose feed (Tasaka et al., 2007).

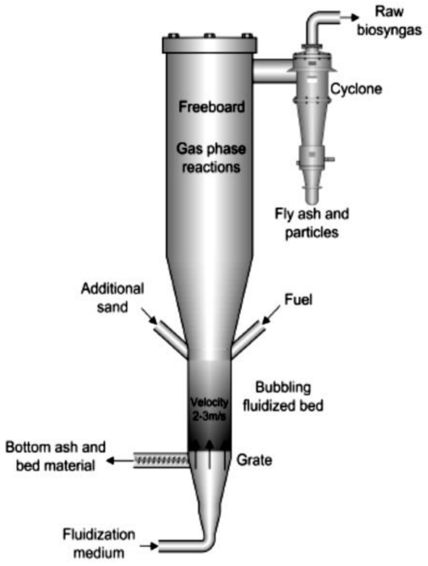


Figure 5. Bubbling fluidized bed (Puig-Arnavat, 2011)

1.3.2.2.2- Circulating fluidized beds

This type is a development of the bubbling bed fluidization type. It has higher velocity of fluidizing air than the final setting velocity of the bed material. So the entire material (biomass + inert material, e.g. sand) exit with the fluidizing air and the exhaust gases of the gasifier is a relatively lean mixture of solids and gas. This exhaust stream is fed into a cyclone separator to isolate solids from the gas that are returned to the bed by downward pipe, as shown in Figure 6. Either one stage or multi-stage cyclone is used, working according to the solids concentration and size distribution. Circulation of the biomass particles is carried-out until the particles are reduced in size due to combustion/gasification. An advantage that circulating fluidized bed design offers is that gasifier can be operated at elevated pressures.

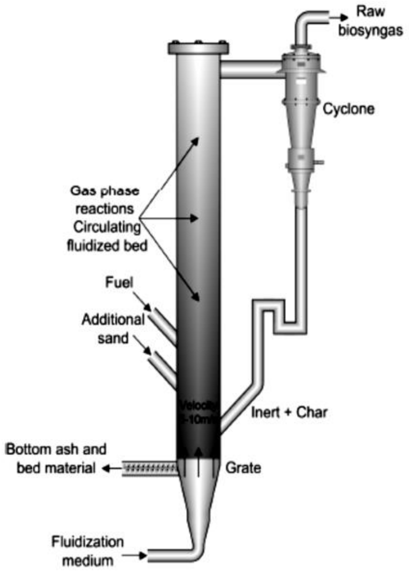


Figure 6. Circulating fluidized bed (Puig-Arnavat, 2011)

There is another type of technology called dual fluidized bed (DFB) which has been developed in Austria using steam as the gasification agent and providing the heat for the gasification reactor by circulating bed material (Pfeiffer et al., 2009). As shown in Figure 7, biomass enters a DFB gasifier where the steps of drying, devolatilization, and heterogeneous char partially gasification take place at temperatures of 850-900 °C. Residual biomass char leaves the gasifier together with the bed material through an inclined, steam fluidized chute towards the combustion reactor.

The combustion zone (riser) serves to heat up the bed material and is designed for high solid transport rates controllable by staged air introduction. After particle separation from the flue gas in a cyclone, the hot bed material flows back to the gasifier via a loop seal (Proll et al., 2007).

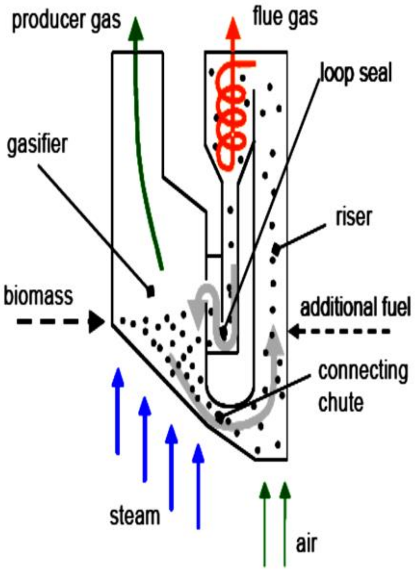


FIGURE 7. DUAL FLUIDIZED BED STEAM GASIFICATION REACTOR (PFEIFER ET AL, 2009).

Dual circulating fluidized beds have been commercially demonstrated in coal-fired power stations (Osowski et al., 2006). There are still issues concerning circulating fluidized bed gasifiers: (1) particle content in the raw gas is close to the one in fixed beds while tar formed is higher; (2) investment and operating costs are higher than in fixed bed gasifiers (Corella et al. 2007; Osowski et al., 2006). Furthermore, gasification systems in an integrated plant for synthetic natural gas production shows that dual circulating bed gasifiers are more suitable overall due to a more advantageous energy conversion related to the composition of the synthesis gas (Gassner and Maréchal, 2009).

1.3.2.3- Advantages/disadvantages of the different gasification reactors

There are a limited number of studies that directly compare fluidized and fixed-bed reactors. A comparison based on technology, use of material, energy, environment and economy, shows that there is no significant differences between the two systems (Warnecke, 2000). The choose of a particular gasifier type and its design depend on close scrutiny and of many other factors, such as the properties of the feedstock (both chemical and physical), the quality of product gas required, the heating method and the various operational variables involved (Demirbas 2004). The features of a fluidized bed gasifier that make it appear less attractive are the more complex design and operation, and the energy expenses needed for biomass particle size reduction. Particle size reduction as well entails the formation of dust unsuitable for fluidization. The synthesis gas contains as well a high tar content requiring extensive external gas cleaning. High plant costs make fluidized bed gasification only economical at the 5-10 MW scale.

In comparison to fluidized bed gasifiers, the fixed bed gasifier appears the most adaptable for the production of low calorific value gases in small-scale power generation stations with gas turbines. The fixed bed gasifier plant is simpler in this application and has no or very few moving parts (McKendry et al. 2002c).

The following are key criteria that need to be addressed when selecting a gasifier reactor: (1) capital costs; (2) operation and maintenance; (3) robustness of the gasifier configuration and absence of moving parts; (4) avoidance, as much as possible, of feedstock preparation such as drying, separation, size reduction or pelletization.

1.3.3 - Operation and performance of gasification design

1.3.3.1- Fixed-bed

Generally, fixed-bed gasifiers have simple designs, but the disadvantage of low calorific values (CV). The composition of this gas is typically around 40–50% N_2, 15–20% H_2, 10–15% CO, 10–15% CO_2 and 3–5% CH_4, with a net CV of 4–6 MJ/Nm^3. When using air as the gasifying agent (as in the previous composition values), the volume of the synthesis gas is higher than when oxygen is used, due to the higher N_2 content, increasing the need for downstream gas cleaning equipment of larger capacity. Typically, biomass has moisture contents in the range 5-30 WT % (wet basis) and to get the optimum calorific value, biomass moisture should be under the level 15-20 WT%. Fixed bed gasifiers generally produce outlet gases with a lower particulate loading (e.g. ash, tar, char) than fluidized bed gasifiers, which will be analyzed in the next sub-section (Gordillo et al 2009).

1.3.3.2- Fluidized bed

The major operational difficulty experienced with fluidized bed gasifiers is the possibility for slagging off bed material, depending on ash content of the biomass. In particular, an important feature of biomass is its alkali content, which is a real problem with biomass from herbaceous annual plants. So, to avoid slagging generation, the bed temperature can be reduced, but this causes an increased loss of char with the removed ash.

The gas formed in the gasifier contains impurities like particulates, tar, nitrogen compounds, Sulphur compounds and alkali compounds. The final uses of the gas determine the degree of clean-up required, achievable by cold or hot gas cleaning. The advantage of hot gas cleaning is the possibility of recovering energy from the gas, which poses significant technical challenges. On the other hand, cold gas cleaning is more straightforward, but produces wastewaters contaminated with tar, which may pose a disposal problem (McKendry, 2002c).

1.3.3.3- Tar removal

The need for research on technologies for post-treatment of synthesis gas is the generation of undesirable pollutants, like tars, particles, nitrogen compounds and alkali metals (Banowetz et al., 2009). Tar consists of a combination of condensable hydrocarbons, which includes single ring to 5-ring aromatic compounds with other oxygen-containing hydrocarbon species (Tasaka et al., 2007). These product species condense in gasifier pipe outlets, leading to its closure and, in particulate filters, leading to filter clogging. Tar may lead further to downstream problems with occlusion in fuel lines and injectors in internal combustion engines. In addition, tars also contain convenient amounts of energy that could be transferred to the fuel gases (but are not), such as H_2, CO, CO_2, CH_4, etc. According to Milne et al., 1998, "*tar is the most cumbersome and problematic parameter in any gasification commercialization effort*".

Until now, there are essentially two methods to remove tar from the synthesis gas, which have been classified as I) direct synthesis gas treatment inside the gasifier and ii) hot gas cleaning after the gasification process (secondary methods) (Devi et al., 2003). The methods for primary treatment are those with higher interest as they may stop the necessity for installation and maintenance of downstream processing steps using hot-gas cleaning technology. There are many factors that must be considered in the same manner to develop an effective primary treatment method: (a) the right choice of operating parameters, (b) the kind of additive/catalyst used and (c) gasifier amendment to prevent tar accumulation (Devi et al., 2003). Tar can simply be thermally decomposed; however, it needs very high temperatures (> 1000 °C). But to prevent ash agglomeration it is very desirable to keep the operating temperature of the gasifier below 700 °C. Ash frequently contains CaO, K_2O, P_2O_5, MgO, SiO_2, SO_3, and Na_2O that can sinter, agglomerate, and deposit on surfaces, and assist the erosion and corrosion of the gasifier. Furthermore, alkaline metals react readily in the gasifier with silica forming silicates, or with sulfur producing alkali sulfates, leaving a sticky deposit, in many cases causing bed sintering and defluidization (Wang et al., 2008; Banowetz et al., 2009; Liao et al., 2007).

According to Devi et al. 2003, catalytic reforming of tar into gaseous products is an effective method for tar removal, avoiding costly tar disposal. In this regard, catalyst Ni-based have a wide activity for tar conversion, as well as for water-gas-shift reaction to reduce the amount of nitrogenous compounds for instance ammonia. However, several damping mechanisms occur with Ni-based catalysts like substances poisoning (by Sulphur, chlorine and alkali metals) and sintering of Ni particles and coke formation (Albertazzi et al., 2009). Ni-based catalysts deactivate rapidly due to coke formation and catalyst attrition. While coke can be removed by combustion, if not carefully performed it can lead to poor catalyst activity and selectivity and to limited catalyst life.

1.3.4 - Gasification Conditions

The operating conditions play a very important role in biomass gasification in all respects, including carbon conversion, product gas composition, tar formation and tar reduction. The most important influencing parameters include temperature, pressure, moisture, gasifying medium, catalyst and additives, and residence time. The selection of these parameters also depends on the type of gasifier used. A homogeneous bed temperature profile and well-functioning bed fluidization are of the utmost importance in avoiding disturbances in the operation of a fluidized bed gasifier.

1.3.4.1- Moisture

High moisture is a typical characteristic of biomass. The root of a plant biomass absorbs moisture from the ground and pushes it into the sap wood. Then the moisture is transmitted to the leaves through the capillary passages. Photosynthesis reactions use some of the available moisture in leaves, and the remaining is released to the atmosphere through the transpiration process. For this reason, there is more moisture in the leaves than in the tree trunk. To reduce the moisture from the biomass, energy is needed to accomplish that. In a gasification plant, the energy used in the vaporization is not recovered. So, this is an important parameter that is needed to evaluate the cost of energy penalty in the drying zone of biomass gasification. The moisture in biomass can remain in two forms: (1) free, or external; and (2) inherent, or equilibrium. Free moisture is that above the equilibrium moisture content. It generally resides outside the cell walls. Inherent moisture, on the other hand, is absorbed within the cell walls. When the walls are completely saturated, the biomass is said to have reached the fiber saturation point, or equilibrium moisture. Equilibrium moisture is a strong function of the relative humidity and weak function of air temperature. For example, the equilibrium moisture of wood increases from 3 to 27% when the relative humidity increases from 10 to 80%. The determination of the moisture content is done by weighing the sample before being heated in an air oven at 103 °C and weighted again after cooling. This process should be repeated many times until the weight remains unchanged. The difference in weight between the dry and fresh sample gives the moisture content. The moisture content of some biomass fuels is given in Table 5. High moisture content leads to decreased biomass consumption rate, increasing the energy requirement for drying and reducing biomass pyrolysis. Thus, moisture content greatly affects the operation of the gasifier and the quality of the synthesis gas. However, the limitations of moisture content for gasifier fuels are dependent on the type of gasifier used. So, the standards for updraft and downdraft gasifier are different. For example, while higher values of moisture content can be used in updraft systems, the highest rate acceptable for a downdraft reactor is generally considered to be around 40% on dry basis (Bhavanam and Sastry, 2011).

In Table 5 are given the moisture content (MC) of some biomass fuels used in the gasification process (Bhavanam and Sastry, 2011).

TABLE 5 - BIOMASS MOISTURE CONTENT

Biomass	**Corn stalks**	**Wheat straw**	**Rice straw**	**Rice husk**	**Dairy cattle manure**
MC (WT %, wet basis)	40-60	8-20	50-80	7-10	88
Biomass	**Wood bark**	**Saw dust**	**Food waste**	**RDF pellets**	**Bagasse**
MC (WT %, wet basis)	30-60	25-55	70	25-35	40-50

1.3.4.2- Temperature

The temperature in biomass gasification is very important, since it is a parameter that can control gas composition, tar concentration, reaction rate, and ash build-up, among others. Thus, it needs to be highly controlled (Taba et al., 2012). Low temperature gasification leads to high tar content and to low CO and H_2 contents in the synthesis gas (Gómez-Barea et al., 2013; Kirnbauer et al., 2013). Thus high temperature gasification is needed to obtain high yield of CO and H_2, also decreasing the tar content. However, gasification temperature above 1000 ºC lead to these two main problems: (1) ash melting when using biomass with high ash content, such as wheat straw (ash content around 20%); (2) the requirement of hard reactor specifications. Therefore, numerous studies have been conducted to investigate the gas composition, tar concentration and other requirements in the temperature range of 750–900 ºC. For instance, an attempt has been made to produce H_2 for charging a solid oxide fuel cell (SOFC) from saw dust in a downdraft gasifier at a temperature range of 750–1150 ºC under atmospheric pressure (Abuadala et al., 2013). An increase in CO and H_2 contents and a decrease in CO_2 and CH_4 were observed when temperature was increased from 650 to 800 ºC in a bubbling fluidized bed gasifier. The raising of temperature from 750 to 850 ºC in a fluidized bed gasifier significantly reduced the tar (Asadullah, 2014).

1.3.4.3- Pressure

Based on the downstream application of the synthesis gas, the gasification of biomass is made often under atmospheric or high pressures. Some downstream applications, such as the conversion of gas to methanol or to synthetic diesel using Fischer–Tropsch synthesis, need high pressure to improve processes performance. Increasing pressure inside the gasifier is helpful to reduce the tar yield in the synthesis gas. There is some investigation in fluidized bed gasifiers aimed to reduce the concentration of tar in the product gas, mainly naphthalene, this reduction increasing with increasing pressure in the gasifier (from 0.1 to 0.5 MPa), but simultaneously decreasing CO concentration, while CH_4 and CO_2 are increased. A model gasification coupled to a SOFC (solid oxide fuel cell) and gas turbine was made to show that a moderate pressure, for instance up to 4 bar, does not have a major impact on the gasification process. Specifically, it affected turbine efficiency and the unit's overall efficiency increased from 23% to 35% (Asadullah, 2014).

1.3.4.4- Gasifying medium

As commented for updraft and downdraft gasifiers, the gasification process consists of four different physical and chemical processes: (1) in the drying zone of the gasifier, biomass is dried and the moisture is released as steam; (2) in the pyrolysis zone of the gasifier, the volatile organic matter distills out from the fixed bed carbon; (3&4) in the oxidation and reduction zones, the volatiles and solid carbons introduce successively or vice versa, depending on the gasifier type, while they react with gasifying agents to produce product gases. Air, steam, carbon dioxide and pure oxygen are commonly being used as gasifying agent, which entirely depends on the requirement of the synthesis gas quality for different downstream applications.

The most used gasifying agent is air, as single gasifying agent, because of low cost, leading to a synthesis gas with low concentration of H_2 and CO, due to the large amount of N_2 available in air. However, air also lowers the heating value of the syngas produced. But if steam is used with air as gasifier agent, H_2 concentration is increased due to the occurrence of the water–gas shift reaction. However, the addition of steam implies the reduction of the thermal efficiency of gasification. Pure oxygen usage as gasification agent is appropriate for synthesis gas with high concentration of CO and H_2 and low concentration of tar, but the usage of pure oxygen alone is an expensive option as gasifying agent. Carbon dioxide also acts as a gasifying agent to react with carbon to produce carbon monoxide. However, the reaction is slow (Asadullah, 2014). Steam or CO_2 requires heat supply for the endothermic gasification reactions. This can be done indirectly, circulating a hot material or using heat exchangers, or directly, feeding the gasifier via air (Carlo et al 2013) or O_2 (Gil et al 1997) to partially burn the biomass. Biomass steam gasification has gathered a big interest in recent years since it leads to the production of gaseous fuels with high contents of hydrogen, enabling it be used for industrial applications, both for highly efficient electricity production and as a feedstock for chemical synthesis. Also, steam gasification has other advantages: (1) produces a gas with higher heating value, (2) reduces the diluting effect of N_2 from air and (3) eliminates the need for an expensive oxygen plant when both air and oxygen are used as gasification mediums (Franco et al., 2003).

1.3.4.5- Residence time

Residence time has a great influence on the amount and composition of the produced tars. According to Kinoshita et al., 1994, the increase of residence time helps to decrease the fraction of oxygen-containing compounds. On large scale, yields of one and two aromatic ring compounds (except benzene and naphthalene) decrease with residence time whereas that of three and four ring species increases. Corella et al., 1999, observed a decrease in the total tar content when the residence time was augmented in biomass gasification with a bed of dolomite. As a summary, the advantages and technical challenges of different gasifier designs, gasifying agents and other operating parameters, for syngas production, are compiled in Table 6 (Dhepe and Fukuoka, 2008).

TABLE 6 - ADVANTAGES AND DISADVANTAGES WITHIN GASIFIER DESIGN, AGENT AND OPERATION CONDITIONS FOR SYNGAS PRODUCTION

	Main Advantages	**Main Technical Challenges**
Gasifier design		
Fixed/moving Bed	1. Simple and reliable design 2. Capacity for wet biomass gasification 3. Favorable economics on a small scale	1. Long residence time 2. Non-uniform temperature distribution 3. High char or/and tar contents 4. Low cold gas energy efficiency 5. Low productivity
Fluidized bed	1. Short residence time 2. High productivity 3. Uniform temperature distribution 4. Low char or/and tar contents 5. High cold gas energy efficiency 6. Reduced ash-related problems	1. High particulate dust in syngas 2. Favorable economics on a medium to large scale
Gasifying agent		
Air	1. Partial combustion for heat supply of gasification 2. Moderate char and tar contents	1. Low heating value (4-6 MJ/Nm^3) 2. Large amount of N_2 in syngas (e.g., > 50% by volume)
Steam	1. High heating value of syngas (13–20 MJ/Nm^3) 2. H_2-rich syngas (e.g.,> 50% by volume)	1. Require indirect or external heat supply for gasification 2. High tar content in syngas 3. Require catalytic tar reforming
Carbon dioxide	1. High heating value syngas 2. High H_2 and CO in syngas, and low CO_2 in syngas	1. Require indirect or external heat supply 2. Require catalytic tar reforming
Gasifier operation		
Increase of temperature	1. Decrease char and tar contents 2. Decrease methane in syngas 3. Increase carbon conversion 4. Increase heating value	1. Decrease energy efficiency 2. Increase ash-related problems
Increase of pressure	1. Low char and tar contents 2. No costly syngas compression required for downstream utilization of syngas	1. Limited design and operational experience 2. Higher costs of a gasifier at a small scale

1.4 - Modelling biomass gasification processes via UniSim Design

UniSim Design is a software program with a graphical interface, which provides a complete integrated solution to chemical processes. In the particular case of reactor simulation, it can be used with different thermodynamic models, which include equilibrium and kinetic rate models. The different reactor types defined in UniSim are used to model each zone of gasification. From the UniSim unit operation set of models, the RStoic reactor mode is selected to model the drying zone of the gasification process, and the pyrolysis process which involves solid, liquid and gas phases is modeled using the RYield reactor. This model calculates the yield distribution of the products without the need to specify reaction stoichiometry and kinetics, which are less understood for the pyrolysis process. Experimental data of the composition of the biomass are used to estimate the yield distribution. Nikoo and Mahinpey, 2008, model the combustion and reduction zones of gasification using the Gibbs reactor model and assuming equilibrium reactions.

Simulation of the heat and mass balances of solids process requires a physical properties model suitable for solid components (De Souza-Santos, 2004). Therefore, the special physical property package feature of UniSim simulator for non-conventional solids is utilized for defining physical and chemical properties of feedstock material, rather than simply representing the biomass with the general chemical formula such as CHxOy.

UniSim design is similar to Aspen Plus and specifically to Hysys packages, which are used for the simulation and optimization of general chemical processes. Most of the literature found in the field of biomass gasification simulation relates to studies using the Aspen Plus package. On the other hand, only a few studies dealing with UniSim Design can be found in this particular field of biomass gasification simulation, in spite of the fact that these simulators provide very similar tools to accomplish this objective.

De Kam et al., 2008, studied the potential of co-products of the dry grind ethanol process and corn Stover to generate combined heat and power (CHP) using Aspen Plus. Atnaw et al., 2011, studied simulation of downdraft gasification of oil palm fronds using Aspen Plus. Ersoz et al, 2006, developed a model by integrating fuel cells with coal or biomass gasification, and simulated it for the generation of electricity. Mansaray et al., 2000, developed and analyzed a model for gasification of rice husks using a fluidized-bed gasifier. Ramzan et al., 2011, developed a steady state simulation model for gasification also using Aspen Plus. They inferred that the model can be used as a predictive tool for optimization of the gasifier performance. The investigations were carried out based on the influence of equivalence ratio, temperature, and level of preheating of the air, on gas composition and its heating value.

Chapter 2 – Model Development

2.1 - Process simulator: UniSim Design

Honeywell’s UniSim® Design Suite is a software modelling application used in many fields of engineering and management, in order to create steady-state and dynamic models for plant design, performance monitoring, troubleshooting, business planning, and asset management.

2.1.1- What is it

UniSim Design Suite is a Software Program which enables the construction of steady state and dynamic simulation process models, within an integrated graphical environment. It also includes powerful tools which allow engineers to develop process optimization designs with lower project risks, prior to committing to capital costs.

2.1.2- What problems does it solve?

With UniSim Design, users benefit from:

- Improved Process Design: UniSim Design enables engineers to assess the impact of their design decisions earlier in the project. For new designs, users can construct several models quickly in order to assess many scenarios.
- Equipment Performance Monitoring: UniSim Design allows users to rapidly determine whether the equipment is performing below specification.
- Reduced Engineering Costs, by creating models that can be improved throughout the plant lifecycle, from conceptual design to detailed design, rating, training and optimization.

2.2 - First Model Description

In this work it was considered the gasification of a biomass feedstock typical of Trás-os-Montes region (almond shell) using fluidized bed gasification.

To simulate the fluidized bed gasification, the developed model considers a number of process blocks implemented in UniSim Design, namely blocks to simulate the processes of drying, pyrolysis (decomposition), volatile reactions, char gasification and gas-solid separation. The general model flowsheet for the simulation of biomass gasification simulation is shown in Figure 8.

The feed of Almond Shell, the dry feed and the ashes are described as non-conventional components in UniSim Design and defined in the simulation model by using the ultimate and proximate analysis obtained from literature and given in Table 7 (Juan et al., 2005).

The input parameters of the corresponding gasifier operating conditions, similar to experimental measurements, are shown in Table 8.

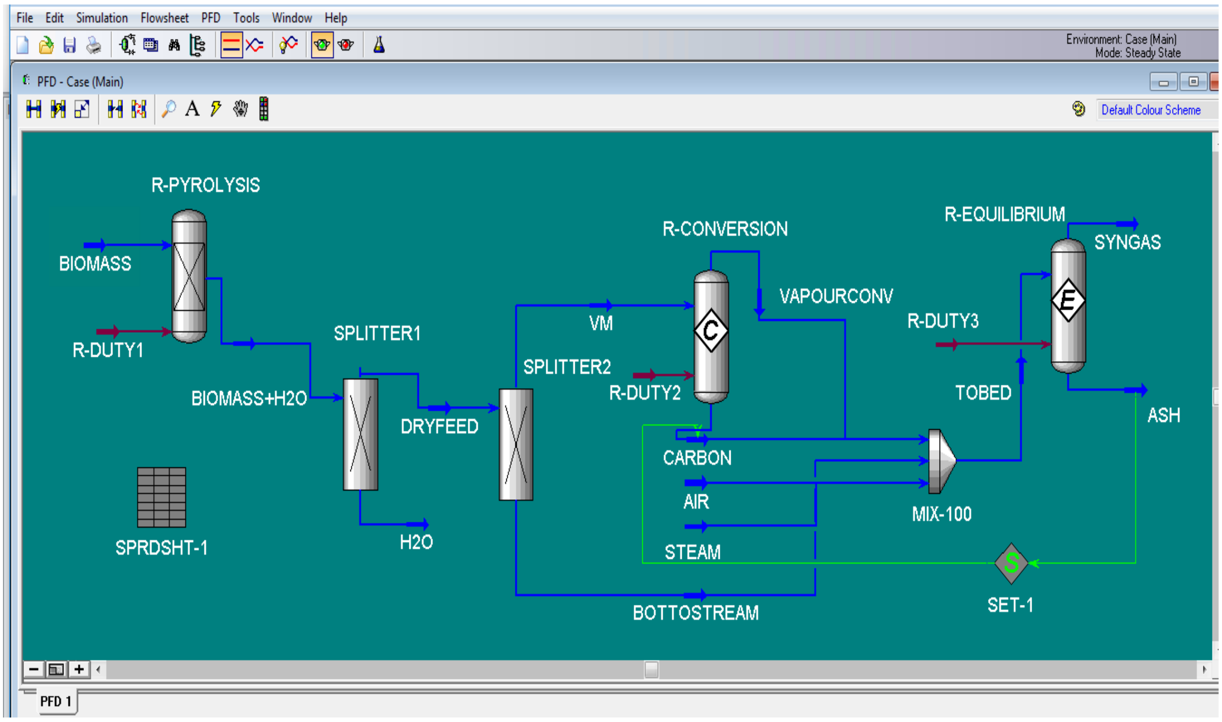


FIGURE 8. GENERAL MODEL FLOWSHEET FOR THE SIMULATION OF BIOMASS GASIFICATION IN UNISIM DESIGN: FIRST MODEL

Table 7 - Proximate and ultimate analysis for almond shell (Juan et al., 2005).

Proximate analysis (wt %) (Dry basis)		Ultimate Analysis (wt %)		HHV, MJ kg^{-1}
fixed carbon	15.87	**C**	50.50	18.2
volatiles	80.28	**H**	6.58	
ash	0.55	**N**	0.21	
moisture	3.30	**S**	0.006	
		O	42.654	
		Cl	0.05	

Table 8 - Gasifier operating parameters. (Begum et al., 2014)

Stream	**Variable Type**	**Value**	**Stream**	**Variable Type**	**Value**
Feed	Flow rate	4.5 kg/h	**steam**	Flow rate	2.5kg/h
	Pressure	0.3 MPa			
	Temperature	25 °C			
Air	Flow rate	1 kg/h			
	Pressure	0.3 MPa		Pressure	0.3 MPa
	Temperature	350 °C		Temperature	200°C
Gasifier	Pressure	0.3 MPa	**dryer**	Pressure	0.3 MPa
	Temperature	700–1100°C		Temperature	400°C
Decomposition	Pressure	0.3 MPa			
	Temperature	400°C			

2.2.1- Physical Property Method

“In UniSim Design, the important information related to pure component flash and physical property calculations is contained within the Fluid Package; this approach allows the definition of all the required information inside a single entity” (UniSim@ Design 2012). The advantages of this approach are as next:

- All associated information is defined in a single location, allowing for easy creation and modification of the information.

- Fluid packages can be used in any simulation, and can be exported and imported as completely defined packages.

- Fluid Packages can be cloned, which facilitates the introduction and test of small changes in complex fluid packages.

- In the same simulation it can be used Multiple Fluid Packages, however they must be all defined inside the common Simulation Basis Manager.

In the simulations carried out the model was set to assume ideal behaviour, suitable for systems at vacuum pressures and isobaric systems at low pressures. In these cases, the vapour phase was modelled with the ideal gas law, with small deviations being allowed to occur at low pressures and very high temperatures (pressures below atmospheric pressure or at pressures lower than 2 bar). Ideal behaviour in the liquid phase was considered to model either molecules with very small interaction or by molecules with interaction that cancel each other out. The IDEAL property method is generally used for systems with and without non-condensable components.

For oil, gas and petrochemical applications, the Peng-Robinson equation of state is generally the recommended property package. The enhancements to this equation of state improve its accuracy for a variety of systems over a wide range of conditions. It strictly solves most single phase, two phase and three-phase systems with a high degree of efficiency and reliability. (UniSim@ Design 2012) This model is ideal for VLE (vapour liquid equilibrium) calculations as well as calculating liquid densities for hydrocarbon systems. However, in situations where highly non-ideal systems are encountered, the use of Activity models is recommended. (UniSim@ Design 2012). Therewith the Peng Robinson was used in our model as a Fluid Package.

2.2.2- Model Sequence

In UniSim Design, the overall gasification process was divided in several model blocks. The main process block consists in three reactors: YIELD REACTOR, CONVERSION REACTOR and EQUILIBRIUM REACTOR. In addition, a MIXER and a number of

SEPARATOR blocks were also incorporated in the simulation model to complete the whole process. The entire gasification consists of four processes, namely drying, decomposition, volatile reactions and char gasification or combustion. These steps will be described in detail in the next sections.

2.2.3- Decomposition and Drying

This step is the first step of the simulation process and is aimed to reduce the moisture from the feed to improve gasifier performance. The block Yield Reactor (block ID: R-PYROLYSIS in Figure 8) in Unisim Design was used to set the composition of almond shell (C, O, H) and the moisture. Almond Shell is fed to the process unit, and through the increase of temperature, the water bound to the biomass is vaporized. The yield of the water is specified by the water content in the proximate analysis of Almond Shell. The moisture content of Almond Shell is 3.3%. Accordingly, the mass yield of gaseous water is set as 3.3%, due to the assumption that the physically bound water is vaporized completely in the drying process. The mass yield of dried Almond Shell is correspondingly equal to 100% − 3.3% = 96.7%. After this process, water and dried Almond Shell flow into the gas and solid separator, (Block ID SPLITTER1 in Figure 8. The separated water is drained out of the process and the DRYFEED continues to the next block, where the second step of gasification starts with the decomposition of the dried feed.

2.2.4- Separation

The splitter (block ID: SPLITTER2 in Figure 8) is used to separate the dried feed into solids and volatile matter. This block allows splitting the feed directly from the knowledge of the compositions, without the need to define reaction stoichiometry and reaction kinetics.

2.2.5- Volatile Reactions

In this study, the Conversion Reactor was used to simulate the volatiles combustion, in which most of the methane reacts with steam to produce hydrogen, carbon monoxide, and carbon dioxide. Decomposed Almond Shell is mainly consisting of C, O_2, H_2, N_2, HCl, H_2S, moisture and ash. Here, C will partly compose the gas phase to take part in de-volatilization and the remaining part of C comprises the solid phase (char) and consequently is later introduced in the char gasification reactor. A separator was used before Conversion Reactor to separate the volatile materials (in VM Stream in Figure 8) and solids (in BOTTOMSTREAM Stream in Figure 8) from the decomposed components. Conversion reactor performs the volatile reactions of separated volatile materials.

The UniSim Design reactor, Conversion Reactor (block ID: R-CONVERSION in (Figure 8) uses energy to convert volatile matter under a known temperature and pressure for each stream of volatile matter (in VAPOURCONV Stream in Figure 8) and carbon (in CARBON Stream in Figure 8). Then, the generated streams get through the mixer with air (in AIR Stream 100 in Figure 8) and steam (in STEAM Stream 100 in Figure 8) to perform a perfect mixing in the reactor (block ID: MIX-100 in Figure 8) and to start the new level of the process, which is the gasification step.

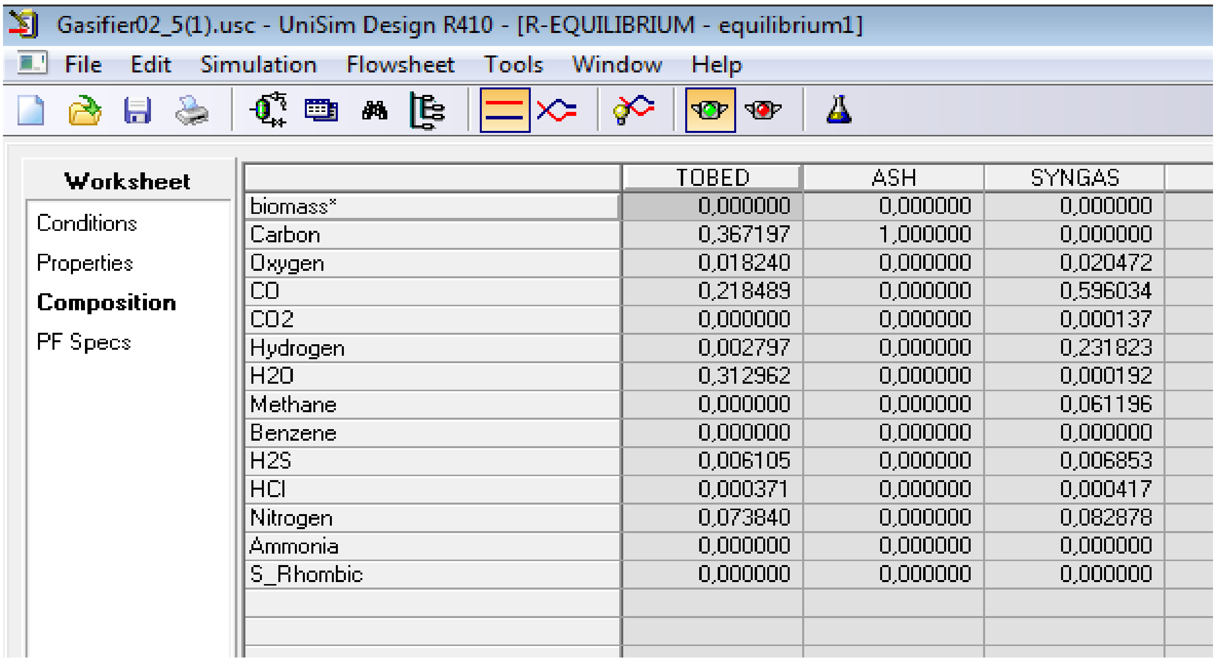
2.2.6- Char gasification

In the UniSim Design an Equilibrium Reactor (block ID: R-EQUILIBRIUM in Figure 8) is considered to model the gas phase reactions during the gasification of char particles. Those reactions are, respectively, the partial combustion reaction of combustible gases (CO, H_2), the water-gas shift reaction and the steam-methane reforming reaction. These reactions are simulated by minimizing the Gibbs free energy in R-EQUILIBRIUM Reactor. From this unit leaves the syngas stream (in SYNGAS Stream100 in Figure 8) and the ash (in ASH Stream100 in Figure 8).

2.2.7 - Compositions results of first gasification model

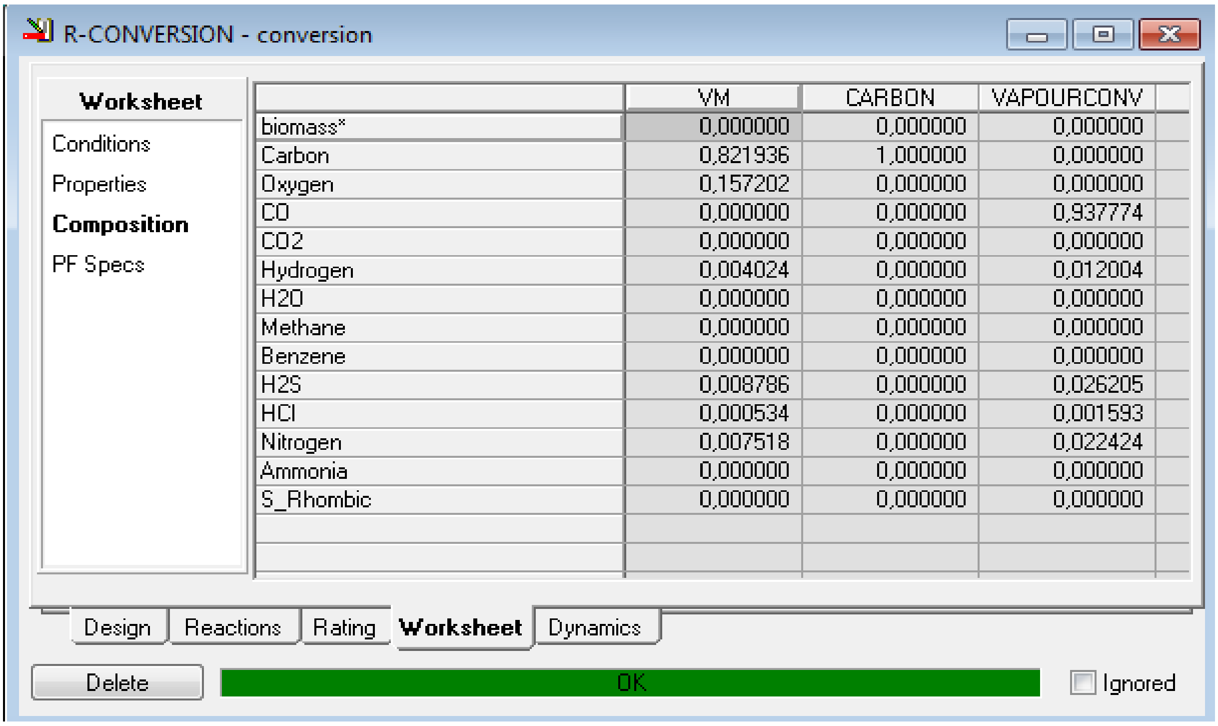
As seen in Figure 8 the reactors in the process are: Conversion, Equilibrium, and Yield Reactor. Those Reactors are the main reactors, which represent the several steps of the gasification process. The mole compositions of the inlet and outlet streams for each Reactor are presented in Tables 9, 10 and 11. Those results correspond to the conditions mentioned before in Tables 7 and 8.

TABLE 9. THE COMPOSITIONS OF THE GAS IN THE EQUILIBRIUM REACTOR



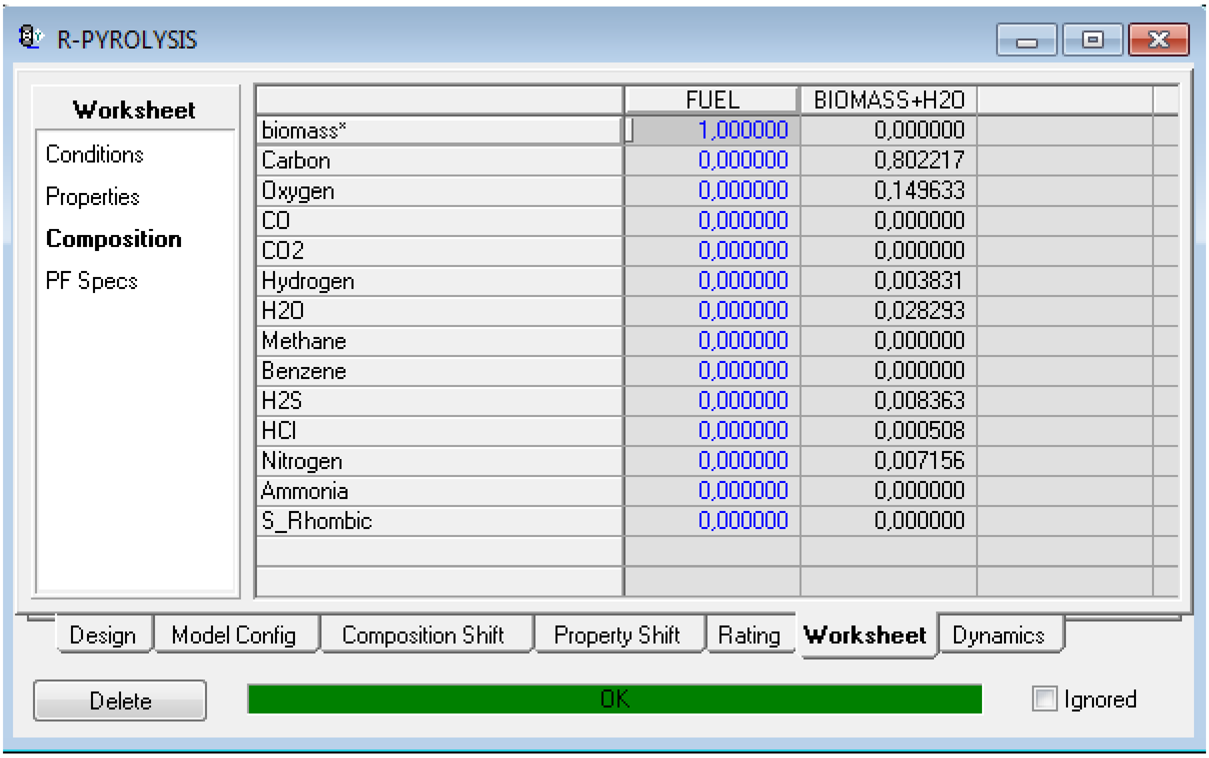
	TOBED	ASH	SYNGAS
biomass*	0,000000	0,000000	0,000000
Carbon	0,367197	1,000000	0,000000
Oxygen	0,018240	0,000000	0,020472
CO	0,218489	0,000000	0,596034
CO2	0,000000	0,000000	0,000137
Hydrogen	0,002797	0,000000	0,231823
H2O	0,312962	0,000000	0,000192
Methane	0,000000	0,000000	0,061196
Benzene	0,000000	0,000000	0,000000
H2S	0,006105	0,000000	0,006853
HCl	0,000371	0,000000	0,000417
Nitrogen	0,073840	0,000000	0,082878
Ammonia	0,000000	0,000000	0,000000
S_Rhombic	0,000000	0,000000	0,000000

TABLE 10. THE COMPOSITIONS OF THE GAS IN THE CONVERSION REACTOR



	VM	CARBON	VAPOURCONV
biomass*	0,000000	0,000000	0,000000
Carbon	0,821936	1,000000	0,000000
Oxygen	0,157202	0,000000	0,000000
CO	0,000000	0,000000	0,937774
CO2	0,000000	0,000000	0,000000
Hydrogen	0,004024	0,000000	0,012004
H2O	0,000000	0,000000	0,000000
Methane	0,000000	0,000000	0,000000
Benzene	0,000000	0,000000	0,000000
H2S	0,008786	0,000000	0,026205
HCl	0,000534	0,000000	0,001593
Nitrogen	0,007518	0,000000	0,022424
Ammonia	0,000000	0,000000	0,000000
S_Rhombic	0,000000	0,000000	0,000000

TABLE 11. THE BIOMASS COMPOSITIONS IN CONVENTIONAL BASED ON MASS BALANCE



	FUEL	BIOMASS+H2O
biomass*	1,000000	0,000000
Carbon	0,000000	0,802217
Oxygen	0,000000	0,149633
CO	0,000000	0,000000
CO2	0,000000	0,000000
Hydrogen	0,000000	0,003831
H2O	0,000000	0,028293
Methane	0,000000	0,000000
Benzene	0,000000	0,000000
H2S	0,000000	0,008363
HCl	0,000000	0,000508
Nitrogen	0,000000	0,007156
Ammonia	0,000000	0,000000
S_Rhombic	0,000000	0,000000

2.3 - Second Model Description

This model was designed in Unisim Design software to simulate an alternative Almond Shell gasification process to produce Syngas. The Peng Robinson as used again as the fluid package for this model. The biomass introduced into the gasifier is already dried and pyrolyzed releasing all gaseous portions at relatively low temperature. The remaining char is oxidized when it arrives to the bed in order to supply the heat for the drying and gasification zones.

The modelling scheme is shown in figure 9. Stream BIOMASS was treated as a nonconventional stream. The proximate and ultimate analyses are defined in Table 7, and the standard operating conditions are mentioned in the Table 9.

TABLE 12 - STANDARD OPERATING CONDITIONS DURING THE GASIFICATION PROCESS.

	Temperature	Pressure
Gasification operating condition	T=700 °C	P=1 bar
Biomass input condition	T=25 °C	P=1 bar
Steam input condition	T=400 °C	P=1 bar
Air input condition	T=25 °C	P=1 bar

R-YIELD block (block ID: R-YIELD in figure 9) is used for devolatilization stage, a thermal decomposition process, in which the biomass is converted to volatile matter and solids such as H_2, N_2, O_2, C (carbon), S (sulphur), and ash. This block used to model the devolatilization stage, is defined by specifying the yield distribution, which is determined using the ultimate analysis of Almond Shell. The enthalpy of the product stream (Stream ID: DRIEDBIOMASS in figure 9) and feed stream (Stream ID: BIOMASS in figure 9) of R-YIELD block does not match due the Heat Stream (Stream ID: R-DUTY in figure 9) inserted to simulate the decomposition heat of the Biomass Stream.

The product of the thermal decomposition process ((stream ID: DRIEDBIOMASS in figure 9) reacts with steam (Stream ID: STEAM in figure 9) in the gasification reaction block, which is called (block ID: R-GIBBS1 in figure 9).

In the gasification block there are introduced various reactions, which represent the gasification process. The gasification mechanism is a complex reaction system from which there were selected 8 reactions (see table 4) which typically simulate a simpler gasification process. This reaction set is divided into two sections: the first one includes reaction 1 to reaction 4 (heterogeneous reactions) and the second section comprises reaction 5 to reaction 8 (homogeneous reactions). The heterogeneous reactions represent gasification processes for char particles that produce CO, H_2, and CH_4. The homogeneous reactions are gas phase reactions that tune the composition of the produced syngas.

Incomplete Oxidation	$\mathbf{C + 0.5O_2 \rightarrow CO}$	Equation (1)
Boudouard	$C + CO_2 \rightarrow 2CO$	Equation (2)
Heterogeneous shift	$C + H_2O \rightarrow CO + H_2$	Equation (3)
Hydrogasification	$C + 2H_2 \rightarrow CH_4$	Equation (4)
Partial combustion of carbon monoxide	$CO + 0.5O_2 \rightarrow CO_2$	Equation (5)
Partial combustion of H_2	$H_2 + 0.5O_2 \rightarrow H_2O$	Equation (6)
Water-gas shift	$CO + H_2O \rightarrow CO_2 + H_2$	Equation (7)
Steam-methane reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	Equation (8)

- Reaction (1) is the partial combustion or incomplete oxidation of carbon and it is exothermic reaction where; all the heat from first reaction is supplied to the second reaction.
- Reaction (2) is the Boudouard reaction, and it is an intensive endothermic process.
- Reaction (3) is the heterogeneous shift reaction,
- Reaction (4) is the hydrogasification reaction and it describes the equilibium of the hydro gasification reaction processes, which depends on the volatile matter in the feedstock.
- Reactions rates of reactions 1, 2, and 3 are known to be lower than the reaction 4 rate.
- Reaction (5) is the combustion of CO and it is exothermic.
- Reaction (6) is the combustion of H_2 and it is exothermic.
- Reaction (7) is the water-gas shift reaction and it is an exothermic reaction.
  Reaction (8) is the reforming reaction and it is endothermic.

In RGibbs blocks: (block ID: R-GIBBS1) and (block ID: R-GIBBS2) the reactions are simulated by minimizing the Gibbs free energy. The second block (block ID: R-GIBBS2 is added to control the temperature of the system. The splitter block (block ID: SPLITTER in figure 9) is used to remove the ash after the gasification process, to give the (Stream ID: PRODUCT-GAS in figure 9) and the (Stream ID: BOTTOMSTREAM3 in figure 9), where all the ash is removed from Bottomstream3. The stream PRODUCT-GAS sent to separator block ((Block ID: SEPERATOR IN FIGURE 9) represents the cyclone separator with 90% efficiency, to separate H_2O from the PRODUCTGAS in the Stream (Stream ID: BOTTOMSTREAM4 in figure 9) and finally the remainder makes up the Syngas stream (Stream ID: SYNGAS in figure 9).

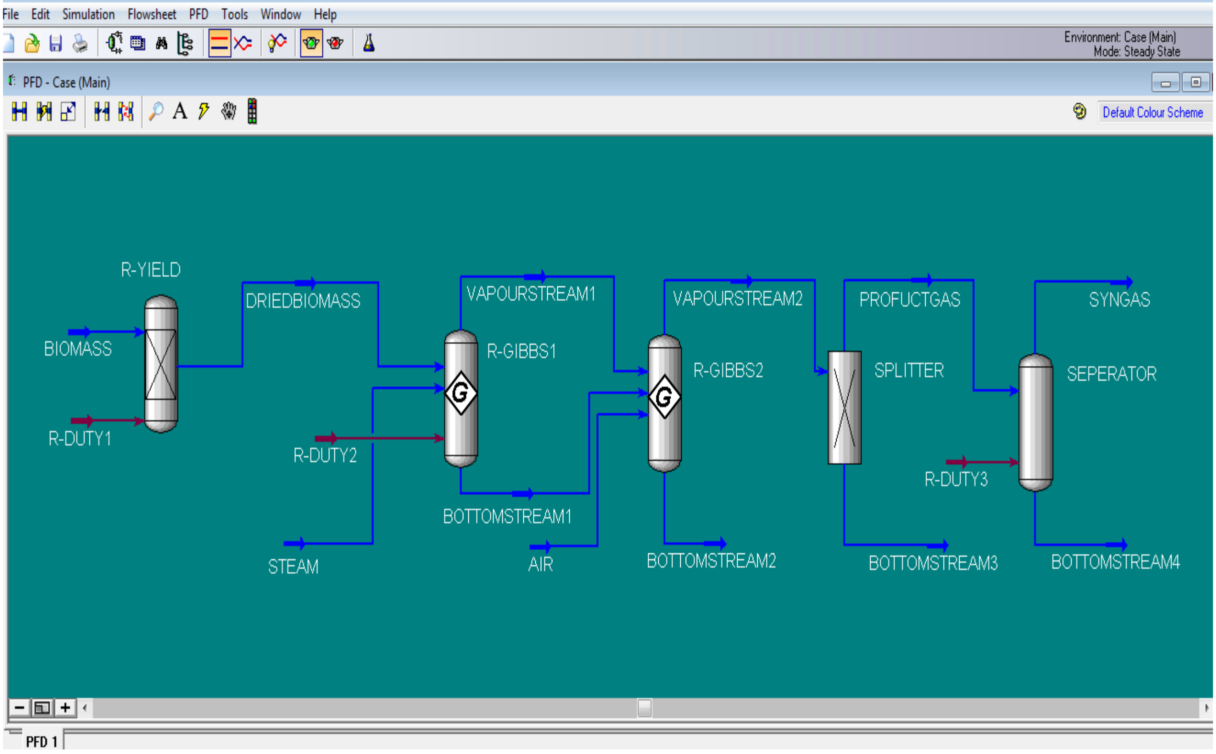
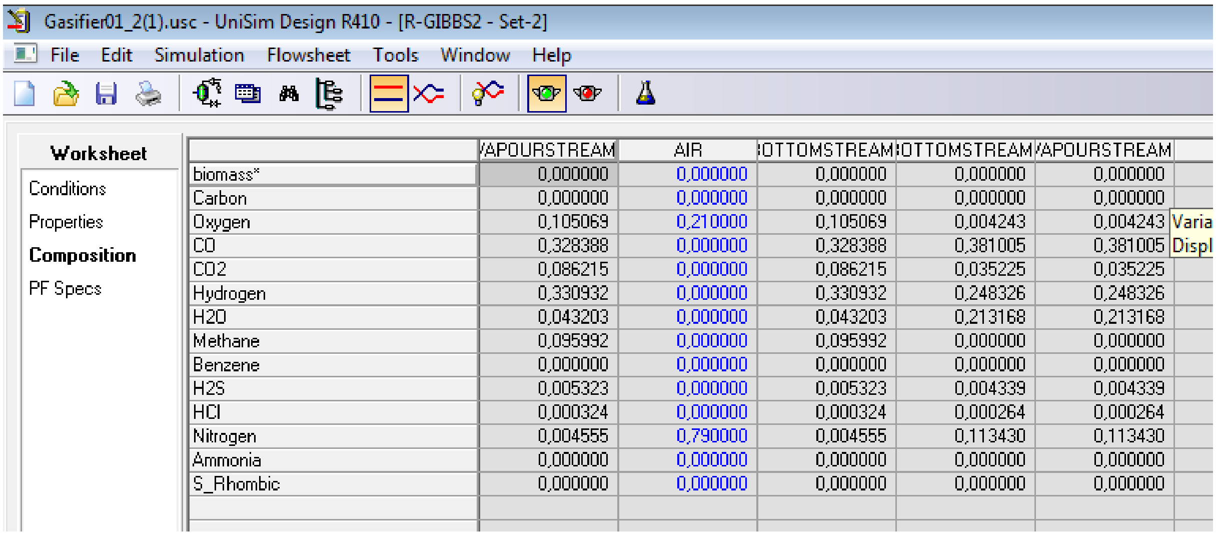


FIGURE 9. GENERAL MODEL FLOWSHEET FOR THE SIMULATION OF BIOMASS GASIFICATION IN UNISIM DESIGN FOR SECOND SIMULATION OF ALMOND SHELL.

2.3.1 - Compositions result of second gasification model

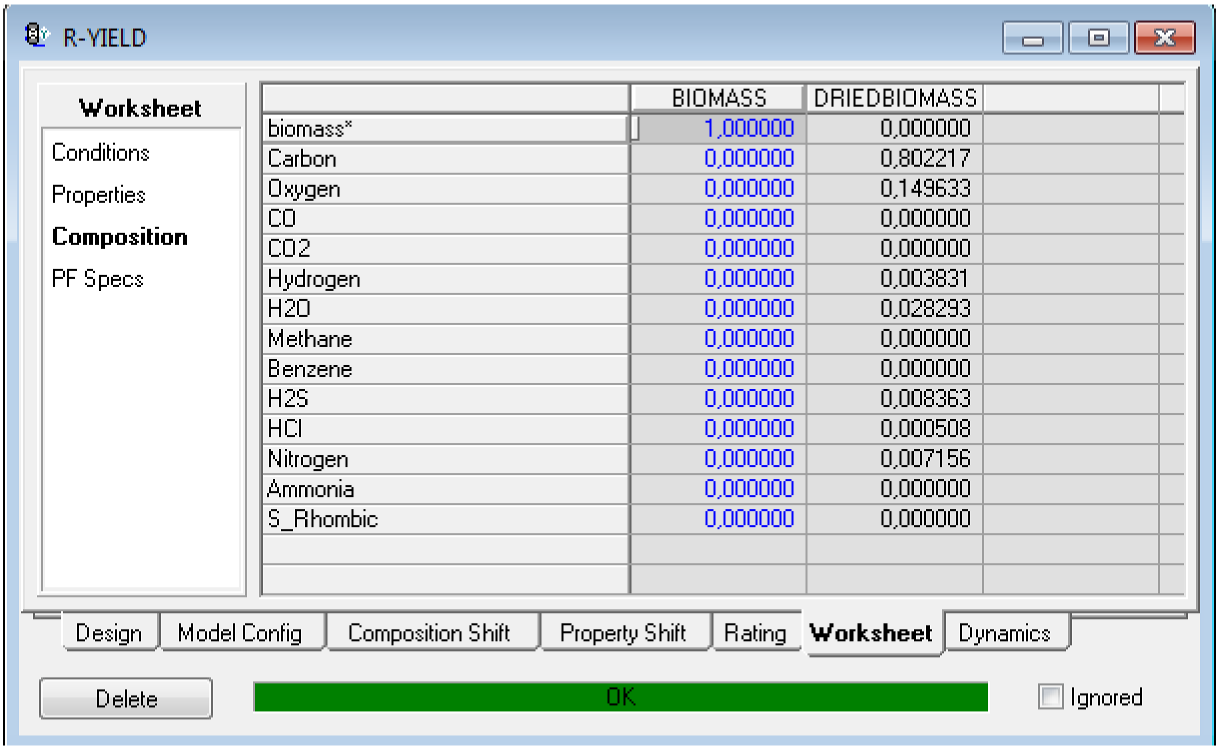
As seen in Figure 9 there are the reactors and separator: Yield Reactor, two Gibbs Reactors and Separator. The inlets and outlets streams in each process, expressed in mole compositions, are shown in Tables 13, 14 and 15.

TABLE 13. GAS COMPOSITIONS IN THE INLET AND OUTLET STREAMS OF R-GIBBBS2 REACTOR



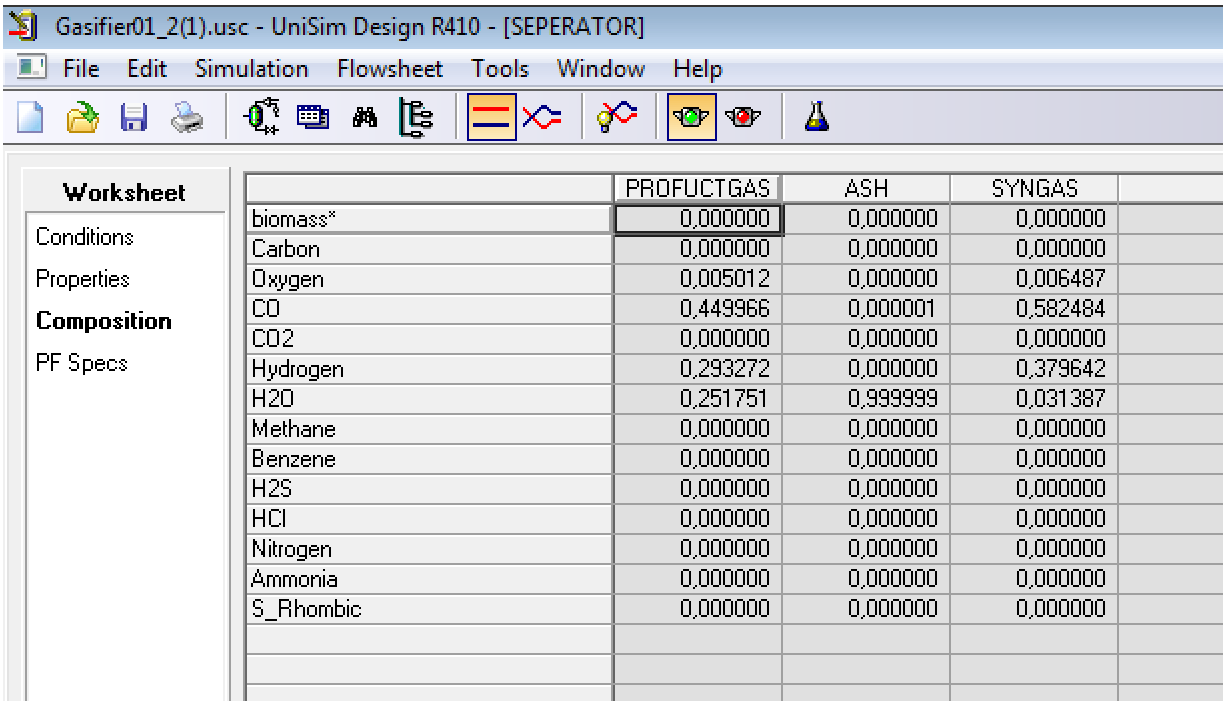
	APOURSTREAM	AIR	OTTOMSTREAM	OTTOMSTREAM	APOURSTREAM
biomass*	0,000000	0,000000	0,000000	0,000000	0,000000
Carbon	0,000000	0,000000	0,000000	0,000000	0,000000
Oxygen	0,105069	0,210000	0,105069	0,004243	0,004243
CO	0,328388	0,000000	0,328388	0,381005	0,381005
CO2	0,086215	0,000000	0,086215	0,035225	0,035225
Hydrogen	0,330932	0,000000	0,330932	0,248326	0,248326
H2O	0,043203	0,000000	0,043203	0,213168	0,213168
Methane	0,095992	0,000000	0,095992	0,000000	0,000000
Benzene	0,000000	0,000000	0,000000	0,000000	0,000000
H2S	0,005323	0,000000	0,005323	0,004339	0,004339
HCl	0,000324	0,000000	0,000324	0,000264	0,000264
Nitrogen	0,004555	0,790000	0,004555	0,113430	0,113430
Ammonia	0,000000	0,000000	0,000000	0,000000	0,000000
S_Rhombic	0,000000	0,000000	0,000000	0,000000	0,000000

TABLE 14. BIOMASS COMPOSITIONS IN CONVENTIONAL BASED MASS BALANCE



	BIOMASS	DRIEDBIOMASS
biomass*	1,000000	0,000000
Carbon	0,000000	0,802217
Oxygen	0,000000	0,149633
CO	0,000000	0,000000
CO2	0,000000	0,000000
Hydrogen	0,000000	0,003831
H2O	0,000000	0,028293
Methane	0,000000	0,000000
Benzene	0,000000	0,000000
H2S	0,000000	0,008363
HCl	0,000000	0,000508
Nitrogen	0,000000	0,007156
Ammonia	0,000000	0,000000
S_Rhombic	0,000000	0,000000

TABLE 15. GAS COMPOSITIONS OF THE SYNGAS



	PROFUCTGAS	ASH	SYNGAS
biomass*	0,000000	0,000000	0,000000
Carbon	0,000000	0,000000	0,000000
Oxygen	0,005012	0,000000	0,006487
CO	0,449966	0,000001	0,582484
CO2	0,000000	0,000000	0,000000
Hydrogen	0,293272	0,000000	0,379642
H2O	0,251751	0,999999	0,031387
Methane	0,000000	0,000000	0,000000
Benzene	0,000000	0,000000	0,000000
H2S	0,000000	0,000000	0,000000
HCl	0,000000	0,000000	0,000000
Nitrogen	0,000000	0,000000	0,000000
Ammonia	0,000000	0,000000	0,000000
S_Rhombic	0,000000	0,000000	0,000000

Chapter 3 – Results and Discussion

3.1- First Process

In this section the results obtained with the gasification first model presented in Chapter 2 are displayed. The Syngas leaving the unit is composed by hydrogen, carbon monoxide, oxygen, methane and small amount of H_2S, HCl and N_2. Starting from this base scenario it was studied the effect of air/biomass ratio and of steam/biomass ratio versus gas composition. The effect of temperature on the performance of the gasification process was also studied. The results of these studies are presented in the following sections.

3.1.1- The effect of air-biomass ratio

The effect of air-biomass ratio on product gas composition was examined. Simulation results for syngas composition *versus* air-biomass ratios covered a range of 0 to 1.1 (where the value of biomass mass flow is fixed at 4.5 kg/h and air mass flow is ranged between 0 to 5 kg/h). In Figure 10 it is noticeable that the production of both H_2 and CO decreases with the increasing amount of air, while the volume of the inert gas N_2 in the syngas increases.

The decreasing in hydrogen and carbon monoxide contents was expected, and it is due to a nitrogen dilution effect.

Air-biomass ratio not only represents the O_2 quantity introduced into the reactor, but also affects the gasification temperature under the condition of auto thermal operation. Higher air-biomass ratios can cause syngas quality to degrade because of an increased oxidation reaction. Alternatively, higher air-biomass ratios mean a higher gasification temperature, which can accelerate the gasification and improve the product quality to a certain extent.

FIGURE 10A. EFFECT OF AIR FLOW VS SYNGAS COMPOSITIONS (CO AND H_2).

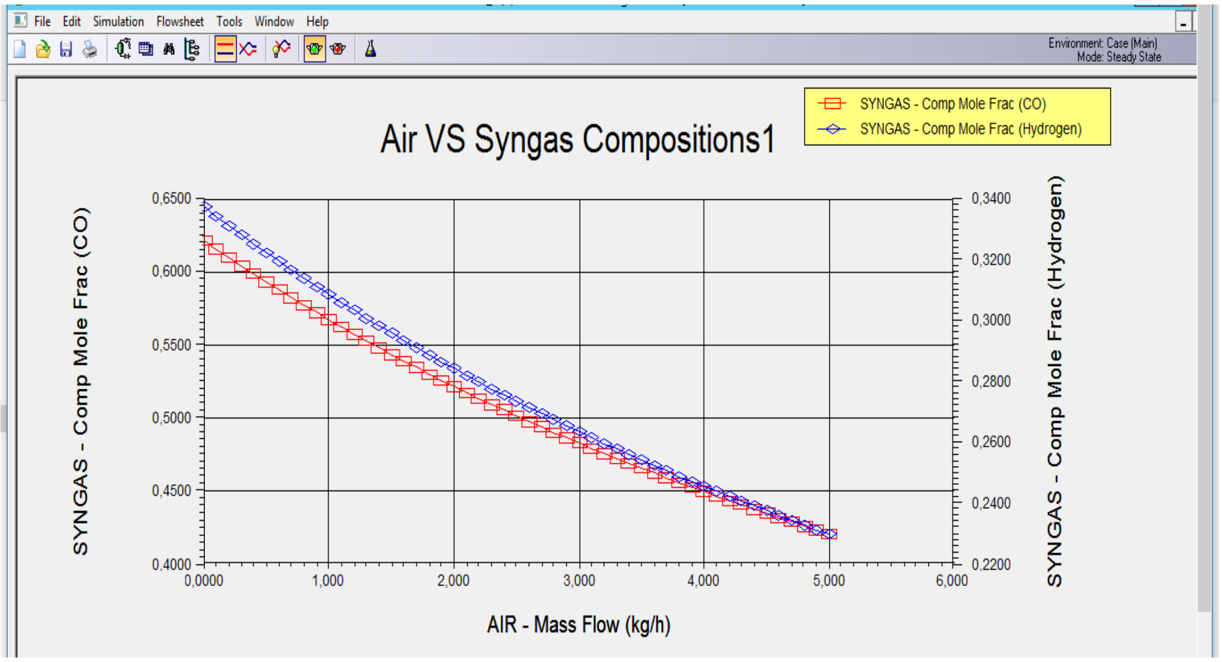
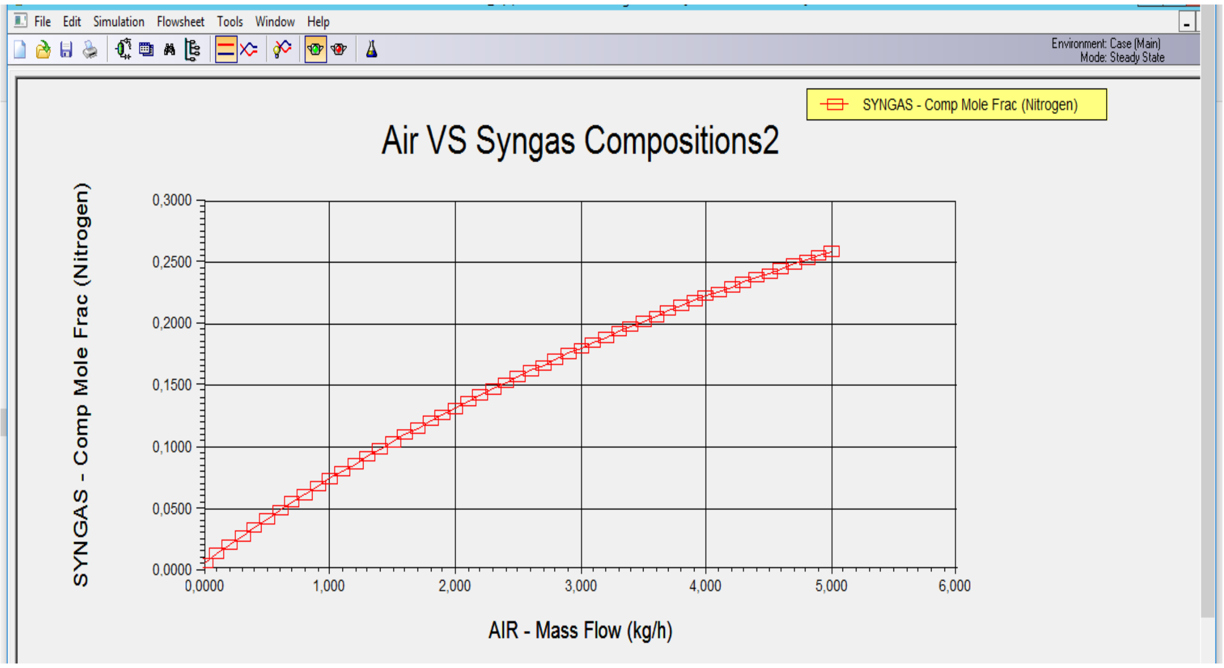


FIGURE 11B. EFFECT OF AIR FLOW RATIO VS SYNGAS COMPOSITIONS (N_2).

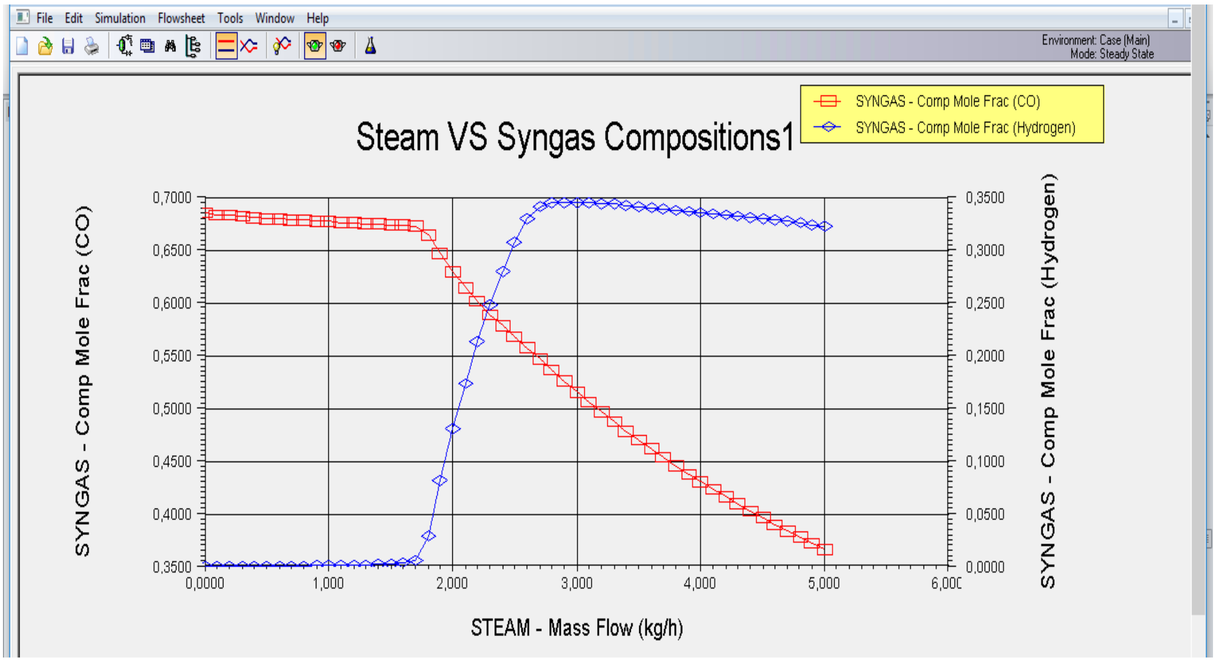


3.1.2 - The effect of steam-biomass ratio

The effect of steam-biomass ratio in the range of 0.44 to 1.11 versus syngas composition is shown in Figure 11 (where the value of biomass mass flow is fixed at 4.5 kg/h and steam mass flow range between 2 to 5 kg/h). The concentration of CO decreases and H_2 concentration increases in this process while we get more H_2O by increasing the Steam/Biomass ratio, as there is only a fixed amount of air supplied at 1 kg/h with increasing steam-biomass ratio.

When the gasifier is operated at a high ratio of steam to biomass it needs higher energy for increased steam production. For this model with this conditions studied the optimal value for the H_2 production is S/B ratio of 0.6 to 0.82 for a steam mass flow from 2.7 to 3.7 kg/h. Within this range a hydrogen mole fraction of 34% in synthesis gas is generated.

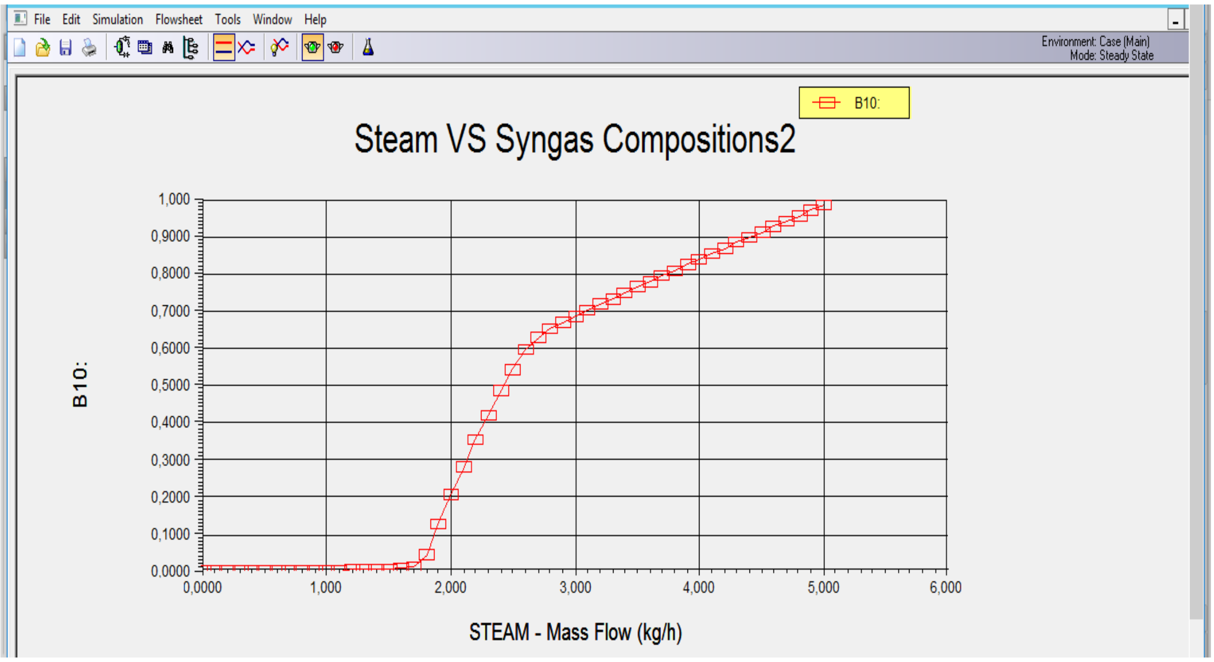
FIGURE 12A. EFFECT OF STEAM FLOW VS SYNGAS COMPOSITIONS (CO AND H_2).



In Figure 11B, the variable B10 express the H_2/CO ratio in the Syngas stream.

It is noticeable that the ratio of H_2/CO increases with the rise of the amount of steam and as it was considered a range of steam flow between 2.7 and 3.7 kg/h, the range of this ratio H_2/CO is between 0.63 and 0.79 for this model.

FIGURE 13B. EFFECT OF STEAM FLOW VS SYNGAS COMPOSITIONS2.

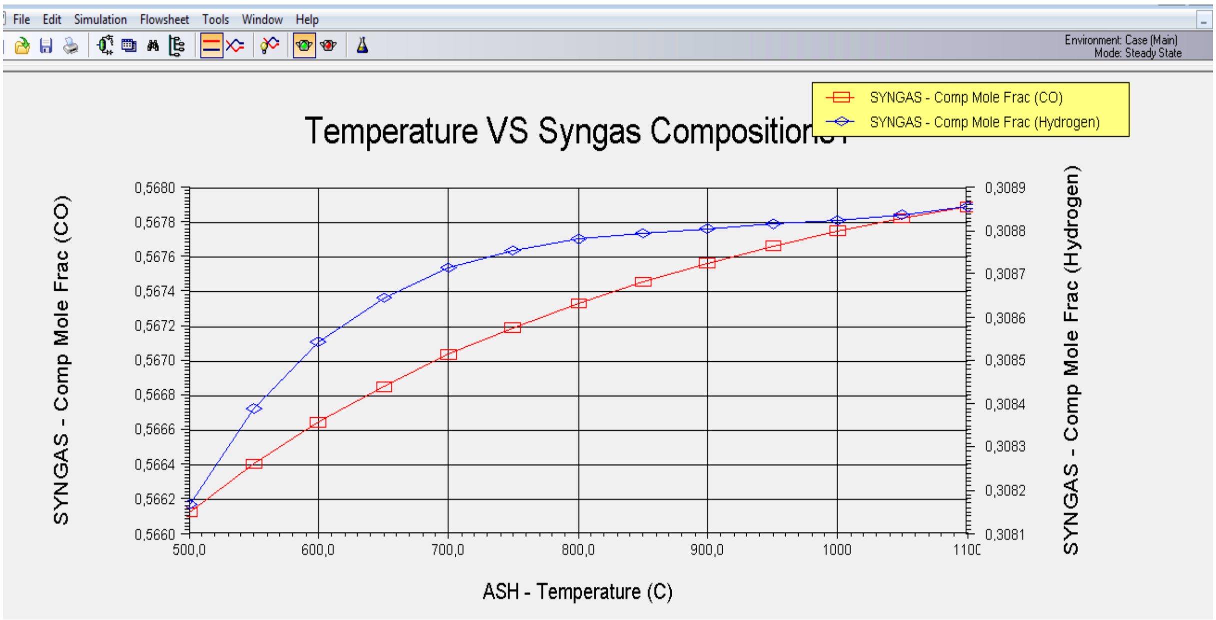


3.1.3 - Effect of Temperatures on syngas compositions

The effect of gasifier temperature on produced syngas composition is shown in Figure 12. The temperature considered varies from 500 °C to 1100°C. The concentrations of CO and H_2 rise with increasing gasifier temperature.

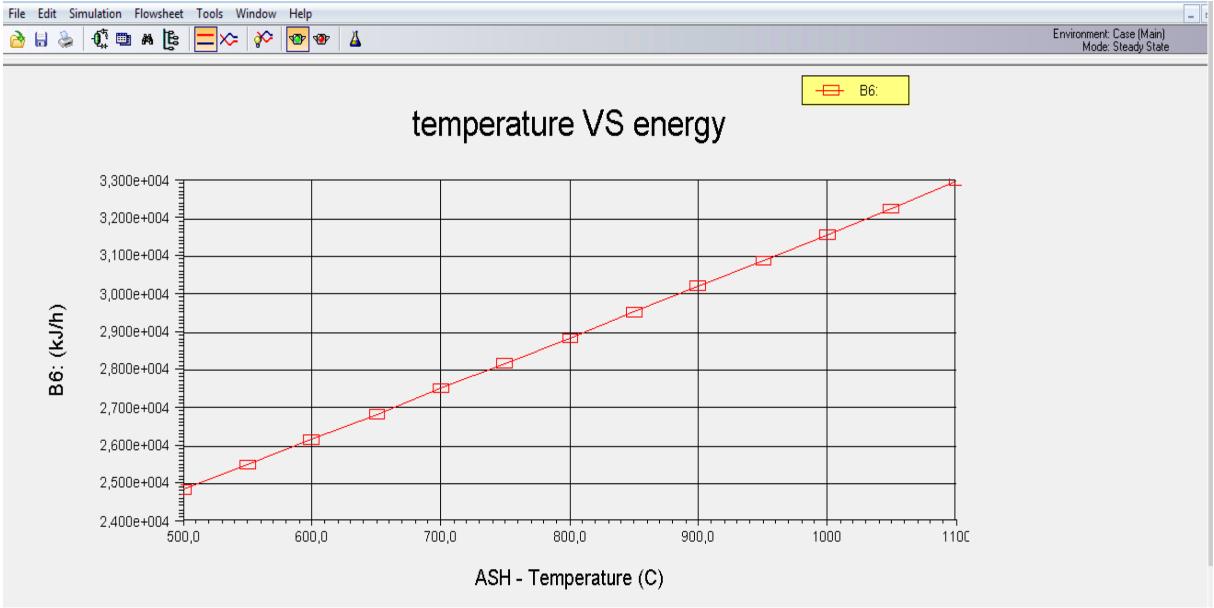
However, the increasing in hydrogen and carbon monoxide content is negligible.

FIGURE 14A. EFFECT OF TEMPERATURES VS SYNGAS COMPOSITIONS (CO AND H_2).



In Figure 12B: variable B6 express of the whole heat flow of the process. The heat demands during the gasification process rise with increasing the gasification temperature as it can be seen in Figure 12B.

FIGURE 15B. EFFECT OF TEMPERATURES VERSUS TOTAL ENERGY PROCESS BALANCE.



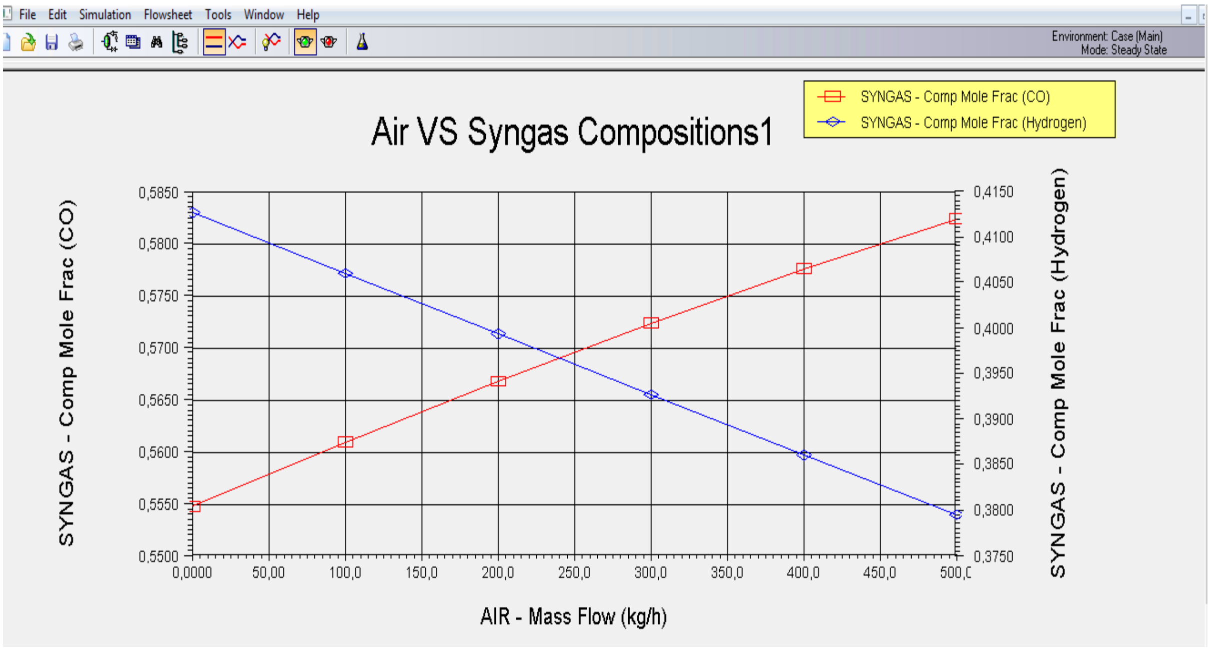
3.2 – Second Process

In this section the results obtained with the gasification second model presented in chapter 2 are displayed. The syngas leaving the unit is composed by hydrogen, carbon monoxide, and oxygen. The model is also divided into three zones Pyrolysis, Gasification, and Combustion, where the drying zone is considered included in the Pyrolysis Zone, due to Almond Shell showing low moisture content. Starting from this base scenario it was studied the effect of air/biomass ratio and of steam/biomass ratio versus gas composition. The effect of temperature on the performance of the gasification process was also studied. The results of these studies are presented in the following sub-sections.

3.2.1 - The effect of air-biomass ratio

The effect of air-biomass ratio ranges between of 0 and 0.5 on the Syngas compositions is shown in Figure 13, where it is shown the ratio of Syngas composition versus the air-biomass. The air flow range is between 0-500 kg/h and the mass flow of biomass is fixed at 1000 kg/h. In Figure 13 the production of H_2 decreases with the increasing amount of air, while the composition in CO rises when the amount of air increase.

FIGURE 16. EFFECT OF AIR FLOW VS SYNGAS COMPOSITIONS (CO AND H_2).



3.2.2 - The effect of steam-biomass ratio

Gas composition variation with Steam/biomass ratio is shown in Figure 14A. As the air feed is maintained at fixed values of 500, and biomass feed is maintained at fixed values of 1000 kg/h, with increasing of the steam/biomass ratio between 1 to 2 kg/h results into increase in H_2 and decrease in CO concentrations.

Figure 14B shows decreasing in dry gas production with increasing the steam/biomass ratio. The steam/biomass ratio effect on gasification efficiency and carbon conversion efficiency is shown in Figure 14C. The gasification efficiency and carbon conversion efficiency is decreased with the increase of the steam/biomass ratio. The best steam/biomass ratio is determined considering the highest gasification efficiency of H_2 as we see in the Figure 14A the H_2 is 0.45 at the 2000 kg/h Steam Flows

FIGURE 17A. THE EFFECT OF STEAM FLOWS VS SYNGAS COMPOSITIONS (CO AND H_2).

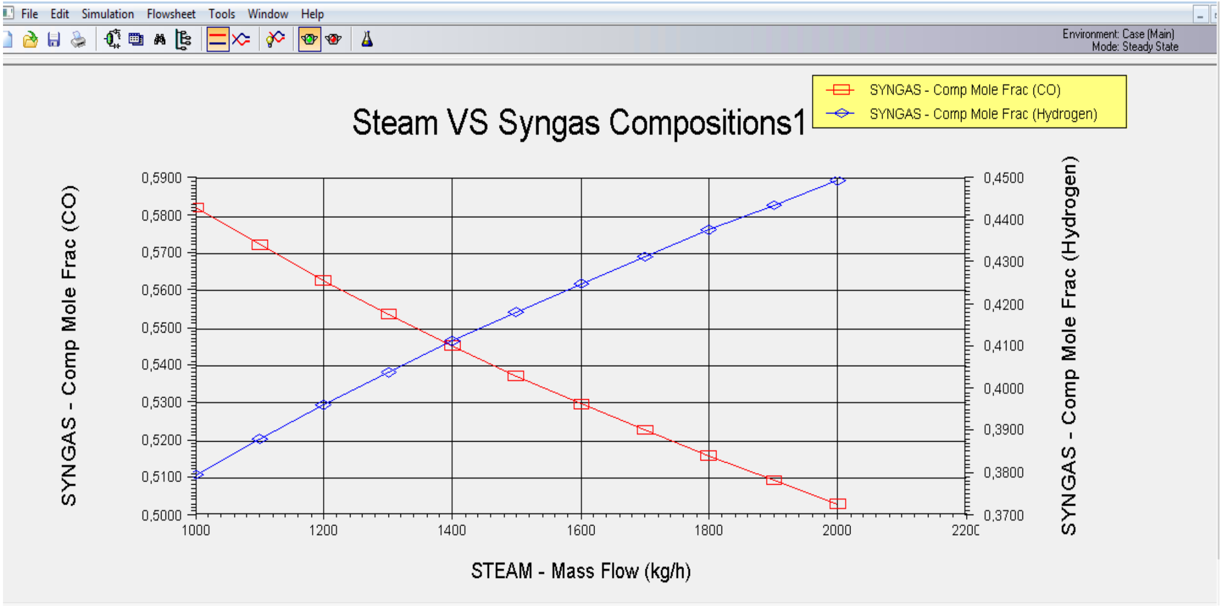


FIGURE 18B. EFFECT OF STEAM FLOW RATIO VS SYNGAS MASS FLOW.

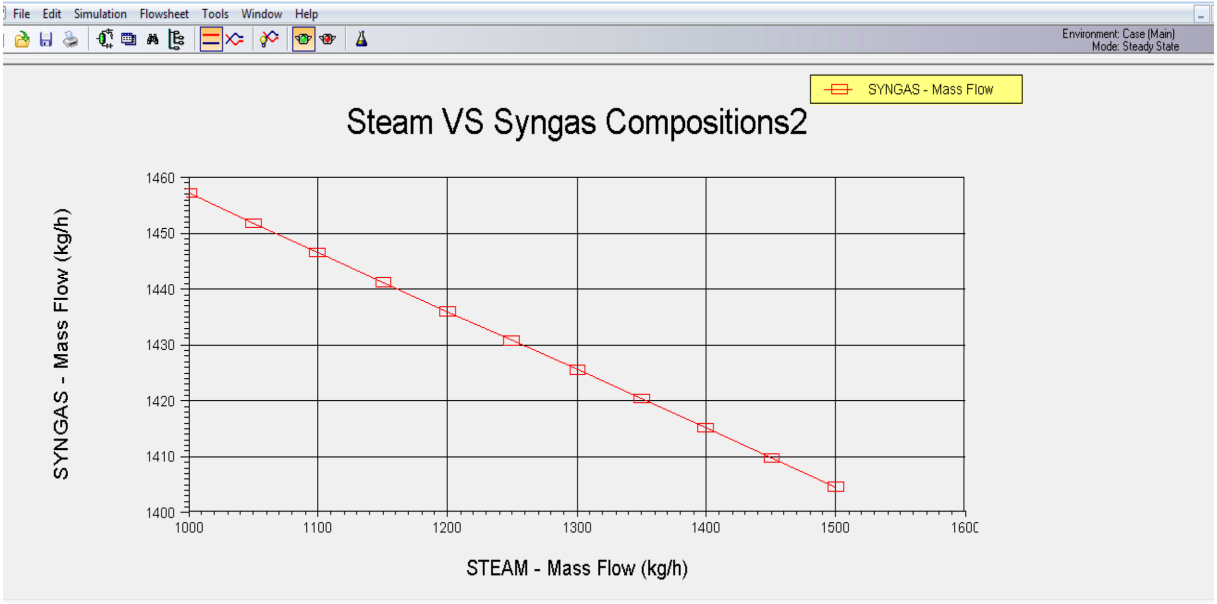
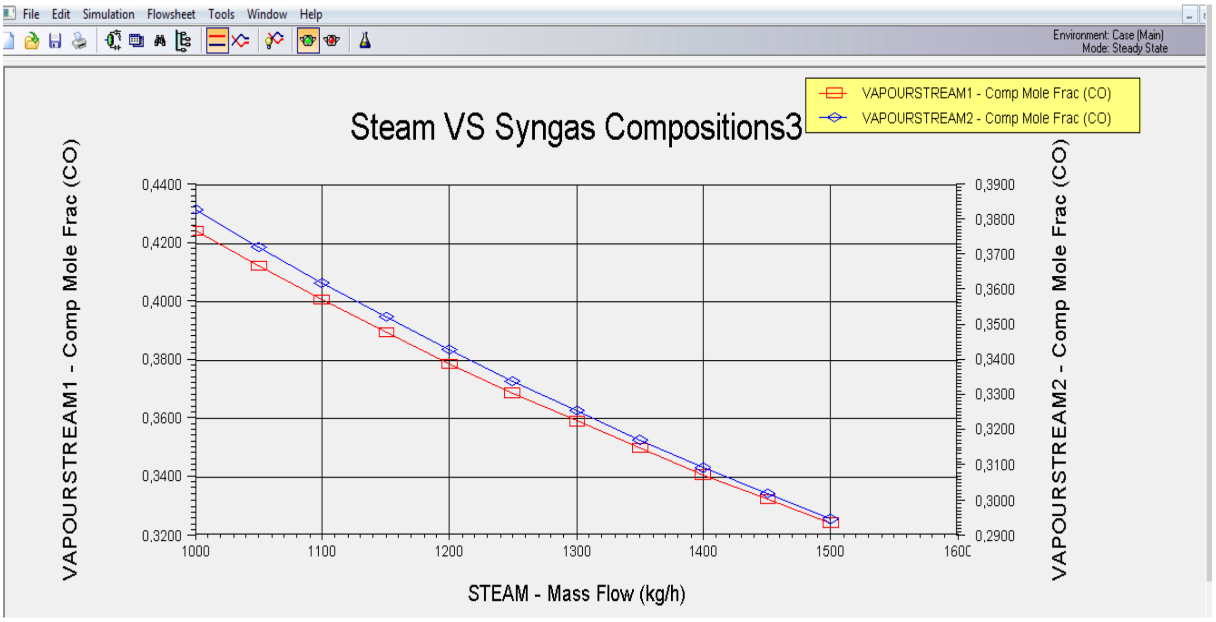


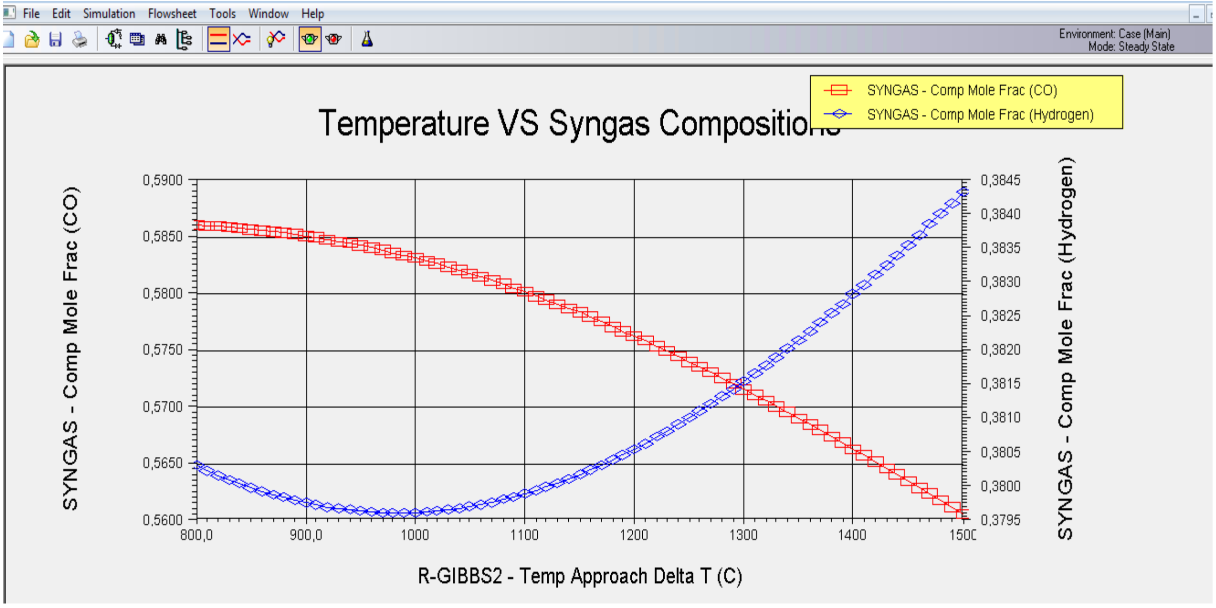
FIGURE 19C. EFFECT OF STEAM-BIOMASS RATIO VS MASS FLOW OF THE GAS OF THE BOTH GIBBS REACTORS.



3.2.3 - Effect of Temperatures on syngas compositions

The temperature of the gasifier is crucial for producing H_2-rich synthesis gas from biomass. As we see in the Figure 15 the Hydrogen decreases slightly for lower temperatures until 1000 °C and rises after this temperature and while the CO drops with increasing temperature.

FIGURE 20. EFFECT OF TEMPERATURES VS SYNGAS COMPOSITIONS (CO AND H_2).



Chapter 4 – Conclusions

This work presents a study regarding the modeling and simulation of almond shell gasification processes. There were developed two simulation processes in order to study the effect of primary parameters on the H_2 and CO production in Syngas.

In case of the first model using a 4.5 kg/h mass flow of biomass it was observed that an increase in temperature in the range 500-1100 °C promoted a rise in H_2 and CO mole contents in the syngas stream, to 0.3 and 0.56, respectively. For the air/biomass ratio study, both H_2 and CO mole fractions in the syngas stream decreased to 0.23 and 0.42, respectively, for a fixed value of steam flow, with significant amounts of N_2 in syngas. However, for the steam/biomass ratio study, at fixed value of air, the H_2 content in syngas increased and peaked at a mole fraction of 0.34 for a mass flow of steam of 2900 kg/h, and the CO content reduced gradually with increasing ratio of steam/biomass. So, the best values for the mole composition in the syngas stream are 0.34 and 0.5 for H_2 and CO, respectively.

For the second model, using 1000 kg/h mass flow of biomass, H_2 content in syngas increased and CO content decreased by increasing the temperature in the range 1000-1500 °C, reaching mole fractions of 0.38 and 0.56 for H_2 and CO, respectively. The same conclusion was obtained for the steam/biomass ratio study but with mole fractions in the syngas of 0.45 and 0.5 of H_2 and CO respectively, changing the steam/biomass ratio in the range 1000-2000 kg/h. However, for the air gasifying agent studies the results were different because when increasing the air biomass ratio from the corresponding mass flows of air of 0 to 500 kg/h, the H_2 mole content decreased to 0.38 and the CO content increased to 0.58, at fixed value of steam/biomass ratio.

There are small differences between H_2 and CO content obtained by these two models. Using the second model, it is obtained a H_2 content higher than the corresponding in the first model, for the temperature study. Regarding the effect of steam as gasifying agent, the conclusion is similar. However, analyzing the effect of air as gasifying agent the H_2 and CO contents obtained with the second model are higher with than the corresponding for the first model.

For future work, it is suggested the study of the recirculation of the non-converted carbon to the reaction system, for the second process.

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