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Scuola di Ingegneria Industriale

**Dipartimento di Chimica, Materiali e Ingegneria Chimica
"Giulio Natta"**

STUDY OF COAL AND BIOMASS GASIFICATION

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1 Introduction

The research for new combustibles and the attempt to find and reuse urban and agricultural wastes brought the development of new and alternative processes. In this way must be read the use of coal and biomass gasification, which transform residues or products with a low value in products with a high value (i.e. syngas and hydrogen for further processes for the chemical industry).

In this thesis there will be a particular attention for coal and biomass, because they give products of high value to the market (especially the syngas) and for this reason a specific attention will be posted to the H2/CO ratio of the syngas leaving the reactor and other important parameters.

In chapter 2 are described the proofs and motivations that allow to perform gasification and also the economical motivations, in terms of a better calorific value of the products and a good reliability of the plant.

The third chapter is dedicated to the description of the raw materials involved in the gasification processes, which is coal and biomass, with an analysis of their qualities, components and structure.

The fourth chapter is dedicated to the reactor analysis, in which are described all the reactor types, their working principles and their characteristics.

Then in chapter 5 are presented the simulations of coal and biomass gasification with the program "D-Smoke", in which the combustion and gasification of this two combustibles is analyzed, reaching the thermodynamic equilibrium of the system and studying the products that leave the reactor in this condition.

Chapter 6 summarizes the analysis done in chapter 5 and improves the model of the gasification process with the help of the tool "GAS-DS", which allows to simulate the operating conditions of a gasifier by means of a kinetic analysis of the gasification phenomena involved into coal and biomass thermal degradation. This model underlines what are the kinetic limitations involved in the gasification processes and gives the opportunity to improve the solid feedstock in order to be compliant with

the product specifications of syngas. This work, (in chapter 5), allowed to dimension the reactor of gasification and to discover the right quantities of utilities (steam and air) necessary to the process.

Finally, in chapter 7 is presented a conclusion of the work of thesis, the main achievements are resumed, giving a high view of the whole gasification process and explaining what are the best operating conditions of the gasifier to reach an optimum in terms of different parameters (H2/CO ratio, steam feed flowrate, calorific value of the outlet syngas).

2 Gasification benefits

Gasification is a chemical process that converts carbonaceous materials like biomass into useful convenient gaseous fuels or chemical feedstock. Pyrolysis, partial oxidation, and hydrogenation are related processes.

Combustion also converts carbonaceous materials into product gases, but there are some important differences. For example, combustion product gas does not have useful heating value, but product gas from gasification does. Gasification packs energy into chemical bonds while combustion releases it. Gasification takes place in reducing (oxygen-deficient) environments requiring heat; combustion takes place in an oxidizing environment releasing heat.

The purpose of gasification or pyrolysis is not just energy conversion; production of chemical feedstock is also an important application. In modern days, gasification is not restricted to solid hydrocarbons. Its feedstock includes liquid or even gases to produce more useful fuels. Pyrolysis, the pioneer in the production of charcoal and the first transportable clean liquid fuel *kerosene*, produces liquid fuels.

In recent times, gasification of heavy oil residues into syngas has gained popularity for the production of lighter hydrocarbons. Many large gasification plants are now dedicated to production of chemical feedstock from coal or other hydrocarbons.

Hydrogenation, or hydrogasification, which involves adding hydrogen to carbon to produce fuel with a higher hydrogen-to-carbon (H/C) ratio, is also gaining popularity.

This chapter introduces the subject of biomass gasification with a short description of its historical developments, its motivation, and its products.

2.1 *Historical background*

The history of gasification (Figure 2-1) may be divided into four main periods, as described in the following:
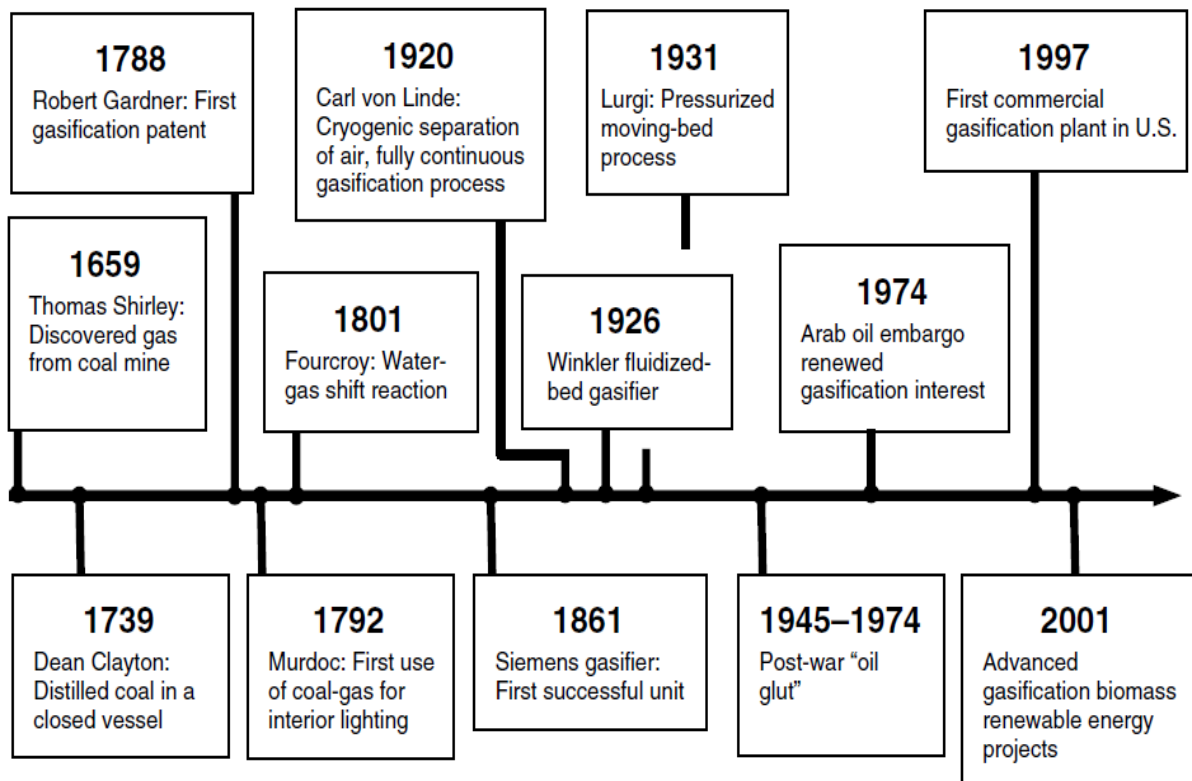
Figure 2-1: Milestones in gasification development.

1850–1940: During this early stage, the gas made from coal was used mainly for lighting homes and streets and for heating. Lighting helped along the Industrial Revolution by extending working hours in factories, especially on short winter days. The invention of the electric bulb circa 1900 reduced the need for gas for lighting, but its use for heating and cooking continued. With the discovery of natural gas, the need for gasification of coal or biomass decreased.

All major commercial gasification technologies (Winkler's fluidized-bed gasifier in 1926, Lurgi's pressurized moving-bed gasifier in 1931, and Koppers-Totzek's entrained-flow gasifier) made their debut during this period.

1940–1975: The period 1940–1975 saw gasification enter two fields of application as synthetic fuels: internal combustion and chemical synthesis into oil and other process chemicals. In the Second World War, Allied bombing of Nazi oil refineries and oil supply routes greatly diminished the crude oil supply that fueled Germany's massive war machinery. This forced Germany to synthesize oil from coal-gas using the Fischer-Tropsch and Bergius processes ($nC + (n + 1)H_2 \Rightarrow C_nH_{2n+2}$). Chemicals and aviation fuels were also produced from coal. A large number of cars and trucks in Europe operated on coal or biomass gasified in onboard gasifiers. During this period over a million small gasifiers were built primarily for transportation. The end

of the Second World War and the availability of abundant oil from the Middle East eliminated the need for gasification for transportation and chemical production.

1975–2000: The third phase in the history of gasification began after the "Yom Kippur" War, which triggered the 1973 oil embargo. On October 15, 1973, members of the Organization of Arab Petroleum Exporting Countries (OPEC) banned oil exports to the United States and other western countries, which were at that time heavily reliant on oil from the Middle East. This shocked the western economy and gave a strong impetus to the development of alternative technologies like gasification in order to reduce dependence on imported oil. Besides providing gas for heating, gasification found major commercial use in chemical feedstock production, which traditionally came from petroleum. The subsequent drop in oil price, however, dampened this push for gasification, but some governments, recognizing the need for a cleaner environment, gave support to large-scale development of integrated gasification combined cycle (IGCC) power plants.

Post-2000: Global warming and political instability in some oil-producing countries gave a fresh momentum to gasification. The threat of climate change stressed the need for moving away from carbon-rich fossil fuels. Gasification came out as a natural choice for conversion of renewable carbon- neutral biomass into gas. The quest for energy independence and the rapid increase in crude oil prices prompted some countries to recognize the need for development of IGCC plants. The attractiveness of gasification for extraction of valuable feedstock from refinery residue was rediscovered, leading to the development of some major gasification plants in oil refineries. In fact, chemical feedstock preparation took a larger share of the gasification market than energy production.

2.2 *A view on the global markets and their previsions*

In this paragraph the markets view is analyzed to understand better why using coal and biomass as sources for the gasification and why biomass are forecast to have a great expansion in the near future. At the beginning the attention is set on the global consumption of fossil and non-fossil fuels and then a single panoramic for the coal and biomass is done. At the ending the previsions for the future are made, with the relative graphics.
A primary example of the world consumption of fuels is explained below (Figure 2-2 and Figure 2-3).
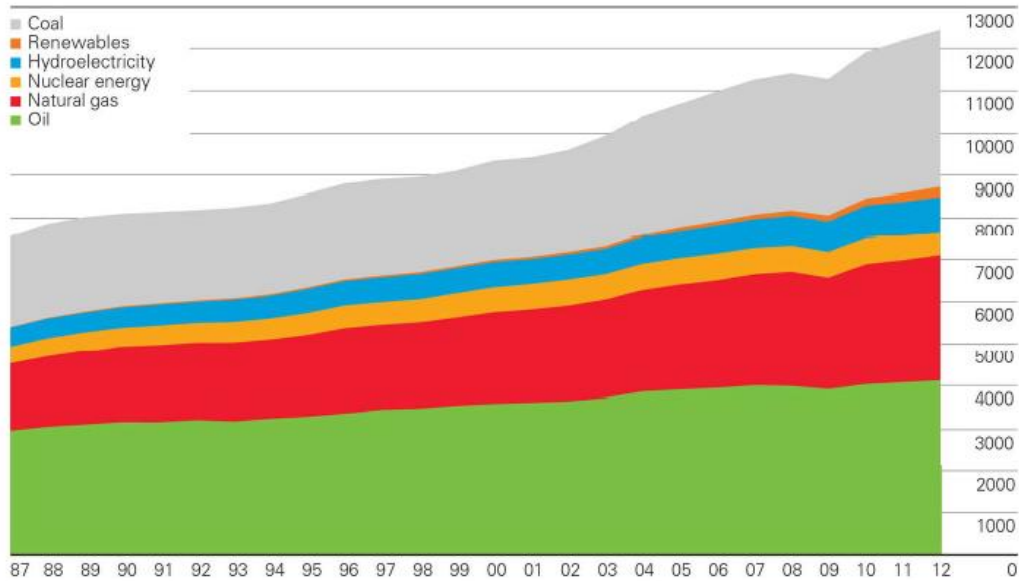
Figure 2-2: Energy world consumption.
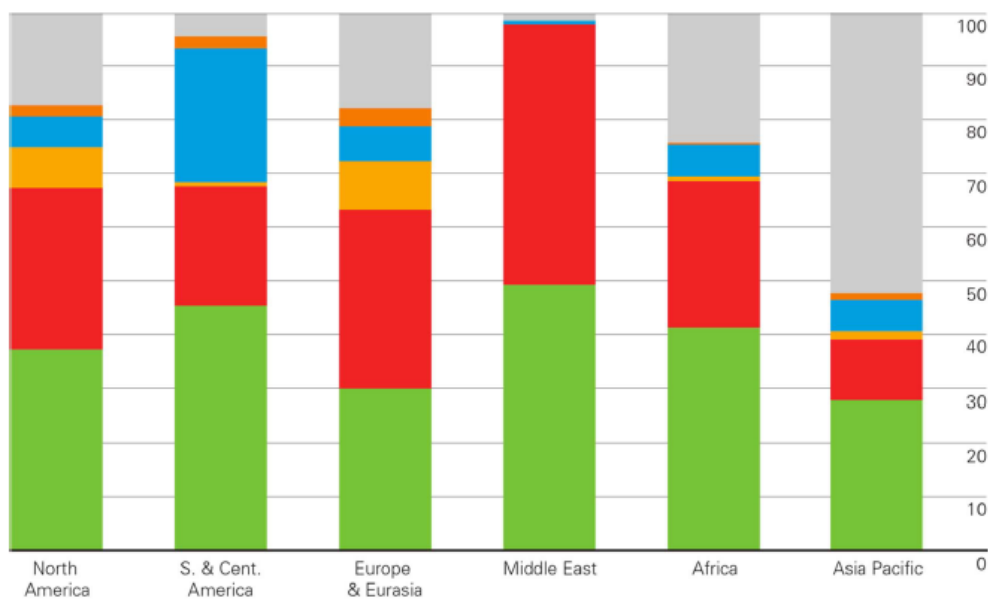
Figure 2-3: Energy regional world consumption.

In these two graphics there is the trend of the fuels consumption in 2012 all around the world and then for specific areas. The first thing to notice is that oil, natural gas and coal are the three major fuels used by the market, but it is also evident that renewable sources are growing very quickly and they are reaching an important space between the other fuels.

Now the second part of this paragraph is focused on the future previsions of the markets as expressed by Figure 2-4, Figure 2-5 and Figure 2-6.

Shares of primary energy

2013-35 increments by fuel

Billion toe

*Includes biofuels
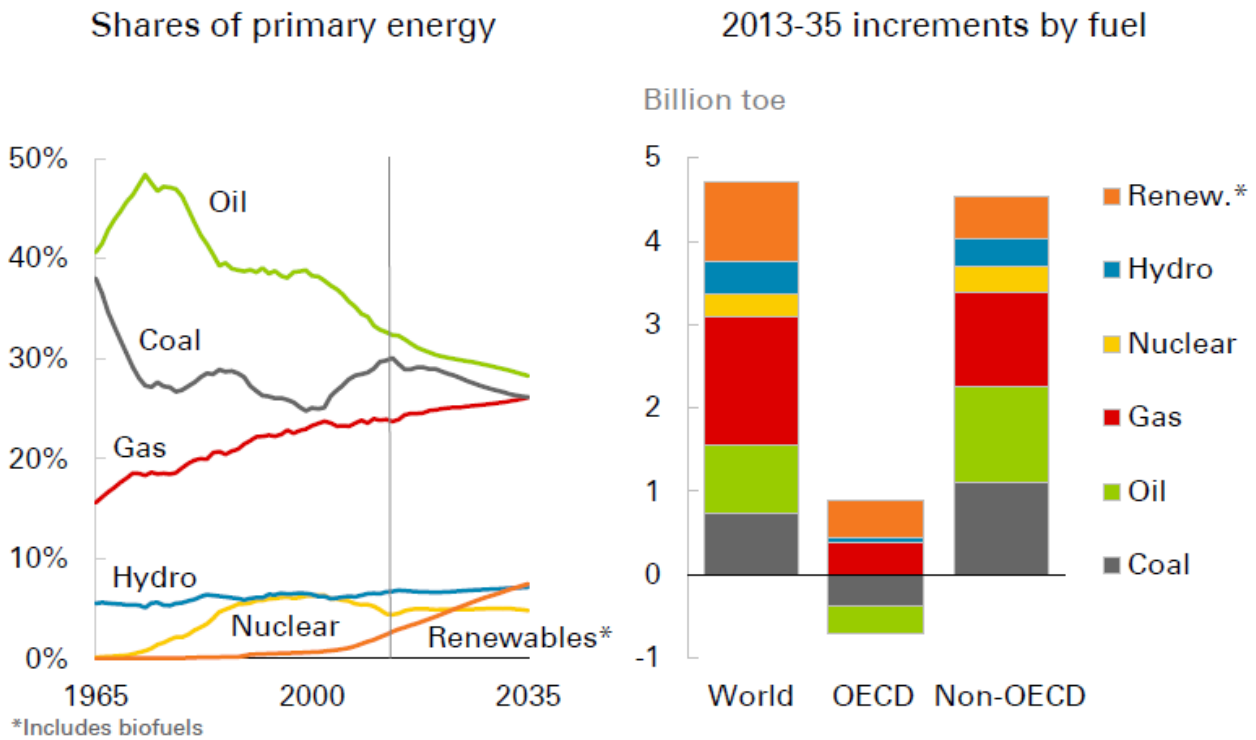
Figure 2-4: Forecasts of fuels consumption.

Inputs to power as a share of total primary energy

Primary inputs to power
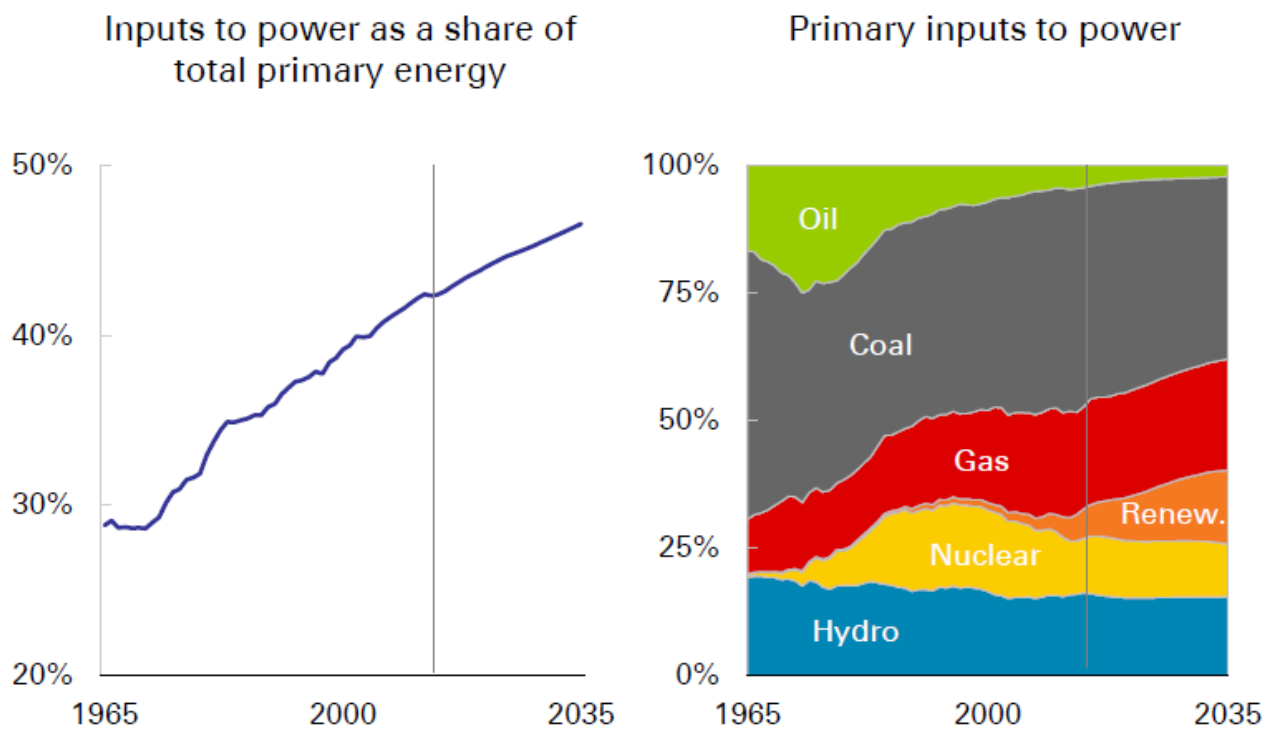
Figure 2-5: Forecasts of fuels' consumption.

Primary energy production

Billion toe

Legend:
- Europe
- FSU
- N America
- Middle East
- Africa
- S & C America
- Asia Pacific

New energy forms

Billion toe

Legend:
- Renewables in power
- Shale gas
- Tight oil, oil sands, biofuels
- % of total (RHS)
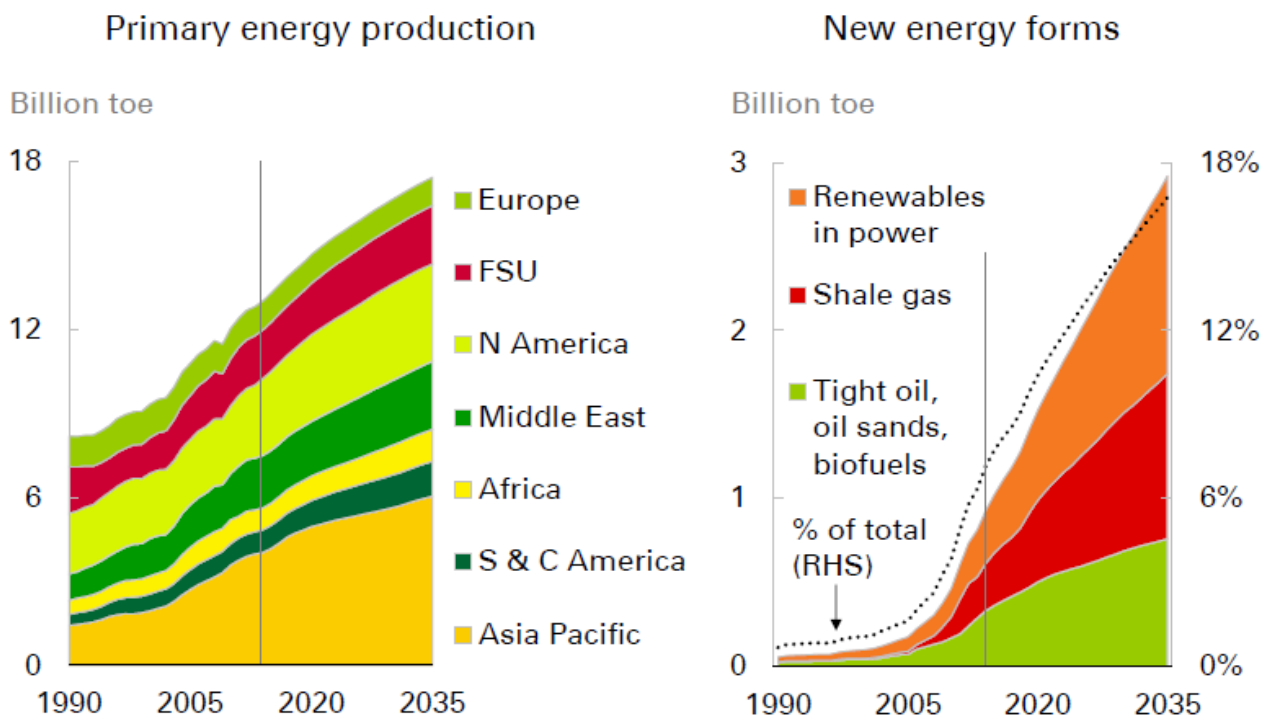
Figure 2-6: New energy forms in 2035.

These graphs explain that in the next years it is very probable a change in the global assets and a gradual passage from the conventional fuels to new sources such as biomass and other non-fossil fuels and a return to the use of coal, especially through the gasification process, which gives us a product and a combustible much more clean. That's why the gasification process of both coal and biomass, which can produce syngas and then synthesis fuels or other products would be so important in a few years.

It is also evident the decrease in the use of oil and a static trend for the nuclear energy, which won't be able to replace the oil losses.

2.3 _Thermochemical conversion of the fuel_

In thermochemical conversion, the entire fuel is converted into gases, which are then synthesized into the desired chemicals or used directly. The Fischer-Tropsch synthesis of liquid transportation fuels is an example of the catalytic conversion of syngas to valuable products.

Production of thermal energy is the main driver for this conversion route that has four broad pathways:

- Combustion;

- Pyrolysis;
- Gasification;
- Liquefaction;

Combustion involves high-temperature conversion of biomass in excess air into carbon dioxide and steam.

Gasification, on the other hand, involves a chemical reaction in an oxygen-deficient environment.

Pyrolysis takes place at a relatively low temperature in the total absence of oxygen. In liquefaction, the large feedstock molecules are decomposed into liquids having smaller molecules. This occurs in the presence of a catalyst and at a still lower temperature.

2.3.1 Combustion

Combustion represents perhaps the oldest utilization of fuels, given that civilization began with the discovery of fire. The burning of forest wood taught humans how to cook and how to be warm. Chemically, combustion is an exothermic reaction between oxygen and the hydrocarbon in biomass and coal. Here, the fuel is converted into two major stable compounds: water and carbon dioxide.

Heat and electricity are two principal forms of energy derived from biomass and coal. Electricity, the foundation of all modern economic activities, may be generated from fuels combustion.

The most common practice involves the generation of steam by burning fuel and coal in a boiler and the generation of electricity through a steam turbine. In some places, electricity is produced by burning combustible gas derived from fuels through gasification.

2.3.2 Pyrolysis

Unlike combustion, pyrolysis takes place in the total absence of oxygen, except in cases where partial combustion is allowed to provide the thermal energy needed for this process. Pyrolysis is a thermal decomposition of the biomass and coal into gas, liquid, and solid. It has three variations:

- Torrefaction, or mild pyrolysis;
- Slow pyrolysis;
- Fast pyrolysis;

In pyrolysis, large hydrocarbon molecules of fuels are broken down into smaller hydrocarbon molecules.

Fast pyrolysis produces mainly liquid fuel, known as bio-oil; slow pyrolysis produces some gas and solid charcoal (one of the most ancient fuels, used for heating and metal extraction before the discovery of coal). Pyrolysis is promising for conversion of waste biomass into useful liquid fuels. Unlike combustion, it is not exothermic.

Torrefaction, which is currently being considered for effective biomass and coal utilization, is also a form of pyrolysis. In this process (named for the French word for roasting), the two fuels is heated to 230 to 300 °C without contact with oxygen.

2.3.3 Gasification

Gasification converts fossil or non-fossil fuels (solid, liquid, or gaseous) into useful gases and chemicals. It requires a medium for reaction, which can be gas or supercritical water (not to be confused with ordinary water at subcritical condition). Gaseous mediums include air, oxygen, subcritical steam, or a mixture of these.

Presently, gasification of fossil fuels is more common than that of non-fossil fuels like biomass for production of synthetic gases. It essentially converts a potential fuel from one form to another. There are three major motivations for such a transformation:

- To increase the heating value of the fuel by rejecting noncombustible components like nitrogen and water;
- To remove sulfur and nitrogen such that when burnt the gasified fuel does not release them into the atmosphere;
- To reduce the carbon-to-hydrogen (C/H) mass ratio in the fuel.

In general, the higher the hydrogen content of a fuel, the lower the vaporization temperature and the higher the probability of the fuel being in a gaseous state. Gasification or pyrolysis increases the relative hydrogen content (H/C ratio) in the product through one the followings means:

Direct: Direct exposure to hydrogen at high pressure.

Indirect: Exposure to steam at high temperature and pressure, where hydrogen, an intermediate product, is added to the product. This process also includes steam reforming.

Pyrolysis: Reduction of carbon by rejecting it through solid char or CO_2 gas.

Gasification is carried out generally in one of the three major types of gasifiers:

- Moving bed (also called fixed bed);
- Fluidized bed;
- Entrained flow;

Downdraft and updraft are two common types of moving-bed gasifier. A survey of gasifiers in Europe, the United States, and Canada shows that downdraft gasifiers are the most common (Knoef, 2000). It shows that 75% are downdraft, 20% are fluidized beds, 2.5% are updraft, and 2.5% are of various other designs.

2.3.4 Liquefaction

Liquefaction of solid biomass into liquid fuel can be done through pyrolysis, gasification as well as through hydrothermal process. In the latter process, biomass is converted into an oily liquid by contacting the fuel with water at elevated temperatures (300–350 °C) with high pressures (12–20 MPa).

2.4 Motivations for biomass and coal conversion

Gasification is almost as ancient as combustion, but it is less developed because commercial interest in it has not been as strong as in combustion. However, there has been a recent interest in conversion of biomass and coal into gas or liquid due to three motivating factors:

- Renewability benefits;
- Environmental benefits;
- Sociopolitical benefits;

2.4.1 Renewability

Fossil fuels like coal, oil, and gas are good and convenient sources of energy, and they meet the energy demands of society very effectively. However, there is one major problem: fossil fuel resources are finite and not renewable.
Biomass, on the other hand, grows and is renewable. A crop cut this year will grow again next year; a tree cut today may grow up within a decade. Unlike fossil fuels, then, biomass is not likely to be depleted with consumption. For this reason, its use, especially for energy production, is rising fast. We may argue against cutting trees for energy because they serve as a CO_2 sink. This is true, but a tree stops absorbing CO_2 after it dies. On the other hand, if left alone in the forest it can release CO_2 in a forest fire or release more harmful CH_4 when it decomposes in water.

2.4.2 Environmental benefits

With growing evidence of global warming, the need to reduce human-made greenhouse gas emissions is being recognized. Emission of other air pollutants, such as NO_2, SO_2, and Hg, is no longer acceptable, as it was in the past.

Biomass has a special appeal in this regard, as it makes no net contribution to carbon dioxide emission to the atmosphere.

Regulations for making biomass economically viable are in place in many countries. For example, if biomass replaces fossil fuel in a plant, that plant earns credits for CO_2 reduction equivalent to what the fossil fuel was emitting.

When burned, biomass releases the CO_2 it absorbed from the atmosphere in the recent past, not millions of years ago, as with fossil fuel. The net addition of CO_2 to the atmosphere through biomass combustion is thus considered to be zero.

Even if the fuel is not carbon-neutral biomass, CO_2 emissions from the gasification of the fuel are slightly less than those from its combustion on a unit heat release basis.

For example, emission from an IGCC plant is 745 g/kWh compared to 770 g/kWh from a combustion-based subcritical pulverized coal (PC) plant.

Sequestration of CO_2 is becoming an important requirement for new power plants. On that note, a gasification-based power plant has an advantage over a conventional combustion-based PC power plant.

In an IGCC plant, CO_2 is more concentrated in the flue gas, making it easier to sequestrate than it is in a conventional PC plant.

Coal gasification may offer a further environmental advantage in addressing concerns over the atmospheric buildup of greenhouse gases, such as carbon dioxide. If oxygen is used in a coal gasifier instead of air, carbon dioxide is emitted as a concentrated gas stream in syngas at high pressure. In this form, it can be captured and sequestered more easily and at lower costs.

2.4.3 Sulfur removal

Gasification from coal or oil has an edge over combustion in certain situations. In combustion systems, sulfur in the fuel appears as SO_2, which is relatively difficult to remove from the flue gas without adding an external sorbent.

In a typical gasification process 93 to 96% of the sulfur appears as H_2S with the remaining as COS. We can easily extract sulfur from H_2S by absorption.

Furthermore, in a gasification plant we can extract it as elemental sulfur, thus adding a valuable by-product for the plant.

2.4.4 Nitrogen removal

A combustion system firing fossil fuels can oxidize the nitrogen in fuel and in air into NO, the acid rain precursor, or into N2O, a greenhouse gas. Both are difficult to remove. In a gasification system, nitrogen appears as either N2 or NH3, which is removed relatively easily in the syngas-cleaning stage.

2.4.5 Dust and other hazardous gases

Highly toxic pollutants like dioxin and furan, which can be released in a combustion system, are not likely to form in an oxygen-starved gasifier. Particulate in the syngas is also reduced significantly by multiple gas cleanup systems, including a primary cyclone, scrubbers, gas cooling, and acid gas–removal units.

2.4.6 Sociopolitical benefits

The sociopolitical benefits of biomass are substantial. For one, biomass is a locally grown resource. For a biomass-based power plant to be economically viable, the biomass needs to come from within a certain distance from it. This means that every biomass plant can prompt the development of associated industries for biomass growing, collecting, and transporting. Some believe that a biomass fuel plant could create up to 20 times more employment than that created by a coal- or oil-based plant. The biomass industry thus has a positive impact on the local economy.

2.5 *Commercial attraction of gasification*

A major attraction of gasification is that it can convert waste or low-priced fuels, such as biomass, coal, and petcoke, into high-value chemicals like methanol. For example:

- Downstream flue-gas cleaning in a gasification plant is less expensive than that in a coal-fired plant with flue-gas desulphurization, selective catalytic reducers (SCRs), and electrostatic precipitators.
- Polygeneration is a unique feature of a gasifier plant. It can deliver steam for process, electricity for grid, and gas for synthesis, thereby providing a good product mix. Additionally, for high-sulfur fuel a gasifier plant produces elemental sulfur as a by-product; for high-ash fuel, slag or fly ash is obtained, which can be used for cement manufacture.

- For power generation, an IGCC plant can achieve a higher overall efficiency (38–41%) than can a combustion plant with a steam turbine alone. Gasification therefore offers lower power production costs.
- Carbon dioxide capture and sequestration (CCS) may become mandatory for power plants.

An IGCC plant can capture and store CO2 at one-half of what it costs a traditional PC plant.

Other applications of gasification that produce transport fuel or chemicals may have even lower CCS costs.

- Established technologies are available to capture carbon dioxide from a gasification plant, but that is not so for a combustion plant.
- A process plant that uses natural gas as feedstock can use locally available biomass or organic waste instead, and thereby reduce dependence on imported natural gas, which is not only rising sharply in price but is also experiencing supply volatility.
- Gasification provides significant environmental benefits.
- Total water consumption in a gasification-based power plant is much less than that in a conventional power plant.
  - Furthermore, a plant can be designed to recycle its process water.
  - For this reason, all zero-emission plants use gasification technology.
- Gasification plants produce significantly lower quantities of major air pollutants like SO2, NOx, and particulates.
- An IGCC plant produces lower CO2 per MWh than a combustion-based steam power plant.
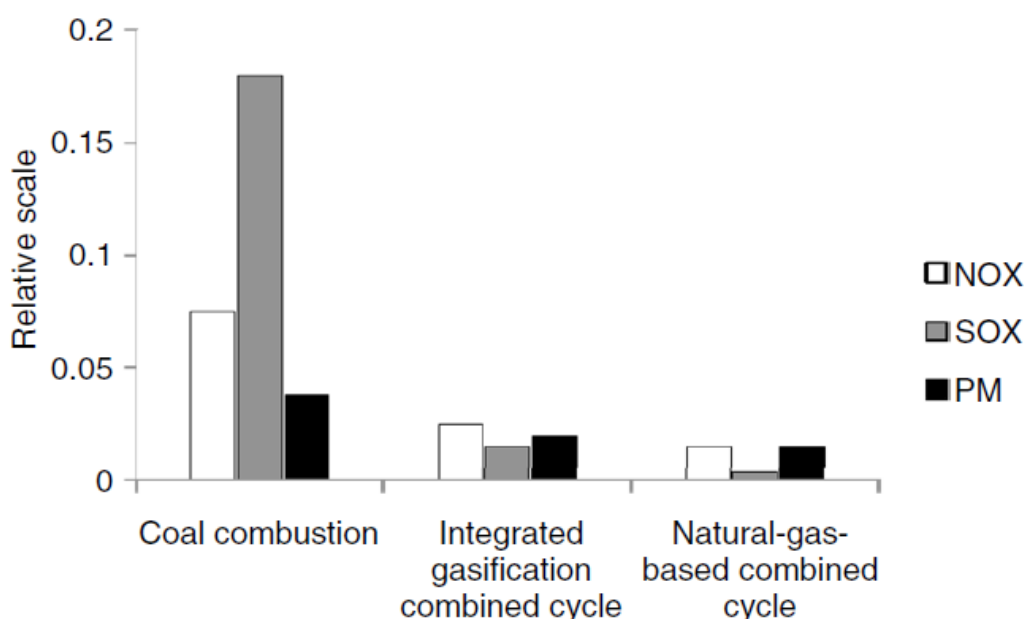
Figure 2-7: Comparison of pollutant emissions.

2.6 *Comparison between gasification and combustion*

With heat or power production, the obvious question is why a solid fuel should be gasified and then the gas burned for heat, losing some part of its energy content in the process.

The comparison is based, where applicable, on an IGCC plant and a PC-fired plant, both generating electricity with coal as the fuel.

- For a given throughput of fuel processed, the volume of gas obtained from gasification is much less compared to that obtained from a direct combustion system. The lower volume of gas requires smaller equipment and hence results in lower overall costs.
- A gasified fuel can be used in a wider range of application than can its precursor solid fuel.
  For example, sensitive industrial processes such as glass blowing and drying cannot use dirty flue gas from combustion of coal or biomass, but they can use heat from the cleaner and more controllable combustion of gas produced through gasification.
- Gas can be more easily carried and distributed than a solid fuel among industrial and domestic customers.
  Transportation of synthetic gas, or the liquid fuel produced from it, is both less expensive and less energy intensive than transportation of solid fuel for combustion.
- The concentration of CO_2 in the product of gasification is considerably higher than that of combustion, so it is less expensive to separate and sequestrate the CO_2 in IGCC.
- SO_2 emissions are generally lower in an IGCC plant. Sulfur in a gasification plant appears as H_2S and COS, which can be easily converted into saleable elemental sulfur or H_2SO_4. In a combustion system sulfur appears as SO_2, which needs a scrubber producing ash-mixed $CaSO_4$, which has less market potential.
- Gasification produces much less NOx than a combustion system. In gasification, nitrogen can appear as NH_3, which washes out with water and as such does not need a SCR to meet statutory limits. A PC system, on the other hand, requires SCR for this purpose.
- The total solid waste generated in an IGCC plant is much lower than that generated in a comparable combustion system. Furthermore, the ash in a slagging entrained-flow gasifier appears as glassy melt, which is much easier to dispose of than the dry fly ash of a PC system.

- For mechanical work or electricity in a remote location, a power pack comprising a gasifier and a compression ignition engine can be employed. For a combustion system, a boiler, a steam engine, and a condenser might be needed, making the power pack considerably more bulky and expensive.
- The producer gas from a gasifier can be used as a feedstock for the production of fertilizer, methanol, and gasoline. A gasification-based energy system has the option of producing value-added chemicals as a side stream. This polygeneration feature is not available in direct combustion.
- A gas produced in a central gasification plant can be distributed to individual houses or units in a medium-size to large community.
- If heat is the only product that is desired, combustion seems preferable, especially in small-scale plants. Even for a medium-capacity unit such as for district heating, central heating, and power, combustion may be more economical.

2.7 *Brief description of gasification and related processes*

When biomass or other carbonaceous materials are heated in a restricted oxygen supply, they are first pyrolyzed or decomposed into solid carbon and condensable and non-condensable gases.

2.7.1 *Pyrolysis*

The solid carbon as well as the condensed liquid enters the gasification reaction with carbon dioxide, oxygen, or steam to produce combustible or synthetic gas. To illustrate the different reactions we take simple carbon as the feedstock.

$$C_nH_mO_p + \text{ Heat} \Rightarrow \sum \text{liquid } (C_a\,H_b\,O_c) + \sum \text{gas } (C_x\,H_y\,O_z) + \sum \text{solid } (C) \tag{1}$$
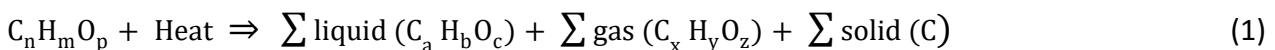
2.7.2 *Combustion of carbon*

When 1 kmol of carbon is burnt completely in adequate air or oxygen, it produces 394 MJ heat and carbon dioxide. This is a combustion reaction. The positive sign on the right side (+Q kJ/kmol) implies that heat is absorbed in the reaction. A negative sign (-Q kJ/kmol) means that heat is expelled in the reaction.

$$C + O_2 \rightarrow CO_2 \quad -393,770\ KJ/Kmol \tag{2}$$

2.7.3 Gasification of carbon

Instead of burning it entirely, we can gasify the carbon by restricting the oxygen supply. The carbon then produces 72% less heat than that in combustion, but the partial gasification reaction shown here produces a combustible gas, CO, as we can observe by the reaction below:

$$C + 0.5\,O_2 \rightarrow CO \qquad -110,530\;KJ/Kmol \tag{3}$$

When the gasification product, CO, subsequently burns in adequate oxygen, it produces the remaining 72% (283 MJ) of the heat. Thus, the CO retains only 72% of the energy of the carbon, but in complete gasification the energy recovery is 75 to 88% owing to the presence of hydrogen and other hydrocarbons.
The producer gas reaction is an endothermic gasification reaction, which produces hydrogen and carbon monoxide from carbon. This product gas mixture is also known as synthesis gas, or *syngas*. Producer gas reaction:

$$C + H_2O \rightarrow CO + H_2 \qquad +131,000\;KJ/Kmol \tag{4}$$

Production of heavy oil residue in oil refineries is an important application of gasification. Low-hydrogen residues are gasified into hydrogen. Heavy oil gasification:

$$C_nH_M + (0.5n)O_2 \rightarrow nCO + (0.5m)H_2 \tag{5}$$
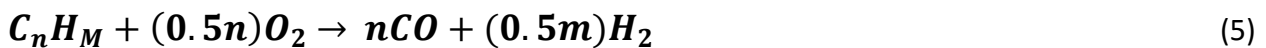
This hydrogen can be used for hydrocracking of other heavy oil fractions into lighter oils. The reaction between steam and carbon monoxide is also used for maximization of hydrogen production in the gasification process at the expense of CO and it is called the water gas shift reaction (WGSR). Shift reaction:

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad -41,000\;KJ/Kmol \tag{6}$$

3 Biomass and coal classification and properties

3.1   *General classification of solid fuels*

Classification is an important means of assessing the properties of a fuel. In evaluating gasification feedstocks, the following properties are generally useful: water content, proximate (thermo-chemical behavior) and ultimate (elemental composition) analysis.

The proximate analysis classifies the fuel in terms of its moisture (M), volatile matter (V), fixed carbon (FC) and ash. The moisture content of a solid is expressed as the quantity of water per unit mass of the dry solid.

The thermal behavior of biomass was studied by measuring the rate of weight loss of the sample as a function of time and temperature (thermo gravimetric analysis TGA). The observed rates are not only functions of time and temperature, but also of the size and the density of the sample. The dynamic TGA measurements yield data equivalent to a standardized proximate analysis.

The ultimate analysis generally reports the elemental carbon (C), hydrogen (H), nitrogen (N), sulphur (S) composition and oxygen (O) very often by difference in the solid fuel. In order to avoid confusion and to give a good representation of the fuel itself, an ultimate analysis is performed and reported on a dry basis, because otherwise moisture is indicated as additional hydrogen and oxygen.

A number of instruments have been developed to determine the elemental C, H, N, S and O composition. In some cases C, H, N and S can be determined simultaneously.

There are three other methods of classifying and ranking fuels using their chemical constituents: atomic ratios, the ratio of ligno-cellulose constituents, and the ternary diagram.

All hydrocarbon fuels may be classified or ranked according to their atomic ratios, but the second classification is limited to ligno-cellulose biomass.

Classification based on the atomic ratio helps us to understand the heating value of a fuel, among other things. For example, the higher heating value (HHV) of a biomass correlates well with the oxygen-to-carbon (O/C) ratio, reducing from 38 to about 15 MJ/kg while the O/C ratio increases from 0.1 to 0.7. When the hydrogen-to-carbon (H/C) ratio increases, the effective heating value of the fuel reduces. The atomic ratio is based on the hydrogen, oxygen, and carbon content of the fuel.

The figure below (Figure 3-1), plots the atomic ratios (H/C) against (O/C) on a dry ash free basis for all fuels, from carbon-rich anthracite to carbon-deficient woody biomass.

This plot, known as "Van Krevelen diagram", shows that biomass has much higher ratios of H/C and O/C than fossil fuel. For a large range of biomass, the H/C ratio might be expressed as a linear function of the (O/C) ratio.
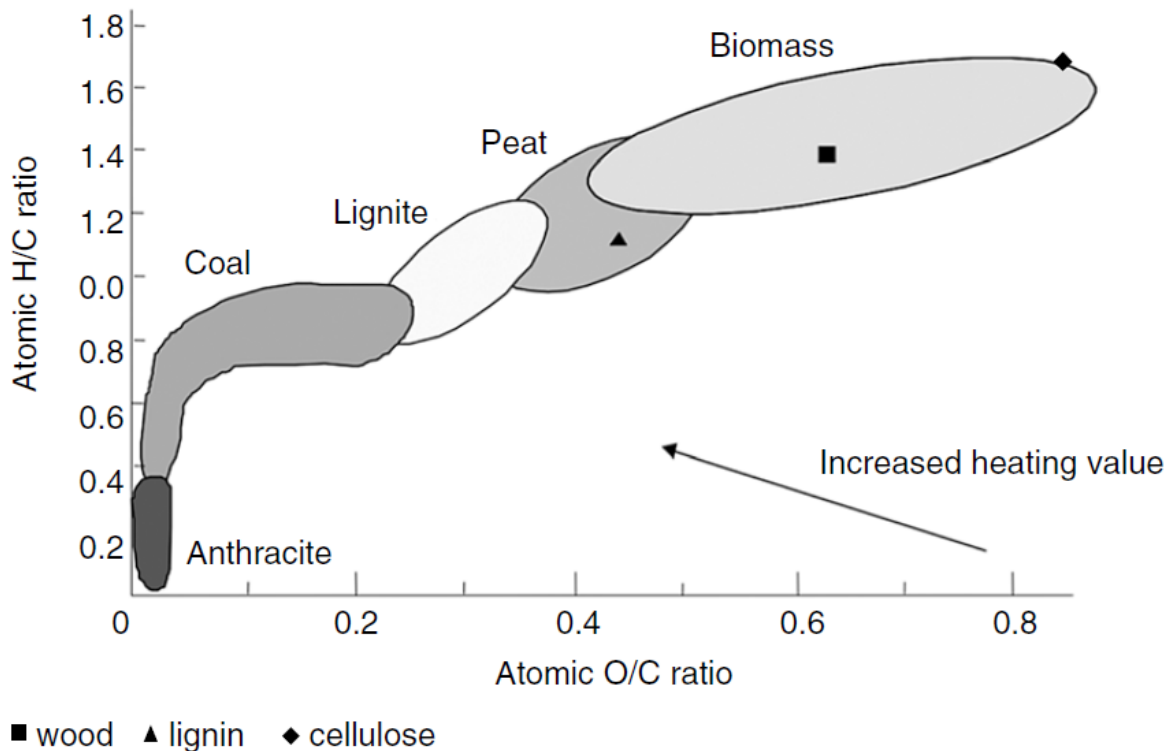
Figure 3-1: Van Krevelen diagram

Fresh plant biomass like leaves has very low heating values because of its high H/C and O/C ratios. The atomic ratio of a fuel decreases as its geological age increases, which means that the older the fuel, the higher its energy content.

Anthracite, for example, a fossil fuel geologically formed over many thousands of years, has a very high heating value. Its lower H/C ratio gives higher heat, but the carbon intensity or the CO_2 emission from its combustion is high.

Among all hydrocarbon fuels biomass is highest in oxygen content. Oxygen, unfortunately, does not make any useful contribution to heating value and makes it difficult to transform the biomass into liquid fuels. The high oxygen and hydrogen content of biomass results in high volatile and liquid yields, respectively. High

oxygen consumes a part of the hydrogen in the biomass, producing less beneficial water, and thus the high H/C content does not translate into high gas yield.

3.2 _Biomass characterization_

Biomass refers to any organic materials that are derived from plants or animals. Biomass also includes gases and liquids recovered from the decomposition of non fossilized and biodegradable organic materials.

As a sustainable and renewable energy resource, biomass is constantly being formed by the interaction of CO_2, air, water, soil, and sunlight with plants and animals. After an organism dies, microorganisms break down biomass into elementary constituent parts like H_2O, CO_2, and its potential energy.

Because the carbon dioxide, a biomass releases through the action of microorganisms or combustion was absorbed by it in the recent past, biomass combustion does not increase the total CO_2 inventory of the Earth. It is thus called greenhouse gas neutral or GHG neutral. Biomass includes only living and recently dead biological species that can be used as fuel or in chemical production. Botanical biomass is formed through conversion of carbon dioxide (CO_2) in the atmosphere into carbohydrate by the sun's energy in the presence of chlorophyll and water. Biological species grow by consuming botanical or other biological species. Plants absorb solar energy in a process called photosynthesis (Figure 3-2).
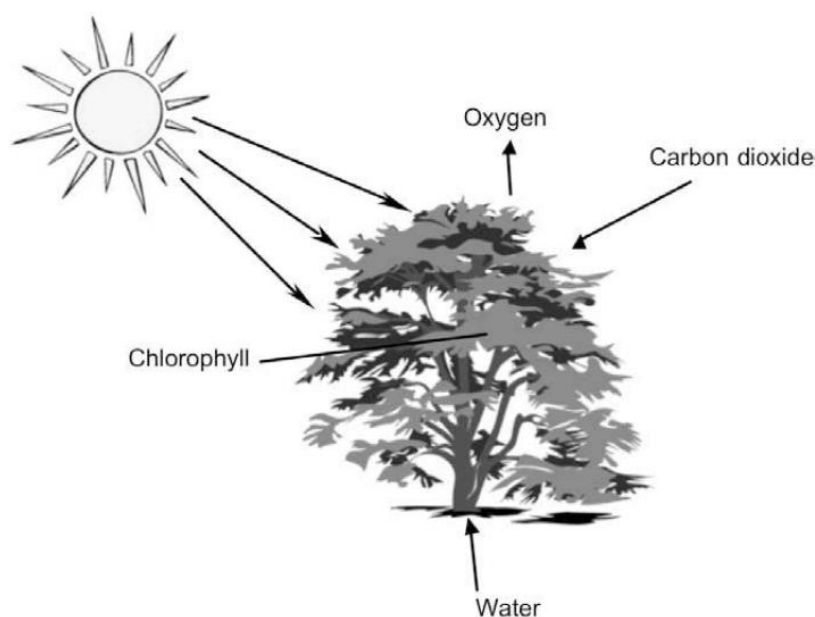

Figure 3-2: Biomass growth.

3.2.1 Structure of biomass

Biomass is a complex mixture of organic materials such as carbohydrates, fats, and proteins, along with small amounts of minerals such as sodium, phosphorus, calcium, and iron. The main components of plant biomass are extractives, fiber or cell wall components, and ash.

Extractives: Substances present in vegetable or animal tissue that can be separated by successive treatment with solvents and recovered by evaporation of the solution. They include protein, oil, starch, sugar, and so on.

Cell wall: Provides structural strength to the plant, allowing it to stand tall above the ground without support. A typical cell wall is made of carbohydrates and lignin. Carbohydrates are mainly cellulose or hemicellulose fibers, which impart strength to the plant structure; the lignin holds the fibers together.
These constituents vary with plant type. Some plants, such as corn, soybeans, and potatoes, also store starch (another carbohydrate polymer) and fats as sources of energy, mainly in seeds and roots.

Ash: The inorganic component of the biomass. Wood and its residues are the dominant form of the biomass resource base.
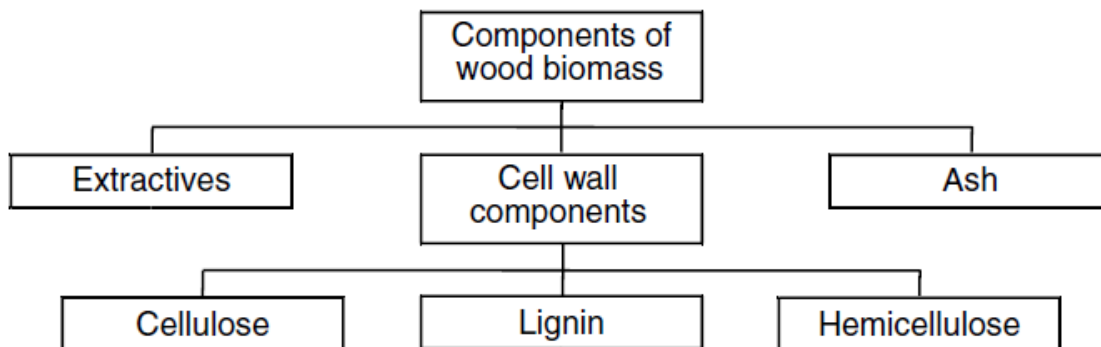

Figure 3-3: Major constituents of a woody biomass.

3.2.2 Constituents of biomass cells

The polymeric composition of the cell walls and other constituents of a biomass vary widely, but they are essentially made of three major polymers: cellulose, hemicellulose, and lignin.

Cellulose

Cellulose, the most common organic compound on Earth, is the primary structural component of cell walls in biomass. Its amount varies from 90% (by weight) in cotton to 33% for most other plants.

Represented by the generic formula $(C6H10O5)n$, cellulose is a long chain polymer with a high degree of polymerization and a large molecular weight. It has a crystalline structure of thousands of units, which are made up of many glucose molecules. This structure gives it high strength, permitting it to provide the skeletal structure of most terrestrial biomass. Cellulose is primarily composed of d-glucose, which is made of six carbons or hexose sugars (Figure 3-4).

Cellulose is highly insoluble and, though a carbohydrate, is not digestible by humans. It is a dominant component of wood, making up about 40 to 44% by dry weight.
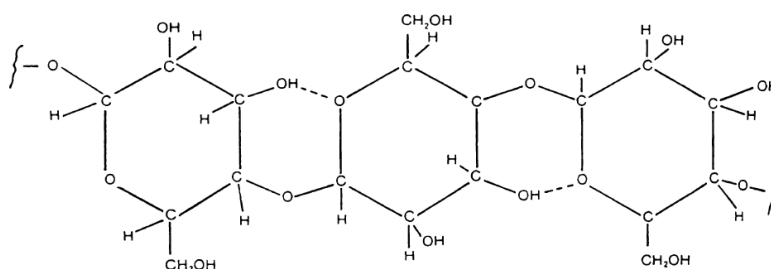
Figure 3-4: Molecular structure of cellulose.

Hemicellulose

Hemicellulose is another constituent of the cell walls of a plant. While cellulose is of a crystalline, strong structure that is resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength.

It is a group of carbohydrates with a branched chain structure and a lower degree of polymerization (between 100–200), and may be represented by the generic formula $(C5H8O4)n$. Figure 3-5 shows the molecular arrangement of a typical hemicellulose molecule, xilan.

There is significant variation in the composition and structure of hemicellulose among different biomass. Most hemicelluloses, however, contain some simple sugar residues like d-xylose (the most common), d-glucose, d-galactose, l-ababinose, d-glucurnoic acid, and d-mannose. These typically contain 50 to 200 units in their branched structures.

Hemicellulose tends to yield more gases and less tar than cellulose. It is soluble in weak alkaline solutions and is easily hydrolyzed by dilute acid or base.

It constitutes about 20 to 30% of the dry weight of most wood.

Figure 3-5: Molecular structure of a typical hemicellulose, xylan.

Lignin

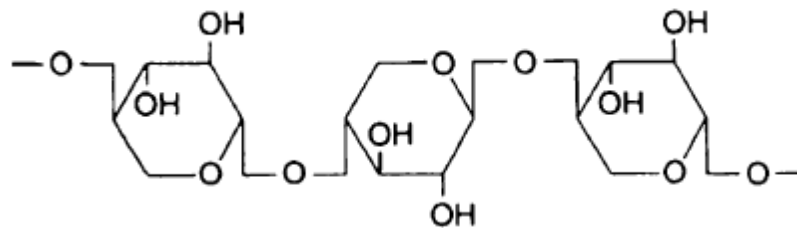Lignin is a complex highly branched polymer of phenylpropane and is an integral part of the secondary cell walls of plants. It is primarily a three-dimensional polymer of 4-propenyl phenol, 4-propenyl-2-methoxy phenol, and 4-propenyl-2.5-dimethoxyl phenol. It is one of the most abundant organic polymers on Earth (exceeded only by cellulose). It is the third important constituent of the cell walls of woody biomass.

Lignin is the cementing agent for cellulose fibers holding adjacent cells together. The dominant monomeric units in the polymers are benzene rings.
It is similar to the glue in a cardboard box, which is made by gluing together papers in special fashion. The middle lamella, which is composed primarily of lignin, glues together adjacent cells or tracheids.
Lignin is highly insoluble, even in sulphuric acid. A typical hardwood contains about 18 to 25%, while a softwood contains 25 to 35% by dry weight. In addition, lignin is further detailed as a combination of three reference components with different methoxylation degree, LIGH, LIGO, and LIGC, which are richer in hydrogen, oxygen and carbon, respectively (Figure 3-6).
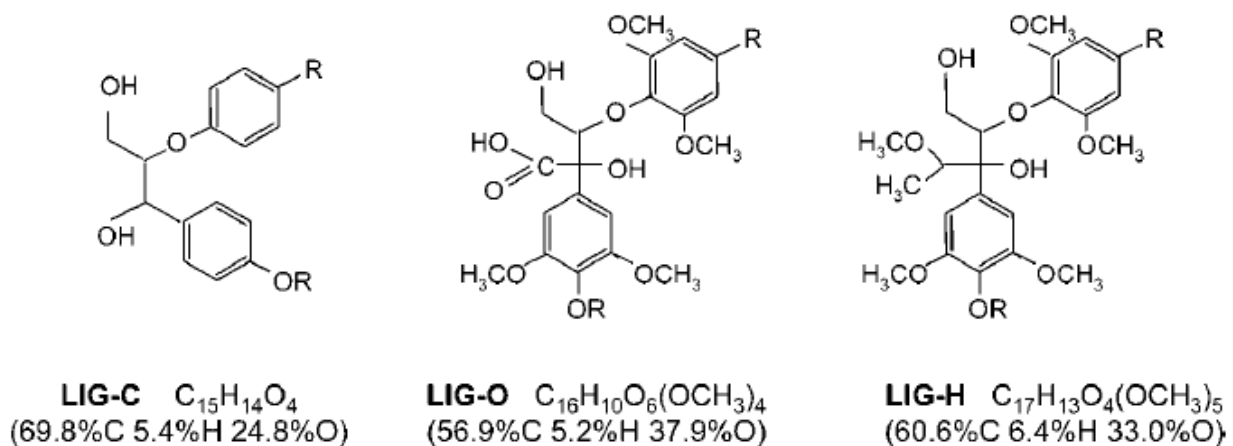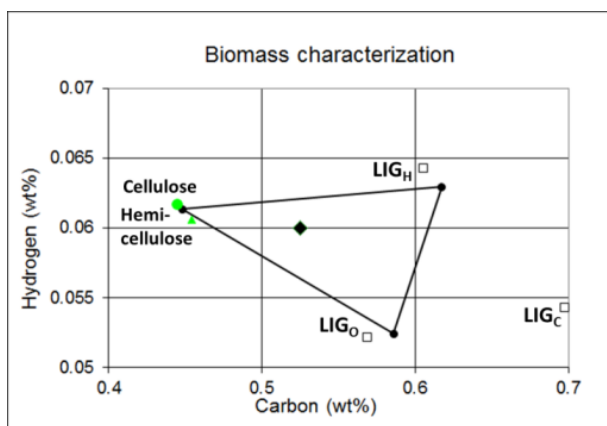

LIG-C $C_{15}H_{14}O_4$
(69.8%C 5.4%H 24.8%O)

LIG-O $C_{16}H_{10}O_6(OCH_3)_4$
(56.9%C 5.2%H 37.9%O)

LIG-H $C_{17}H_{13}O_4(OCH_3)_5$
(60.6%C 6.4%H 33.0%O)

Figure 3-6: Structures of LIG-C, LIG-O, and LIG-H.

The biochemical analysis of biomasses provides information on cellulose, hemicellulose, and lignin content together with extractives and ash. Phenolic compounds, alkaloids, nonproteic amino-acids, terpenes, and fatty acids are just a few examples of the species involved in this fraction.

The characterization of a biomass is then reduced to the definition of the composition of its reference components.

When the biochemical analysis is available, it is possible to derive the proper biomass composition details in terms of ash, cellulose, hemicellulose, and lignin content. If only elemental analysis in terms of C/H/O content is accessible, then a suitable combination of the reference species can be derived by atomic balances.

Weight fraction of reference components:

(daf basis)

Cellulose	$-C_6H_{10}O_5-$	0.329
Hemicellulose	$-C_5H_8O_4-$	0.179
LIGH	$-C_{22}H_{28}O_9-$	0.253
LIGO	$-C_{20}H_{22}O_{10}-$	0.175
LIGC	$-C_{15}H_{14}O_4-$	0.064

Figure 3-7: Biomass characterization using three reference components.

With the diagram expressed above (Figure 3-7), it is possible to reproduce the exact composition of the biomass feedstock entering the gasifier.

The C/H plot of Figure 3-7 is thus divided in three triangles, and each coal lies inside one of them. Any individual biomass is then considered as a simple linear combination of the three closest reference compounds, and its devolatilization is considered a straightforward weighted combination of the pyrolysis of the reference biomass components.

3.3 *Kinetic models of biomass thermochemical conversion*

Beside heat and mass transport processes, a mechanistic kinetic model of biomass gasification and pyrolysis should focus on three different facets of the overall process:

- (i) biomass pyrolysis or devolatilization, that is, the decomposition of the solid into permanent gases, condensable vapors (tars) and solid residue (char);

- (ii) secondary gas phase reactions of the released gas and tar species;

- (iii) char gasification and combustion, that is, the overall set of heterogeneous reactions of the gases (steam, O2, etc.) with the solid residue.

During the gasification process, the chemical evolution of the system has been described by means of detailed kinetic schemes for solid fuel devolatilization and pyrolysis, residual solid (char) gasification with steam, CO2 and oxygen, and finally, secondary gas phase reactions.

At first, the solid fuel, either biomass or coal, is heated up until devolatilization and pyrolysis occur. During this first stage the solid fuel is progressively converted to three main product groups: light gases, tar species and a residual solid, mainly composed by ashes and char, with a residual content of volatiles trapped within the porous matrix. For both kinetic schemes, the solid feedstock is characterized as a mixture of reference lumped species.
After this first step, the carbonaceous residual solid is partially subject to gas-solid gasification reactions with steam and oxygen, with the preferential production of carbon monoxide and hydrogen. Moreover, volatiles, especially heavy tar species, as soon as are released in the gas phase, are cracked to lighter gaseous species through gas-phase secondary reactions.

A detailed kinetic scheme has been adopted, the POLIMI_1310, available on the *creckmodeling.chem.polimi.it* website. This kinetic scheme (Figure 3-8), including the pyrolysis and combustion of tar and oxygenated species and successive reactions of aromatic and polycyclic-aromatic species, involves more than 450 species and about 15,000 reactions.
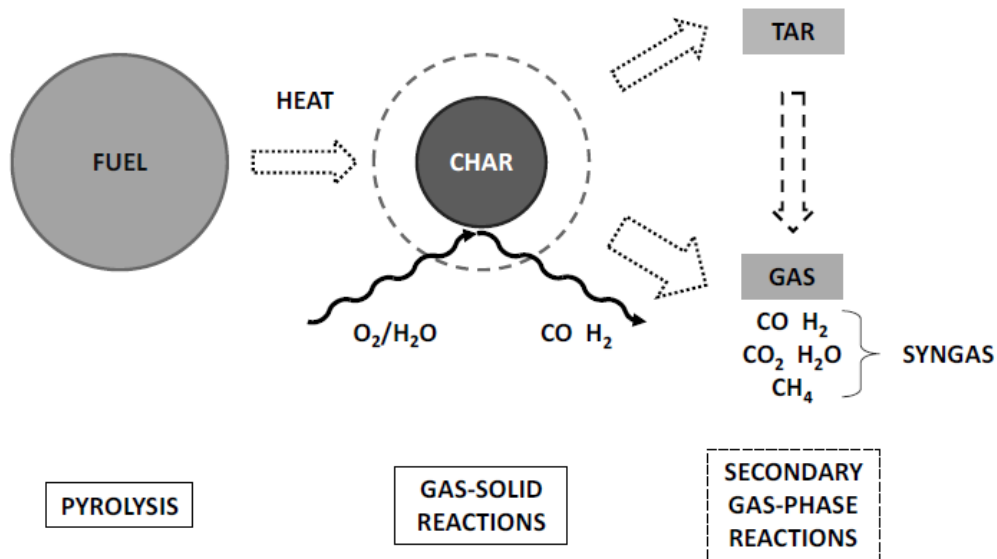
Figure 3-8: Solid fuel devolatilization and gasification.

3.3.1 Multi-step kinetic model of biomass pyrolysis

Pyrolysis of cellulose

The pyrolysis of reference components, presented and described in this paragraph, consists of a limited number of devolatilization reactions, which are applied to predict not only the rate of weight loss, but also the expected composition of species released in the gas and vapor phases.

The proposed kinetic scheme adopts both grouping of similar components and lumping of reactions as a compromise capable of satisfactorily describing a variety of biomasses. However, a flexibility in the level of simplification is maintained for the aim of a better comparisons between model predictions and experimental measurements.

Figure 3-9: Multistep lumped mechanism of cellulose pyrolysis.

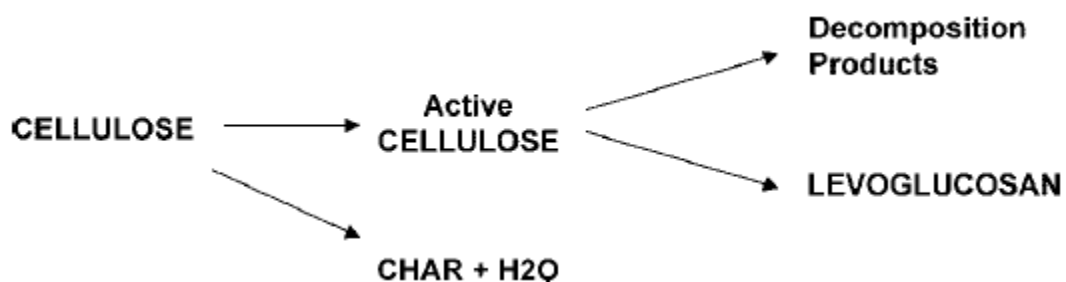Figure 3-9 schematically shows the pyrolysis of cellulose, a regular polymer of glucosidic monomers $(C_6H_{10}O_5)n$. This mechanism refers to the initial formation of an intermediate active cellulose (CELLA), as suggested by several authors. Levoglucosan (LVG: 1,2-anhydro-α-D-glucopyranose, $C_6H_{10}O_5$) is then formed from cellulose degradation through a chain-end depolymerization reaction.

The lumped species HAA is supposed to also contain the isomer component acetic acid. The char residue is usually below 5%, depending on operating conditions. Levoglucosan is always a major product and mainly prevails at low temperatures; its successive vaporization, at about 260 °C, might be a rate-limiting step. The higher the temperature is, the greater the importance and the formation of the remaining degradation products. Among them it is worth mentioning HAA, which becomes significant at temperatures higher than 450-500 °C. Mass transport resistances in the solid matrix and in the melt phase also increase the relative importance of the successive decomposition reactions and char formation.

Pyrolysis of hemicellulose and lignin

Similarly to cellulose, the hemicellulose and lignin pyrolysis processes were investigated. The same approach and methodologies adopted for cellulose were also applied for these components.

Decomposition of hemicellulose (HCE) starts at a temperature lower than that at which cellulose does and forms a 20-25% residue that slowly releases H_2 and CO at higher temperatures.

Lignins are complex racemic polymers mainly derived from hydroxycinnamyl alcohol monomers with different degree of methoxylation. The complex chemical structure of lignins requires the adoption of different reference components: this means that the lignins are approximated, case to case, by a mixture of reference components. They are identified by LIGC, LIG-O, and LIG-H, which recall their characteristic of being richer in carbon, oxygen, and hydrogen, respectively. All the reference components are based on the typical O-4 skeleton.
The reference components decompose, release gases, and form intermediate components that are involved in substitutive additions and cross-linking reactions with a progressive charification of the solid residue. Phenol and phenoxy species become typical products of lignin decomposition.

3.3.2 Secondary reactions in the gas phase

The volatile components may undergo successive decomposition or combustion reactions in the surrounding gas phase. The description of the involved reactions was obtained by enlarging an existing kinetic scheme for the pyrolysis and oxidation reaction of hydrocarbon species.

Typically, they are initiation and H abstraction reactions of these species and their successive decomposition reactions until the formation of intermediate products already present in the existing kinetic scheme.

3.4 *Coal characterization*

Coal combustion and gasification are complex processes, which involve many interactions of chemical and physical phenomena. The coal pyrolysis and devolatilization is always the first step and plays a fundamental role. Coal rank and properties significantly influence heat and mass transfer as well as reaction rates.
Therefore, times, yields, and pollutant emissions depend on the original source. The key to understanding the phenomena occurring inside the process units thus lies first in the characterization of the initial coal and then in describing the primary devolatilization phase and the released products.

Coal consists of aromatic clusters with several bridges, side chains and functional groups on peripheral positions. Coal composition and structure strongly differ from coal to coal; low rank coals contain large amounts of oxygen, longer side chains and smaller aromatic clusters. Increasing the rank (i.e., increasing the age of the coal) oxygen content decreases, side chains become unlikely and shorter while the aromatic clusters gradually increase evolving towards graphite like structures. The pyrolysis and devolatilization process is similar to the aging process: all the coals become progressively more aromatic, the carbon content increases and the apparent rank of the char or solid residue also increases.

The description of coal pyrolysis process first requires the characterization of the initial structure in terms of atoms, bonds and average or lumped chemical structure. The coal devolatilization model discussed in this work simply refers to the elemental analysis of the coal, in the usual form C, H, O, S, N and ashes. S and N are usually present in a relatively small amount and they do not affect too much the overall devolatilization process.

Ashes, whose composition and weight are strongly dependent on the coal grade and origin, do not affect coal devolatilization process. They are treated as inert and they remain in the solid residue. Catalytic effects of the different metals contained in the ashes are not considered.

As a first step of the coal characterization method, the elemental analysis of the coal is corrected and simply normalized to the C, H and O content, on dry, ash (and S, N) free basis.
Carbon content is always higher than 60–65 wt%, while hydrogen content is usually lower than 7 wt%. The rank of the coal increases with the rising carbon content, moving from the low rank of lignite, to average values for bituminous coals, up to the high rank and high carbon content of anthracite.
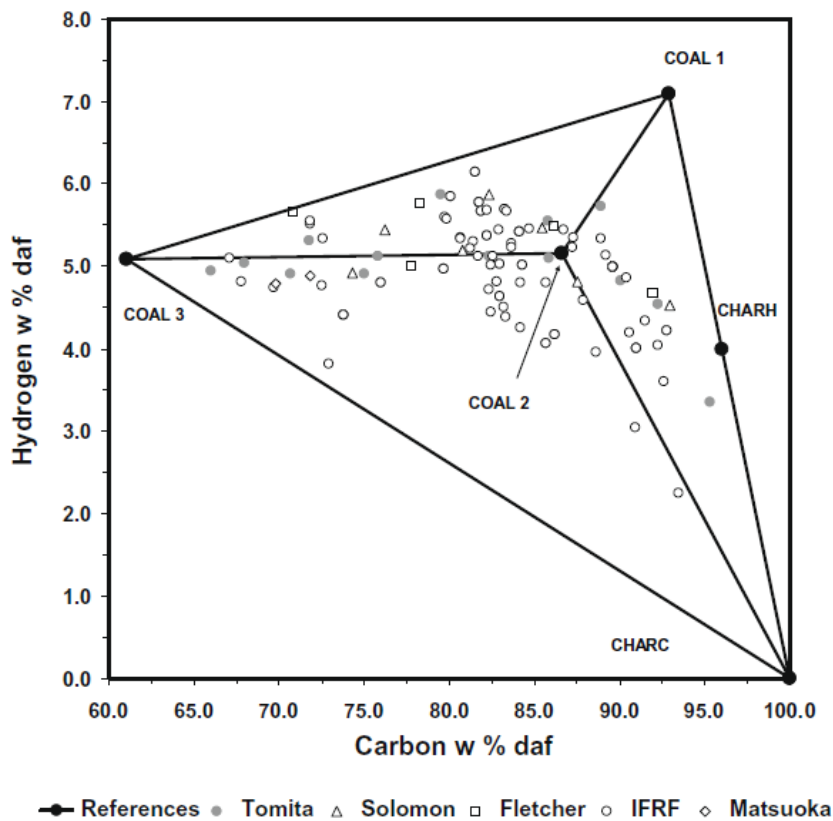
Figure 3-10: Diagram of reference coal component.

All the coals reported in Figure 3-10 can be included in a triangle whose vertexes are pure carbon (CHARC), and two reference coals: a lignite with high oxygen content (COAL3) and a reference coal without oxygen and particularly rich in hydrogen (COAL1). A third reference coal (COAL2) has been selected in the middle of in this triangle, close to a great number of bituminous coals.

These reference coals can be described by three lumped or equivalent monomer structures which stand for reference configurations, saving the elemental C/H/O composition.
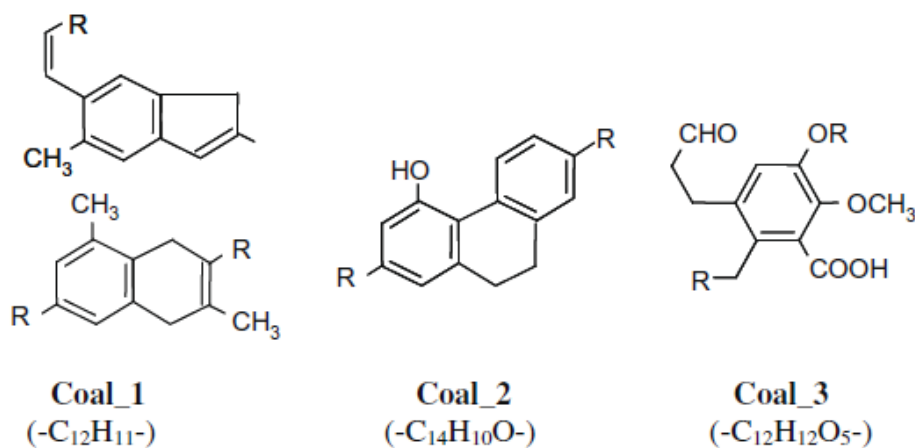

Figure 3-11: Reference coals and reference monomer structures.

Figure 3-11 sketches the average structures of the reference monomers which represents COAL1 (–C12H11–), COAL2 (–C14H10O–) and COAL3 (–C12H12O5–), respectively. COAL1 is indeed considered as a 50/50 mol mixture of (–C12H10–) and (–C12H12–). The multi-step kinetic model discussed in next paragraph will describe the pyrolysis of these reference coals.

The C/H plot of Figure 10 is thus divided in three triangles, and each coal lies inside one of them. Any individual coal is then considered as a simple linear combination of the three closest reference coals, and its devolatilization is considered a straightforward weighted combination of the pyrolysis of the reference coals.

3.5 *Kinetic models of coal thermochemical conversion*

3.5.1 *Multi-step kinetic model of coal pyrolysis*

As already mentioned, all the coals of possible interest are simply considered as a linear combination of the reference coals and the same linear combination applies to devolatilization process and released products.

A multi-step devolatilization mechanism is assumed for the reference coals, with different product distributions and different kinetic parameters.

Initially the coal forms a metaplastic phase, then, with different mechanisms at low and high temperatures, gas and tar species are released (Figure 3-12).
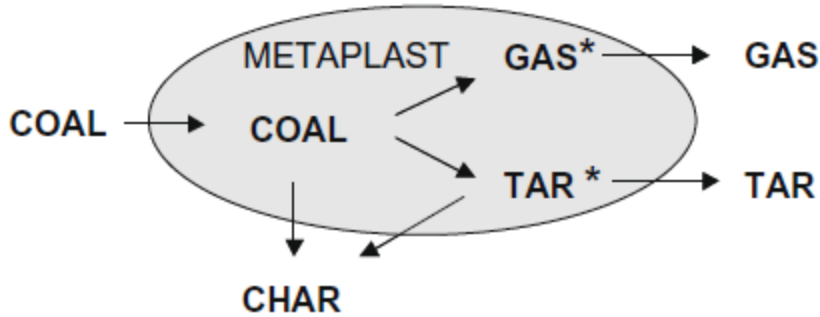
Figure 3-12: Coal decomposition and devolatilization mechanism.

At low temperatures (or low heating rates), the reference coals initially form char and volatile species (tar* and gas*), which still are in the condensed phase. The apparent activation energy of this thermal decomposition is of about 33,000–40,000 cal/mol. The tar* in the condensed phase can be released with a proper kinetic rate or can interact with CHAR in cross-linking and reticulation reactions, which increase the residual char and produce further gas.

The tar release reactions account for gas–liquid equilibrium in a simplified form which does not explicitly include the tar molecular weight. At high temperatures (or high heating rates) the reference coals more directly decompose to gas and tar, and always form more aromatic char structures.

Lignitic coals (COAL3) first move through an activate state in the condensed phase (COAL_ 3) and then undergo a real decomposition reaction. The activation energy of the high temperature decomposition reactions of different coals is in the range of 65,000–70,000 cal/mol. The transition temperature, where gradually high temperature decomposition prevails, is about 800 K for COAL2 and COAL3 and becomes higher than 1200 K for COAL1, because of its aromatic structure.

The description of gas species is simplified. As observed in the literature, light hydrocarbon gases are H2, CH4 and a mixture of C2–C5 hydrocarbons (C2–5), here lumped as a single pseudo-components with the equivalent formula (–CH2–). Experimental comparisons are only limited to ethylene, here considered as 15–20% of this mixture. Main oxygenated products are CO, CO2 and H2O. Other oxygenated species are present at lower concentrations. Tar species from the different coals are grouped in pseudo-components, whose elemental composition reflects that of the corresponding initial coal (Figure 3-13).
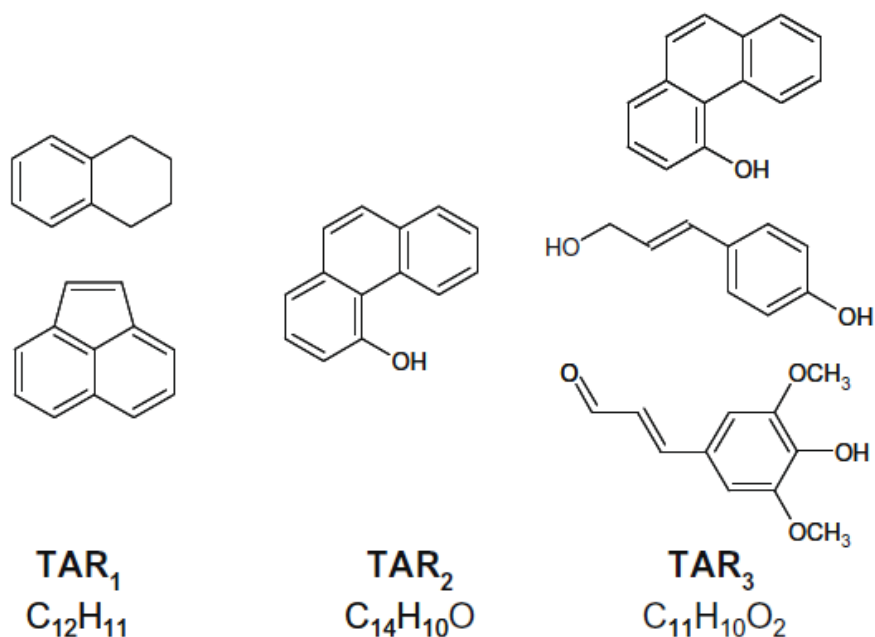
Figure 3-13: Reference lumped structures of tar components.

BTX fraction is also accounted in terms of a single lumped component, standing for a molar B:T:X ratio 6:3:1, with the equivalent formula C6.5H7.

In order to describe the devolatilization rate and the wide and spread release of gas and tar species, mainly at low temperatures, several gas and tar species are considered as pseudo-species trapped in the condensed phase and/or in the solid matrix which are prone to be released as gas or tar components, with suitable kinetic rates.

Pyrolysis studies carried out at low heating rate show that the overall release of hydrogen and methane, but also of CO and permanent gases, seems the result of several reactions.

As already mentioned, at high temperatures the direct release of tar species prevails on cross-linking and reticulation reactions. The oxygenated coals that undergo early cross-linking are less fluid, produce less tar with a lower molecular weight compared with coals that do not experience early cross-linking.

The yield of the fast released CO2 is a factor controlling the thermoplastic behavior of coals. On these bases, the formation of tar components from the oxygenated reference COAL3 is very limited at low temperatures, while it becomes relevant only at high temperatures with an immediate release of CO2 and H2O.

Tar release from the bituminous COAL2 is less affected by the different temperatures, even if a thermosetting effect due to the released CO2 is accounted for in the kinetic scheme. A direct interaction between CO2 and TAR2 promotes a further cross-linking with char formation and gas release.

Finally, in order to account for a possible annealing effect, the solid carbon structure is described by using two different equivalent or reference species. The reference coals can either form a partially hydrogenated char (CHARH, brute formula C2H, which stands for a coronene-like structure) or the more graphitic and completely carbonaceous structure (CHARC, brute formula C).

The description of the gas-phase reactions is obtained by using an already available detailed kinetic scheme of pyrolysis and oxidation of hydrocarbon species. Due to its modular and mechanistic nature, the inclusion of the new tar species was performed by adding the primary propagation reactions of these new compounds down to the formation of components already contained in the kinetic scheme (Figure 3-14).
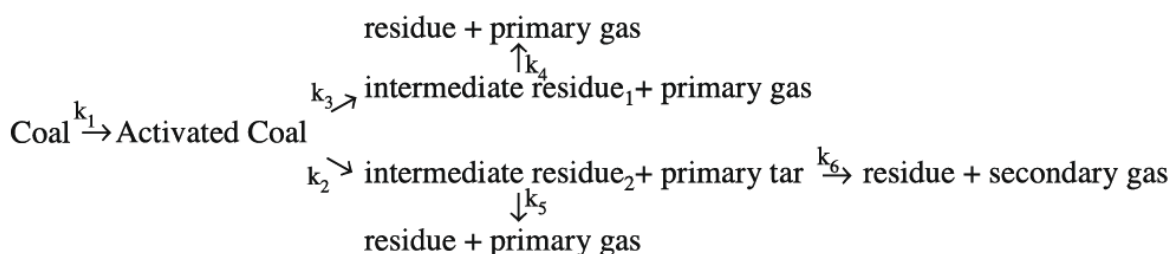
$$\text{Coal} \xrightarrow{k_1} \text{Activated Coal} \begin{cases} \xrightarrow{k_3} \text{intermediate residue}_1 + \text{primary gas} \xrightarrow{k_4} \text{residue + primary gas} \\ \xrightarrow{k_2} \text{intermediate residue}_2 + \text{primary tar} \xrightarrow{k_6} \text{residue + secondary gas} \\ \xrightarrow{k_5} \text{residue + primary gas} \end{cases}$$

Figure 3-14: Kinetic scheme of coal devolatilization and pyrolysis.

The whole kinetic scheme, constituted by more than 100 molecular and radical species involved in several thousands elementary and lumped gas phase reactions, with relating thermodynamic properties is available online in CHEMKIN format at the web site: (www.chem.polimi.it/CRECKModeling/).

3.5.2 Secondary reactions in the gas phase

The effect of secondary gas-phase reactions is to convert tar fraction into gases and heavy components. Carbon content in tar fraction increases up to 86%, further improving the agreement with experimental measurements. These results, in terms of reactivity, gas production and progressive formation of heavy PAH and soot precursors are only scarcely affected by the specific hypothesis on the different internal de-lumped distributions of tar components.

Light gases obtained from this gas phase decomposition easily sum up to 10% of the initial mass of tars. Tar reactivity affects from one side the proper evaluation of volatile species in the experiments but also the molecular weight distribution of tar fraction.

4   Gasification reactors

4.1 *Introduction*

Gasifiers are classified mainly on the basis of their gas–solid contacting mode and gasifying medium. Based on the gas–solid contacting mode, gasifiers are broadly divided into three principal types: (1) fixed or moving bed, (2) fluidized bed, and (3) entrained flow.
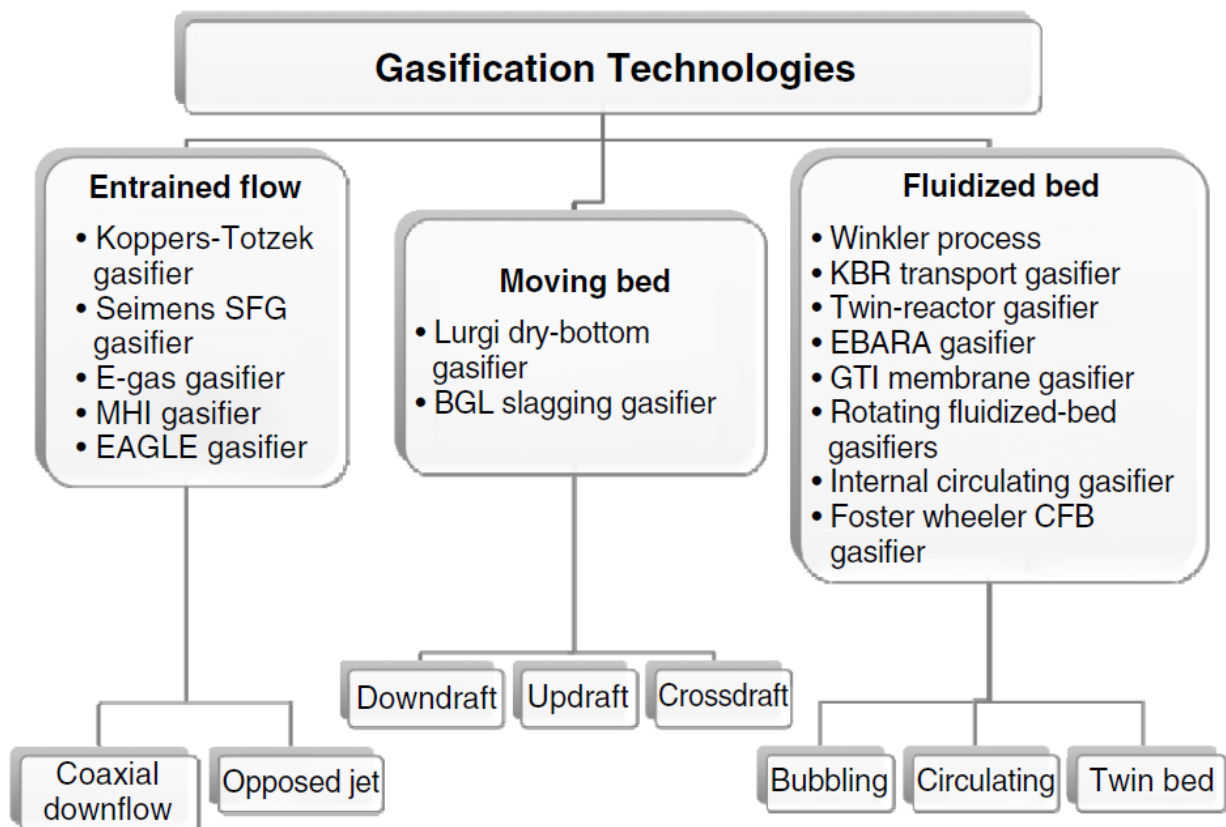Each is further subdivided into specific types as shown in Figure 4-1.

Figure 4-1: Gasification technologies and their commercial suppliers.

One gasifier type is not necessarily suitable for the full range of gasifier capacities. There is an appropriate range of application for each. For example, the moving-bed (updraft and downdraft) type is used for smaller units (10 kWth– 10 MWth); the fluidized-bed type is more appropriate for intermediate units (5 MWth–100 MWth); entrained-flow reactors are used for large-capacity units (>50 MWth).
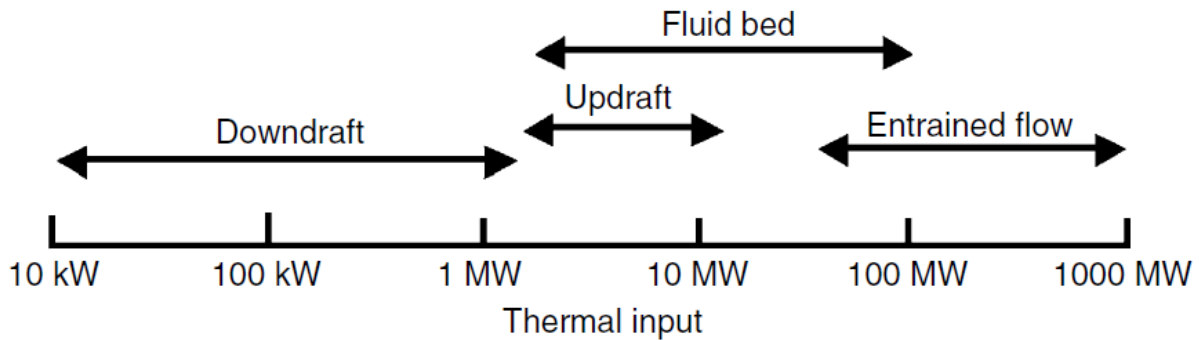

Figure 4-2: Range of applicability for biomass gasifier types.

Figure 4-2 shows the overlapped range of application for different types of gasifiers. Crossdraft gasifiers are for the smallest size while entrained flow are the largest size gasifiers.

4.2 *Fixed bed gasifiers*

In entrained-flow and fluidized-bed gasifiers, the gasifying medium conveys the fuel particles through the reactor, but in a fixed-bed (also known as moving-bed) gasifier the fuel is supported on a grate (hence its name). This type is also called moving-bed because the fuel moves down in the gasifier as a plug.

Fixed-bed gasifiers can be built inexpensively in small sizes, which is one of their major attractions. For this reason, large numbers of small-scale moving-bed biomass gasifiers are in use around the world.
Both mixing and heat transfer within the moving (fixed) bed are rather poor, which makes it difficult to achieve uniform distribution of fuel, temperature, and gas composition across the cross-section of the gasifier. Thus, fuels that are prone to agglomeration can potentially form agglomerates during gasification. This is why fixed-bed gasifiers are not very effective for biomass fuels or coal with a high caking index in large-capacity units.
There are three main types of fixed- or moving-bed gasifier: (1) updraft, (2) downdraft, and (3) crossdraft.

4.2.1 Updraft gasifiers

An updraft gasifier is one of the oldest and simplest of all designs. Here, the gasification medium (air, oxygen, or steam) travels upward while the bed of fuel moves downward, and thus the gas and solids are in countercurrent mode. The product gas leaves from the top as shown in Figure 4-3.
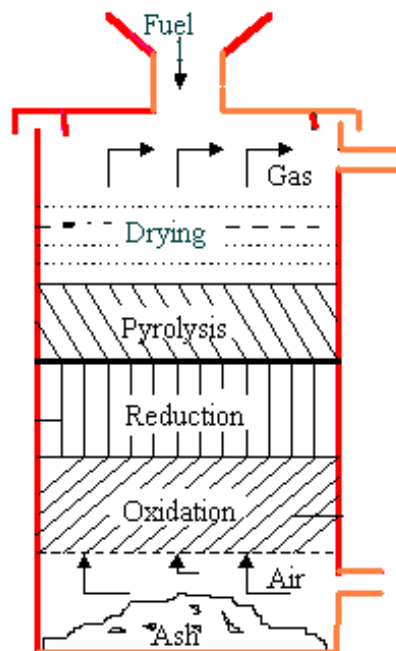

Figure 4-3: Updraft gasifier.

The gasifying medium enters the bed through a grate or a distributor, where it meets with the hot bed of ash. The ash drops through the grate, which is often made moving (rotating or reciprocating), especially in large units to facilitate ash discharge.

Updraft gasifiers are suitable for high-ash (up to 25%), high-moisture (up to 60%) biomass. They are also suitable for low-volatile fuels such as charcoal.

Tar production is very high (30–150 g/nm^3) in an updraft gasifier, which makes it unsuitable for high-volatility fuels.

On the other hand, as a countercurrent unit, an updraft gasifier utilizes combustion heat very effectively and achieves high cold-gas efficiency. Therefore, it is more suitable for direct firing, where the gas produced is burnt in a furnace or boiler with no cleaning or cooling required. Since the gas is not fired in an engine or stored, the tar produced does not have to be cleaned. Updraft gasifiers find commercial use in small units like cooking stoves in villages and in large units like South African Synthetic Oils (SASOL) for production of gasoline from coal.

4.2.2 Downdraft gasifiers

A downdraft gasifier is a co-current reactor where air enters the gasifier at a certain height below the top. The product gas flows downward (giving the name downdraft) and leaves through a bed of hot ash (Figure 4-4).
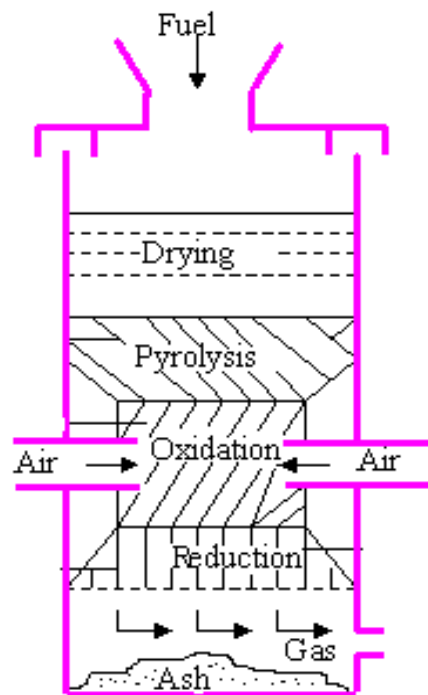

Figure 4-4: Downdraft gasifier.

Since it passes through the high-temperature zone of hot ash, the tar in the product gas finds favorable conditions for cracking. For this reason, a downdraft gasifier, of all types, has the lowest tar production rate.

Air from a set of nozzles, set around the gasifier's periphery, flows downward and meets with pyrolyzed char particles, developing a combustion zone (zone III) of about 1200 to 1400 °C.
Then the gas descends further through the bed of hot char particles (zone IV), gasifying them. The ash produced leaves with the gas, dropping off at the bottom of the reactor.

The first, or uppermost, zone receives raw fuel from the top that is dried in air drawn through the first zone. The second zone receives heat from the third zone principally by thermal conduction.

During its journey through the first zone, the biomass heats up (zone I). Above 350 °C, it undergoes pyrolysis, breaking down into charcoal, non-condensable gases (CO, H_2, CH_4, CO_2, and H_2O), and tar vapors (condensable gases).

The pyrolysis product in zone II receives only a limited supply of air from below and burns in a fuel-rich flame. This is called flaming pyrolysis.

Most of the tar and char produced burn in zone III, where they generate heat for pyrolysis and subsequent endothermic gasification reactions.

Zone III contains ash and pyrolyzed char produced in zone II. While passing over the char, hot gases containing CO_2 and H_2O undergo steam gasification and Boudouard reactions, producing CO and H_2.

The temperature of the downflowing gas reduces modestly, owing to the endothermic gasification reactions, but it is still above 700 °C.

Downdraft gasifiers work well with internal-combustion engines. The engine suction draws air through the bed of fuel, and gas is produced at the end.

Low tar content (0.015–3 g/nm^3) in the product gas is another motivation for their use with internal-combustion engines. A downdraft gasifier requires a shorter time (20–30 minutes) to ignite and bring the plant up to working temperature compared to the time required by an updraft gasifier.

4.2.3   Crossdraft gasifiers

A crossdraft gasifier is a co-current moving-bed reactor, in which the fuel is fed from the top and air is injected through a nozzle from the side (Figure 4-5).
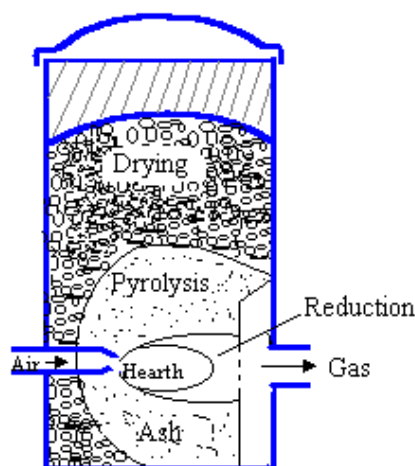

Figure 4-5: Crossdraft gasifier.

It is primarily used for gasification of charcoal with very low ash content. Unlike the downdraft and updraft types, it releases the product from its side wall opposite to

the entry point of the air for gasification. Because of this configuration, the design is also referred to as sidedraft.

High-velocity air enters the gasifier through a nozzle set at a certain height above the grate. Excess oxygen in front of the nozzles facilitates combustion (oxidation) of part of the char, creating a very-high-temperature (>1500 °C) zone.

The remaining char is then gasified to CO downstream in the next zone (Figure 5). The product gas exits from the opposite side of the gasifier. Heat from the combustion zone is conducted around the pyrolysis zone, so the fresh biomass is pyrolyzed while passing through it.

This type of gasifier is generally used in small-scale biomass units. One of its important features is a relatively small reaction zone with low thermal capacity, which gives a faster response time than that of any other moving-bed type.

Moreover, startup time (5–10 minutes) is much shorter than in downdraft and updraft units.

These features allow a sidedraft gasifier to respond well to load changes when used directly to run an engine. Because its tar production is low (0.01–0.1 g/nm^3), a crossdraft gasifier requires a relatively simple gas-cleaning system.

Crossdraft gasifiers can be very light and small (<10 kWe). Since layers of fuel and ash insulate the walls from the high-temperature zone, the gasifier vessel can be constructed of ordinary steel with refractory linings on the nozzle and gas exit zone.

The crossdraft design is less suitable for high-ash or high-tar fuels, but it can handle high-moisture fuels if the top is open so that the moisture can escape.

Particle size should be controlled, as unscreened fuel runs the risk of bridging and channeling. Crossdraft gasifiers work better with charcoal or pyrolyzed fuels.

For unpyrolyzed fuels, the height of the air nozzle above the grate becomes critical.

4.3 *Fluidized-bed gasifiers*

Fluidized-bed gasifiers are noted for their excellent mixing and temperature uniformity. A fluidized bed is made of granular solids, called bed materials that are kept in a semi-suspended condition (fluidized state) by the passage of the gasifying medium through them at the appropriate velocities.

The excellent gas–solid mixing and the large thermal inertia of the bed make this type of gasifier relatively insensitive to the fuel's quality.

Along with this, the temperature uniformity greatly reduces the risk of fuel agglomeration.

The fluidized-bed design has proved to be particularly advantageous for gasification of biomass. Its tar production lies between that for updraft (~50 g/nm^3) and downdraft gasifiers (~1 g/nm^3), with an average value of around 10 g/nm^3.
There are two principal fluidized-bed types: bubbling and circulating.

4.3.1 Bubbling fluidized-bed gasifier

The bubbling fluidized-bed gasifier, developed by Fritz Winkler in 1921, is perhaps the oldest commercial application of fluidized beds; it has been in commercial use for many years for the gasification of coal and biomass (Figure 4-6).
Because they are particularly suitable for medium-size units (<25 MWth), many biomass gasifiers operate on the bubbling fluidized-bed regime.
Depending on operating conditions, bubbling-bed gasifiers can be grouped as low temperature and high-temperature types. They can also operate at atmospheric or elevated pressures.
In the most common type of fluidized bed, biomass crushed to less than 10 mm is fed into a bed of hot materials. These bed materials are fluidized with steam, air, or oxygen, or their combination, depending on the choice of gasification medium.
The ash generated from either the fuel or the inorganic materials associated with it is drained easily from the bottom of the bed. The bed temperature is normally kept below 980 °C for coal and below 900 °C for biomass to avoid ash fusion and consequent agglomeration.
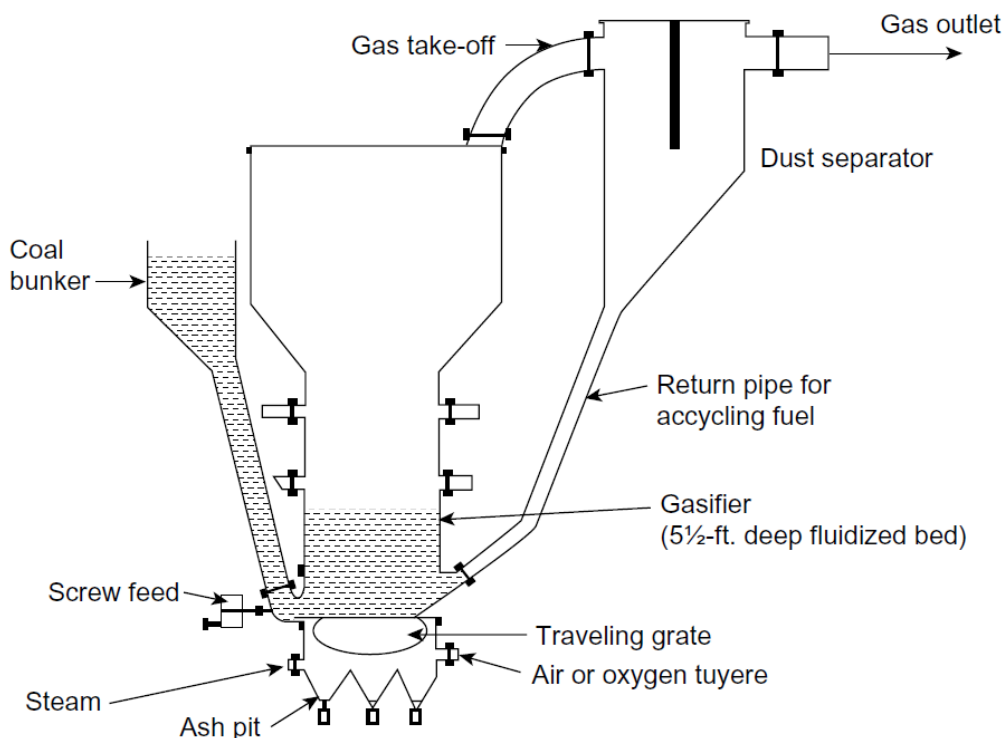

Figure 4-6: Bubbling fluidized-bed gasifier.

The gasifying medium may be supplied in two stages. The first-stage supply is adequate to maintain the fluidized bed at the desired temperature; the second stage supply, added above the bed, converts entrained unreacted char particles and hydrocarbons into useful gas.

High-temperature Winkler (HTW) gasification is an example of high-temperature, high-pressure bubbling fluidized-bed gasification for coal and lignite.

The gasifying medium (steam and oxygen) is introduced into the fluidized bed at different levels as well as above it. The bed is maintained at a pressure of 10 bars while its temperature is maintained at about 800 °C to avoid ash fusion.

The over-bed supply of the gasifying medium raises the local temperature to about 1000 °C to minimize production of methane and other hydrocarbons.

The HTW process produces a better-quality gas compared with the gas that is produced by traditional low-temperature fluidized beds.

4.3.2   Circulating fluidized-bed gasifier

A circulating fluidized-bed (CFB) gasifier has a special appeal for biomass gasification because of the long gas residence time it provides. It is especially suitable for fuels with high volatiles.

A CFB typically comprises a riser, a cyclone, and a solid recycle device. The riser serves as the gasifier reactor (Figure 4-7).

The circulating and bubbling fluidized beds are significantly different in their hydrodynamic. In a CFB, the solids are dispersed all over the tall riser, allowing a long residence time for the gas as well as for the fine particles. The fluidization velocity in a CFB is much higher (3.5–5.5 m/s) than that in a bubbling bed (0.5–1.0 m/s). Also, there is large-scale migration of solids out of the CFB riser. These are captured and continuously returned to the riser's base.

The recycle rate of the solids and the fluidization velocity in the riser are sufficiently high to maintain the riser in a special hydrodynamic condition, known as fast fluidized bed. Depending on the fuel and the application, the riser operates at a temperature of 800 to 1000 °C.

The hot gas from the gasifier passes through a cyclone, which separates most of the solid particles associated with it, and the loop seal returns the particles to the bottom of the gasifier.
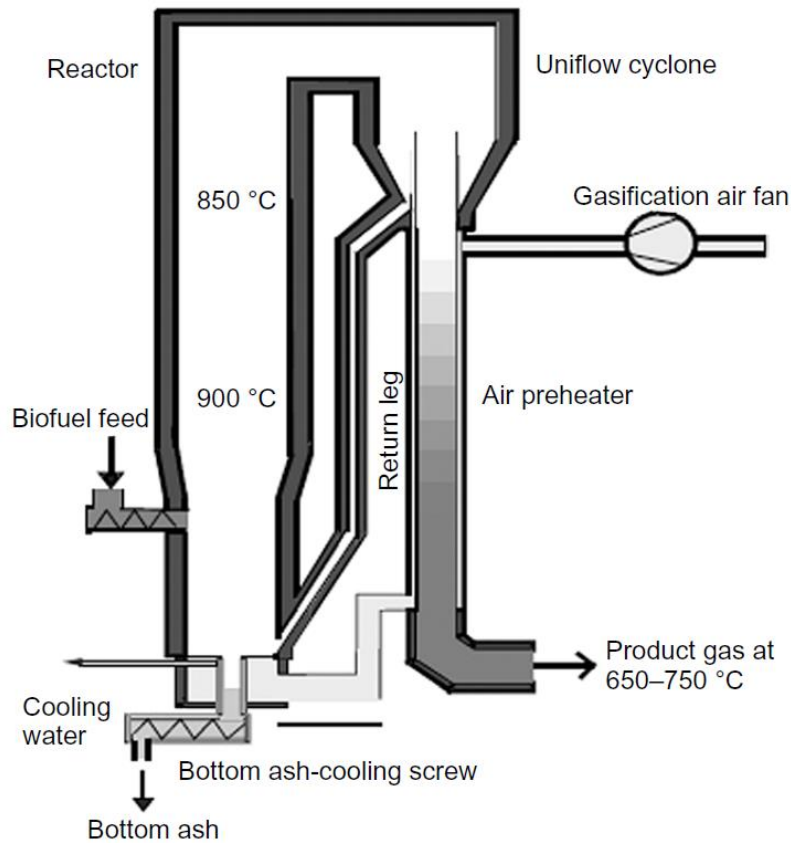
Figure 4-7: Circulating fluidized-bed gasifier.

4.4 *Entrained-flow gasifiers*

Entrained flow is the most successful and widely used gasifier type for large-scale gasification of coal, petroleum coke, and refinery residues. It is ideally suited to most types of coal except low-rank coal, which, like lignite and biomass, is not attractive because of its large moisture content.

High-ash coal is also less suitable because cold-gas efficiency decreases with increasing ash content. For slurry-fed coal, the economic limit is 20% ash; for dry feed it is 40%.

The suitability of entrained-flow gasification for biomass is questionable for a number of reasons. Owing to a short residence time (a few seconds) in entrained-flow reactors, the fuel needs to be very fine, and grinding fibrous biomass into such fine particles is difficult.

For biomass with CaO but no alkali, the ash-melting point is high, and therefore it has a higher oxygen requirement.

The melting point of biomass ash with a high alkali content is much lower than that of coal. This reduces the oxygen required to raise the temperature of the ash above its melting point.

However, molten biomass ash is highly aggressive, which greatly shortens the life of the gasifier's refractory lining.

For these reasons entrained-flow reactors are not preferred for biomass gasification. Still, they have the advantage of easily destroying tar, which is very high in biomass and is a major problem in biomass gasification.

Entrained-flow gasifiers are essentially co-current plug-flow reactors, where gas and fuel travel.

The hydrodynamics is similar to that of the well-known pulverized-coal (PC) boiler, where the coal is ground in a pulverizing mill to sizes below 75 micron and then conveyed by part of the combustion air to a set of burners suitably located around the furnace.

The reactor geometry of the entrained-flow gasifier is much different from the furnace geometry of a PC boiler. Additionally, an entrained-flow gasifier works in a sub-stoichiometric supply of oxygen, whereas a PC boiler requires excess oxygen.

The gasification temperature of an entrained-flow gasifier generally well exceeds 1000 °C. This allows production of a gas that is nearly tar-free and has a very low methane content.

A properly designed and operated entrained-flow gasifier can have a carbon conversion rate close to 100%.

The product gas, being very hot, must be cooled in downstream heat exchangers that produce the superheated steam required for gasification.
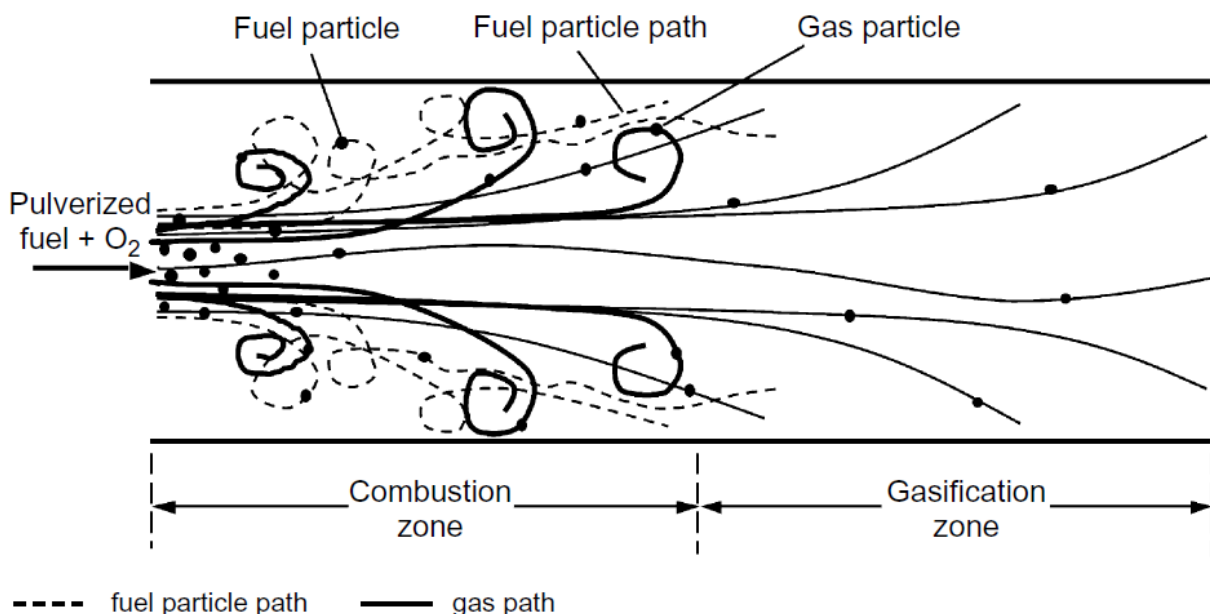

Figure 4-8: Simplified sketch of gas–solid flow in an entrained-flow gasifier.

Figure 4-8 describes the working principle of an entrained-flow gasifier by means of a simplified sketch. The high-velocity jet forms a recirculation zone near the entry point.

Fine fuel particles are rapidly heated by radiative heat from the hot walls of the reactor chamber and from the hot gases downstream, and start burning in excess oxygen.

The bulk of the fuel is consumed near the entrance zone through devolatilization; here the temperature may rise to as high as 2500 °C.

The combustion reaction consumes nearly all of the oxygen feed, so the residual char undergoes gasification reactions in CO_2 and H_2O environments downstream of this zone.

These reactions are relatively slow compared to the devolatilization reaction, so the char takes much longer to complete its conversion to gases. For this reason, a large reactor length is required.

Entrained-flow gasifier design may be classified into two broad groups: (1) the top-fed down-flow (used by GE Energy and Siemens SFG); and (2) the side-fed up-flow (used by Koppers-Totzek, the Shell gasification process, Prenflo, and the Lurgi multipurpose), shown below (Figure 4-9).
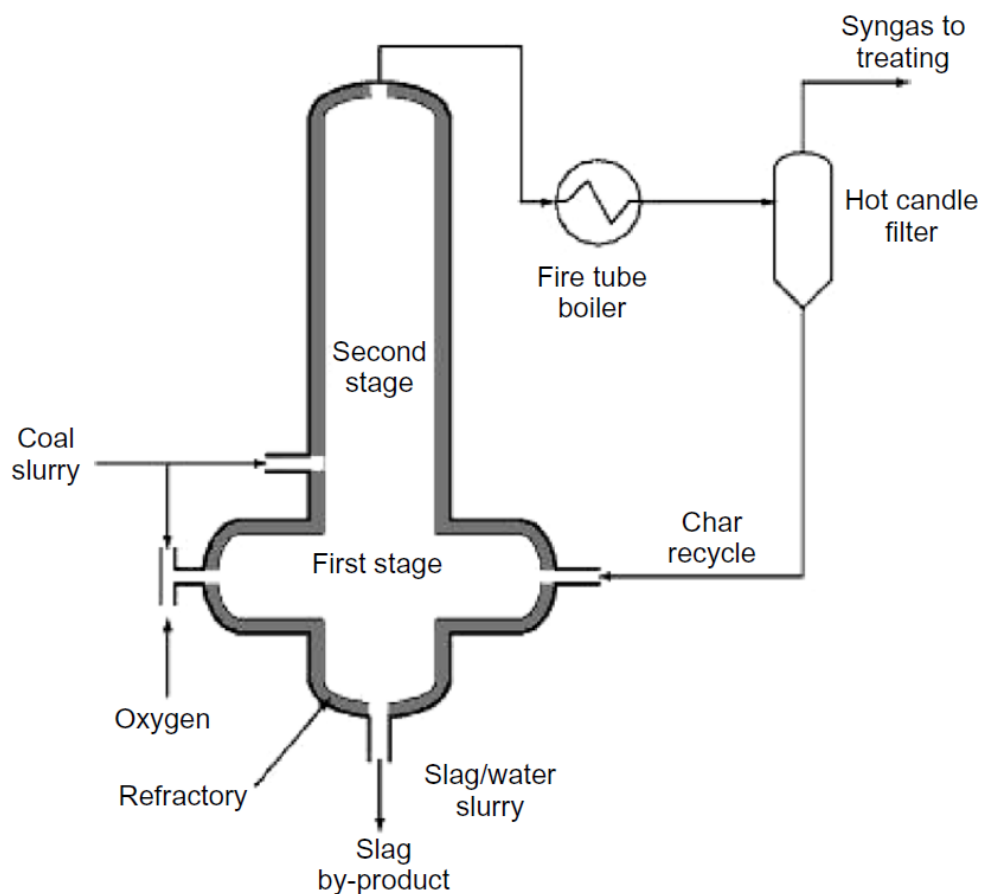

Figure 4-9: A side-fed entrained-flow gasifier.

Entrained-flow gasifiers have several advantages over other types:

- Low tar production;
- A range of acceptable feed;
- Ash produced as slag;
- High-pressure, high-temperature operation;
- Very high conversion of carbon;
- Low methane content well suited for synthetic gas production;

4.5 *Plasma gasification*

In plasma gasification, high-temperature plasma helps gasify biomass hydrocarbons. It is especially suitable for MSW and other waste products.

This process may also be called "plasma pyrolysis" because it essentially involves thermal disintegration of carbonaceous material into fragments of compounds in an oxygen-starved environment. The heart of the process is a plasma gun, where an intense electric arc is created between two electrodes spaced apart in a closed vessel through which an inert gas is passed (Figure 4-10).
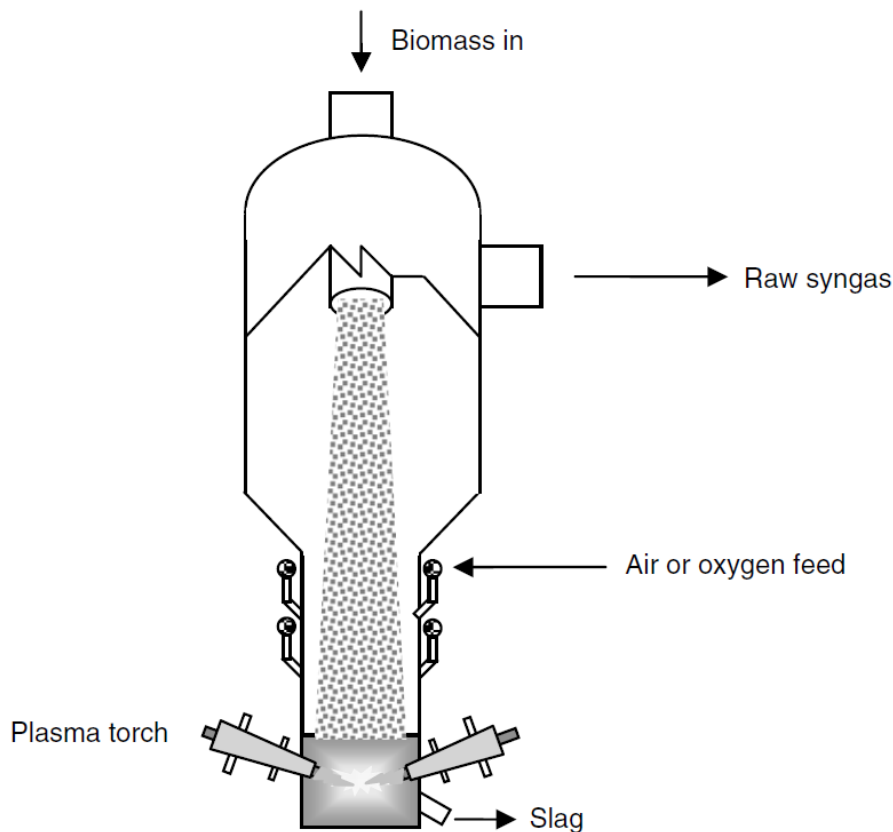
Figure 4-10: Plasma gasifier.

Though the temperature of the arc is extremely high (~13,000 °C), the temperature downstream, where waste products are brought in contact with it, is much lower (2700–4500 °C). The downstream temperature is still sufficiently high, however, to pyrolyze complex hydrocarbons into simple gases such as CO and H2. Simultaneously, all inorganic components (e.g., glass, metals, silicates, heavy metals) are fused into a volcanic-type lava, which after cooling forms a basaltic slag. The product gas leaves the gasifier at very high temperatures (1000–1200 °C).

A typical plasma reactor provides a relatively long residence time for the gas in the gasifier. This and the high temperature cause the tar products to be cracked and harmful products like dioxin and furan to be destroyed.
Owing to the high reactor temperature and the presence of chlorine in wastes, the life of the reactor liner is an issue. However, an attractive feature is that plasma gasification is relatively insensitive to the quality of the feedstock. This is the result of an independent energy source run by electricity instead of partial combustion of the gasification product.

4.6   *Process design*

The design of a gasifier involves both process and hardware. The process design gives the type and yield of the product, operating conditions, and the basic size of the reactor. The hardware design involves structural and mechanical components, such as grate, main reactor body, insulation, cyclone, and others, that are specific to the reactor type.

For any design, specification of the plant is very important. The input includes the specification of the fuel, gasification medium, and product gas.
A typical fuel specification will include proximate and ultimate analysis, operating temperatures, and ash properties.
The specification of the gasifying medium is based on the selection of steam, oxygen, and/or air and their proportions. These parameters could influence the design of the gasifier, as follows:

- The desired heating value of the product gas dictates the choice of gasification medium.
- Hydrogen can be maximized with steam, but if it is not a priority, oxygen or air is a better option, as it reduces the energy used in generating steam and the energy lost through unutilized steam.
- If nitrogen in the product gas is not acceptable, air cannot be chosen.

- Capital cost is lower for air, followed by steam. A much larger investment is needed for an oxygen plant, which also consumes a large amount of auxiliary power.
- Equivalence ratio.

For the product gas, the specification includes:

- Desired gas composition;
- Desired heating value;
- Desired production rate (Nm^3/s or MWth produced);
- Yield of the product gas per unit fuel consumed;
- Required power output of the gasifier, Q;

The design outputs of process design include geometry and operating and performance parameters.

Basic size includes reactor configuration, cross-section area, and height (hardware design).

Important operating parameters are: (1) reactor temperature; (2) preheat temperature of the steam, air, or oxygen; and (3) amount (i.e., steam/ biomass ratio) and relative proportion of the gasifying medium (i.e., steam/ oxygen ratio). Performance parameters of a gasifier include carbon conversion and cold-gas efficiency.

4.7 *Energy balance*

Unlike combustion reactions, most gasification reactions are endothermic. Thus, heat must be supplied to the gasifier for these reactions to take place at the designed temperature.

In laboratory units, this is not an issue because the heat is generally supplied externally.

In commercial units, it is a major issue, and it must be calculated and provided for. The amount of external heat supplied to the gasifier depends on the heat requirement of the endothermic reactions as well as on the gasification temperature (Figure 4-11). The latter is a design choice, and it is discussed next.

Because lignin, a refractory component of biomass, does not gasify well at lower temperatures, thermal gasification of lignocellulosic biomass prefers a minimum gasification temperature in the range 800 to 900 °C.

For biomass, an entrained-flow gasifier typically maintains a gasification temperature well exceeding 900 °C. For coal, the minimum is 900 °C for most gasifier types.

A higher peak gasification temperature is chosen for an entrained-flow gasifier. The higher the ash-melting temperature, the higher the design value of the gasifier temperature. This temperature is raised through the gasifier's exothermic oxidation reactions, so a high reaction temperature also means a high oxygen demand.
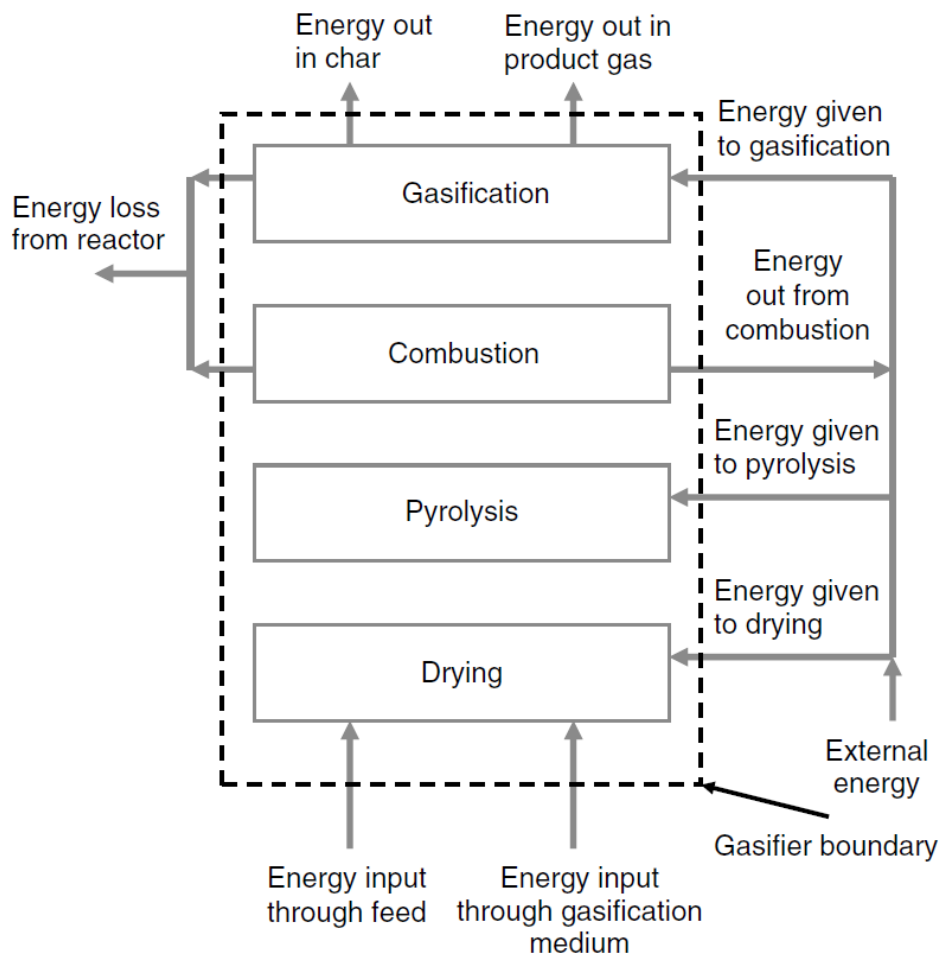

Figure 4-11: Energy flow in and out of a gasifier.

In entrained-flow gasifiers, the peak gasification temperature is typically in the range 1400 to 1700 °C, as it is necessary to melt the ash; however, the exit gas temperature is much lower. The peak temperature of a fluidized-bed gasifier is in the range of 700 to 900 °C to avoid softening of bed materials. It is about the same as the gas exit temperature in a fluidized-bed gasifier.

In a crossdraft gasifier the gasification temperature is about 1250 °C, whereas the peak gasification temperature is about 1500 °C.

The exit-gas temperature of a downdraft gasifier is about 700 °C, but its peak gasifier temperature at the throat is 1000 °C.

The updraft gasifier has the lowest gas-exit temperature (200– 400 °C), while its gasification temperature may be up to 900 °C.

5 Simulation of coal and biomass gasification with thermodynamic equilibrium models

5.1 *Introduction*

In the following chapter it will be treated the biomass gasification into an entire gasification reactor (gasifier).

This thing is related with the consideration of all the possible reaction paths, involving the description of a heterogeneous system, with reactions in both gas and solid phase and thus, a multiplicity of compounds and species connected.

These things described above were related each other and brought to a non-linear system, with many problems for its solution, because it was possible to find a correct solution, which approximated quite good the real conditions of a gasifier, only with simulations of 4 or 5 reactor layers, then the simulations were too long as calculation time and they could have many problems also for the convergence to a steady-state solution.

For these reasons it has been decided in this chapter to take a step inward and describe only the system such as a homogeneous system in gas-phase to see the various solutions with different feedstocks, arriving to the thermodynamic equilibrium, and at the end a final discussion of the results has been proposed.

First of all, to consider only the gas-phase reactions and a homogeneous system, a few simplifications has been made, which can be considered reasonable and explained below.

The greatest simplification was to consider only the gas-phase reactions in these new simulations and not all the reactions, which concerned also solid reactions, and so the original biomass was considered divided in three main components (cellulose, hemicellulose and lignin), which were yet broken into other components (volatiles in the gasification conditions).

So the biomass was considered to have yet accomplished the pyrolysis reactions and the three original components of the biomass were just divided into other components.

Before of this passage there was an investigation of the various components' activation energies in which the biomass was broken following the pyrolysis reactions and three main paths were created for each component, because both cellulose, hemicellulose and lignin gave primarily only a component in gas phase.

Noticed the three main components released by the solid biomass into the gas phase, the simulations were ready to start.
Then in the next paragraph the same thing was done for the coal, always trying to reach the thermodynamic equilibrium, with the same simplifications, using different components in the gas phase, because released by the coal and not by the biomass.

5.2 *Simulations of biomass gasification*

First of all it will be defined the program used for the simulation, which is "dsmoke82.exe". This program is able to simulate various reactors, solving the mass and energy balances and giving the outgoing conditions in any point of the reactor, even if we are interested to the final conditions at the end of the reactor, after a certain residence time, because we are looking for the thermodynamic equilibrium in the simulations.

The program has not a predefined graphic interface and to be able to use it, two main things must be compiled: the first one is the "file.dat", where it has been put all the inlet feedstocks of the simulation with their flows and their mass or molar percentage; the second important thing to compile is the "RUNBAT", which is the program that execute the simulations and in which are included the "file.bin", the "file.dat" and the type of "D-Smoke" version which has to be used for the simulations of the reactor.

In addiction it is here underlined that this type of program is simulating only heterogeneous conditions inside the reactor, because we are working only with gas species and this is a very high degree of simplification respect to the previous programs and simulations of the entire gasifier, which were done simulating both the solid and gas phases.

So in these simulations only three main components released by the biomass into the gas phase were used (from cellulose, hemicellulose and lignin to LVG, xylan and FE2MACR), with the same composition assigned to the original biomass, due to the hypothesis.

An adequate temperature was assumed for the biomass entering in the reactor, respecting the hypothesis.

In the next step other 2 entering flows must be assigned, air and water feedstocks, essential for the simulation of the gasification conditions.

The other fundamental passage is the assignment of the operative conditions in which we want the reactor to work (for example if we want an auto-thermal reactor or an adiabatic reactor and/or if we want the pressure constant or variable).

It is here underlined that these simulations must always arrive to the thermodynamic equilibrium, because of the strategic importance to see the outlet streams only in that condition, which is extremely important for the evaluation of the results obtained.

Finally the program needs the introduction of the "file.bin", with the kinetics of the gas phase reactions, which involves many species (about 70) and it will be used the file "BIO1201.BIN".

It is posed the attention at the beginning on the study of the compositions of the outlet gases, working with only an oxidative pyrolysis lower in oxygen, then changing the conditions and simulating a biomass gasification with only water and finally a gasification with both oxygen and water.

5.2.1 Simulation with stoichiometric air

In this simulation it will be used the biomass species released by the biomass three main components with their molar fractions (cellulose 0.46, hemicellulose 0.31, lignin 0.23) and the air (O_2 0.21and N_2 0.79), with a stoichiometric ratio between fuel and air (stoichiometric respect to the oxidative pyrolysis). It will be used an inlet flow of biomass of 0.0004 (Kg/s) and an inlet flow of air of 0.00044 (kg/s).

In this simulation thermodynamic equilibrium will be reached, and it will be used in the "file.dat" the "TYPE 12", which is a PFR of reactor which allows to reach in a few calculation seconds the steady-state conditions and the thermodynamic equilibrium.

Then we have to choose the conditions for the reactor and the simulations will be made the first with a constant pressure (1 atm) and with the command "CONH" and the others with the command "CONT", because of the evaluation of the sensibility of the parameters in different conditions, even if it will be reported in this work only the simulations with the command "CONH".

The last parameters of the system are the inlet flows and reactor temperatures and this is a parameter which could be very critical during the simulations.
In fact the start-up with inlet flows and reactor temperatures which are too low could bring the system to have solid residues and this is a thing to avoid, because of the need of the highest gasification efficiency and from the other side the lack of a plant for the use and conversion of solid carbon (char).

Now defined all the operative conditions, the simulation can run, but it will be reported only the simulation with the command "CONH", always with constant pressure of 1 atm, and the results and the graphics are showed below, interfaced with a discussions.
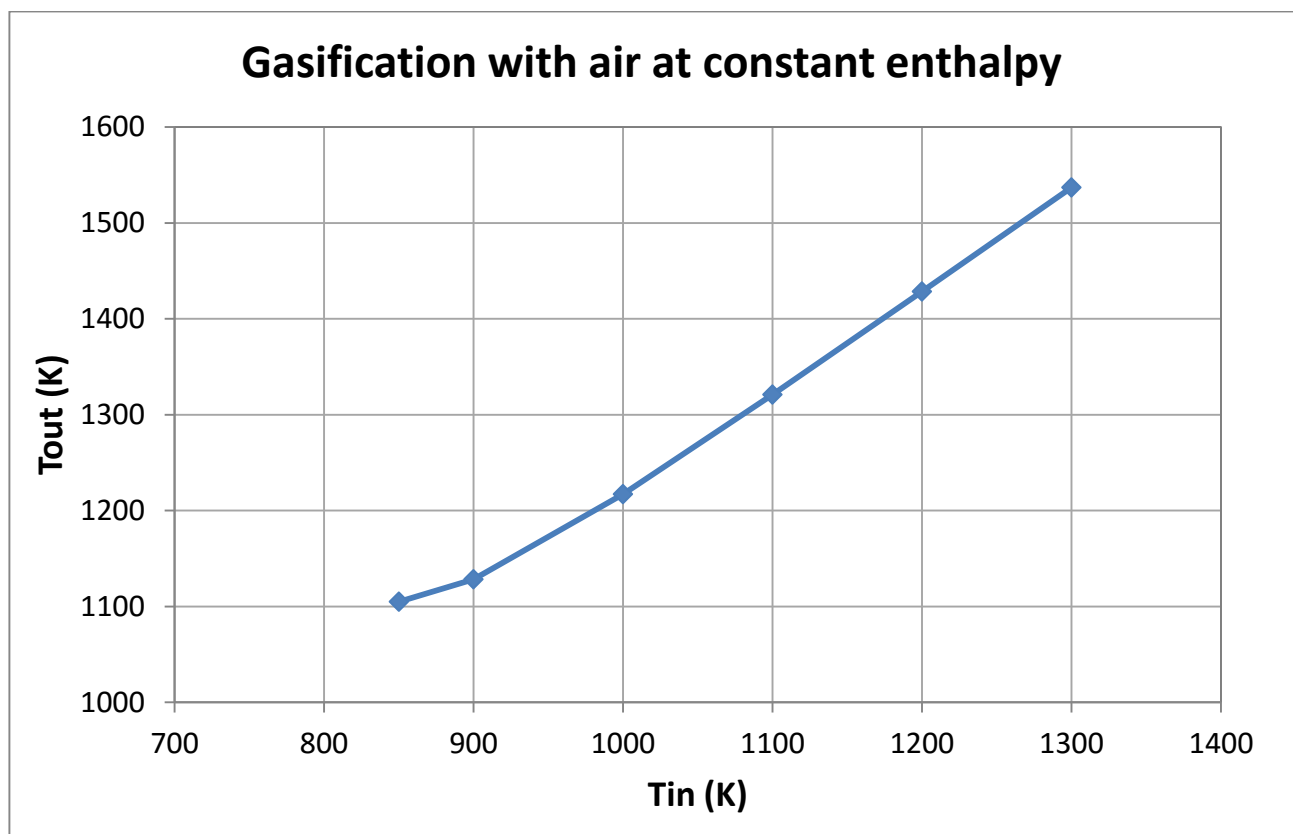
Gasification with air at constant enthalpy
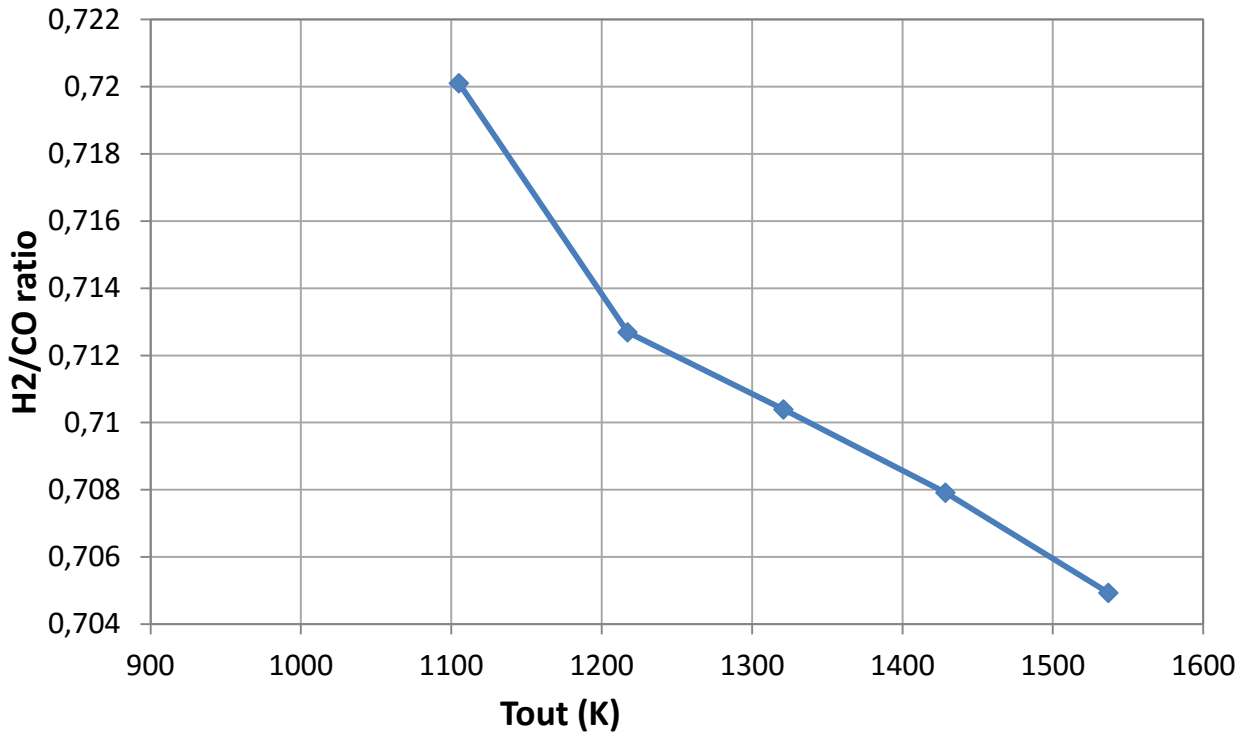
Gasification with air at constant enthalpy
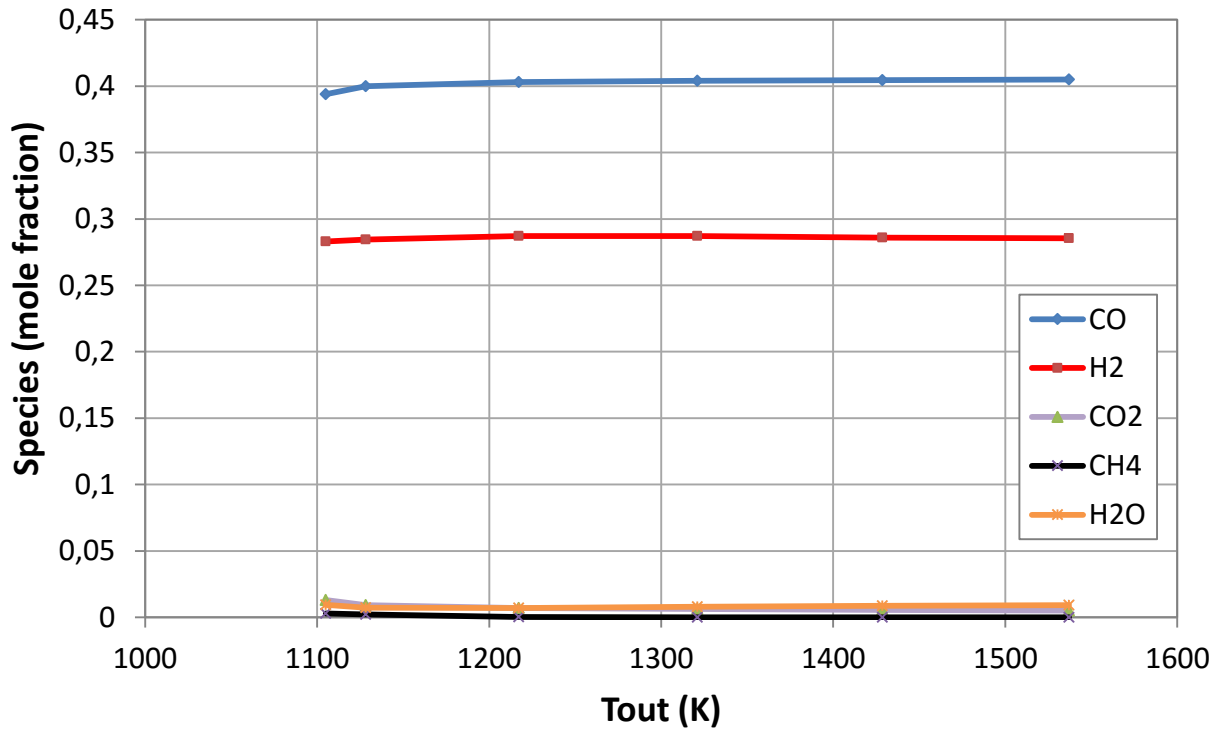
In the graphics above it is showed the H2/CO ratio, which is a fundamental parameter for the biomass gasification, because of its strategic importance for a high number of industrial applications downstream the gasification and the formation of the syngas (for example for the "Fischer-Tropsch synthesis" in which the H2/CO ratio must be 1.8-2).

It is notable that with the only oxidative pyrolysis of the biomass with air must lead to a H2/CO ratio of about 0.72-0.7, which is very similar to the theoretical ratio which must be 0.75.

It is important to explain here that the theoretical H2/CO ratio was obtained oxidizing the biomass with less air, so the products will be CO and H2 and the combustion/gasification will not be complete until the formation of CO2 and steam.

Now this is only the most simple simulation, but now let's move from this and try to simulate the same biomass with the presence of the only a bit H2O, that is in conditions of poor gasification.

After that it will be showed some complete and more interesting simulations with both air and steam, trying to investigate the various parameters and the differences varying the ratio air/steam for a gasification system.

5.2.2 *Simulation with air and a stoichiometric quantity of steam*

Now in the second simulation, the gasification of a biomass will be reproduced, but this time with the same quantity of air (0.00044 kg/s) and a small quantity of steam (0.000022 kg/s).
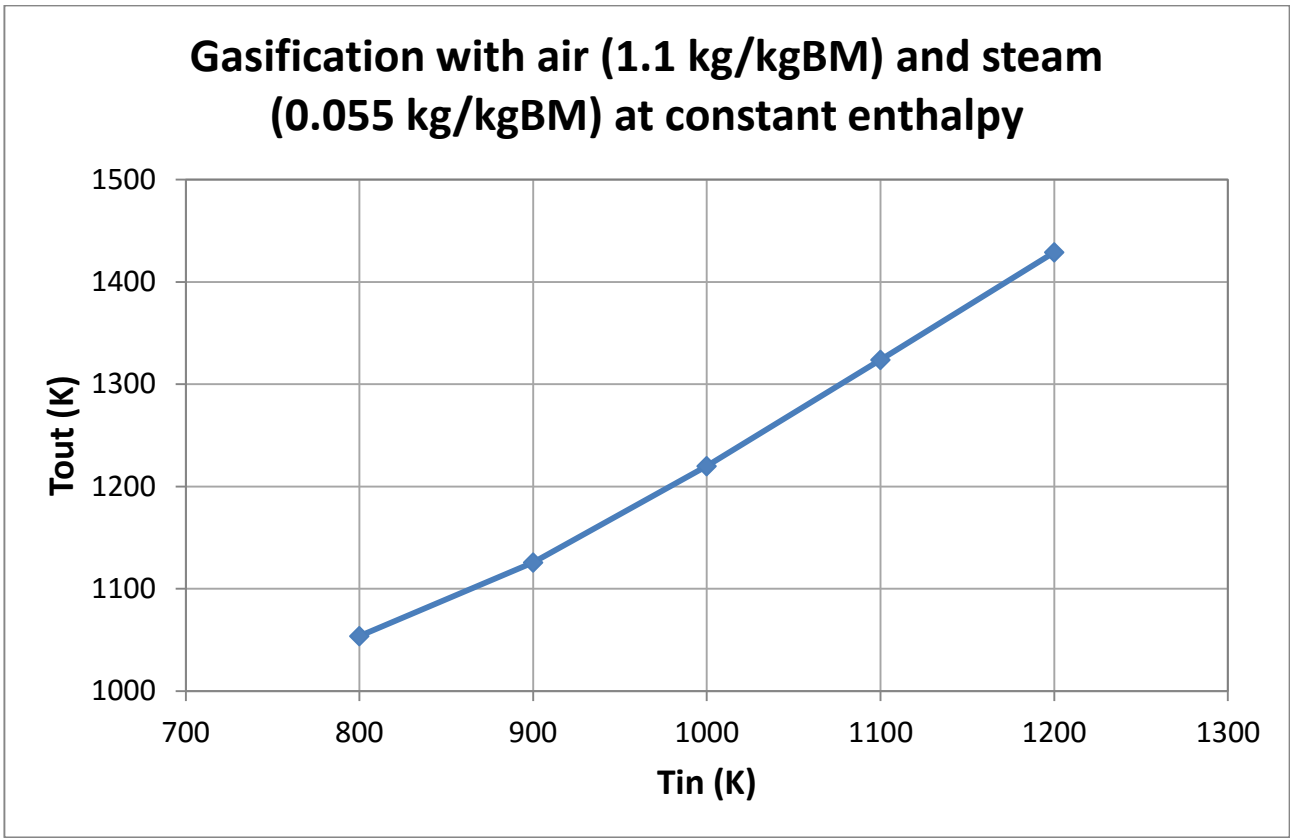
In the proceeding of the chapter it will be used the quantity of biomass as unitary (1) and all the other physical quantities will be described in terms of the biomass scale, dividing all for the biomass unit of measure (kg/kgBM), where BM stands for biomass. So in this case, there will be a term 1 for the biomass, 1.1 for the air and 0.055 for the steam.
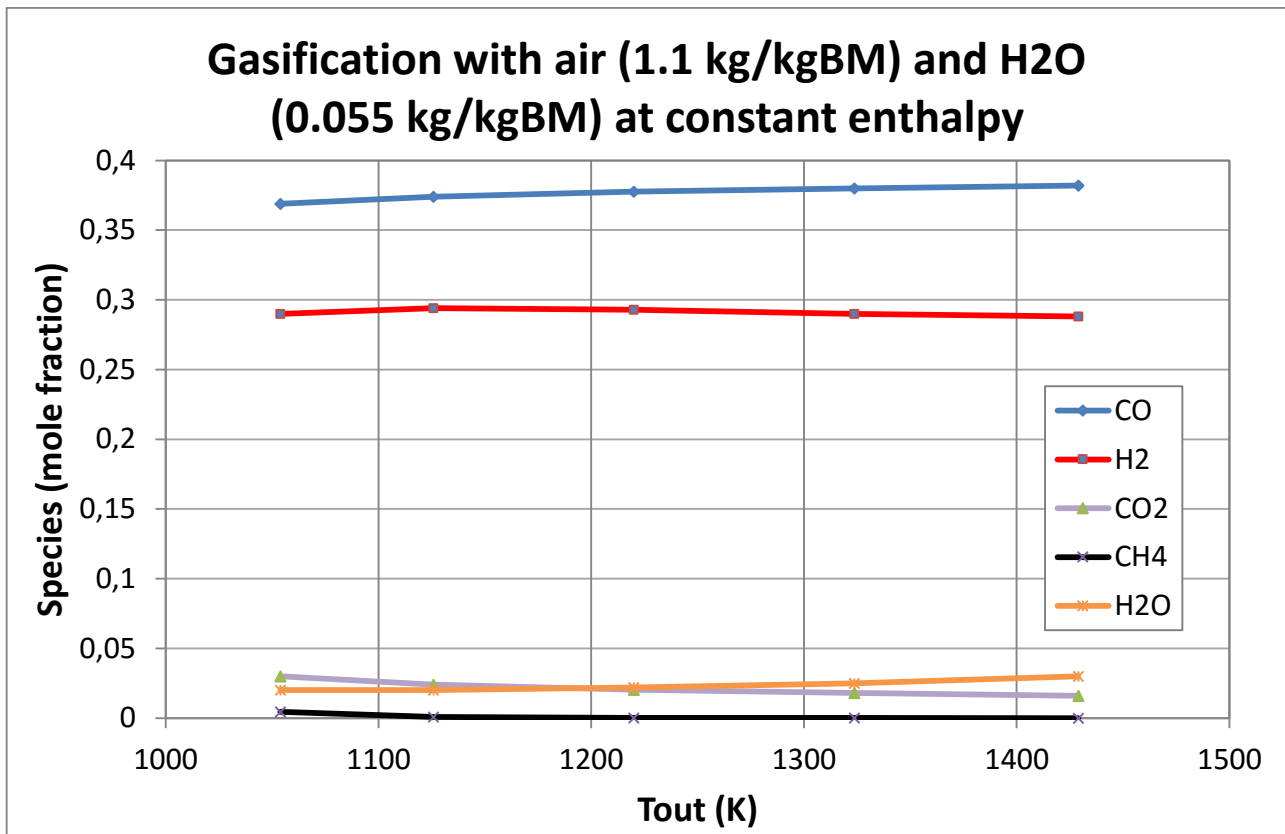
It is notable the achievement of the thermodynamic equilibrium and the lack in the production of solid residues, thus an adequate start-up temperature is needed.
In this simulation it is expected a major quantity in the syngas of H2 and so on a higher H2/CO ratio, due to the steam current in the inlet flow.
As usual the simulation is done in a certain range of temperatures to see how the parameters change, maintaining the same initial condition of constant pressure (1

atm) and with the command "CONH". The graphics of the simulations are reported below.

Gasification with air (1.1 kg/kgBM) and steam (0.055 kg/kgBM) at constant enthalpy

Gasification with air (1.1 kg/kgBM) and H2O (0.055 kg/kgBM) at constant enthalpy

Gasification with air (1.1 kg/kgBM) and H2O (0.055 kg/kgBM) at constant enthalpy
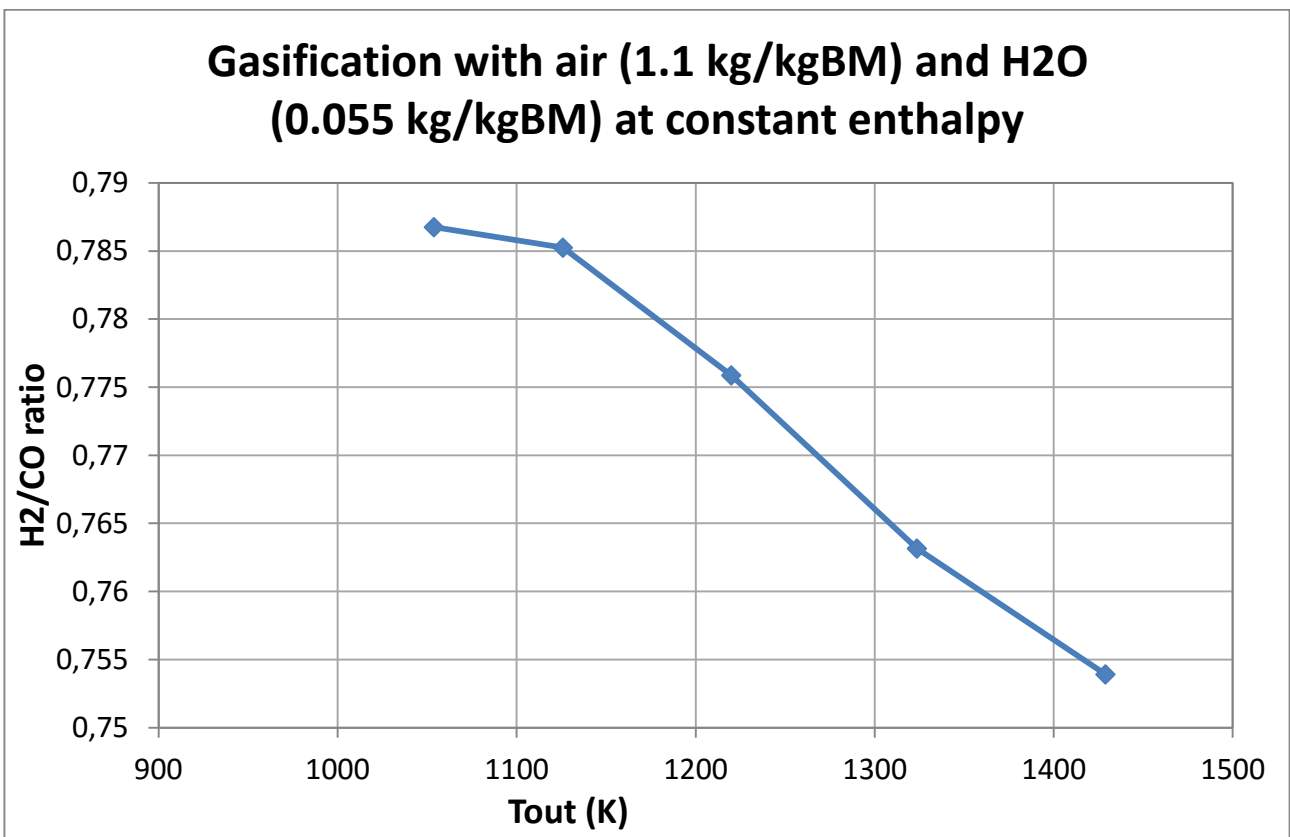
Here in the second simulation it is easy to capture a higher level of the H2/CO ratio, as expected, due of the presence of H2O in the inlet flow.

Another interesting thing is that the temperature used for the simulation is lower at the beginning and this is always thanks to the steam, which is an efficient gasifying agent and reduces the presence of carbon residues (char) in the outlet flow and allows to work with a lower reactor temperature. Once again the H2/CO ratio is about 0.79-0.73, which is very similar to that one expected in ideal conditions of gasification.

Also in this case it is showed a graphic for the gas species leaving the reactor and there are some differences in the product distribution, with a higher quantity of CO2 and steam in the gases.

Now let's increase the quantity of steam in the inlet flow and decrease the quantity of air. In this procedure a particular care must be placed in the fact that for a mole of O2 we need 2 moles of steam, due to a ratio (½) in the stoichiometric coefficients.

5.2.3 Simulation with air and steam

Here there is the need to try and see the parameters changes with the use of a major quantity of steam. This will be done for many aspects, which will be described later.

The same conditions are used (constant pressure of 1 atm and "TYPE 12" for the reactor) and the type "CONH", to simulate as usual the adiabatic conditions along the reactor.

The other difference in the following graphics is the presence of another parameter ("etaC"), which is the efficiency of conversion of carbon. Thus the parameter "etaC" allows to obtain information of how much of carbon has gone to form CO and how much to CO_2 and CH_4, two undesired products during the production of syngas. The graphics of the simulations are reported below.
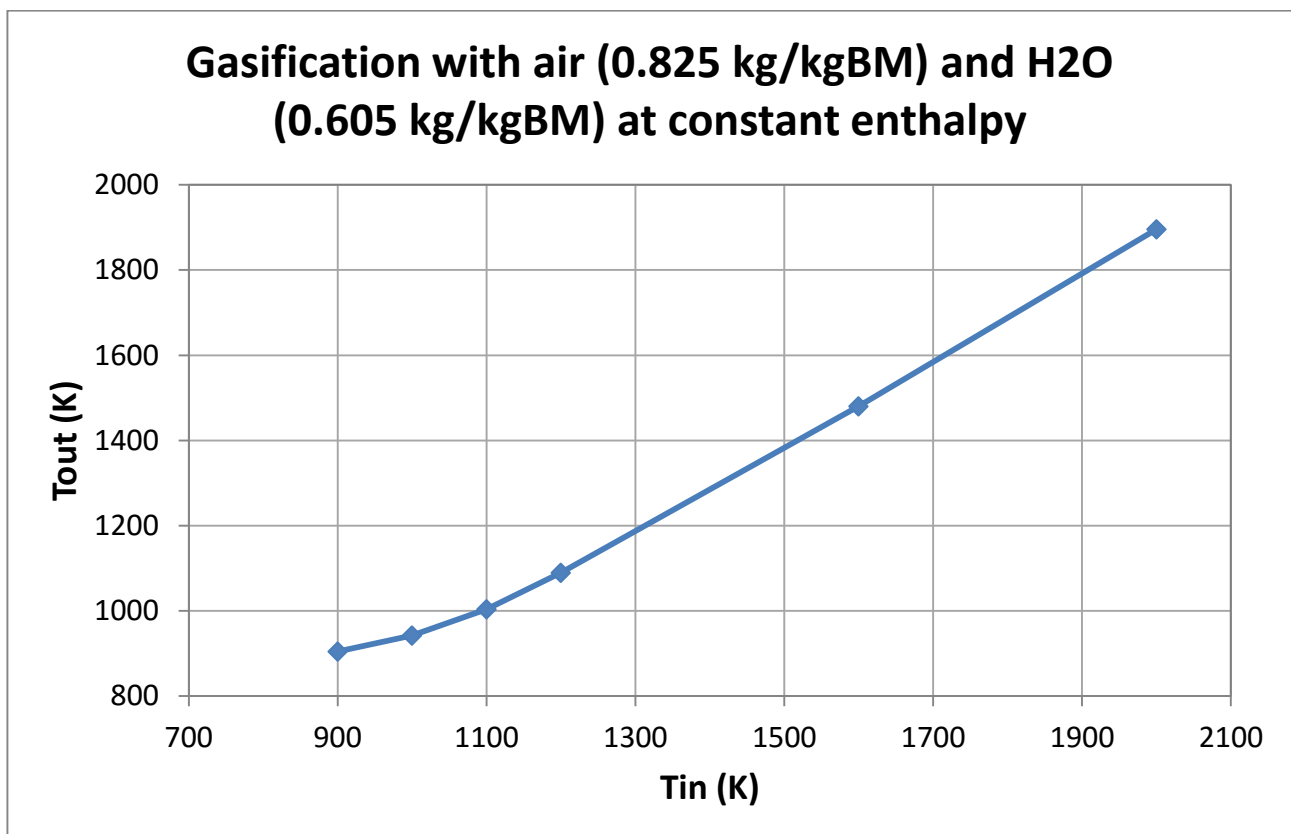
Gasification with air (0.825 kg/kgBM) and H_2O (0.605 kg/kgBM) at constant enthalpy

Gasification with air (0.825 kg/kgBM) and H2O (0.605 kg/kgBM) at constant enthalpy

Gasification with air (0.825 kg/kgBM) and H2O (0.605 kg/kgBM) at constant enthalpy
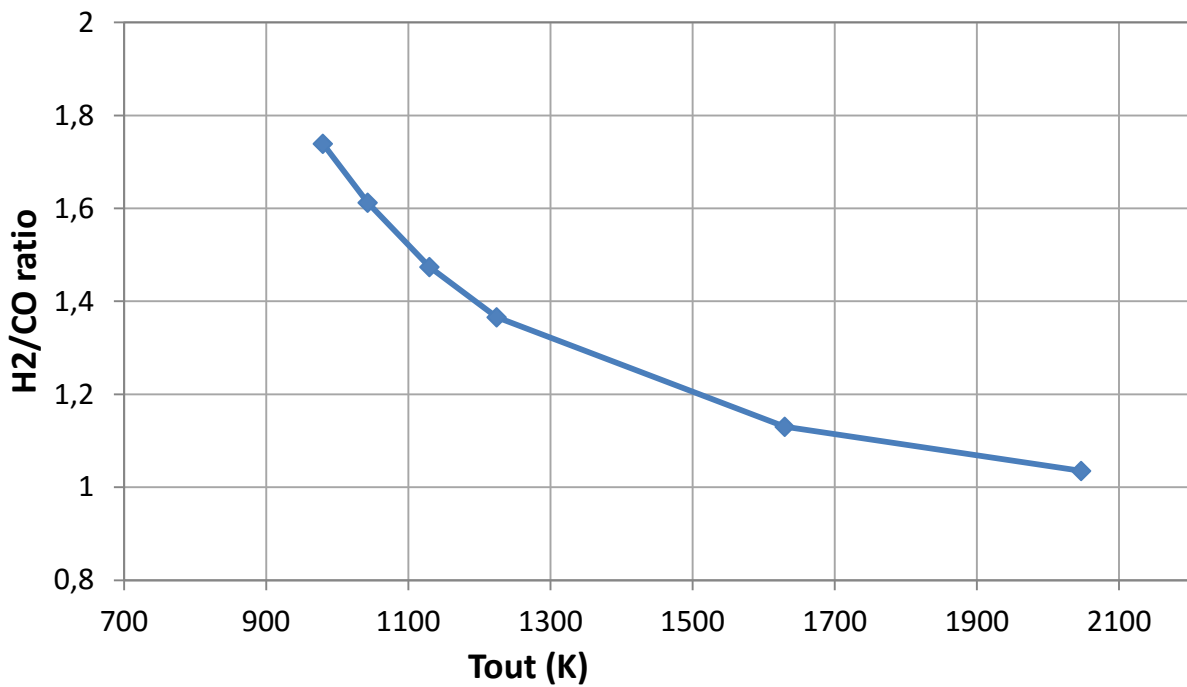
Gasification with air (0.825 kg/kgBM) and H2O (0.605 kg/kgBM)
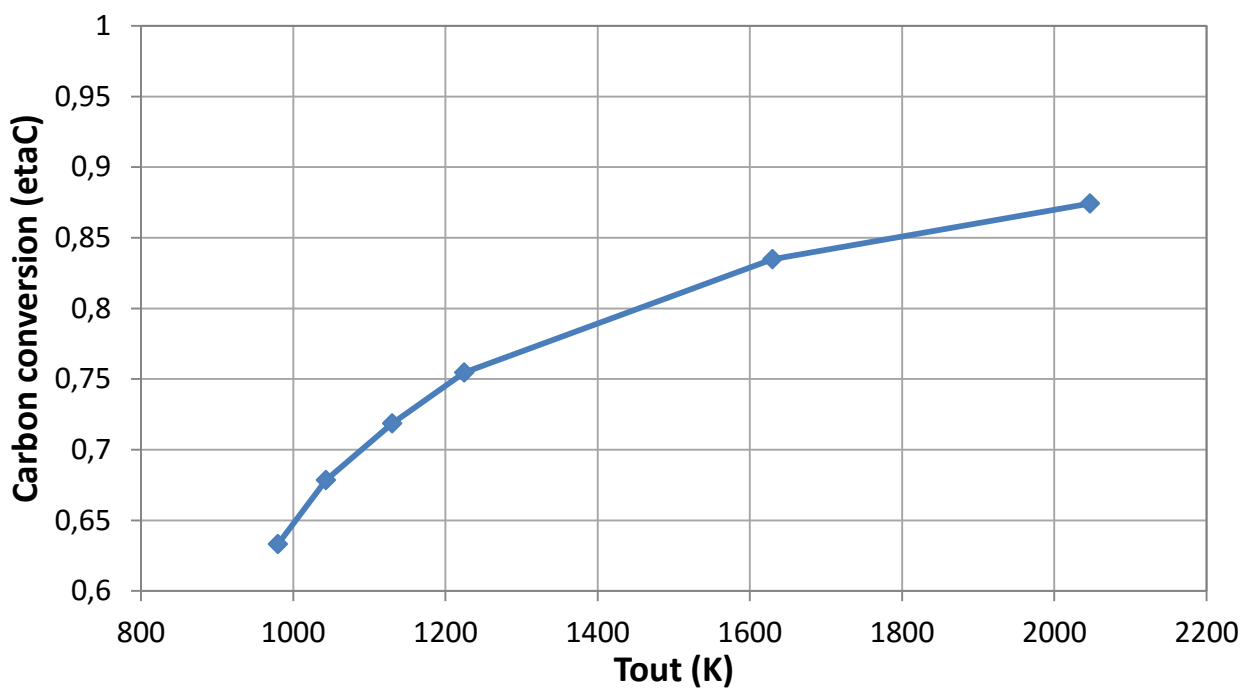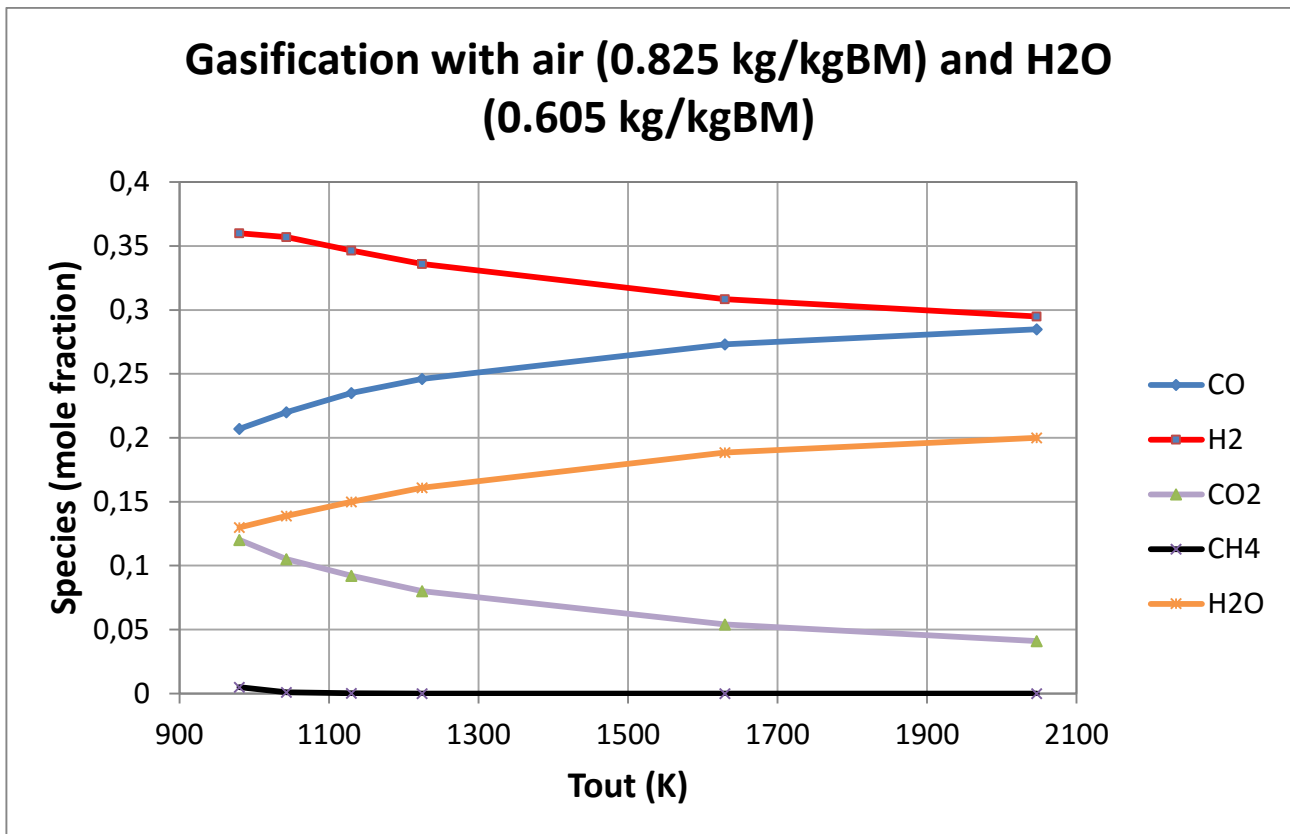
In this simulation there is the presence of more parameters than in the previous simulations.

First of all there is the presence of a higher level of steam and thus the outlet flow is modified by this, due to a high H2/CO ratio and a higher level of CO2.

Two things are very important to be noticed: the first one is the water that favors the reaction to give H2 and CO2, the so called WGS (water-gas shift), because there is a shift in the products from CO and H2O to CO2 and H2.

The second very important thing is that at higher temperatures (above 1500 K), the production of CO is always higher than that of CO2, but with the gasification process the temperatures are not so high (generally between 900 and 1400 K).

The fact that with a higher level of water in the inlet flow, there is a prevalence in the production of H2 is very good and the H2/CO ratio is very high (between 2 and 1).

There is to consider also the fact that with a large quantity of H2O and thus of the reaction of WGS, there a major presence in the syngas of CO2, in high quantity and this is not a good news.

In fact the presence of CO2 into the syngas decreases its energetic value and we have a poorer outlet syngas as composition, so it is very preferable to use not so much water with the addiction of air in the gasification.

Next simulations will see the use of more steam and a lower quantity of air to forecast the change of the parameters and confirm the trend of the previous ones.

Let's move to the last simulations of this paragraph, which will be focused on the increase of the quantity of steam and the reduction of air.
Now the parameters change with a ratio about 1/1 between steam and biomass and thus it is expected an increased H2/CO ratio, a higher level of CO2 in the outlet gases and of consequence a reduced "etaC", because of the major formation of CO2 and not of CO.
This time the air flow is placed to 0.00022 (kg/s) and the steam flow to 0.000462 (kg/s), with the same biomass quantity of 0.0004 (kg/s); for this reason air and steam are divided for the quantity of biomass (kg/kgBM) and it results air (0.55 kg/kgBM) and H2O (1.155 kg/kgBM). Also in this simulation, there is the use of the command "CONH", which means working with adiabatic conditions into the reactor. Here the graphics below explain the trend of the simulation.
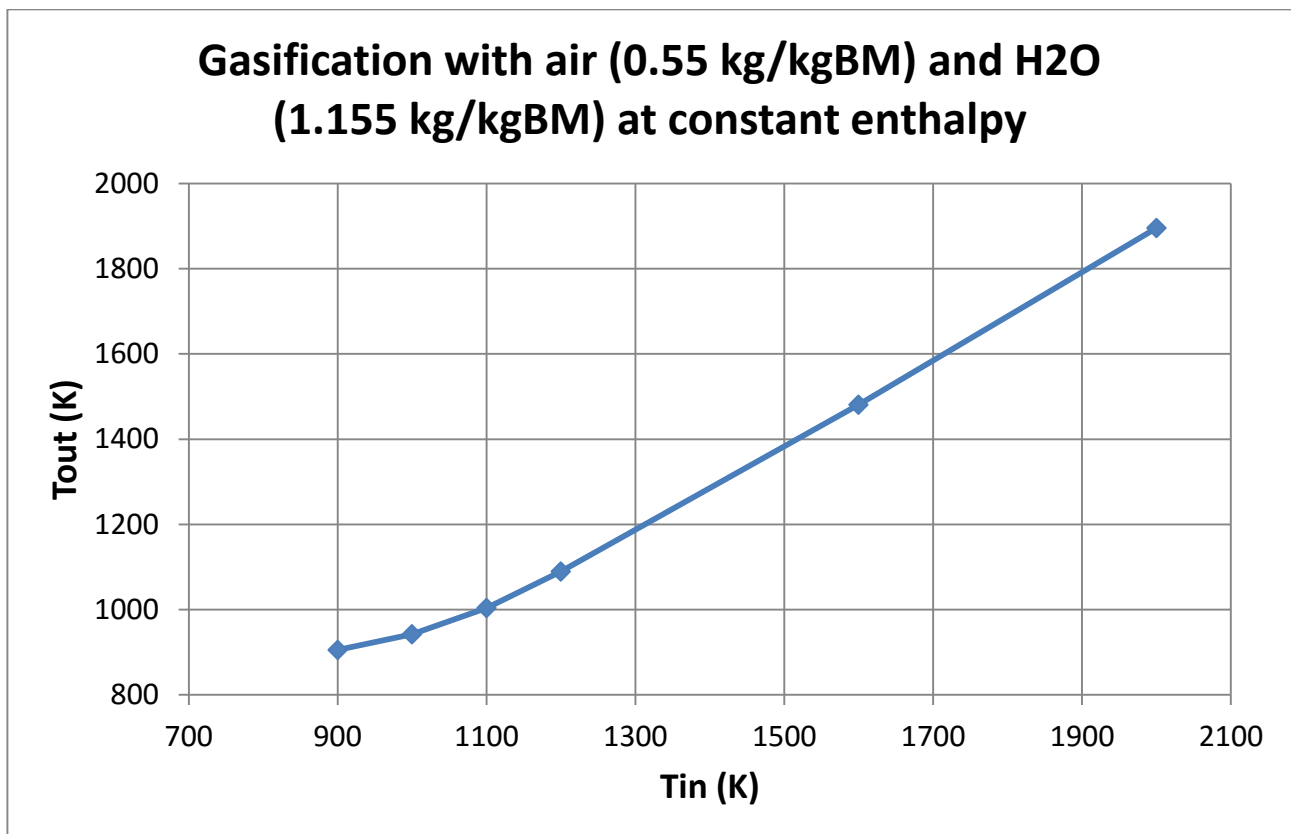
Gasification with air (0.55 kg/kgBM) and H2O (1.155 kg/kgBM) at constant enthalpy
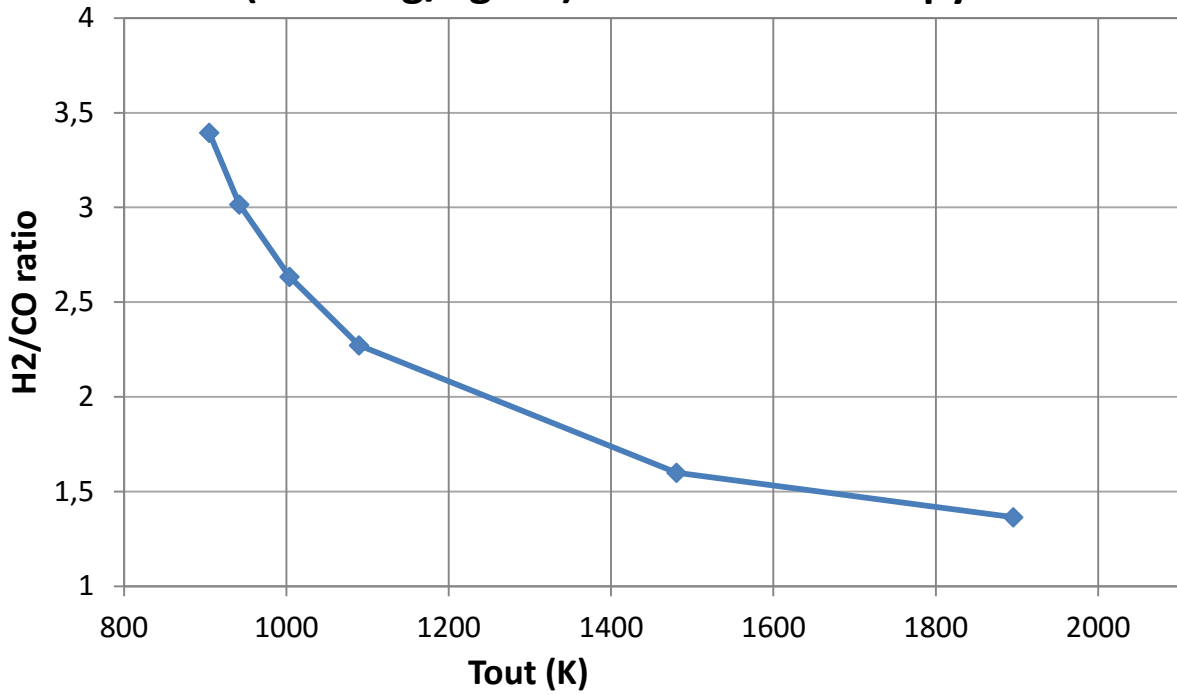
Gasification with air (0.55 kg/kgBM) and H2O (1.155 kg/kgBM) at costant enthalpy

Gasification with air (0.55 kg/kgBM) and H2O (1.155 kg/kgBM) at constant enthalpy

Gasification with air (0.55 kg/kgBM) and H2O (1.155 kg/kgBM)
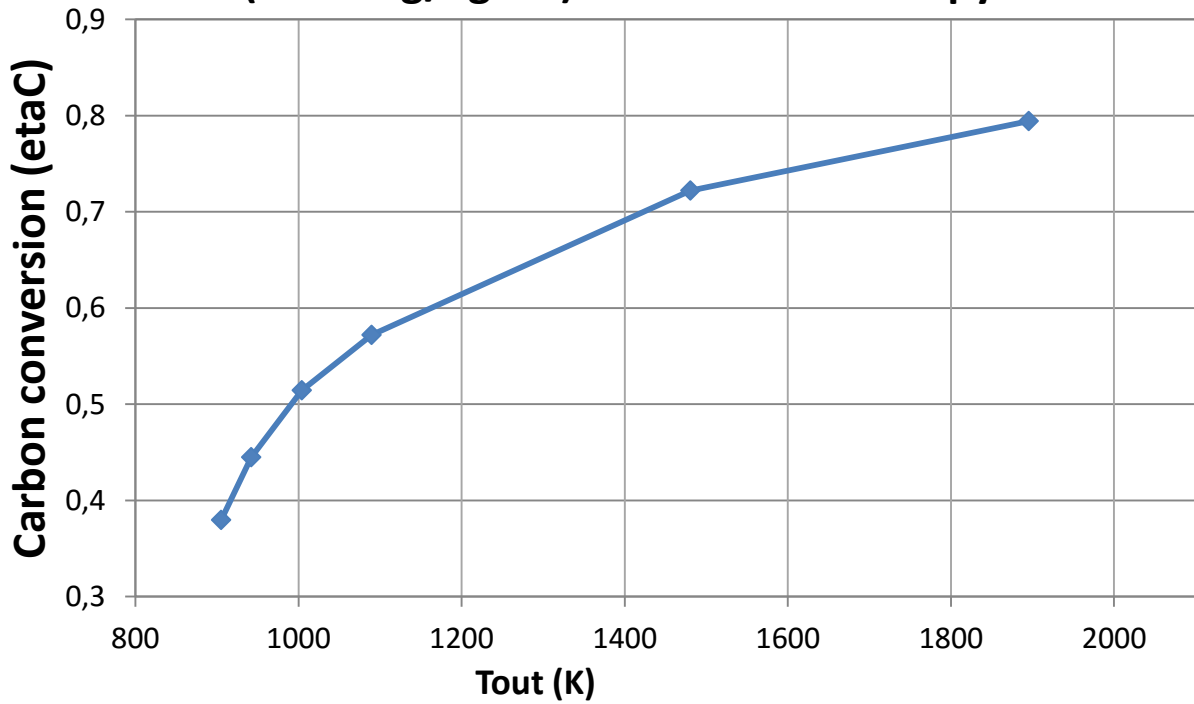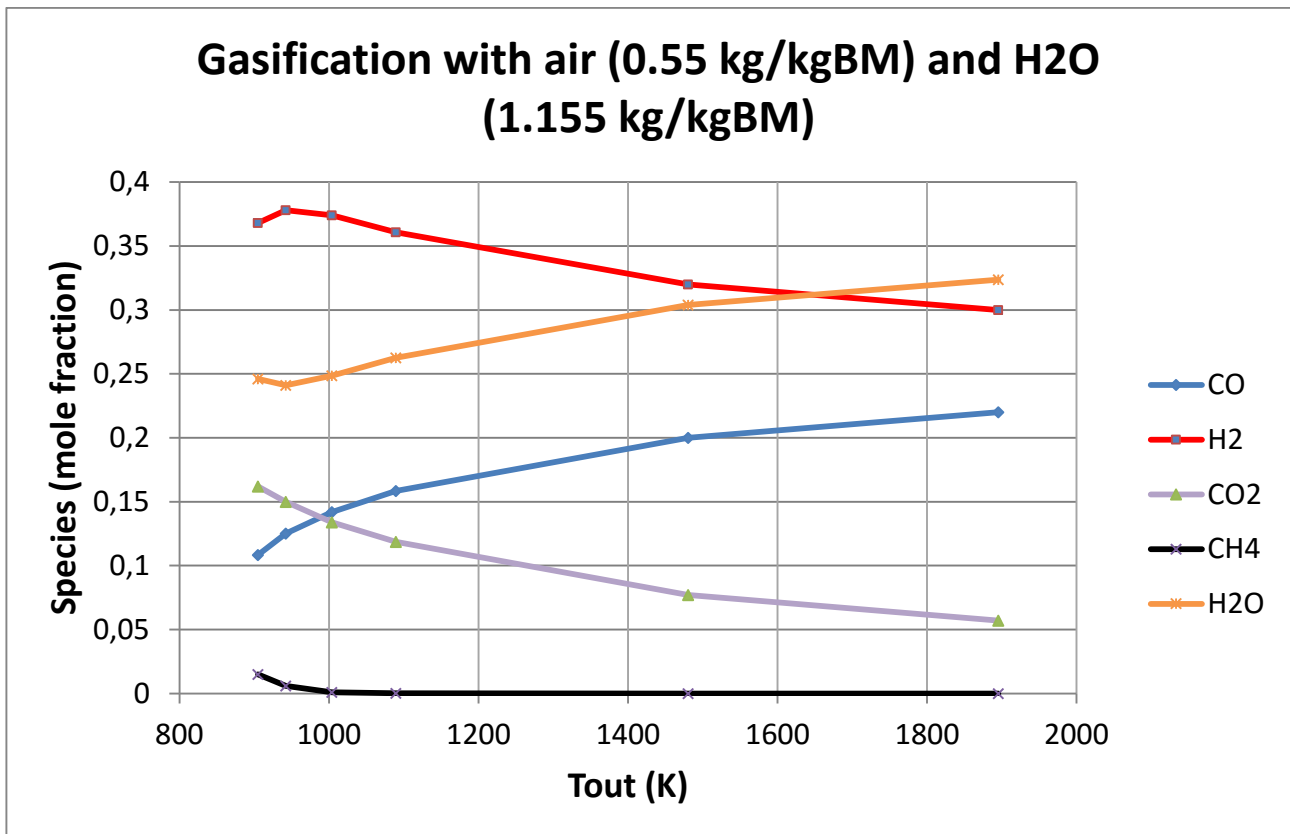
Through the graphs appears immediately a further increase in the H2/CO ratio, as expected, and on the other hand a lower "etaC", because of a higher quantity of CO2 in the gases.

This is explained once again by the fact that with a higher quantity of steam in the inlet flow, we have an increase of the reaction of WGS and so a higher production of CO2 and H2 and a consumption of CO and steam.

All the considerations done before are very well explained in the graphs, especially the one with all the gas species leaving the reactor.

5.2.4   Results and discussion

In this chapter there was an extensive investigation of the biomass gasification, but not analyzing all the complete phenomena involved in the reaction, rather than using only a simplified model to described it.

In fact with the adoption of a program, which worked only in homogeneous conditions, and using a simplified kinetics, which accounted for the reactions in the gas phase and not for all the reactions described in the gasification.

This was possible thanks to the hypothesis that all the three main components of the biomass (cellulose, hemicellulose, lignin) release three main volatile components in the gas phase (LVG, xylan, FE2MACR) and then with these

components it is possible to use a simplified kinetics only for the gas phase and not also for the solid phase, paying attention to the hypothesis.

The second important thing is the fact that the simulations needed to arrive to the thermodynamic equilibrium, due to the strong interest to the outlet gas composition, so the program and the reactor were modeled to reach this condition. Subsequently after compiling the program, the simulations started, using at the beginning only biomass and air (oxidative pyrolysis) and then starting to use a small quantity of steam, till reaching a high quantity of steam and a reduced quantity of air, in conditions which were similar to the normal conditions of gasification. At the beginning the objective was to reach the conditions of ideal oxidative pyrolysis using only air (in terms of H2/CO ratio) and then the water content was augmented and the simulations reached a higher level of H2/CO ratio.

Adding water to the inlet flow was good for the H2/CO ratio, which is very important for the downstream processes, but the presence of the WGS reaction, which is favored with a higher content of water and brings a higher quantity of CO2 in outlet gases, which is something to avoid, because of the depletion for the syngas of its calorific value and the "etaC", due to the presence of CO2 and a less quantity of CO.

Another important fact is that the WGS reaction is exothermic, thus it is interested by equilibrium and favored at low temperatures. In fact as showed in the graphs, the production of CO2 is higher at low temperatures and this for the presence of WGS, which has a major role at low temperatures and also because above 1900 K there is another important reaction which seizes the CO2 and turns it into CO. In the graphs below it is possible to noticed all what was mentioned before; in addiction it is evident the competition between the simulations with a value of 0.000242 kg/s of steam and 0.000462 kg/s of steam (so with an equivalent ratio of steam of 0.605 and 1.155).

The graphs are made for the "CONH" simulations, with the command "CONH" and "CONT", to underline the sensitivity of the parameters, but only the graphs for the "CONH" simulation will be showed, because of the similarity of the data found.

Costant enthalpy simulations
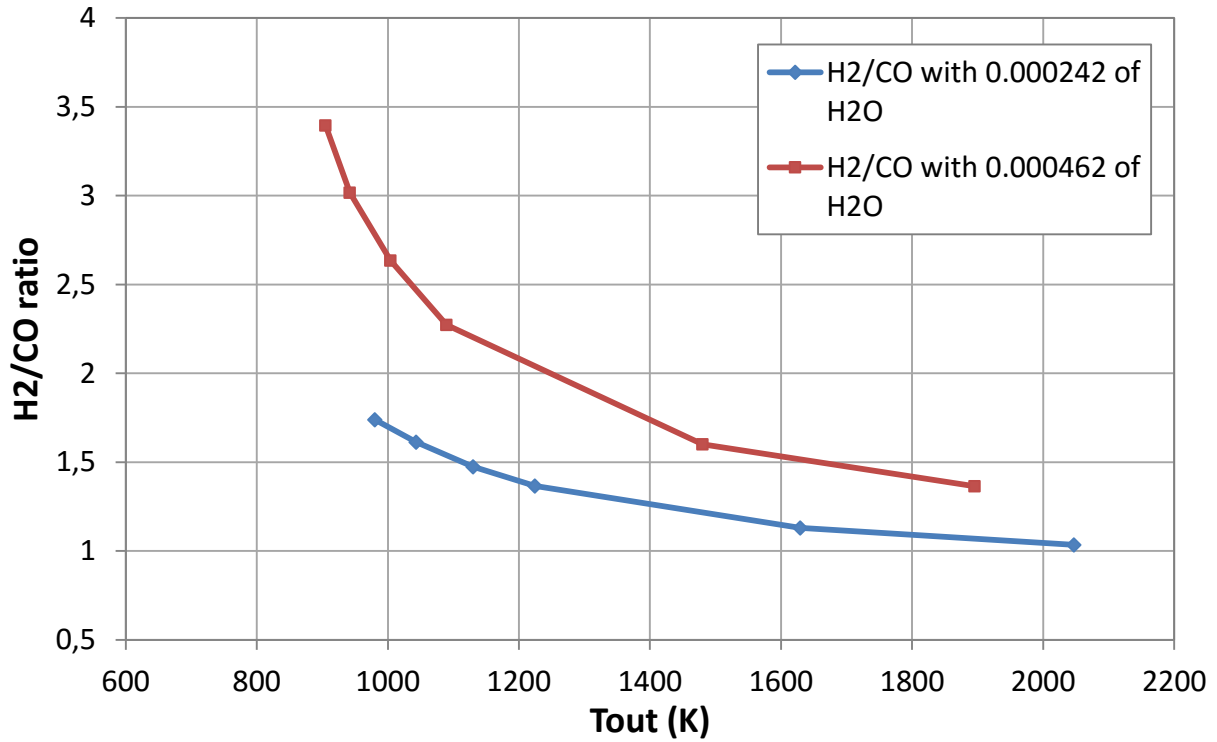
Costant enthalpy simulations
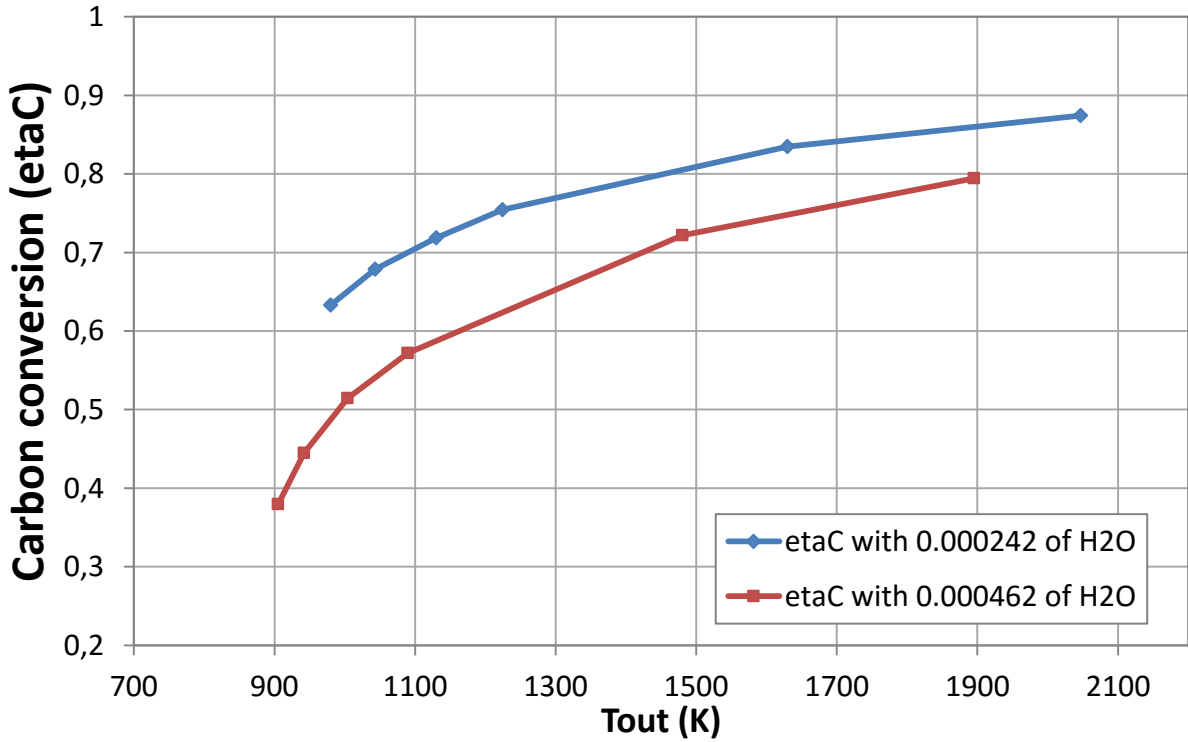
Just a particular mention to the fact that normally the gasification is done into a range of temperature of about 900-1400 K, thus the high temperature reactions are not so dominant.

In the final results it is very interesting to notice that with a quantity of water which is ½ of the quantity of the biomass it is reached a better compromise between the H2/CO ratio and the level of CO2 in the outlet gases.
In fact the gasification cannot be conducted only in presence of water, due to the formation of a higher level of CO2 in the gases and so a lower calorific value.
In addiction the best H2/CO ratio for the syngas is about 1.8-2.2, because in this range can be done many processes downstream and it is avoidable to adjust the ratio with another reactor, which means a great saving in terms of plant costs.

5.2.5 Study of the combustion and gasification regimes

In the second part of the chapter it will be investigated the effect of the variation of the inlet flow of air on the gasification, without using steam.

In fact starting the simulations with a value of the biomass which is similar to the previous simulations (0.0004 kg/s) and using this as a calculation base, the biomass will be 1 and then also the current of air entering the reactor will be rescaled.

At the beginning the system works with an inlet flow of air of 1.5 (that is 0.0006 kg/s), because of a testing approach with lower values of that current and in that condition is notable a fixed coal residue (char) and this is a thing to avoid, thus there is the need to work at least with that value of air.
Then during the simulations the value of the inlet air is increased till reaching the maximum value of 6.25 and the reader can notice many important things about the gasification and the combustion regime, which are reflected also in the gases species leaving the reactor.
We also introduced an important coefficient to measure the gasification and the combustion regime, that is lambda (λ), which gives the ratio between the inlet air flow and the stoichiometric air required for the complete combustion of the biomass (producing CO2 and steam).
For the simulations it is used also in this time the "D-Smoke" program, which is able to simulate homogeneous reactions in gas phase and was created the same input file ("file.dat") in which was inserted all the inlet flows entering the reactor.

In the "file.dat" is used a current of biomass with cellulose, hemicellulose and lignin in the same proportions of the other time, and a current of air (80% N2 and 20% O2).

The differences in these simulations point out the necessity to avoid the use of steam in the inlet flow and the different temperature of the inlet flows, both biomass and air, which are at 300 K at the beginning of the simulation and than the outlet temperature will vary, due to the variation of the lambda coefficient.

Of course both the two commands "CONH" and "CONT" are used, to simulate adiabatic conditions and constant temperature into the reactor, even if the graphs will be reported only for the "CONH" simulations.
The graphs and the discussion of the results can be found below.

Lambda variation at constant enthalpy
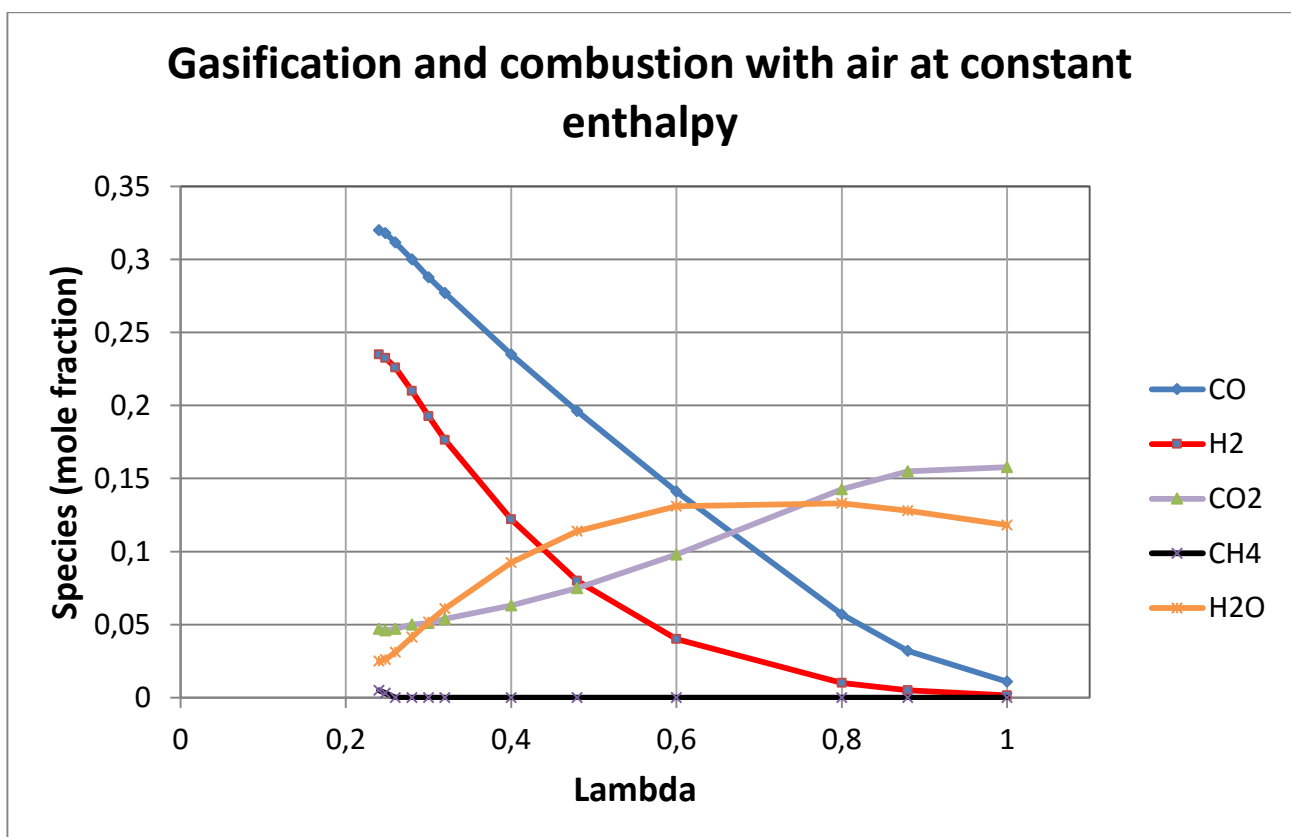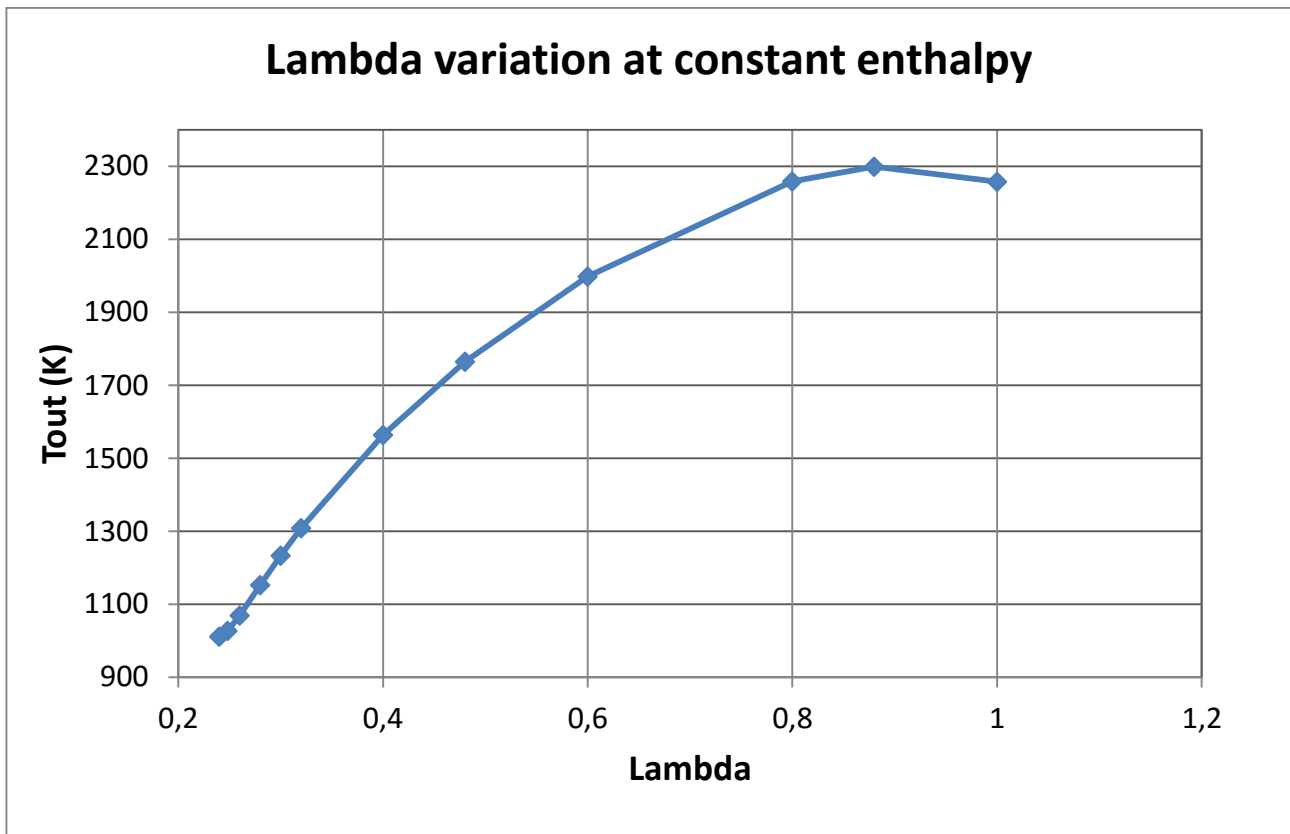
Here in the graphs it is notable the variation of the species and the outlet temperature referred to the parameter lambda.

It is very interesting to notice that at higher lambda values (nearly 1), there is a predominance of the combustion regime and as a consequence also the temperatures are higher; thus into the outlet gases there are high quantities of CO_2 and steam, vice versa at lower lambda values (0.35-0.25) the system reach the conditions of complete gasification and products and temperatures are different, with a predominance of CO and H_2.

Now it is interesting to reason about the correct lambda to choose for the gasification regime, considering that it is essential to avoid an excessive flow of air into the inlet current, not to oxidize too much the syngas and producing too much CO_2, but it is essential also not to work with too poor lambda values for the previous mentioned problems with a coal residue in the outlet gases leaving the reactor.

So the reactor will work with a lambda of about 0.28.

This value allows to have a good H_2/CO ratio and in addiction an outlet temperature enough high (1153 K) not to give a coal residue into the outlet flow.

In addition working with a higher lambda is not an advantage also for an economic optimum, because of a higher air flow entering the reactor and so higher costs for pumping the gases and higher costs of construction of the plant, with bigger tubes.

Also for the downstream processes is better a lower lambda, because it allows a good H2/CO ratio and a low quantity of CO2 and steam into the outlet gases, which signifies lower costs of purification for the syngas.

5.3 *Simulations of coal gasification*

In the previous paragraph it has been made an analysis of the conditions of thermodynamic equilibrium for a biomass of reference and the operative conditions in terms of air and steam needed to have a satisfying gasification, in terms of syngas produced with a good H2/CO ratio, useful for other downstream processes.

Now, always using the same computational tools ("D-Smoke"), let's start to approach a feasible analysis for the coal gasification, always with some simplifications, considering an homogeneous system with only a gas phase and considering only the most important compounds freed from the solid to the gas phase to simplify the calculation efforts.

First of all it will be determined, using a fixed inlet temperature and doing a gasification with only air as gasifying agent, a correct λ value (ratio between the input air and the stoichiometric air for the complete combustion), then using that λ the analysis continues with the variation of a few parameters (for example the H2/CO ratio or the eta C) and the inlet temperature of the reactor.

After this it will be introduced a steam dilution of the system, working with both air and steam, and the effects of this dilution on many parameters will be parameterized, finding the correct quantity of steam which is useful for the gasification and trying to work with adiabatic conditions and a H2/CO ratio about 2.

Finally let's move from a thermodynamic and equilibrium approach and pass to a kinetic approach, which accounts for both the two phases (solid and gas) and let's make other simulations with the "GAS-DS" tool, using many parameters and initial conditions developed and reached with the thermodynamic equilibrium approach.

An important thing is that at the beginning only a simplified coal (only COAL2) is considered to launch the simulations, even if there are no results here, because it was used only to test the sensibility of the parameters and verify then the

simulations done with a more complex type of coal, which included both the three main type of coals (COAL1, COAL2, COAL3).

5.3.1 *Operative conditions of the first simulation*

First of all it is important to mention the fact that for these simulations the same computational tool ("D-Smoke") is used; for this reason there is the need to create the same structure of the previous simulations made with the biomasses.

Thus the work will be done with the program "dsmoke82.exe", which will simulate our reactor.

All the simulations included in this chapter will be done with the command "CONH", which simulates an adiabatic reactor.

The following step is to create the "file.dat", in which will be specified the input conditions of the simulation (inlet flows of coal and air, temperature, pressure and the composition of all the flows).

After this it will be compiled and executed the file "RUNBAT", which includes the "file.bin", with the kinetics of the gas phase reactions and involves many species (about 70) and in this case it is used the file "Coal_1201.BIN".

Of course this new "file.bin" is different from the other one used with the biomass, because now includes only the gas-phase reactions involved in the coal gasification.

The coal used in these simulations is made by a mixture of COAL1 (4.5%), COAL2 (62.0%) and COAL3 (24.6%) and a part of ASH (9%), which is equally divided and split in the three coals.

This is very important, because also during the first analysis the gas phase compounds took part from these type of coals (in fact we have from COAL1 FUEL1, from COAL2 FENAOH and from COAL3 a mixture of FENAOH, FE2MACR and COUMARYL).

At the beginning λ values will vary, with a constant inlet temperature (300 K), and an analysis is requested to discover which fits at the best the data to have a correct gasification and a good outlet temperature to run the gasifier with adiabatic conditions.
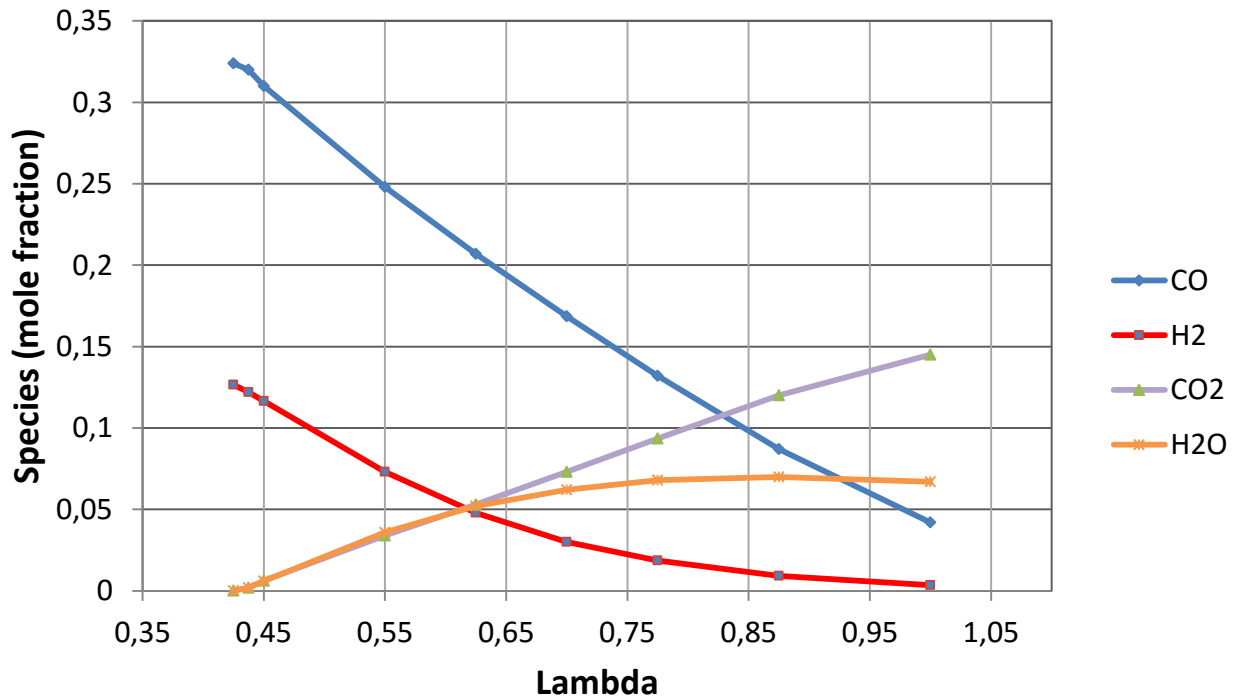
Now everything is ready for the start-up of the simulations with a fixed quantity of coal (0.0004 kg/s).

The results and the discussion are shown below.

Lambda variation at constant enthalpy
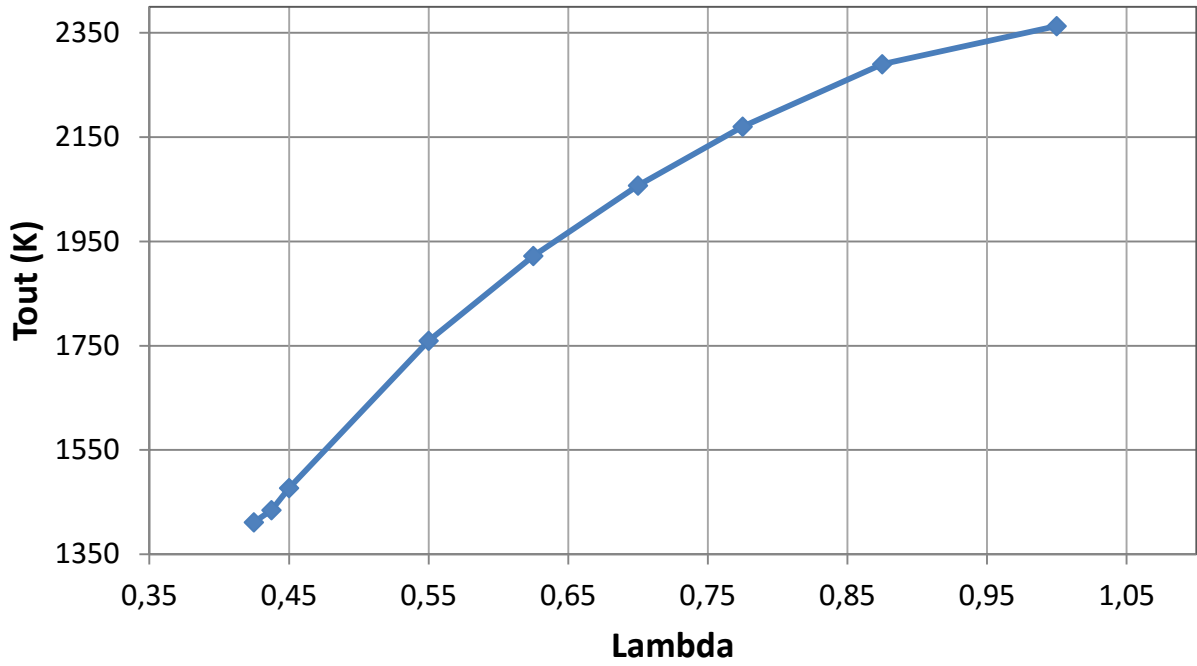
Gasification and combustion with only air

As showed by the graphs above, there is a combustion regime with λ values of about 1 and then diminishing λ it is possible to approach the gasification regime.

If the λ values are equal to 1 (and so with a quantity of air which is equal to the stoichiometric value) there is a combustion regime and a predominance of steam and above all of CO2, but then when passing to lower λ values (0.5-0.4), it is notable a prevalence of the gasification regime and a predominance of CO and H2.
The most important fact is determine a λ optimum for the gasification reaction, because of a great production and an optimization of CO and H2, but also to ensure a high temperature, necessary to run the reactor and the entire process in an adiabatic way; in addiction to ensure the consumption of all the carbon, avoiding solid residues at the outlet of the gasifier.
With these informations it is possible to choose a proper condition of λ = 0.438, which allows to reach at the exit of the gasifier the temperature of 1435 K and have no solid carbon leaving the reactor.

Starting by this value of λ, there is the possibility to find the value of ϕ (1/λ), which is 2.286 and this is the ratio between the stoichiometric air to have a complete combustion and the air used in this case for the gasification.

5.3.2 Simulations with a fixed λ and varying the inlet temperature

Discovered a correct λ (0.438) and continuing to use this during next simulations, let's start to change the inlet temperature of the reactor (Tin).

In fact if at the beginning it was used a fixed Tin (300 K) for the simulations, then in these new simulations is changed within an open range of values (500-1000 K), because of the need to test and verify the sensibility of the parameters, such as the H2/CO ratio or the overall species involved (CO, H2, CO2, H2O, CH4).
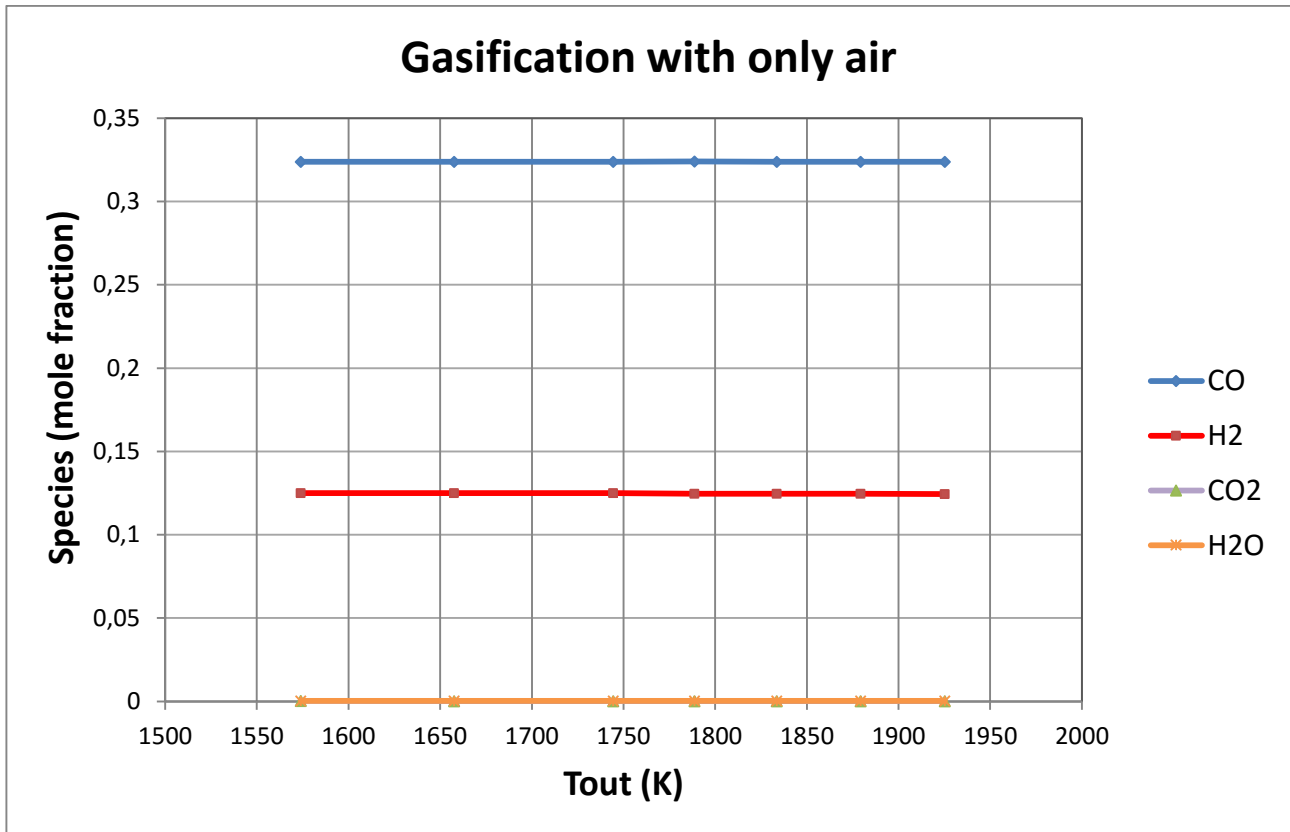Always remember that for this fixed λ, there is the need in the reactor a stoichiometric quantity of air for the complete gasification (0.00173 kg/s). In the following pages are shown the graphs and a discussion of these simulations.

Gasification with air at constant enthalpy

Gasification with air at constant enthalpy
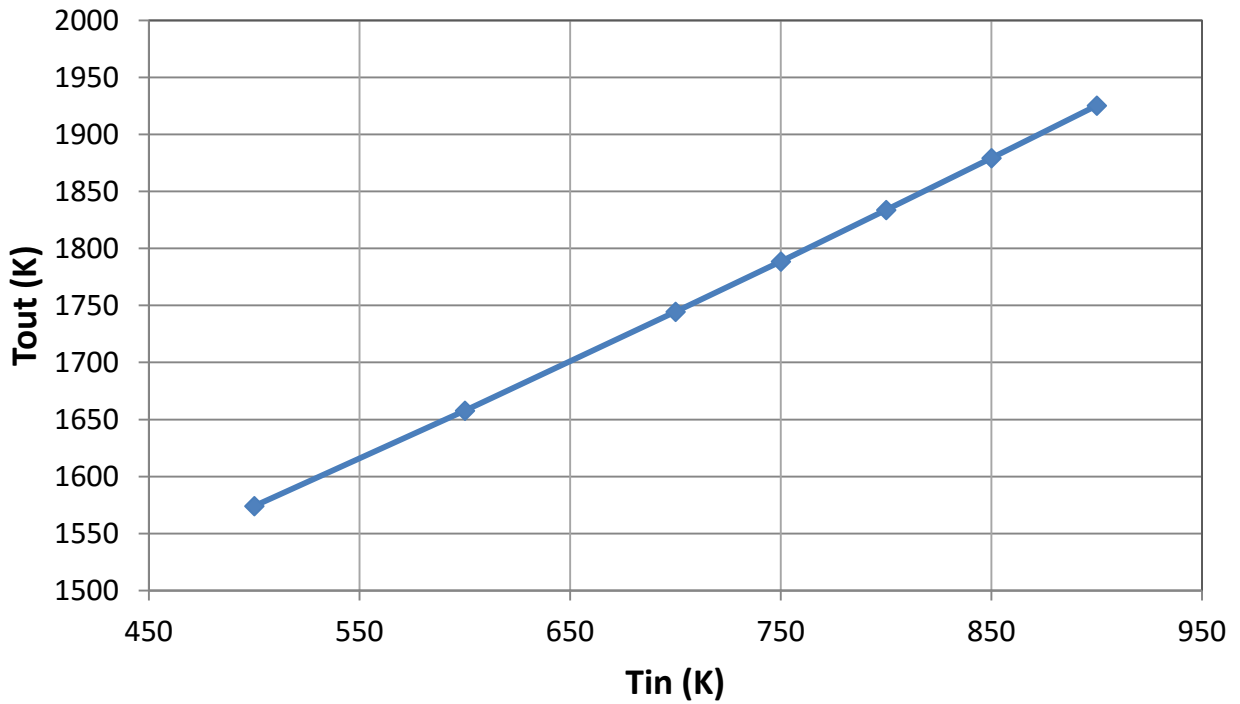
Gasification with only air
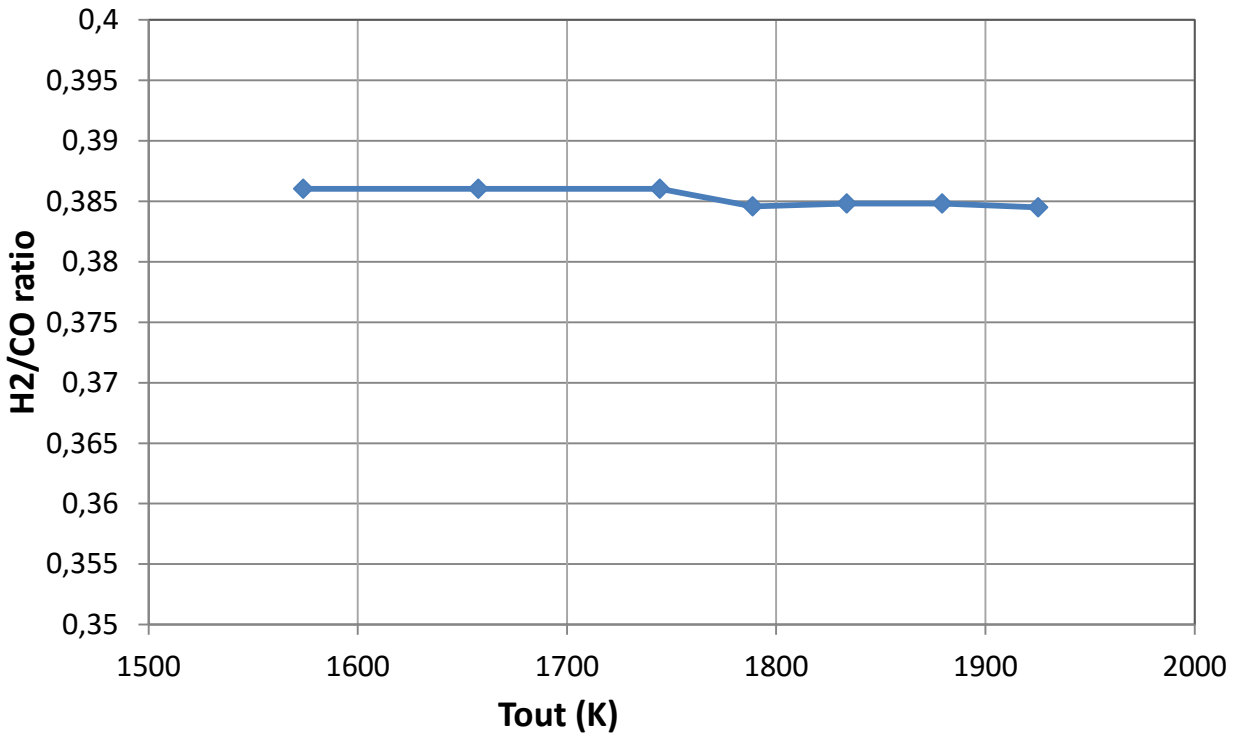
There is not a significant change in the gasification regime and conditions with the temperature. In fact the H2/CO ratio is nearly the same (0.384-0.387) while the temperature varies from 500 K to 1000 K.

This constant evolution in the ratio H2/CO can be seen also from the graph with all the species, where there is a predominance of CO and H2 and lower levels of CO2 and steam, in according with the gasification regime.

Also the trend of Tin (inlet temperature) and Tout (outlet temperature of the reactor), it is underlined how is a linear profile, in which varying the Tin, the Tout is always quite linear in changing.

This is important because in adiabatic conditions, there is not a change of the exothermic reactions and so of the heat produced, rising the inlet temperature (Tin).

5.3.3   *Simulation with air and a stoichiometric quantity of steam*

Now using always the same quantity of air, there is the need to study the gasification of coal with the implementation of a stoichiometric quantity of air into the system. First of all it is studied alone the reaction of steam gasification, which starts from coal and steam and leads to CO and H2 and it is possible to discover the stoichiometric quantity of steam requested to add at the system to reach the complete conversion of the solid coal in gas products. The stoichiometric quantity of air is always 0.00173 kg/s, while the stoichiometric quantity of H2O is 0.000416 kg/s and the coal is 0.0004 kg/s. In the following pages the quantity of air and steam will be expressed as divided by the base of calculus of the coal quantity and so they will be expressed as kg/kgC (kilograms on kilograms of coal). Then let's change the "file.dat", because this time there is the need to introduce not only the gas species for the coal (FUEL1, FENAOH, FE2MACR, COUMARYL) and the air, but also the steam and mixing the three flows at the same temperature (Tin) before entering the reactor. After it is possible to start the simulations, investigating a wide range of operative conditions for the inlet temperature (500-1000 K) and noticing the change in the gases species exiting from the reactor. The graphs are showed below with their respective brief discussion.
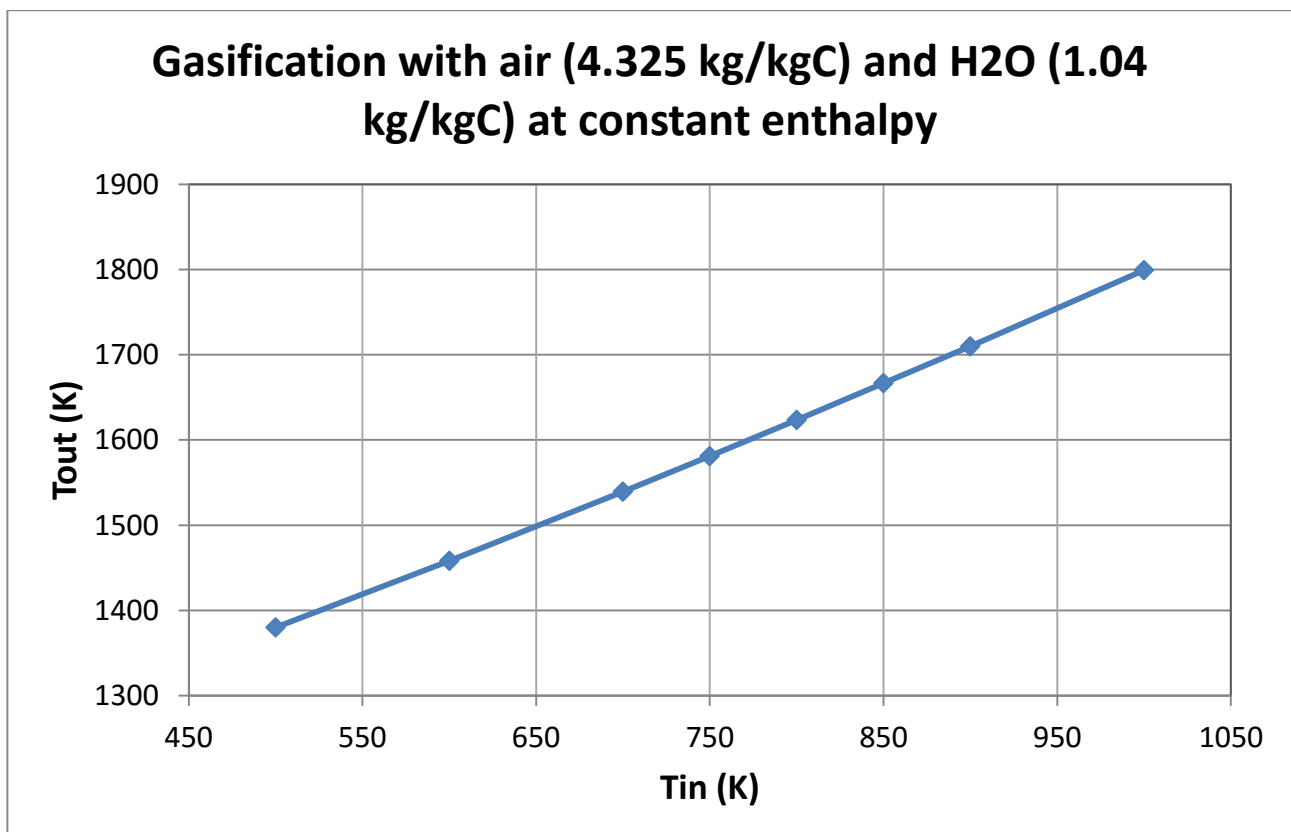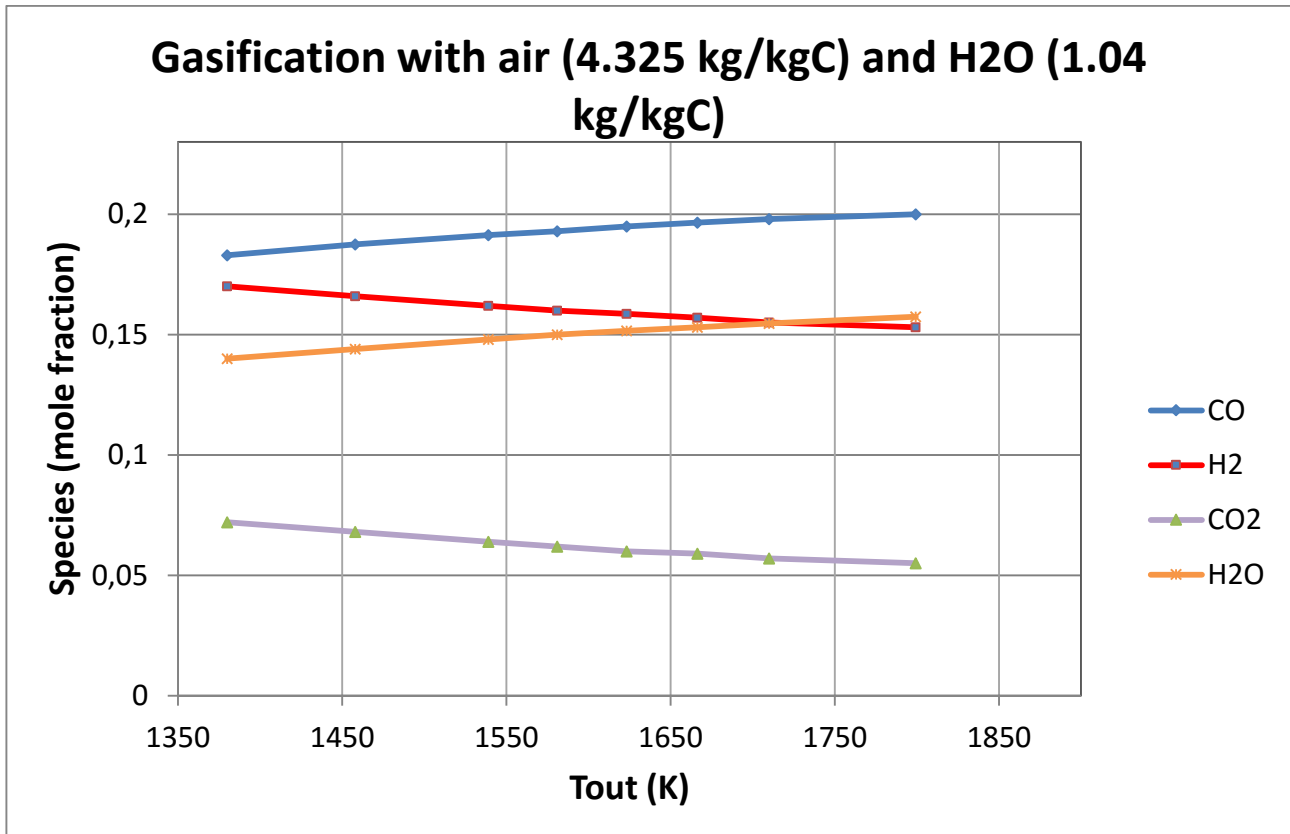

Gasification with air (4.325 kg/kgC) and H2O (1.04 kg/kgC) at constant enthalpy
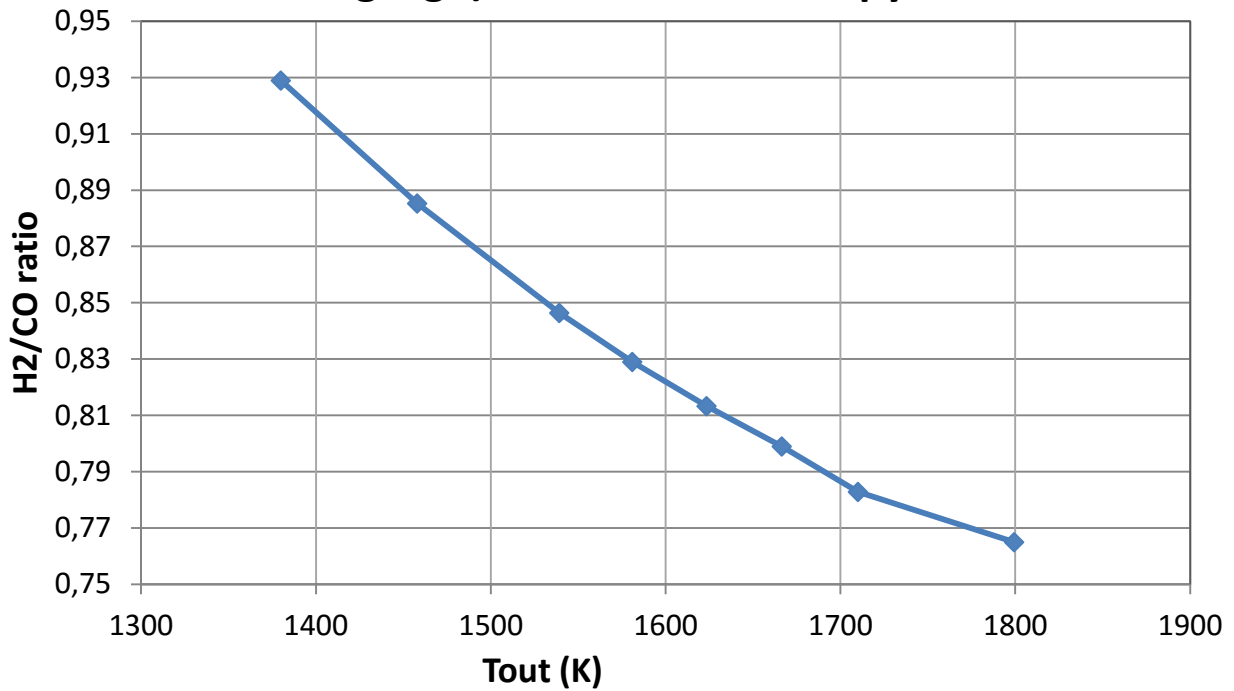
Gasification with air (4.325 kg/kgC) and H2O (1.04 kg/kgC) at constant enthalpy

Gasification with air (4.325 kg/kgC) and H2O (1.04 kg/kgC) at constant enthalpy

Gasification with air (4.325 kg/kgC) and H2O (1.04 kg/kgC)
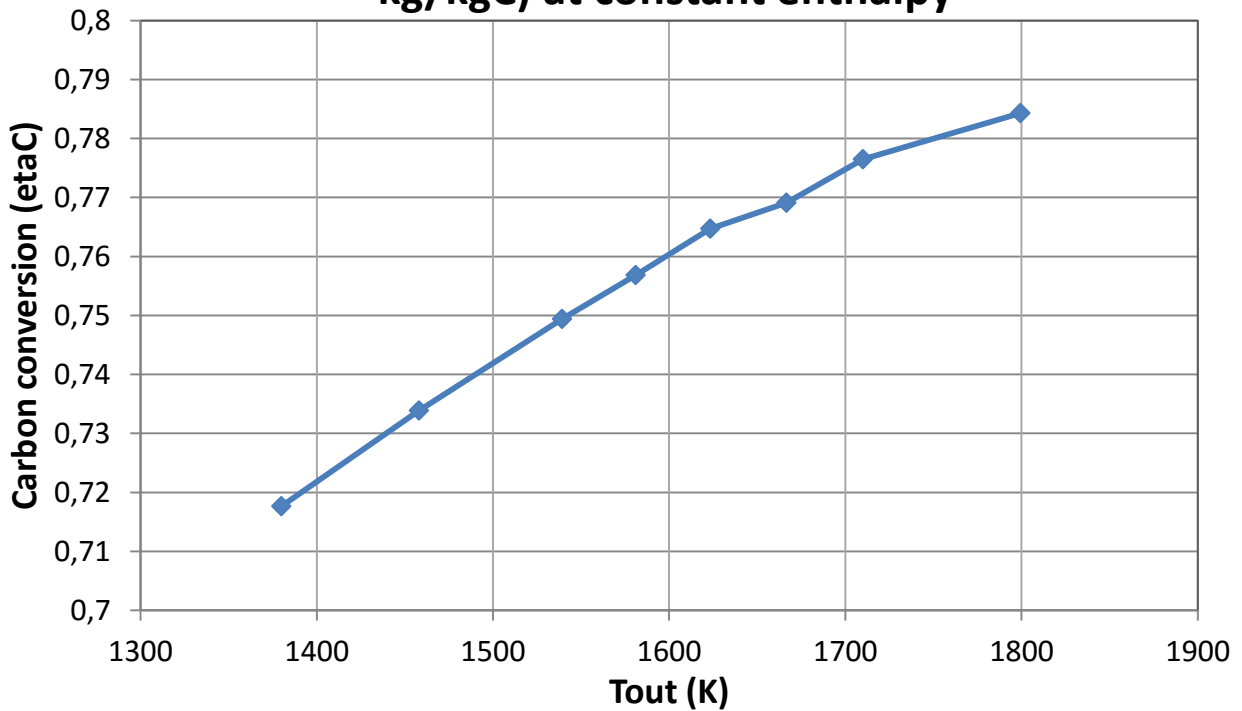
First of all there is a high change in this new configuration, with the adding of steam to the inlet flows. In fact a higher level of H2 is noticed into the outlet gases; thus also a higher H2/CO ratio.

Another interesting thing is the presence of a higher quantity of CO2 (0.08-0.06%) and a higher quantity of H2O and the major presence of these two species can be explained with the adding of steam which increases the quantity of oxygen and hydrogen in the system.

The two main things shown by the graphs are that now the H2/CO ratio is higher (0.8-1), but it is not enough to reach the ratio of 2, which is very good for the downstream processes (especially for the processes related to the FT or the methanol synthesis) and this evidence is confirmed also by the parameter etaC, which gives us the quantity of carbon converted in CO (0.71-0.79).

A higher level of CO and H2O with the increase of the temperature and the decrease of CO2 and H2, due to the reaction of CO2 which gives CO at high temperatures (significantly above 1900 K), and above all due to the reaction of RWGS which gives CO and steam starting from CO2 and H2.

The other important thing is that with the adding of steam the reaction and the system is less exothermic and operates with more facility in auto-thermic

conditions, because the heat provided by the oxidation is used for the endothermic reactions with the steam.

Now in the next simulations it is kept constant the quantity of air as usual and it will be added more steam to the system from a side, while from the other it will be decreased the air, keeping constant the quantity of steam entering the reactor and it will be noticed from the changing of our parameters what is the best way to exercise the gasifier in terms of H2/CO ratio, temperature reached (Tout), etaC.

5.3.4 Simulations with air and steam

In these new simulations the system starts from the previous values reached before keeps constant the quantity of air (4.325 kg/kgC), increasing the quantity of steam introduced into the reactor (passing from 1.04 kg/kgC to 2.69 kg/kgC).

As usual the evaluation of the sensibility of many parameters will be done, expecting a higher level of the H2/CO ratio as a consequence of the higher H2O entering the system. Of course the simulations are made varying the Tin into a wide range of temperatures (500-1000 K) to test and verify the trend of the parameters.

The graphs and a brief discussion are shown below.
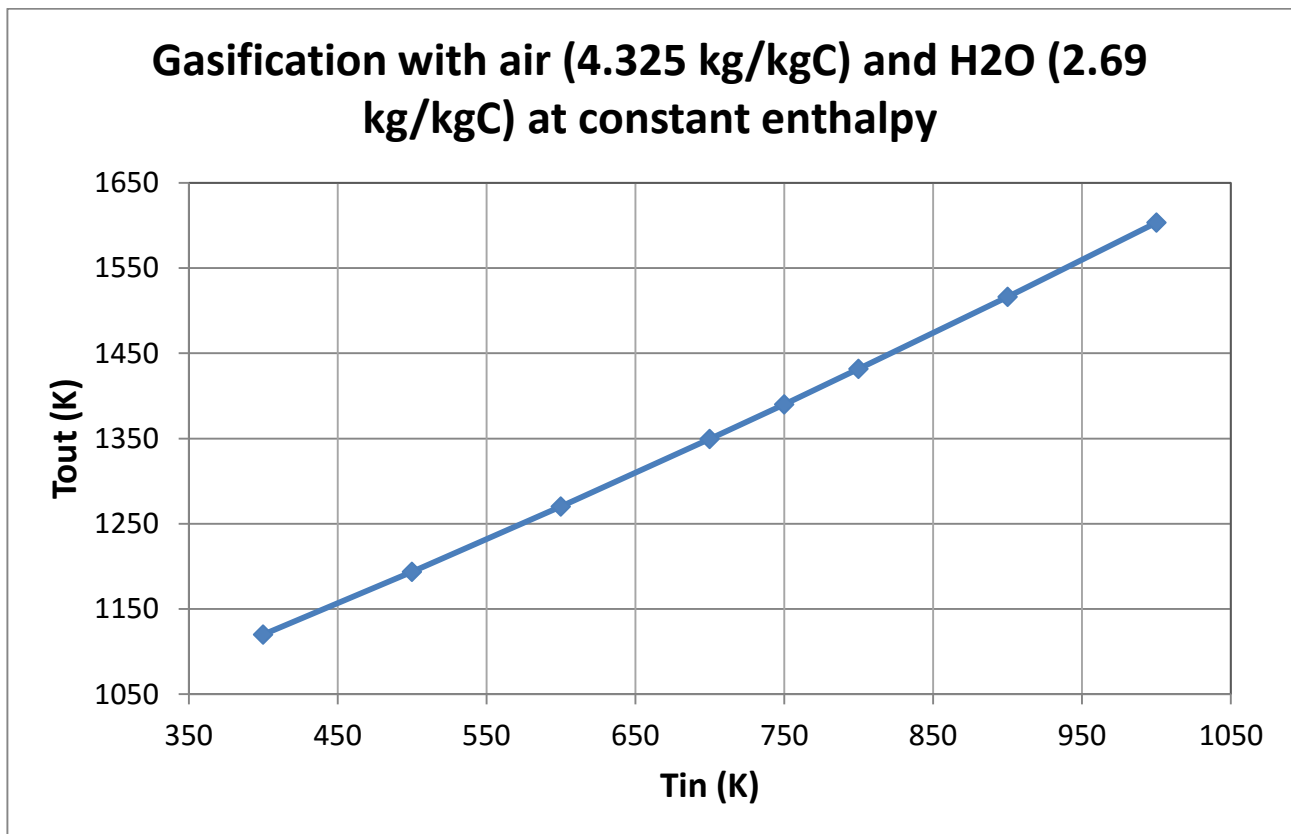
Gasification with air (4.325 kg/kgC) and H2O (2.69 kg/kgC) at constant enthalpy

Gasification with air (4.325 kg/kgC) and H2O (2.69 kg/kgC) at constant enthalpy
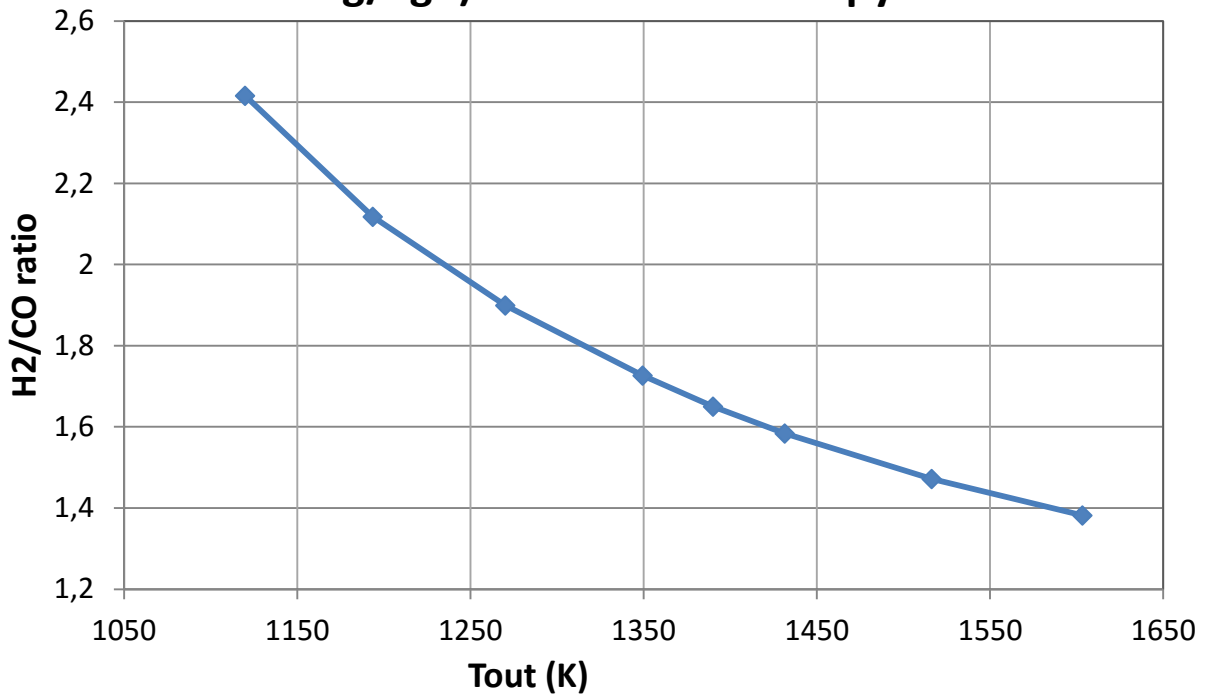
Gasification with air (4.325 kg/kgC) and H2O (2.69 kg/kgC)
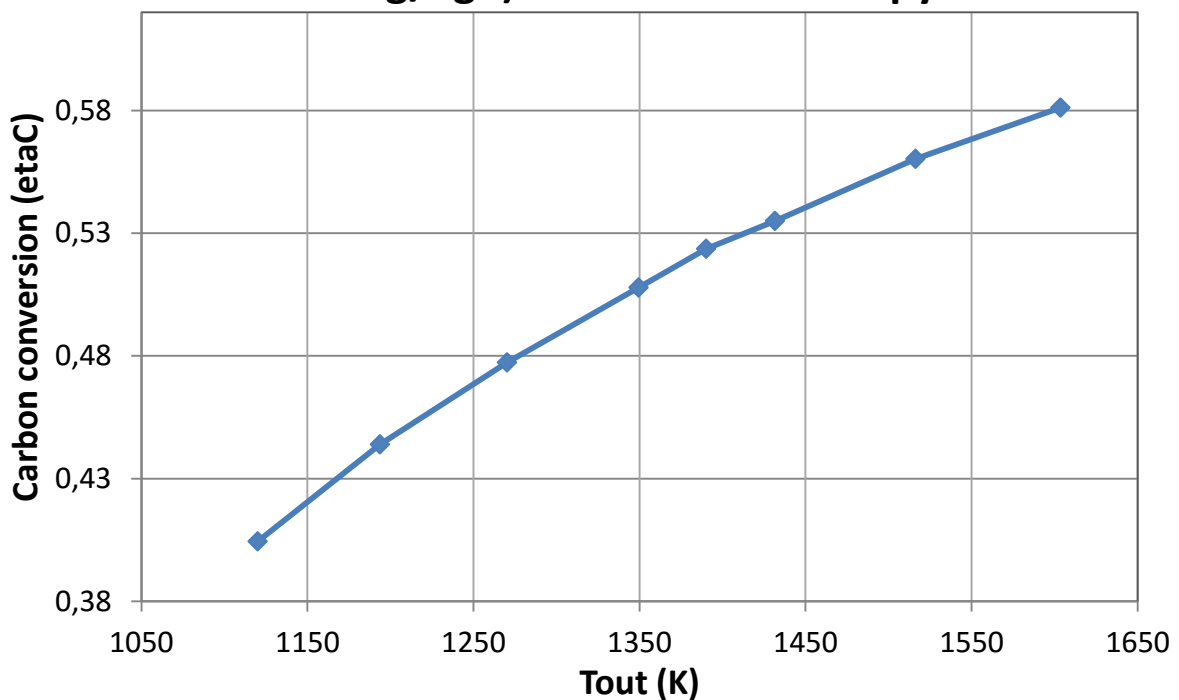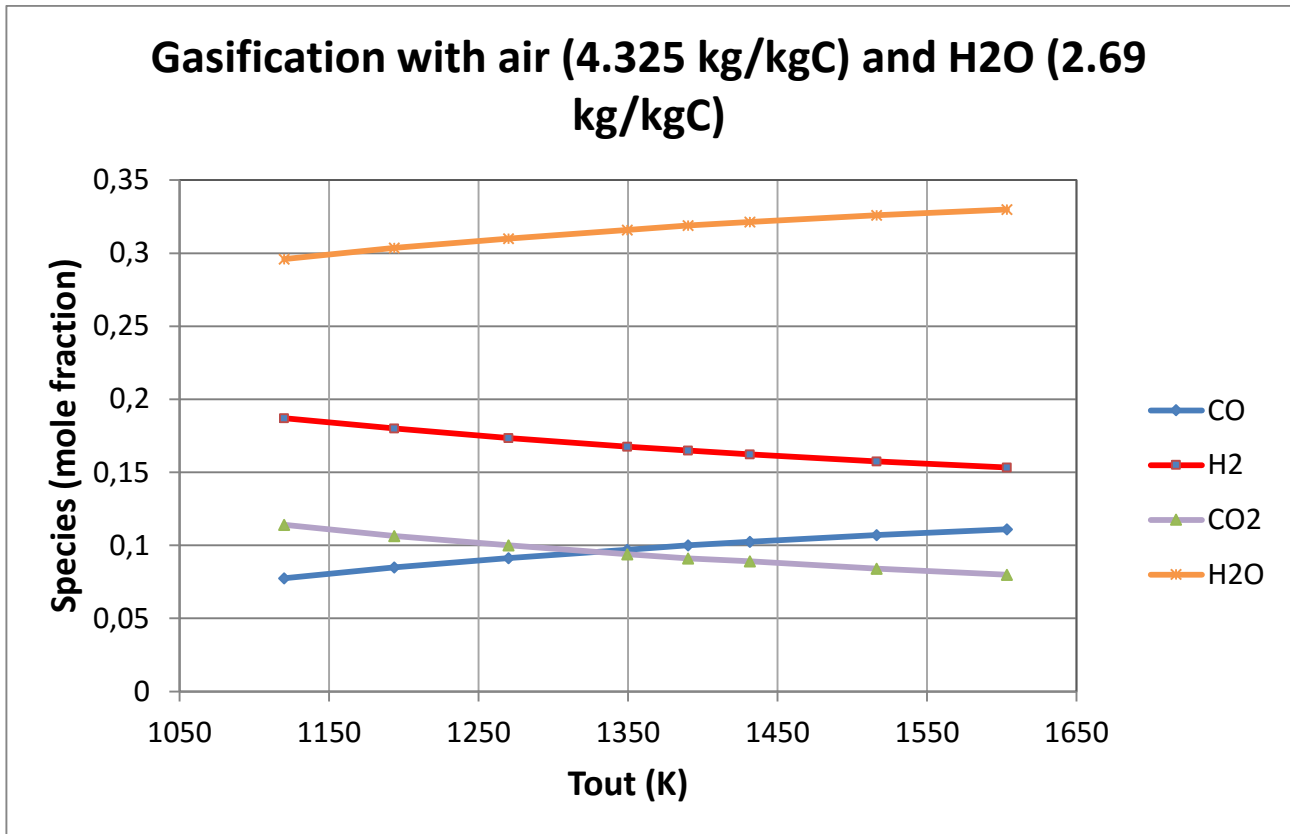
The first important thing in these simulations it is the presence of a higher level of the H2/CO ratio as expected and mentioned before, due to the adding of a major quantity of steam into the reactor.

The H2/CO is about 2.5-1.5 (an optimal ratio is 2) and this because there is a decreasing in the quantity of H2 because of the reaction of RWGS which transforms the CO2 and the H2 in steam and CO and in fact it is interesting to notice also an increase of the steam in the gas species leaving the reactor.

The second important thing is that for a high H2/CO ratio, there is a lower etaC, because of a higher level of CO2 and so as a consequence a lower conversion of carbon in CO.

This is a bad news, because if the gases leave the system with a high level of CO2, this means that our syngas has a lower calorific value and needs to be purified more for the production of fine chemicals.

Now, with these parameters introduced above, gasification loses its exothermicity respect to the previous simulations, due to an addition of a higher quantity of steam, which produces endothermic reactions; instead there is the advantage to operate with lower temperatures without having a solid residue of carbon. It is important to repeat the concept of the willing to operate in auto-thermic conditions

and the intention to avoid an excessive decreasing of the temperatures due to a lot of steam added to the system.

After seeing the case with the same quantity of air (and so with the same fixed λ = 0.438), now let's investigate the case in which it is used a lower quantity of air in the inlet flow and the same quantity of steam of the previous simulations. It is expected a decrease of the temperatures in the reactor zone, due to a higher percentage of steam and so the predominance of the endothermic reactions with steam and not the exothermic reactions of oxidation with air. The work has always been done with the same coal flowrate (0.0004 kg/s) with a steam to coal ratio of 2.69 kg/kgC and an air to coal ratio of 3.5 kg/kgC. As usual the start-up of the reactor has been done with a wide range of temperatures to see the influence of many parameters (H2/CO ratio, etaC, Tout). In addiction it is expected a higher level of H2 and steam in the gases leaving the reactor, because of the introduction of a higher quantity of steam in the reactor at the beginning. Below are shown the graphs of the simulations and a brief discussion of them.
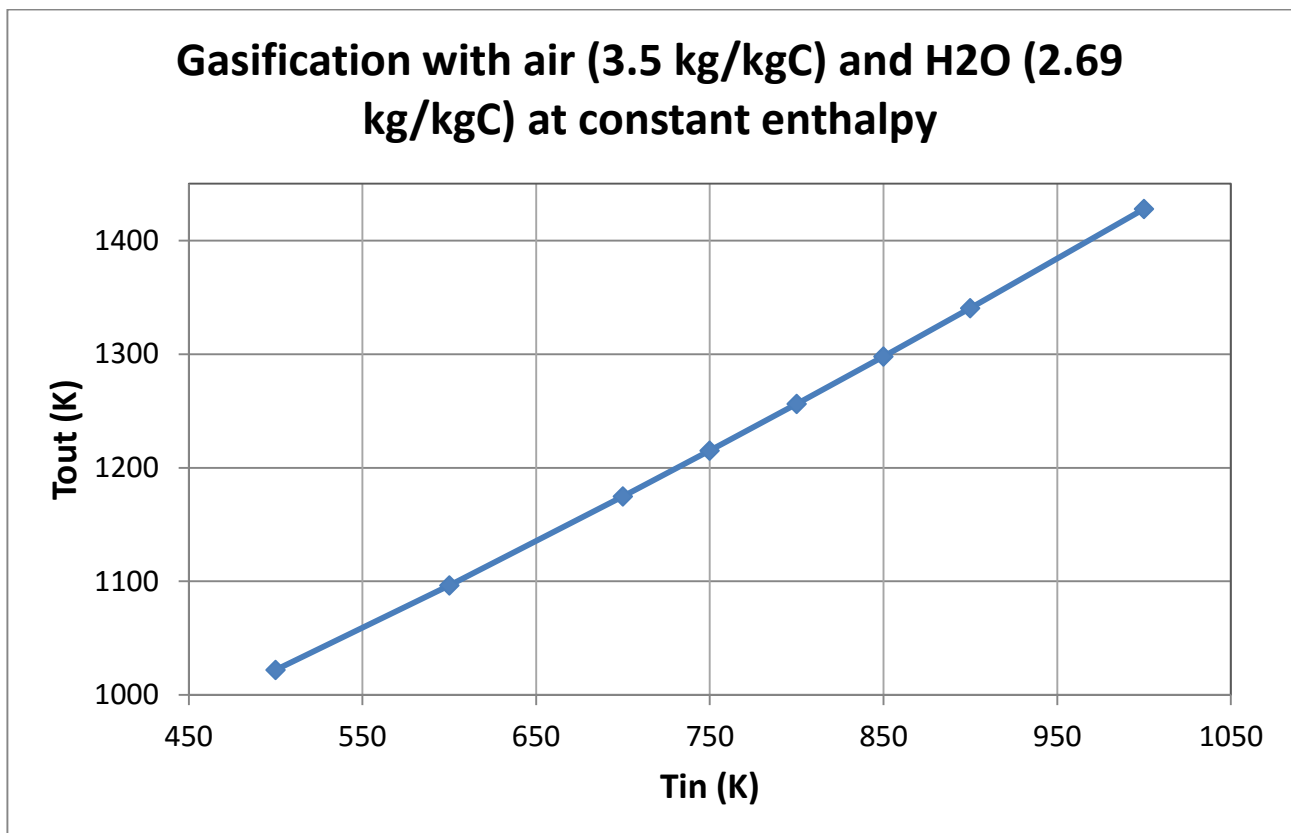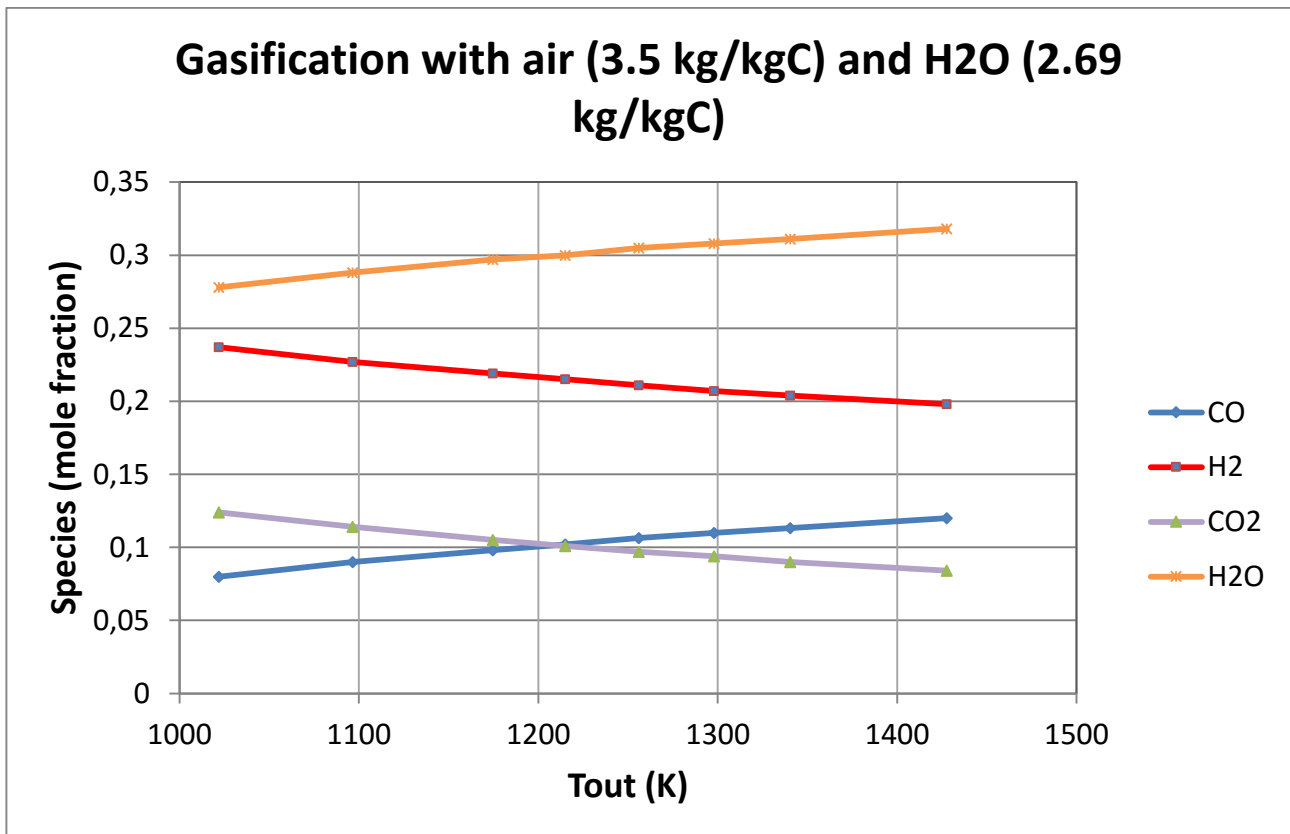

Gasification with air (3.5 kg/kgC) and H2O (2.69 kg/kgC) at constant enthalpy
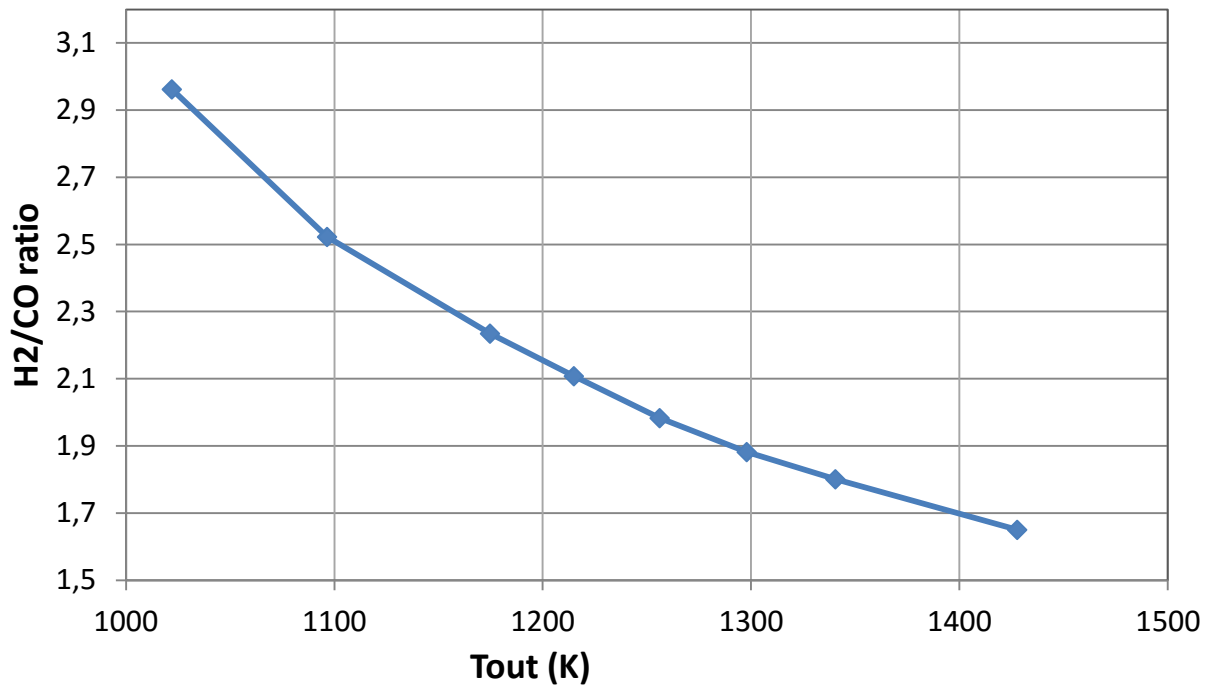
Gasification with air (3.5 kg/kgC) and H2O (2.69 kg/kgC) at constant enthalpy

Gasification with air (3.5 kg/kgC) and H2O (2.69 kg/kgC) at constant enthalpy

Gasification with air (3.5 kg/kgC) and H2O (2.69 kg/kgC)
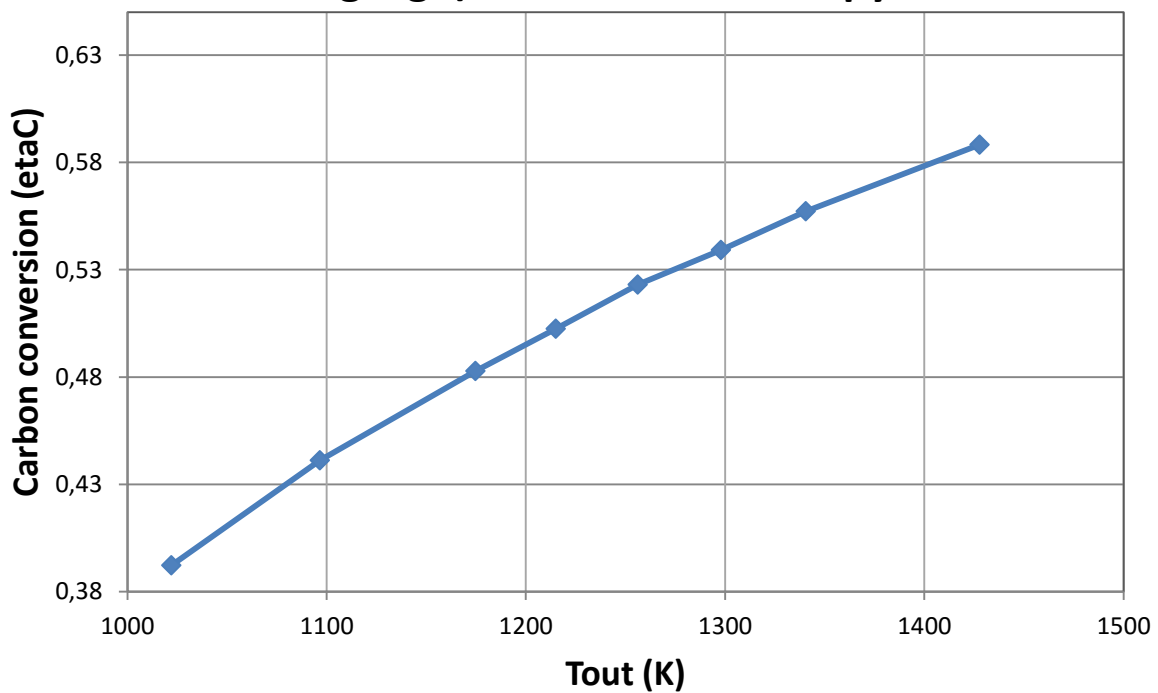
In these new simulations there are many interesting things.

First of all, as expected, there is once again a linear trend for the graph of the Tout in function of the Tin, but it is notable a high decrease of the outlet temperatures (Tout), because this time the quantity of air has been decreased and so there is a predominance of endothermic reactions with the steam.

The second important thing is that in the graph with the gas species leaving the reactor, there is a higher quantity of H2, while the quantities of steam, CO2 and CO are nearly the same of the previous simulations.

This fact is proved by the other two graphs: in fact if from a side there are higher values for the H2/CO ratio (2.9-1.6), from the other side the parameter "etaC" is fixed and it is the same for the quantities of CO and CO2.

 It is also notable a predominance of CO2 at lower temperatures and CO at higher temperatures and this because of the reaction of RWGS, which is endothermic and gives CO and steam and consumes CO2 and H2, added to the reaction of formation of CO starting by CO2 at high temperatures (even if this reaction is very competitive and significant above 1900 K and not so predominant here).

5.3.5 Results and discussion

In this paragraph the coal gasification was investigated, using only a simplified model to describe it, and not analyzing all the complete phenomena involved in the reaction. In fact it was used a program which works only in homogeneous conditions and a simplified kinetics, which accounted for the reactions in the gas phase and not for all the reactions involved in the gasification.

This was possible thanks to the hypothesis that all the three main components of the coal (COAL1, COAL2, COAL3) release four main volatile components in the gas phase (FUEL1, FENAOH, FE2MACR and COUMARYL); then with these components it is possible to use a simplified kinetics for the gas phase and not also for the solid phase, always standing the hypothesis of homogeneous conditions.

The second important thing is that in the simulations the scope was to arrive to the thermodynamic equilibrium, because the outlet gas composition was interesting for the study and it has been modeled the program and the reactor to reach this condition.

Then after having compiled the program, the simulations started, using at the beginning only coal and air (oxidative pyrolysis) and then starting to use a small quantity of steam, till reaching a high quantity of steam with the same quantity of air. Then it was used a reduced quantity of air and always the same quantity of steam of the last case mentioned before, in conditions which were similar to the normal conditions of gasification.

At the beginning there was the intention to reach the conditions of the ideal oxidative pyrolysis, using only air, and then moving the steam value it was reached a higher level of H2/CO ratio.

Here as in the previous chapter for the biomass gasification, the addition of steam to the inlet flow was good for the H2/CO ratio, and as mentioned before it is very important for the downstream processes, but it was also noticed the presence of the WGS reaction, which is favored with the presence of steam and gave a higher quantity of CO2 in outlet gases, which is not a good thing, because the parameter "etaC" is lower, due to the presence of CO2 and a less quantity of CO.

In addition the introduction of steam to the system wants to favor the gasification reaction of solid carbon, which gives CO and H2 from steam and C (solid carbon) and

it is very important for the production of a higher level of syngas and not to decrease the H2/CO value.

Below there are the graphs which discuss the trend of the H2/CO ratio and the parameter "etaC" for different operative conditions in which it is exercised the gasifier.

As usually the graphs are made for the "CONH" simulations, but the simulation were proved with both the command "CONH" and "CONT", to underline the sensitivity of the parameters, even if only the graphs for the "CONH" simulations will be showed, because of the similarity of the data found.

Constant enthalpy simulations
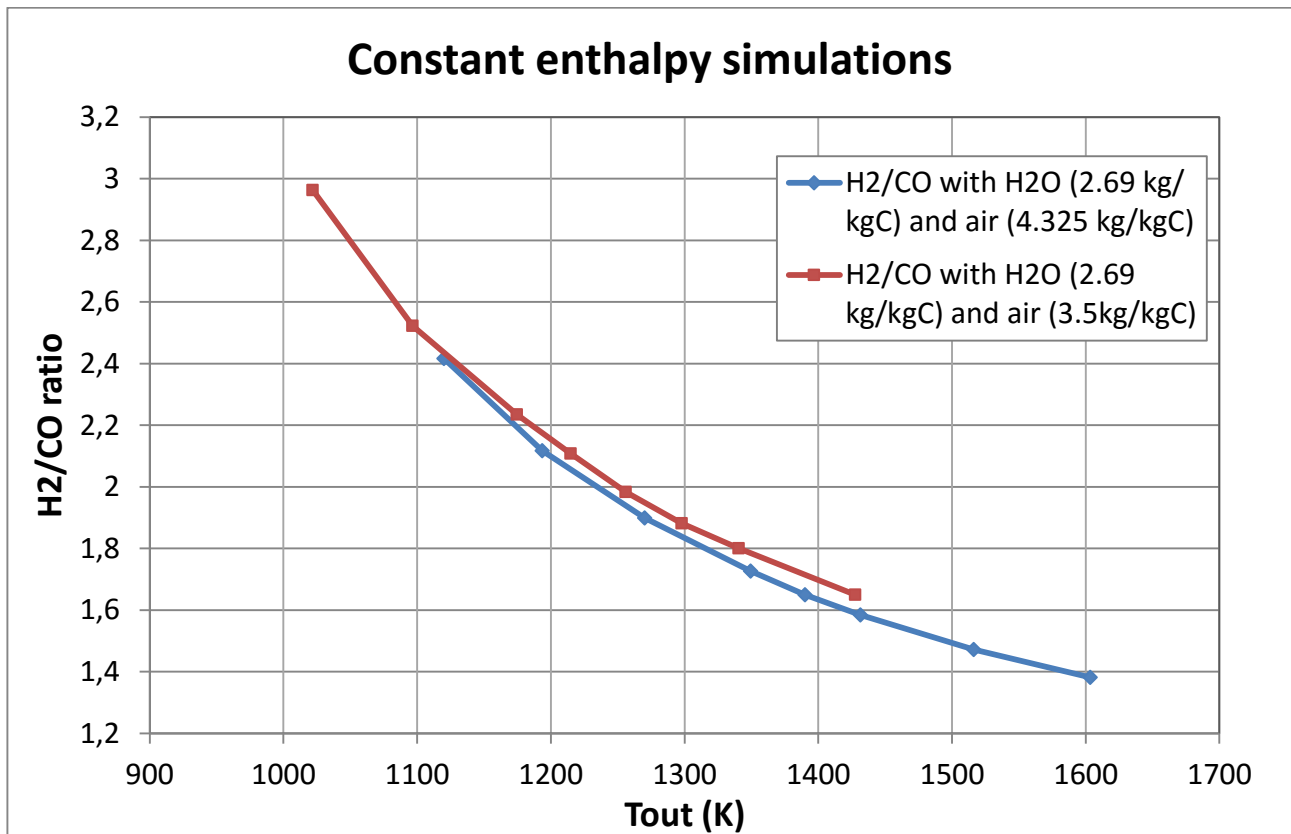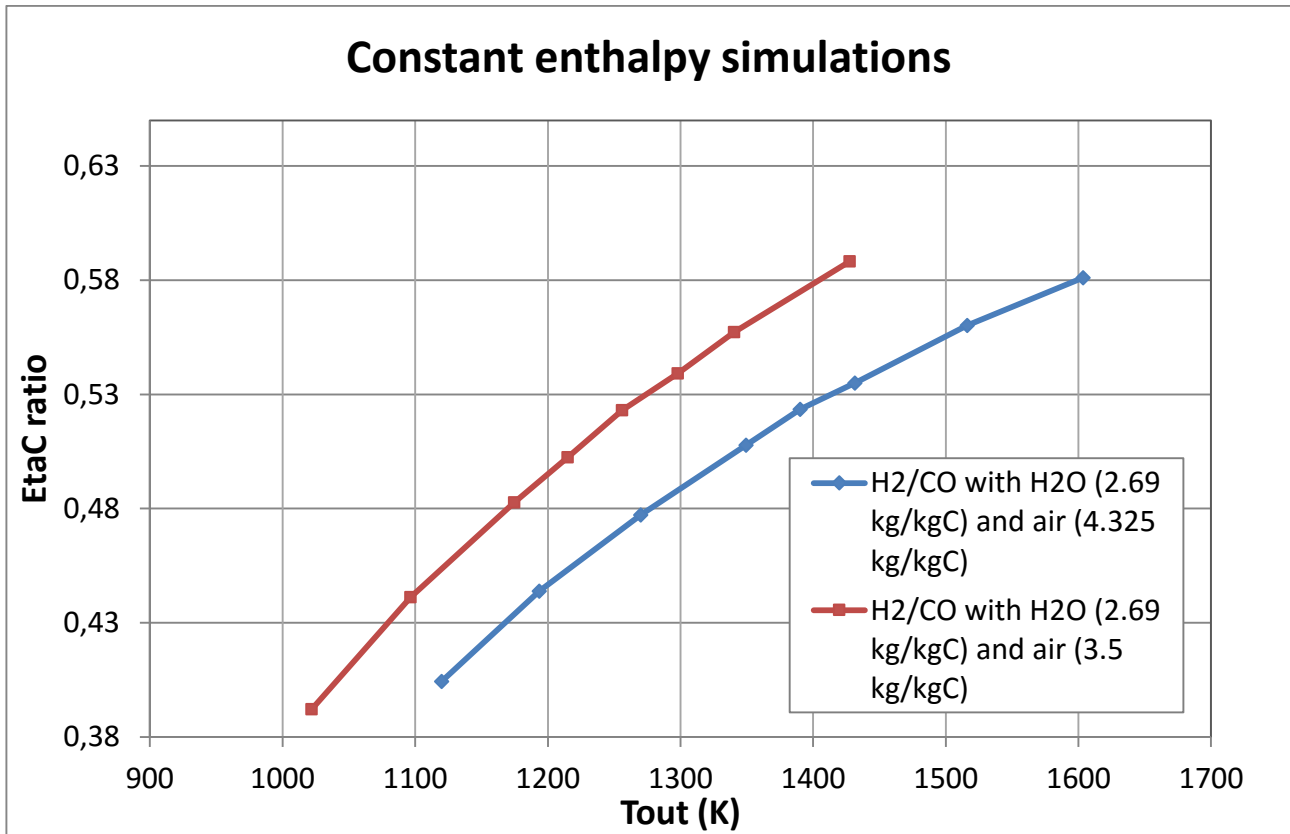
Here these graphs compare two different operative conditions with the same quantity of steam, but with a different quantity of air. The parameter "etaC" is nearly the same, and also the CO and CO2 species have the same values, but it is underlined that the value of H2 is different and increase with the decrease of the quantity of air.

This second fact is also confirmed by the fact that the H2/CO ratio is different during the two simulations and is higher with a less quantity of air, due to the fact that reducing the air there is a lower quantity of H2 which is oxidized to produce steam. The fact of reducing the quantity of inlet air is very important also for the outlet temperatures (Tout) of the reactor and for the conduction of the process; in fact with lower air there is a predominance of endothermic reactions respect to the exothermic ones.

The H2/CO ratio is the other important and fundamental parameter, because of the downstream processes that needs to be executed (the ideal value should be about 1.8-2.2). It is better finally for the gasifier to operate with a level of air of 4.325 (kg/kgC) and steam of 2.69 (kg/kgC), because of the possibility to reach higher outlet temperatures (Tout) and in reason of this a good H2/CO value (about 2.4-1.4).

A lower value of air has a benefit from a side with a better H2/CO ratio (about 3-1.7), but it has the disadvantage of a major endothermicity and lower outlet temperatures and for this reason it is much more difficult to run the gasifier in auto-thermic conditions.

6 Simulation of coal and biomass gasification with kinetic models

6.1 *Introduction*

This chapter will starts from the basis of the gasification in terms of thermodynamic equilibrium and will continue with the dissertation of the kinetic analysis, basing it on the results obtained before with a simplified system. In fact in the previous chapter (using the "D-Smoke" tool), it was investigated the gasification feedstocks (coal, biomass) as a homogeneous system in which the effects were registered only for the gas phase and to do this it was introduced some simplifications.

Now let's start to consider all the complex phenomena involved into gasification and use a new tool called "GAS-DS", which is a software developed by the "POLIMI", which allows to consider a heterogeneous system with many reactions in both solid and gas phase.

Between the two programs ("D-Smoke" and "GAS-DS") there is a great difference in terms of conditions analyzed, precision and computational effort; in fact with the "GAS-DS" program the user is able to consider all the reaction which happens in the gasification system and consider both the two phases (gas and solid), thus with a better precision, but this due to a higher computational effort and a higher time of calculation.

Here in the follow-up there is a brief explication of the kinetic model of gasification into the gasifier, with a description of the mathematical models used and the successive implementation of the algorithm in "GAS-DS".

Then it is shown the simulations done before for coal gasification and for biomass gasification, their results and finally a discussion of its with the conclusions.

6.2   *Particle and reactor model*

In order to model and simulate the gasification process, a suitable particle and reactor model is mandatory for the description of both kinetic and transport phenomena aspects.

This lead to the solution of a multi-scale dynamic system, spanning from the description of kinetic and transport aspects at the particle scale, up to the description of mass and energy transfer as well as secondary reactions at the reactor scale.

To further increase the complexity, the system is intrinsically multi-phase, due to the combined presence of a gas, liquid and solid phase, which can exchange mass and energy among themselves.

The structure of the system is outlined in Figure 6-1, where it is possible to highlight the presence of three main scales. At the particle scale, the system evolves along the radial coordinate, as well as through time.
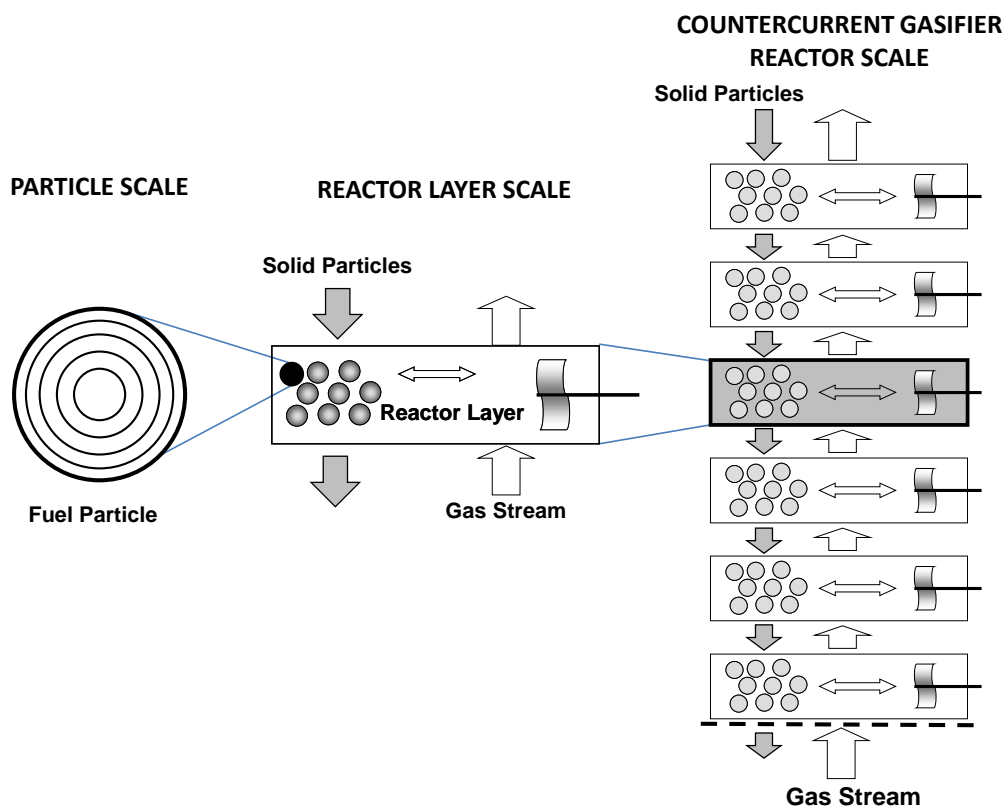
Figure 6-1: Multi-scale structure of the countercurrent biomass gasifier.

The successive scale (elementary reactor layer) accounts for the coupling between isotropic solid particles with an external gas phase, considered homogeneous and perfectly mixed.

Finally, at the reactor scale, several elementary reactor layers are adopted and interconnected to reproduce different reactor configurations.

For instance the counter-current fixed bed gasifier (i.e. updraft) is reproduced through a cascade of elemental reactor layers. In this configuration, which has been selected for the successive studies below in the paper, the solid fuel is fed from the top of the reactor where it encounters a rising gas stream, fed from the bottom of the tower. During the residence within the gasifier, particles are progressively dried, pyrolyzed and gasified, leading to a residual solid stream withdrawn from the bottom and to a gas stream rich in hydrogen and carbon dioxide exiting from the top.

The novelty of this approach relies on a kinetic modelling approach, which can characterize, with a reasonable detail, also the devolatilization and pyrolysis steps, as well as the secondary gas phase reactions.

The best characteristic of the present model relies on an intrinsic flexibility to handle different feedstock and to account for new available experimental data.

This model has been here applied to the gasification process of biomass and coal, considering the counter current fixed-bed reactor.

Now it is mandatory the coupling of the mass and energy balances, which are able to characterize the reactor.

First of all intra and inter-phase heat and mass transfer phenomena need to be considered and coupled with the kinetics when modeling reactors treating thick particles.

Biomass particles shrink by as much as 50% during their conversion. Heat transfer must account for variable transport properties during the pyrolysis process: namely, in virgin biomass, dry and reacting biomass, and the residual char.

The intra-particle mass and heat transfer resistances are simply described by assuming an isotropic sphere.

The mass balance of the solid phase is (1):

$$\frac{dm_{j,i}}{dt} = V_j R_{j,i} \tag{1}$$

where $m_{j,i}$ is the mass of the ith solid component; $V_{,j}$ is the volume of the jth sector; $R_{j,i}$ is the net formation rate of the ith component.

Then we implement the mass balance of the gas phase (2):

$$\frac{dm_{j,i}}{dt} = J_{j-1,i}S_{j-1} - J_{j,i}S_j + V_j R_{j,i} \tag{2}$$

where mj,i is the mass of the ith volatile species within the jth sector; Sj is the external surface of the jth sector; and J is the total fluxes generated by diffusion and pressure gradients.

After this characterization, we describe the energy balance (3):

$$\frac{d\sum_{i=1}^{NCP} m_{j,i}h_{j,i}}{dt} = JC_{j-1}S_{j-1} - JC_jS_j + S_{j-1}\sum_{i=1}^{NCG} J_{j-1,i}h_{j-1,i} - S_j\sum_{i=1}^{NCG} J_{j,i}h_{j,i} + V_j HR_j \tag{3}$$

where hj,i = cPj; T,j is the component partial enthalpy; T,j is the temperature of the jth sector. The term JC accounts for the heat conduction; the term V _ HR accounts for the total reaction heat; NCP is the total number of components; and NCG is the number of gas components.

Mass and heat fluxes within the particle follow the constitutive Fick, Fourier, and Darcy laws (4):

$$JC_j = -k_j^{eff}\frac{dT_j}{dr}\bigg|_{r_j} \tag{4}$$

The boundary conditions at the gas–solid interface become (5):

$$J_{N,i} = k_{ext}MW_i\left(c_{N,i} - c_i^{bulk}\right) + \frac{Da_N}{m_N}\frac{DP}{Dr}\bigg|_N c_{N,i}MW_i \tag{5}$$

$$JC_N = h_{ext}\left(T_N - T^{bulk}\right) + JR_N + \sum_i^{NCG} J_{N,i}h_{N,i} \tag{6}$$

Now there are the mass and energy balances for the reactor scale, into which the solid bed is then simulated as a series of NR elemental layers.

The height of each layer is of the same order of the size of the biomass particle, accounting for the vertical dispersion phenomena. The complete mixing inside the layer both for the gas and solid phase is assumed.

The gas-phase mass balance equations for each elemental reactor are (6):

$$\frac{dg_i}{dt} = G_{in,i} - G_{out,i} + J_{N,i}S_N \eta + V_R R_{g,i}$$ (7)

where g,i is the mass of the ith species within the reactor volume VR; Gin,i and Gout,i are the inlet and outlet flow rate; Rg,i is the net formation from gas-phase reactions; the term JN,i is the gas–solid mass exchange multiplied by the particle surface SN and the number η of particles inside the layer.

The gas-phase energy balance equation for each elemental reactor is (7):

$$\frac{d \sum\limits_{i=1}^{NCG} g_i h_{g_i}}{dt} = \sum\limits_{i=1}^{NCG} G_{in,i} h_{g_{in,i}} - \sum\limits_{i=1}^{NCG} G_{out,i} h_{g_i} + \sum\limits_{i=1}^{NCG} J_{N,i} h_{N,i} S_N \eta + h_{ext}(T_N - T^{bulk})S_N \eta + V_R HR_g$$ (8)

where hg;i = cPiTbulk; Tbulk is the gas-phase temperature; the terms G _ hg are the enthalpies of inlet and outlet flow rates; the term J _ h is the enthalpy flux relating to the mass transfer of a single particle; finally HRg is the overall heat of gas-phase reactions.

6.3 *Start-up procedure of the gasifier*

Let's consider in the start-up procedure a coal or biomass flow, which enters in the reactor at the temperature of about 300 K and an air stream.
The gasifier operates such as a counter-current gasifier.
The dynamic evolution of the system could bring to an ignited or a cold steady-state solution, depending on the start-up policy.
In order to start up the system, an auxiliary fuel is used to heat up the inlet air stream at 1200-1300 K, until the ignition of released volatiles is observed in the gas phase.

Solid particles need to be heated up in order to devolatilize, only then heat generation can occur from the ignition of the volatiles with the cold inlet air flow.
That is why the heat has to be provided by the auxiliary fuel until the exothermic partial oxidation reactions allow the adequate heating of the solid phase.
A feasible start-up procedure is to feed the preheated air stream until fuel particles reach a suitable temperature for the release of the pyrolysis products, with successive   gas-phase reactions.

When these high-temperature operating conditions are achieved, it is necessary to progressively reduce the inlet air temperature by preserving the hot condition, avoiding the system shutdown.

After the first layer reaches a temperature of 1250 K, the air stream was put to about 300 K in a certain time (nearly 600 s), because the ending of the start-up policy, with the gasifier which can operate now into the hot solution.

6.4 *Updraft biomass gasifier*

Biomass is fed continuously from the top, while the steam/air inlet stream enters the bottom of the gasifier.

Gas contact time is in the order of few seconds, while the solid residence time is significantly higher and in the order of the hour.

The resulting large and stiff DAE system, with several thousand equations, is very tough numerically.

At the bottom of the gasifier the gas and the solid temperatures are almost similar. Rising the vertical direction of the bed, the gas is first heated up by the ash and the hot particles and then reaches more than 1400K in the last layers.

In these layers, the exothermic partial oxidation reactions of tar products provide also the heat necessary to biomass devolatilization.

Finally in the last reactor layer, the temperature of the gases leaving the gasifier decreases, due to the heat transfer with the cold biomass entering the unit.

All the processes described above, are schematically represented in the Figure 6-2 below:
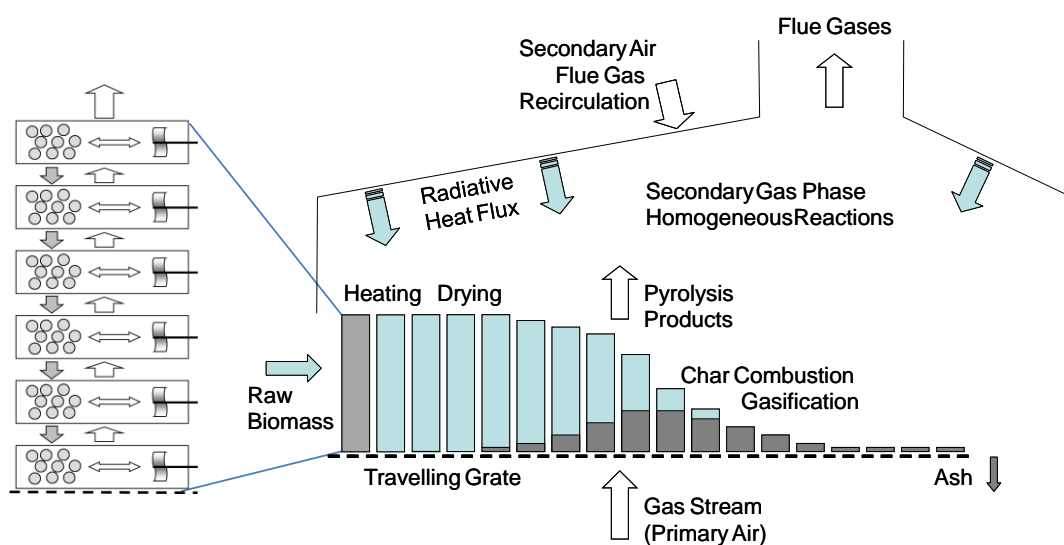
Figure 6-2: Biomass gasifier with the schematized reactor layers.

6.4.1   Jacobian structure of the model and numerical methods

According to the multi-scale nature of the mathematical model, the resulting Jacobian has an embedded highly-sparse and large- scale structure with diagonal-blocks and upper and lower bands, as schematically reported below (Figure 6-3):
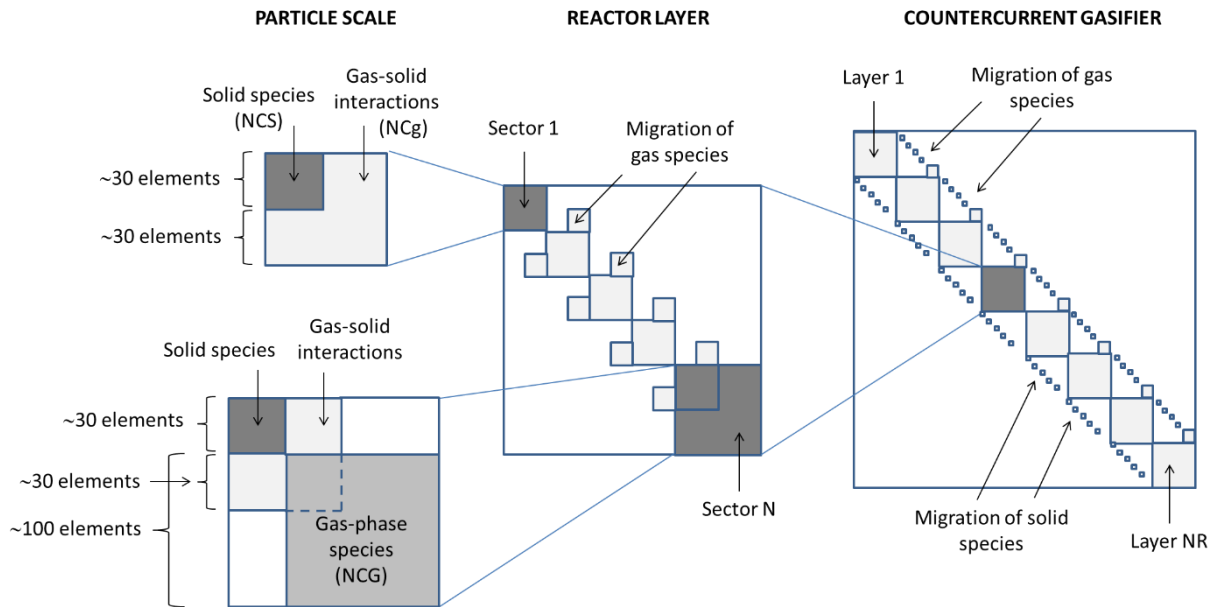
Figure 6-3: Qualitative structure of the Jacobian matrix.

Two different matrices are adopted to first characterize the biomass particle. The first is a (NCS+NCg+1)x(NCS+NCg+1) dense matrix accounting for all the solid species NCS as well as only the gas species NCg (NCg<NCG), that interact with the solid.

It accounts for the intra-particle solid and gas-solid evolution within each sector of the particle. Only the external sector N interacts with all the NCG gas species.

In order to give an idea of the dimension of this problem, let's assume 30solid species, 100gas species, and only 30 gas species really interacting with the solid matrix. The second is a (NCS+NCG+1)x(NCS+NCG+1) partially structured matrix ,of the order of 130x130, accounting for all the solid and gas species in the external sector. Biomass devolatilization, heterogeneous reactions and secondary gas-phase reactions are accounted for.

At the scale of the reactor layer, since the solid species are not diffusing, the upper and lower bands involve only gas species and NCg (30) is the size of the band block. Both the bands are present since gas species diffuse inside the particle. Finally, the external sector accounts for all the gas species.

The dimension of this matrix easily becomes 500x500.

 At the reactor scale, i.e. at the scale of the cascade of reactor layers, each layer interacts with the gas stream coming from the upper or lower layer, depending on

the countercurrent or the concurrent configuration. Similarly, there is the migration of the solid variables across the different layers.

Thus, the numerical structure of the Jacobian for the reactor scale assumes a diagonal- block structure with asymmetric bands.

The asymmetry of lower and upper bands comes from the larger number of gas species (NCG>NCS).

Very often, it is possible to re-order the Jacobian structure so as to achieve a diagonally dominant structure that allows to reduce the computational effort. Ordinary differential and differential- algebraic equation (ODE and DAE) system solvers belonging to BzzMath library (Buzzi-Ferraris and Manenti, 2012; Manenti et al., 2009) are adopted.

6.5 *Simulations of the coal gasifier*

At the beginning of this work is mandatory to specify the first feedstock used is coal and then the same work will be proposed again with the biomass, to see the differences between a thermodynamic model (with all its simplications) and a kinetic and proper model of gasification using the "GAS-DS" tool.

With the coal feedstock it was used as a guideline for the inlet composition a paper by Grieco & Baldi ("Predictive model for countercurrent coal gasifiers", CES, 2011) and it was used their coal classification and developed all the analysis to obtain our optimal conditions of gasification.

There is the need to describe the coal used as feed for the gasifier, which is a mixture of three reference coals (COAL1, COAL2, COAL3) and other compounds (ashes, nitrogen and sulfur).

First of all with the program developed in Excel (which converts the elemental composition into our three reference coals), and starting from the coal composition of the paper "Grieco & Baldi", it was possible to find out the feed composition of the coal to envy to the gasifier for the simulations.

In fact we have an assigned and discovered composition of 0.045 COAL1, 0.62 COAL2, 0.246 COAL3 and 0.09 ASH, which is the input for the solid coal entering the gasifier, with a solid flowrate of 1.44 (kg/h) and a particle diameter of the coal pallets of 2.54 cm.

For the gas stream it was used for this first simulation the data obtained from the thermodynamic equilibrium of coal done with "D-Smoke", and so it was envied a gas

inlet of 0.002598 Nm^3/s (which was converted from the simulations with "D-Smoke", in which was used a different unit of measure) and a molar flowrate composition of 0.4089 N2, 0.1087 O2 and 0.4824 steam.

Then it is mandatory to declare the inlet temperature for the gas (Tgas) and the solid (Tsolid), which were put to 1300 K for the gas and 298 K for the solid, because at the beginning of the simulation it will be the air to preheat the system and then when was reached a condition of stability, in which the system is able to self-sustain, it is possible to decrease slowly the gas temperature till a desired temperature (334 K).

It is important to specify also that in this first simulation it is not requested to have the best accuracy, but it is necessary only to obtain good results and parameters for the next simulations and thus the work is made with 6 reactor layers and 1 particle sector (thus considering the particle isotherm). Finally there is no need to specify the height of our gasifier which it is put equal to 3 meters, with a passage area of 0.05 m^2 and a time of the simulation of 150,000 s. Now everything is ready for the first simulation, with all the graphs and a discussion of its below.

Figure legend: RL 6 PS 1, area 0.05 m^2, gas in 0.002598 Nm^3/s

Gas composition
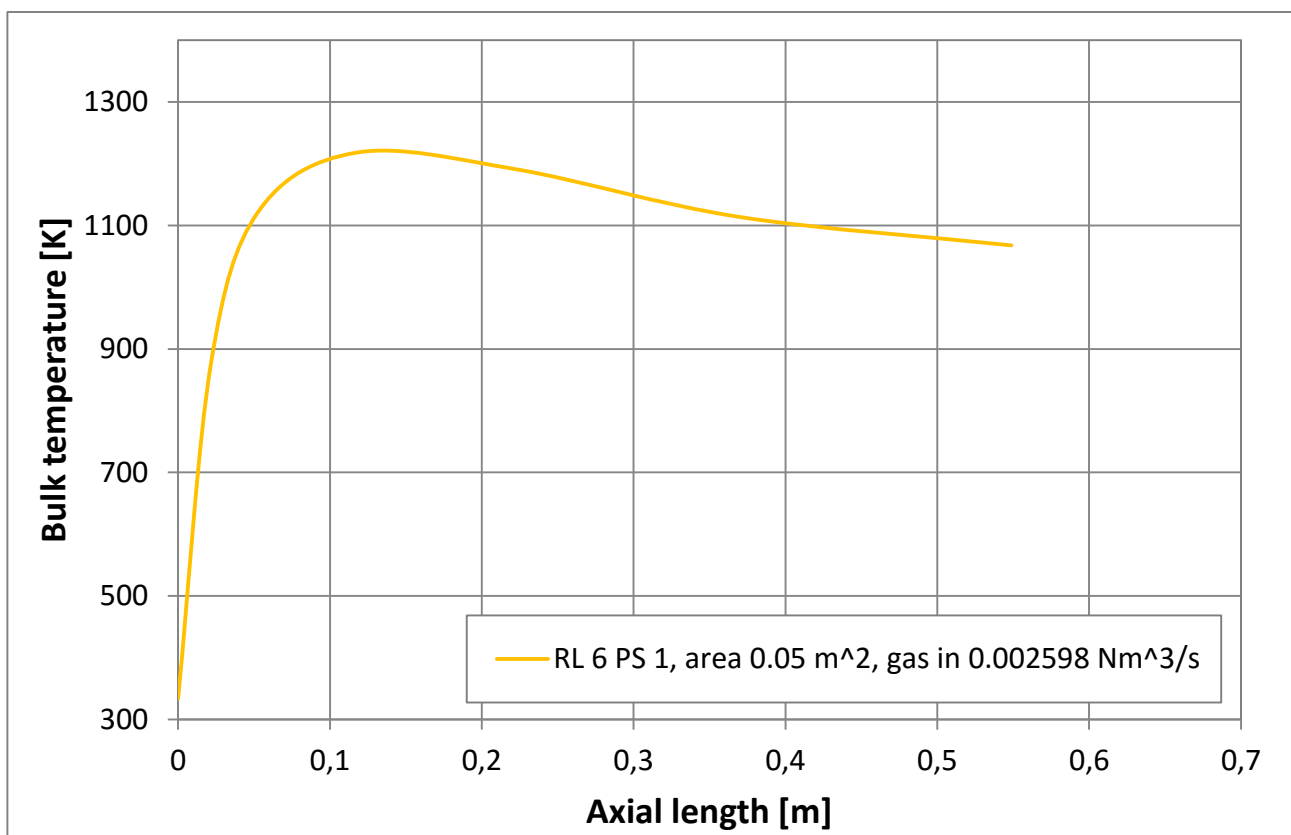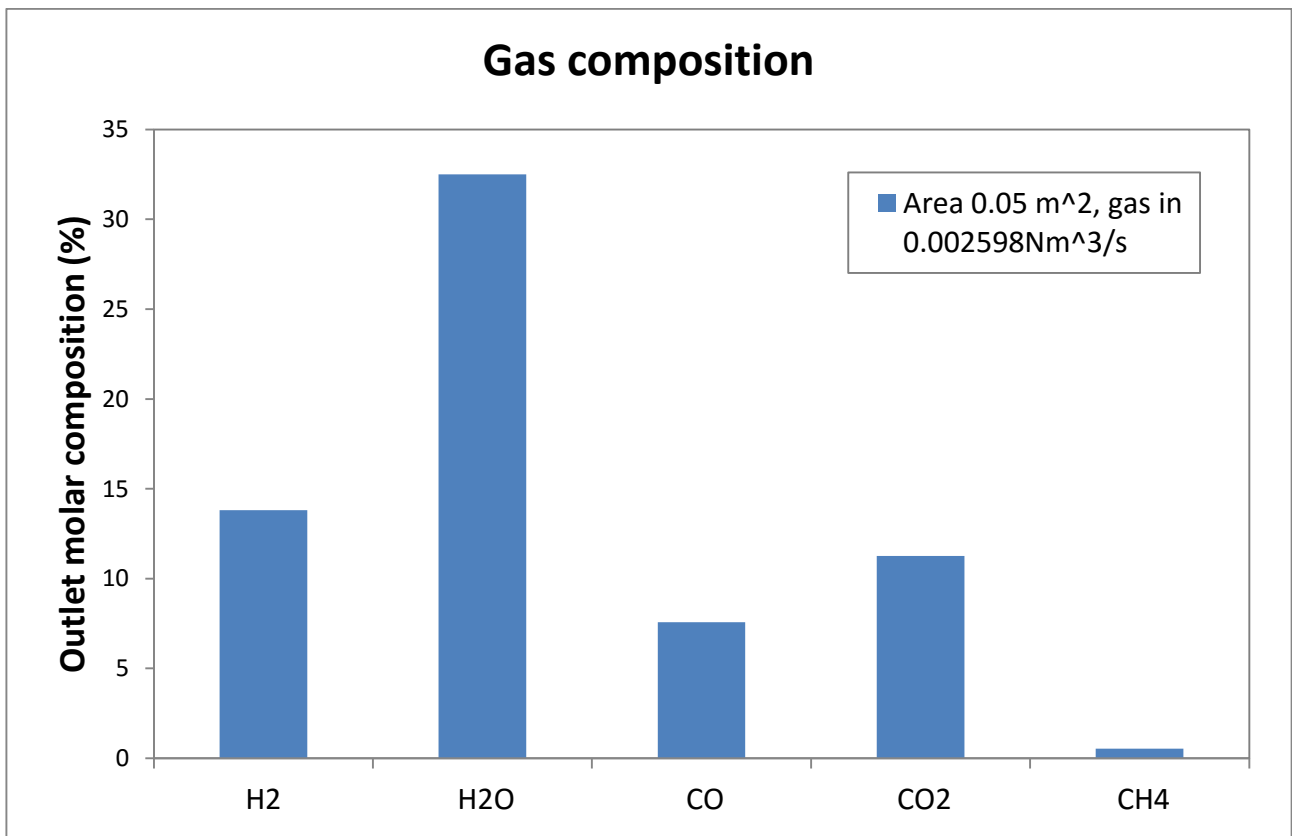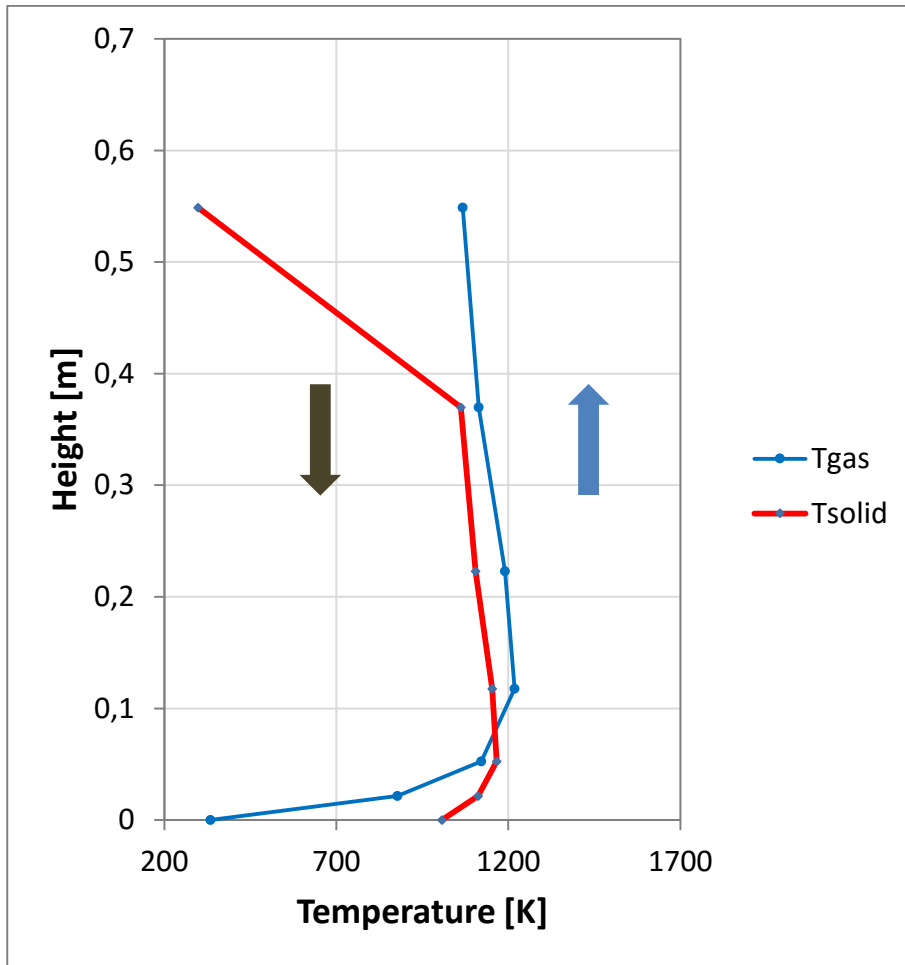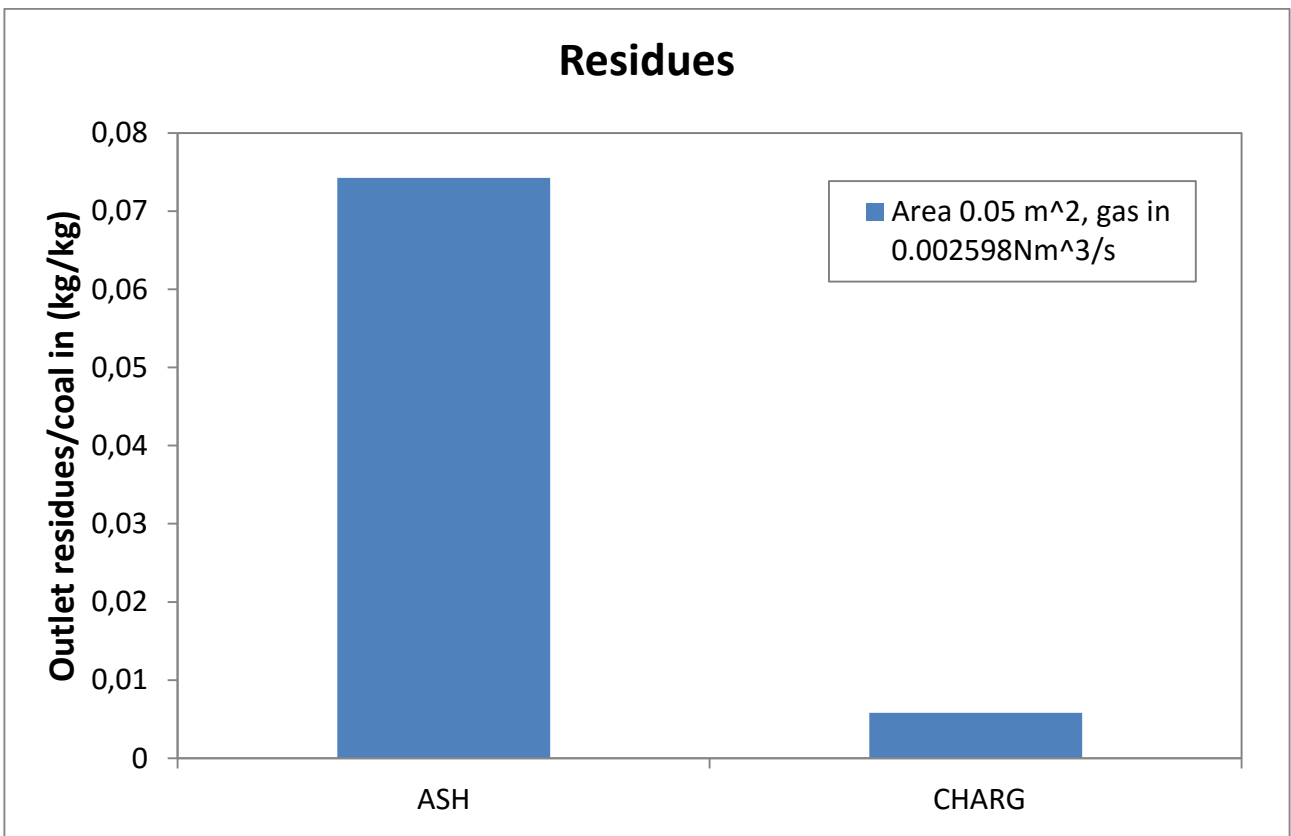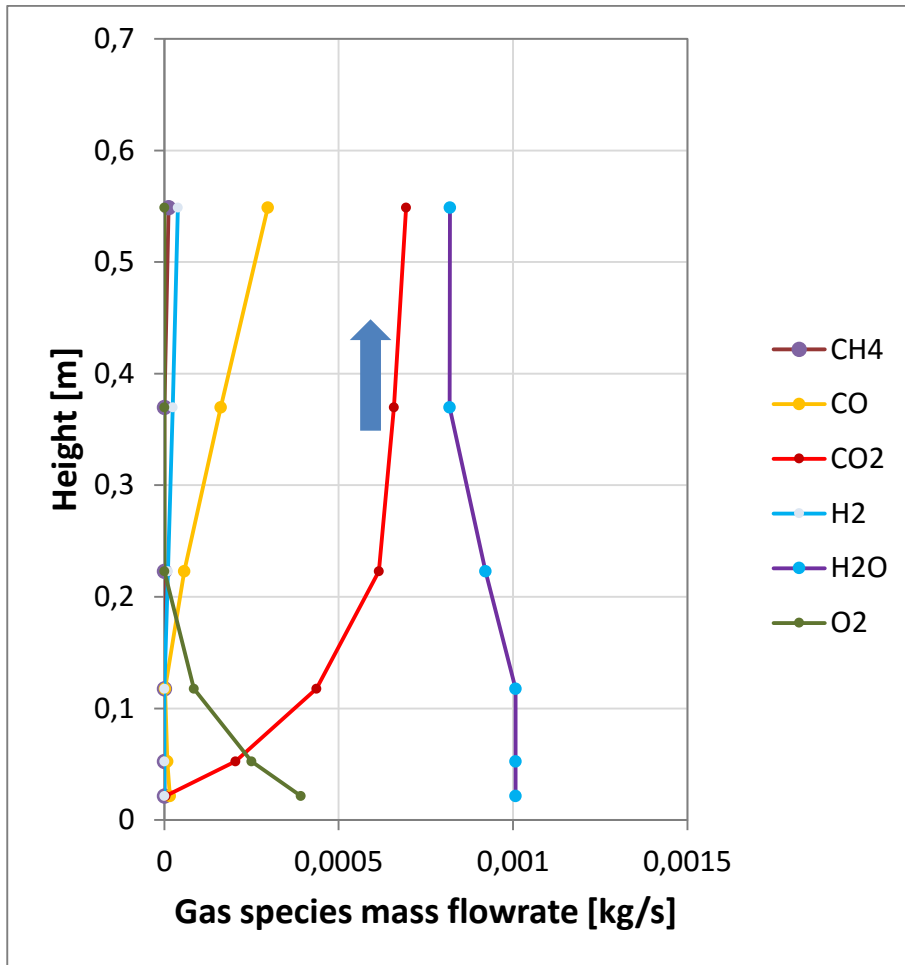
Residues

Here in the first simulation the necessity was to find and point out many things about the composition of the outlet gases, the residue and the residence time.

First thing is that the axial profile of temperature is reasonably good as expected and also the temperature of the gas (Tgas) and solid (Tsolid) are quite good in the graphs respect to the length of the gasifier and this gives the opportunity to predict that the residence time is enough to make all the reactions.

But analyzing better all the graphs and the informations collected from this simulation, it is possible to underline the presence of a residue which is composed by nearly the 90% of ashes and the other 10% by a mixture of chars (char, charh, charg) and this is different from the simulations done with "D-Smoke", in which there was a complete gasification of the coal sphere and any residue was noticed, apart from the ash, which is normal.

The consequence is the need to increase the residence time, diminishing the inlet flow of coal or increasing the area and the quantity of air, thus giving more oxygen to the system to burn and gasify the various chars.

6.5.1 Simulations varying the parameters

So it is necessary to make other simulations, varying the area of the gasifier, the inlet flow of the gas (adding air to the stream) and seeing what are the results.

Above there are the graphs which explain the compositions of the outlet gases found, the residues and the results in terms of optimal conditions obtained.

Of course for every simulation it is absolutely mandatory to change only a parameter, because so it is seen the influence of each one and the sensitivity of the system to the data.
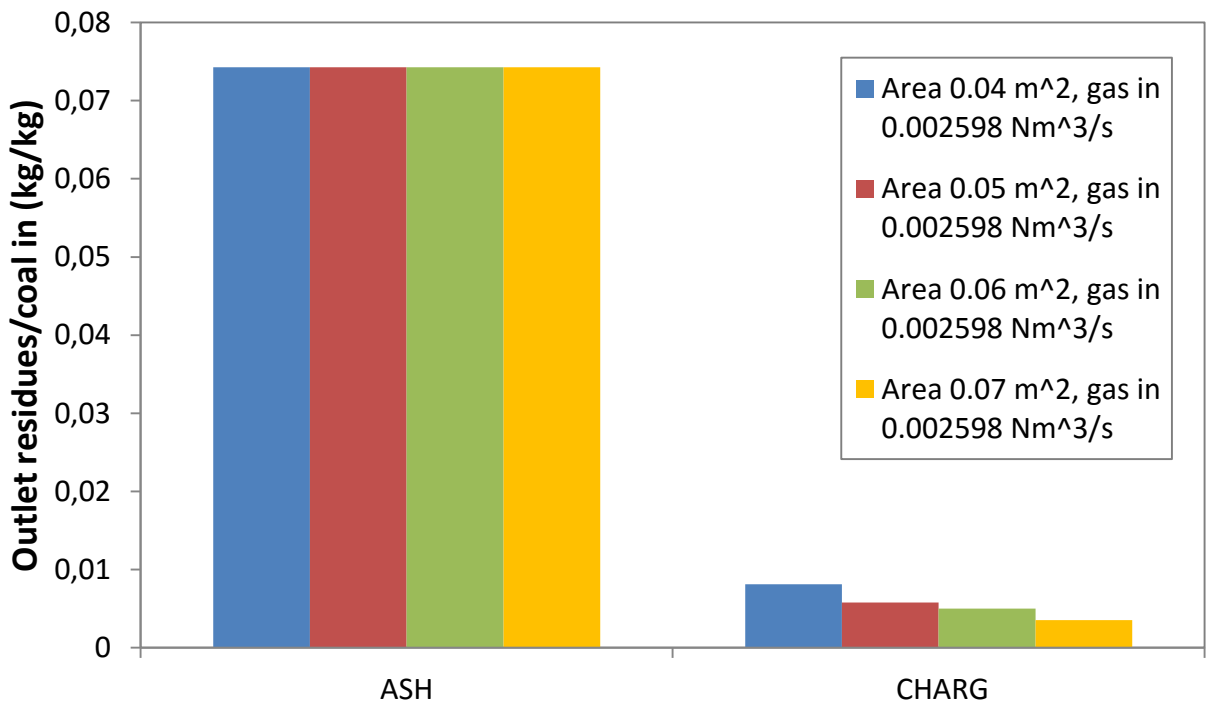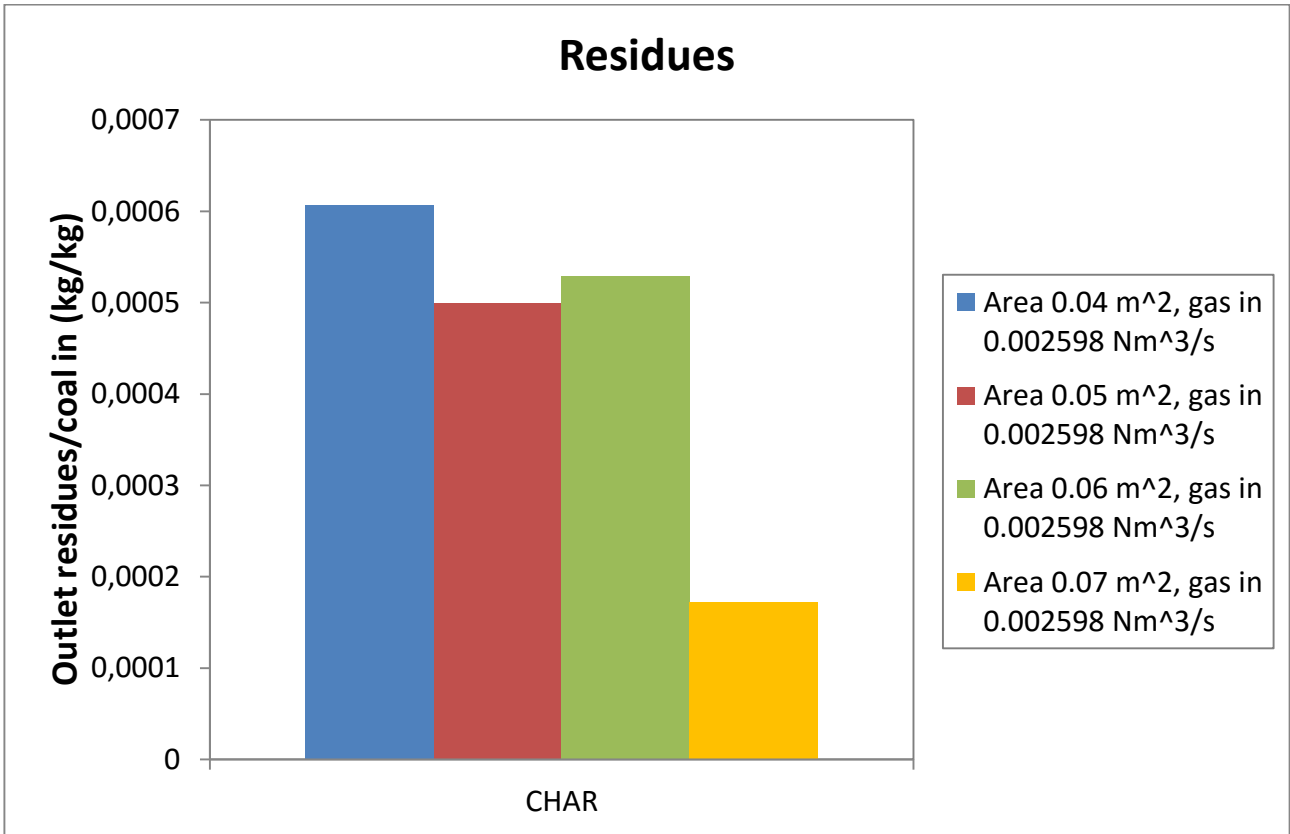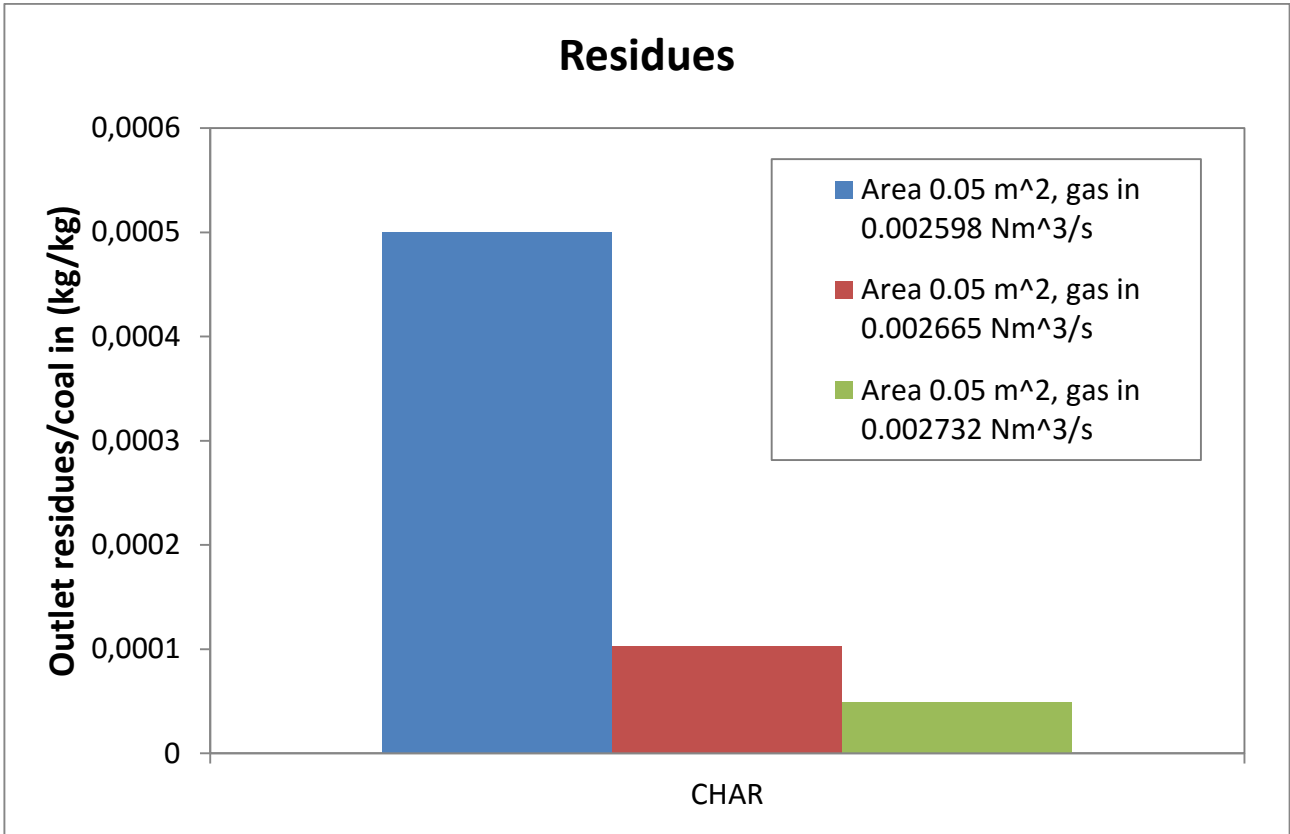
Gas composition

Legend:
- Area 0.05 m^2, gas in 0.002598Nm^3/s
- Area 0.05 m^2, gas in 0.002665 Nm^3/s
- Area 0.05 m^2, gas in 0.002732 Nm^3/s

Y-axis: Outlet molar composition (%)
X-axis categories: H2, H2O, CO, CO2, CH4

Gas composition

Legend:
- Area 0.05 m^2, gas in 0.002598Nm^3/s
- Area 0.04 m^2, gas in 0.002598 Nm^3/s
- Area 0.06 m^2, gas in 0.002598 Nm^3/s
- Area 0.07 m^2, gas in 0.002598 Nm^3/s

Y-axis: Outlet molar composition (%)
X-axis categories: H2, H2O, CO, CO2, CH4

Residues

Outlet residues/coal in (kg/kg)

- Area 0.05 m^2, gas in 0.002598 Nm^3/s
- Area 0.05 m^2, gas in 0.002665 Nm^3/s
- Area 0.05 m^2, gas in 0.002732 Nm^3/s

CHAR

Residues

Outlet residues/coal in (kg/kg)

- Area 0.04 m^2, gas in 0.002598 Nm^3/s
- Area 0.05 m^2, gas in 0.002598 Nm^3/s
- Area 0.06 m^2, gas in 0.002598 Nm^3/s
- Area 0.07 m^2, gas in 0.002598 Nm^3/s

CHAR

Gas temperature

Gas temperature

Here in the graphs it is possible to notice a few important things.

First of all increasing the area of the gasifier there is a decrease in the quantity of the chars (especially CHAR and CHARG), due to the increase of the residence time; thus the residual chars have a major time into the gasifier to react with the oxygen and give gasification products.

Second important thing is that increasing the time, there is in the gasifier the same quantity of air and this leads to a decrease of the char, due to the fact that we have a better quantity of O2 which can reduce the char to CO and CO2 and this is visible in the outlet composition, in which there is a higher quantity of CO and CO2 and a lower quantity of char.

A major quantity of air in the inlet gases brings the syngas to a reduced quantity of H2 and steam, because of the higher quantity of O2 in the inlet gas and thus a higher temperature of the gas (Tgas) into the gasifier; this thing can be noticed by the profiles of temperature along the reactor.

Another important thing to notice is that as expected there are no traces of other hydrocarbons (C2, C3, C4) in the gas species leaving the reactor, in accordance with the simulations made with the "D-Smoke" tool, reaching the thermodynamic equilibrium.

After having seen all the graphs and analyzed many operative conditions, it was decided the optimal way to exercise the gasifier and it was used the maximum area (0.07 m) and an intermediate quantity of gas (0.002665 Nm^3/s), because with these data, increasing the production of CO, there is a less quantity of char, which is an undesired product and gives enormous problems in the pipes due to the deposition.

6.5.2   Simulation with optimal conditions

Here it is possible to see the graphics of this simulation (done with a coal particle of 2.54 cm, 1 particle sector, 6 reactor layers, an area of the gasifier of 0.07 m^2 and with an inlet gas flowrate of 0.002665 Nm^3/s) and then a brief discussion of the results obtained.

RL 6 PS 1, area 0.07 m^2, gas in 0.002665 Nm^3/s

Gas composition

Residues
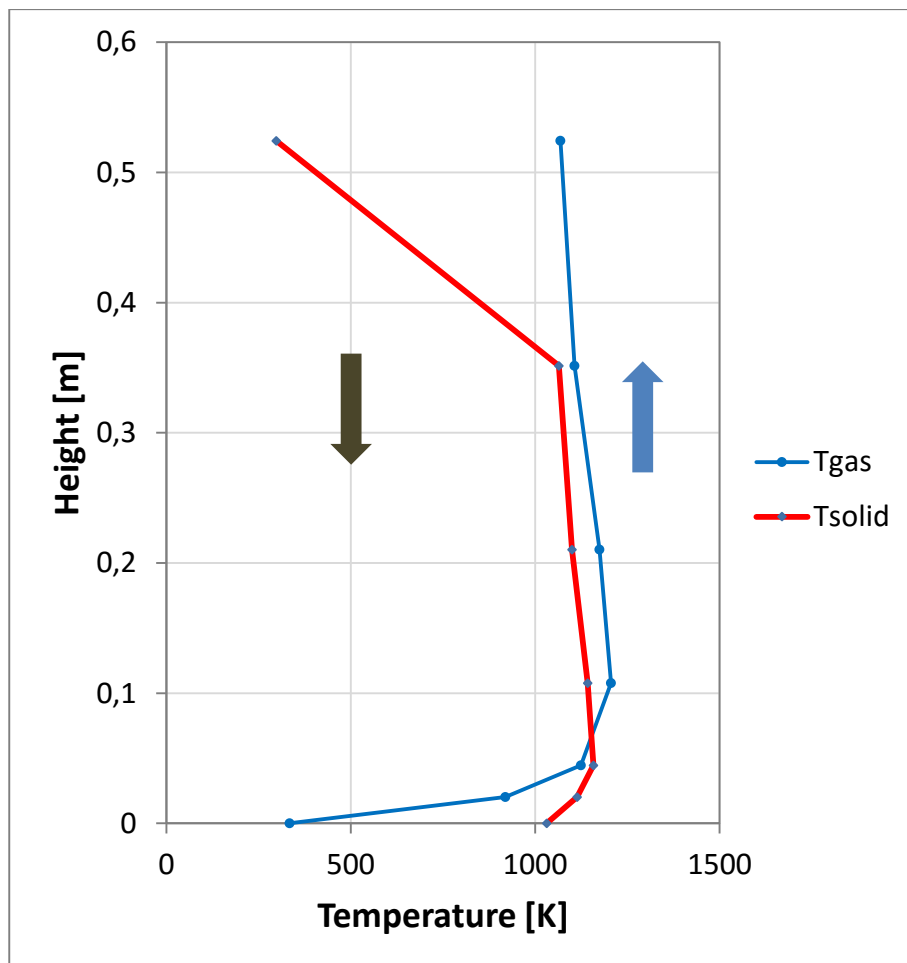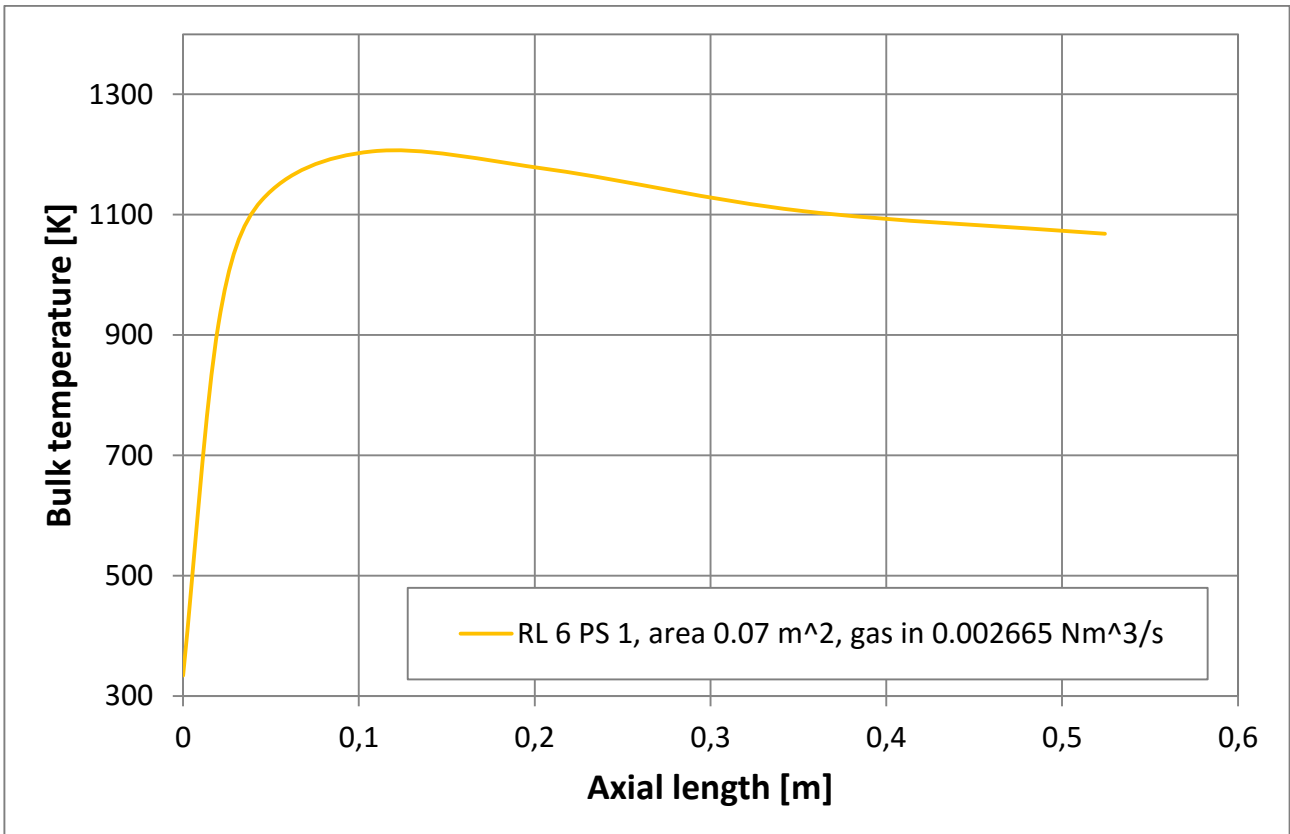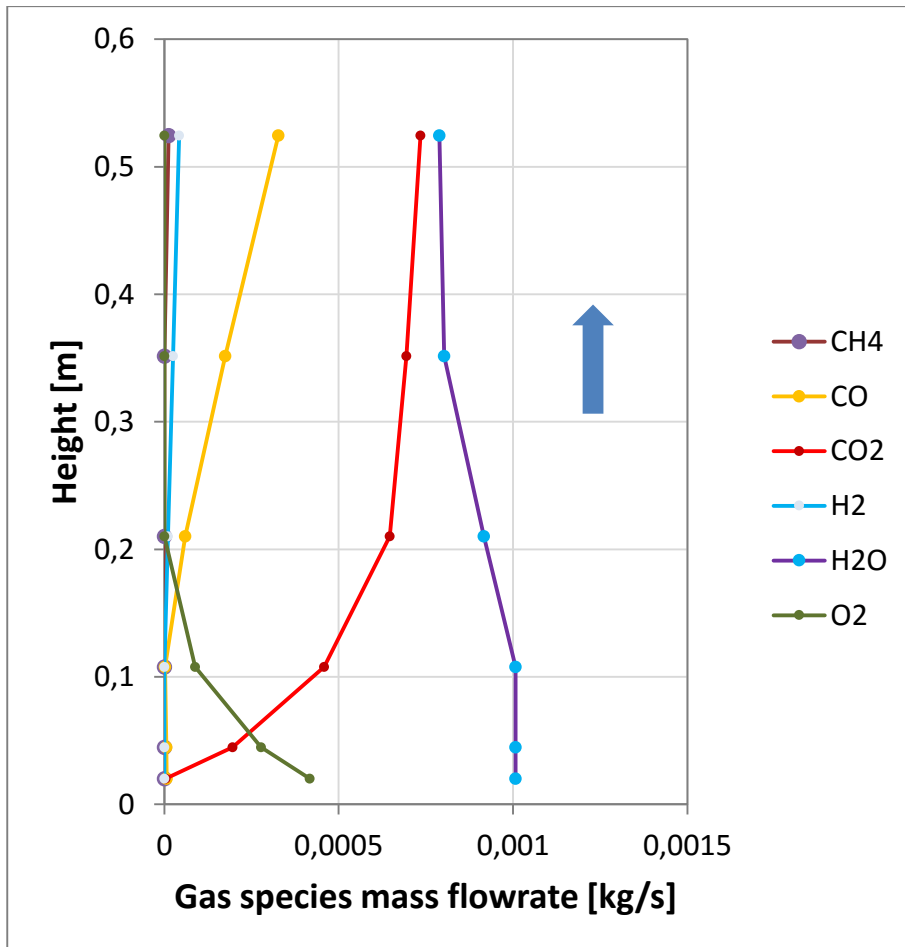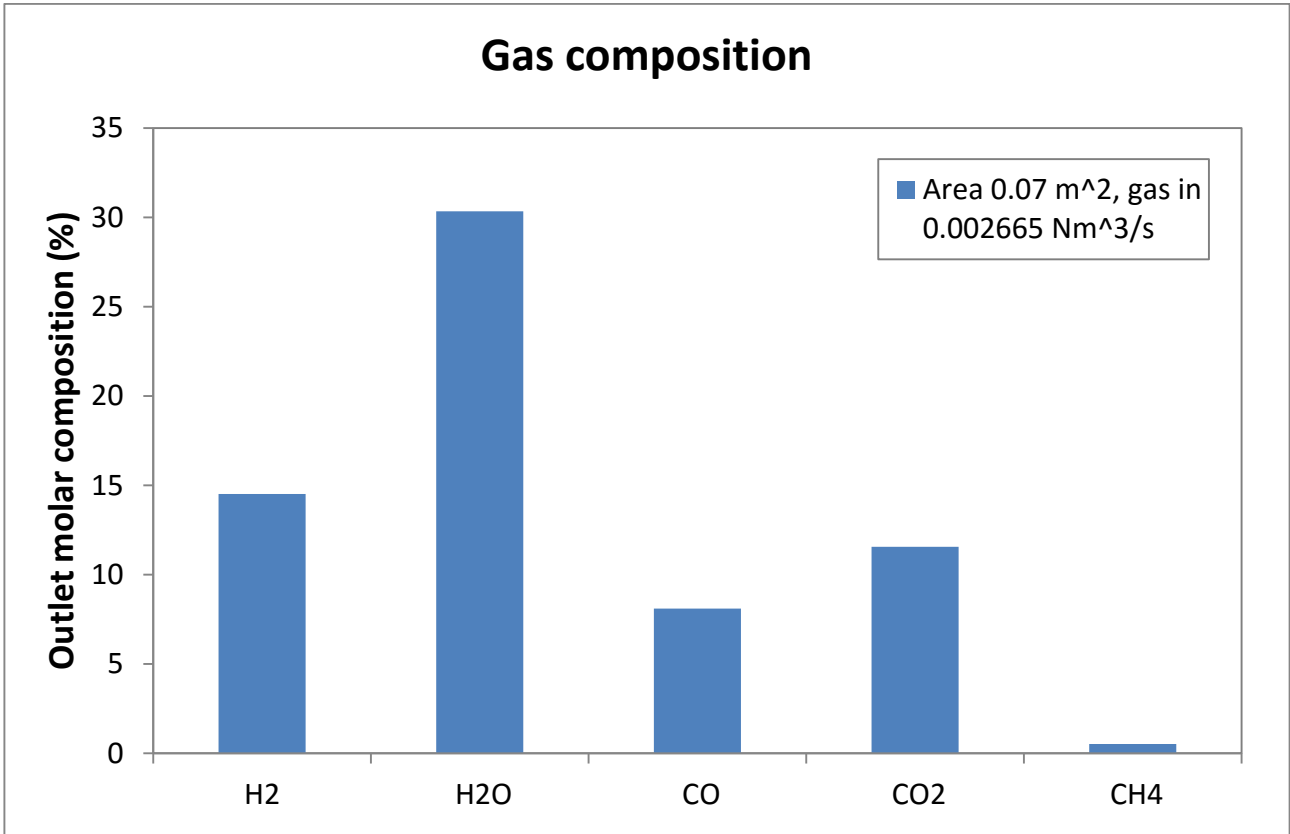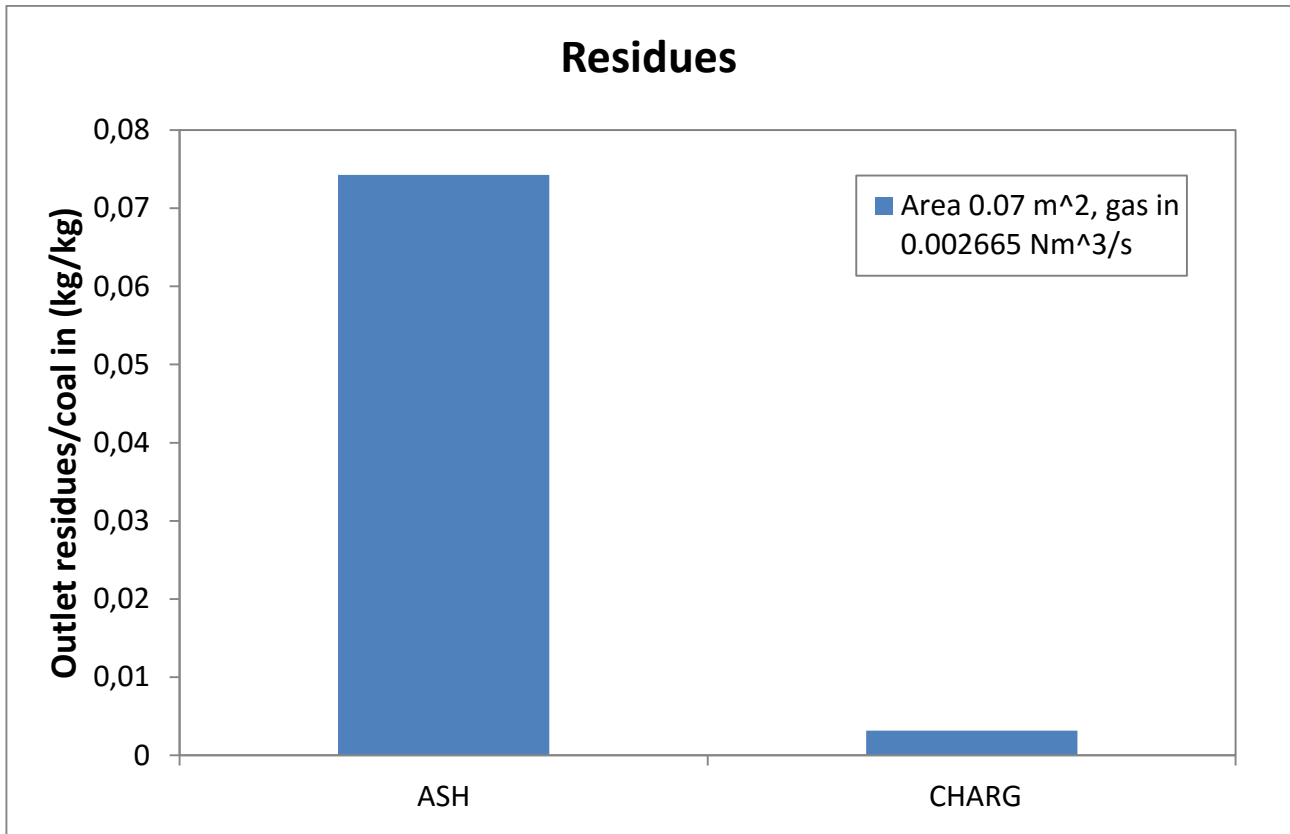
In this simulation it is notable the greater production of CO and CO2 and a decrease of H2 and steam, due to the increased inlet air (5%) respect to the previous simulations (we passed from a gas in of 0.002598 to 0.002665 Nm^3/s).

This fact is reflected also in other two things: the first one is that into the molar composition of the inlet gas there is a higher percentage of O2 and N2 respect to the steam (thus we can explain the decrease of H2 and steam in the outlet gases leaving the reactor).

The second thing is that with the increase of the oxygen into the inlet gas, there is a lower quantity of residual char and this is well underlined by the graphs of the residues.

Then the production of char (above all CHARG), was diminished with the increase of the area of the gasifier (0.07 m^2) and with this also the residence time of the gases in the reactor, giving time to the char to gasify and burn at contact with the O2. So with these operative conditions it was possible to find a reasonable compromise between all our parameters.

6.5.3   *Simulations to test the optimal conditions*

Reached the optimal conditions for our gasifier, which give the right quantities of products in terms of gas species (CO, CO2, H2, H2O, and CH4) and in terms of residual chars exiting by the plant, it is possible to continue the simulations seeing the effect of a few parameters and how they change varying the operative conditions. In fact in the follow-up of the chapter it will be explained what happens when we won't consider anymore the coal particle as isotherm, but two particle sectors will be introduced for a better discretization of the system, to text the properties of the coal particle and see if really the temperature of the solid can be considered uniform.

Then other experiments will be considered, in which it will be notable the effect of the size of the coal particles and, trying to increase or diminish the coal particle from the original dimension of 2.54 cm to two new dimensions (4 and 2 cm) it will be reported the effect of this change on the residence time, on the composition of the gas species and above all on the residual char, paying a particular attention to the profiles of temperature.

Finally it will be possible to simulate the gasifier with the same optimal conditions reached before (gas in 0.002665 Nm^3/s, area 0.07 m^2), but this time it will be used a major number of reactor layers into which the gasifier will be divided, to have a better discretization of the reactor and a major confidence and precision with the results of the simulation.

After all these simulations it will be possible to forecast with a quite good confidence the best conditions that satisfy our requests and then the activity will be switched to dimension the gasifier with all the specifics.

6.5.4   *Simulation with two particle sectors*

In this simulation it is mandatory to text if adding one particle sector to the coal particle and do not considering isotherm the coal particles changes the parameters of the system and above all if it is necessary to consider two different temperatures for the solid (Tsolid1 and Tsolid2) or these two temperatures are nearly the same. Below it is notable the graph that explains very well the results of the simulation in terms of temperatures along the reactor.
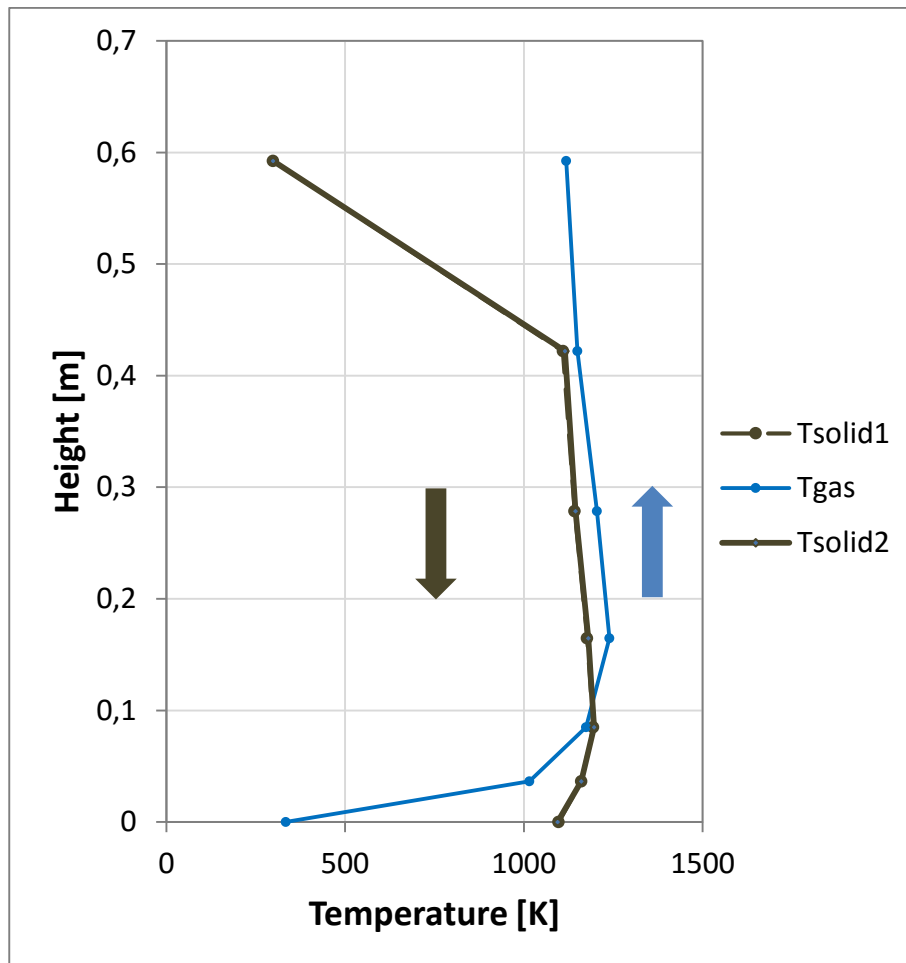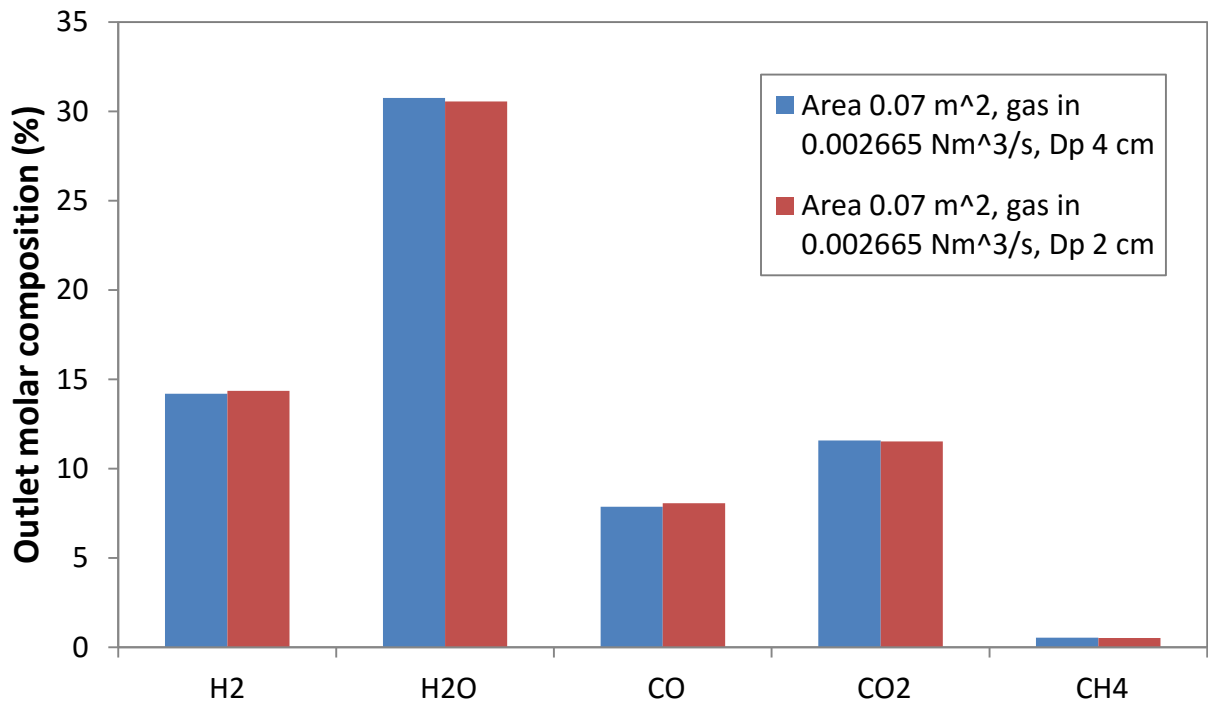
As it is possible to notice from the graph above the temperatures of the two different particle sectors (Tsolid1 and Tsolid2) are nearly the same, due to the overlapping of the Tsolid1 and Tsolid2 and so the conclusion is that the coal particle can be considered isotherm.

Then during next simulations it will be used this hypothesis, thus considering always the coal particle as mono-sector.
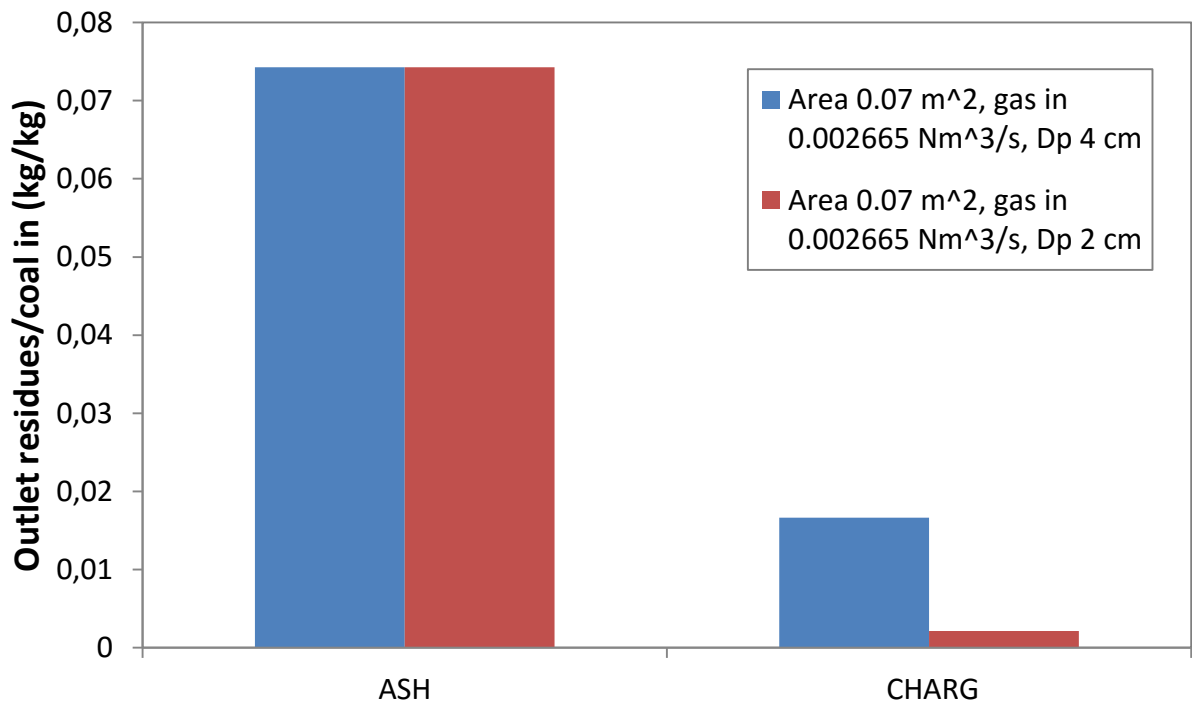
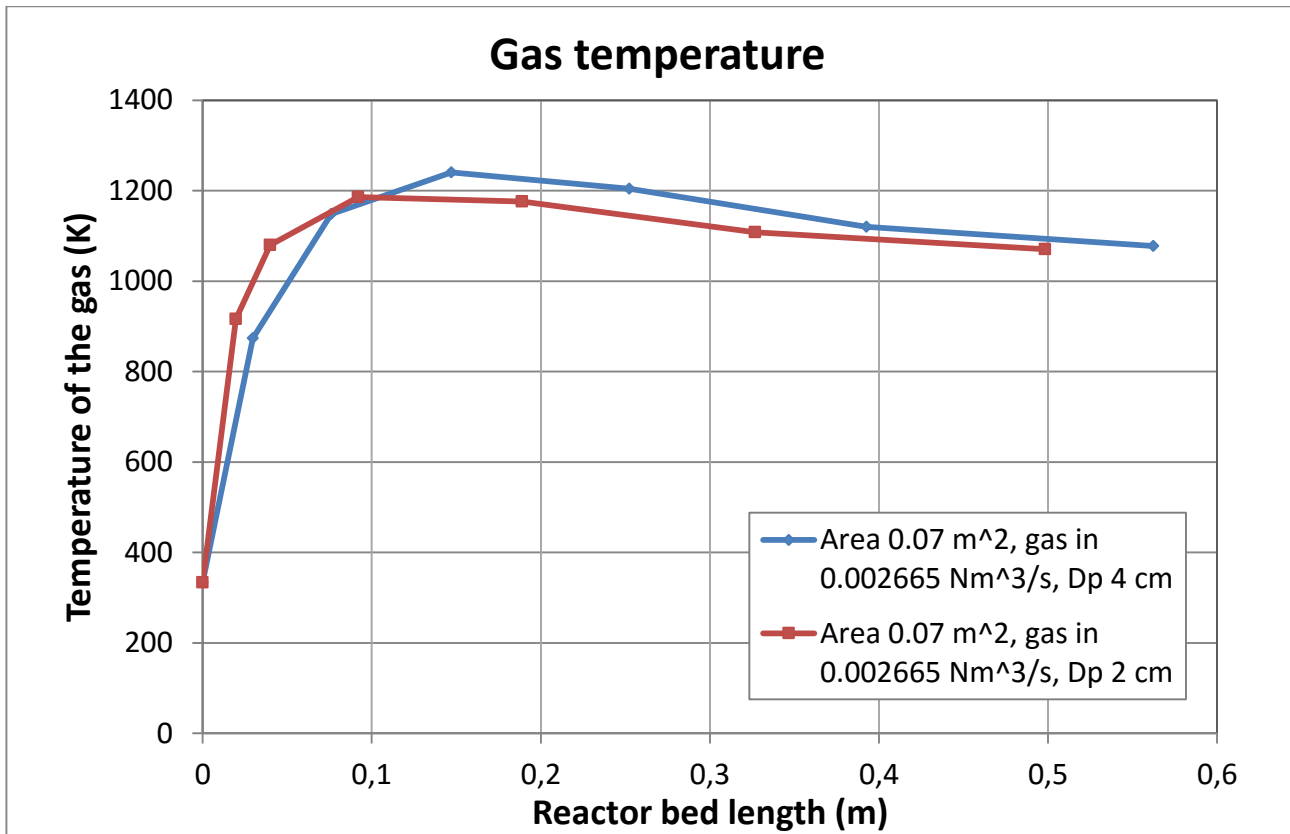### 6.5.5 Simulations changing the diameter of the coal particle

In these simulations there is the need to text what happens changing the diameter of the coal particle in terms of gases composition, temperature of the gases and residual char exiting from the gasifier. Below the graphs of the simulations are shown, with a brief discussion.

Gas composition

Residues

Gas temperature

Legend:
- Area 0.07 m^2, gas in 0.002665 Nm^3/s, Dp 4 cm
- Area 0.07 m^2, gas in 0.002665 Nm^3/s, Dp 2 cm

The graphs above shows some interesting things. First of all it is notable a higher residual char in the simulation with a diameter of the coal particle of 4 cm, due to size of the coal particle, which is greater and so it is more difficult to consume all the coal with the same residence time and oxygen of the previous simulations. In fact this difference it is well underlined both in the residual char results (in which is higher the char for the coal particle of 4 cm) and also in the gases composition with a lower level of CO and H2 and an increase of steam.

The other important thing is the graph of the temperatures, into which the profiles of the two simulations are expressed and it is immediately possible to notice that the profile of temperature for the coal particle of 4 cm is shifted to the right and has a higher maximum of temperature, due to the particle size once again, because with the increasing of the size the particle needs more time to burn the char and gasify; that's why the temperature profile is shifted.

As always all these simulations were done to check the sensitivity of the parameters and see the trend of parameters and operative conditions.

Now let's move to the last two simulations.

### 6.5.6 Simulations with 8 and 10 reactor layers

In these two simulations there is again an area of 0.07 m^2, an inlet flowrate of 0.002665 Nm^3/s and 1 particle sector, but these time the simulations are made with 8 and 10 reactor layers to check another time the sensitivity and the precision of the data. Here below there are the graphs and a brief discussion of its.

Gas composition
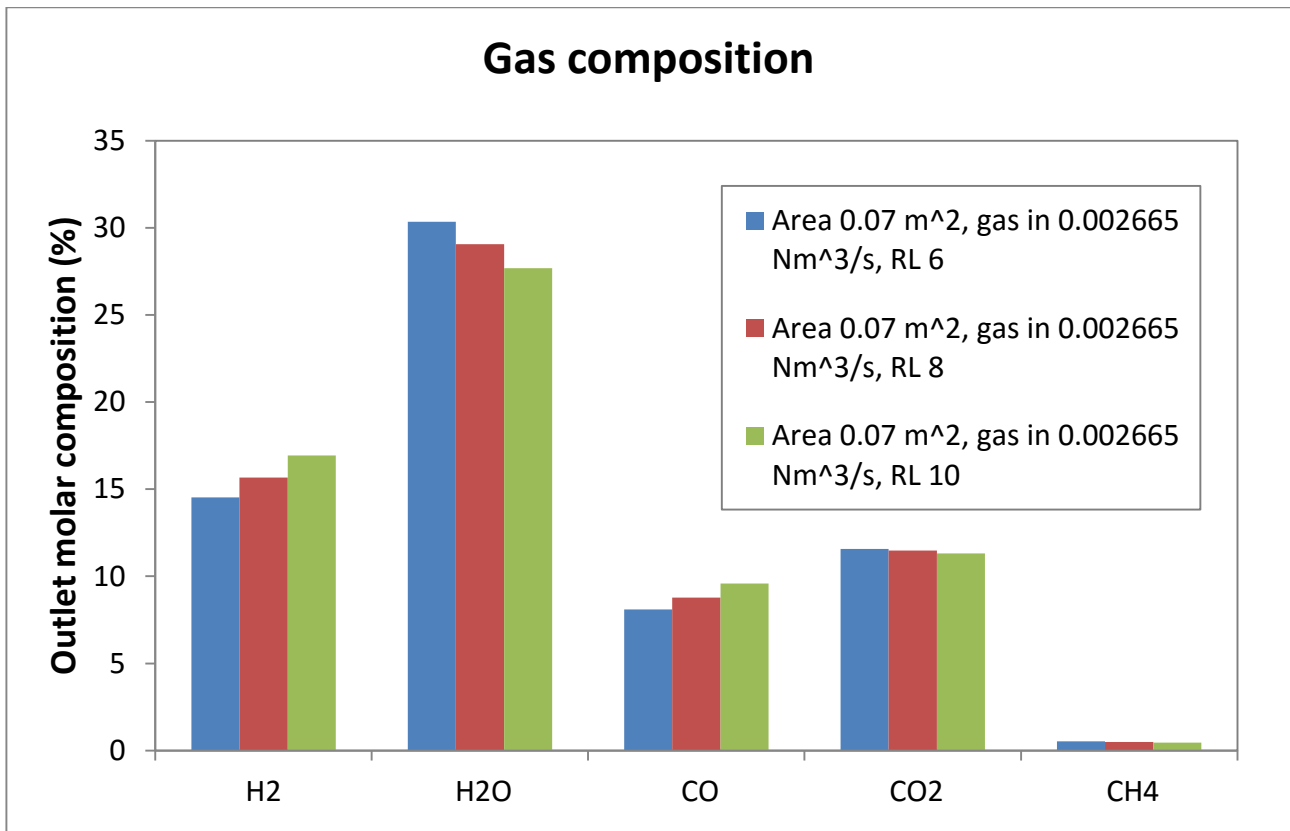
Residues
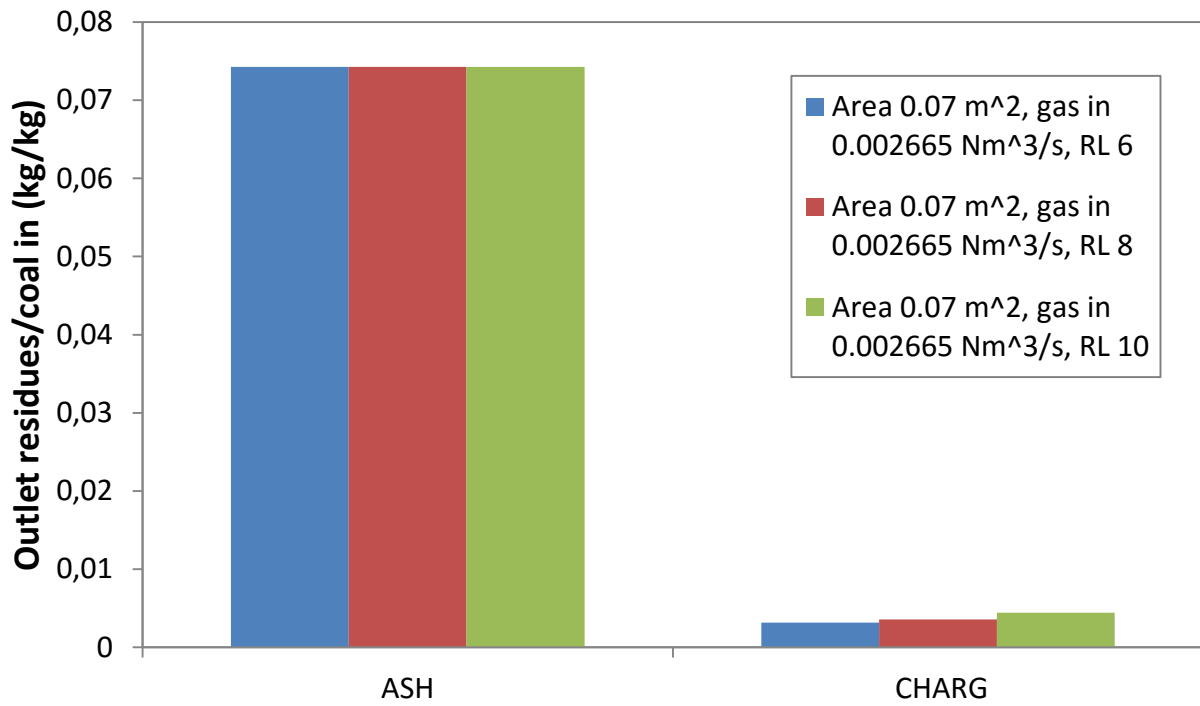
Gas temperature
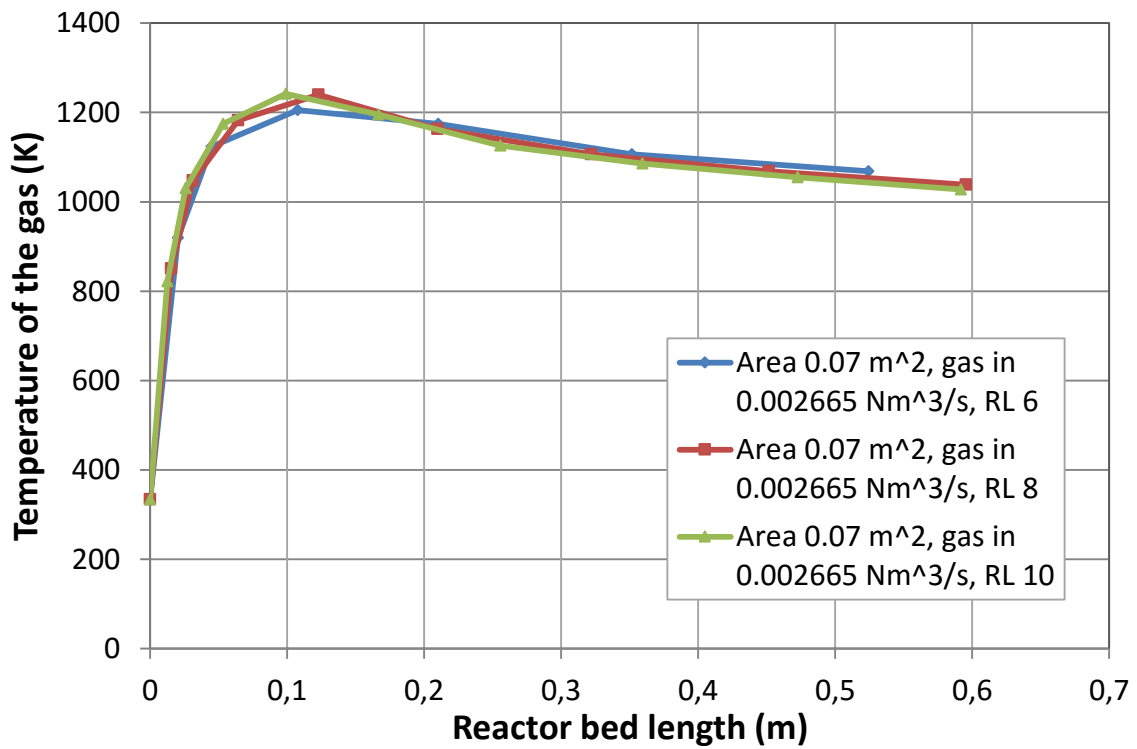
The simulations were done to check the parameters and the sensitivity of the system and the answer was very good.

In fact all the results of the simulations don't vary too much and always in a restricted range of values.

Of course with 10 reactor layers there is a better precision on the outlet gases composition and higher values of H2 and CO and lower values of steam and CO2 are registered, while the value of CH4 is stable.

Also the residual char is quite constant, even if a little increase is noticed with the simulation with 10 layers.

At last the graph of gases temperature shows that the three profiles are nearly the same once again and there is a good accordance on the results as wanted.

6.5.7 *Results and discussion*

In these part of the chapter various simulations and operative conditions of the gasifier were analyzed and discussed.

Starting from the conditions obtained in the previous chapter with the analysis of the thermodynamic equilibrium, made with the "D-Smoke" tool, it was possible to continue that analysis with a more complicated software called "GAS-DS", which is able to simulate and exercise a gasifier with some specified conditions (the "initial conditions") and which makes a kinetic analysis of the system.

The procedure was iterative with the simulations and started with an inlet flowrate of 0.002598 Nm^3/s, an area of 0.05 m^2, a height of 3 m, 6 reactor layers and 1 particle sector for the coal particle.

In those conditions there was no possibility to simulate adequately the gasifier, because with a kinetic system such this one the results showed a higher quantity of residual char that it was not accounted for in the previous simulations.

At this point the choice was to increase the area of the reactor, because the purpose was an increased residence time of the gases in the reactor and the simulations were made with an area of 0.07 m^2, even if there was again a not negligible quantity of char leaving the reactor.

The other possibility was to increase also the quantity of inlet air to have a major quantity of oxygen to burn and gasify the char to CO and CO2 products and the value of air passed from 0.002598 to 0.002665 Nm^3/s, with an improvement in the results obtained.

With these conditions of area (0.07 m^2) and inlet gas (0.002665 Nm^3/s) it was decided to vary other parameters, such as the number of reactor layers or particle sectors, to verify the sensitivity of the gasifier and the results.

It was obtained a desired performance of the gasifier and the simulation with 10 reactor layers was the best one in terms of molar composition of the exiting gases and profile temperature, even if it was very expensive for computational effort (12 hours).

Above there is a graph in which there are the compositions obtained with the simulation of the "GAS-DS" with 10 reactor layers and the simulation obtained with "D-Smoke".
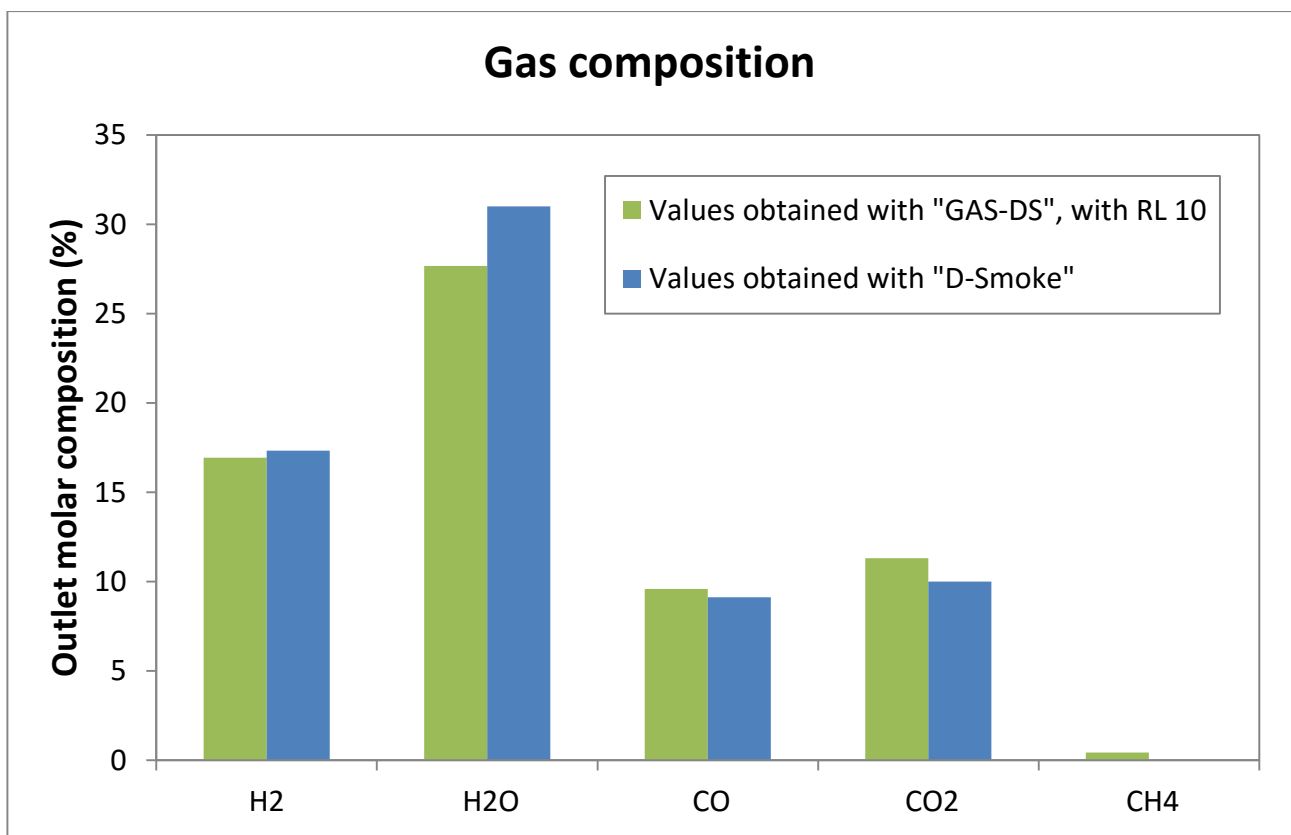
The results showed in the graph above are quite similar in the two types of simulations, but there are some differences.

The first one is the gas composition, which with the simulation done with "GAS-DS", has higher values of CO and CO_2 and lower values of steam and H_2 and a little percentage of methane (0.05 %), due to the higher values of air introduced in the inlet gases and so the lower quantity of steam present in the molar composition.

The other fact is the residual char, which was not predicted with the simulations done with "D-Smoke" and for this reason with "GAS-DS" it was implemented a major quantity of air into the inlet gases, to burn and gasify the char to CO and CO_2.

In addiction, the outlet gases of the gasifier still have a little percentage of residual char (4%), even if this is the lowest possible quantity to exercise the gasifier with conditions that give a good outlet gases composition in terms of H2/CO ratio and in terms of calorific value.

Thus if one goal and aim was to discover the good and feasible conditions to exercise the gasifier, the other goal was to seize the gasifier with this kinetic analysis and both the two requests were obtained.
In fact, discovered the optimum conditions (inlet flow gas of 0.002665 Nm^3/s, 10 reactor layers, 1 particle sector), it was also dimensioned the gasifier (area of 0.07 m^2 and height of 3 m).
This was the major objective of the work and it was reached.
Now let's move and try to do the same thing with a biomass gasifier, seeing if it is possible to have the same good results.

6.6 *Simulations of the biomass gasifier*

The experimental activity was focused on the reproduction of the Di Blasi article ("Countercurrent fixed-bed gasification of biomass at laboratory scale", CES, 1999).
The aim was starting with 10 reactor layers and only 1 particle sector, because of the hypothesis of considering the isotropic properties of the biomass and the relatively small diameter of the particles (5 mm).
The ratio between air and biomass flowrate is fixed at 1.131 and the height of the gasifier must be fixed at 0.45-0.5 m during all the process, trying to reproduce the conditions of the Di Blasi simulation.
Thus the air feed will contain 1.56 Kg/h, while the biomass feed will contain 1.38 Kg/h.
The time used to run the simulation was 100000 s.

The program used for the simulations was a POLIMI software ("GASDS"), into which were integrated the mass and energy equations, using the "BzzMath" library.
The first simulations with 10 reactor layers didn't give satisfying results, because of the impossibility of the program to calculate the dynamic behavior of the simulation due to numerical problems in the codes.
At this point the problem was rescaled, trying this time with only 4 reactor layers, and so with a less grade of precision.
The simulation ran and gave some interesting results, which can be described in terms of temperatures profiles of gas and solid along the reactor and in terms of gases species exiting from the reactor.

6.6.1 First simulation with 4 reactor layers

Below there are all the graphics, an explanation of its and an evaluation of the model data respect to the experimental data.
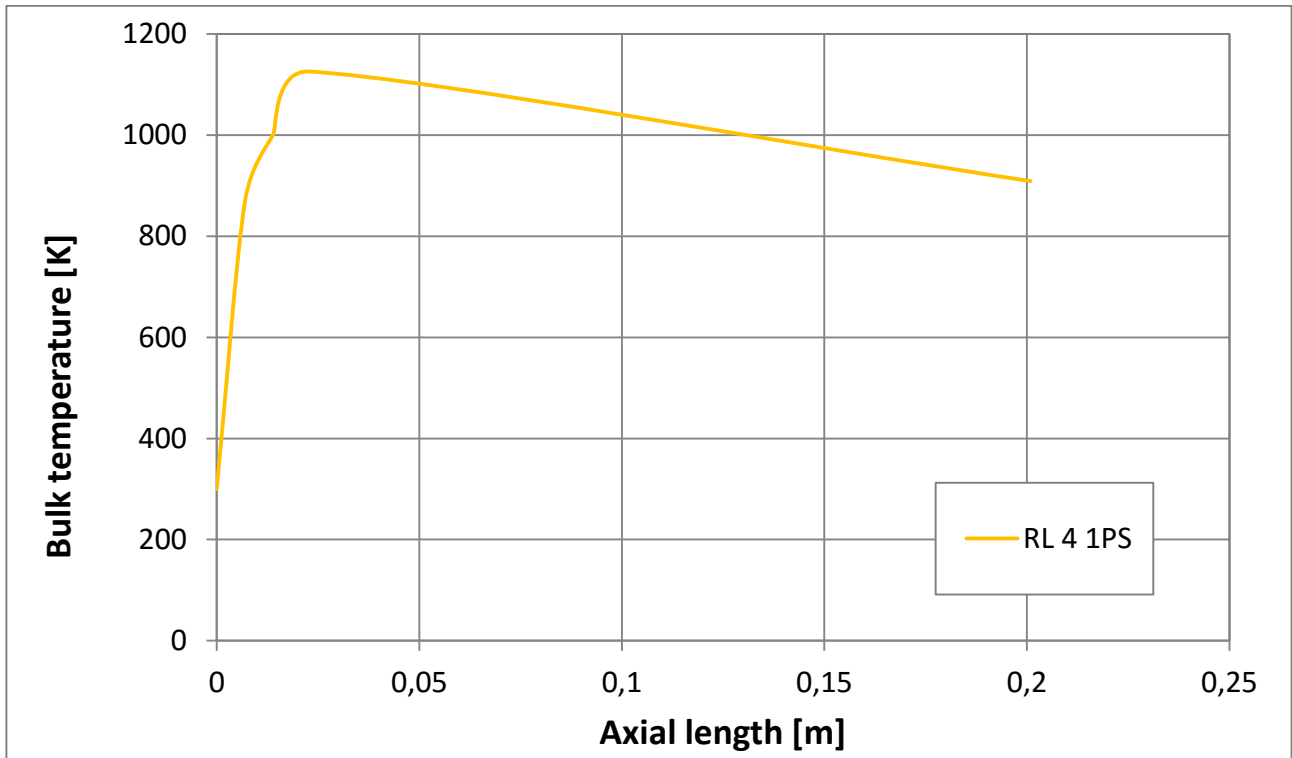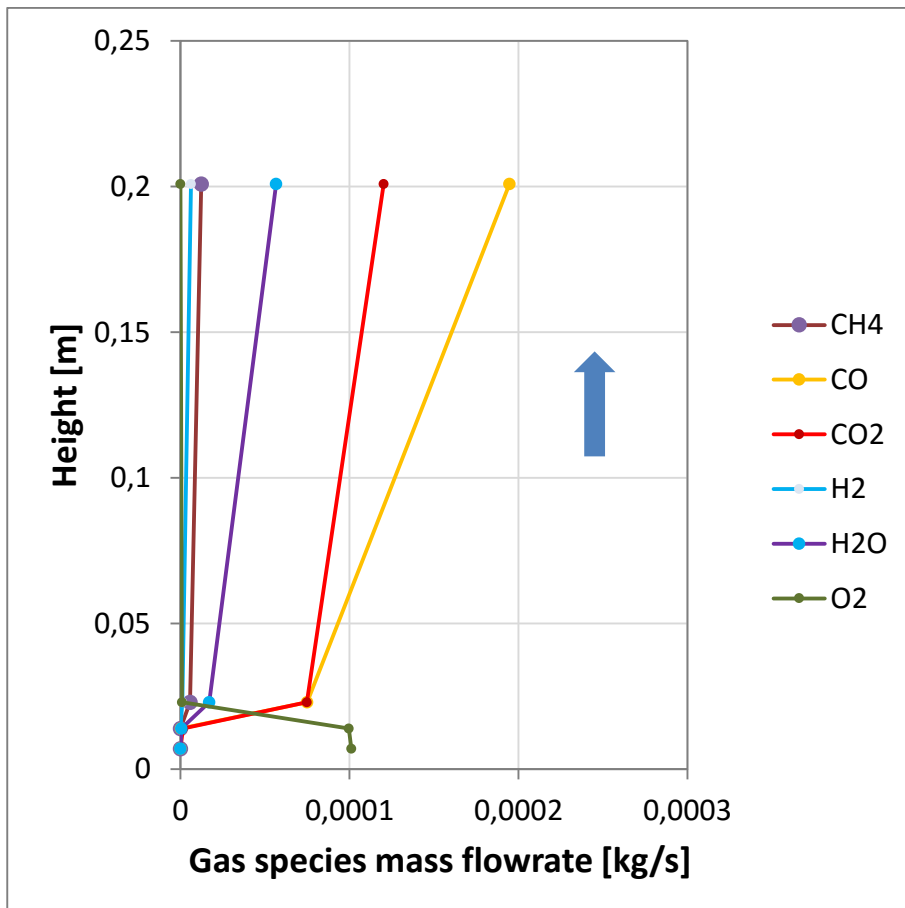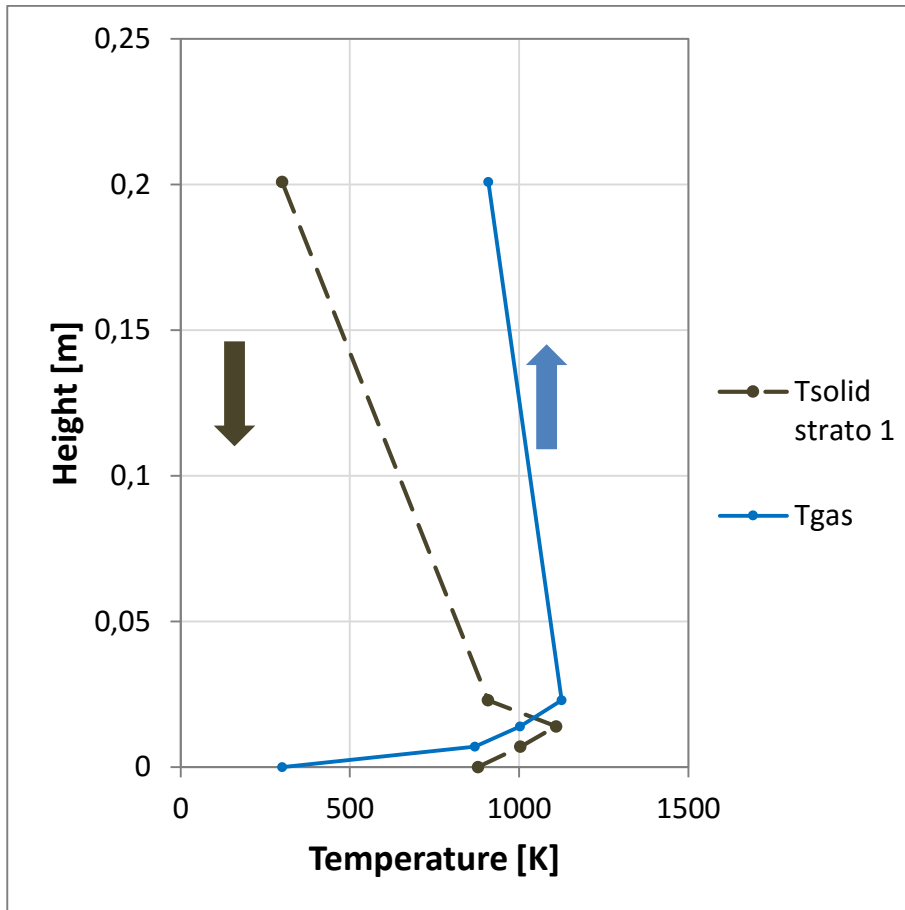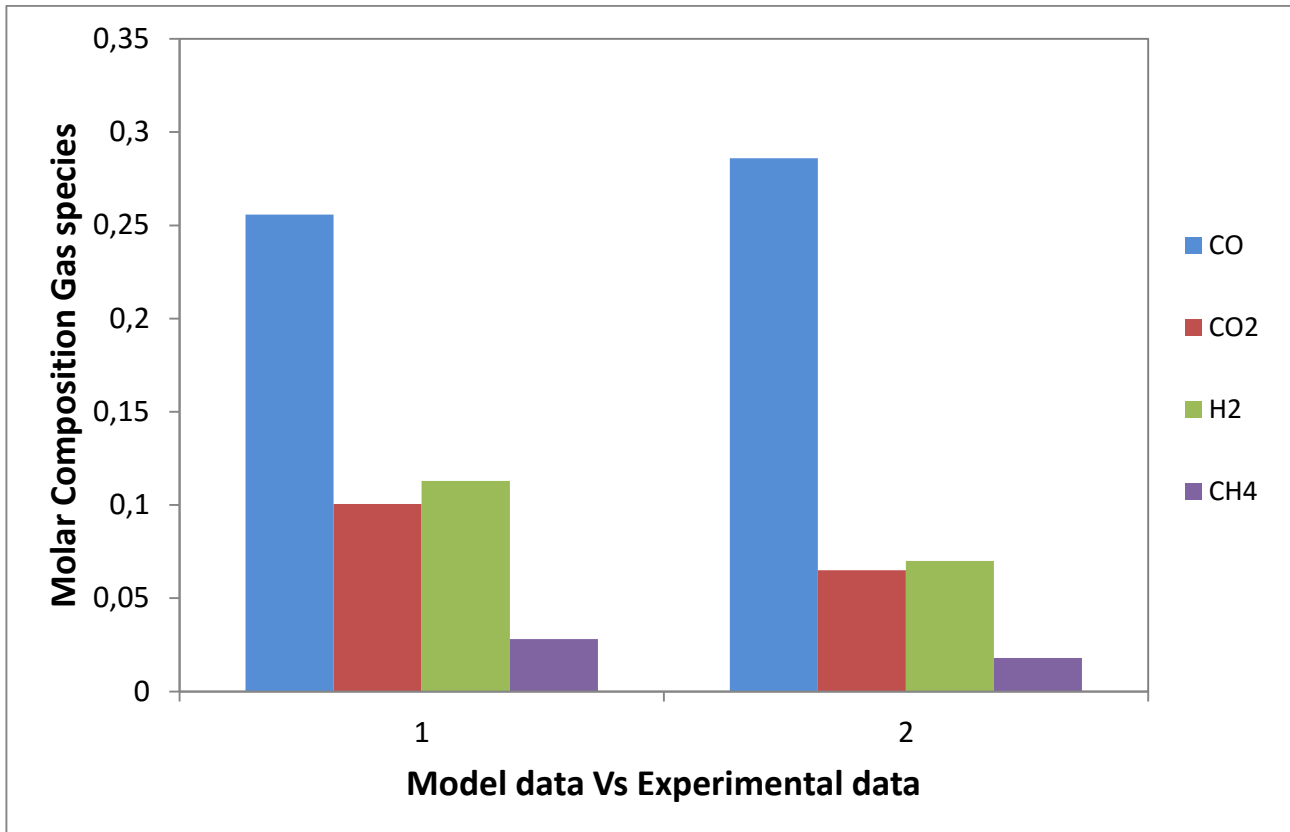
In the graphs above it is interesting to notice the temperature profiles of gas and solid and it is also very interesting to notice the gradually reduction of the reactor bed.

In this direction it is very important to notice that the first two reactor layers where used only by the biomass to pre-heating the air stream and only in the third and fourth reactor layers there is the effective gasification and combustion of the biomass with the hot gas.

It is also very interesting the composition of the outlet flow, in which it's important to highline how the model overestimates H_2, CO_2 and CH_4, while there is a value of the CO which is underestimated, even if the values are in according with the experimental data.

In addiction the residual content of char is negligible, due to the fact that with this flowrates the carbon efficiency is close to 100 %.

6.6.2   Simulation with 5 reactor layers

Below it is reported the graphs of the new simulations, done this time with 5 reactor layers and a major complexity of the system concerning the calculation effort, which is very time consuming.

The initial reactor bed height is always 4 m.
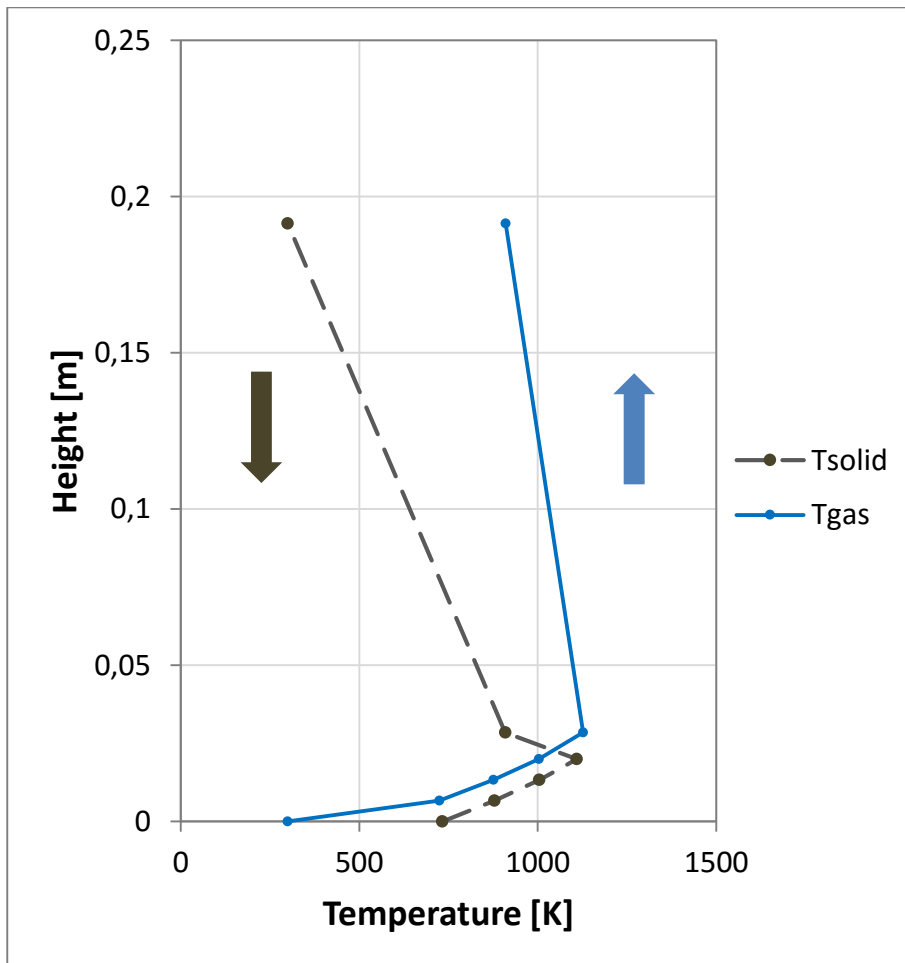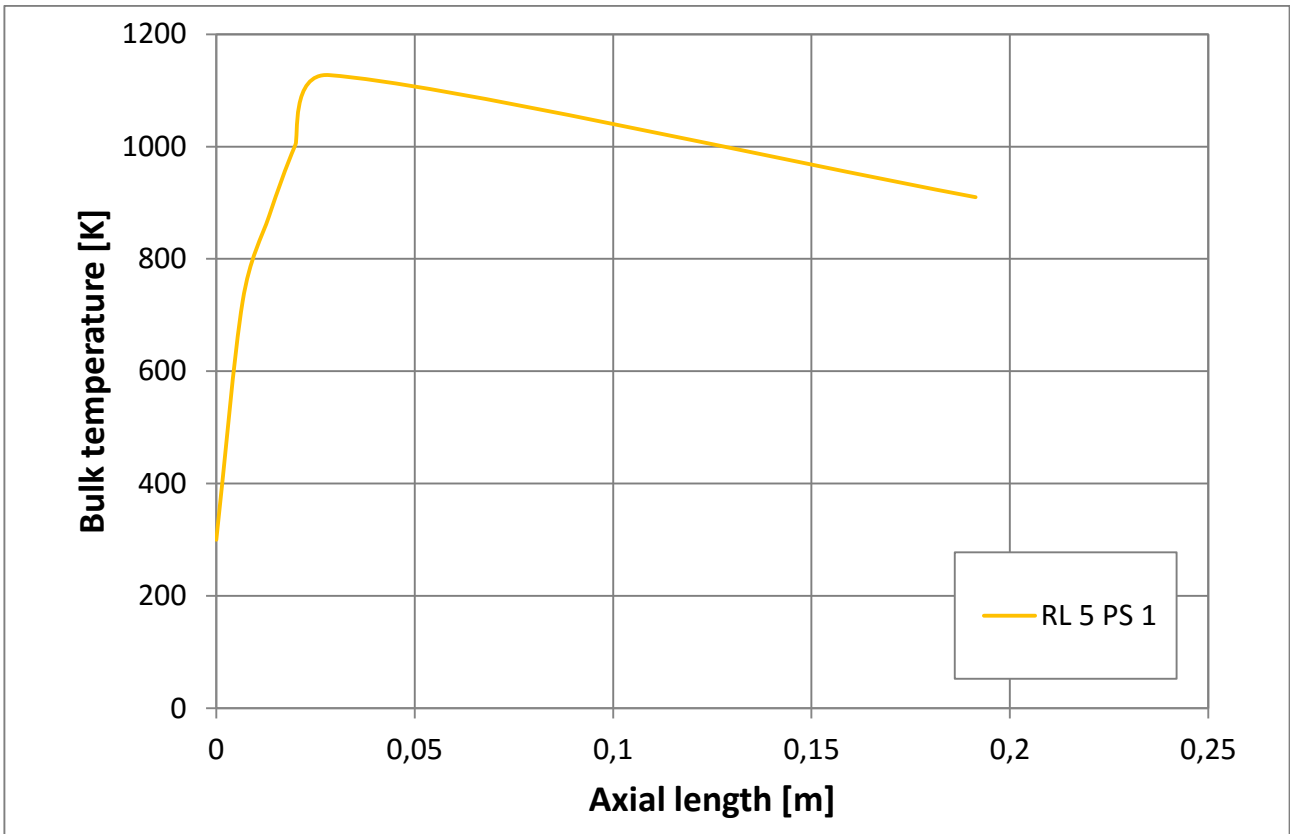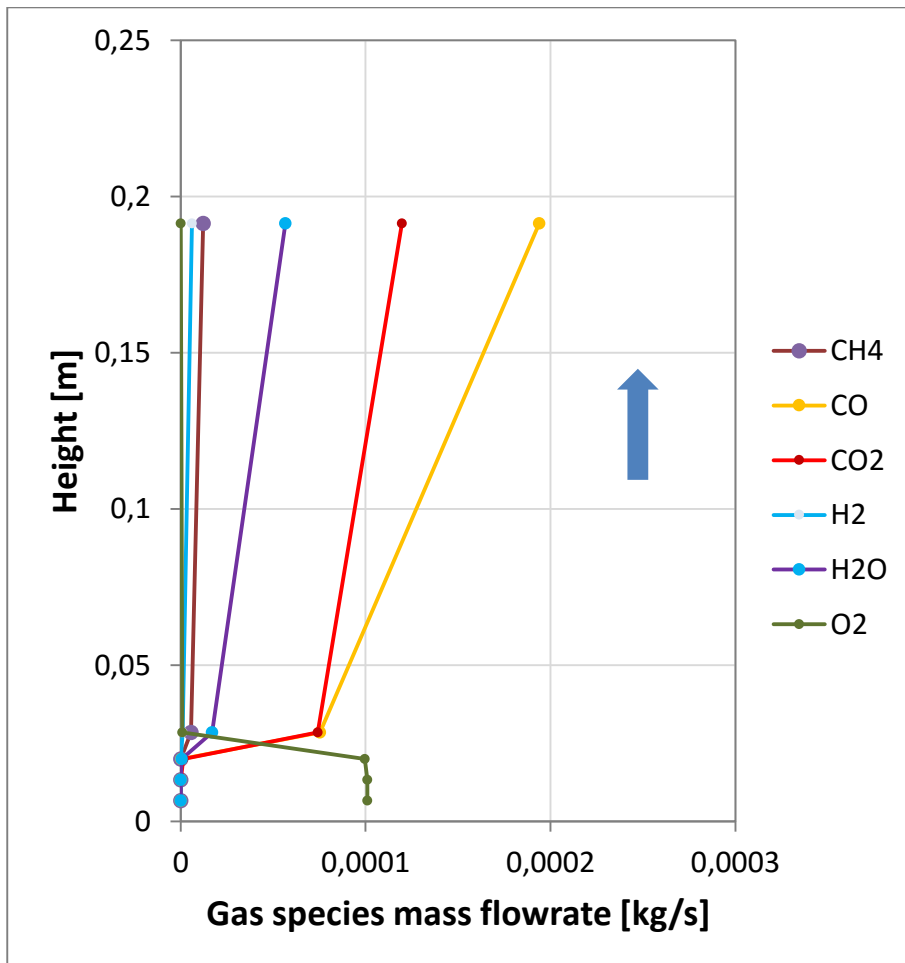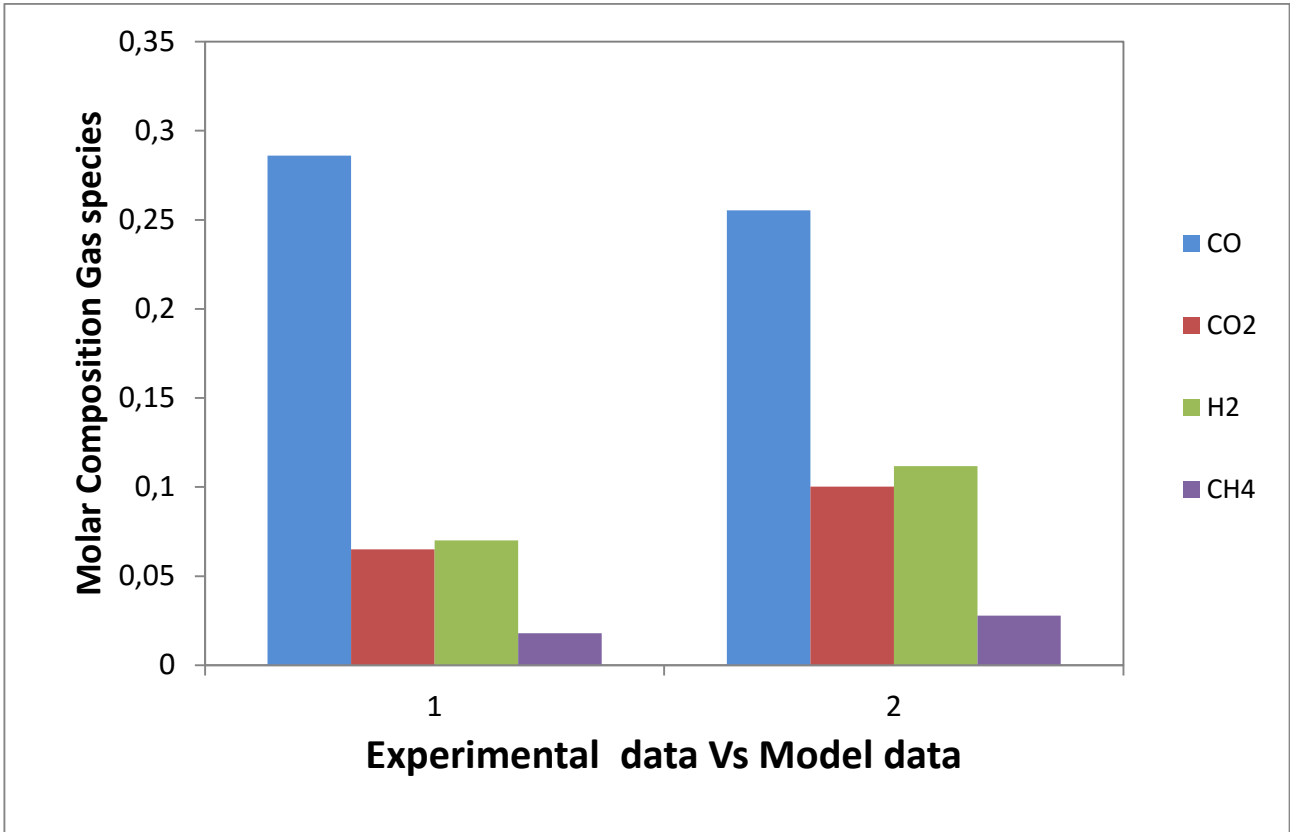
In this simulation with 5 reactor layers, the graphs above shows again the temperature profiles of gas and solid and the outlet species from the reactor.

Also with the new configuration of the reactor, the model data predict quite good the experimental data, but there is always an underestimation of CO and an overestimation of CO2, H2 and CH4.

The second important thing is that now with a more level of discretization, the bed height at the ending of the simulation is a little bit lower (0.191 m, against 0.20 of the simulation with 4 layers), but this can be due to the more complex level of investigation of the system and in the same time the two values are very similar.

Another important thing to notice is that in this simulation the first 3 reactor layers are used by the biomass to pre-heat the air stream till a temperature of about 1000 K, which is in according with the data of the other simulation, in which the first 2 layers where used for the pre-heating of the air by the biomass.

Also in this case, even if it wasn't reported the graph, there is a level of residue char that is negligible.

So it was possible to obtain a lot of data and some considerations explained before.

The next step is now try to do another simulation, in which there is the hypothesis to consider only the upper part of the reactor (2 layers).

The other part of the hypothesis is to divide each one of this two layers into another two and so the result is a simulation with 4 reactor layers again, but in this case we're considering 4 layers just for the upper part of the reactor and the entire reactor will be in this case made by 8 layers.

The results of the hypothesis is reproduce a reactor with more layers and a more level of complexity and to do this, with the numerical problem treated before, the reactor was divided into two portions, for the necessity have a better discretization of both.

6.6.3 *Simulation of the upper portion of the reactor with 4 layers*

Now let's consider the operative conditions supposed for this new simulation. First of all the air entering the reactor is now at 1000 K and it will not be reduced after a certain time, because the simulation is concerning only the upper section of the reaction and so the air stream was yet pre-heated by the hot biomass. The second supposition is that the height of the rector this time was put to 2 m, because of the interest to consider only a portion of the reactor. The graphs below show the results of the simulation.
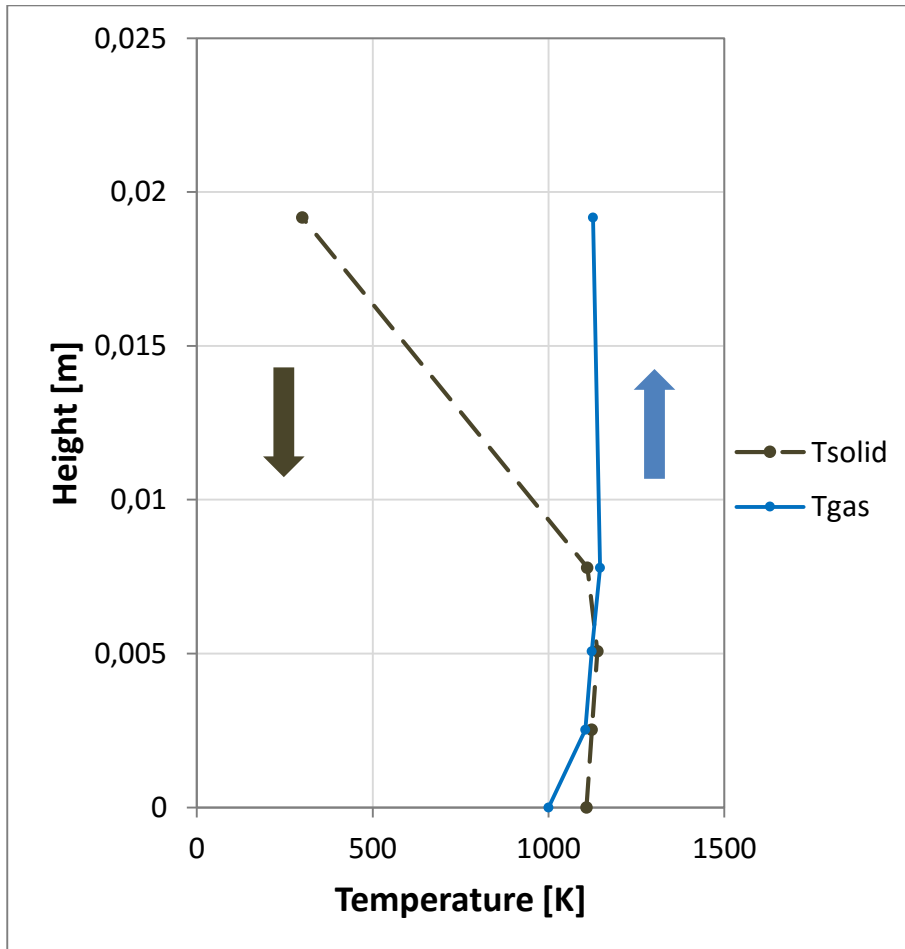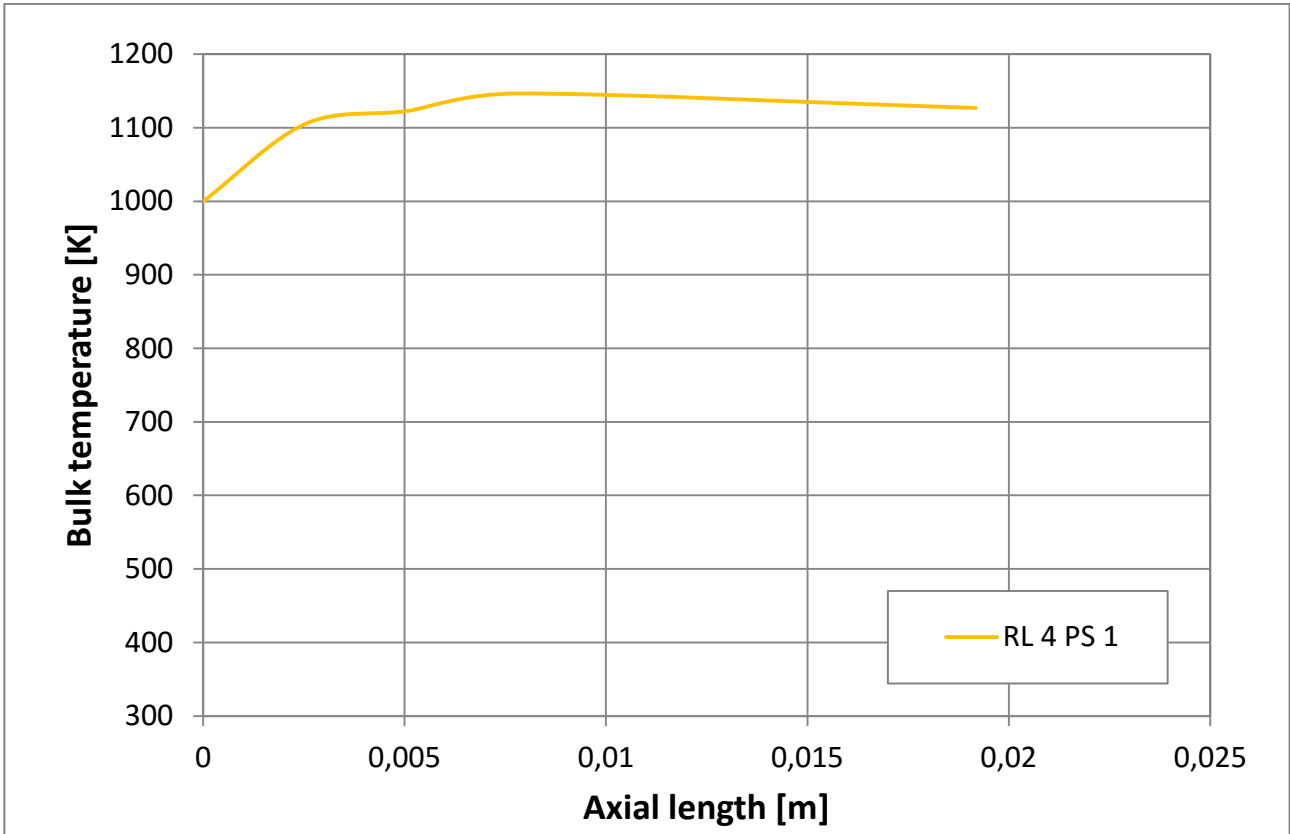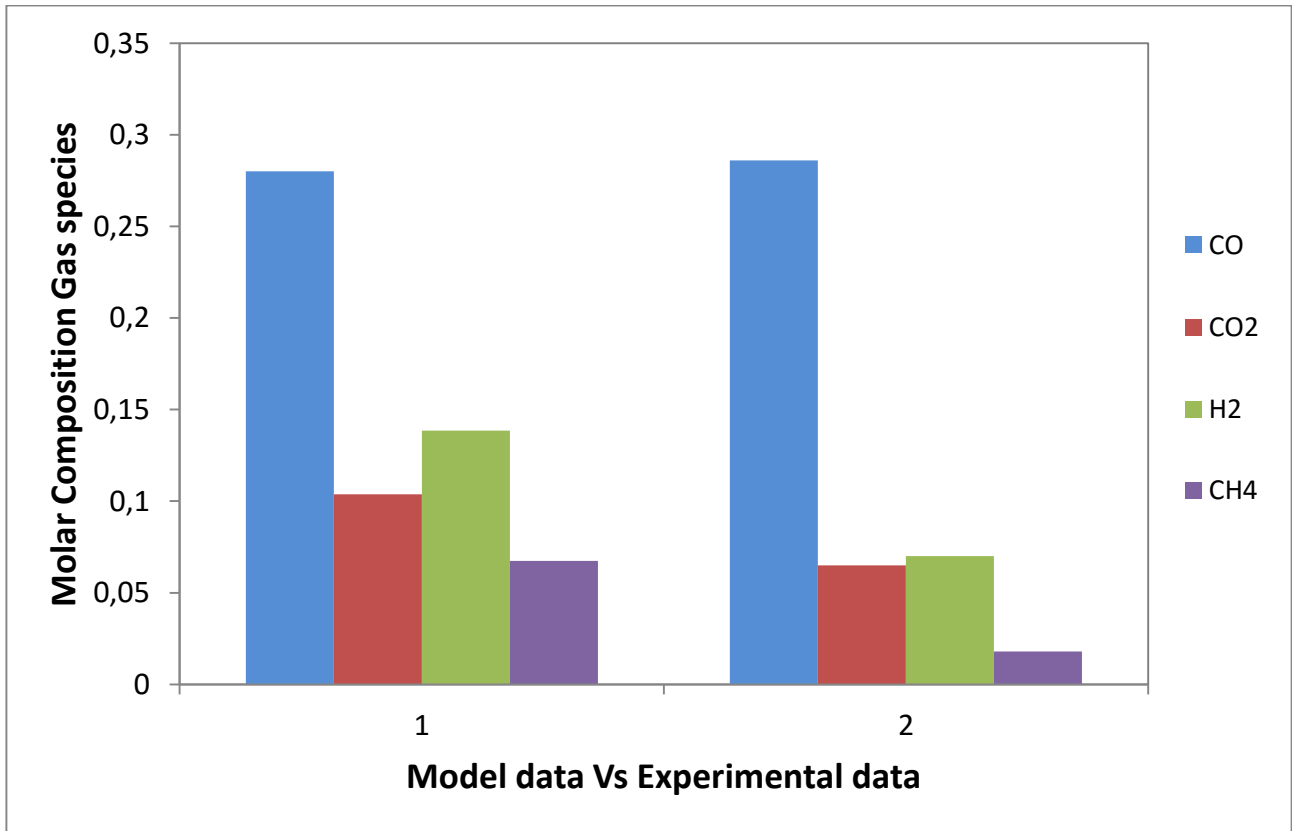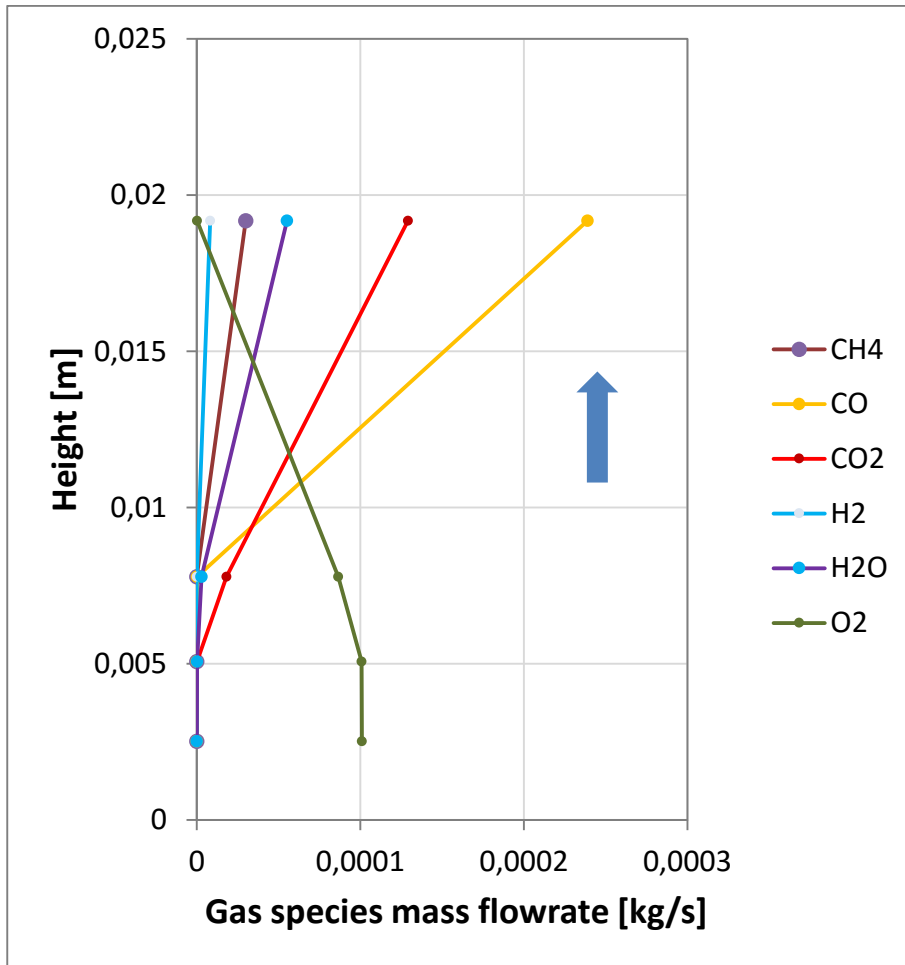
The graphs of the new simulation show always the temperature profiles of gas and solid and the composition of the outlet gases exiting from the reactor.

At the beginning it was noticed a great difference between the model data and what was expected.

First thing in this new simulation the composition of the outlet gases shows that the combustion and the gasification regime are settled only in the fourth layer and this is clearly showed by the consumption of O2, while it was expected that considering only the upper portion of the reactor the combustion and gasification regime should be present since the second layer. In addiction the residual content of char is negligible.

After the results underlined by this simulation, there was the evidence to test again and with other parameters the sensibility of the reactor to clarify the real behavior and all the aspects of the model.

The next parameter it be will texted and checked its behavior is the flowrate entering in the reactor, both biomass and air stream.

In fact in the next simulation there will be a simulation of the complete reactor and not only of the upper portion, varying this time the inlet flow.

6.6.4   Simulation with 4 reactor layers and varying the inlet flowrate (x4)

In this new simulation it was put the same height of the reactor (4 m), while the inlet flowrates of both biomass and air were changed, maintaining otherwise the ratio (A/F) fixed at 1.131 such as in the paper Di Blasi.

In fact the inlet flow rate was multiplied by four times the previous flowrate.

In the following pages there are the results and the comments at this analisys, with the graphs explained.
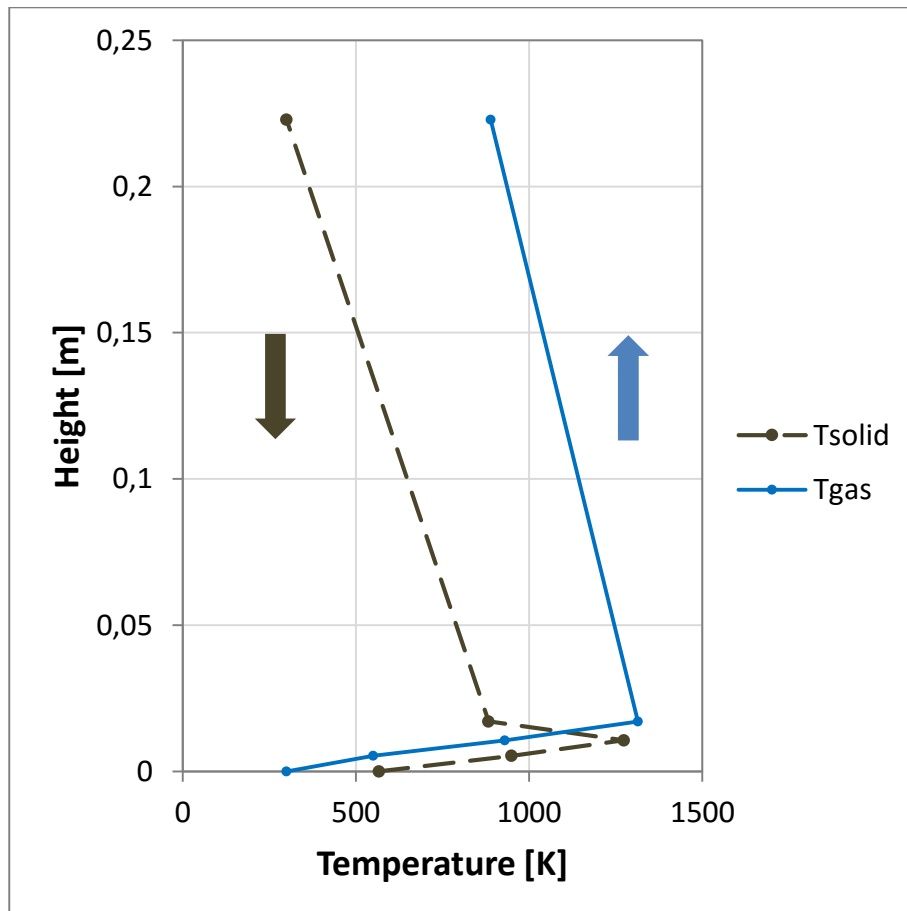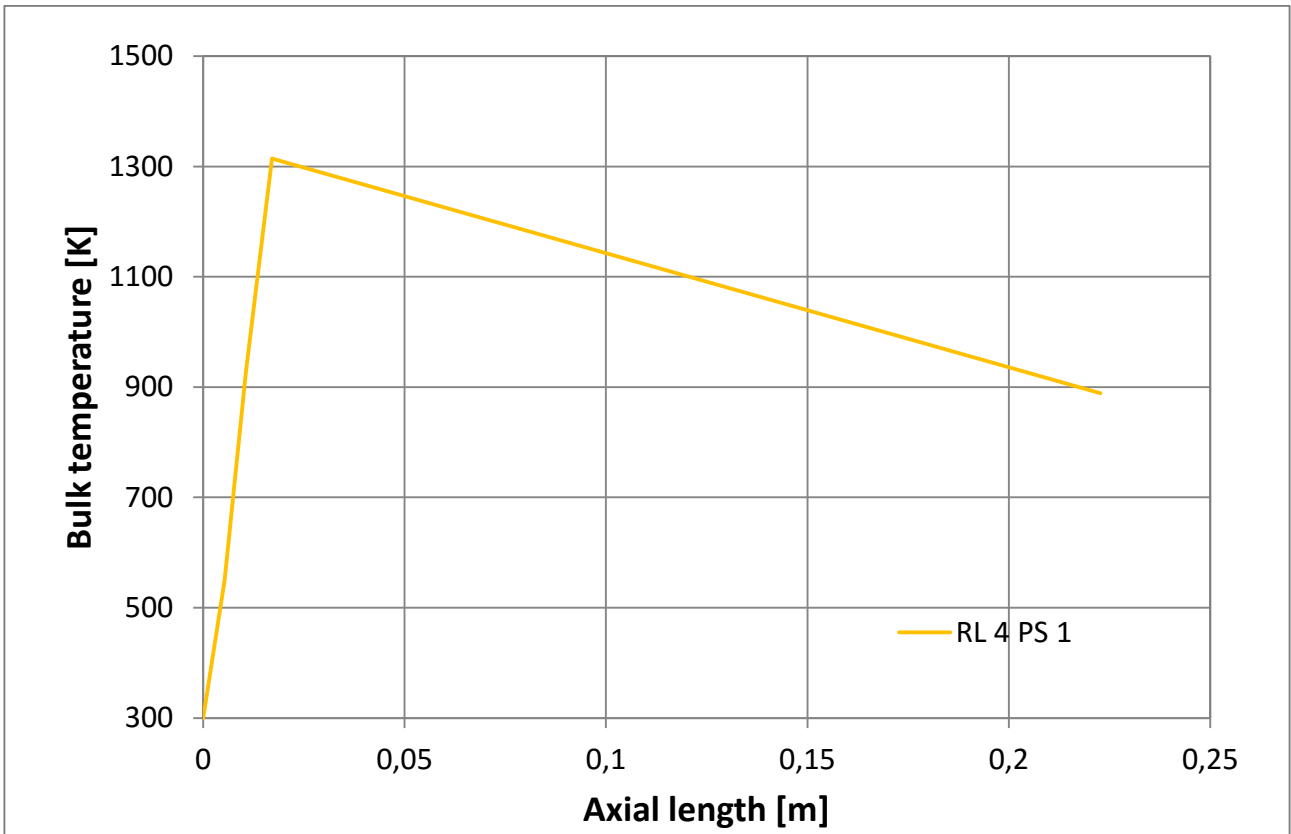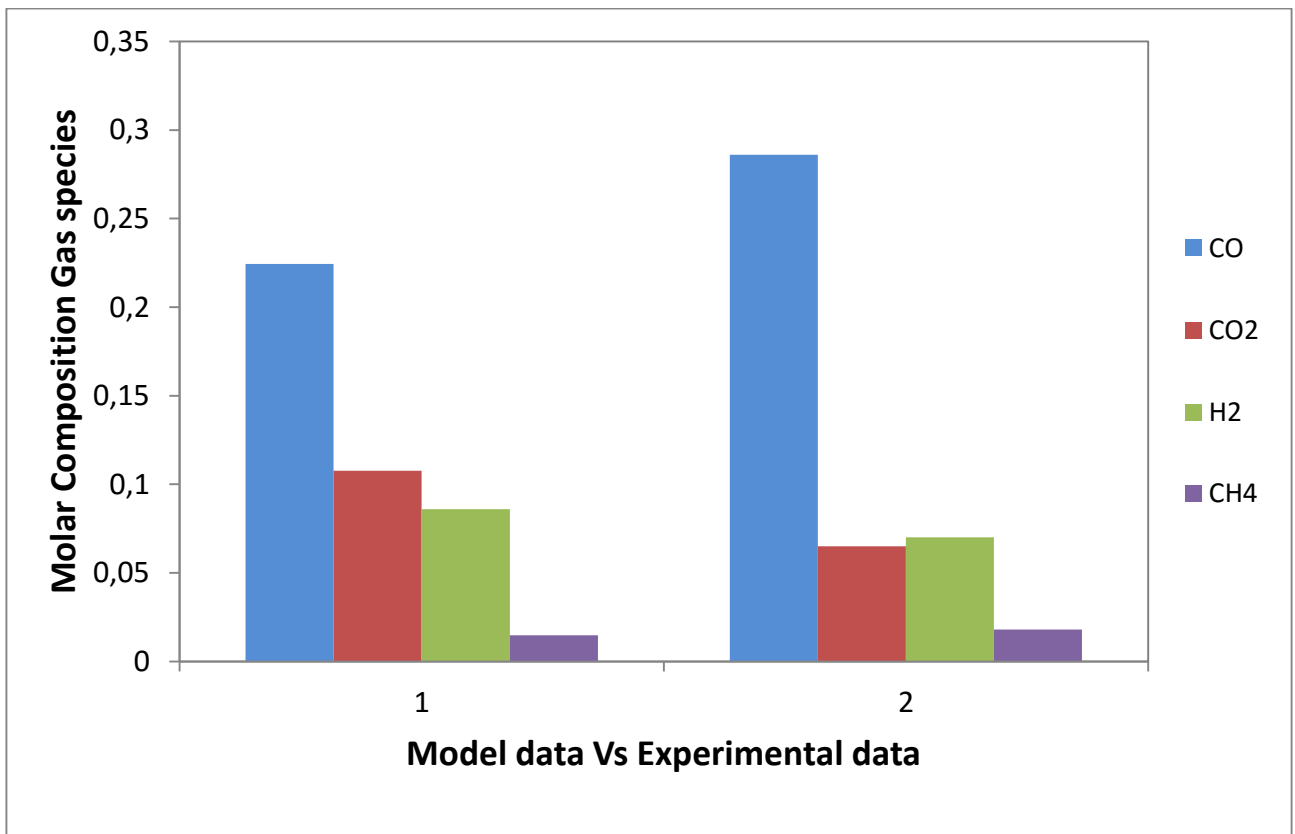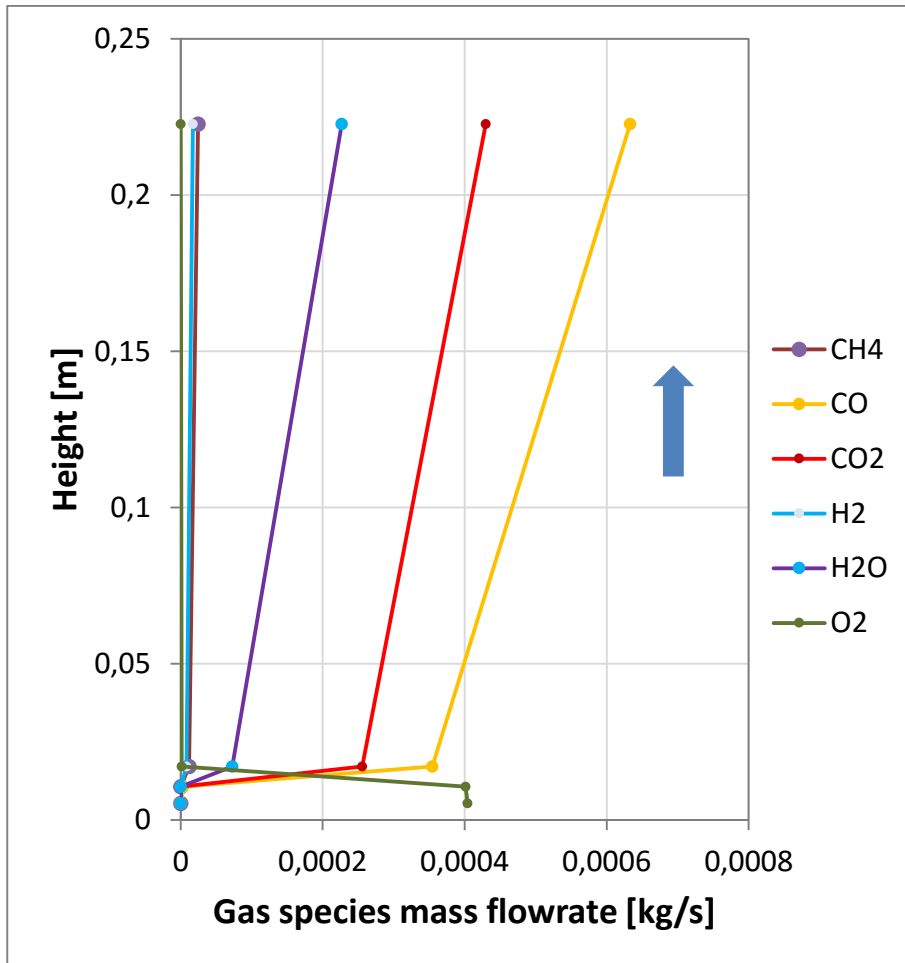
First of all in this simulation the temperature profiles of gas and solid are correlated and there is a difference between them, because of the great increase in the inlet flowrate.

As described better from the graphic below, it is notable that with an increase in the flowrate, the temperature of the solid (Tsolid) increases slower in the first two layers, but then reaches higher temperatures.

The same can be noticed for the temperature of the gas (Tgas), which reaches higher temperatures in the third layer, because that is the layer of combustion and gasification.
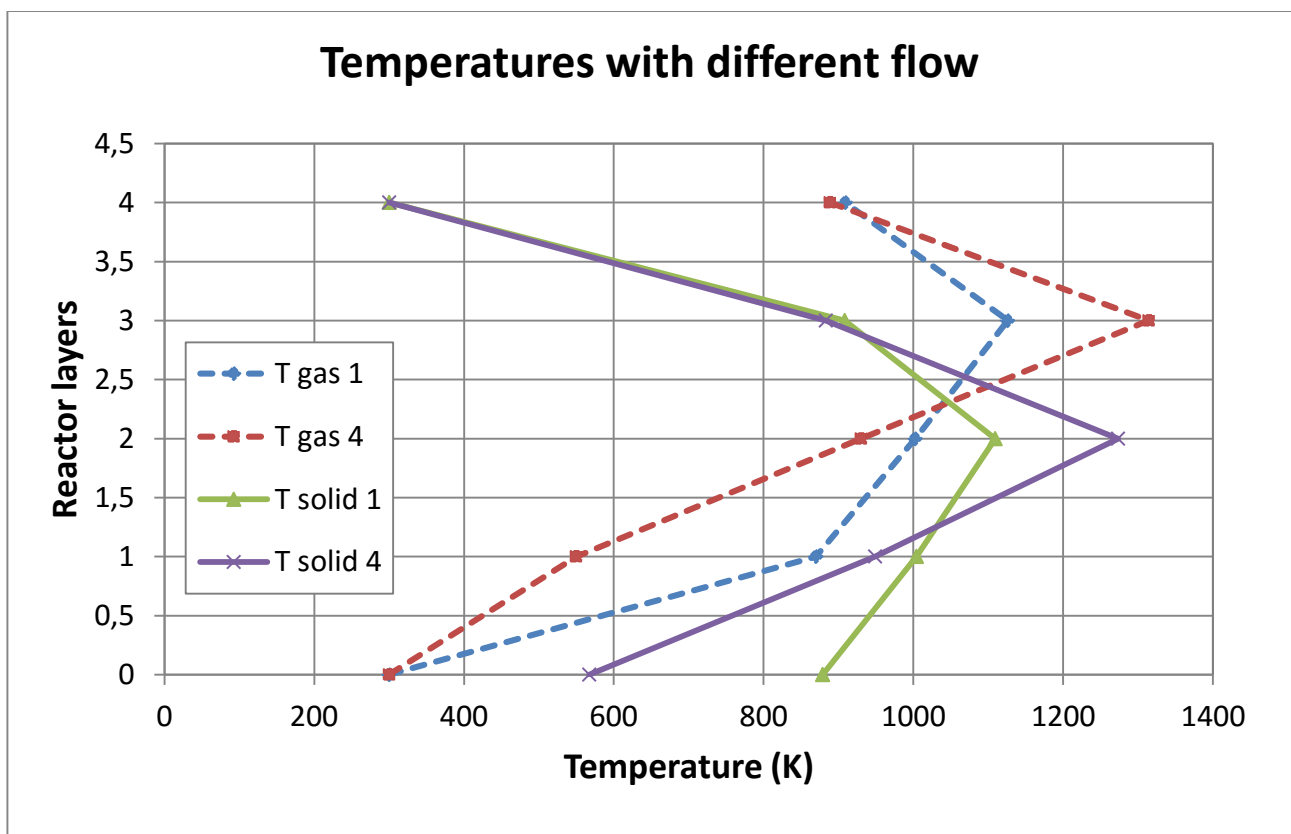
At the same time the outlet compositions are similar switching by the model to the experimental data, even if the CO is less underestimated than the CO2, while the value of CH4 is lower than the experimental data.

Then it is necessary to highline that an increase in the flowrate means a greater velocity in the dynamic of the system; in fact the time to reach the stationary state is decreased by a factor four, with a linear proportion, as expected.

Another thing to notice is that the value of the residual char is negligible also this time, thus the potentiality of the gasifier can be increased, till there will be an accumulation of char in the outlet composition of the solid and that's why in the next simulation there will be another increase in the value of the inlet flowrate.
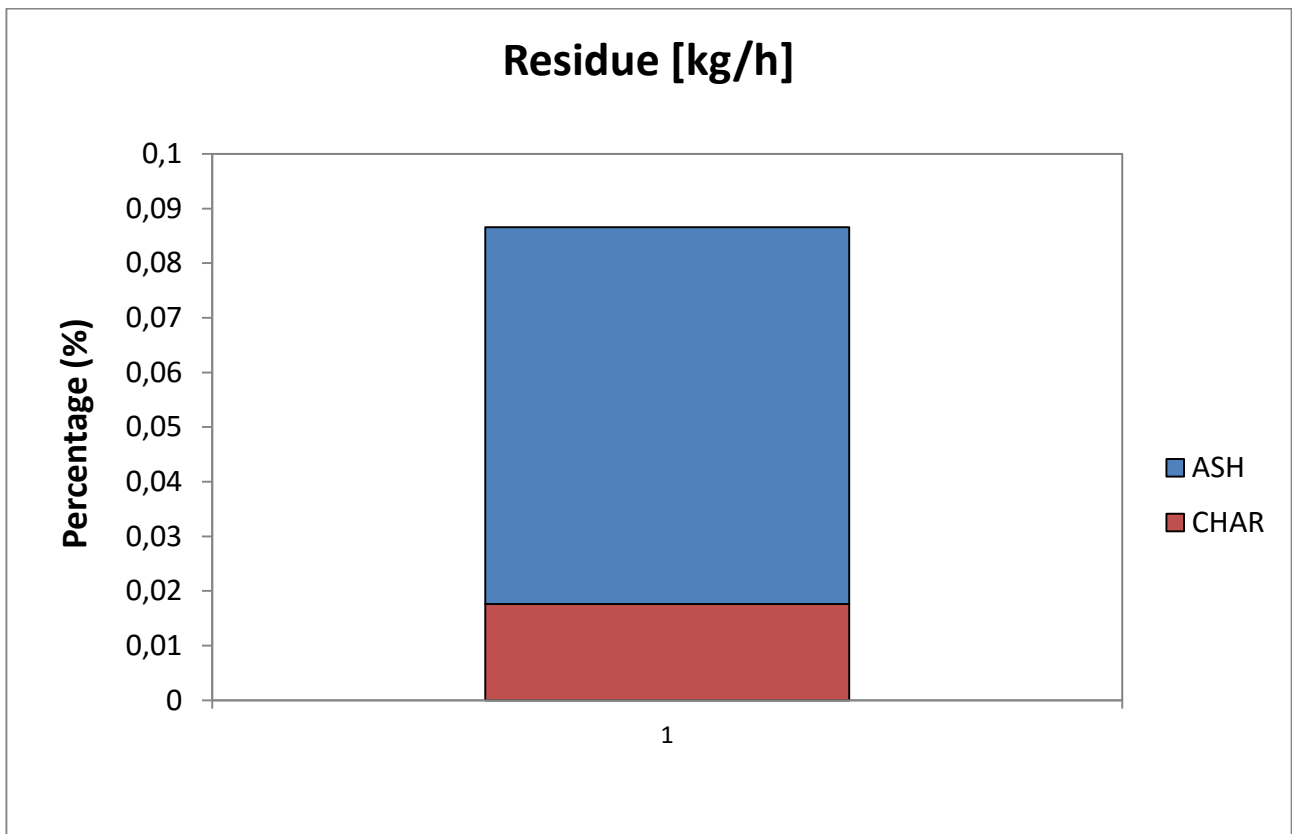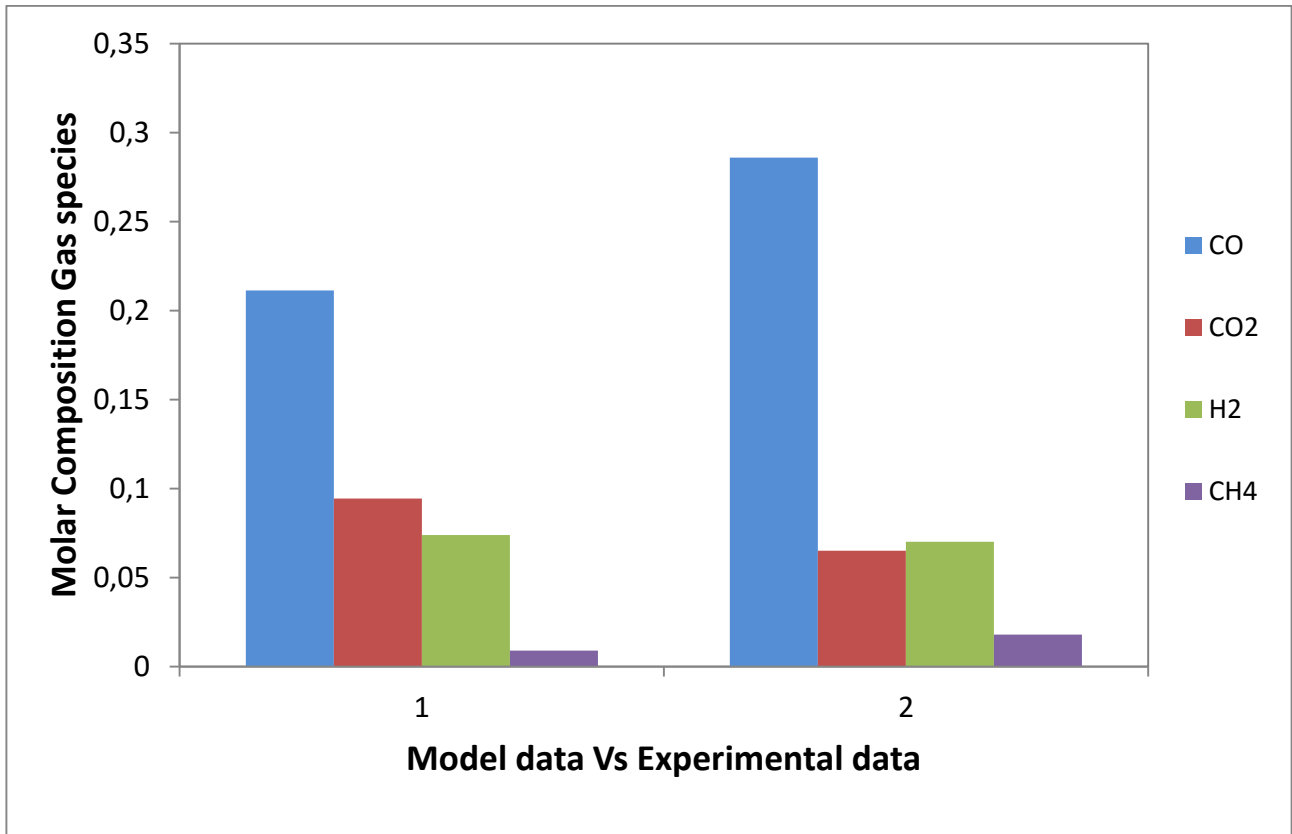
6.6.5 Simulation with 4 reactor layers and varying the inlet flowrate (x10)

This time the simulation will be done with the same initial height (4 m), but increasing the inlet flow and multiplying the initial value by ten times, always using the ratio (A/F) of 1.131.
The graphs below show the trend of the simulation.

Residue [kg/h]
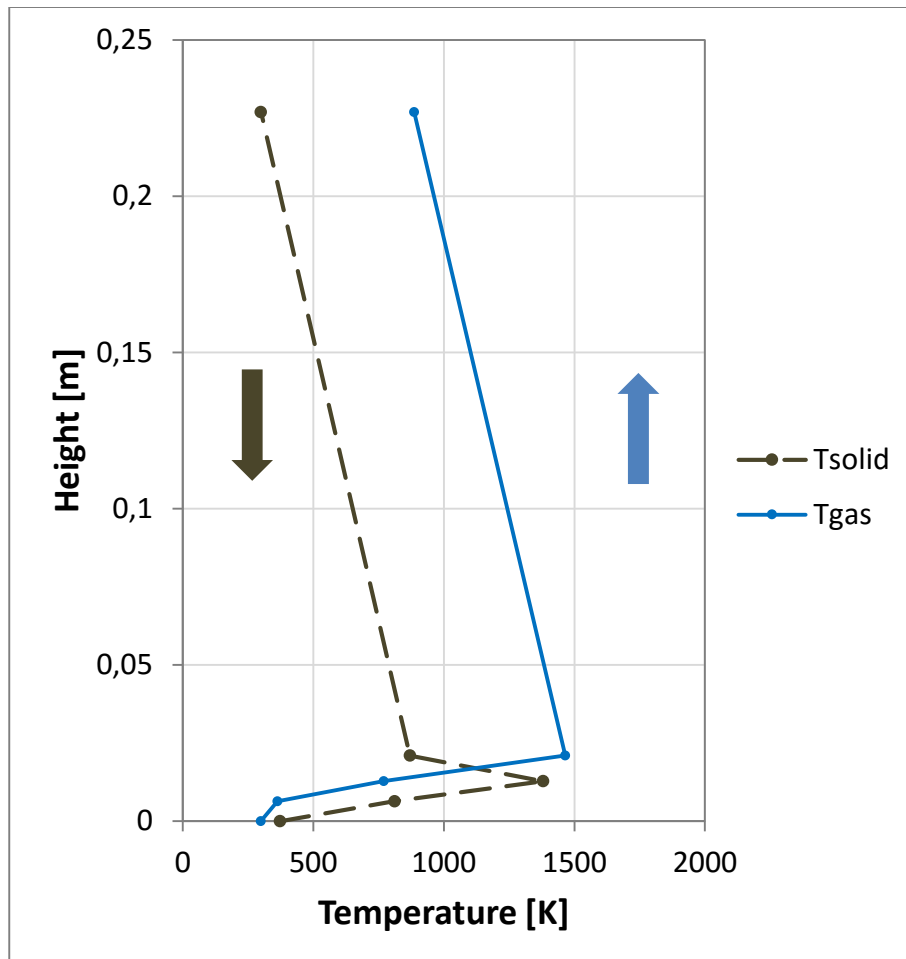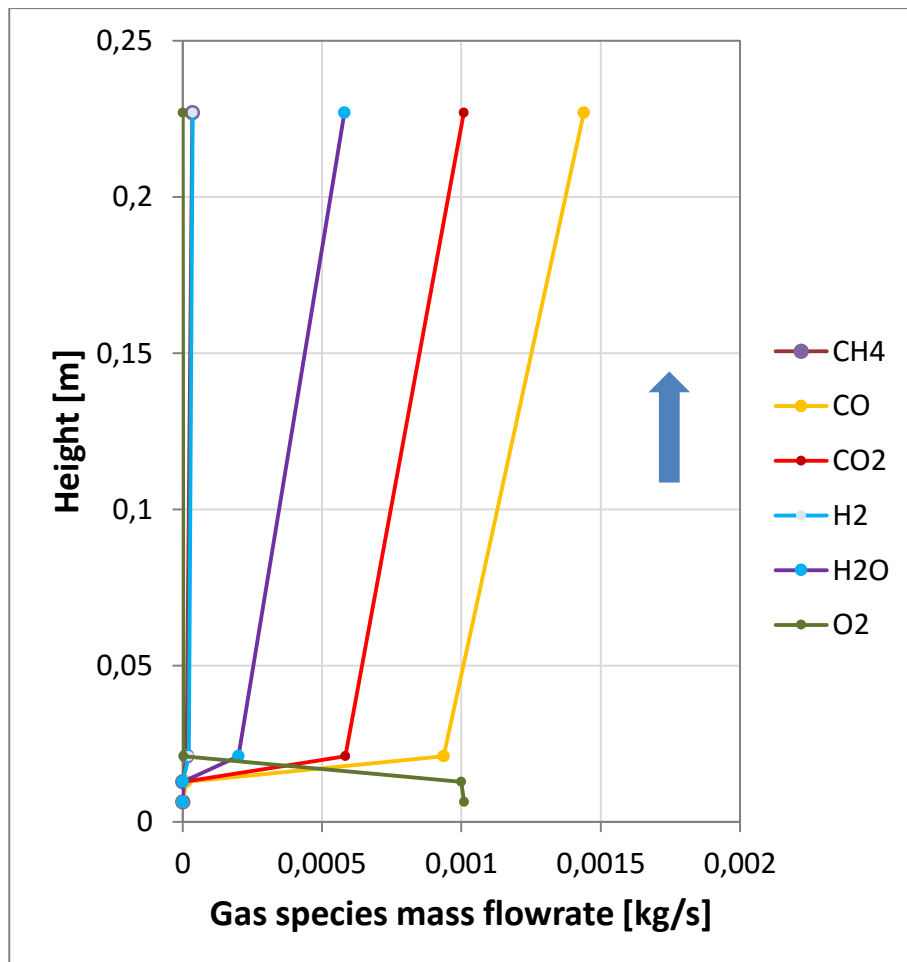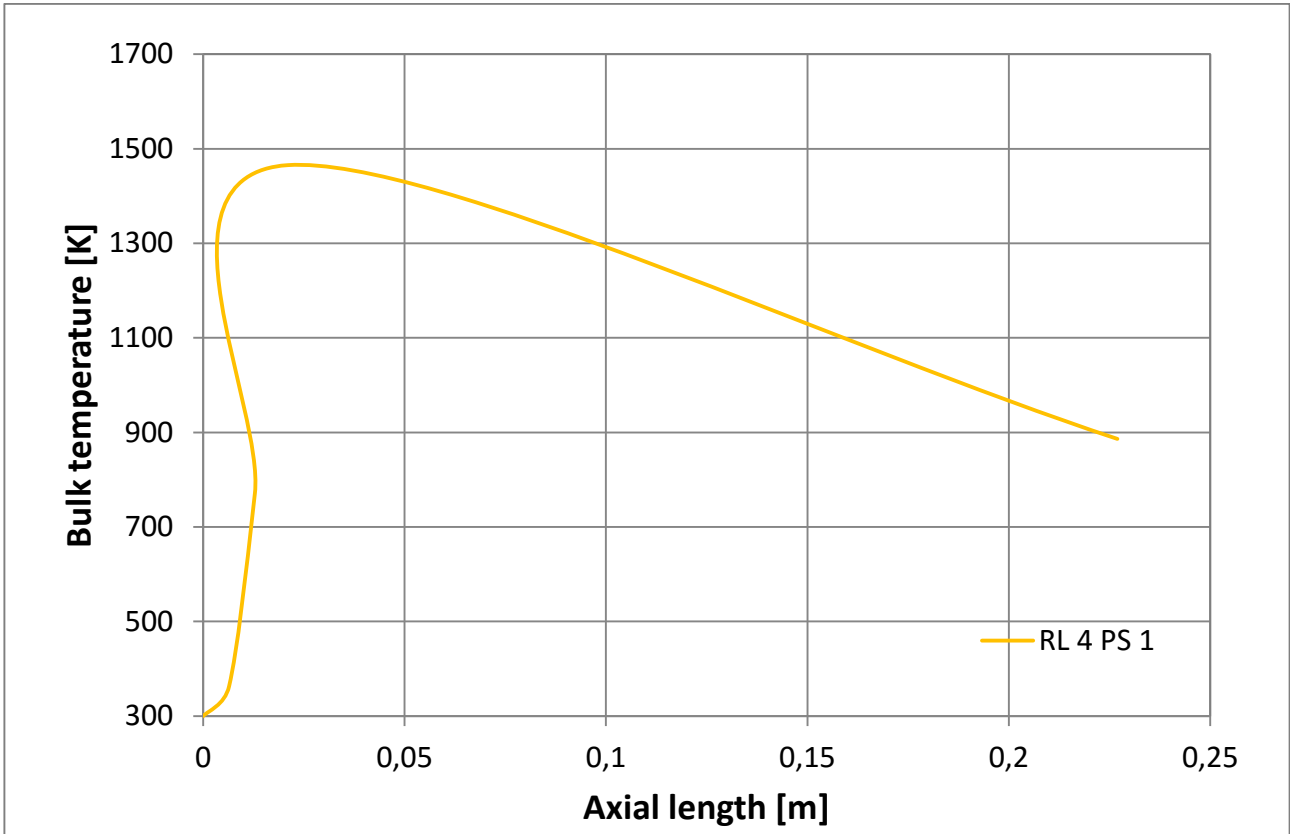
In the graphs above there is the presence this time of a greater value of the residual char, so it is important not to neglect its value.

This result gives also the possibility to focus on a residual high char value, which means that there was a better exploitation of the gasifier and its potentiality, but also that it is mandatory not to increase anymore the inlet flowrate, because of the possibility of an incomplete conversion of the biomass particle.

In addiction there is another time a faster dynamic involved in the fact that the flowrates are greater.

Also this time such as in the previous simulations, the values of CO and CH4 are underestimated respect to the experimental data, while the values of CO2 and H2 are overestimated.

6.6.6   Results and discussion

In the simulations with the biomass there was an interest to reproduce the "Di Blasi" paper, helped by the "GAS-DS" tool, which allows to exercise a gasifier with good precision, but with a great computational effort.

Respect to the simulations with coal, here it was immediately clear that with 10 reactor layers the computational effort was too long (about a week), thus the attempt to make some simulations with 4 or 5 layers.

The results were quite good and also the precision and the sensitivity were enough consistent, even if the accuracy was not the best due to the only 4 or 5 reactor layers.

However with the coal good results were obtained in dimensioning the gasifier and reaching the optimum conditions of the gasification process, both in terms of H2/CO ratio and calorific value of the syngas leaving the reactor.

In addiction with this more complicated and detailed analysis of the gasification process it was possible to optimize the feedstock entering the reactor and reach a residual char which is nearly negligible (less than 4% of the solid exit).

With this analysis many points done with the previous "D-Smoke" tool (it is remembered once again the hypothesis of the previous chapter, that is reaching the thermodynamic equilibrium and the assumption of a homogeneous system) were confirmed and helped to understand with more detail the system, finding out the points were the kinetic gave some interesting and different results to improve the behavior of the gasifier.

7 Conclusions

The work presented here proposes a study of coal and biomass gasification, through the simulation of the thermodynamic equilibrium respect to the combustion and gasification of both the two fuels and then the simulation of a more complex system involving kinetic conditions and seeing how the system reacted to the change of many parameters.

Therefore the first part of the work, which simulated the condition for the system of thermodynamic equilibrium, was conducted using the software "D-Smoke" and doing a few simplifications to the system, with the introduction of a homogeneous phase (only a gas phase), thus neglecting the solid phase.

In the second part of the thesis, starting by the results obtained during the simulations with "D-Smoke", it was considered a kinetic analysis of the entire gasifier and so a more complex system, in which there were two phases (both gas and solid phases), reaching important results.

In fact it was possible to determine the exact feedstock values (in terms of coal, biomass, water and air) and outlet compositions (in terms of syngas produced, H2/CO ratio, calorific value of the products, efficiency of gasification) of the gasifier.

Finally it was important to determine the stability and the sensitivity of the system, changing a few parameters and producing satisfying results for coal gasification, even if the system highlighted some problems for biomass gasification.

This will be the opportunity for future improvements in the software "GAS-DS" and in the biomass kinetic models.

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