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Testing, Modeling and Performance Evaluation of a Sewage Sludge Fluidized Bed Gasifier

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*Ai miei genitori, a mio fratello
e a tutti coloro che credono in me...*

*So let the people talk
This Monday morning walk
Right past the fabulous mess we're in.
-Patrick Wolf*

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Abstract

Biomass is one of the main alternative sources of energy and its use has been gaining more attention in the last decades. Sewage sludge, in particular, is produced at a fast pace by wastewater treatment plants; a good way to process it consists in gasification for syngas production.

Fluidized bed gasifiers are appropriate for this purpose, as they achieve conditions comparable to perfect mixing, between biomass and gasifying agent, thus allowing for a good heat and mass transfer. By performing experiments on a laboratory scale plant, it was possible to collect data and information to develop a model of the process.

This study focuses on equilibrium-based modeling, which uses Gibbs free energy minimization to calculate the syngas composition. By dividing the process in multiple steps, also taking account for non-equilibrium corrections, a simulation of the system capable of reflecting reality was elaborated.

Validation against experimental data sets and an extensive sensitivity analysis were carried out. Predictions of the overall performance and efficiency of sewage sludge gasification helped in the evaluation of the optimal operating conditions, in order to produce high quality syngas.

Sommario

La biomassa è una delle principali fonti alternative di energia e il suo utilizzo ha suscitato via via più attenzione negli ultimi decenni. I fanghi da acque reflue, in particolare, sono prodotti in grande quantità dagli impianti di depurazione e possono essere sfruttati in modo vantaggioso tramite gassificazione, per la produzione di syngas.

I gassificatori a letto fluido risultano particolarmente adatti a tale scopo, poiché operano a condizioni paragonabili a miscelazione perfetta, fra biomassa e agente gassificante, permettendo un buon trasferimento di massa e energia. Eseguendo esperimenti su di un impianto in scala di laboratorio, è stato possibile ottenere dati e informazioni per sviluppare un modello per questo tipo di processo.

Il presente studio si concentra sulla modellazione basata sull'approccio di equilibrio, che fa uso della minimizzazione dell'energia libera di Gibbs per calcolare la composizione del syngas. Suddividendo il processo in molteplici stadi, anche tenendo conto di correzioni di non equilibrio, si è elaborata una simulazione del sistema di gassificazione, in grado di riflettere la realtà.

Sono state effettuate una validazione del modello con più set di dati sperimentali e un'estesa analisi di sensitività. Le predizioni della performance e dell'efficienza della gassificazione di fanghi da acque reflue hanno aiutato nella valutazione delle condizioni operative ottimali, per una produzione di syngas di alta qualità.

1 Introduction

1.1 Energy Sustainability

Energy sustainability is a cause that has been gaining more and more attention in the last decades. This master's thesis work is part of the EAGLES program (Engineers As Global Leaders in Energy Sustainability), which has the aim of increasing interest and knowledge about different ways and technologies to produce sustainable energy.

1.2 State of the Art

An overview of the main concepts about biomass, sewage sludge is presented in this paragraph. Then, process modeling is introduced, with specific attention to the present case.

1.2.1 Biomass

Biomass is a term that refers to a wide range of biological materials, derived from living or recently living organisms.

Some of the numerous different sources are plant-based materials, such as virgin wood, energy crops, agricultural residues, or come from food waste or industrial waste.

Biomass is based on carbon and is composed of organic compounds containing hydrogen, oxygen, but also nitrogen and sulfur and minor quantities of heavy metals.

The main difference with fossil fuels, i.e. coal, oil and gas, is the time that has passed since the material was in a living form, compared to the moment it is used. Fossil fuels subtracted CO₂ from the atmosphere millions of years ago; therefore, when burned, they release CO₂, causing an overall increase of carbon dioxide in the system. Biomass, instead, absorbs CO₂ as it grows, and releases it back when it's used, but as the time scale is smaller, the rate of growth can balance the use, thus maintaining a closed cycle [1].

1.2.2 Sewage Sludge

Sewage sludge is the residue generated in wastewater treatment plants [2]. It can have a liquid or semi-liquid form and is originated by all the waste, municipal or industrial, that goes through the sewer. Sludge comes in many forms and, depending on treatments applied, is often divided into two classes. Class A, which refers to the sludge that is dried and pasteurized to reduce the content of bacteria, and Class B, which comprises the sludge that isn't digested and contains volatile compounds. Other than organic material, sludge also contains other "conventional pollutants", such as nitrogen and phosphorous, as well as heavy metals. Because of growth population and industrialization, production of sewage sludge is in constant increase; as a consequence, its disposal represents an issue that is gaining more attention and has to be dealt with. Despite the many possibilities, USA and European legislations prohibit its direct use as fertilizer or disposal in landfills [3,4]; in addition, public opinion is strongly opposed to incineration. For these reasons, alternative routes, that can be more socially accepted, but also economically advantageous, such as gasification, have to be studied and developed.

1.2.3 Gasification

Gasification is a thermal process that consists in the conversion of organic material to combustible gas containing mainly hydrogen, carbon monoxide and carbon dioxide. This mixture is called *syngas* (from ‘synthesis gas’). This process happens at high temperature ($T > 700^{\circ}\text{C}$), in a reducing environment, with a controlled amount of gasifying agent (usually air, oxygen or steam), in order to avoid direct and complete combustion [5].

The two conditions that limit the gasification range are pyrolysis and combustion. The former develops in complete absence of oxygen, leading to the formation of char and volatiles, while the latter requires the presence of stoichiometric or excess quantity of oxygen.

Gasification is often preferred to these other processes, because the syngas formed can be burned at higher temperatures than the original biomass, thus the thermodynamic upper limit for efficiency is higher or not holding (Eq 1.1) [6,7].

$$\eta_{Carnot} = 1 - \frac{T_C}{T_H} \quad \text{Eq 1.1}$$

where T_C is the temperature of the cold reservoir and T_H the one of the hot reservoir.

1.2.3.1 The Stages of Gasification

The process can be divided into phases that can correspond to different zones of the reactor.

Initially, in the *drying stage*, the biomass is heated and loses the moisture; then, in the *pyrolysis stage*, the volatiles contained in the biomass evaporate and form pyrolysis gases, which mostly contain tar; at the same time the non-volatile compounds remain in the solid

char. Subsequently the pyrolysis gases pass through the *partial combustion zone*, in which most of tar is destroyed via thermal cracking; the produced gases ($T > 1000^{\circ}\text{C}$) release heat to *gasification reactions*, which transform the stream into syngas ($600^{\circ}\text{-}700^{\circ}\text{C}$).

1.2.3.2 Gasification Reactors

Gasification can be performed in different kinds of reactors [8,9]; these are distinguished by the type of bed (where the actual process takes place) and are:

- Fixed bed reactors
- Moving bed reactors
- Fluidized bed reactors.

Fixed bed reactors are characterized, by definition, by an immovable area in which the biomass (and the catalyst, if present) is placed, while a stream of air, or other gasifying agent, flows through the material. Depending on how the biomass and flow of air interact with each other, these reactors can be categorized in updraft, downdraft and cross-current, although more complex configurations can be designed.

Moving bed reactors are quite similar, although the bed is either dragged through the process by a moving grid, or by its own weight, because of gravity.

Finally fluidized bed reactors are the most used for biomass gasification. The bed is formed by biomass, inert material (such as silica sand) and possibly some catalyst; fluidization is achieved by blowing the gasifying agent (air or steam) from the bottom of the

tank, at a fixed velocity, so that the particles are suspended and behave as a fluid [10]. While there are many kinds of fluidized gasifiers (bubbling bed, circulating bed, dual bed), they all have many advantages if compared to other types of reactors. As gasification is a multiphase process, the fact that fluidization allows for more uniform conditions has to be taken into account. Fluidized beds present better heat and mass transfer; indeed, contact between phases as well as even temperature are favored by the constant movement circulation of the particles, assimilating the system to perfect mixing conditions. This is a great advantage when dealing with gasification, as the process involves exothermic reactions, the heat of which is to be used by endothermic reactions [11].

On the contrary, fixed and moving bed reactors do not allow even distribution and transfer of mass and heat, therefore the process is harder to control and predict; certainly, the possible formation of cold or hot spots, which can lead to product degradation, is not desirable.

Some disadvantages of fluidized bed can be represented by the require of power for pumping the material and contrasting pressure drop, the increased reactor size and the possible erosion of reactor components, due to fluid-like behavior of the solid particles. Nonetheless, a great advantage is that fluidized beds can be easily scaled up, overcoming the limitations of small units [12].

Overall, fluidize beds are certainly preferable to other kinds of reactors, thus, for the present study, a fluidized bed reactor has been considered and will be presented in the following chapters.

1.2.4 Reactor Modeling

Mathematical modeling is the best way to study the phenomena involved in gasification in a fluidized bed reactor. A model is based on physical, chemical or empirical relationships and has the purpose of simulating reality. If well developed, a model can be used to predict trends and behaviors that are typical of a certain system at fixed condition. It is a design instrument that allows engineers to study and understand different features of a process, without having to build an experimental setup specific for every case, thus constituting an economic advantage. By analyzing the response of the model under various conditions, a complete characterization can be elaborated and efficiency can be assessed.

Different kinds of models can be studied, depending on the aspects it has to be focused onto, and the two main groups are certainly kinetic-based and equilibrium-based models.

Kinetic-based models are developed when the kinetics of a process are known. This requires quite a thorough amount of experimental data, such as axial and radial profiles of temperature and concentration of the species within the reactor vessel. This allows the creation of multi-dimensional models, which can represent the evolution of the process in each point of the system.

When dealing with fluidized beds, this type of characterization can be hard to elaborate, also because of the complex hydrodynamics and phase regimes that add up to the calculations. For these reason an approach focused on equilibrium-based modeling has recently gained more attention [13].

A common instrument used for model development is the Aspen Plus Process Modeling software. This tool helps representing a

system by dividing it into multiple blocks, which simulate a stage or a unit operation of the process; the blocks are set to match the operating conditions and, if possible, are configured with appropriate correlations.

Petersen et al. [10] developed a kinetic-based model for sewage sludge gasification in a circulating fluidized bed, using Aspen Plus. It includes a complete reaction network and hydrodynamics characterization, elaborated from experimental data that was collected from a pilot plant.

When using equilibrium approach, instead, the model is zero-dimensional. For gasification, most studies develop the simulation using minimization of the Gibbs free energy of the system; it is the case of Nikoo et al. [14], who modeled gasification in fluidized beds and validated the work against experimental data. Ramzan et al. [15] similarly studied biomass gasification and analyzed the influence of different kinds of fuels.

Both approaches to modeling are valuable and present advantages of their own; in the case of kinetic-based models, it is evident that reactions are profiled carefully and the evolution of each stage of gasification can be thoroughly described. Nevertheless, equilibrium-based models allow for easier prediction, require less calculation time and are more suitable to evaluate the overall response of the system.

1.3 Aim of the work

The aim of this master's thesis is to develop a model, using Aspen Plus, to simulate sewage sludge gasification in a fluidized bed gasifier.

This work will analyze the stages of biomass gasification and a method for faithful representation of a real system in a modeling environment. First of all, the equipment, the materials and methods, which were used to collect experimental data, will be introduced. In particular, the laboratory scale plant, comprising a bubbling fluidized bed reactor, will be described; furthermore, details about sewage sludge and the treatments it underwent will be explained.

Subsequently, the development of the model will be illustrated, with particular emphasis on the assumptions taken into consideration, the steps in which the process was split and the methods, based on Gibbs free energy minimization and equilibrium restriction, used to predict the outlet composition of the syngas.

Moreover, a validation of the model against multiple sets of experimental data will be showed, coupled with an extensive sensitivity analysis, which will show the trends of the predictions for different operating conditions.

Finally, the energetic assessment of the process will be presented, in order to show the performance of the model and evaluate the efficiency of this kind of biomass gasification.

2 Experimental equipment and methodology

2.1 Equipment

2.1.1 Materials

Sewage sludge used for gasification can be in two forms: dehydrated or dried. In the first case, the sludge, which usually comes from a wastewater treatment plant, contains about 70-80 % of water and has to undergo a drying step in a separate unit operation before further treatment [16]. If this were neglected, gasification would obviously become highly unfavorable, because of the significant amount of heat that would be spent to evaporate the excess of water. Dried sewage sludge, instead, typically contains 10-20 % of water and can be processed directly into the gasification reactor, where the moisture can vaporize and take part in the reactions.

For the present studies dried sewage sludge has been used. Proximate and ultimate analyses, which followed the UNE-EN standards for analytical methods, were conducted on samples, following the “analysis in triplicate” pattern (see Table 2.1). While proximate analysis expresses the weight percentages of ash, volatiles, fixed carbon and moisture (on a dry basis, except for moisture), the ultimate analysis reports the elemental composition of the biomass,

indicating weight percentages of nitrogen, hydrogen, sulfur, oxygen and carbon, to which ash is added. Finally, the content of heavy metals was observed (Cd, Cu, Ni, Pb, Zn, Hg, Cr).

Parameter	Value for sludge
Moisture	7.0 %
Organic Matter	56.0 %
Ash	44.0 %
pH	6.9
Carbon	27.3 %
Nitrogen	4.1 %
Hydrogen	4.8 %
Sulfur	0.9 %
Oxygen	18.9 %
Heavy Metals:	
(mg/kg)	
Cd	2.7
Cu	402.5
Ni	58.0
Pb	159.5
Zn	1227.5
Hg	2.8
Cr	163.5

Table 2.1 Analysis of sludge. Values are on a dry basis, except moisture and pH

Such analyses permitted the calculation of the lower heating value (LHV) of the sludge following the modified Dulong's formula [17].

$$LHV = 8.060C + 33.910 \left(H - \frac{O}{8} \right) + 2.222S + 556N \left(\frac{kcal}{kg} \right) \quad \text{Eq 2.1}$$

The sewage sludge samples that were used for testing presented spherical particles of approximately 2-5 mm in diameter. The particle size was reduced to 300-500 μm by crushing the sludge with a blender and passing it through a sieve. This was done in order to overcome the possible mass and heat transfer limitations that can become evident at larger scale.

The fluidized bed material consisted of silica sand, with the same particle size of the sludge.

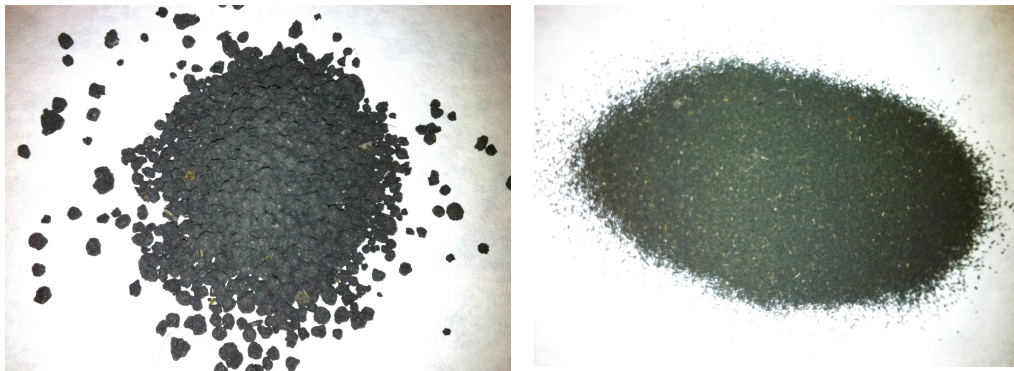


Figure 2.1 Samples of sewage sludge as received (left) and after crushing and sieving (right).

2.1.1 Laboratory scale plant

The gasification tests were run in the plant shown in Figure 2.2. The dosing system consisted of a hopper and two screw feeders, respectively a vertical dosing screw and a horizontal launch screw. The latter was inserted directly into the reactor through a pipe (outer diameter 12.7 mm), which was equipped with a water-cooling system, in order to prevent biomass to pyrolyze before reaching the reactor.

The gasification section of the plant comprised a stainless steel (AISI 316 L) fluidized bed reactor (700 mm of height, 32 mm of inner diameter) and a freeboard (46 mm of inner diameter), located at the top of the reactor. These two elements were heated by an electrical furnace.

The bed was held in place inside the reactor by a distributor plate, with a pore size of 0.1 mm, which also had the function of providing a uniform flow of gasifying agent to the reactor, impeding the creation of preferential paths.

Through the distributor plate passed a concentric tube, which fixed the height of the bed (100 mm) by allowing for the ashes to fall into a lower collector tank.



Figure 2.2 Laboratory scale plant at Universidad Polit cnica de Madrid.

The gasifying medium, which was used in the tests, was air or a mix of air and steam. The bed achieved fluidization through the airflow that was set to a specific fluidization velocity with the aid of a flow controller.

Two rotameters split the flow and diverted part of it to the dosing system to facilitate the feeding of the reactor. When gasifying with air and steam, a peristaltic pump at the bottom of the reactor fed water to the system.

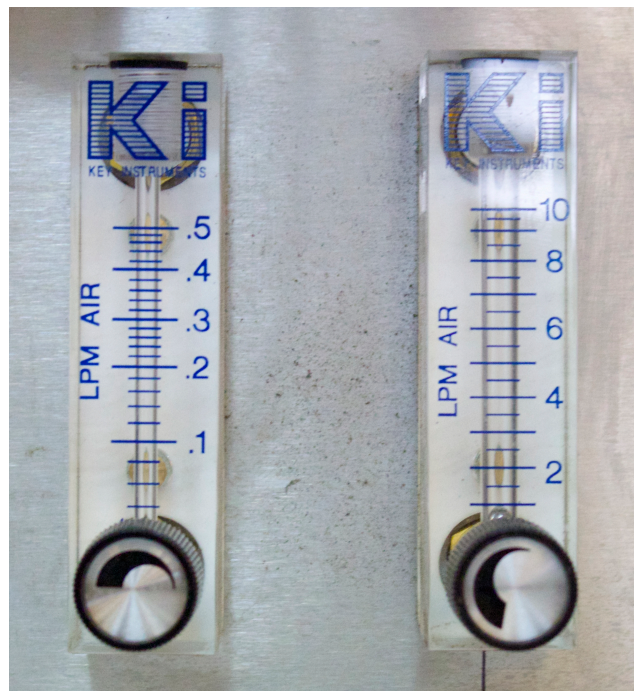


Figure 2.3 Rotameters for splitting flow of air between dosing system and feed of gasifying agent.

A preheating system set the temperature of air and steam to 450° C prior to the reactor.

Downstream of the furnace a hot box contained the separation system, which comprised a cyclone and a micronic filter. The box

was kept at 250° C in order to prevent condensation of tar in the pipes and consequent fouling of the system.



Figure 2.4 Hot box containing cyclone, fan, micronic filter.

The elimination of tar and moisture from the syngas was achieved by feeding the outlet of the hot box to a train of five condensers (bubbling flasks), in which the water bubbled through isopropanol, positioned in an ice bath. Finally a water filter was responsible for completing the cleaning of the gas.

Although gasification can be an autothermic process, most of the laboratory and pilot scale plants are run allothermically, meaning that parameters such as temperature, air-to-biomass ratio and steam-to-biomass ratio can be set independently [18].



Figure 2.5 Train of bubbling flasks in ice bath. In the background: peristaltic pump.

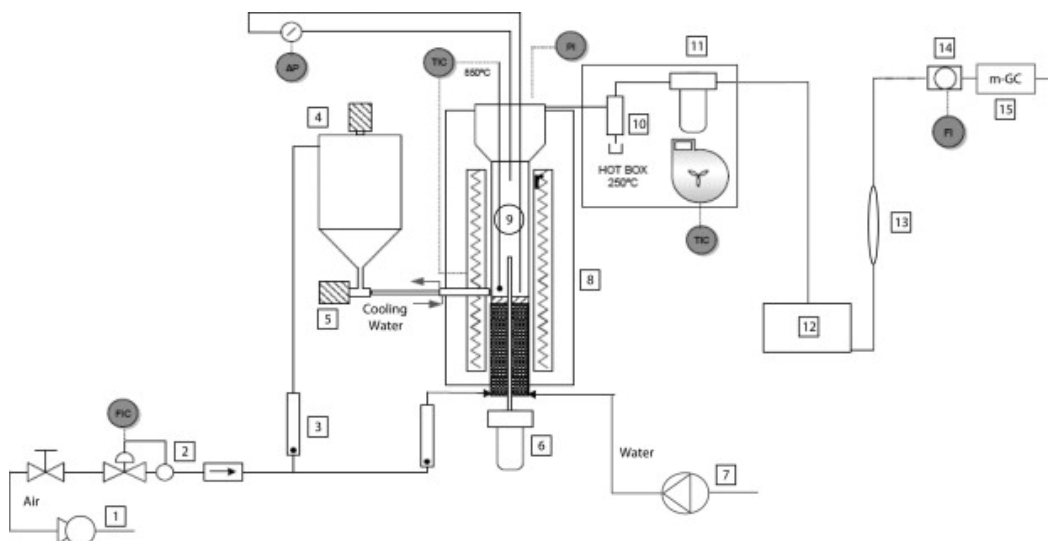


Figure 2.6 Diagram of the laboratory scale plant. 1. Compressor; 2. Mass flow controller; 3. Rotameter; 4. Feed hopper; 5. Screw feeder; 6. Ash hopper; 7. Peristaltic pump; 8. Furnace; 9. Reactor; 10. Cyclone; 11. Hot filter; 12. Condensation train; 13. Water filters; 14. Mass flow meter; 15. Micro gas-chromatograph.

2.1.1 Analysis & Instrumentation

The plant was monitored and controlled by various devices connected to a distributed control system (DCS), also connected to a computer.

The instruments included pressure indicators (PI), differential pressure cells (ΔP), flow indicators-controllers (FIC), mass flow meters (MFM) and thermocouples (TC).

The composition of the syngas was determined with a micro gas chromatograph equipped with two channels and TCD-type detectors (thermal conductivity detector). Helium was used as carrier gas for samples, for both columns. The first column contained a molecular sieve MS5A and analyzed H_2 , O_2 , N_2 , CO and CH_4 , while the second column (Porapak Q) analyzed CH_4 , CO_2 , C_2H_6 and C_2H_4 .

The calibration of the two channels were performed using two different gas mixes, called patrons, which were specifically characterized with the expected composition to be detected.

Tar was analyzed gravimetrically, by distilling the isopropanol of the condensers and weighing the dried residue.

This procedure only takes into account the heavy portion of tar, while the light volatiles are neglected.

An alternative is analysis via gas chromatography of tar, which would detect the light fraction, but not the heavy compounds. Nevertheless, because of the possibility of fouling of the column, this technique has not been considered.

The char content was determined according to the method used by Rapagnà et al. [19]: because char tends to accumulate mainly in the gasifier, its quantity is calculated by weighing the bed before and

after burning off all the carbonaceous residue contained after each test run.

2.2 Methodology

The steps of a test run are:

- start-up of the plant
- preparation of the sample
- gasification
- shut-down

2.2.1 Start-up of the plant

To start up the plant a few steps were followed in a precise order. The DCS system and the computer were turned on and synced with the plant; the one-way valve was open to allow the flow of air in the system and the streams of air and cooling water were started, while the furnace was set to about 85 % of its power in order to reach the desired temperature (750-850° C was the range used for this study). In addition, the hot box and the air and water pre-heaters were also set to the target values, 250° and 450° C, respectively.

In the meantime, a calibration of the micro-GC was performed with the two patrons as reference.

Once the flow of air was started, each condenser was connected to the outlet of the hotbox, in turns, checking that the pressure drop was constant with each addition (~ 4-5 mbar/flask).

A fixed amount of silica sand, which forms the bed, was then introduced in the reactor.

When fluidization was achieved and the temperature of the test was reached, the outlet base flow was measured, in order to assure

that all the parts of the plant were properly sealed. This was done by comparing the inlet and outlet stream of air: if the difference is greater than 15 %, the seals of the connections were checked.

2.2.2 Preparation of the sample

The sample of sludge was weighed with a balance and an appropriate quantity of sand was added to it. After carefully mixing the two compounds, the sample was put into the hopper and the test was started.

The amount of sand added to the sludge sample was calculated as a fixed percentage that is usually 10-20 % of the weight of biomass. This procedure allows the fluidization to be constant and uniform throughout the whole run, because, by introducing new sand together with biomass, an early and excessive presence of ashes is avoided and fluidization is sustained.



Figure 2.7 Introduction of the sample in the dosing system.

2.2.3 Gasification

Once the gasification test was started, a gas sample was analyzed by the online micro-GC every five minutes and the mass flow was measured as well, thanks to a rotameter. By checking the composition of the syngas, it was possible to tell if the correct gasification regime had been reached.

Tests were run for 60 minutes and the quantity of biomass introduced in the dosing system was measured in order to have a constant mass flow throughout the run, maintaining a fixed equivalence ratio (ER). For this reason the data collected was considered valid if the test duration was within the 55-65 minutes range. Moreover, a closure mass balance was estimated, taking into account the air, water and sludge introduced, and the products obtained; the test was validated only if the balance was no less than 95 % or no more than 105 %.

During the run, the observed variables were kept under control to maintain the set point. The temperature of the bed was kept constant by adjusting the power of the electric furnace and represented a parameter to evaluate the proper developing of the gasification.

2.2.4 Shut-down

After the completion of the test, the furnace was turned off while the stream of air was kept running, in order to facilitate the cooling of the system. The preheaters for air and water were turned off immediately while the hot box was kept for longer, in order to avoid condensation of residual tar.

Once cooled off, the plant was disassembled and cleaned while the bed, the ashes and the residues were collected.

After mixing the isopropanol of the five condensers and taking a sample of 100 ml for distillation, tar was collected and dried for 24 hours.

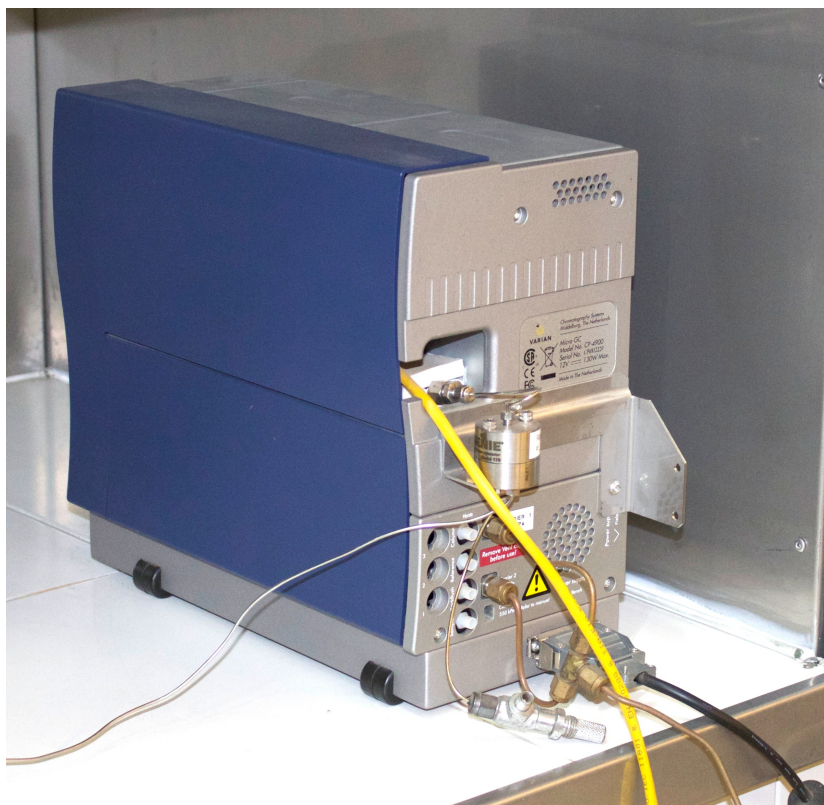


Figure 2.8 Micro gas chromatograph for syngas analysis.

3 Process Modeling

In the second chapter, the experimental equipment and methodology for running gasification tests are described. These experiments were taken as a starting point to develop a model for the process of sewage sludge gasification. Using Aspen Plus Process Modeling software, the whole system has been characterized and simulated. The large amount of experimental data collected by de Andrés et al. [20] allowed for a detailed validation and assessment to be performed.

The proposed model is based on equilibrium correlations and Gibbs free energy minimization. Unlike multi-dimensional models, which analyze the evolution of the system inside the reactor, simulating reactions and production or consumption of species in space and time, this model is developed as zero-dimensional.

A zero-dimensional model takes into account the input of a system and the operational conditions at which the simulation is run. By setting mathematical correlations and some constraints into the code, it is then possible to develop the features that characterize the model.

In the present study the input is represented by biomass, the fuel that has to be gasified, in form of dried sewage sludge, and air and water, which constitute the gasifying agents for the fluidization process.

The operational conditions are determined by pressure, gasification temperature, equivalence ratio and steam-to-biomass ratio. They are set independently, as previously explained, because the system is run allothermically.

The part of the model that simulates the actual gasification of the sludge uses Gibbs free energy minimization to reach chemical equilibrium of the system. This approach best suits the case in study, as it doesn't require any additional information other than the inputs and conditions discussed; indeed it isn't necessary to specify either the complex kinetics of the reactions involved or the hydrodynamics of fluidization.

The objective function to minimize is the expression of the total Gibbs free energy given by:

$$\min_{n_i} \frac{G}{RT} = \sum_{i=1}^c n_i \left(\frac{G_i^0}{RT} + \ln \frac{n_i}{\sum n_i} \right) \quad \text{Eq 3.1}$$

where n_i represents the number of moles of component i , s is the total number of species, R is the gas constant and G_{0i} is the Gibbs free energy of pure component i at temperature T . This operation has to be carried out while considering the constraints of the atomic balance for each element that is present in the system, expressed by the generic formula:

$$n_i = \sum_j^{species} \nu_{ij} c_j \quad \text{Eq 3.2}$$

where n_i is the total number of moles, ν_{ij} is the stoichiometric coefficient of element i in gas species j and c_j is the number of moles of the species j in the gas phase [21].

As gasification involves multiple phases, the model must take account for the phase equilibrium as well. For this reason Gibbs minimization is applied to all the present phases, couple with global mass balance and multi-phase equilibrium. The aim of the whole calculation, which is done at constant temperature, is to approach the minimum thermodynamic potential of the entire system [21].

3.1 Aspen Plus

To quantitatively model the characteristic equation of equilibrium the Aspen Plus Process Modeling software was used. Aspen Plus is a popular tool that has been developed by Aspentech to design and simulate many sorts of industrial processes. This software can predict flow rates, compositions and properties of the streams, the operating conditions and the sizes for the equipment; there are two main modes in which the software can be run; sequential modular (SM), which solves each unit operation in a certain sequence, and equation oriented (EO), which requires the user to insert equations that are then simultaneously solved. For the present study the sequential modular mode was selected.

In the Setup section the global features of the simulation were set. With regards to the units-set, which comprises the units that will be used by default in the entire simulation, Metric Engineering units-set (MET) was selected. The MET units-set includes Celsius degree ($^{\circ}\text{C}$) for temperature, bar for pressure, kilogram per hour (kg/hr) for mass flow and kilomole per hour (kmol/hr) for molar flow.

The Stream Class is another important parameter to be set. It describes the type of stream that will be used in the simulation; the selection of certain stream classes allows the edition of multiple

substreams, depending on the kind of component modeled (see Table 3.1).

Stream Class	Description
CONVEN	No solids are involved
MIXCISLD	Conventional solids are present, but no particle size distribution is specified.
MIXNC	Non-conventional solids are present, but no particle size distribution is specified.
MIXCINC	Both conventional and non-conventional solids are present. No particle size distribution is specified.
MIXCIPSD	Conventional solids are present, with particle size distribution.
MIXNCPSD	Non-conventional solids are present, with particle size distribution.

Table 3.1 List of Aspen Plus stream classes.

MIXCINC stream class was chosen for the simulation, as the process includes conventional gas and liquid phases, conventional solid phase (for solid carbon and sulfur), as well as non-conventional solid phase (for biomass and ashes).

Subsequently the components of the process were defined. All the reactants and final products, as well as the intermediate products of the different steps have to be specified.

The Aspen Plus has two different kinds of database from which the components can be defined, alongside physical and chemical properties: enterprise databases or legacy databases. The enterprise databases were available in the version used for the present study.

The gaseous and liquid components are considered *conventional components*, thus are easily defined in the database by their chemical name. This kind of component enters the streams in the *MIXED*

substream. Examples of conventional components are H₂, O₂, N₂ and H₂O.

The solids can be either *conventional* or *non-conventional*. Conventional solids have been widely studied and used in experiments and processes, their standard properties are known and defined and thus they appear in the *CISOLID* substream. Examples of conventional solids are graphite (solid carbon) and sulfur.

Non-conventional solids are not standardized compounds, whose properties are not known. For this reason they have to be defined by the user and are grouped in the *NC* substream.

The Aspen Plus software provides different correlations that can be adopted to set the properties of the solid. This category is used to define certain kinds of coals, fuels or other compounds, by setting two main algorithms, one for enthalpy and one for density. Sewage sludge belongs to this sort of solids and was defined, in the case of the present study, through the *DCOALIGT* algorithm for density and *HCOALGEN* algorithm for enthalpy. As their ID suggests, these algorithms are suitable for the characterization of coal and, more in general, of carbonaceous fuels. If more specific correlations for the feed used aren't available to the user, these are certainly the most appropriate.

DCOALIGT refers to IGT (Institute of Gas and Technology) Coal Density Model:

$$\rho_i = \frac{\rho_i^{dm}}{[\rho_i^{dm}(0.42w_{A,i}^d - 0.15w_{Sp,i}^d) + 1 - 1.13w_{A,i}^d - 0.5475w_{Sp,i}^d]} \quad \text{Eq 3.3}$$

$$\rho_i^{dm} = \frac{1}{a_{1i} + a_{2i}w_{Hi}^{dm} + a_{3i}(w_{Hi}^{dm}) + a_{4i}(w_{Hi}^{dm})^3} \quad \text{Eq 3.4}$$

$$W_{Hi}^{dm} = \frac{10^2(W_{Hi}^d - 0.013w_{A,i}^d + 0.02w_{Sp,i}^d)}{(1 - 1.13w_{A,i}^d - 0.475w_{Sp,i}^d)} \quad \text{Eq 3.5}$$

where w_{xi}^d is the weight fraction, on a dry basis, of constituent j in component i , while the superscript dm is used when the fraction is calculated on dry and mineral-matter-free basis. Capital letters refer to molar fractions.

Symbol	Value
a_{1i}	0.4397
a_{2i}	0.1223
a_{3i}	-0.0175
a_{4i}	0.001077

Table 3.2 Values of coefficients of IGT density model[22].

HCOALGEN is a General Coal Enthalpy Model and includes a number of different correlations. The user can choose among various relationships by setting four different option codes.

By setting the option codes to 6-1-1-1 for enthalpy, the correlation is based on a user-input value for the heat of combustion (*HCOMB*)

For sewage sludge, the value of *HCOMB* was equated to the LHV of the sample of sludge used for the test.

Both density and enthalpy correlations require the input of *PROXIMATE*, *ULTIMATE* and *SULFUR* analyses, in order to calculate physical and chemical properties.

Ramzan et al. [15] modeled gasification for different types of biomass with Aspen Plus. In their work HCOALGEN and DCOALIGT algorithms were used to define the properties for ash and sludge, which are both non-conventional components.

Analysis Type	ID
PROXANAL	MOISTURE FC (fixed carbon) VM (volatile matter) ASH
ULTANAL	ASH CARBON HYDROGEN NITROGEN CHLORINE SULFUR OXYGEN
SULFANAL	PYRITIC SULFATE ORGANIC

Table 3.3 Description of analyses in Aspen Plus

Another parameter that has to be set, in order for the simulation to run properly, is the *physical property method*. Indeed, Aspen Plus calculates physical properties for each component, by means of the method chosen, which comprises an ensemble of equations of state (EoS).

Because the system deals with multiple phases, as well as conventional and non-conventional solids, the *Ideal Gas* method cannot be chosen, thus the *Peng Robinson – Boston Mathias modified* (PR-BM) method was selected. This correlation is recommended for simulating hydrocarbon processing such as gas synthesis from combustion of coal or other carbonaceous fuels; it was therefore selected for the present case [23].

The equation used by this method is:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)} \quad \text{Eq 3.6}$$

where:

$$b = \sum_i x_i b_i \quad \text{Eq 3.7}$$

$$a = a_0 + a_1 \quad \text{Eq 3.8}$$

$$a_0 = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - k_{ij}) \quad \text{Eq 3.9}$$

$$a_1 = \sum_{i=1}^n x_i \left(\sum_{j=1}^n x_j ((a_i a_j)^{0.5} l_{ij})^{\frac{1}{3}} \right)^3 \quad \text{Eq 3.10}$$

k_{ij} and l_{ij} are binary parameters that are determined from VLE data.

The parameters a and b are calculated using component parameters which are based on a function α_i . The Boston-Mathias extrapolation adapts the method to situations in which temperatures are higher than critical [24]:

$$\alpha_i(T) = [\exp[c_i(1 - T_{ri}^d)]]^2 \quad \text{Eq 3.11}$$

The component list set up for the simulation appears in Table 3.4.

Substream	Component
Conventional	H ₂
	O ₂
	N ₂
	H ₂ O
	CO
	CO ₂
	CH ₄
	H ₂ S
	NH ₃
	C ₁₀ H ₈
	Conventional Solid
S	
Non-conventional	Sludge
	Drysludge
	Ash

Table 3.4 List of components.

3.2 Assumptions

In order to develop an accurate and easy model for sludge gasification, a number of different assumptions were made:

1. The process is considered to be steady-state, no transient state is modeled;
2. Gasification is assumed to be run isothermally;
3. The model is zero-dimensional and kinetic-free;
4. Devolatilization occurs instantaneously at the entrance of the reactor;
5. Syngas is modeled as a mixture of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and moisture (H_2O);
6. All the nitrogen (N) and sulfur (S) present in the sludge react entirely to yield ammonia (NH_3) and hydrogen sulfide (H_2S), respectively;
7. Tar is not modeled, but is considered as a non-equilibrium component.

To assume that the process is steady-state is reasonable, because fluidized beds allow for nearly perfect and rapid mixing of the fuel with the bed and the gasifying agent, thus the system is not influenced by transient states that express the disturbance represented by the feeding of biomass. For the same reason, an isothermal condition can be assumed, as the hydrodynamics of fluidization and the particle size of the biomass allow for a uniform heat distribution and transfer [14].

The model comprises a zero-dimensional, kinetic-free reactor, according to the fact that at laboratory scale it is preferred to investigate the overall production and efficiency, rather than the evolution of the compounds within the system, using an equilibrium-based approach [25].

The release of volatiles compounds from the bulk of the biomass is one of the stages of gasification. Because of the high temperatures of the system and small size of the particles, it is acceptable to assume that this process is instantaneous, once the sludge enters the bed [14].

The syngas produced from the laboratory scale plant used for creating the present model contains mainly hydrogen, carbon monoxide, carbon dioxide, methane and water, but in smaller percentages also ethane (C_2H_6) and ethylene (C_2H_4). The formation of these two compounds stands in devolatilization as well as tar undergoing a cracking process. To simplify the development of the simulation and because the tar species are not distinguished by the instrumentation used, tar are not modeled. This prevents the devising of cracking reactions that would lead to formation of ethane and ethylene, thus these compounds are not considered as relevant in the syngas composition.

Sewage sludge also contains nitrogen and sulfur in different forms; these two elements could form nitrogen oxides, sulfur oxides or combinations with carbon as well. Nevertheless, the studies of de Jong et al. [26] show that during gasification of coal and different kind of biomass, within an environment characterized by oxygen deficiency and in different conditions of air-to-fuel ratio, either the fuel releases the nitrogen as is, during devolatilization, or the nitrogen is converted to ammonia, due to the presence of proteins and amino acids. Moreover, the work of Schuster et al. [27] points out

that disregarding the formation of sulfur compounds different from hydrogen sulfide is acceptable, given that possible inaccuracies are negligible, due to the low content of sulfur in the biomass.

Tar represents the impurities of the gas, a complex mixture of organic compounds that forms during gasification. Although not modeled, tar can be represented as non-equilibrium component, contributing as a correction to the thermodynamics-based model. Typically the amount of tar that is formed during biomass gasification with the present experimental configuration is 5-10 g/m³ on a dry basis; the major component considered in this study is naphthalene (C₁₀H₈) [28].

3.3 Chemical Reactions

Gasification includes numerous chemical reactions that are partially unknown or unpredictable, due to the vast variety of fuels that can undergo this process. However, the main and most important reactions involved have been widely studied and known for long time. The model includes combustion and gasification reactions, which are shown in Table 3.5. Homogeneous reactions include hydrogen combustion, steam reforming, water gas shift and ammonia formation, while heterogeneous reactions are carbon combustion, Boudouard's reaction, methanation, water-gas reaction and hydrogen sulfide formation.

Reactions of hydrogen and carbon combustion (R-1, R-5) are exothermic, meaning that they release energy in form of heat while occurring. Reaction 5, in particular, is the basic reaction that develops after the *pyrolysis* (or devolatilization) process.

During *combustion*, indeed, both the volatile matter and the char react with oxygen to form carbon dioxide and, in minor quantities, carbon monoxide. The heat released in the system by the combustion process is used by the endothermic reactions, such as steam reforming, water-gas and Boudouard's reactions, which are favored at high temperature, as part of the *gasification*. This step also involves exothermic reactions, i.e. water gas shift and methanation, which also take part in the conversion of char.

Reactions R-4, R-9 and R-10 are responsible for the formation of non-equilibrium components, i.e. ammonia, hydrogen sulfide and naphthalene, which represents tar. These reactions didn't take part to the equilibrium-based modeling part of the simulation, but were

applied to other sections, in order to fulfill the conditions stated by the assumptions proposed for the work.

Reaction	Name	Reaction #
Homogeneous reactions:		
$H_2 + 0.5O_2 \rightarrow H_2O$	Hydrogen combustion	R-1
$CH_4 + H_2O \rightarrow CO + 3H_2$	Steam reforming	R-2
$CO + H_2O \rightarrow CO_2 + H_2$	Water Gas Shift	R-3
$0.5N_2 + 1.5H_2 \rightarrow NH_3$	NH ₃ Formation*	R-4
Heterogeneous reactions:		
$C + O_2 \rightarrow CO_2$	Carbon combustion	R-5
$CO_2 + C \rightarrow 2CO$	Boudouard	R-6
$C + 2H_2 \rightarrow CH_4$	Methanation	R-7
$C + H_2O \rightarrow H_2 + CO$	Water-gas	R-8
$H_2 + S \rightarrow H_2S$	H ₂ S formation	R-9
$10C + 4H_2 \rightarrow C_{10}H_8$	Naphthalene formation	R-10

Table 3.5 List of reactions. *The nitrogen involved in ammonia formation comes solely from the fuel.

3.4 Parameters and Variables

The development of a model required the definition and observation of variables and parameters, characteristic for gasification, which were implemented in the calculations, in order to set operating conditions, as well as to study the sensitivity and response of the system in different scenarios.

3.4.1 Temperature

Temperature is one of the most important variables of gasification processes. The different steps and modules of the system are maintained to fixed temperature to ensure, for example, the pre-heating of gasifying agents, the heating of the reactor or the cooling of condensers. The production of certain wanted species is often favored at high temperature, while other secondary and unwanted products are discouraged. The range at which gasification usually is performed goes from 700°C to about 1000°C. The present study focuses on the range 750°-850°C.

3.4.2 Equivalence Ratio

The *equivalence ratio* (ER) is a typical variable that is manipulated in air gasification systems. For the process to develop in the required way, complete combustion of the fuel has to be avoided. For this reason, air has to enter the reactor in such a proportion that the oxygen that is present in the system is less than the stoichiometric quantity, which would be used for complete combustion. The equivalence ratio is therefore defined as the ratio between the flow of air that is fed to the reactor and the stoichiometric flow of air calculated for complete combustion of the biomass.

$$ER = \frac{\text{air fed to the system}}{\text{stoichiometric air for combustion}} \quad \text{Eq 3.12}$$

As gasification occurs in deficiency of oxygen, the air that enters to the system has to be less than the stoichiometric value, thus the equivalence ratio will be smaller than 1.

3.4.1 Steam-to-Biomass Ratio

The *steam-to-biomass ratio* (SB) is a common variable used when gasification is achieved with steam or mixtures of air and steam. SB is defined as the ratio between the flow rate of steam fed to the reactor and the flow rate of biomass fed, on a dry ash-free basis. This variable determines how much steam is present in the system, with respect to the quantity of biomass. This causes the equilibrium of the reactions involving water (R-1, R-2, R-3, R-8) to be significantly modified. The presence of steam in the system results in a more prominent production of hydrogen, although an excess could lead to higher heat dilution and thus to higher energetic costs.

$$SB = \frac{\text{steam fed to the reactor}}{\text{biomass fed to the reactor (daf)}} \quad \text{Eq 3.13}$$

3.4.2 Lower Heating Value

An observed variable is the *lower heating value* (LHV) of the biomass and of the syngas produced. It represents the amount of heat released during the combustion of the substance under consideration, thus its energetic potential. LHV of biomass is calculated with modified Dulong's formula ($LHV = 8.060C + 33.910\left(H - \frac{O}{8}\right) + 2.222S + 556N \left(\frac{kcal}{kg}\right)$ Eq 2.1), while LHV of syngas is calculated

as a weight-average of the different gas components, by multiplying the volume fraction of each component for its calorific value (Table 3.6).

Compound	Lower Heating Value (kJ/Nm ³)
CO	12.618
CO ₂	0
CH ₄	35.807
H ₂	10.779
N ₂	0
H ₂ S	71.718
H ₂ O	0

Table 3.6 Lower Heating Value of syngas compounds.

3.4.1 Gas Yield

Another parameter that is evaluated when studying and modeling biomass gasification is the *gas yield*. It represents the production of syngas with respect to the quantity of fuel fed to the reactor and it is important to assess the overall process. In the present case it was defined as the volume of syngas produced for each kilogram of sludge (on a dry and ash-free basis) entering the system.

$$Y = \frac{\text{volume of syngas produced [Nm}^3\text{]}}{\text{mass of sludge fed [kg daf]}} \quad \text{Eq 3.14}$$

3.4.1 Carbon Conversion

A parameter that indicates the extent to which the gasification has come is *carbon conversion*. Seeing how much of the elemental

carbon contained in the biomass is converted to syngas, helps understanding how the process develops, and the possible modifications to introduce. It is defined as the ratio between the weight carbon present in the syngas produced and the weight of carbon in the sludge fed to the system.

$$\chi_C = \frac{\text{kg of C in syngas}}{\text{kg of C in biomass introduced}} \quad \text{Eq 3.15}$$

3.4.2 Cold Gas Efficiency

Cold gas efficiency is the ultimate parameter to evaluate gasification. It expresses the energy content of the syngas with respect to the biomass used and is thus based on the ratio of their lower heating values.

$$CGE = \frac{\text{LHV of syngas}}{\text{LHV of biomass}} \quad \text{Eq 3.16}$$

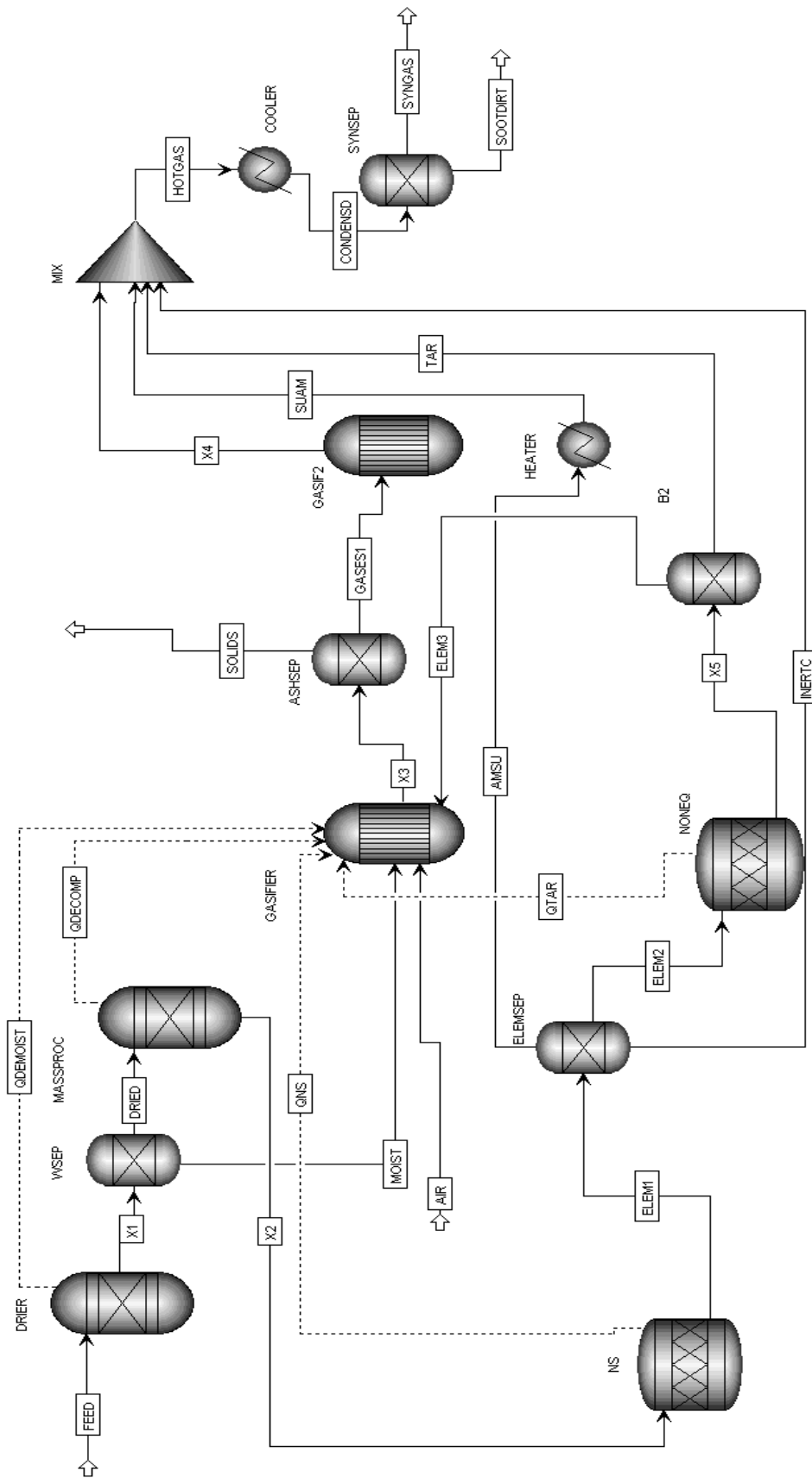


Figure 3.1 Flowsheet of gasification model in Aspen Plus[®]

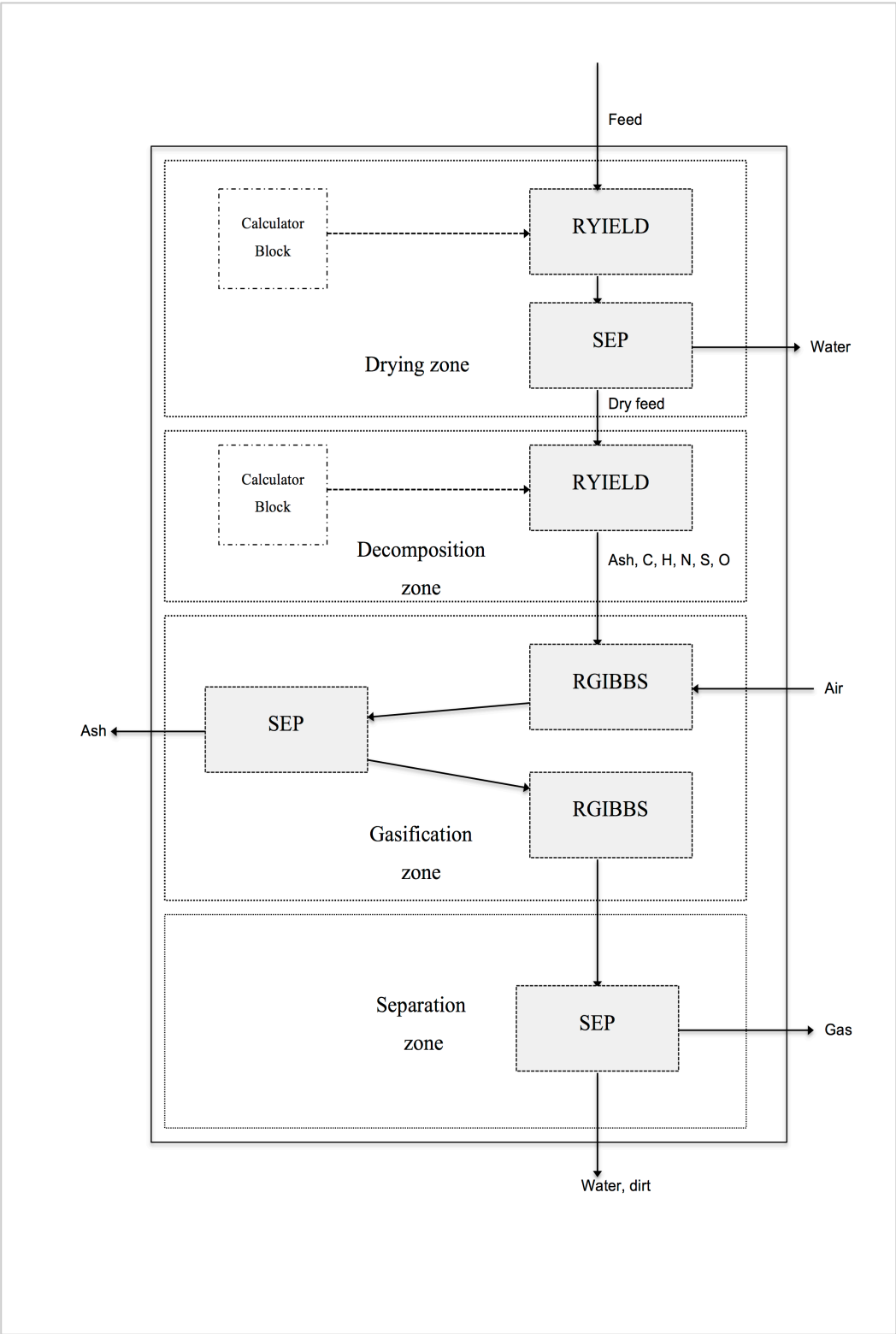


Figure 3.2 Diagram of calculation procedure.

3.1 Flowsheet development

The gasification process occurring in the laboratory scale plant was simulated with Aspen Plus, by combining and coupling different modules, in order to represent the different parts of the experimental configuration, as well as the different steps of the process.

The fluidized bed reactor was modeled as divided into multiple blocks, which correspond to the different phases occurring. These comprise drying of the feed, decomposition of the biomass, non-equilibrium modeling and gasification. This was followed by a separation and cooling section. A reproduction of the flowsheet is showed in Figure 3.1.

3.1.1 Drying

Drying consists in the removal of the residual moisture in the biomass, due to the increasing temperature. A RYIELD block, named 'DRIER', is responsible to simulate this step; it is a block that can simulate reactions of which the stoichiometry and kinetics are unknown, by basing on a yield distribution or correlation. The inlet stream 'FEED' is characterized by the non-conventional substream containing the component 'sludge' at ambient pressure and temperature (1 atm, 298 K). The yield distribution is set to the RYIELD by a calculator block, which is configured to import the component attributes of the feed (its proximate analysis) and export the value of the moisture content as the yield of water. In this way the outlet of the 'DRIER' is a stream containing water, as a conventional component, and 'DRYSLDG' representing the dried biomass, still in form of a non-conventional component. The temperature of the block is set to the gasification value. A SEP block then separates the moisture from the rest of the feed and sends it to the gasifier.

3.1.1 Decomposition

The following step consists in the decomposition of the non-conventional biomass into conventional elements, in order to perform reactions and other transformations. This step takes place in a second RYIELD block called 'MASSPROC'. The same calculator block previously mentioned sets the mass yields by importing the ultimate analysis of the feed. The outlet stream contains hydrogen, nitrogen, oxygen in the MIXED substream, solid carbon and sulfur in the CISOLID substream and non-conventional ash in the NC substream.

The temperature of decomposition is the same of gasification stage.

3.1.2 Non-Equilibrium Modeling

As mentioned in the assumptions of the model, all the nitrogen and sulfur contained in the sludge react to yield ammonia (NH_3) and hydrogen sulfide (H_2S), respectively.

For this purpose, reactions R-4 and R-9 were initially included in 'GASIF2' (see section 3.1.3), but, as nitrogen from air also input, the restricted equilibrium was biased and didn't allow for a good prediction to be made. Therefore a RSTOIC block was set up in the flowsheet. RSTOIC block simulates a stoichiometric reactor in which kinetics are unknown or unimportant, while stoichiometry and extent of reaction are known. The 'NS' block models the complete conversion of the elemental nitrogen and sulfur of the sludge, following reactions R-4 and R-9 [26,27]. The outlet stream enters a separator 'ELEMSEP', which diverts the reacted ammonia and hydrogen sulfide from the rest of the reaction stream to the final MIXER. This block also separates 10 % of the carbon contained in

the sludge ('INERTC'), to represent the quantity of unreacted carbon that is observed in the experimental tests [28].

The rest of the reaction stream, 'ELEM2', enters a second RSTOIC non-equilibrium reactor, 'NONEQ'. This block is set by a calculator block to represent the formation of tar. Trends of tar formation in different conditions of temperature and equivalence ratio were observed from the experimental data and configured in the calculator block, by means of an Excel spreadsheet. These trends set the extent of reaction for the 'NONEQ' block (R-10). This procedure allows the excluding from the reaction stream of a portion of elemental carbon, which converts to tar instead of syngas.

A SEP block 'B2' is responsible for the separation of tar, which is sent to the final MIXER, by the rest of the elements. The temperature of both 'NS' and 'NONEQ' blocks is set to match the gasification temperature, by means of a calculator block.

3.1.3 Gasification

The reaction stream enters a first 'RGIBBS' block called 'GASIFIER'. A RGIBBS block is an equilibrium reactor, which is capable of handling multiple-phase physical equilibrium as well as chemical equilibrium, without the need of specified kinetics or extent of reaction. It is based on minimizing Gibbs free energy. GASIFIER has no operating temperature specified; this value is automatically set according to the four heat streams that enter this block, transporting the heat developed by DRIER, MASSPROC, NS and NONEQ blocks. This is done to model the way the combustion and processing of biomass lead to production of energy used by gasification reactions [15]. Once the equilibrium is reached, the outlet stream enters a SEP block, 'ASHSEP', in which the ashes are removed by

the bulk, simulating the way the bed reaches the concentric tube inside the reactor, causing the ashes and other materials to pour into the collector tank.

Subsequently the stream enters a second RGIBBS block, which is called 'GASIF2'. This RGIBBS is set by a 'Design Specific' block, to the desired gasification temperature, as it has no inlet heat stream. This also allows setting a *restricted equilibrium*, by specifying chemical reactions, with different temperature approaches (ΔT), and possible inert components. Following a method widely studied and established by Gumz [29], as the desired reactions do not really reach complete equilibrium, an appropriate temperature approach is specified for each reaction, in order to set a sensible syngas composition. By doing so, the equilibrium of each specified reaction can be modified, thus restricted, in order to make the model capable of realistic predictions.

Aspen Plus requires to set reactions that are linearly independent, in order to perform the minimization; because of this constraint, two different sets of reactions were selected to model two different situations.

When running air gasification simulations, the specified reactions are hydrogen and carbon combustion, water gas shift, Boudouard's reaction, methanation and water-gas reaction (R-1, R-3, R-5, R-6, R-7, R-8).

In air-steam gasification tests, nevertheless, the steam reforming reaction becomes more relevant for the overall process and it is thus included. In order to keep all reactions linearly independent, hydrogen combustion and Boudouard's reaction are excluded (R-2, R-3, R-5, R-7, R-8).

In the early stages of the present study, only the first RGIBBS was included in the model, with no sort of equilibrium restriction.

Figures 3.3 and 3.4 show how the model was unable to predict the trends of any of the different components of syngas, due to an unrealistic simulation of the gasification step.

Subsequently, the outlet stream is mixed with the streams of inert carbon, tar, ammonia and hydrogen sulfide by means of a MIXER block, to simulate the presence of a single outlet. Subsequently a COOLER and a SEP block were coupled to model the ensemble of cyclone, micron filter and train of condensers. This way the particles are separated and diverted in the stream 'SOOTDIRT' and the gas is cooled under 100° C, which is the typical range required for applications in internal combustion engines[30].

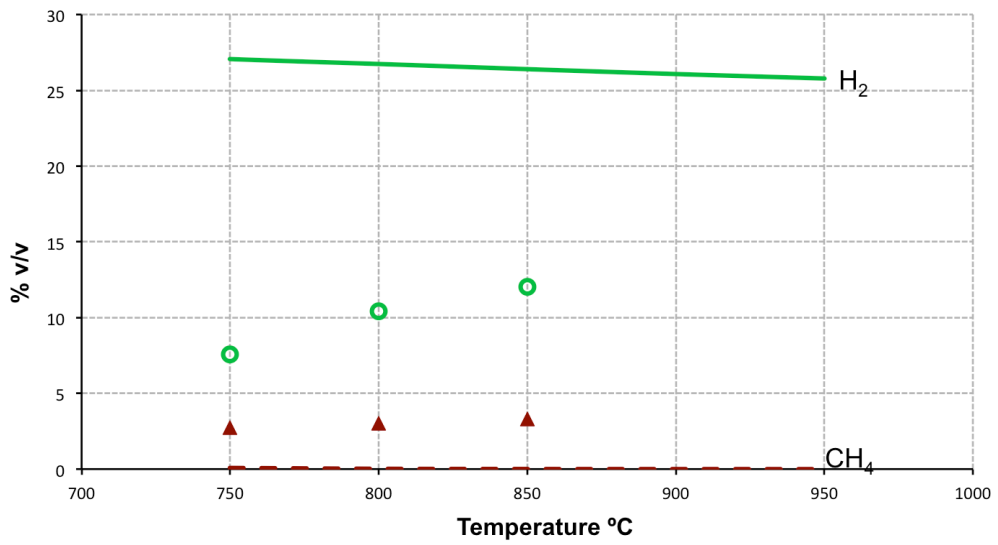


Figure 3.3 Model prediction in case of unrestricted equilibrium. Experimental data: $\circ = \text{H}_2$ $\blacktriangle = \text{CH}_4$.

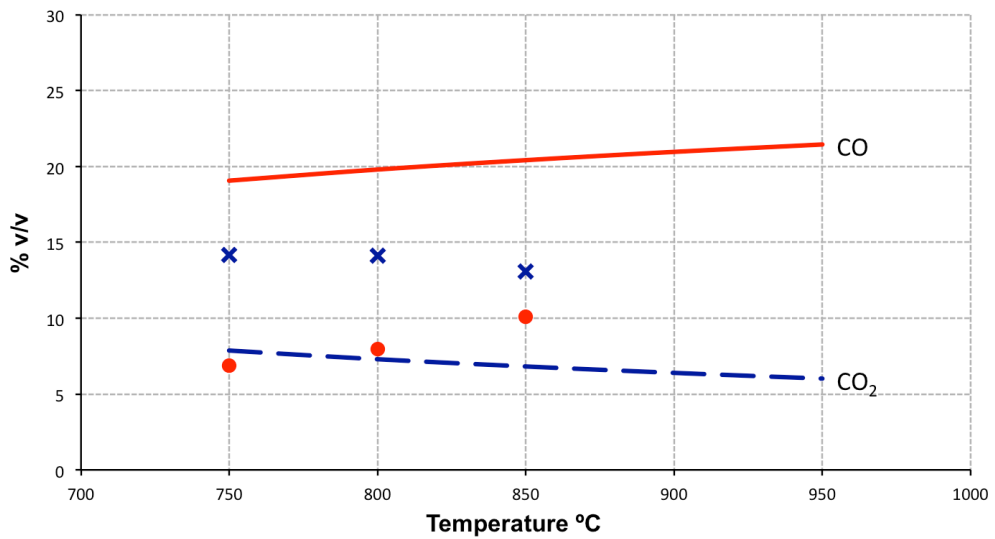


Figure 3.4 Model prediction in case of unrestricted equilibrium. Experimental data: $\times = \text{CO}_2$ $\bullet = \text{CO}$.

4 Results and Discussion

4.1 Experimental Results

The model was validated against the experimental results that were collected from the laboratory scale plant. In previous studies the research group observed the plant running under different conditions and collected the results shown in Table 4.1.

It was witnessed that the major difficulty in running the experiments consists in calibrating the dosing system, as it is sensitive to the disassembling-reassembling of the plant for cleaning and to the particle size of the sludge.

The production of syngas was calculated as a weight-average of the measurements collected every five minutes.

4.2 Validation

The base case selected for the Aspen Plus simulation was air gasification at 800° C, ER= 0.3. By activating the ‘Data Fit’ in *Model Analysis Tools*, a set of matching experimental result was input and a regression was run, in order to find the best temperature approaches for each reaction considered. By tuning the values of standard deviation, more restrictive for hydrogen, carbon monoxide and carbon dioxide, more loose for the other compounds, a proper set of temperature approaches was found (Table 4.2). For steam gasification a similar procedure was adopted, with the base case at SB=0.5.

Parameter	Units	Test #														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Temperature	°C	750	800	850	750	800	850	750	800	850	750	800	850	750	800	850
ER	-	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.3
SB	-									0.5	0.5	0.5	1	1	1	1
Sludge	g/min	2.16	2.16	2.16	1.44	1.44	1.44	1.08	1.08	1.08	1.44	1.44	1.44	1.44	1.44	1.44
H ₂	%	9.8	14.0	16.4	7.6	10.44	12.1	3.2	8.5	9.7	9.9	11.0	15.5	10.0	12.0	16.1
N ₂	%	60.9	52.2	47.7	65.1	60.8	57.7	74.9	65.3	63.3	60.8	59.2	53.8	60.4	58.5	53.1
CH ₄	%	3.7	4.9	5.7	2.7	3.0	3.3	1.0	2.4	2.1	2.8	3.1	3.2	2.9	2.7	3.0
CO	%	7.2	10.7	12.6	6.9	8.0	10.1	4.3	6.9	8.2	7.7	8.4	10.4	7.8	8.6	10.1
CO ₂	%	14.2	13.6	13.0	14.1	14.1	13.1	14.1	13.8	13.9	14.8	14.8	14.1	15.6	15.2	14.7
C ₂ H ₆	%	0.15	0.10	0.07	0.14	0.09	0.04	0.09	0.07	0.03	0.07	0.04	0.03	0.06	0.03	0.02
C ₂ H ₄	%	2.6	3.2	3.3	2.1	2.2	2.4	0.8	1.5	1.4	1.9	2.0	1.5	1.8	1.6	1.5
LHV _{gas}	MJ/Nm ³	3.4	4.8	5.6	2.8	3.3	3.9	1.3	2.7	2.9	3.2	3.5	4.2	3.2	3.5	4.2
Y _{gas}	Nm ³ /kg _{sludge,daf}	1.77	1.89	1.91	2.32	2.37	2.45	2.76	2.92	3.07	2.44	2.60	2.75	2.46	2.62	2.77
Tar	Mg/g _{sludge,daf}	30.48	26.53	19.50	27.35	18.07	10.55	18.36	13.89	9.13	11.18	18.61	10.94	26.89	18.16	10.77
χ _c	%	59.42	74.18	79.90	71.86	77.36	84.40	64.40	84.69	91.03	77.46	85.47	91.15	79.59	84.38	91.12
CGE	%	28.5	43.0	50.4	30.2	37.2	45.2	16.5	37.9	42.1	35.2	41.0	53.1	35.6	41.1	53.0

Table 4.1 Experimental results.

Reaction #	Temperature approach [$\Delta^{\circ}\text{C}$]	
	Air gasification	Steam gasification
R-1	-148	-
R-2	-	-280
R-3	100	0
R-5	-73.5	-350
R-6	-227	-
R-7	-500	-350
R-8	-307.5	-110

Table 4.2. Temperature approaches.

The results of the simulation of the base case were compared with experimental results and, as Table 4.3 shows, they are in very good agreement. The percentage error is always below 12 %.

The model was also validated against a secondary set of experimental data, originated by a similar study on the same laboratory scale plant, with a different sludge [31]. Table 4.4 reports the comparison between experimental data and prediction and, once again, the two sets are in very good agreement.

	Experimenta I	Model	Relative Error %
Composition (%) v/v)			
H ₂	10.40	10.40	0
CO	7.97	8.03	0.75
CO ₂	14.10	14.00	-0.71
CH ₄	3.01	3.24	7.64
N ₂	60.81	58.18	4.52
LHV _{gas} (MJ/Nm ³)	3.33	3.72	11.71
CGE (%)	37.25	38.89	4.40

Table 4.3 Comparison of base case with experimental data.

	Experimenta I	Model	Relative Error %
Composition (%) v/v)			
H ₂	10.27	10.47	1.96
CO	8.98	7.54	-19.04
CO ₂	13.57	12.49	-8.65
CH ₄	3.31	3.25	-1.77
N ₂	59.51	60.57	1.75
LHV _{gas} (MJ/Nm ³)	3.58	3.81	6.04
CGE (%)	39.29	42.63	7.83

Table 4.4 Comparison of model prediction with secondary set of experimental data.

4.3 Sensitivity Analysis

Sensitivity analyses were performed with the aim of investigating the influence of various parameters on the results. In particular the present study focuses on the influence of temperature, equivalence ratio, steam injection on the syngas yield and composition and on the carbon conversion.

4.3.1 Effect of Temperature

Figures 4.1 and 4.2 show the effect of changing temperature on the composition of the syngas, within a range of 750°-950°C, at a constant equivalence ratio (ER=0.3). As an overall trend, it can be seen that the gas yield increases with temperature (Figure 4.3). The concentration of hydrogen and carbon monoxide increases with increasing temperature, while the concentration of carbon dioxide decreases. Moreover, the concentration of methane shows a maximum around 850°C, while the production of syngas increases with temperature.

These observations can be justified by the fact that the carbon conversion is higher, at higher temperatures (Figure 4.4). Also, the reverse methanation reaction and Boudouard's reaction are thermodynamically promoted at higher temperatures. Finally, the water-gas reaction raises the production of carbon monoxide and hydrogen[20].

The figure also shows that within the model is in very good agreement with experimental data (temperature range 750°-850°C), except for carbon monoxide, which is slightly over predicted at higher temperatures.

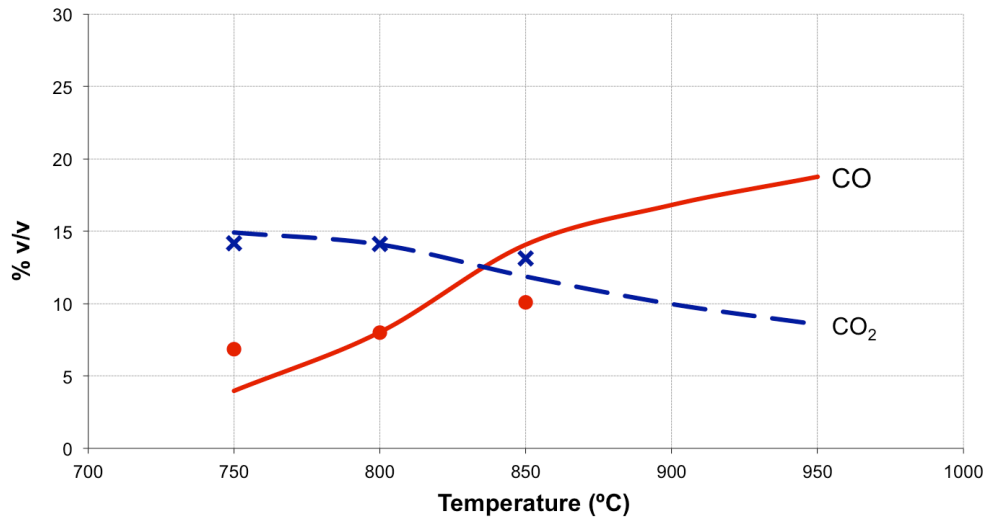


Figure 4.1 Effect of temperature on syngas composition. Experimental data: X= CO₂ • = CO.

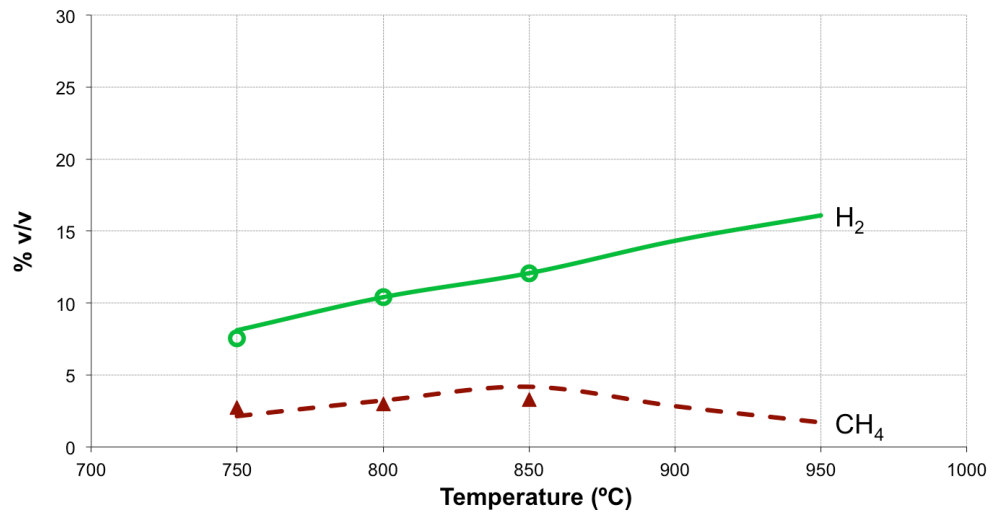


Figure 4.2 Effect of temperature on syngas composition. Experimental data: ○ = H₂ ▲ = CH₄.

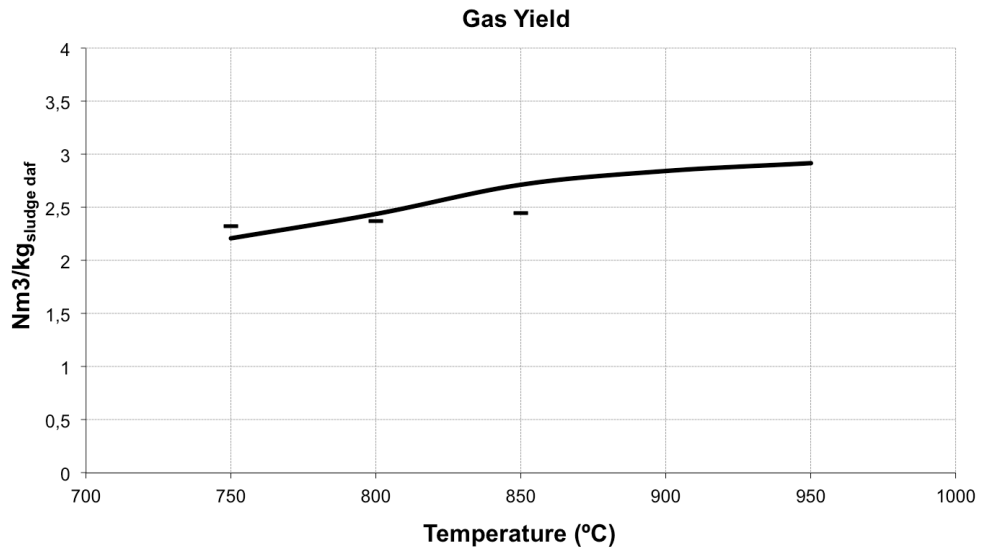


Figure 4.3 Effect of temperature on gas yield. Dots are experimental data, lines are model prediction.

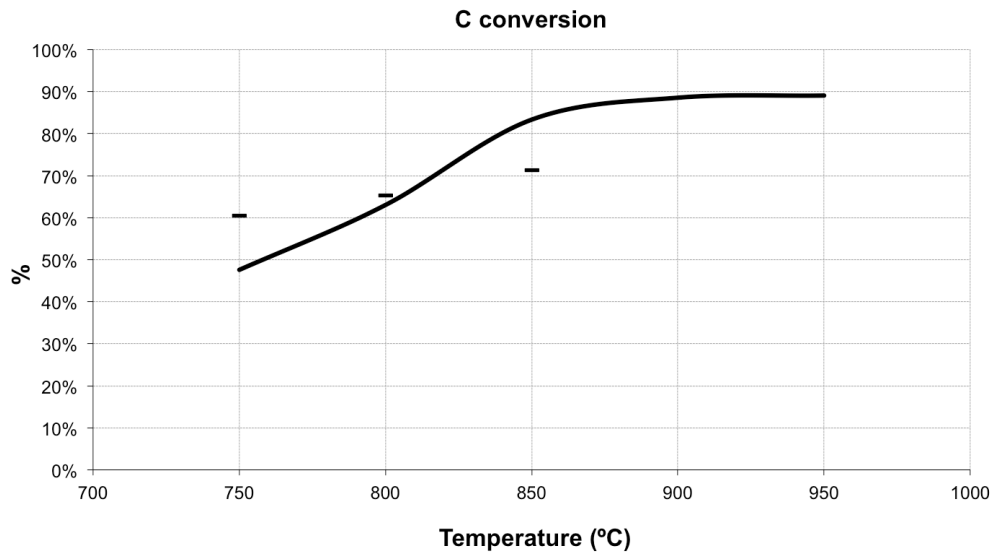


Figure 4.4 Effect of temperature on carbon conversion. Dots are experimental data, lines are model prediction.

The outlet composition obtained by running the simulation using the secondary set of experimental data is shown in Figures 4.5 and 4.6.

Model prediction are, once again, very accurate; carbon monoxide presents a similar, but less evident, over-prediction at high temperature.

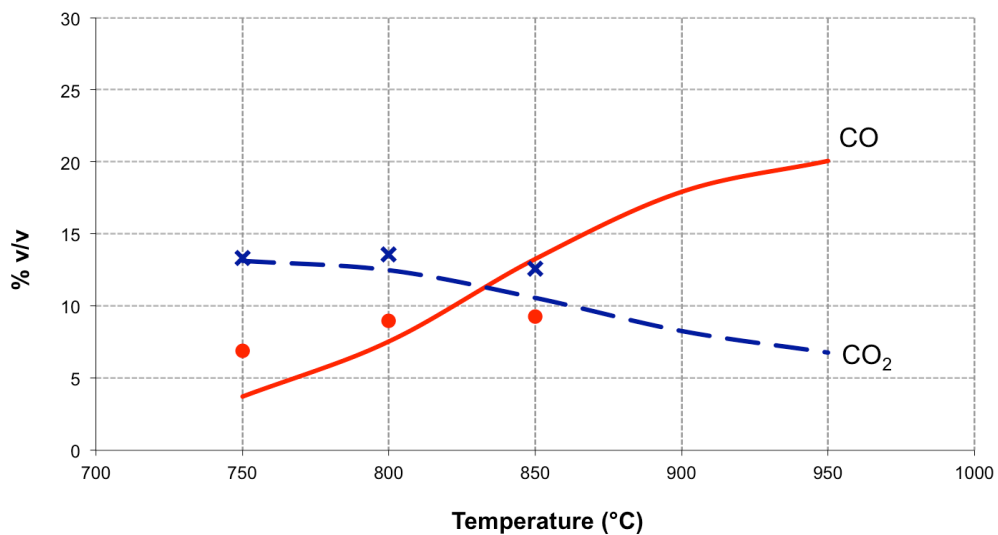


Figure 4.5 Effect of temperature on CO and CO₂ yields. Comparison with secondary set of experimental data: X= CO₂ • = CO.

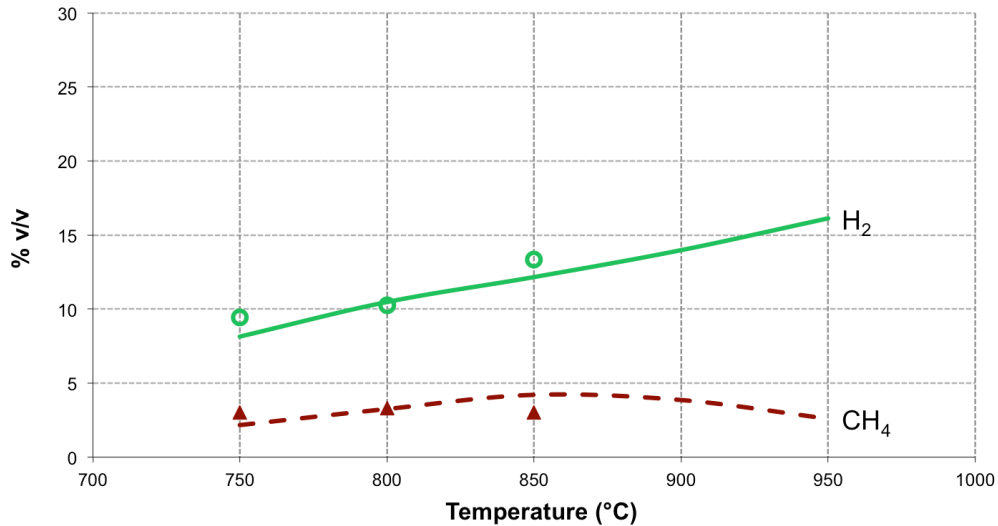


Figure 4.6 Effect of temperature on H₂ and CH₄ yields. Comparison with secondary set of experimental data: ● = H₂ ▲ = CH₄.

4.3.2 Effect of Equivalence Ratio

Figures 4.7 and 4.8 show the effect of varying the equivalence ratio on syngas composition and gas yield, at a fixed temperature (800°C). The choice of ER represents an influence to the promotion of oxidation reactions and can express two extreme conditions. At high ER (ER>1) a high flow of air enters the system, thus promoting complete combustion of the fuel and producing primarily carbon dioxide.

At very low ER the amount of oxygen in the system is low, favoring pure pyrolysis conditions, yielding syngas and char.

It can be seen that the conversion of carbon increases as ER increases, while the production of hydrogen, carbon monoxide and methane decreases (see Figure 4.10).

The total gas yield increases with ER, as a result of a full oxidation of the biomass to CO₂ (see Figure 4.9).

Once again the model predicts very accurately the experimental data (also at higher temperatures, e.g. 850°C).

4.3.3 Effect of Steam Injection

When gasification is achieved with a mixture of air and steam, different reactions become prominent within the process. When SB is high, steam reforming, water-gas and water gas shift reactions are promoted. As a result, a higher amount of hydrogen is produced, while the production of carbon monoxide decreases. In Figures 4.11 and 4.12 the syngas composition at SB=0.5 is shown. Gas yield and carbon conversion are shown in Figures 4.13 and 4.14. Model predictions follow experimental data quite satisfactorily, although with lesser accuracy than air gasification simulations. The model has a similar behavior when the steam-to-biomass ratio is set to 1.

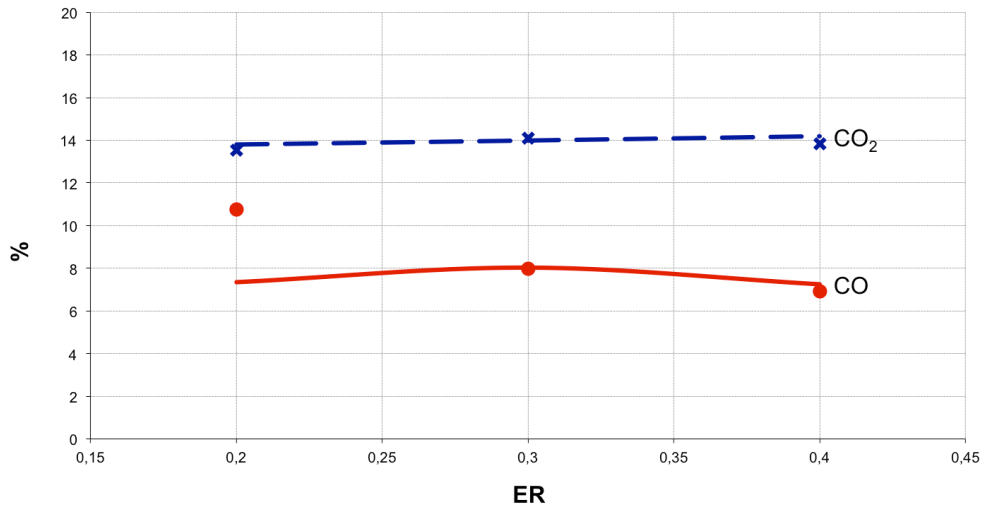


Figure 4.7 Effect of equivalence ratio on syngas composition. Experimental data: X= CO₂ • = CO.

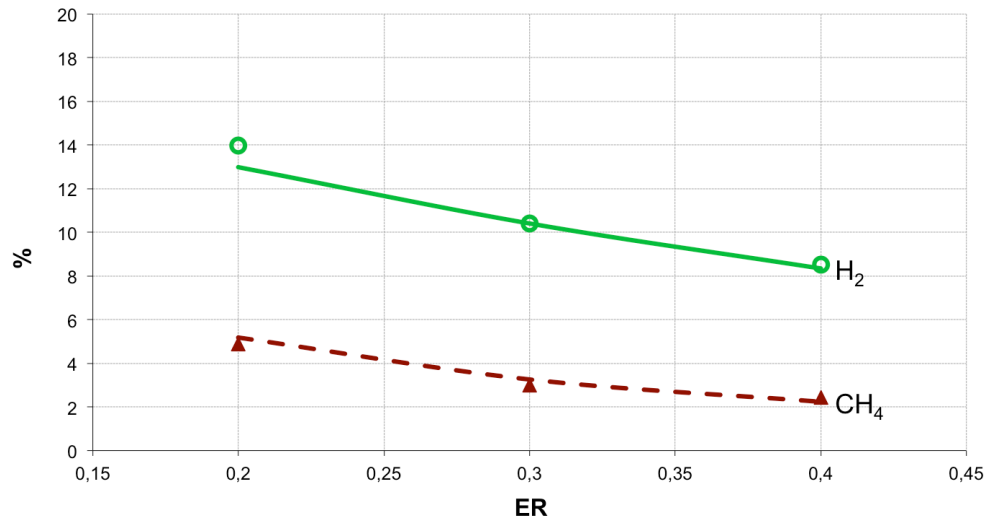


Figure 4.8 Effect of equivalence ratio on syngas composition. Experimental data: ○= H₂ ▲= CH₄.

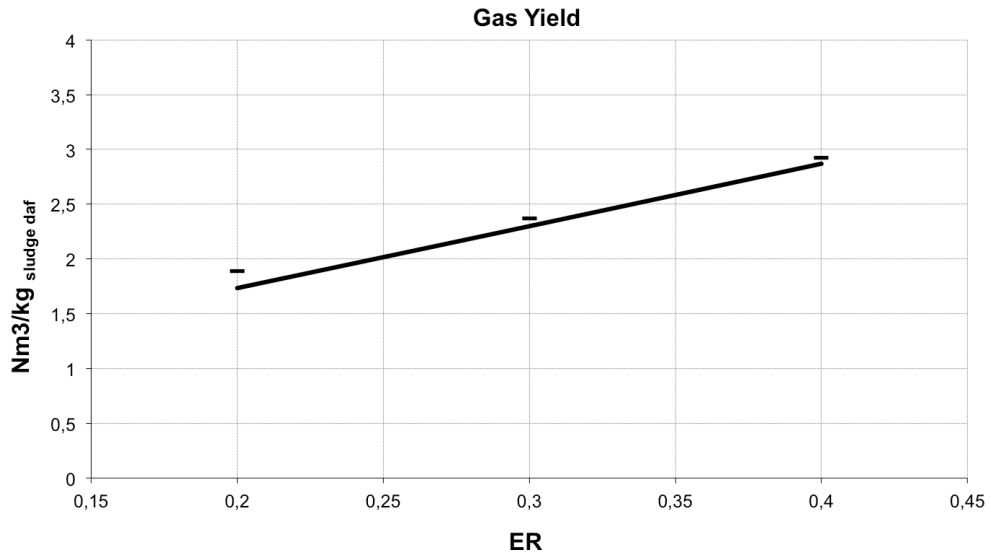


Figure 4.9 Effect of equivalence ratio on gas yield. Dots are experimental data, lines are model prediction.

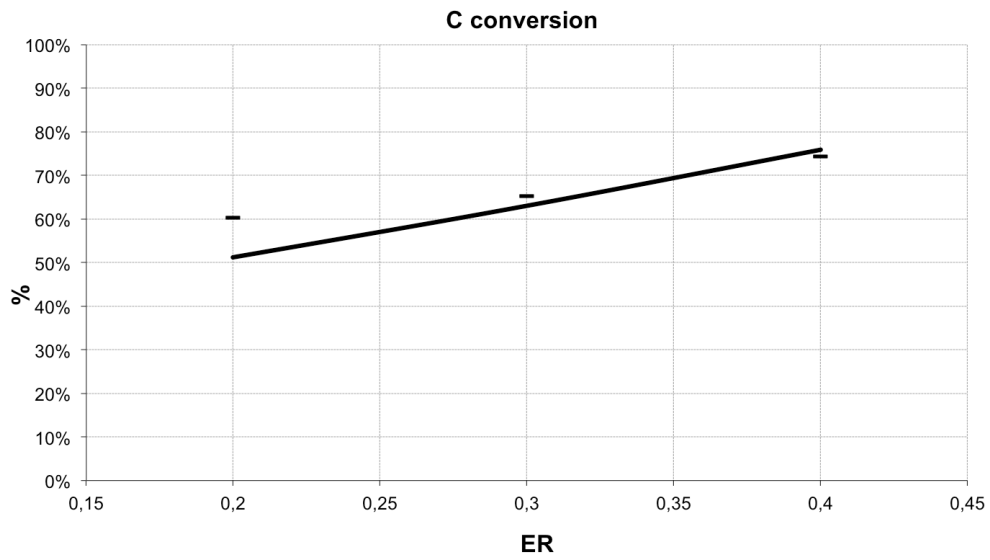


Figure 4.10 Effect of equivalence ratio on carbon conversion. Dots are experimental data, lines are model prediction.

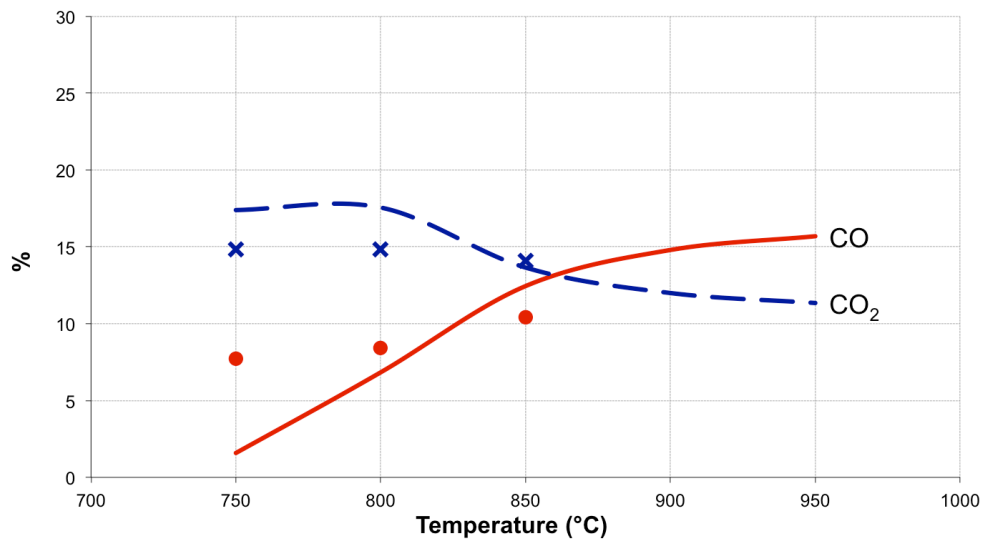


Figure 4.11 Effect of steam injection on syngas composition. SB= 0.5. Experimental data: X= CO₂
• = CO.

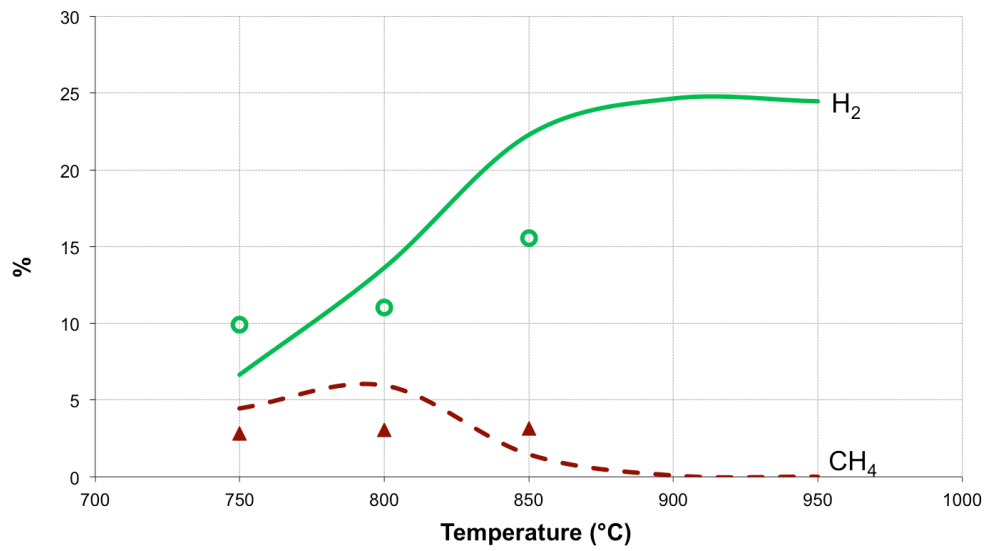


Figure 4.12 Effect of steam injection on syngas composition. SB= 0.5. Experimental data: ○= H₂
▲ = CH₄.

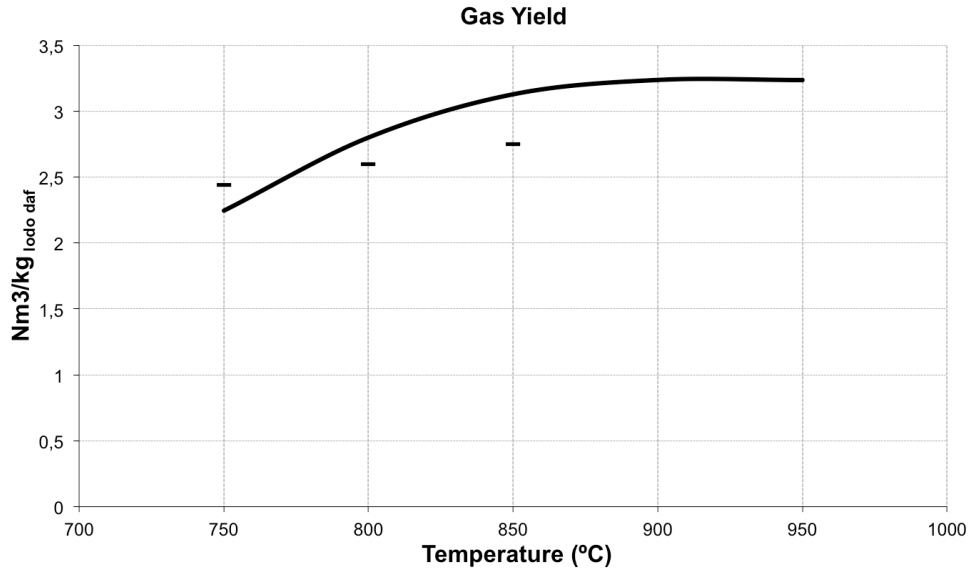


Figure 4.13 Effect of steam injection on gas yield. SB= 0.5.

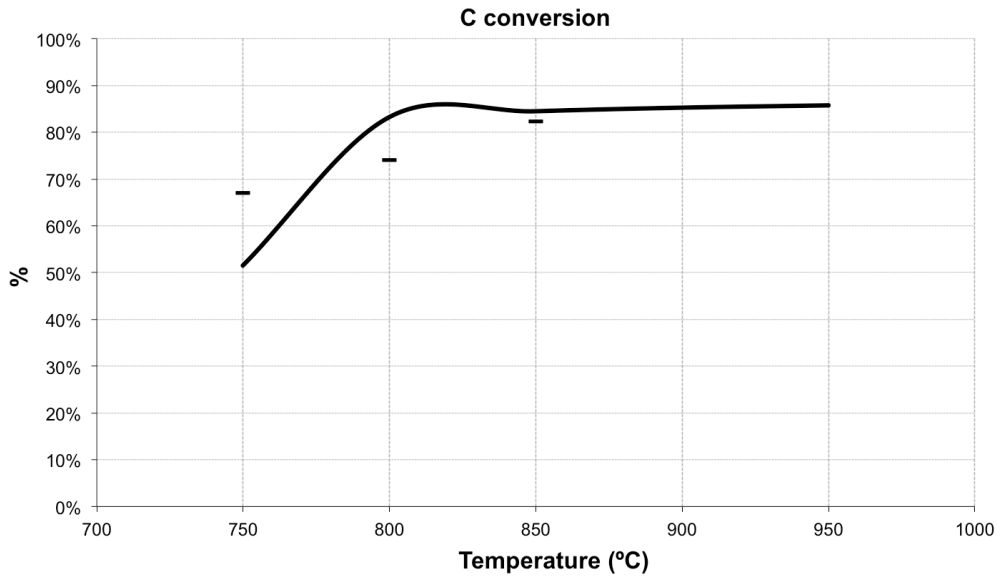


Figure 4.14 Effect of steam injection on carbon conversion. SB= 0.5.

4.1 Energetic Evaluation

Another important goal of the present work is to assess the ability of the model to predict the overall energetic efficiency of the process.

The two parameters that can help in the evaluation of this aspect are the lower heating value of the syngas (LHV_{gas}) and the cold gas efficiency (CGE). After collecting the experimental data[20], a calculator block was configured in the model, with the task of calculating these two values using the outlet composition of the syngas.

4.1.1 Effect of Temperature

It can be seen that an increase of temperature corresponds to an increase of lower heating value and cold gas efficiency (Figures 4.15 and 4.16). This is due to a higher syngas production and to higher percentage of hydrogen and carbon monoxide in the syngas.

Experimental data are fit quite satisfactorily, although it can be seen that the overestimation of CO production at high temperature ($> 850^{\circ}\text{C}$) reflects on the estimation of the energetic parameters as well.

4.1.2 Effect of Equivalence Ratio

The equivalence ratio has a quite a strong influence on the energetic efficiency of the process. As more air is introduced, combustion is favored in spite of gasification, therefore the lower heating value decreases with higher ER and cold gas efficiency also decreases, although less evidently (Figures 4.17 and 4.18).

Model predictions are, once again, in quite good agreement with experimental data.

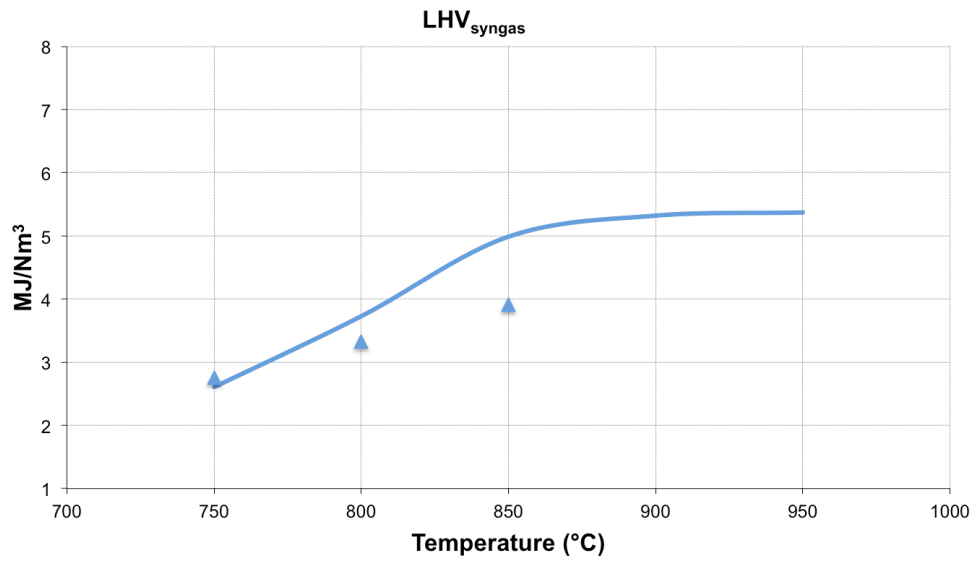


Figure 4.15 Effect of temperature on LHV at ER= 0.3.

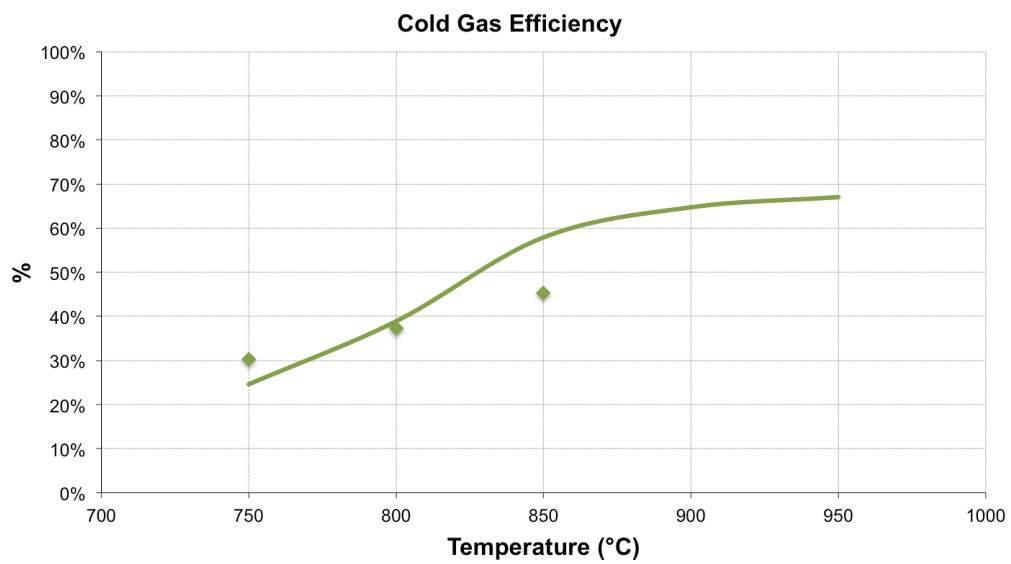


Figure 4.16 Effect of temperature on CGE at ER=0.3.

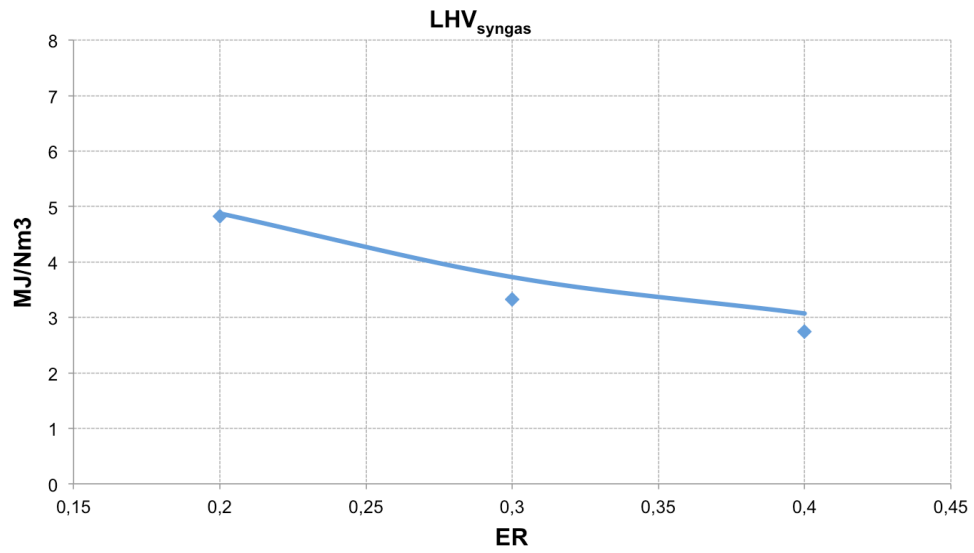


Figure 4.17 Effect of equivalence ratio on LHV at 800°C.

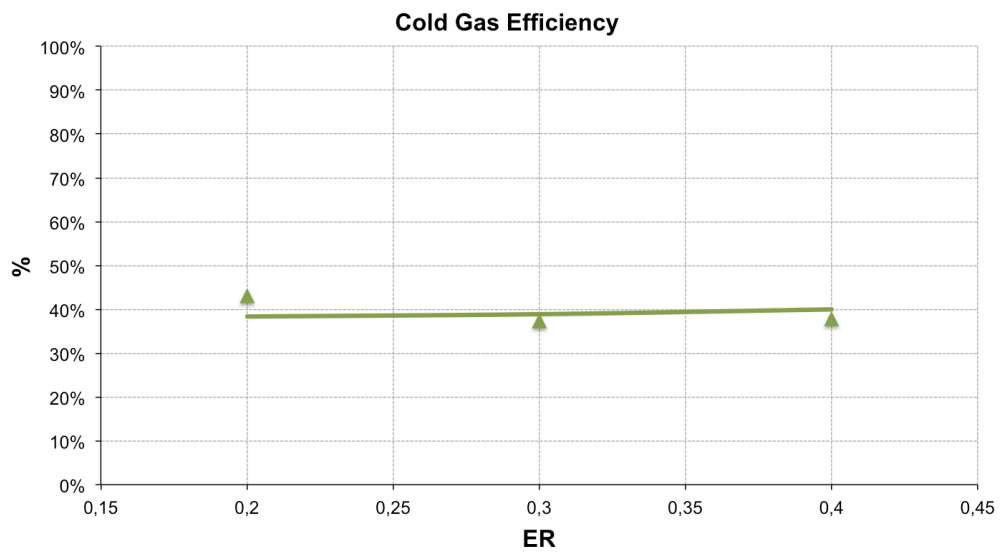


Figure 4.18 Effect of equivalence ratio on CGE at 800°C.

4.2 Selection of ideal case

After having considered all the conditions of gasification it is easy to compare the different situations, in order to understand which case constitutes the optimum configuration for sludge processing.

It is clear that higher temperatures and lower ERs yield higher quantities of hydrogen in the syngas and thus a higher LHV, but less gas is produced because of the lower carbon conversion. Indeed, higher ERs and steam injection yield a higher quantity of total syngas, but lower quantity of hydrogen, carbon monoxide and methane. Nonetheless, the injection of steam raises the yield of hydrogen and the LHV of the syngas.

For these reasons, for the data considered in the present case, the best conditions are a compromise that consists in gasification temperature of 800°C, ER=0.3 and presence of steam injection.

5 Conclusions

In this thesis work, the processes of testing and developing a model for a fluidized bed gasifier were described. At the closure of this study, it can be said that the main objectives have been met. Sewage sludge gasification tests have been completed successfully. Although some obstacles arose when dealing with some parts of the experimental equipment, the results have been collected satisfactorily. Modeling using Aspen Plus has been performed and was proved to be an effective method; the software is both capable of dealing with complex cases, letting the user specify many aspects of a process, and presents a simple interface, which allows for faster comprehension and easier programming.

The process was divided into stages (drying, decomposition, reaction, separation) that were implemented in different blocks and unit operations. The RGIBBS reactor performed the operation of Gibbs free energy minimization, in order to predict the syngas composition, while non-equilibrium components were treated separately, in RSTOIC blocks, which are able to specify a defined extent for each reaction.

Despite some difficulties, which were encountered in dealing with the reactions to be specified in the RGIBBS block, results were satisfactory. The reactions state the way the whole equilibrium is calculated, and the possibility to insert just independent reactions

represents a limit, which affects, for example, the ability to obtain a more precise trend for carbon monoxide.

Nevertheless the overall behavior of the simulation is in good accordance with reality and the model can be successfully used for assessments of many different systems and situations.

5.1 Future work

For future work, some aspects that can be revised, in order to develop more thorough analyses and simulations, can include:

- ◇ Improvement of the dosing system; in particular the screw feeder and launcher can be re-configured, so that the influence of gravity is minimized and the calibration curve is more reliable.
- ◇ The study can be performed on a pilot plant; this would allow for specific temperature and concentration data about multiple stages of the gasification process, thus leading to a more accurate modeling.

6 Acknowledgements

I would like to take this occasion to thank the many people to whom I am so very grateful, and to be able to do this properly I have to use different languages, so... sorry for the mess! The full list would be certainly too long, so to anybody who doesn't appear below, please be sure that you are not forgotten and will always have a place in my mind and heart.

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