Università degli Studi del Molise

DIPARTIMENTO DI BIOSCIENZE E TERRITORIO

DOTTORATO DI RICERCA XXXIV CICLO

Oxygen-blown gasification of sewage sludge and biomass for chemicals synthesis

PhD Thesis

Nicola FRATIANNI
(Matr. 164270)
September 5, 2022

Nicola Fratianni

SSD: FIS/01-CHIM/03

PhD Coordinator:

Prof. Giovanni FABBROCINO

Tutor:

Prof. Vincenzo DE FELICE

Co-Tutor:

Prof. Giovanni Maria PIACENTINO

Prof. Stefano FRIGO

Academic Year 2018-2021

Acknowledgements

I wish to express my sincere gratitude to my supervisor, Associate Professor V. De Felice for his advice, assistance and encouragement throughout this project.

The words are not sufficient to express my gratefulness and deepest thanks to my co-supervisor Associate Professor. G.M. Piacentino, for his continuous guidance, positive discussions, important ideas through this research work and his various support along my study.

Special thanks are also due to Associate Professor. S. Frigo, who co-supervised me during last year of the thesis, for his readiness, precious support, input and advice.

I would like also to thank the research group of the DESTeC Department of the School of Engineering of the University of Pisa. Special thanks to Dr G. Fiori and other technical staff for their supports during experimentation. My thanks for Associate Professor R. Gabbrielli for his help, support and contribution.

I would like to extend my thanks to the Italian Government - Ministry of Education, University and Research, in particular the University of Molise for granting me the opportunity to study and complete the PhD.

I also wish to acknowledge the persons and companies who have financially supported and made the production of part of this work possible, particularly Biosyn srl.

I am greatly indebted to my devoted wife. My gratefulness for her love, care, encourage, support, patience in best and worse conditions. My thanks to my lovely children Vincenzo and Bianca for tolerating my part-time presence in their most needed times. My apology for them.

Finally, my deepest thanks and gratitude to my family, parent, sister and my relatives for their helps, supports and prayers.

Abstract

Sewage sludge management is a current problem of extreme concern in Europe. Till now, the most frequent route for sludge management has been incineration or the reuse by shedding on agricultural land both directly or after composting.

This work, carried out in the context of an industrial research program co-financed by the EU LIFE program entitled LIFE-AUGIA, has been performed in partial fulfillment of the requirements necessary for the achievement of the Doctorate. It concerns a particular line of treatment of sewage and agricultural waste transforming them into gas with a significant energy content and of important economic and industrial value. In fact, a well-known source of material destined for landfill, are forest maintenance waste and sludge from sewage treatment. If waste from forestry and agricultural maintenance can in any way be used as a marginal source of energy, conventional methods such as landfill, incineration and use in agriculture have become less and less exploitable for sewage sludge in the Countries of the European Union (EU). The new directive 99/31 / EEC introduced restrictions for landfilling of biodegradable organic waste. In some countries of the EU, the use of untreated sewage sludge in landfills is already forbidden as well as their use in agriculture.

After an initial description of the treatment methods alternative to gasification, the different gasification methods and their merits and defects are described here in detail according to what can be found in the specialist literature. The following description of the LIFE- AUGIA program introduces to modern methods of gasification in presence of oxygen and carbon dioxide, identifies materials and methods of analysis of the gas and the materials used in the process. Follows a description of components and structure of the AUGIA experimental plant. A conspicuous part of the work has been then dedicated to the creation and running of two simulation models, both developed in the commercial framework Aspen Plus. The first is based on the evolution of gasification at thermodynamic equilibrium and the second instead considers the kinetics of the reactions and more accurately describes the various transformations that happen along the gasifier. Part of the work required the creation and operation, in the Lab of the University of Pisa, of a small-scale reactor with which the oxygen-based gasification has been experimentally tested, allowing the comparison between experimental results and simulations aimed at validating the latter and obtaining the necessary empirical parameters. Finally, the AUGIA industrial reactor has been completely simulated and the results are shown in the last part of this very work. They will be compared with the results of the full-scale LIFE-AUGIA experiment as soon it will be operative in the next future.

Table of Contents

List of Figures

List of Tables

Chapter 1
Introduction

1.1 Background

The use of agricultural waste and sewage sludge represents a well-known and promising alternative for the energy production, allowing at the same time the reduction of the use of sources of fossil origin and the enhancement of the economic value of materials at present classified as waste.

In this work, that is part of the research activity of the LIFE AUGIA Project and represents the PHD Thesis of the Author, attention has been paid to handling and processing of sludge originating from civil wastewater treatment plants, which constitute both a biological matrix and a refuse to be disposed of.

Unfortunately, disposal conventional methods such as landfill, incineration and use in agriculture have become less and less exploitable for sewage sludge in the Countries of the European Union (EU). Indeed, the new directive 99/31 / EEC which replaces the CE 1986 Directive, introduced restrictions for landfilling of biodegradable organic waste. In some countries of the EU, the use of untreated sewage sludge in landfills is already forbidden and it is very likely that in the near future it will achieve a ban on the use of sludge in agriculture in all the EU Countries. In any case, even the European Directive 86/278 / EEC prevents the spreading of row, untreated sewage sludge in agriculture. On the other side the laying of sludge on agricultural land is regulated by laws increasingly restrictive, in consequence of the limits imposed by the EU for the concentration of heavy metals in the soil. These limits are devoted to preventing heavy metal assimilation by plants, animals and consumers of plant foods, but could, as a side effect, prevent the use of sludge on agricultural land. Many Europeans countries are therefore abandoning or have already abandoned the option of disposal of sewage sludge in agriculture even before of an official ban of the use of sludge in agriculture.

As a consequence, the amount of sewage sludge to be disposed every year tends to grow uncontrolled. As reported by Milieu Ltd et al. [1] every year the first 15 Member States of the European Community produce 8,7 million tons of sewage sludge (dry assessment), while the other 12 produce 1.2 million tons. These figures increase as new states adhere to the directives of the European Community and their relative compliance passes from the initial 50% of the collection to the normal rate in other countries which exceeds 95%. The management of sewage sludge is, therefore, one of the problems of greatest concern throughout Europe, above all in view of the renewal of the legislation in a decidedly more rigorous sense, which has become imminent thanks to the commitment of the C.E. in the field of Ecology and the Construction of a Circular, Green, Compatible Economy. In particular, the amount of sewage sludge that regularly goes to landfill must be reduced. Only in 2014 in Italy 25% of the sewage sludge produced was sent directly to the landfill of the residual share 38% was destined for direct agricultural use, 46% was used for the preparation of compost and 6% was incinerated; the remaining 10% had an unknown destination, probably illegal. It appears therefore necessary to develop alternative processes to manage the sewage sludge problem that is growing both for greater production and for the need to resize the method of disposal that has up to now concerned about eighty percent of this waste production. In

In several EU countries, thermochemical processes such as incineration and gasification are emerging as the most promising alternatives. Gasification, in particular, represents a valid alternative to incineration, for the thermal treatment of sludge. Gasification indeed has benefits in common with incineration, i.e. complete sterilization, significant volume reduction, production of a solid residue (ash).

Gasification moreover makes it possible to avoid some problems related to incineration such as emissions of sulfur and nitrogen oxides, heavy metals, fly ash and the potential production of dioxins and furans.

In fact, gasification is a process occurring in a reducing atmosphere thus preventing dioxins and furans production as opposed to the oxidant conditions typical of the incineration.

As previously mentioned, this thesis work has been carried out within the LIFE-AUGIA applied research project funded by the European community. The related gasification plant is under construction at the COSIB Industrial Consortium. In this work I made extensive use of experimental data and process simulations carried out in the LIFE AUGIA context.

In addition to the COSIB consortium, the LIFE AUGIA project, involves the University of Molise (UNIMOL), the University of Pisa (UNIPE), the SIME and BIOSYN companies and some other people.

The present study concerns the gasification of sludge mixed with agricultural waste, performed in a fixed bed downdraft reactor that can be operated at a very high temperature and can be fed for experimental purposes, respectively, with oxygen, steam or carbon dioxide.

Wood chips gasification plants are rather common in northern Europe, but this is not the case for the gasification of sludge.

Preliminary experiments have been conducted with a small pilot plant in order to investigate the efficiency of the oxygen-based gasification of wood pellet with CO2 as moderator. The experimental tests were carried out in Pisa at different values of equivalent ratio (0.25÷ 0.35) and at different ratio O2/CO2 in the feed (between 1÷3, kg/kg), in order to analyze and assess the gasifier behavior and its performances and the effects of using oxygen as gasifying agent.

Two numerical models for simulating sludge and biomass co-gasification have been structured in order to carry out a more in-depth analysis of the process, fitting the available experimental data (both those already available in the context of the LIFE AUGIA project and those obtained in the course of this thesis work) and predicting the behavior of the system with varying operating parameters.

1.2 Motivation and Aims

The gasification process has been identified as a promising technology for the treatment and disposal of sewage sludge and the production of high added-value products such as hydrogen, methanol and methane. However, the complex nature of the gasification process requires a thorough understanding and characterization of the different parameters that affect its performance. The design and development of oxygen-based co-gasification processes of sewage sludge and biomass are still at immature stages. There is still a lot of basic scientific information lacking in the technical literature. The motivation for this PhD thesis is to investigate the potential of using pure oxygen as a gasifying agent in the gasification process of sewage sludge and biomass to contribute to the development of sustainable and efficient technologies for waste management and chemical production. This will be pursued by conducting an experimental and numerical investigation of the aforementioned gasification process in order to better understand the underlying mechanisms and to identify the key parameters that affect the process. The main aims of this study are to:

1. Characterize the physical and chemical properties of the feedstocks (sewage sludge and biomass) that affect the gasification process.
2. Investigate the effect of different operational parameters (such as temperature, pressure, and oxygen concentration) on the gasification process.
3. Develop a detailed mathematical model of the gasification process that can be used to predict the performance of the process under different conditions.
4. Investigate the feasibility of using pure oxygen as a gasifying agent in the gasification process of sewage sludge and biomass.
5. Design and build an experimental set-up for oxygen-based biomass gasification, by revamping and modifying a lab-scale pilot plant and to use this set-up to conduct a comprehensive study of the key parameters that affect the efficiency and yield of the gasification process.
6. Compare the results of the experimental and numerical study to identify the similarities and differences between them and to understand the impact of model assumptions.

Overall, this study aims to contribute to the development of a better understanding oxygen-based gasification process of sewage sludge and biomass and to demonstrate its potential as a sustainable and cost-effective way to convert these waste materials into valuable chemicals and to provide a basis for the optimization and design of future gasification plants.

1.3 Research Hypothesis

The research hypothesis for this PhD thesis is that the use of pure oxygen as a gasifying agent in the gasification process of sewage sludge and biomass can significantly improve the efficiency and yield of the process, resulting in a more sustainable and cost-effective way to convert these waste materials into valuable chemicals. Specifically, it is hypothesized that:

1. The use of pure oxygen as a gasifying agent will lead to a higher gasification efficiency compared to using air or steam, due to the higher oxygen content in the feed.
2. The use of pure oxygen mixed with steam will result in a higher energy output and increased hydrogen yield, as more heat will be generated during the gasification reaction.
3. The gasification of sewage sludge and biomass using pure oxygen will lead to a lower content of pollutants in the produced syngas, due to the absence of nitrogen, which is a common diluent in air.
4. The use of pure oxygen together with the special dual- fire design of the gasifying plant developed, will lead to a reduction in the formation of tar and other heavy hydrocarbons in the syngas, resulting in a cleaner and more valuable end product.

1.4 Layout of the thesis structure

The following sections structures the thesis:

Chapter 1: In this section, the research background, purpose and objectives of the study are presented. The main focus of the research is described, as well as the hypotheses to be verified and the thesis structure.

Chapter 2: The chapter outlines common methods of treating sewage sludge as well as disposal technologies currently in use (disposal in landfills, incineration, etc.). It continues with an analysis of the Italian sludge production by territory and, finally, frames the problem from both an Italian and an international regulatory point of view;

Chapter 3: This chapter introduces the basics of the biomass gasification through a discussion about the reactions involved, a review of the main gasifier types, and an analysis of the parameters affecting the process performance as well as of the main syngas cleaning techniques.

Chapter 4: This section provides an overview of the existing literature on the topic of sewage sludge gasification. In particular, the current state of the art in terms gasification plant is presented, focusing on realizations at each of the of possible scales: laboratory, pilot plant and full scale. The literature review also covers research and development on the most promising gasification techniques such those that entails the use pure oxygen added with CO2 or steam.

Chapter 5: This chapter is devoted to the description of the Life AUGIA project, funded by the European Community under the LIFE+ program, within which the present research work is included. The demonstration plant, which will be built as part of the project and that will be used for the study and investigation of the oxygen-based gasification process of sewage sludge and residual biomass, is described in detail.

Chapter 6: In this chapter, the materials and methods of characterisation that were performed on the feedstock and syngas, are described. In addition, all equipment and accessories for cold and hot rigs are presented. This section includes details on the experimental setup, the materials and equipment used, and the procedures that were followed.

Chapter 7: This chapter displays the simulations models of the proposed oxygen-based gasification process and illustrates their results. In accordance with the approaches commonly adopted in literature, two different numerical models have been developed and simulated. An equilibrium model, relatively simple, based on the assumption that system is at thermodynamic equilibrium during the reactions, in its most stable state at the minimum value of the Gibbs potential. A Pseudo-Kinetic model, more complex, that takes into account the geometry of the reactor and the kinetics of each reaction.

Chapter 8: This chapter details the experimental set-up and describes the procedures that were used during an experimental campaign conducted on a small-scale plant to which the author of this thesis contributed during the research. The parameters of interest and operating conditions for all experimental tests are explained in detail. The chapter includes tables, figures, and graphs to illustrate the results. It also reports the comparison of the results with those obtained through numerical simulations.

Conclusion: This section summarizes the main findings of the study and provide recommendations for future work. The section will also discuss the overall significance of the study and its implications for the field of oxygen-based gasification of sewage sludge and residual biomass.

References: This section will list all the sources cited in the thesis in a proper format.

Appendices: This section will include any additional information or data that is not essential to the main body of the thesis but may be useful for readers. Such as detailed experimental data, calculations, or process flow diagrams.

Chapter 2
Sludge from treatment of municipal wastewater

Domestic and industrial wastewater, conveyed through the sewerage service to treatment plants, must be properly treated before being discharged.

2.1 Wastewater treatment

Wastewater treatment is a process used to remove contaminants from wastewater and convert it into an effluent that can be returned to the water cycle. The treatment process takes place in a wastewater treatment plant.

Industrial waste has such variable characteristics that a generalization of the treatment to which it should be subjected is difficult. In fact, the implementation of an industrial wastewater discharge requires very thorough preliminary investigations. It is also common to provide for specific treatments upstream of the entry of wastewater into the public sewerage system, in order to avoid any serious interference with the final facilities (especially the biological ones). As regards domestic (or similar) wastewater, discharge limits are regulated by Annex 5 to Part III of Legislative Decree 152/2006 (Table 2.1 and Table 2.2).

Table 2.1 - Emission limits for municipal wastewater treatment plants

Plant capacity in PE (Population equivalent)	2.000 ÷ 10.000		>10.000	
Parameters (Daily average)	**Concentration**	**% of reduction**	**Concentration**	**% of reduction**
BOD5 (Without nitrification) mg/1	≤ 25	70 ÷ 90	≤ 25	80
COD mg/l	≤ 125	75	≤ 125	75
Suspended solids mg/l	≤ 35	90	≤ 35	90

Table 2.2 - Emission limits for municipal wastewater treatment plants in sensitive areas

Plant capacity in PE (Population equivalent)	10.000 ÷ 100.000		>100.000	
Parameters (Annual average)	**Concentration**	**% of reduction**	**Concentration**	**% of reduction**
Total phosphorus mg/l	≤ 2	80	≤ 1	80
Total Nitrogen mg/l	≤ 15	70 ÷ 80	≤ 10	70 ÷ 80

The stages that commonly constitute a wastewater treatment process are as follows:

- *Specific treatments* at the outlet of the department in which the effluent is produced; these treatments abate specific contaminants, before they are diluted with wastewater from other departments, as better results are obtained by processing streams of lower flow rate and higher concentration, containing a well-defined class of pollutants. For example, abatement of heavy metals, chemical oxidation of non-biodegradable substances, stripping of organic ammonia vapours, etc.
- *Primary treatment:* the effluent undergoes some coarse treatment, i.e. not sufficient to produce a discharge to specification, but necessary for subsequent treatment to work properly. These may be:
  - flow and pollutant concentration offsets,
  - neutralization,
  - chemical-physical coagulation and flocculation treatment,
  - solid-liquid separation by sedimentation, flotation, filtration.
- *Secondary (biologiacal) treatment:* the effluent undergoes biological treatment (usually aerobic) which results in the removal of BOD and COD. The removal of nitrogen, phosphorous and suspended solids is also achieved. The reactor solutions can be of various types (aerated tanks in different configurations, percolator beds, biodiscs, etc.).
- *Tertiary treatments:* finishing treatments to get specific on all pollutants, with particular reference to:
  - nitrification and denitrification, for the removal of nitrogen,
  - defosphating, for the removal of phosphorus,
  - filtration, for the removal of remaining suspended solids,
  - disinfection, for the elimination of pathogenic microorganisms,
  - adsorption with activated carbon, for the elimination of non-biodegradable substances.
- *Sludge treatment:* the water purification process involves the production of large quantities of sludge, the nature of which (predominantly organic, inorganic, or

composition) depends on the overall structure of the purification process. They require further treatment before they can be finally disposed of. These treatments will be addressed in more detail in the following section.

A block diagram of a domestic effluent treatment line is shown in Figure 2.1.

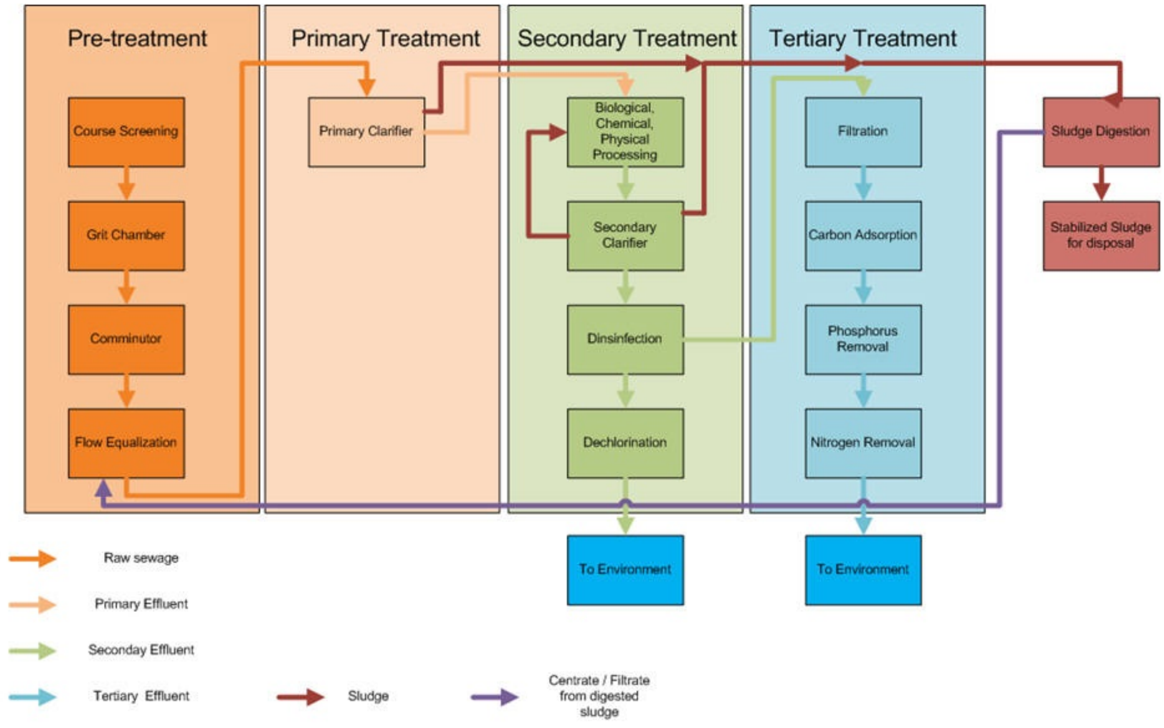


Figure 2.1 - Block diagram of a typical effluent treatment line

2.2 Sewage Sludge Treatment

Aqueous wastewater treatment processes generate a muddy solid residue in which the pollutant load originally present in the liquid wastewater is concentrated. This sludge is collected in the solid/liquid separation processes implemented in the treatment plant and generally requires further treatment before final disposal.

These include, as a minimal intervention for inorganic sludge, thickening and drying. However, organic sludge must also undergo specific treatments to reduce its volatile content before final disposal.

The selection of a particular process over others depends mainly on the nature and characteristics of the sludge, as well as the final disposal method used: for example, sludge from activated sludge processes is more efficiently concentrated by flotation processes than by gravity thickening. A final disposal by incineration, in turn, requires a sufficiently high solids content to maintain self-combustion in the incinerator.

The technologies that can be considered optimal for the final disposal of a sludge, both from a purely technical and economic point of view, are dictated by the physical-chemical characteristics of the sludge itself. In general, sludges of a gelatinous type, such as those resulting from flocculation with alum or from an activated sludge biological process, have lower concentrations of solids than those obtainable in sludges of inorganic origin or from primary sedimentation.

The degree of dehydration achievable in a sludge coming out of a filtration is related to its specific resistance to the same filtration; this characteristic can be modified by the addition of polyelectrolytes, but economic considerations might suggest different treatments as an alternative. Figure *2.2* shows a block diagram of the sludge treatment line.

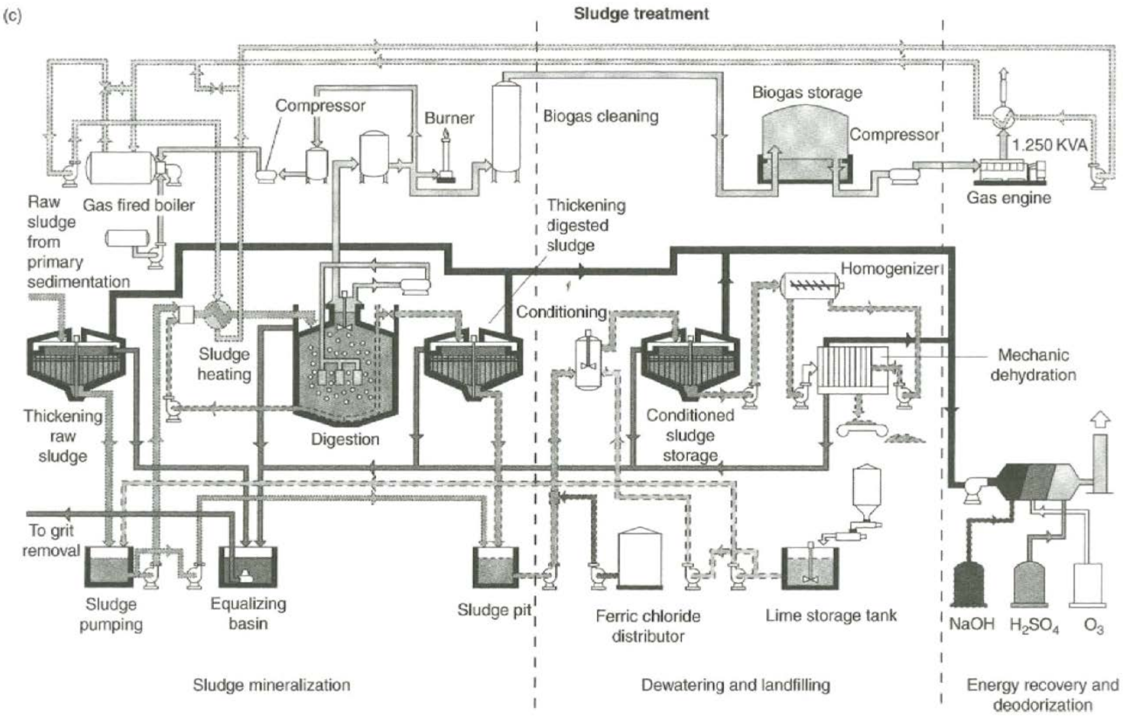


Figure 2.2 - Block diagram of a typical sludge treatment line

2.2.1 Thickening

Preventive sludge thickening is a practice that has long been neglected, but which is finding application in an increasing number of plants. Placed upstream of digestion, it makes it possible to regularise and increase the dry matter concentration of the sludge.

Substantial savings can therefore be made in the sizing of the digestion plant. Prior to dewatering, thickening stabilises and facilitates operation, making it possible to reduce the volume of the conditioning units (particularly important in the case of thermal conditioning), and to increase the capacity of the dewatering devices.

Thickening of primary and activated sludge can be provided separately or simultaneously. In Europe, it is preferred to introduce excess activated sludge at the head of the primary decanters, resulting in a single thickening of mixed fresh sludge.

The thickening of digested sludge requires much more work than that of fresh sludge: the duration of the process can vary from several days to several weeks, depending on the initial and final concentration of the sludge. Consequently, in the case of anaerobic digestion (and in the case of aerobic stabilisation), preliminary thickening is often cheaper, in terms of investment, than subsequent thickening.

For small installations, the thickener can be a simple cylindrical-conical tank with a steeply inclined bottom, but from diameters in the order of 5-6 metres, the installation of a mechanism with a comb scraper is advisable.

The types of thickening generally employed are:

- *Gravity thickening:* the gravity thickening of surplus sludge takes place in a basin equipped with a scraper bridge, which rotates at low speed and destabilises the hydrated agglomerates of sludge particles, improving sedimentation and compaction.
- *Flotation thickening:* sludge thickening by air flotation has become increasingly popular and is particularly suitable for the treatment of gelatinous sludge such as activated sludge. In flotation thickening, small air bubbles released from the solution stick to the sludge floes and become trapped there; the air/solid mixture rises to the surface of the basin, where it is concentrated and then removed.

2.2.2 Biological sludge stabilisation

Sludge digestion or stabilisation can be carried out by two processes:

- *Anaerobic sludge digestion:* this is a biological process used for the treatment of organic sludge in sewage treatment plants for civil sewage and, sometimes, for highly concentrated organic industrial effluents. It is a process of mineralisation, gasification and humification of substances organic processes, which is slower than aerobic processes, but is cost-effective when small volumes with a high organic load must be treated.

  The term mineralisation refers to the attainment of a condition whereby the material present cannot be further degraded biologically, while gasification is the conversion, in this case biologically, of solid and liquid products into gaseous products. Humification refers to the transformation of originally putrescible organic material into a metastable, harmless product subject to very slow decomposition (natural humus).

  In general, the objectives of anaerobic sludge digestion are stabilisation of organic material, destruction of any pathogenic microorganisms, reduction of sludge volumeand facilitation of final disposal.

  During the digestion process, volatile organic material is degraded, through successive stages, to various gases and organic end products: the gases consist mainly of methane and carbon dioxide. Degradation takes place through three basic stages: liquefaction, acid formation and gasification. All processes are conducted by a bacterial flora of an anaerobic nature that develops in the sewage and sludge.
- *Aerobic sludge digestion:* this takes place under conditions of strongly endogenous respiration and is a treatment aimed at stabilising the sludge, i.e. significantly reducing its putrescibility under the action of heterotrophic microorganisms in the presence of air. Another objective is to reduce its volume,

favouring the release of water, so that it can be separated, and finally to achieve a reduction in the bacterial load.

The sludge from the primary and secondary sedimenters, possibly thickened, is fed into mechanically aerated tanks, more rarely by air diffusion, where it remains on average for 15-20 days (hydraulic retention time). Generally, aeration is stopped for 3-4 hours once a day to allow the water to be separated and the digested and thickened sludge to be extracted: more rarely, and in larger plants, thickening takes place afterwards in a separate, continuously operating unit.

Separate aerobic digestion is generally preferred to anaerobic digestion in temperate climate locations and in small plants (where an anaerobic system should operate without heating) and where handling operations have been simplified as much as possible, sometimes even dispensing with thickening of the sludge that is sent directly to the drying beds.

2.2.3 Dewatering

Sludge from municipal wastewater treatment is predominantly organic. Volatile matter accounts for 60 to 75% of dry matter in fresh sludge, and 45 to 60% in digested sludge. Sludge has a high content of colloidal matter and therefore its dewatering by filtration on a filter medium or its centrifugation requires prior conditioning treatment. The sludge must be flocculated so that the finer materials are collected in sufficiently large particles (floes) capable of being retained on the filter cloth or transported by an extraction screw.

In the absence of flocculation, extraction efficiency is poor and clogging of the filter media very rapid. In addition, the Interstitial liquid separated from the dewatered sludge £ highly charged and constitutes, with its recirculation at the head of the plant, an overload for the latter.

Good sludge conditioning is a prerequisite for the proper functioning of the dewatering plant itself, and the overall treatment plant.

In the case of mechanical dehydration, the absence or a reduced dosage of the conditioning reagent can only be envisaged for very lightly loaded plants, but these are in any case poor fallback solutions.

If sludge drainage on natural drying beds is planned, conditioning is not indispensable, as in this case a longer drying time is allowed and, above all, with each removal of dried sludge, the fine layer of top sand adhering to the sludge is evacuated along with it. Preliminary conditioning of the sludge can however, in the case of drainage on beds, decrease the drying time by 5 to 10 times. Drying beds can only be used with digested or stabilised sludge; with fresh sludge, the inconveniences {especially odour) risk quickly becoming unbearable.

Sludge flocculation can occur:

- by addition of mineral reagents,
- by adding organic polymers,
- by baking.

The first two possibilities represent chemical conditioning, the third thermal conditioning.

The following types of mechanical dehydration are practised:

- *Centrifugation:* this operation is used for both sludge thickening and de-watering; in practice it accelerates the sedimentation process that occurs naturally by gravity through the application of a centrifugal force. Centrifugation offers the advantage of dewatering sludge in a totally closed environment and very compact equipment. It is particularly suitable for very colloidal sludge that is difficult to dewater, although in this case the dry material yield is limited. The feeding and production of sludge is continuous, so that it is possible, for example, to directly feed a furnace. Preliminary desanding is often a useful precaution, which reduces the maintenance problems of centrifuges and particularly of extraction screws.

There are basically three types of centrifuges that can be used to dewater sludge: bowl, basket, and disc separators. The basic difference between these types of centrifuges is the method of collecting and expelling the solids from the unit.

- *Filtration:* Among the sludge dewatering processes by filtration, the most widely used are:

a) Filtration on drying beds: it can be used in installations of all the more reduced importance the more unfavourable the climatic conditions are. The cost of land immobilisation today limits this technique in practice to populations of a few thousand unless mechanical dewatering is planned at the same time for the bad season. Rectangular and circular beds equipped with wet sludge distributor bridges and dry sludge extractors are made.

b) Vacuum filtration: can be applied to different types of residual sludge; the achievable dry content varies depending on the type of sludge treated, the feeding of the sludge to the vacuum filters is generally discontinuous, while the production of the filtration panel is continuous.

c) Pressure filtration: two types of equipment are commercially available for this type of filtration. The belt press is a two-belt pre-pressure filter, preceded by preliminary flocculation using polyelectrolytes. It usually consists mainly of a flocculator (additive dosing zone), a distribution device, a drip zone, a successive and multi-directional pressing zone, a scraping and evacuation system for the panel, and a cloth washing system. Its adjustment and operation are extremely simple. The filter press, on the other hand, allows maximum dewatering of the panel, as it operates at pressures of up to 15 bar. This equipment often exceeds 45% dryness in mixed fresh or digested sludge, thermally conditioned or with mineral reagents. Generally, the filter press requires very little chemical conditioning of the sludge, but, in any case, adequate to avoid clogging of the cloths, which causes an increase in pressing time and the need for more frequent washing of the cloths.

2.3 Sewage sludge disposal technologies

After the dewatering processes, the sewage sludge is subjected to one of the following solutions, which are the most widely used and sometimes still under development.

1.1.1 Composting

The transformation of sludge into a variety of fertiliser suitable for spreading on agricultural land can be achieved by so-called *composting*. The sludge is generally deprived of water that can be removed mechanically and then mixed with a material that, on the one hand, provides organic matter and, on the other hand, reduces the moisture content of the mixture to facilitate maturation. A rational arrangement of fermentation towers equipped with powerful aeration and recycling devices allows the duration of accelerated fermentation to be reduced to a few days. The carbonaceous input material can be wood sawdust, bark or organic solid waste, although in the latter case prior treatment of the MSW, separating the fraction suitable for the purpose from the others. Favourable market conditions are essential for the adoption of such a solution, while the aspect of potential environmental impact, represented by products not suitable in this respect for the said use, cannot be neglected.

The term composting commonly refers to an aerobic process conducted in variously structured systems:

- use of suitable materials (biomass) alone or in a suitable mixture, provided that they are suitable for obtaining a finished product suitable for use as a soil conditioner on agricultural land,
- aeration and reaching temperatures of around 60°C, so to break down the pathogenic load present, and also reduce moisture from the material,
- permanence of the treated material in repose (maturation phase), with the possible intervention of a further aeration phase,
- refining of the product with possible separation of different materials.

The yield of the process is dictated by moisture conditions, degree of aeration, carbon, nitrogen and nutrient content, pH, and temperature.

The starting material is commonly represented by mixtures of biological sewage sludge and organic fraction of municipal solid waste (MSW) or other organic material, but the systems by which the process is carried out are of various types, depending on the case; the differentiation lies in the way the mass to be transformed into compost is mixed and aerated.

A distinction can be made between open and closed systems. In the former case we see processes based on static heaps or periodically turned over and in any case aerated, or the adoption of discontinuous open reactors equipped with a stirring system to ensure aeration.

In the second case, the process, continuous or discontinuous, takes place in closed reactors with air circulation, mixing or simple handling. Continuous reactors can be of the horizontal or vertical piston flow, or of the mixing type. The advantages of the closed system over the open one He in the fact that in such a configuration the emission of odours and pathogenic microorganisms can be controlled, and the process temperature can be better controlled.

Whichever system is adopted, the ripening phase is always required, even after accelerated fermentation in a reactor. Ripening is conducted either in aerated heaps or in reactors.

1.1.2 Wet oxidation

It consists of the oxidation of organic substances in the absence of flame and in the presence of liquid water. The process is carried out by operating at sufficiently high temperatures

(200-340°C) to carry out the complete oxidation of organic compounds with air or oxygen, but under pressure conditions (80-125 atm) that prevent the water from boiling.

That is, high concentrations of molecular oxygen dissolved in water are realised in the absence of boiling, and the energy required is that due to pressurisation rather than evaporation of the water. In addition to using the heat of reaction to heat the wastewater, the turbine expansion of the steam from the mixture leaving the reactor makes mechanical energy available for compressing the reaction air.

Incineration normally requires the sludge to be well dewatered so that combustion is self-sufficient in terms of fuel supply. In the case of wet oxidation, on the other hand, the degree of dewatering required for biological sludge is lower (about 6 per cent dry). As with all combustion processes, by-products are generated that require further action; these are ash, the resulting aqueous solution, and gaseous products.

The ash is relatively small in quantity, and although it can generate deposits in the equipment, it is largely carried by water. The water produced has a high nutrient and organic content and is recycled to the aqueous effluent treatment plant.

The odors generated, corrosion, and the high energy and maintenance costs of the equipment for this process limit its interest.

1.1.3 Liquefaction

Liquefaction is a thermochemical treatment involving the conversion of feed into a liquid phase, operating at low temperature (T<350°C) and high pressure (P-300 bar).

The process requires a low heat flow, rather long reaction times, possible use of H2, CO and/or catalyst. The main product is an oil with low oxygen content and specific heat of about 35-40 MJ/kg. The use of this process is limited by high costs, high pressure, and the need to separate the product from the solvents used.

1.1.4 Incineration

Sludge incineration consists of combustion with oxygen at high temperature (at least 800°C); it is generally carried out on sludge that has undergone drying treatment.

For heat balance reasons, it would be logical to apply incineration to fresh sludge, when its calorific value is higher than that of digested sludge. However, in the absence of digestion, special protection devices and/or sufficient storage of the panel after dewatering are required for hygienic reasons. In general, to avoid excessive fuel expenditure, it is preferable to condition the sludge and then dewater it mechanically before incineration.

When considering disposal by incineration, the moisture content, the volatile solids content in the sludge and the calorific value (which is typically between 11500 and 23500 kJ/kg), among other things, must be known in order to assess whether the combustion process can be self-sustaining or whether secondary fuel is required.

It is important to conduct combustion in such a way as to minimise the formation of pollutants, and in any case to put in place all operations and equipment suitable for purifying the flue gases of ash and pollutants ini general.

The incineration can be conducted in multi-layer furnaces, in which the sludge is passed through a series of superposed planes in a cascade: in the upper zones, the evaporation of the moisture still contained in the sludge takes place, and the cooling of the flue gases; in the intermediate zones, the combustion of gases and volatile solids takes place, while the fixed carbon bums in the lower zones.

Incineration is a rather expensive technology for the treatment of sludge and generates problems related to the disposal of the solid combustion residue, which amounts to about 30% of the input mass [2]. A dry solid content of at least 33% is required for the process to be autothermal.

The advantages of incineration are:

- significant reduction in sludge volume,
- energy valorization of sludge,
- the recycling of by-products, such as ash and inert materials, which can be used as filler for bitumen or in the manufacture of construction materials,
- the reduced sensitivity to different sludge composition,
- the reliability of the system,
- the minimization of odors using closed high-temperature systems.

The negative aspects are:

- the high cost of the process, which makes it economical only for large plants,
- very stringent legislation on emissions into the air, thus necessitating stringent,
- cleaning treatments of the gases produced,
- the aversion of public opinion.

1.1.5 Pyrolysis

Pyrolysis is a thermal decomposition process in an inert atmosphere (absence of O_2). It can also be the first stage of combustion and gasification processes.

This technology generates liquid, solid and gaseous products. The liquid product, which constitutes about 75% by weight, is composed of an oily substance, called bio-oil, with a chemical composition, specific weight, and heat of combustion similar to a diesel fuel.

The weight percentages of the solid and gaseous products are about 12% and 13% respectively. The solid consists mainly of coal, while the gas generally consists of a mixture of H_2, CO, CO_2, N_2, CH_4 and other low molecular weight hydrocarbons, in varying proportions depending on the type of feed and the operating conditions. Cooling the gas stream results in the condensation of an oily residue, called *tar*.

In general, pyrolysis requires a temperature of 400-800 °C and atmospheric pressure. The proportions of each product depend strongly on the pyrolysis method and reaction parameters. Both the char and the produced gases are burnt to provide for the heat demand in the feedstock drying and pyrolysis processes, thus requiring auxiliary fuel only only to start the process [3].

Limiting the presence of heavy metals (Cr, Ni, Cu, Zn, Cd, Hg. Pb) to ash alone requires adequate temperature control.

Gas formation takes place in three consecutive stages:

a) once a temperature of about 250 ° C is reached, CH_4, CO_2 and acetic acid are are produced,

b) at a temperature around 350°C, hydrocarbons and alcohols are formed,

c) at temperatures above 550°C, mainly H_2, CH_4, CO_2, hydrocarbons and alcohols are produced.

There are three different types of pyrolysis processes, which can be defined as follows:

- *Low-temperature pyrolysis* takes place at temperatures below 325°C and no bio-oil is produced.
- *Medium-temperature (fast) pyrolysis* takes place between 425 and 540°C, producing bio-oil.
- *High-temperature pyrolysis* takes place in the temperature range 650- 980°C, producing ash.

Among these, fast pyrolysis is the most frequently performed; the main characteristics of this type of process are:

- dehydrated feed with a moisture content of less than 10%, in order to minimize water in the oil produced,
- high heating and high heat transfer rate at the reaction interface,
- non-pressurised system,
- accurate temperature control of pyrolysis reactions,
- steam residence time of less than 2 seconds,
- rapid cooling and condensation of pyrolysis steam to produce bio-oil,
- collection and separation of coal (solid product),
- collection of gaseous products.

Efficiency depends on the moisture content of the fed sludge, so that co-pyrolysis of sludge with other waste materials is often used.

In summary, the positive aspects of the pyrolysis process are as follows:

- the coal and gas produced can be used to supply thermal energy to the reactorand to produce the heat needed to dry the sludge,
- bio-oil can be used in diesel engines as is,
- pathogens, viruses and organic chlorinated compounds are completely destroyed,
- unpleasant odour emissions are kept under control,
- NOx emissions can be controlled, heavy metals are limited in the ashes, which can be exploited as land fill or construction materials.

However, the problems listed below limit the development of this technology:

- complexity of the system,
- lack of information on operating costs,
- formation of poor-quality products,
- need to develop a market for bio-oil, which has a higher cost than fossil fuels.

1.1.6 Gasification

Gasification is a thermochemical process, carried out at a high temperature (around 800 °C), in the presence of a sub-stoichiometric quantity of oxygen, which converts solid organic material into gaseous products.

The composition of the produced gas, which is called *syngas*, depends on the characteristics of the feedstock (sludge) and the type of gasification technology employed.

Before being gasified, the sludge must be dehydrated, through a mechanical water removal process, and then dried, as its moisture content must not exceed 25-30 %.

The fact that the main product of the process is a combustible gas that can be readly used makes gasification a more attractive technology than pyrolysis, since a clean gas is more easily used than a combination of gas and oil. The amount of energy produced in the entire process is in excess and auxiliary fuel is only needed at start-up.

Fixed-bed gasifiers are simple to construct and have considerable plant reliability; they have the advantage of high thermal efficiency, but the disadvantage of a difficult process control.

Fluidised-bed gasifiers offer better mass transport and greater flexibility in terms of composition and feed rate than fixed-bed gasifiers but are subject to the problem of solid biomass sintering. Although it has been demonstrated how dried sludge can be treated in fluidised bed gasifiers, commercial applications are currently still under development. It is however possible to state that gasification through this type of equipment is a very promising technology for sludge disposal.

In conclusion, the following considerations can be made regarding the sewage sludge gasification process:

- a significant reduction in the volume of the original material is achieved, producing a residue that can be disposed of and recycled,
- sludge requires drying before treatment to reduce its moisture content, but no preliminary digestion is necessary,
- the process allows the complete destruction of the feedstock organic and pathogenic portions,
- a valuable gaseous fuel (syngas) can be obtained, which can be used for heat and power generation or chemicals production,
- compared to incineration, cleaner gases are produced, with less bituminous residueand lower NOx and CO_2,
- unpleasant odours are minimized,

- systems require small areas for installation,
- data on applications and costs for large-scale plants are still scarce.

2.4 Municipal sewage sludge disposal: current situation

The management of sewage sludge from civil wastewater treatment plants in different European countries is governed by national regulations and guidelines provided by the European Community.

Generally, energy recovery is carried out in plants where sludge is co-combusted with other waste material, although there are plants dedicated to the thermal treatment of sewage sludge alone in Europe.

In Spain, sludge management is regulated by the 2001 National Sludge Plan (NPSA). Reuse in the soil is the most widely used disposal method, although incineration is becoming increasingly important. Energy recovery is in fact one of the main aims of the NPSA and the prior anaerobic digestion of sludge allows its use in medium to large incineration plants. Pre-treatment to increase biogas production and the fate of micropollutants are still topics of study, as is the gasification process, options that have not yet been brought onto an industrial scale [4].

In Switzerland, co-combustion in MSW incinerators accounts for about 21 per cent of the total quantity of sludge subjected to thermal treatment; mono-combustion in sludge-only plants accounts for 55 per cent; the remaining 24 per cent is used in cement plants.

In Germany, the co-combustion of sludge in MSW incinerators, on the other hand, accounts for 3.5% of the total energy recovery. This is mainly due to the different structure of electricity production, which has a considerable fleet of coal- and lignite-fired thermal power plants, which are used with sludge in co-combustion. These power stations absorb, with a high degree of energy efficiency, a considerable share (48.6%) of the sludge quantity for thermal treatment, followed by single-fired power stations (38.4%) and cement plants (5.9%). In Switzerland, this type of power plant is almost non-existent due to the high share of hydroelectric power generation (70%), while the remaining 30% is covered by nuclear power. Consequently, the co-firing of sludge in MSW incinerators in Switzerland and Germany is in each case, albeit with a different share of the total, the optimal solution in several respects [4].

In Austria, with a total production of 260,000 t/y of sludge, 68% is incinerated, of which 43% is in six plants, which treat only sewage sludge. The largest operator in Austria is Femwarme Wien with three waste-to-energy plants including three sewage sludge lines, with an annual capacity of 84,000 t/y of sludge. Waste-to-energy solves the sludge problem through rapid, efficient, safe and systematic disposal, contributing substantially to: energy production and district heating without the use of fossil fuels; the achievement of CO2 emission reduction targets; the reduction of sludge volume to 1% of the original volume; the elimination of hazardous organic substances; and the concentration of nutrients in the sludge. The ashes are collected by a filter system that ensures emissions are below the limit values set by air pollution ordinances. Biological waste ash, especially from sewage sludge, contains not only silicon, calcium and heavy metals, but also phosphorus up to 20 per cent. In a new patented process, ASH DEC, the ash is mixed with a small amount of natural chlorine additives until soft granules are formed in the mixer. These granules are fed to a thermal reactor to be treated at a temperature of 900-1100°C for about 30 minutes. Under these conditions, the additives react with the metal substances to be removed and the resulting chemical compounds vaporise. In this way, up to 99% of mercury, cadmium, lead, zinc and copper, elements that generally make the ash from the waste-to-energy process, can be eliminated. At the reactor outlet, 90% of the ash is in the form of phosphorus-rich granules, while 10% is retained by a filter system in the form of concentrate of metal compounds. In order to produce a fertiliser suited to the needs of the market and cultivated soils, ASH DEC has enriched the granules produced in the pyro-metallurgical process with other nutrients such as potassium, sulphur, and an addition of phosphorus. PhosKraft PK fertiliser with trace elements is of high quality and contains no harmful substances. In fact, the concentration of toxic elements such as cadmium is significantly lower than in most conventional fertilisers with a high phosphorous content. The Austrian Food Protection Authority (AGES) authorised the unrestricted use of PhosKraft in May 2006 on agricultural and forestry land. The first industrial plant with a capacity of 14,000 t/y started up in Austria at the end of 2007 [4].

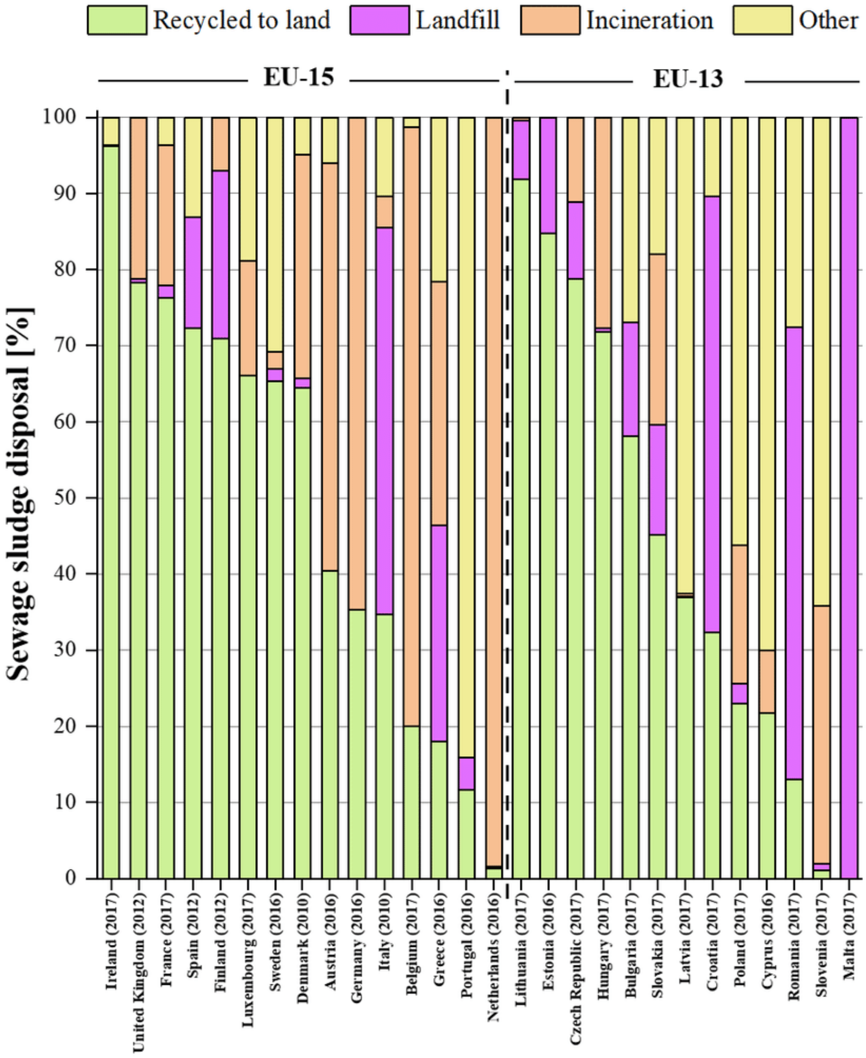


Figure 2.3 - Sewage sludge disposal routes in Europe (2019) [5]

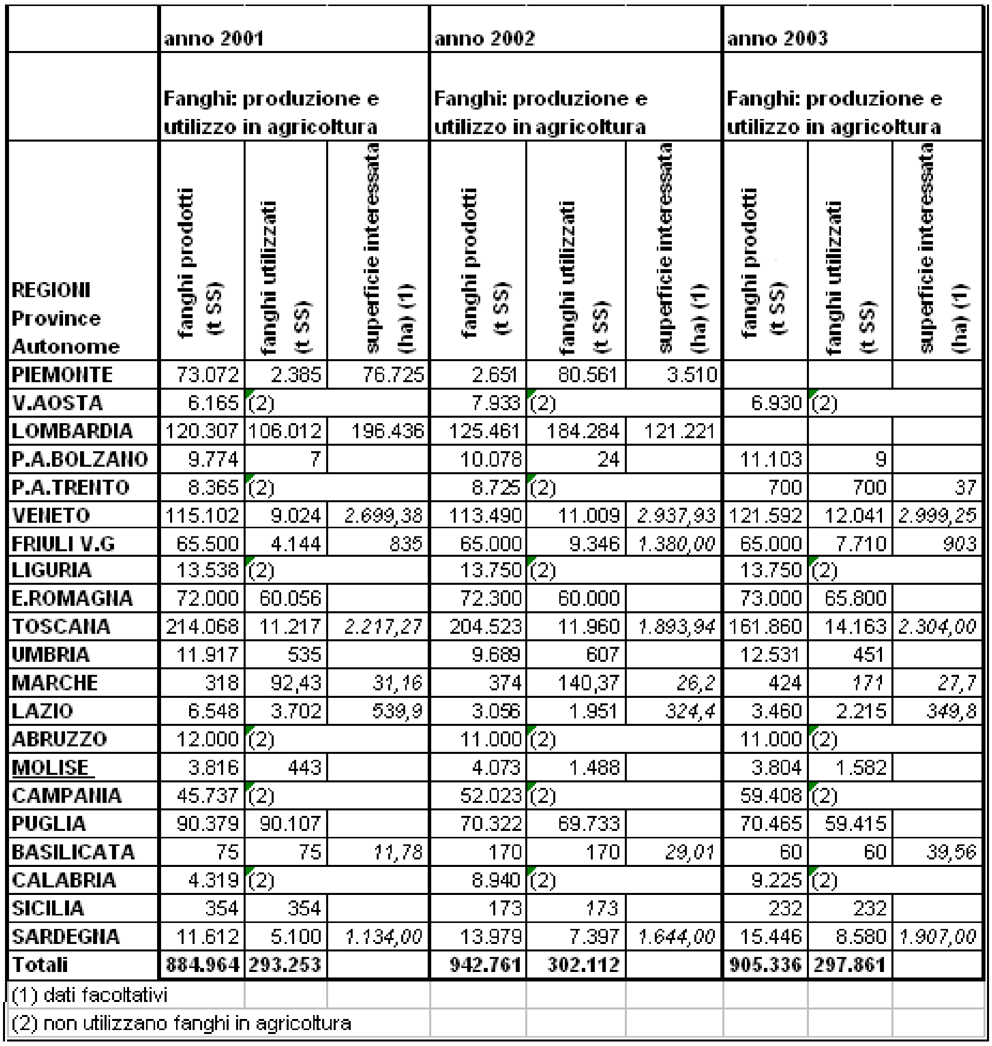
Figure 2.3 summarises the situation in Europe in terms of various sludge recovery routes methods: as can be seen, in most of the countries, landfilling and agricultural land spreading together account for almost the total percentage.

In Italy sludge is generally considered a waste to be disposed of through spreading on land or landfilling. In relation to changing boundary conditions, such as the ever-increasing quantities produced as a result of the growing number of sewage treatment plants and more restrictive regulations, it is necessary to find alternative ways of reusing sludge and the use of new sewage technologies that allow reducing its production.

At EU level, the use of sewage sludge in agriculture, regulated by Directive 86/278/EEC, reaches 40% of the total sludge produced; in Italy, a reuse rate of 32% was reached in 2003.

Table 2.5 shows the data acquired by the Ministry for the Environment and Protection of Land and Sea, transmitted to the European Commission, in fulfilment of the obligations deriving from the implementation of Directive 86/278/EEC, on the production of sludge and its use in agriculture for the years 2001, 2002, 2003.

Table 2.3 - Data acquired by the Ministry of the Environment and Protection of Land and Sea, transmitted to the European Commission, in fulfilment of obligations arising from the implementation of Directive 86/278/EEC



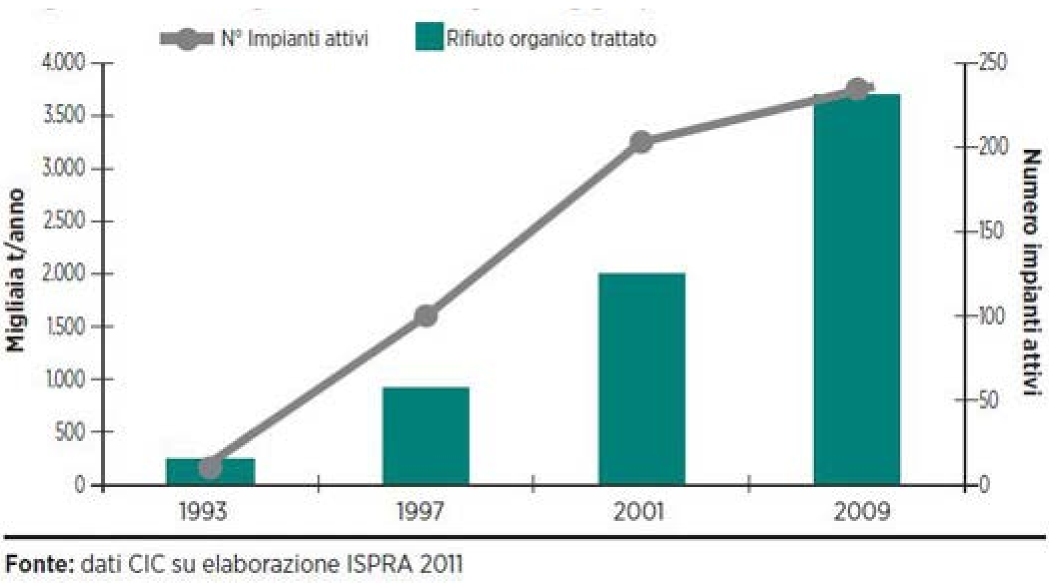
	anno 2001			**anno 2002**			**anno 2003**		
	Fanghi: produzione e utilizzo in agricoltura			**Fanghi: produzione e utilizzo in agricoltura**			**Fanghi: produzione e utilizzo in agricoltura**		
REGIONI Province Autonome	**fanghi prodotti (t SS)**	**fanghi utilizzati (t SS)**	**superficie interessata (ha) (1)**	**fanghi prodotti (t SS)**	**fanghi utilizzati (t SS)**	**superficie interessata (ha) (1)**	**fanghi prodotti (t SS)**	**fanghi utilizzati (t SS)**	**superficie interessata (ha) (1)**
PIEMONTE	73.072	2.385	76.725	2.651	80.561	3.510			
V.AOSTA	6.165	(2)		7.933	(2)		6.930	(2)	
LOMBARDIA	120.307	106.012	196.436	125.461	184.284	121.221			
P.A.BOLZANO	9.774	7		10.078	24		11.103	9	
P.A.TRENTO	8.365	(2)		8.725	(2)		700	700	*37*
VENETO	115.102	9.024	*2.699,38*	113.490	11.009	*2.937,93*	121.592	12.041	*2.999,25*
FRIULI V.G	65.500	4.144	*835*	65.000	9.346	*1.380,00*	65.000	7.710	*903*
LIGURIA	13.538	(2)		13.750	(2)		13.750	(2)	
E.ROMAGNA	72.000	60.056		72.300	60.000		73.000	65.800	
TOSCANA	214.068	11.217	*2.217,27*	204.523	11.960	*1.893,94*	161.860	14.163	*2.304,00*
UMBRIA	11.917	535		9.689	607		12.531	451	
MARCHE	318	92,43	*31,16*	374	140,37	*26,2*	424	*171*	*27,7*
LAZIO	6.548	3.702	*539,9*	3.056	1.951	*324,4*	3.460	2.215	*349,8*
ABRUZZO	12.000	(2)		11.000	(2)		11.000	(2)	
MOLISE	3.816	443		4.073	1.488		3.804	1.582	
CAMPANIA	45.737	(2)		52.023	(2)		59.408	(2)	
PUGLIA	90.379	90.107		70.322	69.733		70.465	59.415	
BASILICATA	75	75	*11,78*	170	170	*29,01*	60	60	*39,56*
CALABRIA	4.319	(2)		8.940	(2)		9.225	(2)	
SICILIA	354	354		173	*173*		232	232	
SARDEGNA	11.612	5.100	*1.134,00*	13.979	7.397	*1.644,00*	15.446	8.580	*1.907,00*
Totali	**884.964**	**293.253**		**942.761**	**302.112**		**905.336**	**297.861**	

(1) dati facoltativi

(2) non utilizzano fanghi in agricoltura

The agronomic reuse of sludge, either directly or after composting, is a valid solution to the problem of sewage sludge disposal and is of considerable interest due to its agronomic and economic effectiveness, as it replaces, in whole or in part, chemical fertilisation or other types of organic fertilisation. To avoid any risk to the environment and health, this way of managing sludge must be practiced in full compliance with the regulation, in particular regarding soil and sludge testing.

The number of composting plants has exceeded 200 for some years now. In 2009, almost 250 composted soil improver production plants were registered, that fulfils the criteria identified by Law No 748/84. If we observe the evolution of the data regarding the "composting system" (Figure 2.4), since 1993 there has been a constant increase in both the quantity of organic waste treated and the number of dedicated plants. The distribution of the plants on the Italian territory is still not homogeneous. In fact, it can be observed (Figure 1.5) that there is a greater concentration of plants in Northern Italy where approximately 2,0000,000 t/year are treated in the regions of Lombardy, Emilia-Romagna, and Veneto alone. The quantities of organic waste treated by composting in Southern Italy are significant, even if the development of separate collection is still a slow process.



Fonte: dati CIC su elaborazione ISPRA 2011

Figure 2.4 - Development of the treatment capacity of organic fractions and composting plants, years 1993-2009

In terms of co-firing sewage sludge, the Italian experience is that of the Piacenza waste-to-energy plant, which already disposed of municipal solid waste, wood and non-recoverable packaging. This plant had to undergo plant adjustments in order to solve the management problems associated with the co-firing of sludge [4],

In the autonomous province of Trento, until the end of the 1980s, the destination of residual sludge from public sewage treatment was controlled landfill. This practice was rather expensive and took up significant volumes in landfills intended for MSW. Since the mid-1980s, new disposal systems were therefore introduced, such as composting first and thermal drying later, to reduce the mass and allow the sludge to be reused in agriculture.

The propensity of the last twenty years to recover sewage sludge for agronomic purposes has, however, recently been questioned, so that future scenarios foresee the increasing use of drying and/or thermo-reduction systems for residues, with an inevitable increase in disposal costs, which are now very low in recovery and reuse practices. An interesting and economically sustainable alternative, even on a medium scale, is represented by wet oxidation processes of the volatile fraction of sludge in superheated and pressurised water. This solution was adopted by the centralised urban sewage sludge treatment plant, with a capacity of 300 t/y in terms of total dry matter, in the update of the waste disposal plan of the Province of Trento [4].

Table 2.4 - Composting of waste, by region (tons), year 2020
(source ISPRA report on municipal waste 2021)

Region	No. of operating plants	Authorized quantity	Total waste treated	Types of waste treated (t/a)			
				Wet fraction	Green waste	Sludge	Other (1)
Piemonte	18	415.899	261.066	74.802	121.770	31.176	33.318
Valle d'Aosta	0	-	-	-	-	-	-
Lombardia	64	1.369.875	983.055	189.851	560.748	68.244	164.212
Trentino-Alto Adige	11	67.760	39.048	11.892	21.960	-	5.196
Veneto	53	560.314	430.516	94.737	199.016	109.778	26.985
Friuli-Venezia Giulia	15	223.292	56.626	7.562	48.623	-	441
Liguria	6	50.852	24.339	77	22.350	-	1.912
Emilia-Romagna	10	247.750	214.696	59.081	129.616	15.595	10.404
North	177	2.935.742	2.009.346	438.002	1.104.083	224.793	242.468
Toscana	18	572.800	321.919	207.596	80.055	20.039	14.229
Umbria	2	87.000	30.841	-	8.876	7.826	14.139
Marche	6	157.400	116.920	75.888	18.886	15.433	6.713
Lazio	17	339.325	138.160	38.982	73.462	15.862	9.854
Centre	43	1.156.525	607.840	322.466	181.279	59.160	44.935
Abruzzo	6	204.450	180.643	139.983	13.689	23.572	3.399
Molise	2	32.400	19.214	15.622	1.895	1.555	142
Campania	4	164.200	98.595	72.428	4.757	13.363	8.047
Puglia	7	284.250	238.173	211.380	15.702	1.152	9.939
Basilicata	0	-	-	-	-	-	-
Calabria	11	144.700	134.909	129.059	5.781	-	69
Sicilia	22	537.285	452.169	257.777	43.387	141.898	9.107
Sardegna	21	337.700	222.045	176.765	37.409	4	7.867
South	73	1.704.985	1.345.748	1.003.014	122.620	181.544	38.570
ITALIA	293	5.797.252	3.962.934	1.763.482	1.407.982	465.497	325.973

(1) Paper, cardboard, wood waste, waste from industrial sectors (agri-food, textiles, paper, wood), waste from aerobic and anaerobic treatment of waste.

Considering the extent of the problem, which is now worldwide, it is interesting to see how it has been addressed by one of the most industrialised countries, such as the United States. Here, each city has the power to decide how to manage the disposal of its biomass, within guidelines from the EPA (Environmental Protection Agency), the state and local regulatory agencies. Popular methods for their disposal include various applications in agriculture and use as filler in soils.

Recently, two federal agencies, the Center for Disease Control and Protection and the National Institute of Occupational Safety and Health, have issued warnings regarding disposal by land application, aimed at limiting workers' exposure to biomass and restricting public access to landfill sites.

The traditional method used to solve this problem is the incineration of biomass with energy recovery. More than 170 plants dedicated to sewage sludge incineration are currently operating in the United States; three types of incinerators are used for this purpose:

- Multiple Hearth (-80% of the total);
- Fluidised Bed (~ 15% of the total);
- Electric Infrared (~ 3% of the total).

The remaining 2% goes to co-firing plants with very small quantities of coal and other waste materials, mostly municipal solid waste (MSW), wood and agricultural waste.

Co-combustion of municipal solid waste-sludge is performed in two different ways: by means of MSW combustion technologies with the addition of dehydrated and/or dried sludge or through sludge combustion technologies with the addition of MSW as an auxiliary fuel.

All oxidation reactions generally take place very quickly in a single combustion chamber. However, together carbon, hydrogen and oxygen, biomass contains other chemical elements that combine with oxygen and nitrogen in the air to give rise to secondary reactions responsible for the production of pollutants.

At high temperatures, nitrogen can combine with oxygen to give rise to nitrogen oxides (NOx); sulphur contained in biomass reacts with oxygen to generate sulphur oxides (SOx), while chlorine and unburnt hydrocarbons can produce dioxins and furans. In addition, at high reactor temperatures, traces of heavy metals, such as mercury and lead, may be vaporised. Secondary reactions may prevent the complete oxidation of hydrocarbons, resulting in the presence of unburnt hydrocarbons and carbon monoxide (CO) in the flue gas.

In the US, atmospheric emissions of pollutants and particulate matter (PM) are regulated and controlled by the US EPA and other national agencies. Incineration plants must therefore necessarily be equipped with devices for flushing and treating gaseous effluents:

- dry or wet scrubbers are used for acid gas elimination,
- a large part of the particulate matter is removed through cyclones,
- while residual particles are captured by means of electrostatic precipitators,
- unburnt hydrocarbons are abated in afterburners or catalytic converters,
- the removal of heavy metals, dioxins and furans is achieved using activated carbon,
- NOx are removed by washing the gaseous stream with an ammonia solution.

In order to limit pollutant emissions while complying with laws, which are even more restrictive in Europe, the costs of exhaust gas treatment equipment can sometimes exceed those for power generation.

2.5 Regulations

In the current scenario of municipal sewage sludge disposal systems, the current italian regulations governing the processes of landfill, composting and reuse in agriculture are increasingly restrictive.

Landfill

The I.D. of 27 July 1984 stated that “non-toxic and noxious sludge, stabilised and palatable, deriving from sewage treatment plants, originating exclusively from civil settlements, as well as sludge with similar characteristics to the above” could be disposed of in first class landfills, together with urban waste, and assimilated without any limitation regarding the content of organic substance and/or contaminants, provided that they are not classifiable as toxic and harmful. With the full entry into force of the Ministerial Decree of 3 August 2005, the presence of organic matter in sewage sludge, for the purposes of its disposal in landfills, has become an issue.

The aforementioned decree prohibits sewage sludge from being disposed of unless the plants use distinct lots separated from the other waste, equipped with technological devices suitable for the management of organic waste, or the managing bodies install thermal drying systems, in order to reduce the moisture content and thus the volumes. Sewage sludge is not mentioned among the wastes that can be accepted in landfills without prior assessment. With regard to this disposal route, the decree itself prescribes the following tests:

- Basic characterisation: this consists of determining the characteristics of the waste by collecting all the information required for safe final disposal. The data to be provided are: source of origin of the waste; information on the process that produced the waste; description of the waste treatment carried out according to Legislative Decree 13 January 2003; data on the composition of the waste and leachate behaviour, if present; appearance of the waste; European Waste List code; for hazardous waste, the properties that make it hazardous; information showing that the waste does not fall under the exclusions in art. 6, paragraph 1 of Legislative Decree 13 January 2003, No 36; category of landfill to which the waste is admissible; any additional prescription; direct control and verification of the possible recycling or recovery of the waste.
- Verification of compliance: this is used to establish whether the waste deemed eligible for a given landfill category, by means of basic characterisation, possesses the characteristics of the relevant category and whether it meets the eligibility criteria set out hi the Ministerial Decree of 3 August 2005; it is carried out by the Operator on the basis of the data provided by the producer during characterisation.
- On-site verification: this consists of the inspection of each load of waste, before and after unloading, carried out by the plant operator and the checking of documentation proving that the waste complies with the eligibility criteria of the decree for the specific category of landfill.

Among the parameters to be checked in the basic characterisation and compliance verification, in addition to organic and inorganic pollutants, are Total Organic Carbon (TOC) on waste as such and Dissolved Organic Carbon (DOC) on eluate. These two parameters are considered by the legislator to be "very sensitive", and therefore very restrictive limit values for landfill admissibility are set out in Table 2.5.

Table 2.5 - Limit values for landfill admissibility [6]

	TOC (Limit value on the as-received waste, with reference to organic substances chemically active)	DOC (limit value on eluate)
Landfills for non-hazardous waste	Max 5%	80 mg/l
Landfills for Hazardous waste	Max 6%	100 mg/l

It is clear that these limit values cannot be respected for sewage sludge from domestic and similar wastewater treatment: in fact, it is considered appropriate to use it in agriculture as soil improver, due to its high contribution of organic substance, both as TOC and DOC. Therefore, there is a real risk that sewage sludge could no longer be disposed of in landfills, neither in those for non-hazardous waste nor in those for hazardous waste.

Composting

Ministerial Decree No. 186 of 5 April 2006 represents the amendment of Ministerial Decree No. 186 of 5 February 1998 and relates to the recovery of non-hazardous waste in a simplified procedure. With the entry into force of this decree:

- the maximum amount of non-hazardous waste accumulable is reduced for the various installations,
- Annex 4 establishes the maximum annual quantities of non-hazardous waste that may be recovered; the quantities may never exceed the authorized capacity, i.e. the capacity indicated in the Notification of Commencement of business, or the plant capacity, which must be respected even when different types of waste are treated.

Reuse in agricolture

The purpose of Legislative Decree 99 of 27 January 1992 is to regulate the use of sewage sludge in agriculture in such a way as to avoid harmful effects on soil, vegetation, animals and man, while encouraging its correct use. The decree defines: 'Sludge: the residues resulting from the purification processes of wastewater coming exclusively from civil settlements, civil and productive settlements, exclusively from productive settlements. [...] Use: the recovery of said sludge by spreading it on the soil or any other application on and in the soil’. According to the decree, sludge may be used in agriculture only if the following conditions are met:

- they underwent specific treatment,
- are suitable for producing a fertilising and/or soil-conditioning effect,
- they do not contain toxic and harmful and/or persistent and/or bioaccumulative substances in concentrations harmful to soil, crops, animals, humans and the environment in general.

The use of sludge is permitted if the concentration of one or more heavy metals in the soil does not exceed the limit values set out in Table 2.6, or if these limit values are not exceeded as a result of the use of the sludge. Sludge can be used which, at the time of its use in agriculture, does not exceed the limit values for concentrations of heavy metals and other parameters also set out in Table 2.6.

Sludge may be applied to soils in doses not exceeding 15 t/ha of dry matter over a three-year period, provided the soils have the following characteristics:

- cation exchange capacity (c.s.c.) greater than 15 meg/100 g,
- pH between 6.0 and 7.5.

If sludge is used on soils whose pH is below 6 and whose c.s.c. is below 15, the quantities of sludge used can be reduced by 50% to take into account the increased mobility of heavy metals and their increased absorption by crops. If the soil pH is above 7.5, the quantities of sludge used can be increased by 50%.

Table 2.6 - Limit values for heavy metals: in agriculture land intended for sludge and in sludge intended for agricultural use [7]

	Maximum heavy metal concentration values [mg/kgSS]	
Heavy metals	In agricultural soils intended for the use of sludge	In sludge intended for use in agriculture
Cadmium (Cd)	1.5	20
Chrome (Cr)	-	200
Copper (Cu)	100	1000
Mercury (Hg)	1	10
Nickel (Ni)	75	300
Lead (Pb)	100	750
Zinc (Zn)	300	2500
Arsenic (As)	-	20

Sludge from the agro-food industry may be used in quantities up to three times the quantities specified in paragraph 4. In this case the heavy metal limits may not exceed values equal to one fifth of those in Table 2.6.

Sludge can be used as a constituent of artificial substrates of floricultural crops on benches, in compliance with the above-mentioned standard, environmental protection and the health of the operators in the sector. In particular:

a) the sludge used must be dehydrated and its moisture content must not exceed the limit of 80% expressed on the as-received basis,

b) the sludge must have an analytical composition within the limits of Table 1.7;

c) the artificial growing medium must contain no more than 20 per cent sludge.

Table 2.7 - Agronomic and microbiological parameters
in sludge intended for use in agriculture [7]

Organic carbon % SS (min.)	< 20
Total phosphorus (P) %SS (min.)	< 0,4
Total nitrogen (N) %SS (min.)	< 1,5
Salmonellae MPN/gSS (max.)	< 1000

Chapter 3
Gasification theory

In this chapter, the basics of biomass gasification and the reactions involved are described. Due to the importance of gasifier design over the conversion process, two common types of gasification technologies are presented and reviewed in some detail with respect to their functioning scheme, advantages, and drawbacks. Then the factors that noticeably affect the gasifier performance such as biomass feedstock type, operating conditions and gasifying agents, are highlighted and explained. The last section introduces and examines the main syngas cleaning techniques.

3.1 Introduction

Gasification is a thermochemical process of partial oxidation that allows the conversion of carbonaceous materials, such as biomass and fossil fuels-based ones, into a gaseous fuel-rich product and small quantities of char and ash. The process is carried out at high temperatures (typically >700 °C), in a reducing environment, using a controlled amount of oxidizing agent (usually air, oxygen or steam), to avoid the direct and complete combustion of the reactants [8].

The resulting gas mixture, called *syngas* (from synthesis gas) or producer gas, is almost entirely composed of carbon monoxide (CO), hydrogen (H_2), methane (CH_4) and traces of non-condensable hydrocarbons as desired products, and of other undesired species like carbon dioxide (CO_2) and water, coming from the completely oxidize part of the feedstock material. If air is used in the oxidization step as a gasifying carrier, then inert nitrogen (N_2) is also present.

The remaining part of the producer gas generally consists of condensable compounds (a complex mixture of heavy hydrocarbons and free carbon called *tar*) and of contaminants such as particulate, alkali metals, ammonia, and inorganic acid gases (H_2S and HCl) [9–11]. The gasification end products also include, to a limited extent, a solid phase, called *ash*, consisting in the inert materials present in the feedstock and the un-reacted char. The char in the ashes is a very low percentage of the total ash amount, generally lower than 1 wt%, the transformation of the carbon matrix in gas being the objective of the overall process [12,13]. A fraction of the unconverted biomass material (ash and char), soot and fines are typically entrained with the gas stream in the form of particulates, which, if not removed, together with tars, can induce severe operational problems and damages.

Among the thermochemical conversion processes, gasification is regarded as the most promising technology that can exploit the embedded energy within various kinds of biomass and transform them into valuable products. It has several advantages over combustion and pyrolysis, mainly related to the possibility of obtaining a final gas mixture that can be suited for second use apparatus and employed as an intermediate with flexibility for many industrial applications.

The limited uses and difficulty in downstream processing of bio-oil produced via biomass pyrolysis have restricted the wide application of this technology [14]. Direct combustion, instead, even being the most common and technically easiest way to extract energy from biomass, can only provide heat or electricity. Moreover, it generally has a lower thermal efficiency than the gasification does [15], because the gas produced by the latter process can be combusted at higher temperatures so that the thermodynamic upper limit to the efficiency defined by Carnot's rule is higher.

Gasification can be considered an upgrading process that takes in a solid which is difficult to handle, strip it of undesirable constituents and convert it into a gaseous product that can be handled with maximum convenience and minimum cost and can readily be purified to a clean fuel or feedstock for synthesis of other chemicals [14].

Syngas is most used for heat production and for generation of mechanical and electrical power, including integrated combined cycles (IGCCs), by using it to fuel boiler burners or in a more efficient way by burning it directly in gas reciprocating engines or by powering gas turbines.

However, its main components, carbon monoxide and hydrogen, can also offer the basic building blocks for producing valuable products as chemicals and fuels. Biomass gasification can therefore target the final production of methanol and hydrogen, dimethyl ether (DME), substitute natural gas (SNG), Fischer–Tropsch synthetic fuels and fertilizers.

Syngas may also be used as the hydrogen source in fuel cells, even if it often requires additional processing and reforming to remove the contaminants and other gases such as CO and CO2. Solid oxide fuel cells can operate on 100% producer gas [16].

For some materials gasification can be an alternative to landfilling and incineration, resulting in lowered emissions of atmospheric pollutants such as methane and particulates. Some gasification processes aim at refining out corrosive ash elements such as chloride and potassium, allowing clean gas production from otherwise problematic feedstock material

The conversion of biomass by gasification into a fuel suitable for various use ranging from production of chemicals, electricity, and heating increases greatly to a large extent the potential usefulness of biomass as a renewable resource [17].

Gasification is a robust proven technology that can be considered as the enabling one for modern biomass utilization. However, challenges remain in biomass gasifier design and gasification model for viable commercial application through reliable model prediction and optimization of the process condition to obtain quality product syngas compositions and maximal efficiencies.

3.2 Chemistry of gasification

As we discussed earlier, gasification takes place in an oxygen-poor environment, meaning it uses typically only 25 to 40 % of the theoretical oxidant (either pure oxygen or air) required for the stoichiometric combustion of the same amount of fuel. In these conditions, the material to be treated undergoes partial or incomplete combustion, while the unoxidized part, in the presence of high temperature (up to 1000 °C) and controlled amounts of gasifying agents, gives rise to a gaseous mixture which still has energy potential. The heat released by partial oxidation provides the chemical energy needed to carry out the whole process of drying and decomposing the incoming feedstock, sustaining the principal endothermic reduction reactions, and increasing the temperature of the final gasification products.

Biomass gasification is a quite complex process involving a series of interconnected chemical and physical phenomena. However, a natural description of a typical biomass gasification takes the form of the following major stages [17-19]:

- Preheating and drying
- Thermal decomposition or pyrolysis
- Combustion and cracking
- Char gasification (reduction)

Though these steps are frequently understood in series as if they were localized in different areas of the reactor, there is no sharp boundary between them, and they often overlap and occur concurrently, which in any case do not affect the validity of the simplified model of the overall process.

The process is initially endothermic, it is therefore necessary to provide a certain activation energy. Once fully operational, the process becomes exothermic and self-sustaining.

A schematic presentation of these processes is shown in Figure 3.1

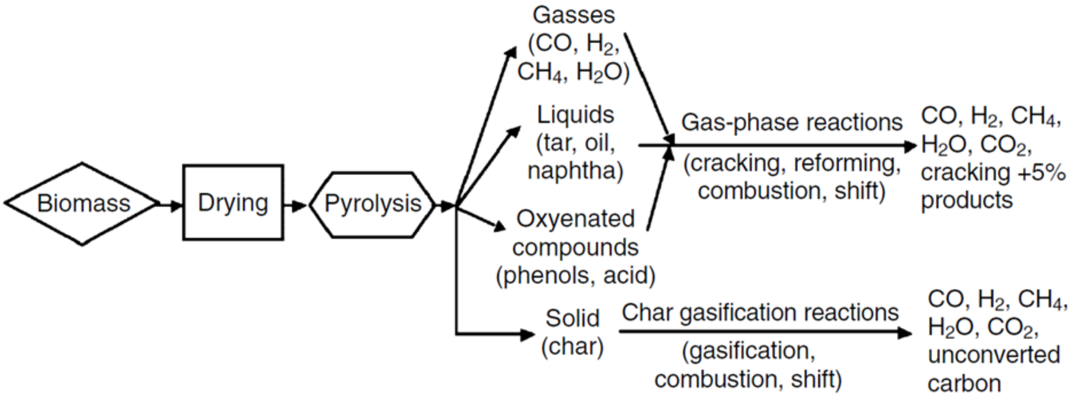


Figure 3.1 - Reaction sequence for gasification of coal or biomass [8].

Preheating and drying

This endothermic stage consists in the evaporation of the water present in the material as moisture. The typical moisture content of biomass ranges from 30 to 60%, and in some rare cases it can reach 90%. To produce a fuel gas with a reasonably high heating value, most gasification systems use dry biomass with a moisture content of 10 to 20%. Pre-drying is therefore necessary to remove as much moisture as possible before the biomass charge is introduced into the gasifier.

The final drying it’s relatively fast and takes place after the feed enters the gasifier, where it receives heat from the hot zone downstream. Above 100 °C, the loosely bound water that is in the biomass is irreversibly removed. As the temperature rises, the low-molecular-weight extractives start volatilizing. This process continues until a temperature of approximately 200 °C is reached.

Pyrolysis

Pyrolysis is a rather complex process, but it is essentially the irreversible decomposition of the organic compounds of the original biomass, in an inert (low oxygen) atmosphere, achieved by heating it to high temperatures ranging from 200 to 700°C [20]: this causes the thermochemical breakdown of its complex hydrocarbon molecules into small and medium-sized ones, but no major chemical reaction with oxygen occurs. The volatile substances are driven off as gases, and the fixed carbon-to-carbon chains are what remains. Upon completion, pyrolysis gives rise to light permanent gases (like H2, CO, CH4 etc), tar (condensable hydrocarbon vapors) and a porous carbon-rich solid residue (*char*) [21]. The proportions of these components are influenced by the chemical composition of the biomass and the operating conditions of the gasifier, such as pressure, temperature, heating rate, residence time and heat losses.

It is seen that the output gas of the gasification process depends upon the properties of the char that is produced in the pyrolysis step. In general, the reactivity of the char determines the rate of the reduction reaction and thus determines the residence time of the gasification process [22].

Combustion

An oxidation zone is formed in the section where the gasifying medium is supplied. The combustible gases (mainly H2, CO and CH4), vapors and char coming from the previous stage react with the oxidizing agent, to primarily form carbon dioxide, water, and small amounts of carbon monoxide. Since the amount of oxygen introduced is lower than the stoichiometric one, it affects only a part of the fuel present.

These combustion reactions are highly exothermic and cause a rapid temperature increase, up to 1000-1200°C. The thermal energy that is generated is essential to ensure the smooth course of the entire gasification process.

The high temperatures produced lead to the simultaneous thermal cracking of the large complex molecules (tars and oils) coming from the pyrolysis zone, into lighter hydrocarbons by exposure to heat. This process is crucial to produce a clean syngas, that is compatible with downstream equipment.

Gasification

Once the oxygen present has been completely exhausted, the hot gaseous products of combustion and the residual char react with each other, giving rise to the gas mixture representing the final product of gasification. This stage involves a series of globally endothermic heterogeneous and homogeneous reactions among which the most important are carbon dioxide-char reduction, steam-char reduction (water–gas reaction) and methanation. The energy needed comes from the oxidation step hence the decrease in the characteristic temperature of this zone (800-1000°C)

Gasification yields combustible gases such as hydrogen, carbon monoxide, and methane [8]. The so-called CO shift reaction can also take place, which increases the hydrogen content of the gasification product at the expense of carbon monoxide. Unconverted carbon and ashes are what remains after the gasification stage.

Gasification proceeds through a great number of simultaneous or consecutive complex reactions. The main chemical reactions could be classified into two major groups, that is, the heterogeneous (gas-solid phase) and homogeneous (gaseous phase) reactions, as shown in the following table 2.1.

Table 3.1 - Typical Gasification Reactions at 25 °C [23]

Reaction equation	**Heat of Reaction** [(a)] (MJ/kmol)	**Reaction Name**	**Type**
Biomass Pyrolysis			
R1 $Biomass + heat \rightarrow Char + Tar + H_2O + Light\ gas$	Endothermic	Devolatilization	heterogeneous
Oxidation Reactions			
R2 $C + \frac{1}{2} O_2 \rightarrow CO$	- 111	Carbon partial oxidation	heterogeneous
R3 $CO + \frac{1}{2} O_2 \rightarrow CO_2$	- 283	Carbon monoxide oxidation	homogeneous
R4 $C + O_2 \rightarrow CO_2$	- 394	Carbon oxidation	heterogeneous
R5 $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	- 242	Hydrogen oxidation	homogeneous
R6 $C_nH_m + n/2\ O_2 \rightarrow nCO + m/2\ H_2$	Exothermic	C_nH_m partial oxidation	homogeneous
Gasification reactions involving steam			
R7 $C + H_2O \leftrightarrow CO + H_2$	+ 131	Water-gas reaction	heterogeneous
R8 $CO + H_2O \leftrightarrow CO_2 + H_2$	- 41	Water- gas shift reaction	homogeneous
R9 $CH_4 + H_2O \leftrightarrow CO + 3H_2$	+ 206	Steam methane reforming	homogeneous
R10 $C_nH_m + nH_2O \leftrightarrow nCO + (n + m/2)\ H_2$	Endothermic	Steam reforming	homogeneous
Gasification reaction involving Hydrogen			
R11 $C + 2H_2 \leftrightarrow CH_4$	- 75	Hydrogasification	heterogeneous
R12 $CO + 3H_2 \leftrightarrow CH_4 + H_2O$	- 206	Methanation	homogeneous
Gasification reaction involving carbon dioxide			
R13 $C + CO_2 \leftrightarrow 2CO$	+ 172	Boudouard reaction	heterogeneous
R14 $C_nH_m + nCO_2 \leftrightarrow 2nCO + m/2\ H_2$	Endothermic	Dry reforming	homogeneous
Decomposition reaction of tars and hydrocarbons [(b)]			
R15 $pC_xH_y \rightarrow qC_nH_m + rH_2$	Endothermic	Dehydrogenation	homogeneous
R16 $C_nH_m \rightarrow nC + m/2\ H_2$	Endothermic	Carbonization	Heterogeneous

[(a)] *A positive sign indicates an endothermic reaction, and a negative sign indicates an exothermic reaction.*

[(b)] *CxHy represents tars and, in general, the heavier fuel fragments produced by thermal cracking and CnHm represents hydrocarbons with a smaller number of carbon atoms and/or a lower degree of unsaturation than CxHy*

The reaction scheme can be split into three processes: pyrolysis, gasification, and combustion. As extensively described above, solid particles are heated to undergo drying and pyrolysis first (R1). Subsequently, the volatile matter, as well as char, are oxidized (R2-R6) or, as in the case of heavier hydrocarbons, decomposed (R15-R16). Once the oxygen is exhausted, since it is supplied only in a fraction of the stoichiometric requirement for complete combustion of the solid fuel, a reducing environment arises, with carbon-containing char acting as reducing agent for the remaining gaseous compounds (R7, R11, R13). Final products contain substantial quantities of carbon monoxide (CO) and hydrogen (H2) and small quantities of methane (CH_4).

The heterogeneous gas-char reactions are the controlling step of the gasification process since they are much slower both than biomass devolatilization (R1), that produces the char, and homogeneous reactions. Achieving an efficient and complete char conversion is therefore of extreme importance in biomass gasification in order to realize a competitive technical performance. Char is present even at high temperatures, and it is in part discharged as unconverted carbon in the rejected ash, so determining loss of conversion efficiency.

Among all the heterogeneous ones, the main reduction reactions between the solid char and the gasifying agents CO2 and H2O are the Boudouard (R13) and the Water-gas (R7) reactions.

Apart from hydrogasification (R5) which is slightly exothermic, char gasification is a globally endothermic process and¬ is favored by increases in temperatures (especially reaction R13). At low temperatures (i.e around 600 °C) the equilibrium shifts excessively towards the formation of CO_2 and H_2O; the gas produced has lower calorific value and the char conversion is negatively affected too.

The exothermic oxidation reactions (R2-R6) provide the main energy source for the overall process. Reaction R4 is the best in this regard as it gives the highest amount of enthalpy (394 kJ) per mol of carbon consumed. The next best is R2, which also produces the fuel gas CO, but produces only 111 kJ/mol of heat. The speed of R2 is relatively slow. When carbon comes in contact with oxygen, both reactions can take place, but their extent depends on temperature.

The relative amounts of fuel, oxidant (air or oxygen), and steam (if used) govern the fraction of carbon or oxygen that enters R2 or R4. Any more oxidant than that needed for the endothermic reaction will increase the gasifier temperature unnecessarily as well as reduce the quality of the product by diluting it with carbon dioxide. Oxygen prefers to react with carbon (to form CO and CO_2) rather than with hydrogen to form water (so hydrogen content increases at higher temperatures).

The rate of gasification of char depends primarily on its reactivity and the reaction potential of the gasifying medium. Oxygen, for example, is the most active, followed by steam and carbon dioxide. The rate of the char–oxygen reaction (R2) is the fastest among the heterogeneous gas-solid reaction under similar conditions. Table 3.2 compares the rate of combustion and gasification for a biomass char at a typical gasifier temperature of 900 °C. The combustion rates are at least one order of magnitude faster than the gasification reaction rate.

The rate of the char–steam reaction (R7) is three to five orders of magnitude slower than that of the char–oxygen reaction. The char–carbon dioxide reaction (R13) is six to seven orders of magnitude slower. The rate of this reaction is insignificant below 750 °C [8]. The rate of the water–gas or water–steam gasification reaction (R7) is about two to five times faster than that of the Boudouard reaction (R13) [24]. The char–hydrogen reaction that forms methane

(R11) is the slowest of all. The presence of hydrogen has a strong inhibiting effect on the char gasification rate in H2O. For example, 30% hydrogen in the gasification atmosphere can reduce the gasification rate by a factor as high as 15 [25].

Table 3.2 - Comparison of the Effect of Pore Diffusion on Char Gasification and Combustion Rates

Particle Size (μm)	**Combustion Rate (min−1)**	**Gasification Rate (min−1)**	**Combustion Rate/ Gasification Rate (−)**
6350	0.648	0.042	15.4
841	5.04	0.317	15.9
74	55.9	0.975	57.3
Source: Adapted from Reed, 2002, p. II-189 [26]			

The homogeneous reactions mainly involve the reactions between the primary gaseous products and the gasifying agents. Carbon monoxide (R3) and Hydrogen (R5) oxidation are the main reactions involving the highly reactive combustible gases generated in the pyrolysis stage. Methane combustion could be considered as the sum-up of reactions R2, R5, and R10, which are mainly carried out under oxygen-sufficient conditions and would release large quantities of energy of up to 803 kJ/mol. The methane formation is a highly exothermic reaction (R12) and is preferred at low temperatures and high pressures. When the system works at atmospheric pressure, as is often required to avoid dangerous leaks of the product gas, the previous reactions reach equilibrium already at temperatures much lower than those usually present in the reaction zone: an excess of CH4 can testify to a too low temperature in the gasifier and a consequent incomplete reforming of the distillates (tar).

The water−gas shift reaction (R8) is of great importance when using steam as a gasifying medium to adjust the H2 and CO ratio of the syngas. Above 1000 °C this low exothermic reaction rapidly reaches equilibrium, but at a lower temperature it needs heterogeneous catalysts.

The highly endothermic reforming reactions of methane with H2O (R9-steam reforming) and CO2 (R13-dry reforming) are also preferred when partially adding steam or CO2 into the gasifying mediums. They progress very slowly and requires relatively low temperature and catalyst. They are limited reaction due to the low concentration of CH4 in the gasifier.

Since all the reactions listed above, apart from the oxidation ones, are equilibrium reactions, they will shift more or less towards the products depending on the operating temperature and pressure and the concentration of reagents. Specifically, an increase in temperature favors the formation of a gas richer in H2 at the expense of CO; an increase in pressure from 1 to 40 atm entails an increase in the methane content of the gases from negligible values up to over 30%, with a simultaneous reduction in the CO and H2 content and with a significant increase in the calorific value. In practice, however, the final composition is determined by reaction rates and by the presence of catalytic effects (particularly important for tar decomposition reactions) rather than by the chemical equilibrium.

Water vapor, deriving from biomass moisture, constitutional water and to a less extend from air humidity, plays a very important role in the entire gasification process. From reactions R7, R8 and R12 it can be inferred that steam acts both by favoring the production of H2 and by inhibiting the formation of CO and CH4, with a consequent increase in the syngas calorific value. Furthermore, the carbon conversion efficiency increases, while the content of unreacted char of tar, water vapor and long-chain hydrocarbons in the gaseous mixture decreases. Steam can also be introduced as gasifying medium.

Methane and other hydrocarbons, at temperatures above 600 ° C such as those in the hot reaction zone, tend to decompose (R15-R16) into gas with small molecules and with low amounts of condensed carbon.: this can also imply a remarkable decrease of tar content but only for temperature higher than 1000 °C. Anyway, a tar-free gasifier does not exist and tar removal and/or conversion is required in most cases [27, 28].

The reactions involving sulfur and nitrogen are not given in the reaction list because these heteroatoms are usually of negligible amounts and thus have little influence on the total gas composition and heating value.

3.3 Syngas characterization

As anticipated in the previous paragraphs, the purpose of gasification is to maximize the conversion of solid biomass materials, usually of little economic and energy value, into usable gas - phase compounds. The result is a synthesis gas mixture which can be utilized in a separate process equipment, even at different times or sites, representing an important fuel resource for energy and chemical industry.

Producing high-quality syngas to meet the requirements of different applications is critical to successful implementation of biomass gasification.

When it comes to the quality of syngas, the parameters typically taken into consideration are its composition, its LHV (low calorific value) and its level of contamination.

The specific composition and quantity of syngas produced depend upon biomass properties, process parameters, and the gasification approach used, both in terms of processing technology and gasifying agent (sub-stoichiometric oxygen or air, steam but also CO2, H2, and mixtures of the different oxidizers).

Table 3.3 - Composition of synthesis gas from biomass gasification [5]

Gasifier	**Biomass**	**Component (% volume, dry)**						
		CO	**H_2**	**CO_2**	**CH_4**	**C_2H_4**	**C_2H_6**	**N_2**
Downdraft	Switchgrass	12-18	7-12	10-17	-	-	-	60
Downdraft	95% hardwood chips	23.9	17	11	1.4	-	-	46.7
Downdraft (air)	N/A	21	17	13	1	-	-	48
Downdraft (O_2)	N/A	48	32	15	2	-	-	3
Downdraft	N/A	22.1	15.2	10.2	1.7	-	-	50.8
Updraft (air)	N/A	21	11	9	3	-	-	53
Multistage hybrid	Coconut shell and charcoal	17-22	11-14	10-15	1-3	-	-	50-60
Bubbling fluidized bed	Empty palm fruit husk	16.6	5.6	19.2	4.3	-	-	54
Fluidized bed	Switchgrass	14.7	4.4	16.5	4.2	2,4	-	56.8

Syngas from biomass gasification typically consists of the combustible components, carbon monoxide (CO), hydrogen (H2), and methane (CH4), along with incombustible components, carbon dioxide (CO2), water (H2O), and nitrogen (N2). Table 3.3 shows the gas compositions obtained for different feedstock, gasifying media, and gasification processes.

In addition to these compounds, raw syngas is generally contaminated by undesired products, such as particulate, ash, volatile condensable compounds (tar), sulfur compounds (H2S, COS and SO2), nitrogen compounds (NH3 and NOx), chlorinated compounds (HCl and others), heavy metals and alkalis [30, 31]. Their content must necessarily be reduced both to mitigate environmental impacts and to avoid problems, blockages, or damages to the subsequent processes to which the syngas is subjected, thus reducing efficiency, and possibly causing the failure of prime movers and other downstream devices and ultimately of the entire gasification system.

Syngas heating (calorific) value (MJ/Nm^3) is a measure of the available thermal energy produced by a gasification process. The calorific value refers to the total amount of energy released when a known volume of gas undergoes complete combustion under standard conditions. From an energy point of view, partial combustion develops only 20-30% of the theoretical calorific value. This means that the syngas retains 70 - 80% of the heating value of the original fuel.

For simply benchmarking purposes, the lower heating value (LHV) is generally considered appropriate to rate syngas quality. LHV considers energy losses such as the energy used to vaporize water. LHV is closely related to syngas chemical composition and its value ranges from 4 up to 40 MJ/Nm^3, mainly depending on the used gasifying agent [32]. It is usually calculated by means of empirical formulas on the base of the content of the combustible compounds.

The performance of the gasification process is assessed with respect to various indicators. The most important are:

- *Cold gas efficiency (CGE)*, defined as the ratio between the chemical energy contained in the product gas and the chemical energy in the incoming feedstock,

$$\mathrm{CGE} = \frac{Q_s \cdot \mathrm{LHV_s}}{\dot{m}_\mathrm{f} \cdot \mathrm{LHV_f}}$$

where Qs is the syngas volumetric flow rate (m^3/h), $\dot{m}_f$ is feedstock mass flow rate (kg/h) and $\mathrm{LHV_s}$ and $\mathrm{LHV_f}$ are the net heating value of the product gas (MJ/m^3) and the incoming feedstock (MJ/kg), respectively.

It is called ‘‘cold’’ efficiency since it does not consider the syngas sensible heat but only its potential chemical energy.

- *Hot gas efficiency (HGE)*, defined as the ratio between the sum of the chemical energy and sensible heat of the syngas (H_{out}) and the sum of the chemical energy and sensible heat (H_{in}) of the feedstock fed to the plant,

$$\mathrm{HGE} = \frac{H_{out} + Q_s \cdot \mathrm{LHV_s}}{H_{in} + \dot{m}_\mathrm{f} \cdot \mathrm{LHV_f}}$$

- *Gas yield (GY)*, represents the volume of syngas produced per unit mass of feedstock consumed in the gasifier on a dry basis (water excluded):

$$\mathrm{GY} = \frac{\mathrm{Q_s}}{\dot{m}_\mathrm{f}}$$

- *Carbon conversion (XC)*, determines the fraction of total carbon from the gasifier feedstock converted to carbon in syngas constituents,

$$XC = \frac{12 \cdot M_{CS}}{w_{C,f} \cdot \dot{m}_f}$$

where M_{CS} is the total mole flow of carbon in all carbon-bearing gaseous components in syngas (i.e. ash and tar excluded) and $w_{C,f}$ is the mass fraction of carbon in feedstock from ultimate analysis. It gives an indication of the amount of unconverted material that must be treated with other technique or sent to disposal, and then provides a measure of chemical efficiency of the process.

- *Tar content* and, when it is possible, tar composition. These are crucial parameter since tars cause problems in the process equipment as well as in the devices for end-use application [33] and moreover reduce the overall efficiency of the process. Therefore, they indicate the energy conversion or chemical synthesis devices that can be reasonably utilized, taking into account the technical and economic performance of the cleaning techniques that can be applied inside the reactor (primary measures) and/or downstream of it (secondary measures) [27, 28].
- Other parameters, such as specific energy production (i.e. the chemical energy of the syngas obtained by the mass unit of feedstock fed to the gasifier, kJ/kgf).

3.4 Key factors affecting the gasification process.

There are several factors affecting the synthesis gas quality and the performance of the gasification process. Generally, these factors are gasifier design, feedstock type and properties and operating conditions. Next each one is described.

3.4.1 Gasifier design

After analyzing the gasification process, it is useful to classify and review the main gasification technologies existing in the industry.

Gasification reactor designs have been researched for more than a century, which has resulted in the availability of several designs at the small and large scales. They can be classified in several ways [35]:

- By gasification agent: Air-blown, oxygen or steam gasifiers.
- By modes of heat transfer: Auto-thermal or direct gasifiers (heat is provided by partial combustion of biomass) and allothermal or indirect gasifiers (heat is supplied by an external source via a heat exchanger or an indirect process)
- By gasifier pressure: Atmospheric or pressurized.
- By reactor design: fixed bed (or moving bed), fluidized bed, entrained flow. The existing gasification technologies and their range of applicability are shown in Figure 3.2.

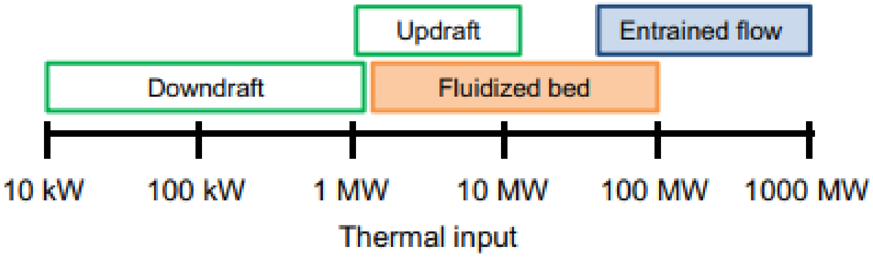


Figure 3.2 - Biomass gasifier types and range of applicability

Entrained flow technology is the most widely used gasifier type for fossil fuel gasification. However, in the case of biomass gasification, entrained flow gasifiers are not yet available on a commercial scale, and a range of other technologies are applied instead.

Two broad categories can be distinguished, with alternative form within each type, based on the characteristics of the motion to which the fuel bed is subject inside the reactor vessel, on the means of supporting the biomass and on the direction of flow of both the biomass and oxidant [36]:

1. *Fixed bed gasifiers* in which the gasifying media and the syngas move through a column of solid fuel particles supported on a gate placed on the bottom of the reactor. The biomass moves slowly downward under gravity as it is gasified. Sometimes the grate moves slowly to facilitate the descent of the fuel, as well as the separation of the ashes for subsequent evacuation. Because of the negligible mixing and heat transfer, temperature and gas composition profiles throughout the reactor are not uniform. Fixed-bed gasifiers are simple to construct and generally operate with high carbon conversion, long solid residence time, low gas velocity and low ash carry-over [37, 38].
2. *Fluidized bed gasifiers*, in which the gasifying agent is blown through a bed of solid particles (inert material and biomass) at a sufficient velocity to keep the particles in a state of suspension. Fuel particles, introduced at the bottom of the reactor, are very quickly mixed with the bed material, and almost instantaneously heated up to the bed temperature. Fluidization of the bed enhances the heat transfer to the biomass particle leading to increases in reaction rates and conversion efficiencies. The fluidized bed temperature must be kept below the ash melting point of the biomass, since a sticky ash might glue together with bed particles causing agglomeration and breakdown of fluidization. Hence, these are better suited for materials having high ash melting point e.g. woody bio-material (above 1000°C).

Around 75% of the commercial biomass gasifiers are fixed bed downdraft, 20% are fluidized bed, 2.5% are fixed bed updraft, and 2.5% corresponded to other designs [39]. Small-scale fixed-bed gasifiers are cost-effective and relatively easy to build and operate. On the other hand, most of the medium- or large-scale gasifiers are fluidized bed reactors, and they offer higher performance than fixed-bed gasifiers but at higher cost and complexity.

A) Fixed bed reactors

There are mainly three types of fixed bed gasifiers, depending on the mode of contact between the feed material and the gasifying agent:

Updraft or Counter-Current gasifier

It is the most common and proven type of gasifier. The gasifying medium enters the lower part of the reactor and ascends the solid biomass bed, with which it reacts, generating product gases that are released at the upper end. [40]

Gases and fuel flows in the opposite direction, in counter-current configuration: the downward flowing feedstock, fed from the top end, is first dried by the hot syngas exiting the reactor. After drying, the solid fuel is pyrolyzed, giving char which continues to move down to be gasified, and pyrolysis vapors which are carried upward by the hot product gas. The tars and hydrocarbons in the vapor either condense on the cool descending fuel or are carried out of the reactor with the product gas, contributing to its high calorific value but also to its high tar content. The extent of this tar bypassing is believed to be up 20% of the pyrolysis products. The condensed tars are recycled back to the reaction zone, where they are further cracked to gas and char. In the lower part of the gasifier the solid char is first reduced and finally partially oxidated near the grate by the incoming air or oxygen (Figure 3.3). The thermal profile varies from 200 ° C to ~ 1000 ° C, reaching a maximum value in the oxidation zone (around 900 ÷ 1000 ° C), and then decreasing.

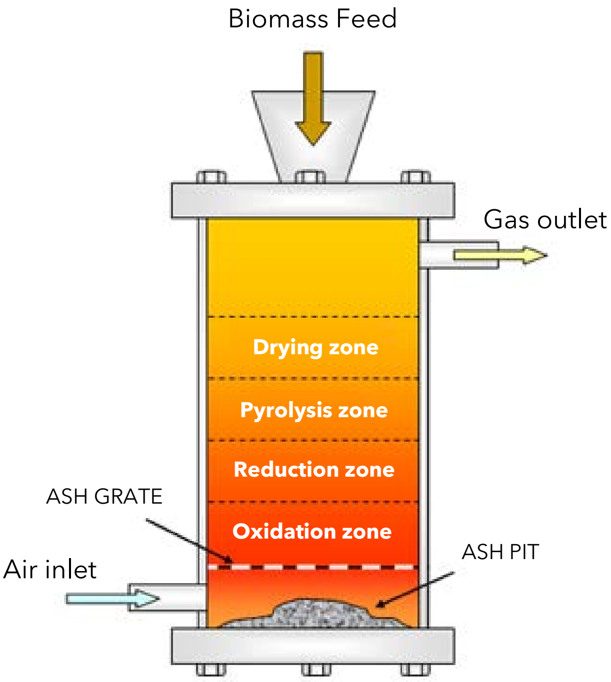


Figure 3.3 - Diagram of updraft gasification

The gasifying agent, rising upwards through the grate, is evenly distributed in the reaction bed, without the need for nozzles: flow velocity is relatively low (2.5 m/s on average) and favor rather long contact times between the reactant phases (around 0.5 s) which allow a final gas composition close to the equilibrium one.

Since syngas yield is proportional to size of the grate, which, as mentioned, acts as a flow distributor, it is easy to make gasifiers of considerable power. The grate, therefore, is an element of great importance: it supports the entire fuel column and withstands remarkably high temperatures being close to the combustion zone. It must be designed so that only the ash and not the pieces of unburnt char pass through and, moreover, it must have good mechanical, thermal and corrosion resistance. In some cases, the use of eccentrically rotating grids favors the fall of the ashes, prevents clinker formation, and facilitates the descent of the fuel column with a slight shaking.

Among its main advantages, this type of gasifier includes a great ease of ignition and high constancy of operation. Moreover, in the counter-current gasifier, the gas produced in the reduction zones undergoes a pre-filtration by the solid bed through which it flows; in this way the gas releases its sensible heat to the fuel, creating a counter-current heat exchange that leads to an overall improvement in the thermal efficiency of the process. The residual enthalpy content of the syngas can be further exploited to preheat the incoming air or oxygen: the temperature of the gas in the outlet section thus varies between 100 and 200 ° C.

Further advantages of this type of gasifier are its relatively simple design, which makes it suitable for a wide range of applications and sizes (0.2 ÷ 10 t/h) as well as its ability to accept feedstock with high moisture content, which give it a rather high potential.

The main problem of the updraft gasifier is, as already mentioned, the high content of tar and pyrolysis products which are carried away by the gas stream without undergoing any cracking.

Downdraft or Co-current gasifiers

The downdraft gasifier features concurrent flow of gases and solids through a descending packed bed. The gasifying agent enters the reactor at a certain height below its top and it mixes with the pyrolysis gas products while flowing downward in parallel with the solids (char and ash) through the oxidation and gasification zones.

The drying and pyrolysis zones lie above the oxidation layer, and they are maintained at the required temperature by conduction of the heat generated from the combustion of pyrolysis vapors (including tar precursors). The gases leaving the oxidation zone, mainly CO2 and H2O, are reduced into CO and H2 on the glowing char in the gasification area. The maximum temperature occurs in the oxidation zone, then it decreases due to the occurrence of the endothermic gasification up to a level at which no further reaction takes place. The unreacted char and the ash are discharged through a grate at the bottom in a collection chamber. The grate is usually shaken at intermitted intervals to remove fines from the char bed which otherwise clog the bed. The synthesis gas is removed from the reactor close to the ash grate. (Figure 3.2).

One of the main advantages of the co-current arrangement is the production of a fuel gas with relatively low quantity of tars (0.015-3 g/Nm3). Downdraft gasifiers can operate at a biomass conversion rate of more than 95 wt% db.

Various designs following the downdraft configuration can be found [8]:

1. Throated (also called constricted, Imbert gasifier, or V-shaped) This is the most common design among the existing downdraft gasifiers. The throated gasifier consists of a vessel with the oxidation zone located at the narrowest part of a throat, which reduces and then expands the cross-sectional area. The design ensures the pyrolysis vapors are forced to pass through the narrow oxidation zone. The gasification agent is introduced above the throat. The reaction products are intimately mixed in the high-temperature region around the throat, which aids tar cracking. Some tar cracking also occurs below the throat on a residual charcoal bed, where the gasification process is completed. This configuration results in a high conversion of pyrolysis intermediates and hence a relatively clean synthesis gas. The temperature levels achieved at the center of the oxidation zone depend on the amount of air/oxygen, blown by the nozzles, that reaches it. Thus, for each nozzles flow rate there is an upper size limit for throat diameter beyond which the air jets cannot penetrate the deeper fuel bed. This aspect practically limits the scaling-up of the Imbert design to larger sizes.
2. Throatless (also called open core or stratified) The throatless gasifier consists of an open-top non constricted cylindrical vessel with the heart at the bottom. Both the biomass and the gasifying agent are supplied from the top and flow downward through the four zones. This design is more flexible than the conventional throated version especially for biomass with troublesome flow characteristics and low bulk densities (eg, agricultural residues such as rice husk). Since all tars must pass through a hot bed of char and hence, they undergo thermal cracking, also this configuration ensures significantly low tar levels.

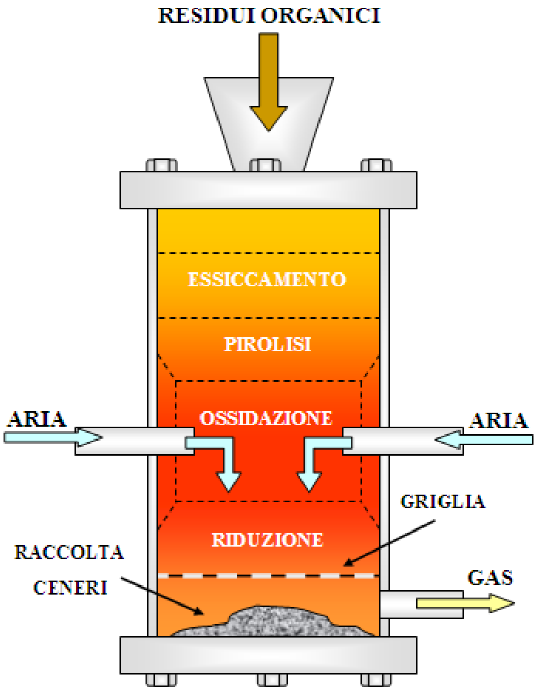


Figure 3.4 - Diagram of downdraft gasification

In the downdraft gasifier, the gas leaves the gasifier at a high temperature causing both problems for its cooling and a general worsening of the overall energy balance, unless the sensible heat of the gas is appropriately recovered, such as preheating the incoming oxidant or the solid particle bed. A further modification of the throated gasifier consists of introducing internal heat exchange by a double-walled vessel. The hot syngas, instead of coming out directly from the bottom, leaves the reactor through a surrounding annular jacket, creating a counter-current heat exchange with the air flowing downwards through a second jacket, coaxial to the first (Figure 3.5). The heat is transferred also to the biomass in the drying and biomass zone.

Another particularly important aspect to consider about this type of downdraft gasifier concerns the fuel refilling methods. The gas produced tends to move down and, even if it comes back towards the top, it does so by passing through an annular cavity not in contact with the external environment. It is therefore possible to open the gasifier to introduce new fuel and close it again without disturbing its operation excessively.

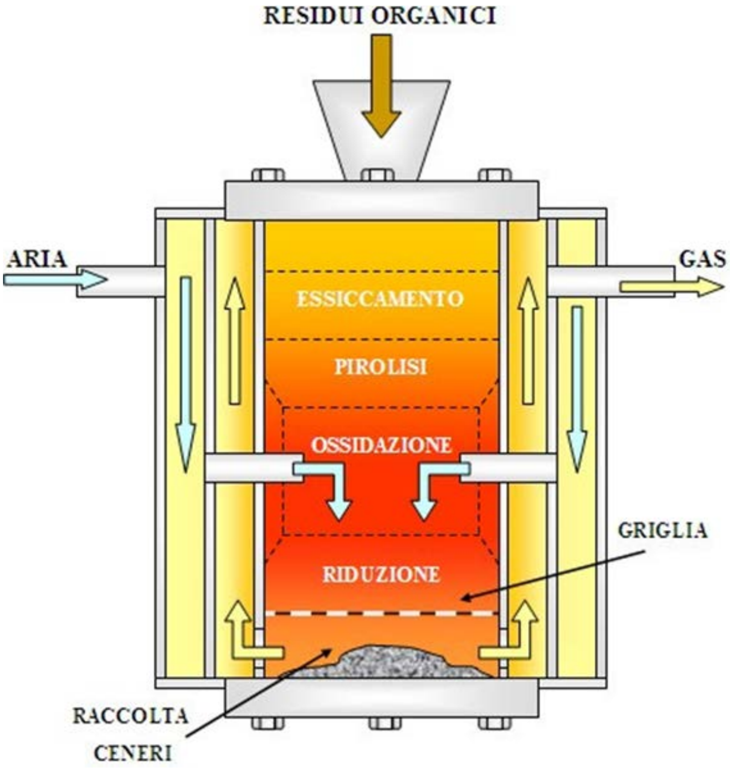


Figure 3.5 - Jacketed downdraft gasifier

The co-current gasifier is particularly sensitive to variations in the moisture content of the biomass fed, that affects both the energy efficiency of the process and the temperature of the gas leaving the reactor. Biomass size constraints are also required, which must be as homogeneous as possible in order to achieve a smooth fuel flow inside the reactor, especially in the throat section.

The high content of ash and particulate matter entrained in the outgoing syngas is another factor playing an important role against this gasifier; the gas passes through the char reduction bed collecting small particles of ashes and unburnt products.

In the Imbert type, the dimensions of the throat section and the control of the oxidant flow are critical factors; even slight variations in the throat diameter and the position of the air nozzles can lead to drastic variations in the composition of the gas and in the percentage of tars present. Furthermore, the reduction in area at the hearth and the protruding nozzles present hazards at which the passage of the fuel can be restricted, thus causing bridging and channeling followed by high tar output, as unpyrolyzed biomass falls into the reaction zone.

Crossdraft gasifiers

The cross-draft gasifier shown in Figure 3.6 is the simplest and lightest gasifier. The biomass feedstock comes from the top end of the reactor, whereas the gasifying agent is fed at high velocity through a single nozzle located on the side of the lower part of the unit. The product gas is extracted at the same level as the oxidant inlet, but from the other side of the gasifier vessel. Combustion takes place at the gasifying agent entrance, where it reacts with part of the char. giving rise to very high temperatures (>1500 °C) in a very small volume. The flue gas is reduced to CO and H2 downstream in the gasification zone. The pyrolysis and drying zones are above the high-temperature area and the heat is transferred from the oxidation zone by conduction. Ash is removed from the bottom.

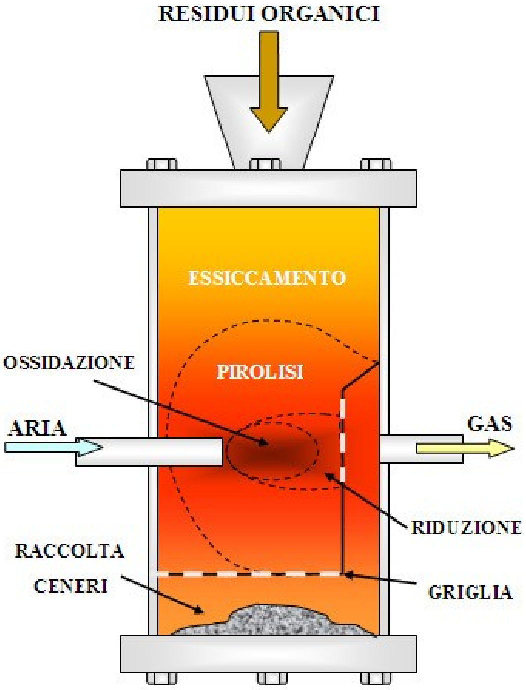


Figure 3.6 - Diagram of crossdraft gasification

Inside the reactor there is a predominance of the drying and pyrolysis areas, while the limited reactive mass present both in the oxidation and reduction areas determines a certain instability of operation. The product gas leaves at temperature around 800–900°C with a high tar content.

This gasifier design is suitable for small-scale applications (<10 kWe) because it presents a short start-up period (5-10 min) and a rapid response to load changes, and it is built with less expensive materials, except the nozzles and grates, as the solid fuel and ash surrounding the oxidation zone acts as insulation for the walls.

The main drawback is that the gas product leaves the unit at around 900-1250 °C which results in the low energy efficiency of the process. In addition, other factors are to be considered against this configuration such as: slagging issues, high levels of carbon in the ash, the possibility of using only well-selected feedstock and the production of a gas rich in particulates and tar

B) Fluidized bed gasifiers

In fluidized bed gasifiers, the biomass is introduced into a hot bed of inert (or catalytic) material which is maintained in a turbulent fluidized state by the gasifying agent (air, oxygen, steam, or their mixture) flowing upward at an appropriate rate. This fluid like bed provides excellent gas–solid mixing and solid–solid contacting to enhance reaction rates and mass/heat transfer thus leading to an isothermal reactor behavior with excellent temperature-controlling possibilities.

Drying, devolatilization, oxidation, tar reforming and gasification occur simultaneously and homogeneously in the gasifier. Fresh fuel is brought into contact with the hot bed material that quickly heat its solid particles to the bed temperature and make them undergo rapid drying and pyrolysis, producing char and condensable and non-condensable gases. Upon entering the bottom of the bed, the oxygen goes into fast exothermic reactions with the char mixed with bed materials. The bed material immediately disperses the heat released to the entire fluidized bed. Subsequent gasification reactions take place further up as the gas rises. The gas bubbles in the fluidized bed serve as the primary conduit to the top where the syngas exits the reactor. The ash is removed dry or as heavy agglomerates that de-fluidize.

Most of the gasification reactions take place within the bed however some conversion to product gas continues outside the bed owing to reactions of entrained small particles and tar cracking.

The gasifiers typically operate at moderately high temperature, between 800° and 900°C to achieve on one hand an acceptable carbon conversion rate (e.g., 90-95%) but on the other hand to avoid ash agglomeration and bed sintering with eventual loss of fluidization. Consequently, tar conversion rates are not very high. Loss of carbon in entrained ash can become significant and fluidized beds are not economical for small scale applications.

Three main configurations of fluidized bed reactors can be identified depending on both the flow rate of the fluidization/gasification medium and the number of stages in which the gasification takes place:

- Bubbling Fluidized Bed (BFB),
- Circulating (or Fast) Fluidized Bed (CFB),
- Dual Fluidized Bed (DFB)

Bubbling fluidized bed gasifier

The bubbling fluidized bed gasifier is one of the most popular designs for biomass gasification, mainly due to its applicability to medium-scale processes (<25 MWth). It is characterized by moderate fluidization velocities and the fluid mechanic behavior is dominated by gas bubbles ascending in the fluidized bed. This configuration is successfully used to process feedstocks with a wide particles size distribution.

The BFB gasifier consists of a vessel with a grid air-distribution at the bottom, through which the gasifying agent is introduced upward at a velocity fast enough (0.5–1.0 m/s) to agitate the bed material and to maintain the required temperature. The bed is initially heated with an external auxiliary burner, then, when a high enough temperature (800 ÷ 900 ° C) is reached, the biomass, reduced in small particles, is introduced continuously by a mechanical feeder in the reactor, where devolatilization occurs. Char particles and volatiles (tar precursors) are gasified and cracked by contact with the hot fluidized bed. Ash and unconverted residues remain in the reactor, except for a certain amount which is entrained by the syngas flowing out of the unit, lowering its carbon conversion efficiency.

A schematic of the bubbling fluidized bed gasifier is shown in Figure 3.7.

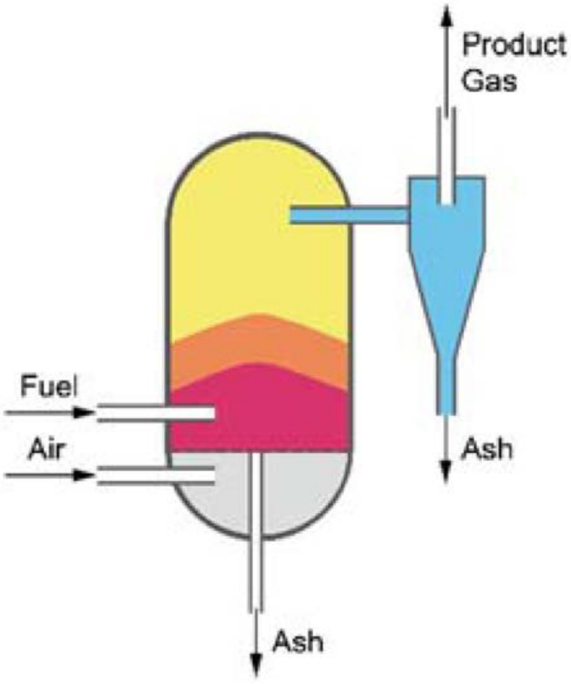


Figure 3.7 - Diagram of bubbling fluidized bed gasification

The optimal amount of gasifying medium needed to fluidize the bed and convert the biomass particles is about one fourth of that required for complete combustion, thanks to the intimate oxidant-fuel mixing that it’s achieved in the bed.

The average operating temperature is lower than the ash melting point and allows to gasify even biomass with a high content of low-melting ashes. This fundamental characteristic opens the way to the gasification of feedstocks for which, otherwise, this process could not be used, due to problems of agglomeration and clinker formation.

The major drawbacks of fluidized bed gasification are:

- Slow response to load changes, as this is connected to difficulties in accomplishing prompt variations in the biomass feeding rate. The amount of outgoing syngas is directly related to the amount of biomass fed. Conversely, increasing the flow of oxidizing agent alone without consequently acting on that of the fuel, would only decrease the energy content of the gas produced.
- The composition of the syngas is strongly dependent on that of the feedstock.
- The outgoing gas is heavily soiled with tars, unburnt carbon particles and ashes contained in the original fuel. Filters are required for their separation.
- •It takes a long time to reach steady state operation, but, on the other hand, the system has a good thermal inertia.
- This type of gasifier is better operated at high pressures, even if slightly higher than the atmospheric one.

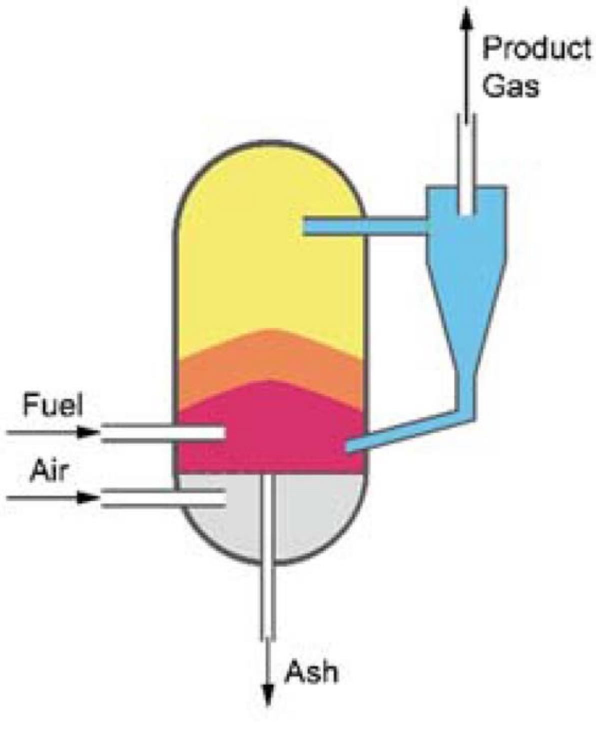


Figure 3.8 - Diagram of Circulating fluidized bed gasification.

Circulating fluidized bed gasifier

The CFB gasifier is arising as a major technology for medium- (a few MWth) to large-scale (100 MWth) biomass gasification processes, mainly due to its long residence time which makes it applicable to biomass with high volatile contents.

The gasifying agent is introduced upward at a velocity fast enough (3.5-5.5 m/s) to move the bed material throughout a circulating loop, full mixing and long residence times being achieved (see Figure 3.8) The solids unconverted residues leaving the top end along with the product gas are separated in an external gas-solid separator unit (cyclone) and returned to the bottom of the gasifier.

The CFB design overcomes some of the disadvantages exhibit by the BFB design. The gas-solid contact is better due to the absence of bubbles and prevents the gas from bypassing the bed. In addition, biomass is heated at a higher rate due to the recirculation loop. Consequently, gasification efficiency and carbon burnout are increased compared to BFB, and tar production during the heating up of the feedstock decreases.

CFB can process feedstock with small particle size (<400 mm) and a wider particle size distribution without the penalty of the entrainment loss and they are reliable over a wider range of feedstock [41]. Another feature is the greater specific gasification potential per unit volume of bed, with a consequent decrease in the size of the gasifier itself (which rather develops upwards).

Furthermore, this configuration is more responsive to external load requests and allows for better control of related parameters.

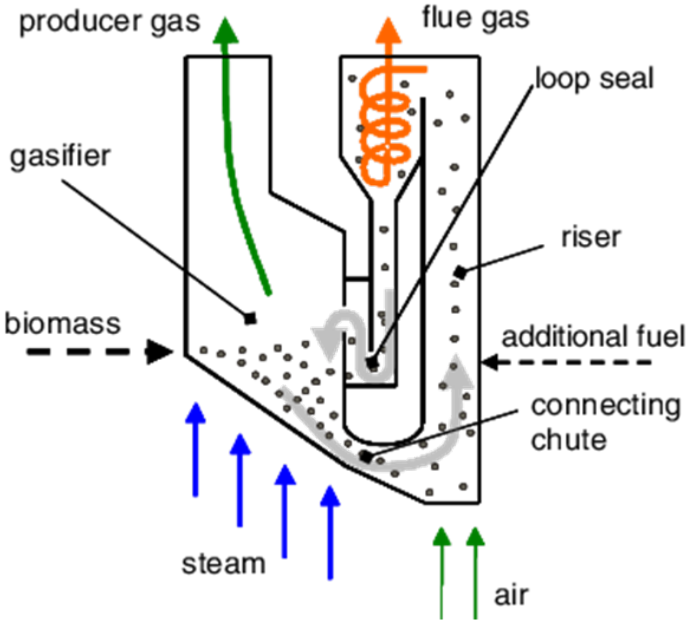


Figure 3.9 - Principle of the dual fluidised bed gasification process

Dual fluidized bed gasifier

The basic idea under this gasification arrangement concept is a recirculating system consisting of two interconnected reactors: a BFB gasifier which operates as a steam pyrolysis device and a CFB combustor (riser) which oxidizes the residual char in presence of a fluidizing medium and provides the heat to the whole process.

The reactors are filled with an inert material, usually silica sand, which also acts as a heat transport medium. Syngas is produced during the pyrolysis and the partial char reduction stages and exits the top of the first reactor with the steam. Gasification take place at bed temperatures of about 850-900°C.

An inclined connecting chute transports by gravity the bed material and the residual char from the pyrolyzer to the combustion reactor. After particle separation from the flue gas in a cyclone, the hot bed material flows back to the gasifier via a loop seal. Both connections, the loop seal and the chute are fluidized with steam, which effectively prevents gas leakage between gasification and combustion zone and also allows high solid throughput.

The process yields two separate gas streams, a high-quality producer gas and a conventional flue gas, at high temperatures. Figure 3.9 shows a simplified scheme of this process.

The system is inherently auto-stabilizing since a decrease of the gasification temperature leads to higher amounts of residual char which results in more fuel for the combustion reactor. The pressure in both the reactors is close to atmospheric conditions.

Table 3.4 shows compare salient features of different biomass gasifiers designs

Table 3.4 - Comparative evaluation of different designs of biomass gasifiers (adapted from [42])

Downdraft fixed bed	**Updraft fixed bed**
Simple and proven technology	*Simple and proven technology*
Fuel specificity in terms of both type and size	*Low exit gas temperature*
Suitable for biomasses with low moisture	*High thermal efficiency*
Producer gas with moderate calorific value and low tar and ash (or particulate) content	*Producer gas with moderate calorific value but high tar and ash (or particulate) content*
High exit gas temperature	*High residence time of solids*
Suitable for capacities of 20–200kW	*High overall carbon conversion*
High residence time of solids	*Extensive gas clean-up required before it can be used in engines*
High overall carbon conversion	*Suitable for capacities up to 250kW*
Limited scale-up potential with maximum capacity of 250kW	*Limited scale-up potential*
Bubbling fluidised bed	**Circulating fluidised bed**
High fuel flexibility in terms of both size and type	*High fuel flexibility in terms of both size and type*
Flexibility of operation at loads lower than design load	*Flexibility of operation at loads lower than design load*
Ease of operation	*Ease of operation*
Low feedstock inventory	*Low feedstock inventory*
Good temperature control and high reaction rates	*Good temperature control and high reaction rates*
Good gas–solid contact and mixing	*In-bed catalytic processing possible*

In-bed catalytic processing possible	*Producer gas with moderate tar levels but high particulates*
Producer gas with moderate LHV but low tar levels and high particulates	*High carbon conversion*
Carbon loss with ash	*Good gas–solid contact and mixing*
High conversion efficiency	*High conversion efficiency*
Suitable for large-scale capacities (up to 1MW or even higher)	*Suitable for large-scale capacities (up to 1MW or even higher)*
Good scale-up potential	*Very good scale-up potential*
Twin fluidised bed	**Cross-draft fixed bed**
Relatively complex construction and operation	*Simple design and small size*
Producer gas with moderate LHV and moderate tar levels.	*Producer gas rich in particulates and tar. High exit gas temperature hence gas cleaning requirements are low*
Cleaning of gas required before it can be fired into engines	*Flexible gas production and very fast response time to changes in load*
In-bed catalytic conversions possible	*Well-selected feedstock needed*
Good gas–solid contact and mixing.	*Very high sensitivity to slag formation*
Relatively low efficiency	*Low energy efficiency*
Suitable for high specific capacities (>1MW).	*Suitable for small-scale applications (<10 kW)*
Good scale-up potential but relatively complex design.	*Limited scale-up potential*
	Carbon loss with ash

3.4.2 Feedstock properties

The characteristics of the biomass feedstock have a significant effect on the performance of the gasifier, especially the following ones:

- *Moisture content:* biomass with moisture content above ~ 30% makes ignition difficult and reduces the calorific value (CV) of the syngas due to the need to evaporate the additional moisture before combustion/gasification can occur. High moisture content reduces the temperature achieved in the oxidation zone, resulting in the incomplete cracking of tars. Increased levels of moisture favors, in presence of CO, the formation of H2 by the water gas shift reaction and, in turn, the increased H2 content of the gas yields more CH4 by direct hydrogenation. The gain in H2 and CH4 of the product gas does not however compensate for the loss of energy due to the reduced CO content of the gas and therefore gives a product gas with a lower CV.
- *Ash content:* Due to its usually high concentration in alkali metals, biomass ash acts as a natural catalyst for char gasification and tar removal, and it is sometimes added as a secondary catalyst to the gasifier. Nevertheless, high ash content is normally undesirable since it complicates the process operation due to clinkering, agglomeration, and slagging of the mineral matter. Alkali metals also react with silica

and sulfur to form silicates and sulfates, respectively. This is particularly relevant to fluidized bed gasifiers since these compounds cause bed sintering and defluidization.

- *Elemental composition:* The elemental composition of the fuel is important with respect to the heating value and the emission levels in almost all applications. The production of nitrogen and sulphur compounds is generally small in biomass gasification because of the low nitrogen and sulphur content in biomass.
- *Volatile compounds:* Besides operating conditions, reactor designs, etc. the amount of volatiles has an impact on the tar production levels in gasifiers. The gasifier must be designed to destruct tars and the heavy hydrocarbons released during the pyrolysis stage of the gasification process.
- *Bulk density and morphology:* Biomass of low bulk density is expensive to handle, transport and store. Larger particles can form bridges which prevent the feed moving down, while smaller particles tend to clog the available void fraction of the bed, leading to a high pressure drop and the subsequent shutdown of the gasifier.

3.4.3 Operating conditions

To obtain the desired product gas composition, low levels of impurities, and to increase the net energy conversion efficiency, the gasification operating conditions need to be optimized.

The following section describes the effects of the main operating conditions on the quantity and composition of the product gas and its impurities.

- Biomass feeding rate: Overfeeding of biomass can lead to plugging and reduced conversion efficiencies whereas starve-feeding results in less gas yield. Hence, an optimum biomass feeding rate is desired for the gasification system to maximize energy efficiency. Optimum biomass feeding rate is dependent primarily on the design of the gasifier and the properties of the biomass.
- Composition and inlet temperature of the gasifying medium, that necessarily affect mass and energy balances of the reactor. The nature of the gasifying agent strongly determines the composition of the fuel gas produced and its calorific value: air gasification leads to a syngas rich in nitrogen (50–65%) and consequently low in calorific value (around 4 ÷ 7 MJ/m3). By replacing air with pure oxygen, steam, or a mixture thereof, a much more valuable gas is obtained with a heating value (HHV) in the range of 10 ÷ 18 MJ/m3 [18]. If oxygen is used as the gasifying agent, the conversion path moves toward a lowering of the hydrogen content and an increase in carbon-based compounds such as CO and CO2 in the product gas. If steam is used as the gasification agent, then, the product gas contains more hydrogen per unit of carbon, resulting in a higher H/C ratio. Some of the intermediate reaction products like CO and H2 also help to gasify the solid carbon. Injection of CO2 may be performed to increase the char reactivity and burnout rates. For a fixed oxidant, the inlet temperature is related both to the temperature profile that must be established along the gasifier and to the possibility/necessity of heat recovery from the hot syngas.
- Air/Oxygen flow rate (equivalence ratio, ER or superficial velocity, SV). Equivalence ratio (ER) and superficial velocity (SV) are measures of the air (or oxygen) flowrate. ER is the ratio of the actual air (or oxygen) supplied to the value required for stoichiometric combustion of the biomass, which indicates extent of partial

combustion. The SV is the ratio of air flow to the cross-sectional area of the gasifier which removes the influence of gasifier dimension by normalization [43]. Hence, both ER and SV are directly proportional to the airflow.
Air flow affects syngas composition, tar content, gas yield, and its chemical energy. It contributes to gasification in different ways: supplies the O2 for combustion (and fluidization in the case of fluidized bed) and effects the residence time. By varying the O2 supply, air flow rate controls the degree of combustion which in turn, affects the gasification temperature. Higher airflow rate results in higher temperature which leads to higher biomass conversion (gas yield) and a higher quality of syngas. But, an excess degree of combustion, on the other hand, results in decreased energy content of the gas produced because a part of biomass energy is spent during combustion [44,47]. Higher airflow also shortens the residence time which may decrease the extent of biomass conversion. As it is shown in Figure 3.10, values of ER around 0.25–0.35 appear to maximize char conversion and then are those typically used in large-scale commercial plants, even though values as high as 0.5 can be used, in particular with moving grate gasifiers [48] and fluidized bed gasifiers operated with wet fuels [49].

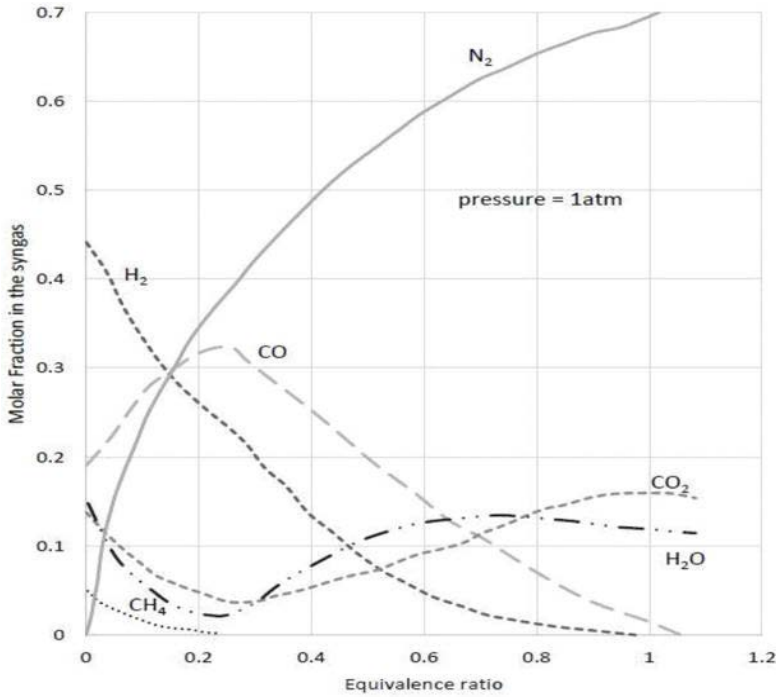


Figure 3.10 - Syngas composition at chemical equilibrium as a function of ER for the gasification of wood at 1 atm [50].

Lower values of ER leave unconverted char and higher tar content while higher values of ER determine the reduction of syngas heating value. Effects of ER on the product gas composition also depend upon other factors such as temperature and steam to biomass ratio. During steam gasification, at high temperature, the H2 yield is more pronounced than the increase in gas yield which results in an increase in H2 content.

- Steam flow rate (steam to biomass ratio, S/B) Supplying steam as a gasifying agent increases the partial pressure of H2O inside the gasification chamber which favors the water gas, water gas shift and methane reforming reactions (R7-R9), leading to increased H2 production [44, 45]. However, the gasification temperature needs to be high enough (above 750–800 °C) for the steam reforming and water gas reactions to be favorable [47]. Higher S/B also leads to higher biomass conversion efficiency [51]. Reduction in tar also is observed at higher steam to biomass ratios, which is attributed to steam reforming of the tar with an increased partial pressure of steam [44]. Since the temperature of the steam supplied to the gasifier is lower than the gasification temperature, a significant amount of heat is needed to raise the steam temperature which, in turn, may lower the temperature of the gasifier bed. Hence with an S/B ratio above a certain threshold, steam had negative effects on the performances. Increasing the temperature of the gasifying agents led to an increase in the heating value of the fuel gas, and reduces the tars, soot and char residues [52]. A preheating is recommended before the introduction of gasifying agents (steam and air/oxygen) to the gasifier to favor higher bed temperature.
- Gasification temperature: Temperature profile along the different reactor sections is one of the most influential process parameters affecting the syngas composition and properties. Higher temperature results in increased gas yield and a subsequent decrease in tar and char yields. The greater amount of gas produced at higher temperatures is explained by the larger release of gases during the initial devolatilization stage, and the secondary reactions undergone by the char and tars. Since the gasification reactions occur simultaneously, the contents and ratios of H2, CO, CO2 and CH4 in the product gas are greatly affected by temperature and partial pressures of reactants. At temperatures above 750–800 °C, the endothermic nature of the H2 production reactions (steam reforming and water-gas reactions) results in an increase in H2 content and a decrease in CH4 content with an increase in temperature. At temperatures above 850–900 °C, both steam reforming and the Boudouard reactions dominate, resulting in increases in CO content. High temperature also favors tar cracking and reforming of tar leading to a decrease in tar content and an increase in gas yield [44, 47]. It was also observed that higher temperatures (700 to 950 °C) increased the gas yield, and carbon conversion efficiencies and overall energy content of the gas [51].
- Pressure: Most of the current gasifiers are operated at pressures ranging from 10 to 100 bars. The operating pressure is normally set depending on the requirements upstream or downstream of the gasifier. High processing pressure saves compression energy and reduces the equipment size. Operating pressure has an influence on product yields and distribution. The amounts of CH4 and CO2 in the fuel gas increase with pressure while the amount of H2, CO and light hydrocarbons decrease. In addition, tar yield decreases with greater pressure due to the inhibition of volatile release from the fuel particles by the physical effect of the external pressure. However, the amount of poly-aromatic hydrocarbons in the tars is larger.

3.5 Syngas cleaning

Gas cleaning is an essential part of any gasification system. Cleaning is intended to achieve high removal efficiencies of impurities, contaminants and other undesired compounds from the product gas stream, such as particulate matters, heavy (and generally condensable) hydrocarbons, inorganic impurities (chlorides, ammonia, sulfur compounds, oxides) and any alkali/heavy metals.

The condensable part may include both water-soluble organic compounds (such as acetic acid) and insoluble organic compounds (such as tars). Particulate matter is generally made up of ashes, fines, sometimes sand and char.

Conventional gas cleaning and conditioning generally involves an integrated, multi-step approach including a combination of physical, chemical, thermal and catalytic technologies.

The extent of gas cleaning required depends on the downstream application of syngas. In general, more stringent conditions on minimum level of impurities in syngas are required for fuel or chemical synthesis compared to combustion of syngas in gas turbine combustion chamber or internal combustion engines, since the activity of the catalysts used in the synthesis process is very sensitive to small amounts of impurities.

When we consider the most common applications of syngas, the requirements in terms of operating conditions are extremely different as well as the issues that may arise. For example, regarding boilers and turbines, a fairly high gas temperature is considered optimal (as high as possible for turbines) while engines require a rather low temperature. As for fuel cells this value is instead strictly linked to the type of used technology. Particulates and tar content is required to be moderate for boilers but low and even zero for engines, turbines and fuel cells. All applications require minimal quantities of contaminants, such as HCl and H2S, with a greater tolerance for boilers.

In general, the cleaning system represents the most complex and heavy part of the gasification plant. A first aspect to consider is the pressure drop occurring in the treatment line which affects the whole system efficiency. The higher the pressure drop, the greater the amount of energy consumed to maintain the desired process flow, requiring a higher horsepower motor.

Recently, gas cleaning has gained significant importance especially when considering the technological complexity of the prime movers to which a gasifier is often connected. Unlike coal gasification, the problem of gas desulphurization does not arise in biomass gasification, but the control of the level of tars and ash becomes predominant.

These substances, combined with the presence of steam in the gas stream, impose further problems to be solved downstream of the gasifier, especially regarding particulates abatement. Particulate deposition in the downstream equipment causes plugging and results in higher wear.

On the other hand, the condensation of steam and distillates (tar), which occurs in the outlet ducts and in the subsequent filtration area, although it can favor a natural washing of the gaseous stream and the removal of solid particles, which are incorporated in the sludge that is formed, at the same time can easily cause equipment clogging and shutdowns. To avoid issues deriving from tar condensation, it is therefore required first a high temperature de-dusting, performed above the dew point of the gas, followed by a separation of the condensate before proceeding to any cold filtration.

3.5.1 Particulate matter

Regardless of the intended use of the product gas, the systems generally adopted for the particulates abatement are:

1. cyclones,
2. electrostatic precipitators,
3. bag filters,
4. ceramic candle filters,
5. wet scrubbers.

Cyclones

Cyclone separators are widely and routinely used to separate the larger particulates (above 5 µm in diameter) at the initial cleaning stage with little pressure drop. Generally, multiple cyclones are used to increase separation efficiency. Cyclones are generally able to remove somewhere between 50-99% of all particulate matter in flue gas. How well they are actually able to perform this task depends largely on particle size. In common cyclone separators, satisfactory abatement efficiency (85% - 95%) is achieved when treating particles over 10 µm. They are beneficial mainly because they are not expensive to install or maintain, they have no moving parts (low maintenance and operating costs) and they can operate even at high temperatures.

Cyclones made of carbon steel are used up to operating temperatures of about 425 °C, while for higher temperatures they must be manufactured with special steels (AISI 304, 309, 310, Hastelloy B or C, Inconel etc.). In the case of particularly high temperatures (above 800 °C), after having properly evaluated their convenience, it is possible to use refractory-lined carbon steel cyclones.

Cyclones can be of the axial or tangential inlet flow type; the former usually have a high capacity but a low separation efficiency, while the opposite is true for the latter. In some cases, by suitably modifying the axial inlet design, it has been possible to build axial cyclones of greater efficiency. In general, for an axial inlet cyclone with 50% of the particulate matter smaller than 10 µm, the separation efficiency ranges from 73 to 85%. Under the same operating conditions, the tangential inlet type can exceed 90% efficiency.

In any case, regardless of the type and size of the inlet particles, the outflow generally has an average particulate content of the order of 100 mg/Nm3

Electrostatic precipitators

An electrostatic precipitator, compared to the cyclone, has a higher efficiency, but, due to its design characteristics, it cannot be used at temperatures higher than 250 ÷ 300 °C.

Other features are:

- low pressure drops,
- minimum maintenance requirements,
- long life-time (of the order of ten years);
- high reliability and elasticity in response to varying flue gas characteristics.

Having clarified that the electrostatic filter cannot operate directly on the gas flow leaving a gasifier (with rare exceptions), if not after cooling it, the particulate content in the outlet gas is of the order of 40 ÷ 50 mg/Nm3.

Bag filters

They are often used in place of electrostatic filters; when operating at the same temperatures they allow to achieve, with the same overall dimensions, higher abatement efficiencies, providing an outlet gas with about 10 ÷ 20 mg/Nm3 of particulates.

When considering biomass gasifiers, a factor limiting the use of bag filters is the presence of tar in the outflowing syngas, even if at the temperatures these filters commonly operate, due to vapors condensation, the gas stream is usually tar-free. Nevertheless, it is preferable that the gas to be sent to a bag filter is previously cleaned from substances capable of clogging it, such as tars.

Ceramic candle filters

This type of filters recently developed and still under study (in the field of the hot gas cleaning, for gasses from coal gasification and intended for use in combined cycles), combine the ability to operate at high temperatures (1200 °C) and the advantage of a separation efficiency that reaches about 99.9%, with low pressure drops (from 200 to 900 mm of water column).

A periodic clean gas flow in counter-current cleans the external surfaces of the ceramic elements in which the particulate matter is deposited, making the solid particles fall to the bottom of the container, where they are collected and removed.

Ceramic filters have been designed to work under pressure (even a few tens of bars).

Wet scrubbers

It is the most common system for the removal of particulate matter from the syngas. Its main features are:

- considerably reduction of the gas temperature and volume, resulting in smaller overall size of equipment.
- no temperature limits or condensation problems
- ability to remove not only particulates, but also other compounds
- need for treatment or reuse of spent liquid
- high power requirements: high collection efficiencies for particulate matter are attainable only at high pressure drops

The dust content in the outgoing gas is very low (of the order of 10 mg/Nm3) and the system is essentially economical and reliable. Wet scrubbers are the most suitable devices if the final use of the gas does not require high temperatures and if the latter contains other pollutants that can be removed with a washing (usually with water only).

Wet scrubbers can be divided into static and dynamic:

- *static*: they are in turn divided into fixed-bed scrubbers (in which the gas flow laps the surface of a pool of liquid) and floating-bed scrubbers (in which the inlet gas stream moves upward in a vessel while the scrubbing liquid is sprayed downwards),

- *dynamic*: among these the “jet scrubber” and the “venturi scrubber” are worthy of note. In the first, the gas is pushed at high speed against a water bed by an ejector and the solid particles to be removed remain in the liquid; in the second, both the gas flow to be treated and the scrubbing liquid under pressure, which nebulizes during expansion, are introduced into a Venturi tube; the solid particles are incorporated into the nebulized droplets to form larger particles, which are then abated in a cyclone downstream. Table 3.5 shows comparative data of the different abatement systems.

Table 3.5 - Comparison of different particulates abatement technologies [53]

Technology	Average grain size of particles captured [μm]	Capture efficiency (%)
Standard cyclone	120 – 220 30 – 60 10 – 20	99 80 50
High efficiency cyclone and multiple cyclones	22 – 35 10 – 15 6 – 10	99 80 50
Electrostatic precipitator	4 – 9 0,3 – 0,7	99 90
Dry filters/separators	5 – 25 0,2 – 1,5 0,1 – 0,3	99 80 50
Wet filters/separators	3 – 15 0,7 – 3 0,3 – 0,9	99 80 50

3.5.2 Sulphur removal technologies

Most biomass contains very little sulphur (<0.5%), which, during gasification, is converted mainly into hydrogen sulphide (H2S) and sulphur dioxide (SO2). Because of the low sulphur content in biomass, as compared to coal, the gas sulphur content in the gas is low enough to meet the needs of most applications. But for a few applications, such as methanol synthesis, even a low sulphur level can irreversibly inactivate the catalysts. Fuels cells and some tar catalysts also are sensitive to sulphur.

SO2 can be removed by wet scrubbing (the same used to abate the particulates) or by calcination processes whereas for H2S removal (H2S is the predominant sulphur compounds in the product gas in the case of gasification) two main methods can be applied:

Wet systems

Wet cleaning processes make it possible to obtain an output gas with H2S contents below 10 ppm. The technologies for the removal of H2S from a gas stream can be based on both chemical and physical absorption. A feature of these systems is that they are often not very selective, thus removing not only H2S, but also other acidic compounds with similar characteristics (CO2, COS and others).

The chemical absorption processes are based on the use of aqueous solutions containing solvents acting as a base (amines, sodium carbonate, etc.); H2S (but also CO2 and COS) tends to chemically bind these substances, thus being removed from the gaseous stream. The solution containing the absorbed sulphur is then regenerated in a special equipment, usually through a thermal process, where the sulphur is separated and suitably recovered. The amount of energy required for thermal regeneration is very high, as a chemical bond need to be broken.

Physical absorption works on the same principle, but no bonds (and therefore compounds) containing sulphur are formed, so regeneration requires less energy.

In general, chemical processes are used to minimize the pollutant content of a starting gas, which already contains very low quantities of the same. On the contrary, physical processes work better in the presence of large quantities of pollutant, tolerating a high H2S absorption per unit of circulating solvent, but without being able to reach a high gas purity. To combine the advantages of the two systems, mixed (chemical-physical) methods have been studied, including the sulfinol approach developed by Shell.

It should be noted that the interest in these processes in relation to biomass gasification is somewhat limited, since these systems, given their cost and complexity, are justified only for large-scale operations.

Dry systems

Such systems can operate at both high and low temperatures and may or may not be regenerative.

Systems working at low temperature (close to the ambient one) are known as molecular sieves. They exploit the ability of some solid substances, often based on alumina, to retain molecules of given dimensions, letting the others pass. These devices, having to operate at low temperatures, make it necessary to perform a preliminary cooling as well as a considerable cleaning (de-dusting) of the gas. They are usually very sensitive to compounds capable of deteriorating the sieve, reducing its life and efficiency. These systems are then regenerated with streams of gas or steam at higher temperatures. They have high installation and operating costs and the base material is also very expensive. Such processes are often used for gas dehydration, but they also work well for the removal of both CO2 (final gas contents below 20 ppm) and H2S (whose final gas content is a few ppm).

In the search for alternative methods to molecular sieves, which are cheaper, work at high temperatures (such as those at the outlet of a gasifier) and tolerate higher particulate content without reducing their efficiency, various technical solutions have been studied. and tested. Some H2S abatement systems based on the passage of a hot gas stream in an iron oxide bed have been already marketed. ZnFeSO4 has been identified as an excellent alternative to iron oxide, as it combines a high affinity to sulphur with an easier regeneration, with a final sulphur content in the gas of less than 10 ppm. The temperatures at which these processes take place are between 800 and 900 °C. Since the reactions involved are globally exothermic, they are controlled using steam as a thermal flywheel.

This system, which as mentioned can purify a gas up to a content of 10 ppm of H2S, has been already developed and is finding application in increasing the efficiency of coal gasification for power generation.

3.5.3 Tar removal systems

Tar is a generic term used for all organic compounds found in the product gas apart from gaseous hydrocarbons. In the EU/IEA/US-DOE meeting on tar measurement protocol held in Brussels in the year 1998, it was agreed to define tar as all organic contaminants with a molecular weight larger than benzene [54].

Tar is a complex mixture of condensable hydrocarbons, which includes single ring to 5-ring aromatic compounds along with mixed oxygenates, other oxygen-containing hydrocarbons and complex poly-aromatic hydrocarbons (PAH).

Its composition shifts from larger molecules to smaller molecules. The major components, present in concentrations clearly higher than 5%, are: toluene (representing all the one-ring compounds), naphthalene (representing two-ring compounds) and, with temperatures below 800 ° C, phenol (representing phenolic and other heterocyclic compounds). There also are traces of numerous other compounds, which, however, taken together may constitute a considerable fraction of the total tar content. Figure 3.11shows the structures of some typical components of tar.

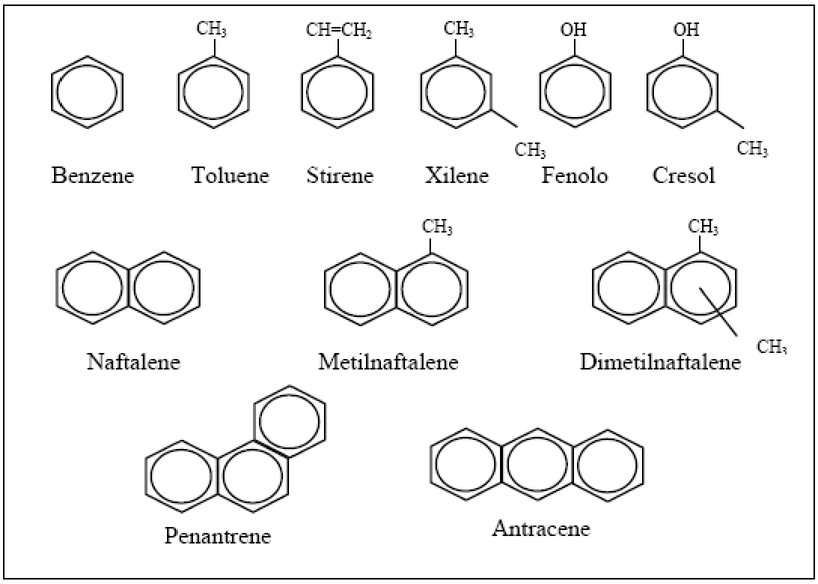


Figure 3.11 - Structures of some typical components of tar

Tar formation is one of the major issues to deal with during biomass gasification. If not removed from the syngas, tar condenses at low temperatures thus blocking, fouling and causing corrosion, erosion, and abrasion of process equipment as well as of downstream prime movers and installations. However, the minimum allowable limit for tar is highly dependent on the kind of process and the end user application. Tar is less problematic for combustion of product gas because tar also can combust and add to the calorific value of the fuel, although less readily and at higher temperatures. Other applications, wherein the gas stream is cooled, result in condensation of the tar. Tars also are detrimental to catalysts used for conversion of syngas and fuel cell applications.

Tar removal techniques can broadly be categorized as primary removal techniques and secondary removal techniques.

- Primary mitigation methods can be defined as all the measures taken inside the gasifier to prevent or convert tar formed. They include: (a) an optimization of operational conditions, (b) the use of suitable additives or catalysts in the gasifier bed, (c) a proper gasifier design.
- Secondary removal technologies are conventionally employed as treatments to the hot product gas from the gasifier. These treatments can be of a chemical or physical type as follows:
    - tar cracking downstream the gasifier either thermally or catalytically,
    - mechanical methods such as use of cyclone, baffle filter, ceramic filter, fabric filter, rotating particle separator, electrostatic filter and scrubber.

Although, downstream gas cleaning methods are reported to be very effective in tar reduction, in some cases they are not economically viable.

A) Primary removal technologies

Effects of operating conditions

Several studies have proven the effectiveness of operating conditions in reducing the amount of tar in the syngas. The most important influencing parameters include temperature profile, pressure, gasifying medium, equivalence ratio (ER), steam to biomass ratio (S/B), total gasifying agent to biomass ratio (GR), and residence time. The selection of these parameters also depends on the type of gasifier used.

A high operating temperature (above 800 °C) results in a product gas with low tar content. In general, with an increase in process temperatures from 700 ° C to 900 ° C, up to 50% less tar is produced. Temperature not only affects the amount of tar formed, but also the composition of tar by influencing the chemical reactions involved in the whole gasification process.

A significant reduction in tar production is related to an increase in the equivalence ratio ER. According to Kinoshita et al. [57], tar yield and tar concentration decreases as the ER increases because of more availability of oxygen to react with volatiles in the flaming pyrolysis zone. The ER is a crucial parameter since its higher value results in lower concentration of H2, CO and higher CO2 content in the product gas, thus decreasing the heating value of the gas.

Herguido et al. [55] reported the effect of steam to biomass ratio (S/B) on the gasification products. When the S/B ratio was increased from 0.5 to 2.5, a sharp reduction in tar (8% yield at 0.5 S/B dropped to almost nil at 2.5) was observed along with a decrease in the lower calorific value attributed by the decrease in CO.

A relationship between ER, S/B and GR values is mentioned for the purpose of comparison by Gil J et al. [56]. Under selected conditions, more tar is formed with pure steam, than that with steam–O2 mixture and less with air as gasifying agent.

Yamazaki, instead, found that, in a downdraft gasifier, a higher superficial velocity (SV) of 0.7 m/s resulted in higher amount of tar as compared to a lower SV of 0.4 m/s [58]. According to the paper, higher SV resulted in shorter residence time and channeling which may have led to higher amounts of tar.

In-bed catalyst

The addition of catalysts such as dolomite, limestone, olivine, alkali carbonates, Ni-based catalysts, metal-oxide catalysts, zeolite or char in the gasifier bed, either with or without sand along with the biomass feed, help reduce tar and increase the extent of reforming reactions in the gasifier, thereby increasing overall carbon conversion efficiency. Addition of active bed materials also prevents the solid agglomeration tendencies and subsequent choking of the bed.

Limestone was one of the first additives used in the gasifier to improve the gasification. Walawender et al. [59,60] performed series of experiments using limestone as bed additive in a fluidized bed gasifier. The authors reported that the gas composition, heating value and yield were all influenced by the presence of 25 wt% limestone in the bed.

Corella et al. [61] mentioned that in-bed use of dolomite results in a similar tar content as using it in downstream catalytic reactor. Rapagnà et al. compared the performances of sand, dolomite and olivine particles as bed materials in a bubbling fluidized bed lab-scale gasifier [62]. They observed that the gas yield increased by more than 50%, tar was reduced by 20 times and char was reduced by 30% when dolomite or olivine was used as a bed material as compared to using sand. However, methane content was almost the same which indicated that the olivine and dolomite catalysed tar destruction, but not methane reforming. Mechanical strengths of olivine and sand were similar, but dolomite resulted in more fines.

In-bed catalysts reduce tar content, but complete tar removal is not achieved without the use of secondary reactors [63]. Also, it should be noted that the optimized operating conditions, gasifier designs and the application of in-bed catalysts for tar reduction using primary methods may not be optimum conditions for yield, composition, and energy content of the syngas. Therefore, the process efficiencies also need to be considered in determining the best operating conditions and gasifier design for obtaining desired product composition.

Gasifier design

The amount and composition of tar at the outlet of a gasifier depend to a large extent on the reactor design. Downdraft fixed bed gasifiers produce a gas with a relatively low tar content, conversely the gas resulting from updraft gasification contains a high level of tar. In a downdraft gasifier, the pyrolysis gases, as already discussed, are forced into the hot reaction zone resulting in an effective tar cracking process. The tar content obtained in the case of fluidized bed gasifiers lies between the two values.

Modification of the gasifier design, such as secondary injection of air or oxygen into the gasifier and two-stage gasification systems, is also very effective in producing a gas with a lower tar content [27].

A higher temperature could be attained due to the secondary air injection with positive effects on tar reduction. The basic concept of the two-stage gasification design is to separate the pyrolysis zone from the reduction zone.

B) Secondary removal technologies

Cleaning by mechanical and physical processes.

Cold gas cleaning can be very difficult. When temperature remains or falls below the dew point of the gas, aerosols are formed which can only be partially removed. The use of barrier filters and cyclone separators has been shown to be ineffective for tar removal since tar aerosol particles are less than 1µm in size and are sticky in nature, making them difficult to remove from the equipment walls. The most important, commonly used systems and their efficiency are shown in Table 3.6.

Table 3.6 - Tar removal potential of some gas cleaning methods

Method	Temperature [°C]	Removal efficiency (%)
Bag filters	~200	max. 25
Sand bed filters	10 – 20	60 – 95
Rotating tower scrubber	50 – 60	10 – 25
Venturi scrubber		50 – 90
Wet electrostatic precipitator	40 – 50	60

The best way to remove tar, among the methods considered, is through sand bed filters. However, the removal efficiency reaches a maximum 95%. To reach the required content of 100 mg/m³, the maximum quantity of tar allowed for the raw gas is therefore 2 g/m³. Relatively high removal rates, up to 90%, can be achieved with the use of venturi scrubbing, which simultaneously removes the particulates. It has been demonstrated that tar concentrations below 20–40 mg/Nm3 can be achieved using a venturi scrubbing system [69]. The exit gas temperature from wet cleaning methods is 35–60 °C, which results in loss of sensible heat and water condensate which requires treatment before disposal.

Wet electrostatic precipitator can remove most of the tar up to about 150 °C but are more expensive. The tar collected using these physical techniques can be burned to produce heat or re-injected into a gasifier.

The shortcomings of wet cleaning are that: (a) the net energy efficiency of the process is decreased, since product gases high temperature is lowered during wet cleaning, (b) the waste water have to be treated extensively before discharge which is a capital-intensive process, and (c) when the syngas end-use applications operate at high temperature, there will be a net loss of energy in cooling and heating the product gas stream [69].

Reforming

A significantly higher reduction of the tar content in the product gas can be achieved with the aid of hot gas cleaning technologies. Hot gas cleaning aims at thermally cracking tars molecules into lighter gases using high temperature. In this process, the gasifier is usually coupled to a subsequent tar reformer, often a catalytic reactor, with a fixed-bed, a fluidized-bed, or a honeycomb design. Tar reforming involves decomposition and partial oxidation of the tar components using air or steam/CO2/O2 to produce hydrogen and carbon oxides and, as mentioned, it is usually carried out with supported transition metal catalysts; high temperature and catalysts provide favourable conditions for reforming and shift reactions. Without a catalyst, the temperature to achieve a sufficiently high tar cracking efficiency is above 850 °C which required a significant energy supply and decreased the overall efficiency. It causes also material issues and produces soot [68].

Several kinds of catalytic reforming materials have been studied, developed and used in removal of tar, such as mineral resource: dolomites, magnesites, zeolites, olivine, mayenite minerals, alkali metal catalysts, Ni-based catalysts and novel metal catalysts [69]. In some cases, dolomite has shown tar reduction rates of over 99.5% and with nickel compounds even up to 99.99%. However, these catalysts, although they showed good activity in tar removal, still have several problems.

Tar removing catalysts are grouped into mineral and synthetic catalysts. The mineral-based catalysts are naturally occurring minerals and inexpensive. They also have fewer disposal problems. Calcined rocks (calcined dolomite, magnesite and calcite), olivine, clay materials and iron ores are mineral-based catalysts. Among these, calcined rocks are the most efficient catalysts. However, calcined rocks are suited only for fixed-bed secondary reactors as they erode in fluidized bed reactors. Olivine has more mechanical strength for attrition but is less efficient than dolomite. Clay materials generally do not withstand temperatures of 800–900 °C, whereas iron ores are rapidly deactivated.

Fluid catalytic cracking (FCC), char, alkali metal-based, activated alumina, and transition metal-based (Pt, Zr, Rh, Ru, Fe, and Ni) catalysts are synthetic catalysts. Transition metals (Ni, Rh, etc.), as well as other synthetic catalysts, are relatively expensive as compared to the mineral catalysts. FCC deactivate rapidly, alkali metals agglomerate in the bed, and transition metals, although very active (8–10 times than dolomite), need gas with low levels of sulfur, tar and char [70]. Numerous efforts have been made to design catalysts for destructing tar and increasing the extents of reforming reactions at the same time.

Operating conditions such as temperature, space time (mass of catalyst per unit flow rate of product gas), catalyst particle size and gas compositions affect tar conversion efficiencies.

3.5.4 Hydrochloric acid

For this compound, as for the tar, the removal systems are of two types:

- wet scrubbing of the gas with water (basic)
- addition of lime in the reactor.

The first is the most used system, and sometimes a scrubbing with water alone is sufficient to obtain low values of HCl concentration in the syngas.

The second system is derived from the experience in fluidized bed combustion. In fact, it became clear how adding calcium in the bed to fix and eliminate the sulphur, acted effectively, even if less markedly, also to inhibit the passage of chlorine in the gaseous stream. Even in this case the fluidized bed gasifier seems to be the most suitable reactor for the use of this application.

Chapter 4

Sludge and oxygen gasification: state of the art

Sewage sludge (SS) is a by-product of wastewater treatment plant (WWTP) operation. Due to fast rates of urbanization and industrialization, and rapid population growth, the world community faces a serious challenge associated with its disposal. There is an urgent need to explore low cost, energy efficient, and sustainable solutions for the treatment, management, and future utilization of SS. Thermal conversion of SS is considered the most promising alternative for sustainable SS management. Among three main thermochemical processes, it seems that gasification (GAS) of sewage sludge has the most advantages,

4.1 Introduction

The thermochemical conversion via gasification of a wide range of residual biomass, waste, and by-products of various industries as wood processing, agri-food industry or even wastewater treatment [71] represents a very promising approach towards circular economy and green transition.

In gasification, due to non-complete oxidation, fewer polluting emissions are produced than in incineration. Furthermore, a globally lower process temperature than incineration provide for most of the pollutants to be retained in the ashes.

In particular, the gasification of sewage sludge has several advantages:

- reduction in the volume of waste products,
- destruction of the pathogenic bacteria present in the sludge,
- low-cost control of atmospheric emissions,
- advantageous energy recovery compared to incineration.

In any case, the main advantage of the process lies in the production of a synthesis gas of stable chemical composition and calorific value, which allow it to be used more efficiently than a solid fuel. Furthermore, by using syngas as a fuel, a significant decrease in CO_2 yield is observed, with the same energy released, compared to combustion of fossil fuels. The major drawback of gasification is the higher content of tar and ash in the product gas [72].

The scientific literature on the gasification of sewage sludge is not very extensive. Below are some examples of realizations at each of the possible scales: laboratory, pilot plant and full scale.

The list does not pretend to be exhaustive and only wants to offer a series of heuristic examples.

4.2 Laboratory-scale experimentation

As a first example of an experimental scale plant for the gasification of sewage sludge we can mention the one built at the Department of Environmental Engineering of the University of Trento (Figure 4.1) [71].

The plant, of a fixed bed type, operates with a discontinuous cycle at pressures between 1 and 10 bar. It is capable of reaching high temperatures (1000 °C). The reactor, into which the material to be gasified is loaded, is housed in a pit furnace with suitable refractory insulation. It consists of a cylinder (internal diameter 142 mm, height 400 mm, thickness 4 mm) in nickel-iron-chromium alloy (Incoloy 800). and is equipped, to close the base sections, with two blind flanges; the 8 small diameter pipes that cross the central chimney exit from the upper flange and are intended for the inlet and outlet of the gas and for the connection of measurement and control instruments.

The control and data acquisition instrumentation are positioned in the upper part of the system.

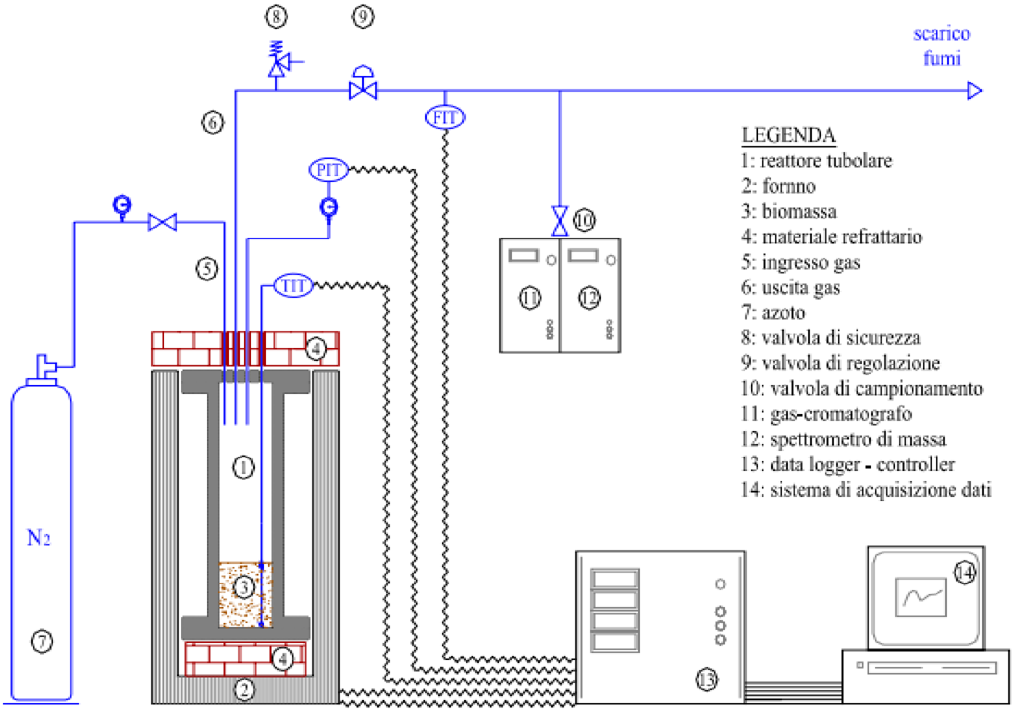


Figure 4.1 - Experimental apparatus for the gasification of sewage sludge of the Environmental Engineering Department of Trento (2006)

In the reactor, the reaction products undergo a washing, carried out by means of a flow of inert gas (nitrogen or helium), which avoids the establishment of secondary reactions and favors their progressive advancement towards the analysis section. This latter contains the system for the removal of condensable compounds (tar), a gas chromatograph and a mass spectrometer for the characterization of the chemical species present in the gas stream.

Temperature, pressure and quantity of air used as a comburent control the composition of the synthesis gas produced. H, the caloric value of the gas produced settles on the typical values of a gasification process and is a decreasing function of the moisture content of the sludge. In fact, the presence of water, on the one hand, increases the purity and quality of the syngas, but on the other hand, it increases the amount of energy absorbed in the conversion reactions.

During the extensive experimentation carried out with this apparatus, the conversion yields of the sewage sludge gasification process were evaluated and simulated using a model that assumes the achievement of thermodynamic equilibrium.

Manyà et al [72] have instead developed a laboratory-scale plant (Figure 4.2) in which the central element is a steel Bubbling Fluidized Bed (BFB).

The sludge is sent to the reactor, together with inert material (sand). At the outlet of the reactor, the gas is sent to a cyclone, to remove the residual coal particles, and is subsequently filtered. The height of the bed is kept constant at predetermined values through a system that collects the ash produced in a tank located below the reactor.

The outgoing gas is sent to a continuous CO/CO_2 infrared analyzer, which monitors the process, and to a micro-gas chromatograph which provides its volumetric composition (N_2, O_2, H_2, CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, H_2S).

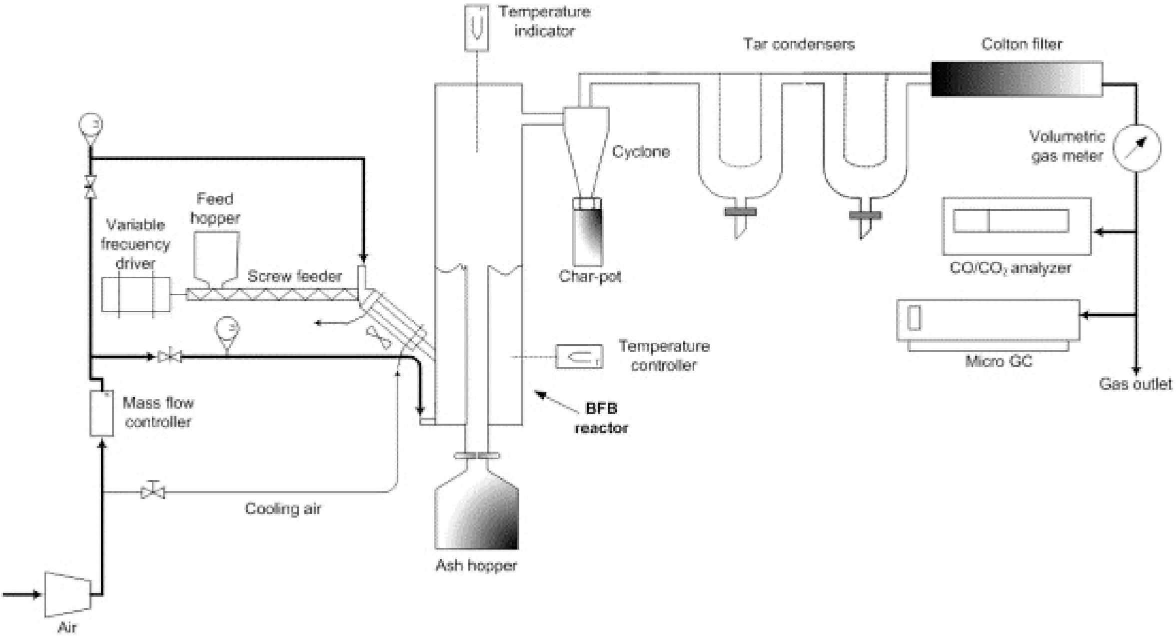


Figure 4.2 - Scheme of the laboratory scale BFB gasifier employed by Manyà et al. (2006)

The purpose of this experiment was to investigate how the gasification process is influenced by the amount of air used and the height of the bed (150 mm and 300 mm), or by the residence time of the sludge in the reactor.

During the experimentation, sludge from an urban wastewater treatment plant, previously subjected to anaerobic digestion and thermal drying and finally reduced to 250-500 µm granules, was used. The trial provided data regarding:

- average composition of the gas produced on a dry basis,
- quantity of gas obtained,

- energy value of the cold gas produced (defined as the ratio between the lower calorific value of the produced gas and the lower calorific value of the fed sludge),
- average percentage of the carbon present in the biomass, recovered in the gas,
- distribution of the mass produced.

The authors found that:

- the concentrations of H_2, CO, CH4, C2H4 and C2H6 increase as the height of the bed increases and decrease as ER increases, defined as the ratio between the quantity of supplied air and the stoichiometric air of the combustion reaction; the concentration of N2 shows an inverse trend,
- the percentage of carbon in the biomass converted into gas and the amount of gas produced increase with the increase of ER (major influence) and the height of the bed (minor influence),
- the value of CGE does not depend on ER, but increases as the height of the bed increases,
- the production of tar and ashes does not show significant trends as a function of ER. and the height of the bed.

4.3 Pilot plants

Dogru et al. [73] carried out the gasification of sewage sludge in a throated downdraft gasifier, to verify the feasibility of using this technology to efficiently produce a clean gas suitable for energy or synthesis purposes. The gasification described by Dogru is autothermal and consists of a series of complex chemical and thermal processes, which occur simultaneously and/or consecutively.

The pilot plant (Figure 4.3) used in this experimentation consists of:

- a downdraft gasifier,
- a packed bed scrubber,
- a filter,
- a fan for the circulation of the gas,
- a pilot burner.

The main stages of the process take place inside the gasifier, in distinct areas: -

- drying area, in which moisture is removed from the sludge by evaporation, by means of progressive heating from 70 to 200 °C,
- pyrolysis area, in which the thermal degradation of dry sludge takes place, conducted at temperatures between 350 and 500 °C, using the thermal energy obtained from the partial oxidation of the pyrolysis products. 60 + 70% of the sludge is converted into a liquid (containing water, tar and oil), a gas (containing CO, CO_2, H2 and light hydrocarbons), ashes and residual carbon,

- oxidation zone, in which the volatile products formed in the pyrolysis zone are oxidized with exothermic reactions, favoring a rapid increase in temperature up to 1000 + 1100 °C. The products, including CO, CO_2, H_2, H_2O, gaseous hydrocarbons, tar and coal, pass into the underlying gasification zone,
- gasification or reduction zone, in which the products, generated in the oxidation zone, are converted into a gas mostly made up of CO and H2, which leaves the gasifier at temperatures close to 700 ° C.

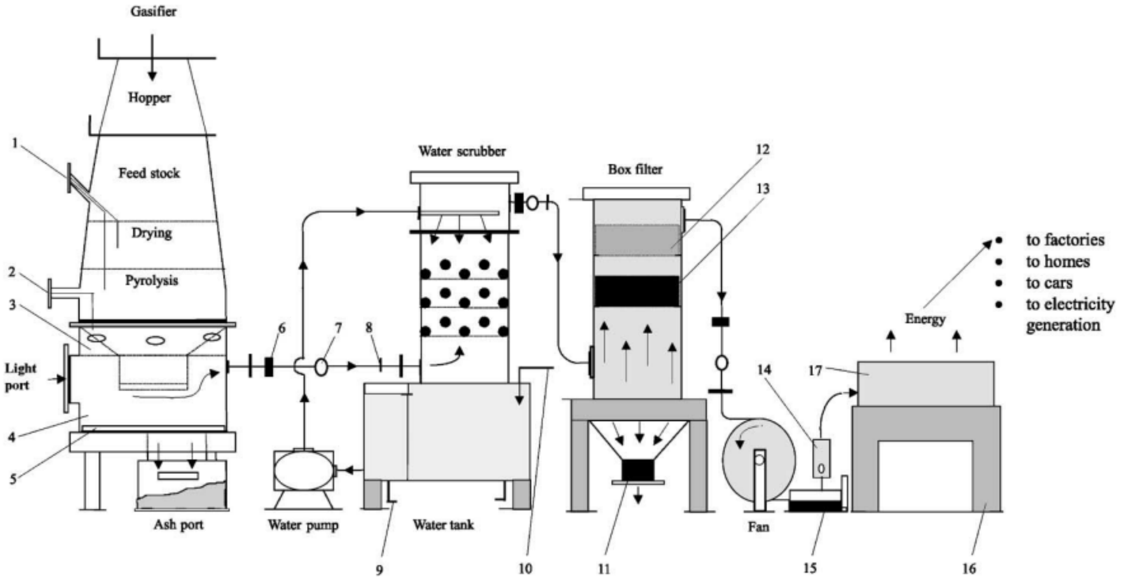


Fig. 1. Schematic figures of the experimental setup. (1) Temperature measurement of drying and pyrolysis zone. (2) Temperature measurement of oxidation zone. (3) Oxidation zone. (4) Reduction zone. (5) Grate. (6) Produced gas outlet temperature measurement. (7) Sampling gas. (8) Pressure measurement of the produced gas. (9) Wastewater outlet. (10) Fresh water inlet. (11) Tar collection chamber. (12) Wood chip. (13) Charcoal. (14) Rotameter. (15) Tar and dust trap. (16) Steal table. (17) Energy generator.

Figure 4.3 - Diagram of the pilot plant used by Do Gru et al. (2002)

The use of a downdraft gasifier allows you to obtain:

- high carbon conversion,
- reduced quantities of ash and tar.

Furthermore, this type of reactor is of simple construction and can be easily used in plants where the co-production of heat and energy is required, as in the case of sludge treatment.

The packed bed scrubber uses water sprays to cool the gases leaving the gasifier, removing 80 ~ 90% of fly ash, dust, tar and condensate.

The subsequent filter allows a washing of the gas and the products eliminated by this stage are recycled as fuel to the gasifier.

During this experimentation, tests were carried out under different operating conditions and with different types of sludge. The outcome of the tests has been then evaluated by quantifying the carbon residue, the ashes and the calorific value of the gas produced.

The ash content of the sludge used was lower than that of coal and, although the ashes were continuously removed from the gasifier, the formation of clinker was observed, due to the high operating temperatures which cause a decrease in the quality of the gas produced.

The gas produced consists of a combustible fraction (20 + 23% by volume), containing H_2, CO, CH_4, C_2H_4, C_2H_6, and a non-combustible fraction (N_2, CO_2).

The gas leaving the gasifier is sent to a scrubber and then to a filter, in order to reduce the content of contaminants (tar, dust and condensate).

The waste products of the gasification process are therefore coal, ash, tar, condensate, and water, while the main product is the synthesis gas.

The temperature plays an important role: higher temperatures allow the use of smaller quantities of air, cause less tar and ash production and above all allow to obtain a synthesis gas of higher quality.

From the experimentation carried out, Dogru et al. drew the following conclusions relating to the pilot plant employed.

- High feeding velocities lead to problems of clinker formation, reduced on the grate of the gasifier, due to an uneven distribution of the temperature in the oxidation zone.
- Due to the presence of contaminants, it is difficult to carry out flow measurements, the gas is then treated in a scrubber and led through a filter to remove tar and condensate.
- The thermal efficiency increases with the increase of the specific digasification rate and the quantity of combustible gas.
- The streams of dry gas and coal increase with the feed rate, while the ashes remain constant.

Petersen and Werther [74] employed another type of pilot plant for sludge gasification, equipped with a circulating fluidized bed (CFB) gasifier.

Gasification and pyrolysis processes have been studied in order to identify reaction mechanisms and kinetics. Although this type of gasifier is very interesting, it goes beyond the main theme of this thesis and therefore I will not add anything else to the simple bibliographic citation.

Phuphuakrat et al. [75] carried out an experiment to characterize the content of tar present in the syngas produced in a down-draft fixed bed gasifier. The authors intend to study how parameter X, defined as the ratio between the amount of air fed and the stoichiometric air of the combustion reaction, affects the yield in tar; the ultimate goal is to structure a process capable of converting the sludge into a clean fuel gas that can be used in a motor diesel for the production of electricity, to be used in the same water purification plant.

The pilot plant (Figure 4.4), designed and developed by King Mongkut's University of Technology (North Bangkok, Thailand) consists of the following equipment: a down-draft gasifier, instrumented with six thermocouples (Figure 4.8); two cyclones, the first downstream of the reactor, the second positioned between the first two traps for the tar; two venturi scrubbers; three tar traps (containing sawdust).

At the beginning of each test, conducted in batches, the reactor is loaded with 300 kg of previously dried mud, reduced to 38-1-50 mm pellets. This sludge contains about 40% volatile material and 11% humidity.

Before switching on, the height of the bed is measured (Figure 4.8) to assess the intensity of the charge and the speed with which it is consumed.

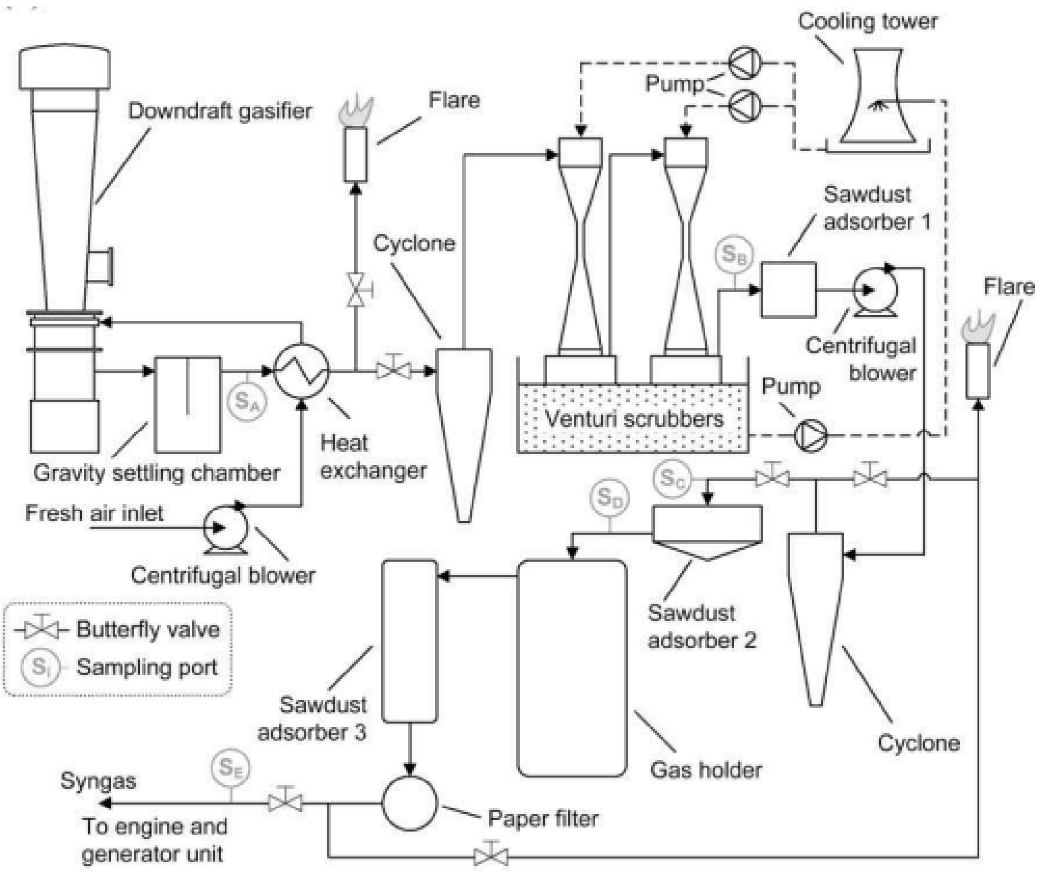


Figure 4.4 - Flowsheet of the pilot plant employed by Phuphuakrat et al (2009)

To start the combustion, a burner is used which remains on for about 3min. During the initial transient, the syngas produced is directly purged from the torch by means of the appropriate bypass valve. As soon as stationary conditions are reached, identified with approximately constant temperatures in the bed, the bypass is closed, and the syngas sent to the washing section; at the same time the gas sampling for analysis begins. The bed level is measured at intervals of about 30 minutes to determine exhaustion.

The syngas, leaving the reactor, passes through a cyclone for the abatement of the dust and, therefore, is washed in two venturi scrubbers with the recirculation water, coming from the basin below them, with a flow rate equal to 100 l / min.

After the scrubbers, the gas passes through three absorbers, interspersed with a cyclone, filled respectively with 1.8, 7.5 and 3.4 kg of sawdust, inside which moisture and tar are captured.

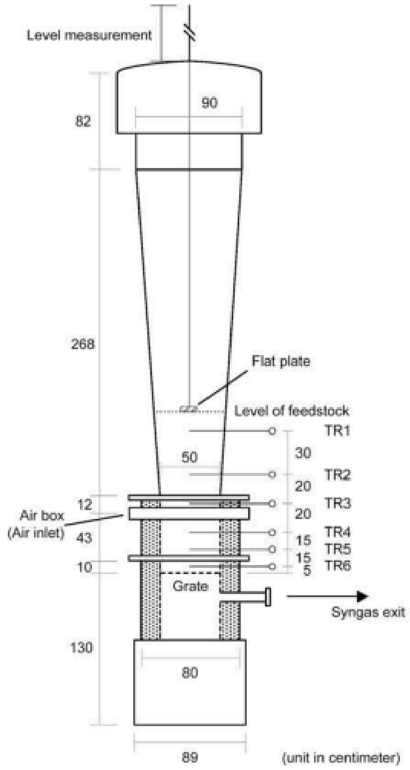


Figure 4.5 - Scheme of the gasified down-draft used by Phuphuakrat et ai (2009)

The last device of the cleaning section is a paper filter, normally used to retain fine particles before sending the syngas to the diesel engine. From the study, the authors found the following:

- The chromatography analysis (SEC) showed that the compounds detected in the tarabbiano have a molecular weight in the 50÷500 range.
- Gas chromatographic analysis coupled to mass spectrometry (GC-MS) indicates the presence of aromatic and polycyclic compounds from benzene to pyrene.
- As the ER increases, the mass of tar produced decreases since the temperature of the oxidation zone increases and with it the cracking and combustion reactions.
- By increasing the ER, there is simultaneous decrease in the tar of compounds with a molecular weight of 50÷300 and an increase in those with a molecular weight of 300÷500: this occurs because the former are easily decomposed as the oxidation reactions increase.
- The efficiency of the syngas purification system depends on the operating conditions, components, and mass of the tar; 26÷53% of the tar can be knocked down in venturi scrubbers, while 14÷36% in absorbers with sawdust. Before leaving the washing section, 44% of the light aromatic hydrocarbons are removed.

4.4 Full-scale plants

Applications and feasibility studies of full-scale plants relating to alternative technologies to incineration, such as gasification and pyrolysis, are currently difficult to find. Following research carried out in scientific literature and on the web, only two interesting applications of sludge gasification have emerged: a system called "KOPF Sewage Sludge Gasification System" in use in Baligen in Germany and a project under study in Philadelphia, Pennsylvania, by Primenergy.

There are also very few applications of pyrolysis of sewage sludge, often abandoned even before having expressed their full potential.

The first innovative sewage sludge gasification plant was set up by KOPF AG in Baligen, Germany, in August 2004. The aim of the process is to valorise the sludge through conversion into electricity and heat, as well as the production of a solid residue in granules free of pollutants, which can be used in many applications.

Sludge, coming from a water treatment plant that treats 10 million cubic meters per year (125,000 inhabitants equivalent), is dried until a residual humidity of 15÷30% is obtained. The energy required for this drying system is supplied by a system of photovoltaic panels and it takes two to eight weeks to obtain the required moisture content.

The plant treats about 230 kg / hour of dehydrated sludge (with a dry sludge content of 160÷180 kg), generating about 70 kW of electricity from the gas produced, of which 15 kW are used for the gasifier. The plant requires natural gas as an auxiliary fuel only during the start-up phase.

The energy value of the cold gas produced (Cold Gas Efficiency, CGE), expressed as the ratio between the energy content of the gas and that of the starting sludge, is 65 ÷70%, depending on the degree of residual moisture in the feed (in practice about 2/3 of the energy contained in the sludge is transformed into fuel gas).

The economic feasibility of the process has been found for small-sized plants, capable of treating a quantity of dewatered sludge less than 1000 ton/year.

The scheme of this process, called Sewage Sludge Gasification System is shown in Figure 4.9. The main equipment of the process is the fluidized bed gasifier, which guarantees a high degree of contact between the reactants, so as to allow the realization of complete, uniform and fast reactions. The only parameter that affects the trend of the reaction is the supply of preheated air: infact it is only added one third of the air needed for complete combustion.

Operating in air conditions sub-stoichiometric, a temperature of about 850 °C is reached, typical of the reactions ofgasification. Under such conditions the high molecular weight organic compounds are decomposed with high efficiency into gaseous compounds, while the inorganic portion generates an inert granular residue.

The ideal feed for the gasifier consists of sludge reduced in grains, of size between 2 and 10 mm, mechanically stable, with low dust content and with residual humidity of 15 ÷ 30%.

The dewatered sludge is taken from the storage and fed into the lower part of the Gas Cooler. The latter has the dual function of cooling and purifying the gas product in the gasifier, fed into the upper part of the equipment, where high pressure nebulized water is also introduced. The very fine drops of water evaporate and quickly cool the gas down to a temperature below 150 ° C, thus avoiding the formation of dioxins and furans. As a result of cooling, the small quantity of oil and tar present in the gas condenses and is adsorbed in the part lower part of the equipment, from the mud granules, which are subsequently fed to the gasifier, crossing it with a residence time of about 30 minutes.

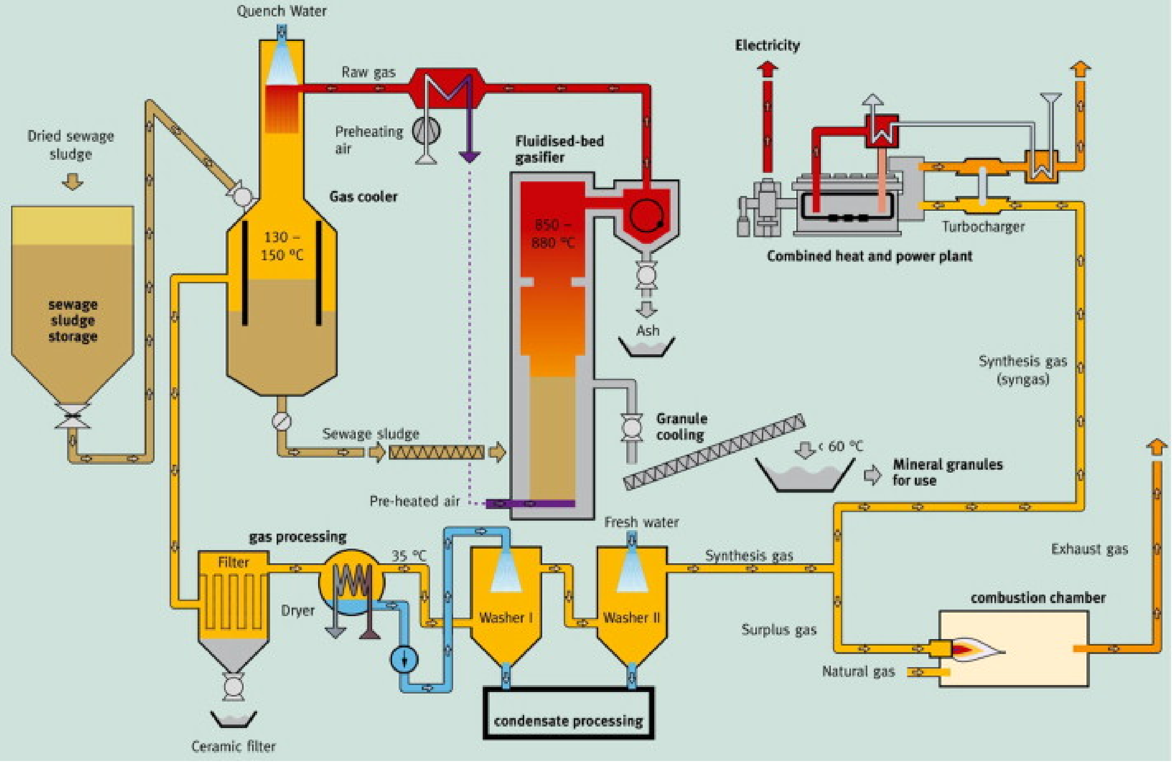


Figure 4.6 - KOPF Gasification of dried sewage sludge

By keeping the fluid bed temperature below the melting point of the ashes, the solid product is free of slag and easy to remove; it comes then cooled to a temperature below 60 ° C and collected in a silo, in the form of granules inert and non-leachable minerals, ready to be used in various applications.

The air necessary for the process is injected into the gasifier from below and, thanks to the presence of atmospheric oxygen, gasification, and oxidation reactions they proceed in parallel. The operating temperature is controlled by adjusting the amount of air fed.

In the cyclone, positioned at the outlet of the gasifier, the gas is separated from the dust coming from the fluid bed. By passing through the next heat exchanger, the gas temperature is lowered to about 600 ° C and at the same time the air supply is preheated up to 400 ° C. This choice of temperatures allows you to avoid condensation of the small quantities of oil and tar present in the gas. How said, except in the start-up phase, thanks to the preheating of the air the process of gasification is energetically self-sufficient.

The produced gas is then sent to the Gas Cooler for further rapid cooling e subsequently to a filter (pore diameter less than 1 mm) to obtain a residual dust content lower than 2 mg/m^3.

Finally, the gas is cooled to a temperature below ambient, so such as to condense much of the moisture contained in it (originating from the reaction of gasification and the atomized water in the Gas Cooler). The smallest drops come eliminated by centrifugation: in this way they condense about 300 liters of water per ton of sludge, which is sent back to water treatment. To lower the relative humidity, and thus avoid condensation downstream, the temperature comes in followed slightly increased.

The process described allows to obtain a gas essentially free of pollutants and containing hydrogen (6-10% by vol.), Carbon monoxide (6-10% by vol.) And methane (3-5% by vol.), The relative percentages of which vary according to the characteristics of the fed sludge. It can then be used as a fuel in a system cogeneration for the production of electricity and heat. The efficiency relating to electricity generation alone is 30%, while if we also consider the production of heat, a value close to 90% is obtained.

In some phases of the process, for example during start-up or run-down, an excess of gas may be produced, which cannot be used in the cogeneration system. That gas comes fed to a post-combustion chamber, operating at about 850 ° C, in which it is eliminated in a way that is not harmful to the environment.

In the start-up phase, natural gas is used to reach the operating temperature in the gasifier, while in the stationary phase the quantity of gas produced is sufficient to maintain this temperature.

As previously mentioned, the mineral granulate, obtained with this gasification process, is totally inert, non-leachable and free of humidity. It is very rich in potassium and phosphorus and therefore can be used in various applications. The mechanical properties of the grains allow the use of this by-product in stabilization landfills, in the production of asphalts and, thanks to the extremely low pollutant content and the richness of minerals, as a filler and substrate in land reconversion projects in agriculture.

4.5 Co-gasification of sludge with other biomasses

In recent years, studies have also been carried out to evaluate the possibility of reusing existing gasification plants, fed with biomass, to gasify sludge mixed with waste biomass or coal.

Paterson et al. [76] showed how, for example, the presence of sludge in coal gasification is technically advantageous, because it increases the yield and the calorific power of the fuel gas produced. The syngas obtained from co-gasification also had higher H2 and CO levels than that obtained from sludge alone; it had, however, a lower content of CH4.

Pinto et al. [77], to study the gasification of mixtures of sludge and coal, built a laboratory-scale plant with a *fluidized bed gasifier* operating at atmospheric pressure (Figure 4.7). The aim of the experiment was also to investigate how the emissions of gaseous pollutants (NH3, H2S e HCl) of the plant vary after mixing the carbon with the sludge.

The gasifier consists of a 1.5 m high column with an internal diameter of 8 cm. The syngas leaving the reactor passes through a cyclone, a condensation system and two filters, to then be collected in bags and analyzed in a gas chromatograph.

The sludge used, thermally dried and reduced to granules, contains about 50% of volatile material and 9% humidity, compared to 25 and 2% for coal. The gasifying medium is a mixture of air and steam, with a steam flow rate equal to 5 g/min and an air that falls in the range 0 ÷ 14 g/min.

The biomass feeding rate, which is kept constant throughout the test period, is of about 5 g daf/min. Tests were made with mixtures with a sludge content from 0 to 100%.

The temperature of the oxidation zone is made to vary from 750 to 900 ° C. From the experimentation the authors found the following.

1. The addition of sludge in coal gasification causes syngas product, an increase in the CO2 content directly proportional to the weight fraction of the sludge; the CO content does not seem to vary. It also decreases the concentration of H2, while that of CH4 and increases hydrocarbons (CnHm).
2. Increasing the quantity of sludge in the mixture decreases the gas yield. Since the ash fraction of the two components is approximately equal, probably the gasification of the mud, compared to that of the coal, takes place more slowly due to the poor reactivity of the char.
3. The temperature increase of the oxidation zone, from 750 to 900 ° C, causes, in syngas, an increase in the content of H2, CO and CO2 and a decrease in that of CH4 and CnHm. Both effects are due to the increase in cracking reactions of hydrocarbons. As for pollutants, with the increase in temperature increases the H2S content but decreases that of NH3; the HCl content remains virtually unchanged.
4. As the equivalence ratio ER increases, the amount of H2, hydrocarbons, decreases light and tar in syngas; however, the concentration of CO increases and, in particular, of CO2. High air ratios also promote reactions combustion, thus leading to a decrease in the calorific value of the gas. However, increasing λ decreases NH3, H2S and HCl, which come oxidized.

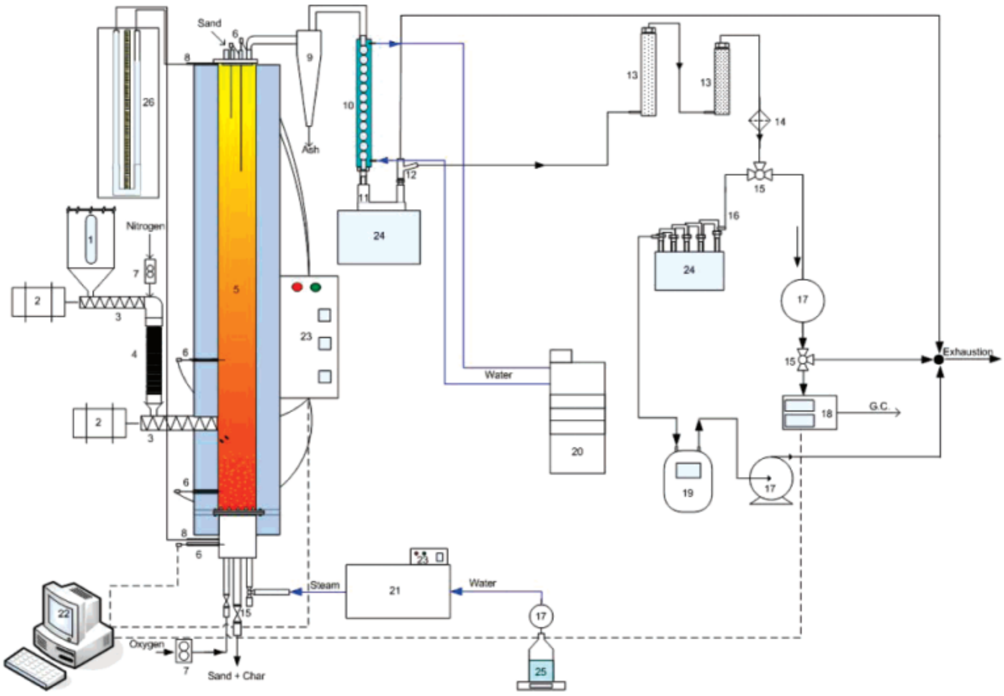


Figure 1. Schematic representation of gasification installation. (1) hopper; (2) motor; (3) screw feeder; (4) drop pipe; (5) gasifier; (6) thermocouple; (7) flow meters; (8) pressure probe; (9) cyclone; (10) condensation system; (11) liquid collector; (12) bypass; (13) glass wool filters; (14) filter; (15) valve; (16) gas sampling; (17) pump; (18) CO/CO_2 on-line analyzers; (19) gas meter; (20) water refrigeration system; (21) steam generator; (22) data acquisition system; (23) gasifier controller; (24) ice bath; (25) water reservoir; (26) pressure indicator.

Figure 4.7 - Scheme of the gasification plant used by Pinto et al (2007)

The authors therefore conclude that already existing gasification plants could be easily used for the gasification of sludge and biomass mixtures of sludge only. The optimal operating conditions for the gasification of the mixture are the following:

- temperature included in the range 850 ÷ 900 ° C;
- low air ratios.

In these conditions, in fact, a syngas with a good calorific value is obtained, due to the higher concentrations of H2, CH4 and CnHm, and low content of pollutants (NH3 and HCl).

4.6 Gasification with oxygen and steam/CO_2

To conclude this section on the state of the art of gasification, let us examine in the following paragraph the gasification process with oxygen, steam and carbon dioxide, a core process in the LIFE - AUGIA program.

This type of gasifying agents, in fact, in recent years, has attracted great attention both considering fixed bed and fluid/entrained bed gasifiers [81-86].

The technology also lends itself to the upgrade of conventional air gasification systems in which to replace, partially or completely, the nitrogen of the oxidizing mixture with steam or carbon dioxide. This allows to improve the operating conditions of temperature control by simultaneously increasing the partial pressure of H2O or CO2 in the gasification process and therefore the percentage of hydrogen and CO in the syngas, factors that favor its use in Sebatier reactors for the production of methane. synthetic [79,80].

S. Wang et al. [81] performed a numerical analysis, validated with literature data, to predict gasification performance using an equilibrium model based on Gibbs free energy minimization. The theoretical methane yield was simulated predicted with equilibrium processes carried out downstream of the gasification.

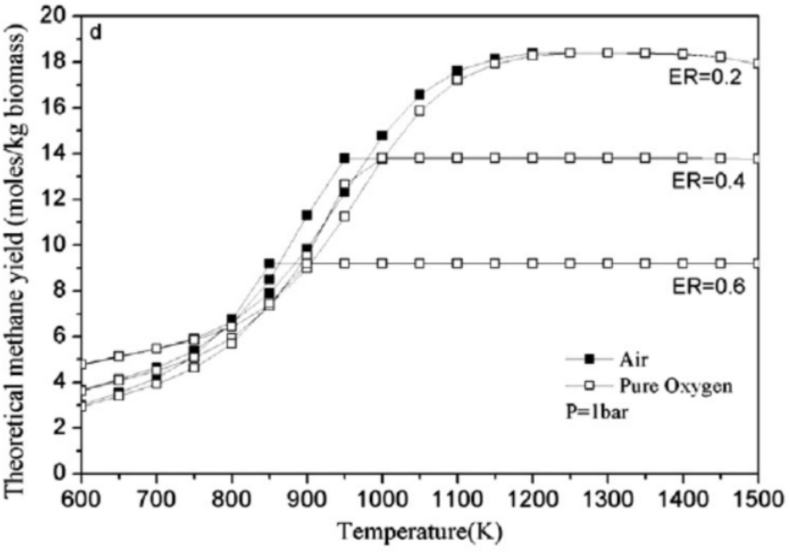


Figure 4.8 – Effect of gasification temperature, pressure, and ER on Methane yield

They also analyzed the gasification performance with varying gasifying agents, considering steam, CO2, O2 or air. The authors note that, regardless of the gasifying agent, when the gasification temperature is below 613 K, H2O, CH4 and CO2 are the main gaseous species. When the temperature is between 613 K and 833 K, hydrogen is added to these species. For temperatures between 833 K and 1173 K, the yields of H2 and CO increase, while H2O, CH4 and CO2 decrease significantly. When the temperature is above 1173 K, CH4 and CO2 hardly exist and the concentrations of H2 and CO satisfy the following relationship:

$$CH_{1,4}O_{0.59} = 0,41C + 0,72H + 0,59CO$$

Figure 4.8 and Figure 4.9 respectively show the methane yield and the composition of the syngas (dry-based) as the gasification temperature varies, for different oxygen/biomass equivalence ratios (ER) and gasification pressures.

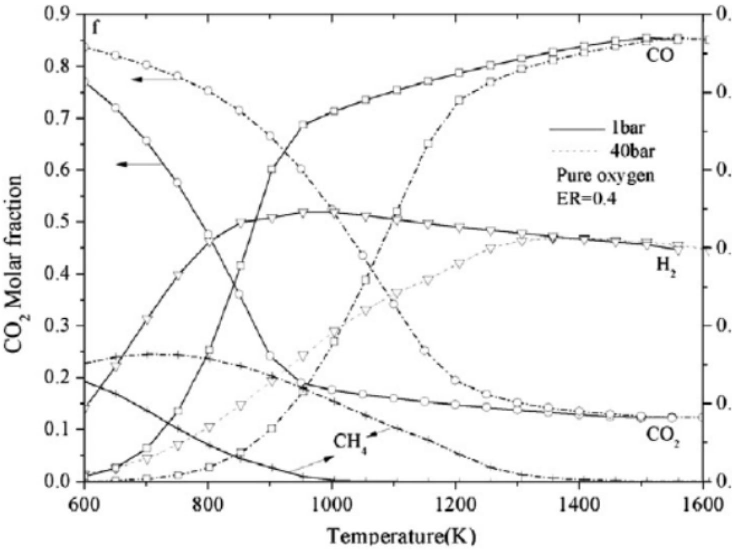


Figure 4.9 – Effect of gasification temperature, pressure, and ER on Syngas composition

Compared to gasification with air or oxygen, gasification with steam can produce syngas with a relatively higher H2 content, maximize gas production, and effectively reduce tar and coal formation. Hence it is a possible option for bio-methane production. Figure 4.10shows the effects of temperature and the vapor / biomass mass ratio (S/F) on the composition of the syngas.

In general, the authors highlight how, as the gasifying agent (air, O2 or steam) varies, the methane yield reaches its maximum when the carbon conversion is maximum. When the carbon is fully converted, the formation of methane is independent of the operating pressure. It should also be noted that for gasification with steam the carbon conversion is maximum and therefore the yield in methane and the H2 / CO ratio are considerably favored. When the ratio by mass of steam / waste (S / F) is ≈1, the yield of methane can reach 22 mol / kg of waste. In conclusion, the authors identify steam gasification as the best system for biomethane production due to the higher H2 / CO ratio in syngas. With steam gasification, however, to maintain endothermic operation, a certain amount of air / oxygen must be added if external heating is not provided.

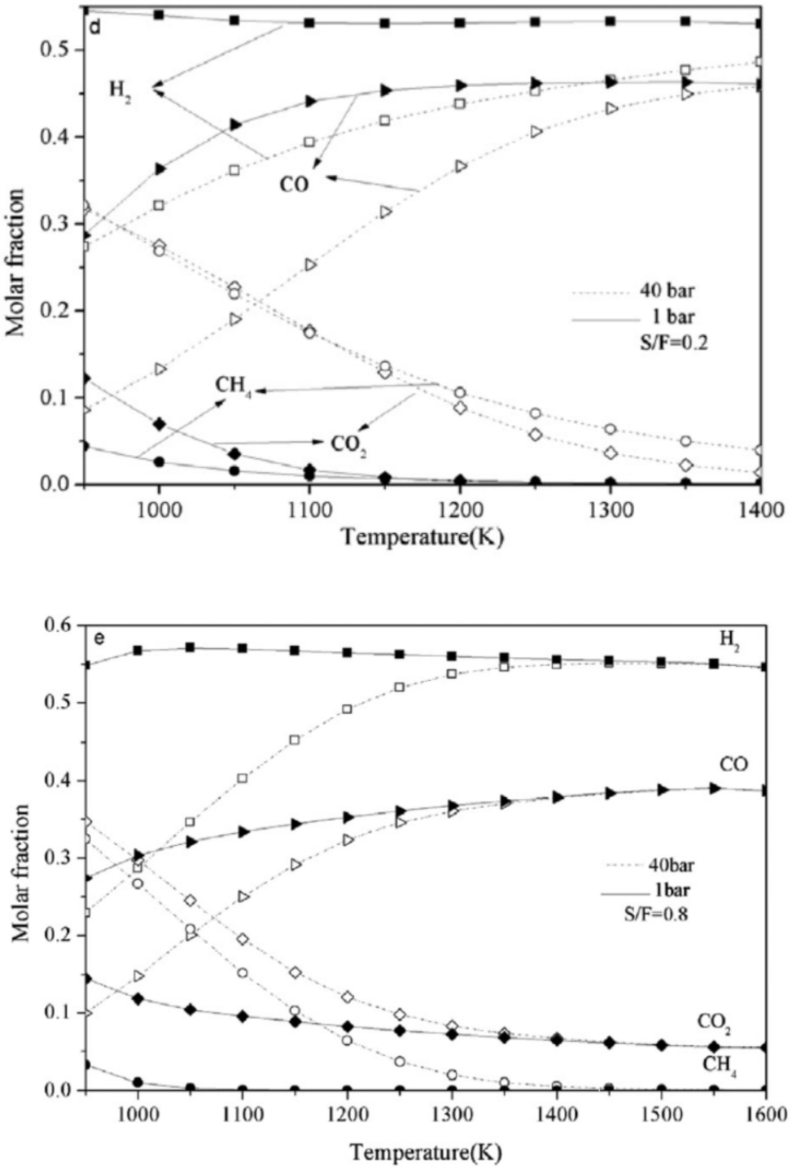


Figure 4.10 – Effect of gasification temperature an S/F ratio on Syngas composition

Again, with a numerical approach, recent studies, such as that of Y. Caoa [82] have further highlighted how oxygen-enriched gasification, using different cellulosic matrices, increases the production of a high-quality gas. Using a model developed in Aspen-Plus, several simulations of the gasification process were performed at different temperatures. For a correct validation, the numerical results were compared with the experimental data. The performance of the process was evaluated based on the flow rate of the syngas produced, the lower calorific value (LHVFG) and the production of TAR. The simulation results indicated that temperature was the most important parameter in the process. At higher temperatures there is an increase in the production of syngas and a decrease in the production of TAR. Indeed, syngas production increased with increasing equivalence ratio (ER) which favors higher temperatures, while LHVFG and TAR production significantly decreased.

The results also showed that the use of oxygen enriched air, with an oxygen/air ratio (OR) that goes from 30% to 90% by mass, favors the quality of the gas and the cracking of the TAR, while decreasing the yield. of syngas. The following figures show the trend of the production of syngas (GY, Syngas Yield) and of the calorific value (LHV) as the OR varies, for an ER of 0.21 and a gasification temperature of 80 °C, for the various lignocellulosic matrices used.

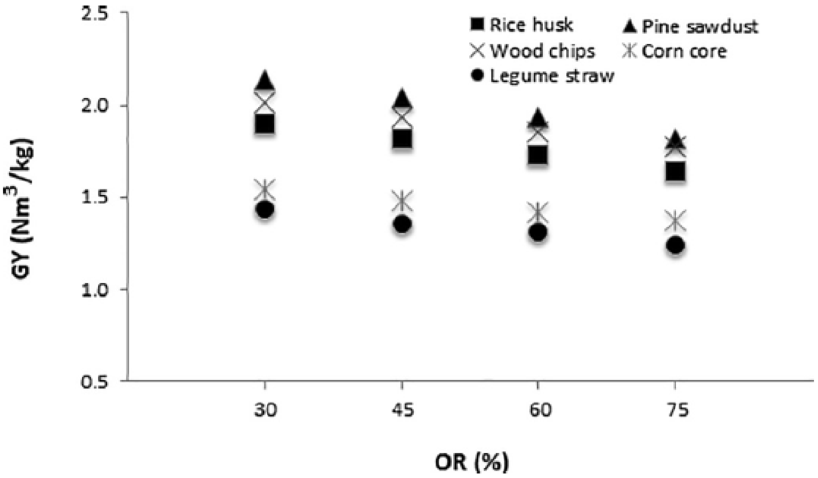


Figure 4.11 – Syngas yield (GY) as a function of the oxygen/air ratio (OR)

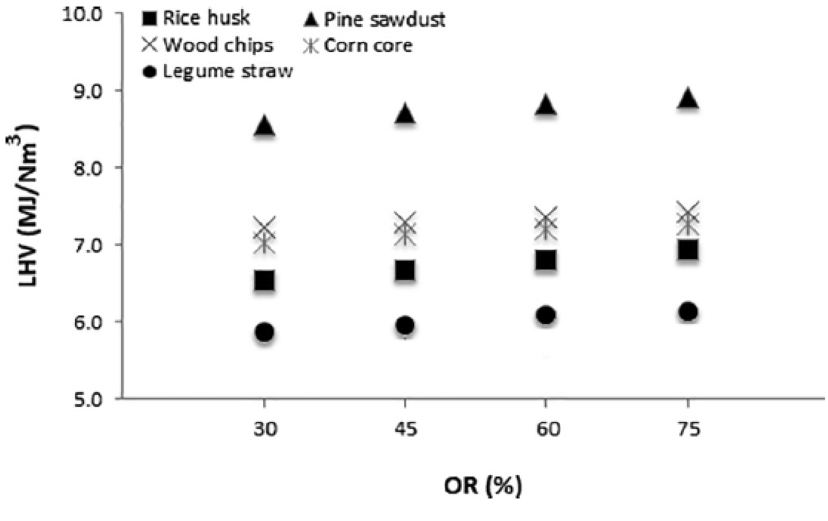


Figure 4.12 – Low Heating Value (LHV) as a function of the oxygen/air ratio (OR)

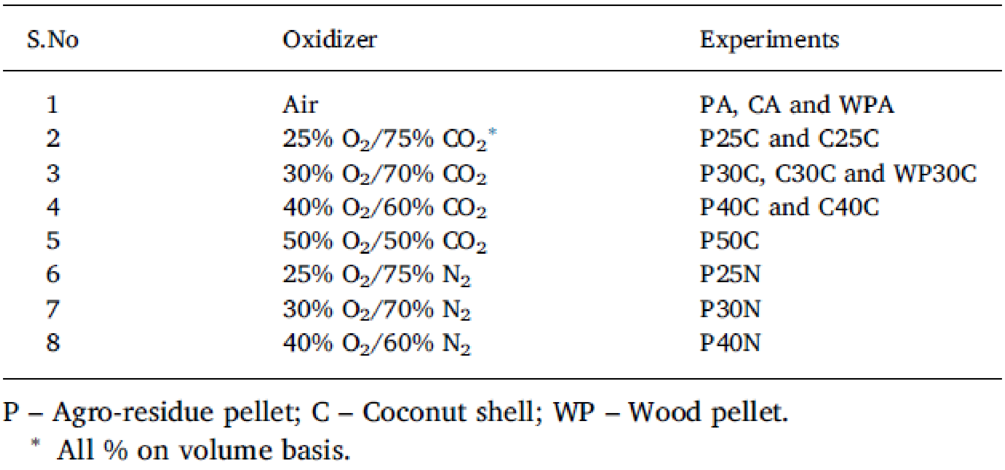
Regarding the specific type of gasifier (fluidized bed, downdraft, etc.), it should be emphasized that, for small gasification plants (<1 MWth), the use of fixed bed gasifiers, in particular those of the downdraft type, it is to be preferred over those with circulating fluid beds, the latter characterized by considerably higher installation and management costs. The "downdraft" type gasifiers, thanks to the relatively long residence times of the volatile oxidation products with the coal within the reaction zone, give rise to a syngas with low levels of TAR and dust. By replacing the N2 of air with CO2 / vapor, the downdraft configuration will lead to a higher CO and H2 yield.

4.6.1 Gasification with oxygen and CO_2

In general compared to a classic gasification process with air, in the oxy-gasification with CO_2, again with reference to the scheme of the gasification reactions already seen, we can note how, at low operating pressures, the presence of CO_2 in the agent gasifier inhibits the gasification reactions (2.5 and especially 2.6), but favors the endothermic reaction 2.7, with the oxygen used for the combustion reactions 2.3 and 2.4 providing the thermal energy necessary for the gasification reactions. In this way, apart from a strong reduction in the concentration of nitrogen in the syngas (replaced by the CO_2 introduced), there is a significant increase in the concentration of CO and a reduction in the formation of hydrogen. The variations in the concentration of these gases involve a partial balancing of the displacement of the balances of the CO-shift process due to the high concentration of CO_2 in the gas.

It should be noted that recently, on new concept plants, gasification processes with CO_2 in the absence of oxygen are also being evaluated. These processes adopt relatively high operating pressures (around 25 bar) and temperatures preferably within the range of 750-1400 ° C). In these conditions the CO_2 diffuses into the char, dissociates and the oxygen radicals react with the carbon giving rise to the formation of CO, according to reaction 2.7 previously seen [A]. Under the same conditions, the water vapor introduced into the reactor as a gasifying agent reacts with the carbon according to reaction 2.6. The thermal energy necessary for the activation of the aforementioned reaction is provided by the combustion of a small part of the syngas produced inside a special combustor (external to the gasifier) whose fumes are injected into the gasification reactor. At low temperatures, the presence of high concentrations of CO inhibits, as previously mentioned, the gasification reactions; an increase in the partial pressure of CO involves a reduction in the efficiency of the gasification process. This phenomenon is much lower for high temperatures, at which the gasification reactions have a negative activation energy [84]. This technology is particularly suitable for use in fluidized bed or, above all, entrained bed gasifiers.

Table 4.1 – Different combinations pf gasifying agent and biomass type in V.M. Jaganathan et al. [96]



S.No	Oxidizer	Experiments
1	Air	PA, CA and WPA
2	25% O_2/75% CO_2*	P25C and C25C
3	30% O_2/70% CO_2	P30C, C30C and WP30C
4	40% O_2/60% CO_2	P40C and C40C
5	50% O_2/50% CO_2	P50C
6	25% O_2/75% N_2	P25N
7	30% O_2/70% N_2	P30N
8	40% O_2/60% N_2	P40N

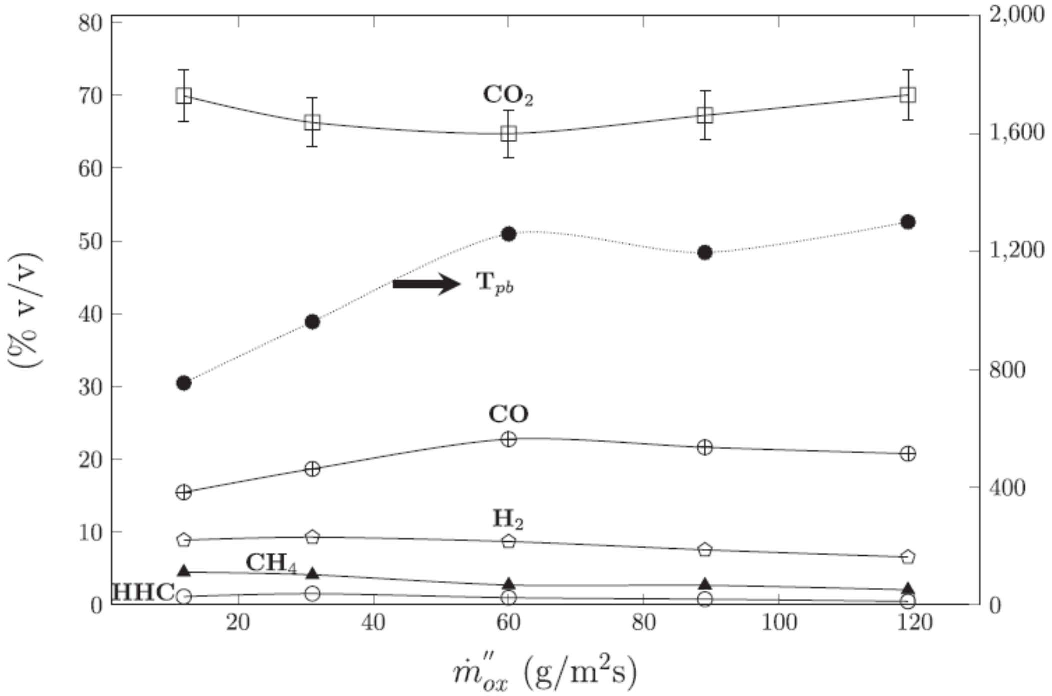
P – Agro-residue pellet; C – Coconut shell; WP – Wood pellet.

* All % on volume basis.

There are few examples available in the scientific literature relating to oxygen-gasification processes with CO_2. Recently, always V.M. Jaganathan et al. [96] experimentally investigated the conversion of CO_2 in an updraft gasifier fueled with biomass and mixtures of oxygen, CO_2, and nitrogen. The experimental scheme is practically the same as that previously reported [94], with the sole exception of the gasifying agent. Different biomass types were used (agro-food residue pellets, coconut shells and wood pellets), with different proportions of gasifying agents, as shown in Table 4.1.

The flow rates of the oxidant streams containing 20, 25, 30, 40 and 50% of O2 (v / v, without CO_2) have been adjusted in order to keep the height of the reaction zone constant, and therefore keeping the surface velocity constant. Under these conditions the following quantities were measured: temperature along the reactor, mass consumption and composition of the syngas. In addition, reference tests were performed using O2 / N2 mixtures to compare the net CO_2 conversion (NCC). In general, the NCC is significant around the stoichiometric point (ϕv = 1) considering the combustion of volatiles, decreasing when the mass flow of oxygen is decreased or increased. The NCC is zero in rich mixture conditions (i.e. when $\phi v \gg 1$), due to the low temperatures of the bed, and also when $\phi v < 1$, due to the oxidation of the coal. A maximum NCC of 627 g / kg of biomass with 30% O2 and 70% CO_2 (v / v) was obtained at ϕv = 0.96 for agro residue pellets. The gasification efficiency (ηg) reaches 85% at maximum NCC.

The composition of the syngas is reported below as the specific flow rate through the reaction section varies, using a mixture of 30% O2 and 70% CO_2 as the gasifying agent, together with the corresponding temperature of the reaction zone.



Chapter 5
The Life-Augia plant

In EU, sewage sludge management remains an open and challenging issue for the Member States. The treatment and disposal of this residual material is an expensive and environmentally sensitive problem. The Sewage Sludge Directive 86/278/EEC has sought to regulate the use of sewage sludge in such a way as to prevent pollution and loss of recyclable materials, reducing the widely adopted method of landfill disposal and encouraging other routes such as landspreading in agriculture. However even though from a policy perspective, farmland is the favoured outlet for sludge, in future it may become practically and economically untenable with the prospect of increasingly stringent quality standards (heavy metals and contaminants content). The challenge is to find cost-effective and innovative solutions whilst responding to environmental, regulatory and public pressures. Oxygen-based gasification, in particular, has been shown to be a promising technology for reducing the environmental impact of sewadge disposal and offering a sustainable and efficient way to convert this waste material into a clean and versatile fuel gas.

5.1 The Life AUGIA project

The LIFE AUGIA project is a European Union funded initiative that aims at demonstrating, over a three-year period, the technical and economic feasibility of an innovative and sustainable solution for the the treatment and disposal of sewage sludge. It utilizes a novel oxygen-based gasification technology to convert sewage sludge together with residual and waste biomass into a gas mixture (syngas), suitable for the subsequent production of very high added-value products such as hydrogen, methanol and methane.

The project is led by a consortium of partners, including research institutions (UNIMOL and UNIPI) and industrial firms (BIOSYN, SIME and COSIB), who will design, construct, and operate a demonstration gasification plant to showcase the capabilities of this technology. The project will also include a detailed assessment of the plant's performance and environmental impact, as well as a study of the economic viability of the technology.

Basically, this project aims to be a first step to the realization of a fully green bio-refinery for the production of environmentally friendly chemicals from organic matters.

Its demonstration character it’s evident as the technologies adopted, namely steam-oxygen gasification and air co-gasification, have been previously applied in other sectors, as documented by many scientific studies, but their combination is a novelty for sewage sludge treatment.

Steam-oxygen gasification process has been already demonstrated using different feedstocks, such as coal, biomass as well as the air co-gasification of biomass with sewage sludge, at least at lab- scale. On the contrary, the steam-oxy cogasification of sewage sludge and biomass for chemicals production can be considered a significant new approach.

For achieving the expected results, specific objectives have been set up as follows, in descending order of importance:

1. converting sewage sludge into a synthesis gas (syngas) with a suitable composition for the production of added value chemicals through oxygen-based co-gasification with residual chipped biomass. This aims at demonstrating the technical and economic feasibility of a more environmentally friendly end use of sewage sludge than those currently in place. Syngas, mainly composed of elementary chemical compounds (CO, H2, CO_2, CH4 and H2O), can be used in the synthesis of various chemicals such as synthetic natural gas (SNG), hydrogen, methanol, liquid hydrocarbons (via the reaction of Fischer-Tropsch). Thanks to the cleaning system that will be used in the plant, the syngas will be completely purified by removing tars and pollutants,
2. demonstrating (up to TRL 7) the operation and reliability of the sewage sludge oxygasification plant for the production of chemicals with a safe, efficient, environmentally friendly and profitable approach. In particular, the stability of the operating conditions, the durability of the equipment materials, the high energy performance and low polluting emissions must be demonstrated. These objectives can be considered effectively achieved if (i) a target of 2000 h of operation with at least 700 h without interruptions is achieved, (ii) the cold gas efficiency of the gasification is greater than 75%, (iii) the carbon content of the ashes is less than 8%, (iv) the emission limits of an equivalent thermoelectric plant fuelled by biomass are respected. In accordance with these objectives, at least 120 t of sewage sludge will be transformed into value-added syngas during the project,
3. obtain the correct setting of the process parameters of the oxygasification plant according to any variable compositions of the sewage sludge and biomass. The reliable operational flexibility of the oxygasification plant will therefore be demonstrated with respect to the variable characteristics of the materials that are fed to the plant. The goal is to reach at least 30% (by mass with biomass) of sewage sludge on the overall mixture.

The project objectives will be achieved realizing and using a full-scale downdraft gasification system with steam-oxygen as gasifying agent and mixture of sewage sludge and residual biomass as feedstock. The system will be composed by a fixed bed downdraft gasifier, with a gross thermal power of about 800-1000 kW (from 200 kg/h of dry feedstock, up to 300 kg/h), a syngas cooling and cleaning system, a pure oxygen supply device, a system for steam supply and injection into the reactor and a flare for the syngas burning.

In the proposed gasifier, which operates at up to 1000 °C, the degree of char conversion reachs very high values, more than 90-95%. The consequent goal is to confine heavy metals, minerals, and contaminants, present in the incoming sewage sludge, almost completely in the residual ash, avoiding hazards.

The plant will be built within the COSIB wastewater treatment plant (industrial area) in the municipality of Termoli (CB).

LIFE AUGIA addresses the topic: “Resource Efficiency, green and circular economy” of the LIFE+ program. Sewage sludge is the residual of the treatment of sewage waters; it contains a large amount of organic material, made mostly of carbon and hydrogen, which represents a valuable resource usually not exploited. In fact, at present, sewage sludge is not seen as an industrial material but mostly as a waste to be disposed. On the contrary, it is a resource to be transformed in a value-added intermediate chemical product, a clear example of circular economy.

Moreover, if successful, the proposed demonstration plant will serve as a model for future fullscale plants in Italy and Europe, giving rise to an industry capable of:

- offering to public and private bodies an alternative in the sludge management policy,
- solving environmental issues connected with landfill disposal,
- mitigating occupational issues.

The project can be also related to another topic, LIFE Projects, Forests, included into the 2013 EU Forest Strategy, which is the “effective and efficient application of tools, methodologies, techniques, technologies and equipment to implement close-to-nature forest management approaches and similar silvicultural alternatives to more intensive forest management”.

The oxy-gasification plant is based in the co-gasification of sewage sludge and woody biomass, and if this last comes from profitable and effective forest maintenance programs it contributes to enrich the local economy, to prevent hydro-geological instability and to reduce the risk of fires. Hence the present project also represents an effective and efficient application of actions dedicated to implement close-to-nature forest management approaches. Considering the energetic aspect of the use of a resource, such as ligno-cellulosic biomass, still largely underused, a considerable advantage could derive from its utilization and the use of thousands of tons of fossil fuels could be avoided. Therefore, the LIFE AUGIA project, which constitutes an example of “circular economy”, has the potential to create many jobs in Europe, while preserving precious and increasingly scarce resources, reducing environmental impacts of resource use and injecting new value into waste products. The plans will extract the maximum value and use from all raw materials, products and waste, fostering energy savings and reducing GHG emissions.

Using an innovative proprietary technology, the project team is interested in the realization of a prototype plant that minimizes char and tar production, completely retaining all metals in the ≈ 8% generated inert ashes. The proposed gasification system competes mainly with the landfill destination but also with land spreading, simple incineration and with the remaining 30% of other disposal routes. It can be considered to candidate as the only alternative to the direct use of sewage sludge as fertilizer.

Typical sewage sludge has an organic-carbon content of about 45- 50% in weight. Nitrogen contributes for some 3%, phosphorus and sulfur for another 2%. Light-weight metals contribute for 4-5%, poisoning metals are collectively responsible for 0.2% (half of what made by Zn). The remaining part consists of hydrogen and oxygen. This means that using and oxygen-based gasification the following results are expected, within the project:

1. the processing of a target quantity of at least 120 t/y of dry sewage sludge,
2. the conversion of about 90% in weight of the annual feedstock in a syngas with a nitrogen contribute as low as 3%,

3. a composition of the produced dry syngas suitable for chemicals production, with an average volume content of hydrogen and carbon monoxide of about 40% and 25%, respectively. Other compounds present in the gas produced are carbon dioxide 30% and methane 5%,
4. resulting (about 8%) carbon free ashes mainly consisting in alkaline metals. Such a composition also stabilizes phosphorus and sulfur preventing the contamination of the produced syngas. Inert ashes can be used in production of concrete without impacting the environment.

From the environmental point of view, the advantage of this gasification treatment is considerable and easy to infer. Indeed, it reduces landfill disposal to zero, recovers a percentage close to 80% in weight of the treated material, producing a gas with high economic value as a raw material for the chemical industry. Moreover, the balance of carbon dioxide, coming from the organic compounds present in the sludge, can be considered at low impact in circular economy because it derives from atmospheric carbon dioxide fixed by the biomass present in the products for human nutrition. So, the carbon of the future chemicals can be considered of renewable origin. Hence, the final chemicals that will be produced via oxy-gasification of sewage sludge and biomass can be fully considered bio-derived renewable chemicals.

5.2 Plant description

As already mentioned, the plant under consideration consists of a downdraft gasification unit followed by a syngas cooler and a gas flaring device. The gasifier will be fueled with suitable mixtures of wooden biomass and sewage sludge, preprocessed and supplied through an automatic loading system. Gasification will be carried out using both air and mixtures of oxygen and steam as oxidizing medium.

In Figure 5.1 is reported the block flow diagram (BFD) of the LIFE AUGIA demonstration plant.

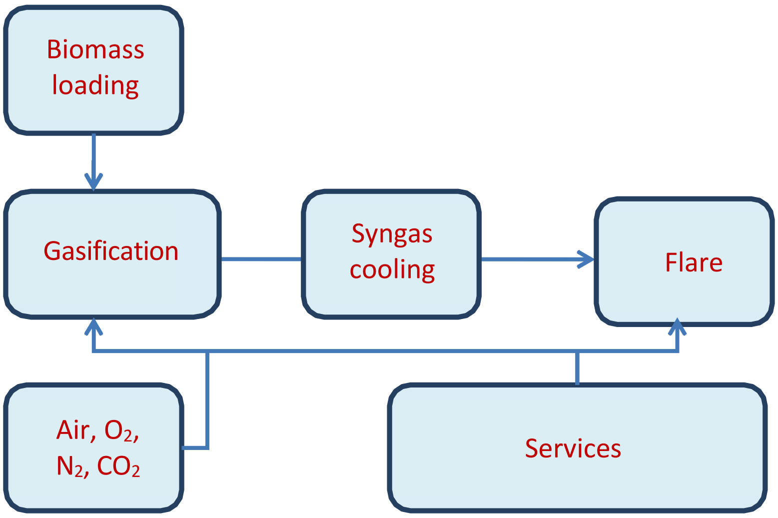


Figure 5.1 - LIFE AUGIA Block Flow Diagram (BFD)

The whole system is designed to be tested in different operating conditions to find its optimal working point according to the intended final use of the syngas; therefore, a very flexible and simple layout has been developed.

The plant layout also includes all the auxiliary services and support systems necessary to its operation as well as the required connections and interfaces with the site existing installations.

The plant, whose process flow diagrams (PFD) are shown in Figure 5.2, 5.3, 5.4, can be divided into five main sections:

1. Feedstock blending and loading system,
2. Gasifier (reaction section),
3. Cooling and cleaning of synthesis gas produced,
4. Services,
5. Support system.

The description of each section can be better followed looking at the PID drawings in appendix A. The plant units with their relative sub-units and the number identification adopted are listed below:

Table 5.1 - Number identification of the plant units

Number	Unit description
100	Feedstock blending and loading system
200	Gasification
300	Syngas cleaning and cooling system
500	Services
510	Auxiliary combustibile gas system
520	Flare system
530	Compressed air system
540	Auxiliaries gas system (N_2, CO_2, O_2)
550	Chilled water system
560	Make-up water treatment system and steam generation
570	Wastewater treatment system
580	Firefighting and safety system
590	Ashes removal and storage
600	Support systems
610	Inbound and outbound weighing of mass
620	Instrumentation
630	Electric system
640	Sewer system
650	Buildings

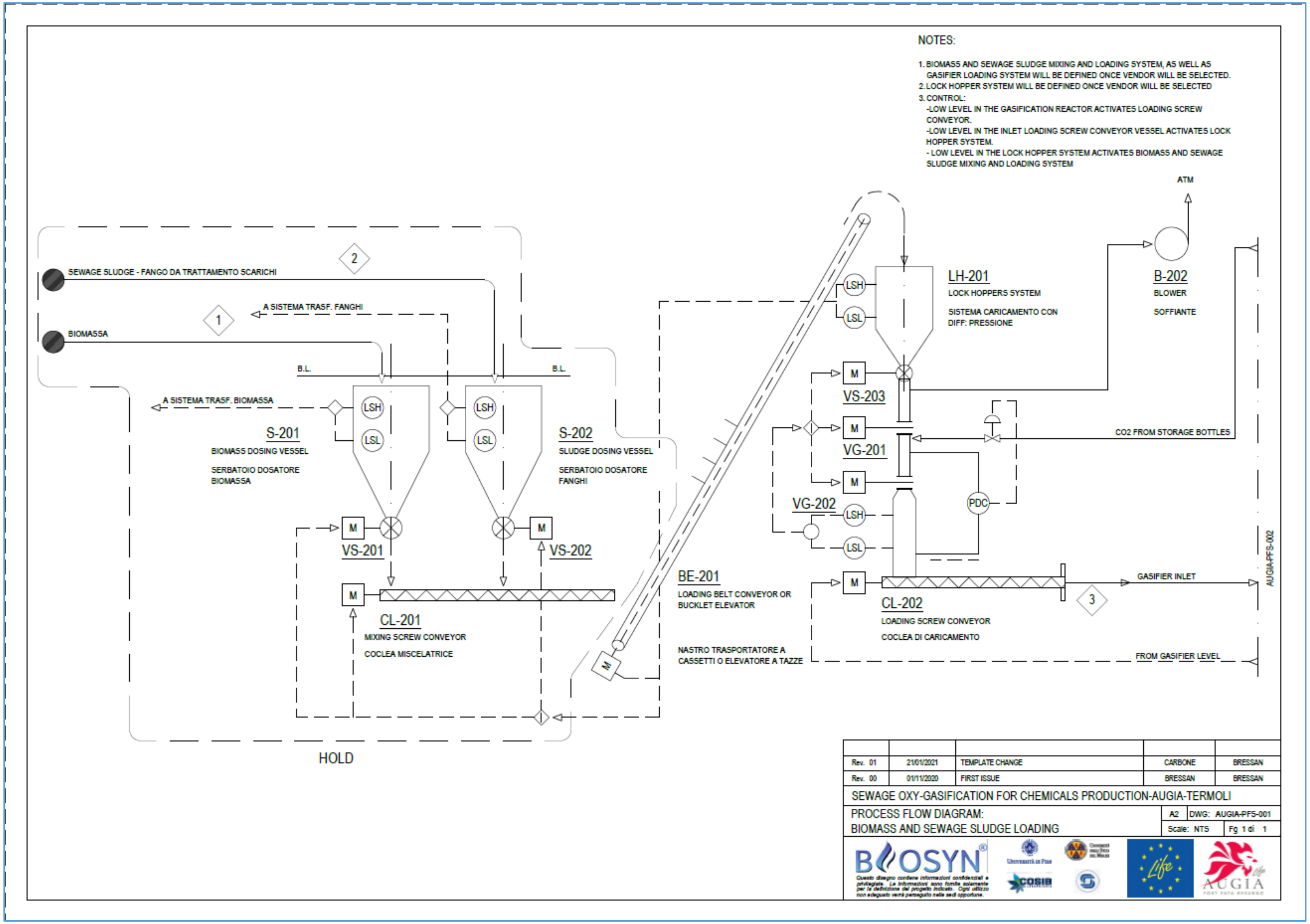
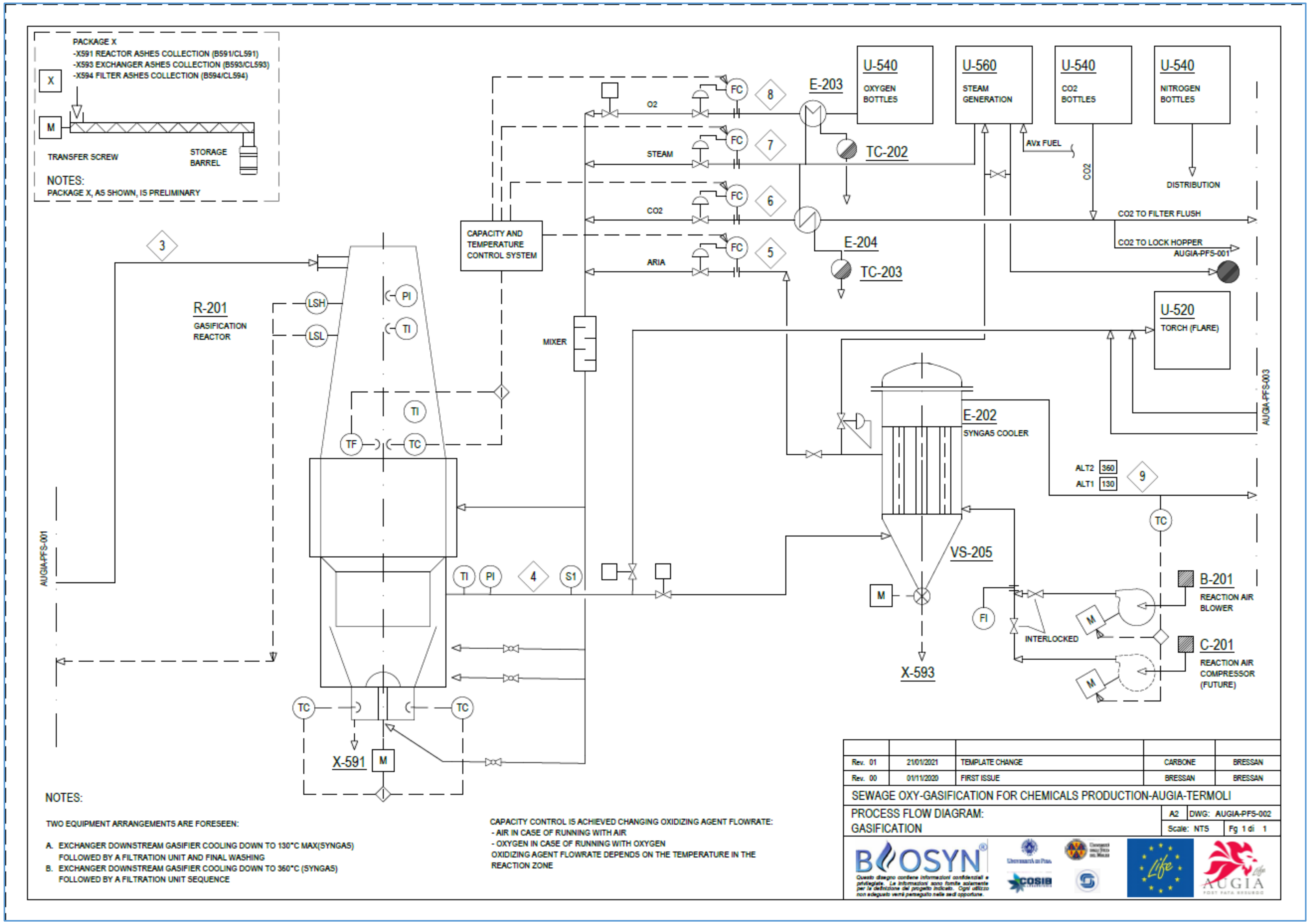


Figure 5.2 – PFD: Biomass and sewage sludge loading



NOTES:
PACKAGE X, AS SHOWN, IS PRELIMINARY

NOTES:

TWO EQUIPMENT ARRANGEMENTS ARE FORESEEN:

A. EXCHANGER DOWNSTREAM GASIFIER COOLING DOWN TO 130°C MAX(SYNGAS) FOLLOWED BY A FILTRATION UNIT AND FINAL WASHING
B. EXCHANGER DOWNSTREAM GASIFIER COOLING DOWN TO 360°C (SYNGAS) FOLLOWED BY A FILTRATION UNIT SEQUENCE

CAPACITY CONTROL IS ACHIEVED CHANGING OXIDIZING AGENT FLOWRATE:
- AIR IN CASE OF RUNNING WITH AIR
- OXYGEN IN CASE OF RUNNING WITH OXYGEN
OXIDIZING AGENT FLOWRATE DEPENDS ON THE TEMPERATURE IN THE REACTION ZONE

Figure 5.3 – PFD: Gasification and syngas cooling

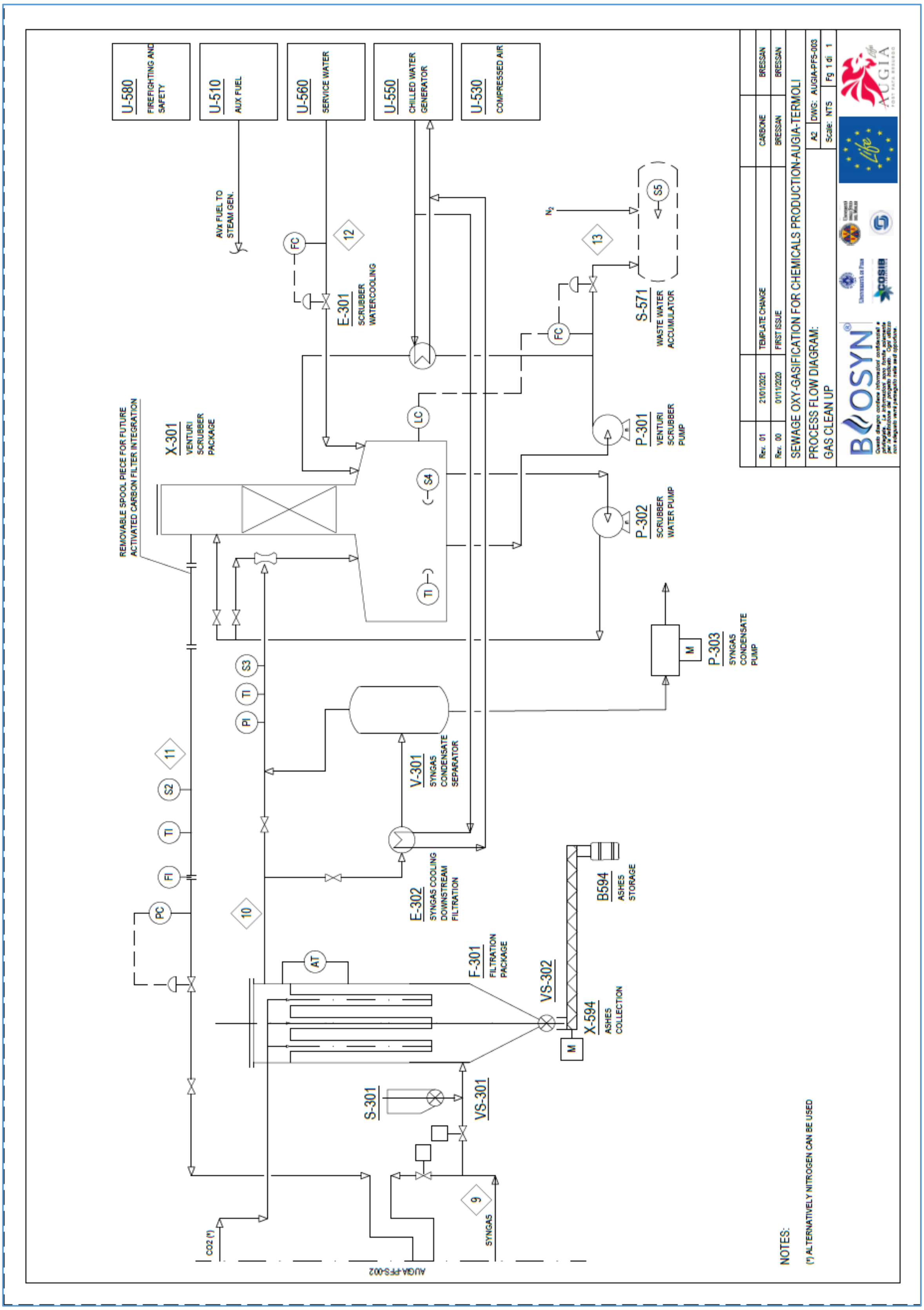


Figure 5.4 – PFD: Gas clean upFeedstock blending and loading system (Unit 100)

The biomass and sludge loading system is composed of the following sequential stages:

- Storage and pre-processing of the two components of the mixture to be gasified (size reduction, drying, densification into pellets or briquettes)
- Composition of the mixture by dosing the components in the required proportion
- Controlled and automatic feeding of the mixture into the gasifier

The system has been designed to ensure a maximum feed rate of 300 kg/h of which up to 30% may consist of sludge. It is important to underline that the addition of sewage sludge is limited by the maximum tolerable ash content in the final mixture sent to gasification. A high amount of ash in the sewage sludge feed may contribute to potential clogging or corrosion of the gasifier and gas pipelines leading to reactor blockage and increasing maintenance costs. Evaluations regarding process efficiency and reliability led to set an ash content limit not exceeding 10%.

The plant will be fueled with feedstocks whose characteristics, determined with laboratory analyses by UNIPI, are shown in Table 5.2 and Table 5.3

Table 5.2 - Results of the characterization of biomass (WOOD CHIPS)

Parameter	**Test method**	**Measurement Unit**		**Result**
Moisture	EN ISO 18134-2:2017	%	as received basis	10.5
Volatile Matter (900°C)	Thermogravimetric method	%	dry basis	82.1
Fixed Carbon	by difference	%	dry basis	16.6
Ashes at 800°C	Thermogravimetric method	%	dry basis	1.3
Carbon (C)	EN ISO 16948:2015	%	dry basis	49.59
Hydrogen (H)	EN ISO 16948:2015	%	dry basis	5.94
Nitrogen (N)	EN ISO 16948:2015	%	dry basis	0.08
Oxygen (O)	by difference	%	dry basis	43.09
HHV	EN ISO 18125:2017	MJ/kg	dry basis	19.83
HHV	EN ISO 18125:2017	MJ/kg	as received basis	17.75
LHV	EN ISO 18125:2017 + EN ISO 16948:2015	MJ/kg	dry basis	18.61
LHV	EN ISO 18125:2017 + EN ISO 16948:2015	MJ/kg	as received basis	16.41

Table 5.3 - Results of the characterization of dewatered sewage sludge

Parameter	Test method	Measurement Unit		Result
Moisture	UNI EN 14346:2007	%	as received basis	78.2
Volatile Matter (900°C)	Thermogravimetric method	%	dry basis	46.4
Fixed Carbon	by difference	%	dry basis	2.7
Ashes at 800°C	Thermogravimetric method	%	dry basis	50.9
Carbon (C)	UNI EN 15407:2011	%	dry basis	22.5
Hydrogen (H)	UNI EN 15407:2011	%	dry basis	2.8
Nitrogen (N)	UNI EN 15407:2011	%	dry basis	3.7
Oxygen (O)	by difference	%	dry basis	20.1
Chlorine (Cl)	EN 15408:2011 + EN ISO 10304-1:2009	%	dry basis	0.17
Sulfur (S)	EN 15408:2011 + EN ISO 10304-1:2009	%	dry basis	0.13
HHV	UNI EN 15400:2011	MJ/kg	dry basis	8.25
HHV	UNI EN 15400:2011	MJ/kg	as received basis	1.80
LHV	UNI EN 15400:2011 + UNI EN 15407:2011	MJ/kg	dry basis	7.66
LHV	UNI EN 15400:2011 + UNI EN 15407:2011	MJ/kg	as received basis	< 1

The feedstock collection and pre-processing system consists of two separate lines, one for the biomass and the other for the sewage sludge. The wet sewage sludge, coming from the COSIB treatment facility, is transported by truck and discharged into a collection tank, from which it is recovered by a motorized auger to be conveyed through a series of conveyor belts (BE-101, BE-102, BE-103) first into a dryer, then into a pelletizer and from there to a dedicated dosing vessel. Similarly, the biomass, already supplied with the right moisture content and size, from a discharge bay is transferred via a specific conveyor belt (BE-104) to the relative dosing vessel.

It is important to control the moisture content of the sewage sludge prior to feed it into the gasification unit. Therefore, upstream the pelletizer, the sewage sludge in dried in a rotating insulated drum to reduce its moisture content to around 10%.

The rotary dryer capacity is 218 kg/h of sewage sludge with a 65% moisture content on a wet basis. A stream of hot air around 330°C (coming from a heat exchanger located on the syngas cleaning lines downstream of the gasifier) is available as direct heat source to dry the sewage sludge. The dryer also offers the option of running on syngas to heat the air or LPG as a backup fuel.

A subsequent pelletizing step transforms the dried sludge into pellets of consistent size and shape (10-12 mm in diameter, 20-30 mm in length) not only to facilitate its handling but also to make its gasification proceeding in a more stable and steady manner.

Biomass and sewage sludge arriving from the pretreatment facilities are temporary accumulated in two separated dosing vessels of limited capacity (1 hour calculated with 20% overdesign) intended for the preparation and the proper adjustment of the fuel blend composition.

Each vessel is equipped with a star valve which, by varying its rotation speed, regulates the downward flow of material and allows it to be dosed and discharged into a screw conveyor (CL-201). The latter acts as a mixing device while transporting the materials to the conveyor belt (BE-201) which in turn loads the resulting mixture into the lock hopper system (LH-201).

The lock hopper is provided to transfer materials from an atmospheric pressure environment to the pressurized gasifier, avoiding contamination with air when running on pure oxygen or rather preventing backflow of gas or ash into upstream feeders and storage devices. The lock hopper acts also as a buffer between the fuel dosing vessels and the gasifier, allowing steady and controlled feeding of fuel into the gasifier, which helps to maintain the efficiency of the conversion process.

A pressurized gas (CO_2) is injected into the lock hopper to regulate its pressure to equal that of the feed hopper at the top of the reactor. The CO_2 stream has the added benefit of not polluting the produced syngas with something that cannot be eliminated from gaseous stream unless unmanageable losses.

A closed inclined auger (CL-202) receives the discharge from the lock hopper system and introduce it into the gasification chamber. The auger feed rate is regulated of by adjusting the rotational speed of the screw through an inverter, which acts on the number of revolutions of the electric drive motor.

The loading systems operates under low level control of the fuel in the upper accumulation section of the gasifier. This truncated conical section is equipped with a paddle switch level sensor as well as an automatic pneumatically actuated shaker to prevent bridging and ratholing phenomena or solid residues sticking to the vessel walls.

5.3 Gasifier (Unit 200)

The core of the demonstration plant is a fixed bed throated downdraft gasifier (R-201) in a dual-fire configuration (Fig.1). This unique design involves the injection of the gasifying agent into two different reactor sections: one, as usual, between the pyrolysis and oxidation zones, immediately above the throat section (primary inlet), the other in the lower part of the reactor, below the mobile grate, with an upward flow hitting the charcoal bed (secondary inlet).

The purpose of this design feature is to create a post-oxidation zone where continuing gasification of those compounds that were not fully involved in the primary conversion process. The positive effects arising on tar reduction, (already favored by the reactor throated configuration), and on carbon conversion efficiency result in a higher yield and improved quality of the final gas.

5.3.1 Reactor layout

As shown in Figure 5.5, the gasifier consists of four main parts; (i) an upper fuel accumulation section, (ii) a reaction chamber, where the solid fuel is converted into gas, (iii) a gas outlet section and (iv) an ash pit, where the non-combustible byproducts of the reaction (ash and unreacted charcoal), are collected and removed through an ash discharge system.

This arrangement ensures the free and continuous flow of the mixture from the top to the bottom of the reactor while undergoing the thermochemical conversion process.

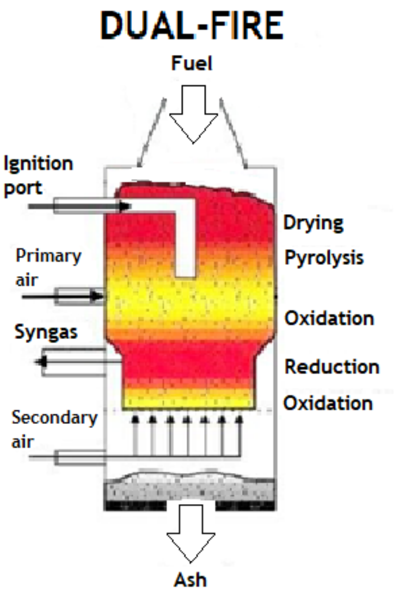


Figure 5.5 – Cross section of the reactor

The solid fuel is continuously fed by a screw conveyor (CL-202) into the upper part of the gasifier from where it moves downwards undergoing drying and pyrolysis. Volatile products from pyrolysis are forced through the heart constriction, where they are partially oxidized by admitting a sub-stoichiometric amount of gasifying medium (air or steam-oxygen) through a set of radially directed intake nozzles. The heat generated is used to drive the entire gasification process. The highest temperatures are reached in this throat section and this causes the condensable organic fraction to decompose into lower molecular weight products, reducing the amount of previously formed tar. The gaseous oxidation products (CO_2 and H2O) are finally passed over a hot pyrolytic charcoal, supported by a perforated movable grate, and chemically reduced into hydrogen (H2) and carbon monoxide (CO). The synthesis gas is extracted, through a circular grid, just below the oxidation zone at a temperature between 550 and 650 °C. A post-oxidation of the charcoal is realized through the secondary injection of gasifying agent in the ash pit, improving carbon conversion and attaining, at the same time, a further thermal cracking of the tar still present.

The perforated ash removal grate located at the bottom of the gasifier prevents ash agglomeration and syntherization. It is driven by an electric motor, which operates at programmable time intervals. The duration of motion and frequency of operation of the grate can be varied depending upon the operating load of the gasifier. The ashes fall periodically through the perforated grate to be collected in a lower chamber (ash pit). From this chamber the ashes are extracted by a screw conveyor and transferred in a storage barrel. The cold gas efficiency was improved by minimizing the amount of charcoal, falling out from the reactor.

5.3.2 Structure of the gasifier.

The gasifier is a cylindrical shell 1.5 m in diameter and about 4 m in height made of alloy steels suitable to withstand the high process temperatures (Figure 5.3).

A sector is appropriately refractory, and the entire mantle is thermally insulated in order to make the process completely adiabatic to prevent heat losses, maintain high temperature level inside the reactor and obtain the appropriate thermal inertia to give maximum stability and efficiency to the process.

Several K-type thermocouple probes are located at different levels along the gasifier to measure and monitor operating temperatures:

- in the reactor top,
- in the gasification zone,
- in the oxidizing medium inlet duct (toroidal)
- at the synthesis gas outlet
- in the ash collection zone

The gasifier is also equipped with pressure gauges for controlling the hydraulic balance of the system and in particular the pressure drop across the gasifier (grate-bed resistance):

- one placed in the reactor top,
- one at the reactor bottom,
- one at the syngas outlet

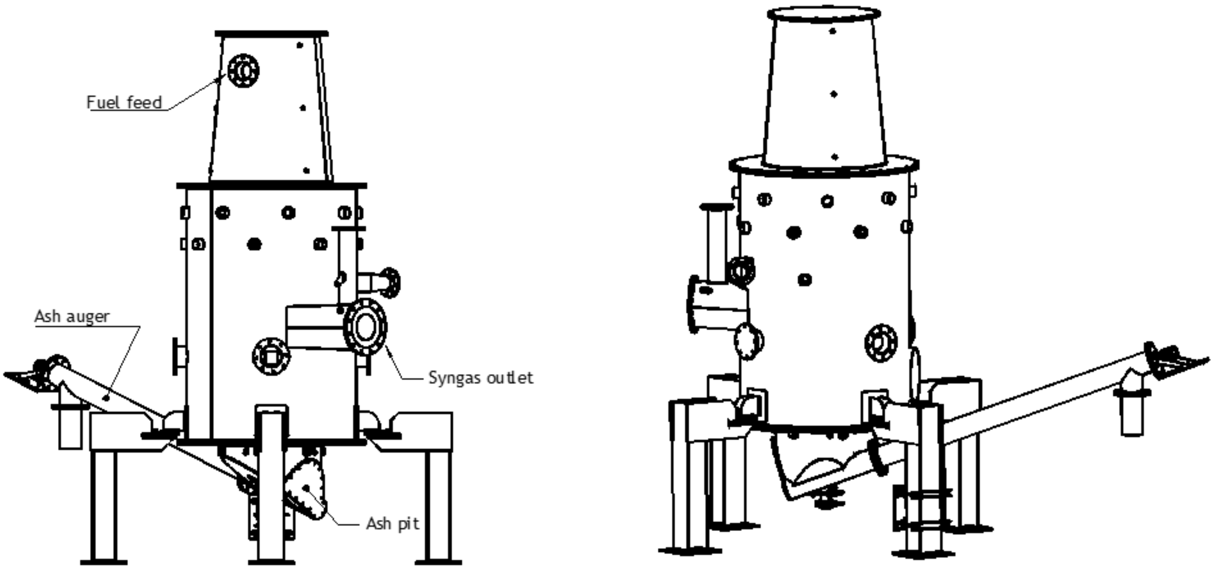


Figure 5.6 – Assembly of the gasifier reactor

5.3.3 Gasifying agent.

Although the system is also set up for using air as gasifying agent, standard operation takes place by supplying pure oxygen adequately mixed with steam, the latter having a dual function, both as a thermal flywheel to keep temperatures within the expected operating range, and to promote desired chemical reactions (water gas shift). CO_2 can also be injected as moderator taking the role of the steam.

Syngas quality is dramatically affected by the purity of the oxygen used in gasification, with increased purity leading to reduced levels of nitrogen and its (toxic) oxides, increased levels of combustible gas components and enhanced calorific values. The calorific value of air-based gasification syngas is typically around 4÷5 MJ/Nm^3 but increases to 10÷12

MJ/Nm^3 with oxygen-based gasification. In addition, gasification performance, as measured by cold gas conversion efficiency, is also affected, with levels rising from 40% for air-based systems to 80% in oxygen-based systems.

The addition of steam promotes the production of a synthesis gas with a high hydrogen content, which is essential for its use in various chemical processes.

The reactor is equipped with an innovative distribution system of process oxygen, subject to international patent filing. The solution adopted makes the oxidative phase very efficient, because it allows a homogeneous distribution of the gasifying agent, maintaining constant temperature and uniform "blast velocity" throughout the oxidation section.

The gasifier is operated with a fan forcing or drawing the oxidizing agent through the reactor. The operating mode selection will depend on the chosen gasification pressure.

5.4 Syngas cleaning and cooling system (Unit 300)

The raw gas leaving the gasifier needs to be cooled and cleaned before any intended application. The high syngas outlet temperature together with the presence of impurities such as solid particles, ash, tar and humidity, can damage the downstream equipment or reduce the efficiency of the overall process. Pollutants may be also present including sulfur compounds, nitrogen compounds, heavy metals and other trace elements.

Cooling is intended to bring the syngas to a safe and appropriate temperature while cleaning pursues the removal of impurities and possibly pollutants, ensuring that the gas can be used effectively without being harmful to the environment.

The adopted syngas cleaning and cooling train entails the following equipment in series: a syngas cooler (E-202), a filtration package (F-301), a heat exchanger (E-302), a condensate separator (V-301) and a final Venturi scrubber (X-301).

The first cleaning stage is performed by a high temperature cyclone inside the syngas cooler (E-202) to mechanically remove the heavier particles entrained by the gas stream. The partially cleaned hot gas is then passed through a vertical shell and tube heat exchanger to decrease its temperature before filtration. The cooling fluid is air, which once heated is partially sent to the gasifier as oxidizing agent and partially routed to plant battery limits for any usage compatible with its heat content, typically sewage sludge drying. Recovery of heat from the syngas is essential for attaining process efficiency. During oxygen-based operation the cooling air stream will be entirely sent to plant battery limit.

The exchanger is of the straight-tube type with one pass tube-side arrangement: air passes through the surrounding shell and the syngas travels through the tubes. Air is preheated up to 400 °C while the synthesis gas gets cooled down from 650-700°C to around 150-180 °C. Part of the test planned on the system is to verify the capability of the exchanger to safely operate for long time cooling down the syngas to about 100-130°C.

Twisted tape turbulators are present inside the tubes in order to improve heat exchanger efficiency and at the same time to reduce the material deposition.

Deposition of crystalline and dry material on the internal walls of the pipes is expected. The deposits are discharged from the bottom of the exchanger in a motorized auger to be conveyed in storage barrel.

The exchanger is equipped with all the facilities to allow putting it out of operation and cleaning the tubes. The upper part of the exchanger has a removable head in order to open it quickly and clean it using suitable cylindrical brushes.

The cooled syngas (and is expected deposition of materials along exchanger pipes) goes to a bag-house filter (F-301) where particulate and fines are removed. The syngas temperature is kept above 120 °C to avoid any condensation inside the filter, which can cause fabric bags clogging with an increase in the pressure drop and a reduction in the gas flowrate. Regeneration of the filtering elements is done by blowing in CO_2. Dust extraction from the collector hopper happens via a foot valve and a screw conveyor connected to a collection barrel.

A second heat exchanger (E-302) is located after the filtration unit to further cool the hot gas. A condensate separator (V-301) is introduced at the exit of the heat exchanger. This separator consists of a two-phase vertical drum with the purpose to trap the mist in the syngas stream formed due to cooling of the gas.

After the condensate separator, a scrubbing system (X-301) based on nebulized cold water is installed to finalize the cleaning of the gas. Being of the Venturi type, the scrubber brings together the scrubbing water and gas stream in turbulent contact, ensuring high abatement efficiency of entrained fine particulates, possibly not separated by the filter, and the condensation and separation from the gaseous flow of the tar present as well as the removal of soluble contaminants such as ammonia and chlorides.

The water used for washing is continuously recirculated by means of a pump (P-302) and diffused inside the scrubber by means of a spiral nozzle. The possibility to chemically treat the circulating water makes the solution capable of achieving cleaning levels adequate for any subsequent chemical reaction steps.

In case the possibility to cool down the syngas exiting the reactor down to 100°C demonstrates unfeasible, the option to cool down to 360°C will be considered. Naturally, due to the high temperature reached, the filtration unit cannot be placed in the previously identified position but must be preceded by the washing phase which will have the further task of cooling down the syngas.

Once out of the Venturi scrubber, the syngas will be sent to the flare to be burned.

A calibrated flange (FT315) is foreseen on the inlet line to the torch for the instant outlet flow measuring. A part of the syngas leaving the plant is conveyed to the analysis section, where its composition is determined using the gas chromatograph.

The gas, which is saturated with water, risks compromising the instrumentation itself, since the capillary columns of the gas chromatograph are equipped with a stationary phase which absorbs water. To overcome this problem, , two special filters capable of dehumidifying the gas are provided in series.

5.5 Services (Unit 500)

Information about the plant auxiliary systems is given below. Where auxiliary services generation is not envisaged in the plant they come from external sources or providers.

5.5.1 Auxiliary combustible gas system (Unit 510)

The plant is completed by the auxiliary system that supply the support fuel. LPG has been chosen to:

- to assist the torch operation
- to purge the torch line
- to eventually operate the biomass drying system
- to provide heat for steam generation.

The supplied LPG will be stored in a dedicated tank.

5.5.2 Flare system (Unit 520)

During transient operations, such as start-up, shutdown, or maintenance, the gasification plant may not be able to process all of the gases being produced. A flare serves as an important safety and environmental control measure to burn off these excess gases. The flare helps to prevent the build-up of flammable gases, which can be dangerous, and also to reduce emissions by burning off any impurities or contaminants, that may be present. In the current configuration of the plant, which does not envisage any downstream syngas utilization system, the flare is used to burn the syngas produced, avoiding its release into the atmosphere. Any gases resulting from purging or inerting the secondary equipment will also be flared.

The flare is equipped with a spark ignition system and, as already pointed, is LPG-assisted for smokeless burning.

5.5.3 Compressed air system (Unit 530)

A compression system for both service and instrument air is planned, featuring a reciprocating compressor (potentially "oil-free"), an accumulation system, and a drying system.

5.5.4 Auxiliaries gas system: N2, CO_2, O2 (Unit 540)

Nitrogen system: The nitrogen system distributes the inert gas to purge the equipment before it is opened for inspection.

CO_2 system: Bottles of CO_2 are provided. CO_2 is used in the lock hopper to purge the feedstock of the air and gain enough pressure to enter the reactor.

O2 system: Bottles of O2 are provided. O2 is used as an oxidizing agent in the gasification reaction.

5.5.5 Chilled water system (Unit 550)

The cooling system is made up of a chilled water circuit, that consists of a pumping station for cold fluid transfer to users and a chilling system. The heat sink is an air cooler with an electrical driven compression unit is. Chilled water is required by the process to capture the low boiling tars (i.e. phenols)

5.5.6 Make-up water treatment system and steam generation (Unit 560)

The make-up water will be drawn from the aqueduct, possibly treating it (softening). In addition, a steam generation system is planned, which will provide the steam needed to moderate the oxygen gasification. For its generation, a boiler powered by LPG will be used.

5.5.7 Wastewater treatment system (Unit 570)

Wastewater derives from the water contained in the biomass fed to the plant, plus the steam introduced as a gasifier minus the water which enters the gasification reactions. Purge water from the scrubbing and dehumidification system must then be considered.

The water will be accumulated in a special vessel where it will be analyzed before being transferred to the COSIB wastewater treatment plant.

In any case, wastewater will be minimized by ensuring the balance between the water fed into the system and the water absorbed by the gasification chemistry.

5.5.8 Firefighting and safety system (Unit 580)

The plant will be equipped with a protection system. The system adequately integrated with the existing facilities will include:

- fire-fighting water used by strategically placed hydrants (accumulation of water for 1 hour autonomy, pumps with safe electrical source, hydrants)
- trolley CO_2 fire extinguishers for intervention on electrical parts
- wheeled powder extinguishers for local interventions
- CO gas alarm system in the plant

5.5.9 Ashes removal and storage (Unit 590)

The ashes collected from the various equipment bottoms and discharged through a star valve will be automatically transferred via a specific auger in metallic barrels suitably insulated and tightly closed to avoid gas leaks. The barrels content will be collected as needed to carry out adequate analysis and later on sent for disposal.

5.6 Support systems (Unit 600)

5.6.1 Inbound and outbound weighing of mass (Unit 610)

The biomass and sewage sludge weighing procedures are performed in the existing installations.

5.6.2 Instrumentation (Unit 620)

The instrumentation system is conceived to perform all control and supervision activities for the gasification plant. The system is particularly important because not only control the plants but transmit to the operators the variable necessary to optimize the plant operation and verify the design data corresponds to the effective plant variables.

5.6.3 Electrical System (Unit 630)

The electrical system is just a distribution system, where electrical loads are collected and brought to the power source.

5.6.4 Sewer system (Unit 640)

Non contaminated water, accurately collected, will be delivered to the existing installations sewerage.

5.6.5 Buildings (Unit 650)

The plant will be placed under a sheltered metal structure for its protection against bad weather and to give plant operators the opportunity to closely monitor the equipment. The control room with instrument and electrical panels is housed in an office site container.

Spaces will be reserved for the gasification plant in the existing plants of the COSIB industrial area.

5.7 Control system

The system is design to operate automatically without operator intervention during normal operations and safety shutdowns. The operator can manually override the controls at any time, excluding interlock logics which must always be active for plant protection.

Return to automatic control occurs from the current state of the variable, not from its value at the time of switching to manual. The system allows for maximum visibility of operations, including waiting times, and easy adjustment of control parameters and sets. The control system of the gasification and syngas cooling unit is designed to allow a quiet and shock-free operation of the plant. Figure 5.7 shows the control system architecture.

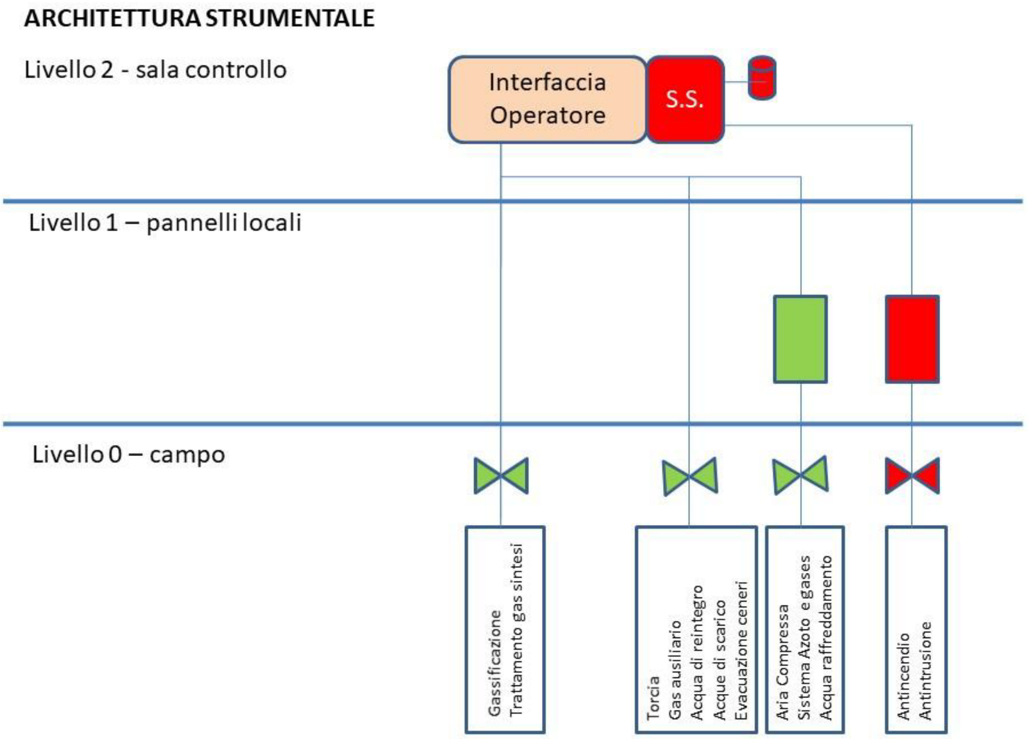


Figure 5.7 – Control system architecture

Plant functions and parameters are monitored through a control room user interface and local panels for field instrument readings. Remote monitoring is possible through interconnection software.

The plant being considered is a demonstration unit where several operating options will be tested to determine the most suitable for achieving the desired outcome. Reference is made to the following conditions:

- Pressurized air - operation at positive pressure within the gasifier, but never exceeding 700 mm H2O.
- Depressurized air - operation under a slight vacuum condition (never below 400 mm H2O).

- Pressurized oxygen - operation at positive pressure within the gasifier, but never exceeding 700 mm H2O.
- Depressurized oxygen - operation under a slight vacuum condition (never below 400 mm H2O).

5.7.1 Operating modes

Four different operating modes are planned based on the type of gasifying agent used:

1. *Operating mode 1* - Oxygen-base pressurized system: The oxygen, pushed by the pressure in the storage cylinders, flows through the gasifier. Under this thrust the produced syngas goes through the cleaning system, bypassing the blower, and reaches the flare, after passing the pressure control valve, which maintains the correct final pressure.
2. *Operating mode 2* - Oxygen-based depressurized system. This mode involves the main blower, which draws the gasification fluids (oxygen and syngas) through the system to the flare, decreasing the circuit pressure below atmospheric level.
3. *Operating mode 3* - Air-based pressurized system. The main blower forces ambient air through the gasifier. Under this thrust the produced syngas flows through the cleaning system, and finally reaches the flare to be burned.
4. *Operating mode 4* - Air-based depressurized system. In this mode, the main-blower sucks in ambient air, while simultaneously drawing time the resulting syngas through the gasifier and the cleaning system to the flare"

5.7.2 Controls Definition

The demonstration gasification plant operates in accordance with some fundamental control logics that were implemented and managed by the governing PLC. These rules logics assure large flexibility from the operative point of view and the possibility to test different configurations. In particular the logics are:

1. Syngas flow control

This control allows the regulation of the syngas flowrate by acting via the electric motor inverter on the rotating speed of the main blower (B-201). The control action also affects the flow of the oxidizing agent (air or oxygen). The control signal passes through a switch which transmits it either to the air supply system or oxygen supply system.

- Air supply system: the control logic is the same for both pressurized and depressurized operating modes. The difference lies in the positioning of the block valves around the blower, which in case of pressurized operation forces the ambient air into the reactor while in case of depressurized operation draws the syngas from the reactor. Operator can change the flowrate also manually.
- Oxygen supply system: it works in a similar way to the air supply case but with some differences. When the system switches to pressure mode, the gasifying agent circulates not by means of the blower, which is by-passed, but thanks to the pressure of the relative storing cylinders. In this case it is necessary to activate a pressure control by acting on the control valve positioned on the line going to the flare. The oxygen

injection is triggered by a signal from the flow control flange located upstream of the pressure control valve. Pressure losses in the circuit determine the actual pressure value in the system. It must be highlighted that the oxygen flowrate is not determined by the inputs received from the flange, but by other signals from the oxidation control system. As with the air supply, the depressurization mode is obtained by letting the blower (B-201) suck from the gasification reactor and regulating its rotation speed to get the desired flowrate. The extent of depressurization depends on the pressure losses within the system.

2. Circuit pressure control

The circuit pressure control regulates the flow rate of the gasifying agent in the pressurized oxygen supply mode when the reaction blower is excluded. Pressure at the control point is determined by the syngas flowrate, given by the pressure losses in the circuit.

3. Gasification temperature control

This control is the most critical one because its failure can cause serious problems for the reactor. It is only enabled during oxygen operation. No temperature control is needed for air-based gasification, as temperature serves only as a control parameter for triggering a flowrate change through the system. The temperature is detected in the gasification section of the reactor.

The control principle is to maintain the temperature set-point through steam injection regulation. To prevent temperature fluctuations and ensure timely steam injection, when necessary, the steam flow is set at a fixed ratio to the oxygen flow.

The same principle applies to CO_2 when used as an alternative to steam as temperature moderator in gasification.

The preset fixed ratio may need to be adjusted when in actual operation no temperature raise is recorded even with an increased oxygen injection deriving from increased load. Two options are available for the operator to follow: manual adjustment or automation. Changes to the ratio are rare unless substantial changes in moisture content or composition of the feedstock occur. It is expected to remain constant under normal conditions. If the ratio is adjusted automatically, it is done stepwise whenever conditions limit the plant. The maximum temperature is a crucial indicator in this process.

When the maximum temperature is reached and plant load is low and not in line with the control request, the ratio should be increased (more steam). Conversely, if the plant load is already at the maximum requested and the temperature is low, the ratio should decrease (less steam).

Fixed ratio reset should only be done after collecting a substantial amount of data on the specific feedstock.

When using enriched air, the control should be either assigned to air or oxygen at the operator's discretion, with the non-controlling agent being fixed.

4. Lock hopper operation

The lock hopper operates in a specific sequence to manage and control the flow of materials within the system. Its functioning requires the use of gate valves and pressure control valves to regulate the flow of biomass and gas (CO_2). The operation is automated and involves the controlled and sequential opening and closing of the valves to flush, pressurize and unload both the transfer and the discharge vessel.

5. Level control in the gasifier

The level control system is governed by two switches: a low-level switch that starts the loading process, and a high-level switch that stops it. The loading process includes a screw conveyor to transfer feedstock from storage, a conveyor belt, a lock hopper system, and a screw conveyor to load the gasifier. The conveyor belt and lock hopper run continuously at optimal speed, while both screw conveyors start and stop simultaneously to control the loading process. Screw conveyors are equipped with an inverter motor to adjust their operating speed.

6. Ash pit temperature control

The periodical ash and unburned char discharge from the reactor to the ash pit is regulated by the rotation of the bottom grate. The grate rotates at regular intervals, controlled by a system that modifies their frequency and duration based on the temperature in the ash pit.

7. Syngas cooler temperature control

Temperature is controlled by a temperature controller that acts on the inverter of the blower (B-201) that in turn change the air flow through the syngas cooler.

8. Temperature control of the air flow inlet to the syngas cooler

To prevent undue cooling of the syngas exiting the cooler, a temperature control is installed to raise the ambient air temperature to 65°C, by recirculating heated air from the cooler.

9. Pressure control in the cooling air circuit

A self-acting pressure control valve is installed in the recirculating air line to the cooler, after diversion of the preheated air.

5.7.3 System Monitoring

A sampling system is provided to check the characteristics of significance fluids for the plant under consideration. The following withdrawal points are foreseen:

- S1 - at the gasifier outlet/syngas cooler inlet to measure the content of tars, dust and micropollutants in the produced gas.
- S2 – at the flare suction side for measuring syngas composition and its content of tars, dusts, micropollutants. The composition of the synthesis gas is detected on a continuous basis by means of a portable gas chromatograph.

5.7.4 Recorders

From the control panel it is possible to monitor the following parameters:

- TI219 R temperature of syngas at reactor outlet
- TI217 R temperature in ashes collection zone
- PI216 R pressure in gasifier bottom
- TI223 R temperature in gasification zone

- TI222 R temperature in midway reactor flow
- TI225 R temperature at reactor top
- PI224 R pressure at reactor top
- FI229 R flow of steam to reactor
- FI228 R flow of oxygen to reactor
- FI227 R flow of CO_2 to reactor
- FI226 R flow of air to reactor
- TI234 R temperature of syngas fron syngas cooler
- TI314 R temperature of syngas to battery limits
- FI315 R flow of syngas to flare
- PI316 R pressure of syngas system proximity of flare
- FI569 R flow of steam
- PI570 R pressure of steam
- TI568 R temperature of steam

5.8 Start-up and shutdown of the plant

The plant will be started on air and switched to operation on oxygen when required. The start-up procedure of the plant will be as described below in outline.

The reactor is loaded with feedstock up to a predefined bed level. The system is then connected to the electricity grid and switched on. The main blower is turned on at a reduced capacity to active a “short” air circulation: the gas treatment system is by-passed and the air at the reactor outlet is sent directly to the flare. An electric heater in the air inlet line brings air temperature to that required for the feedstock mixture ignition.

Once the oxidation reaction has been triggered, the so-called "short" circulation is maintained until reaching proper gasifier operation indicated by the flare flame color. The flare could be in same cases assisted by a gaseous fuel to avoid dark smoke to the atmosphere.

The gas treatment system is then put on-line using the main blower at its maximum flow and closing the "short" circuit with the supporting fan. Finally, the feedstock loading system is started together with the reactor ash removal system.

Immediately after stabilization with air, the plant switches to oxygen operation. Oxygen is injected under control of the reaction temperature with the addition of moderating steam according to a fixed steam to oxygen ratio. Air is slowly reduced, and plant then operates in full-oxygen mode at the intended pressure.

The plant has an automatic shutdown system designed to quickly terminate operation in the event of a problem or when corrections are needed. The shutdown system can be activated by the following events:

a. Control room push button,

b. Reactor elevated platform push button,
c. High Temperature in the reaction zone,
d. High Temperature in the grate area,
e. High Temperature at the reactor syngas outlet.

During plant shutdown, the solid fuel supply stops, and the system is gradually switched back to air keeping anyway the main blower at is maximum flow. The gas produced is sent directly to the flare until the fuel in the gasifier reaches the level of the oxidation zone. All equipment is then switched off and the system is disconnected from the electricity grid.

Chapter 6

Materials and methods

The co-gasification of biomass and sewage sludge is a complex process that involves multiple reactions and interactions between the feedstocks, products, and the environment. Understanding these phenomema is essential to control the product quality and yield of the syngas produced.

The characterization of the feedstocks is therefore a crucial step in this direction, as it allows a better insight in the properties and behavior of the materials during gasification.

Similarly, syngas characterization is essential in determining its composition, properties (LHV) and level of contamination. This information is important in optimizing the gasification process and ensuring the safe and efficient use of the produced gas. Syngas composition can affect the efficiency of downstream processes such as combustion and conversion to chemicals.

Gasification experiments are another significant tool in order to study gasification and to determine the effects of process parameters on its performance. The valuable information they provide can be used to optimize the gasification process, improve its efficiency and sustainability, and develop new technologies.

However, studying experimentally the process can be challenging and costly, and it may not be possible to fully understand the underlying mechanisms and relationships. Therefore, using a simulation model is a further effective way to study gasification in a controlled and comprehensive manner.

In this chapter, we describe the materials and methods used for the characterization of the feedstocks and of the syngas produced.

The gasification experiments performed and the simulation model used to analyze the process are described in details later in the thesis in the dedicated chapters, namely chapter 7 and 8.

6.1 Materials

In order to assess the operability and reliability of the sewage sludge oxygen-based gasification plant and to optimize the process parameters, a fundamental characterization of the feedstock is required.

This characterization is also important to obtain the information needed to perform the experimental data analysis, to develop and run the simulation models and to carry out the mass and energy balances of the process.

The following materials were characterized:

- Wood chips
- Dewatered Sewage Sludge
- Lime stabilized Sewage Sludge

both to obtain useful data for the numerical modeling of the LIFE AUGIA gasifier and the preparation of the related mass and energy balances,

- Woody pellets

to carry out gasification tests on a laboratory-scale pilot plant set up at the University of Pisa

6.1.1 Sewage sludge

The sludge to be used in the demonstration plant envisioned by the LIFE AUGIA project comes from a wastewater treatment plant located in the industrial zone of Termoli (CB) and owned by the Consortium for Industrial Development of the Biferno valley (COSIB).

This plant is used for the treatment of civil wastewater from production sites in the industrial area and has a capacity of around 23,000 population equivalents (PE).

The treatment process includes: screening, equalization, sand removal, sedimentation-degassing, pre-aeration, chemical-physical treatment (removal of colloidal substances through clarification-flocculation), biological treatment, secondary sedimentation, and disinfection using sodium hypochlorite.

The sludge residue is taken from the primary sedimentation tank and undergoes thickening, dehydration, stabilization with calcium oxide, and disposal in a landfill.

Figure 6.1 - Aerial view of the COSIB wastewater treatment.

The sludge sample was first dried to remove ambient moisture, then ground to create a powder from which take portions on which perfom subsequent analyzes.

Figure 6.2 - Picture of the sewage sludge analysed.

6.1.2 Wood chips

The biomass sample analyzed is of the same material that will be fed during the experimental trials to the demostrative LIFE AUGIA plant. It consists of conifer wood chips (Scots pine) from the Trentino Alto Adige region (Italy), obtained from forestry and forest management residues (Figure 6.3).

Woodchips were provided by Biosyn srl one of the associated beneficiaries of the LIFE AUGIA Project.

The sample was first dried to remove ambient moisture, then ground to obtain a powder from which portions could be taken for subsequent analyses.

Figure 6.3 - Picture of the wood chips analysed.

6.1.3 Wood pellet

Given the impossibility of performing gasification tests on the LIFE AUGIA demonstration plant still under construction, an experimental campaign was conducted on a pilot downdraft gasifier, which was set up in the laboratories of the University of Pisa. The purpose of the study was to observe the behavior of the biomass gasification process when using pure oxygen and steam as gasification agents and to collect operative data for the validation of the simulation models developed.

The fir wood pellet used in the start-up tests of the pilot plant and in the subsequent experimental trials is of the type commonly used in domestic stoves (Figure 6.4). The sample underwent the same preparation as for the wood chips.

Figure 6.4 - Picture of the wood pellets used in the experimental champaign.

6.2 Methods

The characterization of the feedstocks was carried out using a variety of methods, including:

- Proximate analysis
- Ultimate analysis,
- Bomb calorimetry (Berthelot-Mahler).

Proximate analysis was used to determine the moisture, ash, volatile matter, and fixed carbon content of the materials. Ultimate analysis was used to determine the carbon, hydrogen, nitrogen, sulfur, and oxygen content of the materials. Bomb calorimetry was used to measure the gross calorific value of the feedstocks.

As regards gas analysis, the following techniques were used:

- Gas-chromatography,
- Tar analysis (condensation and absorption sampling method)

Gas-chromatography has allowed both the separation of the various gaseous compound present in the gas and the qualitative-quantitative analysis of its main components such as: CO, H2, CO_2, CH4, C2H2, C2H4 and C2H6.

6.3 Biomass sample preparation and characterization

In biomass thermochemical conversion, the feedstock composition as well as its energy content greatly influence the process behaviour and its performance. Knowledge of the biomass feedstock characteristics is therefore of considerable importance for designing and operating the biomass utilization system.

Biomass contains a large number of complex organic compounds, moisture, and a small amount of inorganic impurities known as ash. The organic compounds comprise four principal elements: carbon (C), hydrogen (H), oxygen (O), and nitrogen (N). Biomass may also have small amounts of chlorine (Cl) and sulphur (S). [8]

Biomass feedstock proceeds from diverse sources and exhibits variable chemical composition, which has an influence on their specific properties and applicability.

The main analytical parameters typically used for a correct characterization of biomass and an evaluation of its potential as a gasification fuel are:

- Moisture content.
- proportions of fixed carbon and volatiles
- Ash content.
- Chemical constituents: carbon, hydrogen, oxygen, nitrogen, sulphur and total mineral matter.
- Calorific value.

The methods of analysis, the necessary instrumentation and the methodology used to determine the aforementioned properties are illustrated below.

6.3.1 Reporting analytical results

For a more convenient interpretation of the laboratory tests, the sample to be analysed can be divided into two fractions (figure 2.1): a combustible hydrocarbon fraction (C, H), in which are also present oxygen (O) and other quantitatively less relevant heteroatoms (N, S, Cl, etc.), and a second non-combustible fraction consisting of moisture and ashes.

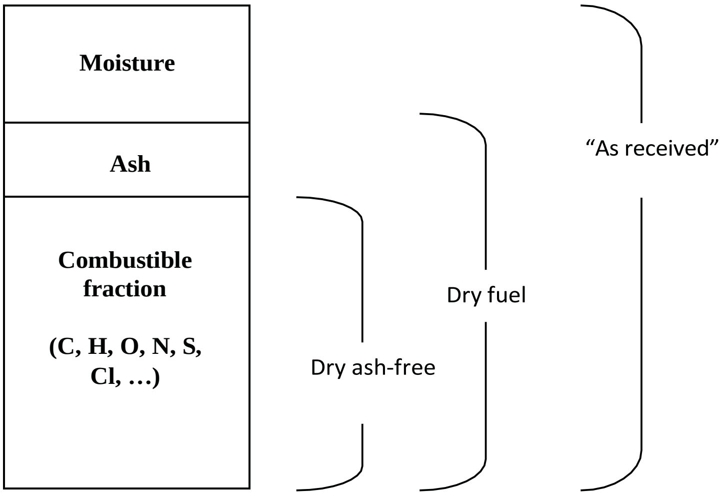


Figure 6.5 - Schematic biomass analysis and results recording bases

This simplified and empirical point of view allows to report the analytical results in different bases, depending on whether they refer:

- to the moisture condition of the biomass sample "*as received*" at the testing facility,
- to the “*dry*” part of the sample,
- to the “*dry, ash-free*” part of the sample.

The results are expressed in percent by weight (% w/w). The AR (as-received) basis puts all components into consideration and uses the total weight of the sample as the basis of measurement. The DB (dry basis) refers to a moisture-free sample. The DAF (dry, ash free) basis neglect moisture and ash constituent and consider only the "combustible fraction".

A comparison between different materials is therefore significant only if data are expressed on a homogeneous basis, which should always be specified. Table 2.1 shows the conversion factors for standard reporting in different bases, as indicated by the technical specification ISO 16993:2016 [97] relating to solid biofuels.

Table 6.1 - Conversion factors of the analysis results in different bases.

Given	**Data to be calculated**		
	As received (ar)	**Dry (d)**	**Dry, ash free (daf)**
As received (ar)	-	$x_{ar} \cdot \frac{100}{100 - M_{ar}}$	$x_{ar} \cdot \frac{100}{100 - (M_{ar} + A_{ar})}$
Dry (db)	$x_{db} \cdot \frac{100 - M_{ar}}{100}$		$x_{db} \cdot \frac{100}{100 - A_{db}}$
Dry, ash free (daf)	$x_{daf} \cdot \frac{100 - (M_{ar} + A_{ar})}{100}$	$x_{daf} \cdot \frac{100 - A_{db}}{100}$	-

where A represents the biomass ash content while M is the moisture content.

6.3.2 Sampling and samples preparation

Operating samples were collected by increments from both woody biomass and sludge to ensure that they could truly represent the properties of the entire body of feedstock. A series of small portions were extracted repeatedly and from different parts of the lot of material being explored. For each feedstock, they were then combined into a gross sample (1 kg or less) that was employed for the application of the laboratory test methods.

Before being used in relevant analytical instruments, the *"as-received"* samples were first dried, to remove moisture, and then ground in order to take as homogeneous and representative sample aliquots as possible for characterization purposes.

Figure 6.6 - RETSCH (SM 100 Model) Cutting Mill

The dried samples were comminuted by means of a laboratory RETSCH cutting mills (fig. 2) until a fine powder was obtained, taking care, at the same time, to avoid a size over-reduction of the sample, to generate excessive heat and to cause significant losses of moisture.

6.3.3 Moisture content

Moisture refers to the quantity of water (free and bound) existing within the biomass at a given temperature. The moisture content is usually determined by measuring the weight loss of a sample upon heating it at 105°–110°C under standard conditions. This method allows to determine the total free moisture given by the sum of the superficial moisture and inherent moisture: the first is due to the thin layer of water retained on the surface of the sample, while the second represents the water present inside its capillaries and pores. Total free moisture does not account for water of thermal decomposition (chemically bond to organic compounds) and water of hydration (associated with the mineral compounds).

Moisture content of biomass in natural conditions varies depending on the type of biomass, the weather conditions, the methods and times of transport and storage.

The moisture content strongly influences some physical properties of the feedstock, with adverse effects both on technical-operational aspects and on some qualitative characteristics of the material such as density and calorific value. It is a critical parameter also for the gasification performance since it has a marked effect on gasifier temperatures and consequently on the carbon conversion efficiency (Kirsanovs V. et al., 2017). Moreover, moisture can also affect the gasifier feeding system causing blockages and unsteady operation.

Experimental procedure and instruments

To determine the moisture content, the as received and unground sample (about 5 ÷ 50 g), was weighed, using suitable containers, in an electronic analytical balance (SCALTEC SBC 31) and then placed in a ventilated drying oven (BINDER GmbH) at 105 °C and hold (about 10 hours) until obtaining a constant weight. After cooling it in a desiccator, the sample was weighed again.

The difference between the dry weight and the initial weight m_o represents the weight loss Δm of the sample. The moisture content, expressed as a percentage by mass, is given by the formula:

$$\frac{\Delta m}{m_o}\, x\ 100$$

The result is given to one decimal place and is calculated as the average of three determinations.

6.3.4 Proximate analysis

Proximate analysis is the determination, by prescribed methods, of the composition of biomass in terms of gross components. The test involves heating the biomass under various conditions for variable amounts of time to determine moisture (M), volatile matter (VM), fixed carbon (FC), and ash yield. Moisture and ashes constitute the non-combustible part of the material while volatile substances and fixed carbon represent the combustible fraction.

Moisture is determined by heating the biomass to a temperature slightly above the boiling point of water (105 °C) and holding it at that temperature until there is no further weight loss.

Volatiles are measured by heating the sample in an inert atmosphere up to a maximum temperature, generally between 800 and 950 °C, under specified conditions (holding time and heating rate) defined according to international standards (ASTM, ISO, DIN, BS). The achieved weight loss (already reduced by the moisture content) allows to determine the amount of the volatiles formed. Volatile matter is the fraction of the sample, excluding free moisture, that is released in a gaseous form and consists of the permanent gases and condensable vapours driven off during pyrolysis.

The residual non-volatile fraction is then completely burned and what results is the inorganic ash content of the initial biomass, called ash.

Ash basically consists of aluminium silicates, iron oxides, lime oxides and traces of alkali metals, titanium oxides and sulphur compounds. Evaluating the ash content is useful since it has a certain influence on the adsorption and desorption phenomena and on char reactivity.

Finally, fixed carbon represents the solid residue obtained after removing the volatile elements, the ash, and the moisture from the initial biomass sample. Since it derives from the decomposition of the organic fraction, it often contains appreciable quantities of nitrogen, sulphur, hydrogen, and oxygen. The determination of fixed carbon is not carried out directly, but as the difference between the original mass of the sample and the total mass of the other components previously measured. This parameter is extremely important in the context of gasification, as it affects the production of char and the oxidant consumption.

In quantitative terms, the contents of volatile matter and fixed carbon are strongly influenced the test conditions of the standardized method used, which must therefore be made explicit.

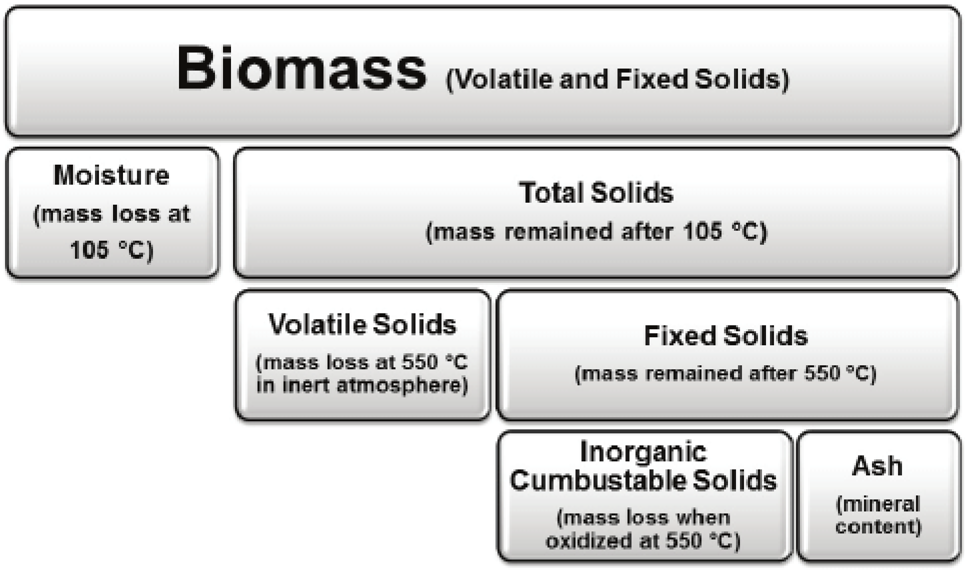


Figure 6.7 - Proximate analysis of biomass (source: Sahito et al., 2013).

Simplifying the process, it can be divided into three distinct phases:

1. Drying of a sample of known mass
2. Devolatilization in inert atmosphere (N2).
3. Oxidation of the solid residue of devolatilization (char) in an oxidizing atmosphere (O2).

The proximate analysis can be performed by means of a thermogravimetric analysis.

Thermogravimetry (TG) or Thermogravimetric Analysis (TGA) involves the continuous measurement over time, of the weight loss of a sample by thermal separation, under a controlled temperature program in a controlled atmosphere. TGA allows to evaluate the temperature ranges in which the tested sample degrades, and the entity of volatile products and solid residues formed. The main advantage this technique is related to the very limited quantity of sample required for the experimental test (of the order of a few mg).

Experimental procedure and instruments

The instrument used for the thermogravimetric analysis is the TA-Q500 thermobalance, shown in Figure 6.8. The analyzer consists of a central body, an external air-water heat exchanger for furnace cooling and a computer unit that allows the equipment control, data recording and processing.

The central unit includes the furnace, the sample loading assembly, the purge gas system, and the balance chamber; it controls the temperature of the furnace in order to impose the desired thermal program to the sample, acquires and records the data of the various tests and transmits them to the computer unit for subsequent processing. The parameters available are time, temperature, mass of the sample and weight loss rate.

Figure 6.8 – TA Instruments TGA Q500

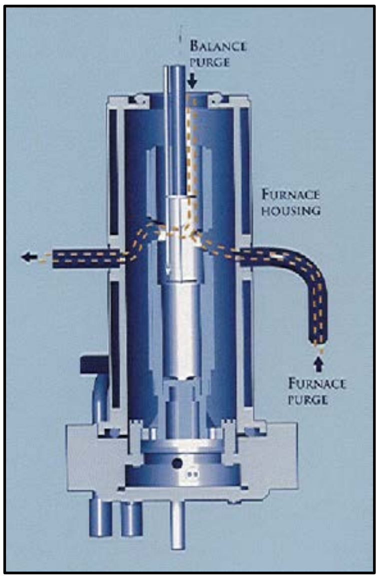


Figure 6.9- Section of the furnace of the TA Instruments TGA Q500 analyzer; purge gas paths are shown.

The sample, both solid and liquid, is placed in an alumina pan, carefully cleaned, which is in turn positioned on the sample platform. The common sample is about 10-15 mg. Solid samples are analyzed only after grinding, as described in par. 2.2. The sample platform pivots the sample pan to the furnace area, where the latter is automatically loaded onto a hang-down wire attached to the balance arm. Finally, the system closes the furnace by moving it up around the sample. The microbalance is positioned above the furnace. Figure 6.9 shows the furnace assembly. The furnace is fluxed by a purge gas (“furnace purge gas”) which allows the conditioning of the atmosphere around the sample and the rapid removal of decomposition products, while a second gas flow ("balance purge gas”) is sent to the balance chamber from which it then passes into the furnace (Figure 6.9). This second gas flow prevents or at least limits the diffusion of the decomposition gasses to the balance chamber.

The temperature control system, essential to ensure the correct implementation of the thermal program, makes use of a thermocouple, that extends through the bottom of the balance chamber, down along the hang-down wire, and is positioned just above the sample pan, where it monitors continuously the sample environment temperature and control the furnace temperature set-point.

The analyzer requires a periodic weight and temperature calibration. The latter is based on the Curie point (temperature at which the magnetic transition or the loss of the permanent magnetic properties of the material occur) of high-purity magnetic standard materials.

The maximum temperature allowed by the system is 1000 °C, while the heating rate can vary from 0.1 to 100 °C / min. The maximum weight capacity is 10 g and the microbalance resolution is 0.1µg.

Depending on the set thermal program, it is possible to execute various experiment both in isothermal and scanning mode by varying the heating rate. The atmosphere in which the tests are conducted can be chosen from several possibilities: nitrogen, air, mixtures with different oxygen or carbon dioxide content, etc.

It is also possible to change the purge gas during the test, for example by carrying out the first part of the test in an inert atmosphere and the subsequent one in an oxidizing environment. The purge flowrate range is 0 ÷ 400 ml/min. In all the tests performed, the purge rate was kept constant at a value of 100 ml/min.

The results of the analysis can be further investigated with the help of the special "Universal Analysis 2000" software, which provides specific functions for displaying the recorded signals both as a function of time and temperature and quickly evaluating some characteristics of the signals themselves.

The following procedural steps were taken in the thermogravimetric analysis:

1. grinding of the sample as described in paragraph 6.1.2,
2. set up of the thermal program on the TGA controller,
3. taring of the sample pan,
4. sample preparation taking care to obtain samples of similar mass (about 10-15 mg) to avoid possible effects related to the difference in mass,
5. positioning of the sample pan on the sample platform and automatic loading into the furnace,
6. start of the experiment on the instrument.

The temperature program to which the sample was subjected in the analyzer is as follows:

1. ramp with heating rate equal to 20 °C/min, from room temperature up to T=105 °C in nitrogen atmosphere,
2. isothermal at T=105°C for 10 minutes in nitrogen atmosphere, to ensure that moisture is completely removed from the sample.
3. ramp with specific heating rate equal to 20 °C/min up to T=900 ° C in nitrogen atmosphere,
4. isothermal at T=900°C for 10 minutes in nitrogen atmosphere, which allows to complete the devolatilization of the sample.
5. equilibrium at T=800 ° C in nitrogen atmosphere,
6. change of purge gas from nitrogen N_2 to air, to carry out a final oxidation phase of the char produced,
7. isothermal for 10 minutes in an air stream, which allows to evaluate the amount of ash contained in the samples.

In any case, two experiments were performed under the same conditions, to confirm the repeatability of the results obtained.

From the experimental data, it is possible to plot the weight loss curve (weight percentage) as a function of time (or temperature) of the various samples. The weight loss curve made available by the "TA Universal Analysis 2000" software, allowed us to determine the composition of each individual sample, in terms of moisture content (M), volatile fraction (VM), fixed carbon (FC), ashes (Ash). Operationally, the values were obtained from the weight loss percentage - time curve. The curve is characterized by horizontal sections in which the weight variation is constant and sections in which the weight decreases over time. By measuring the difference in weight between two horizontal sections, it is possible to obtain the desired values sought.

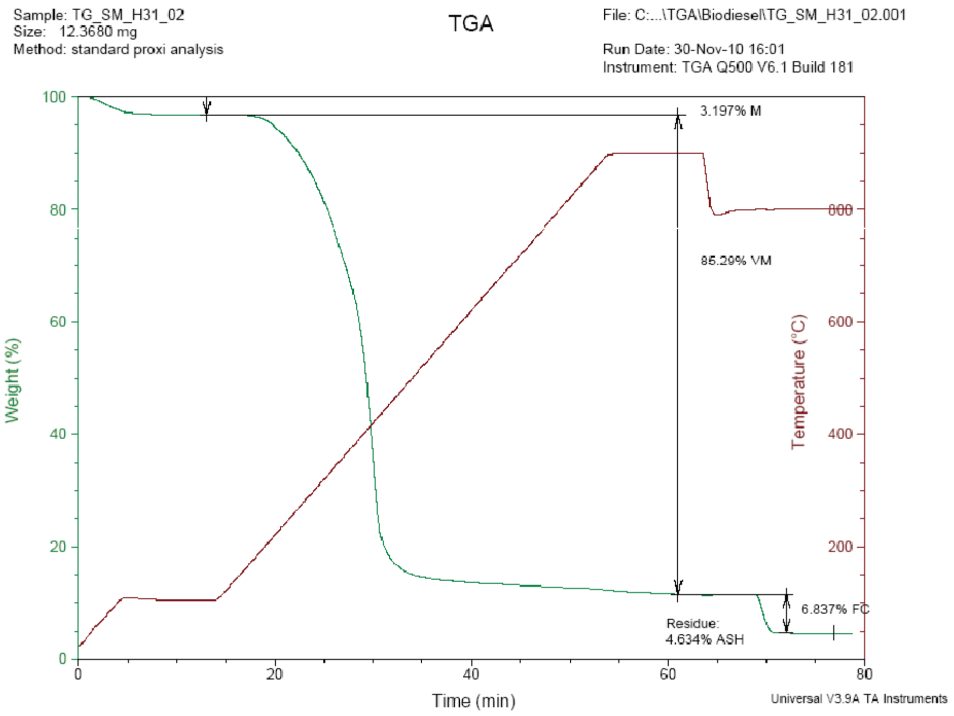


Figure 6.10 - Example of a weight % - time curve

An example of a typical weight loss curve provided by TGA Q500 analyzer is shown in Figure 6.10.

As regards the determination of the moisture content, it was decided not to use the results of the thermogravimetric analysis. Before being subjected to proximate analysis, the samples were prepared and analyzed according to the procedure described in par. 2.3 and 2.4. In fact, with the determination technique that uses the drying oven, more accurate values are obtained than those given by the thermogravimetric analysis on the ground sample, since the mill comminution operations can alter the moisture content of the sample.

The data obtained from the thermogravimetric analysis, recorded on an “as analysis” (aa) basis, are therefore expressed on a dry basis. Based on Table 6.1 and the moisture content measured via the drying oven, it is possible to report the results on an "as received" (ar) basis.

Furthermore, thermogravimetry allows the study of the thermal stability of a material. For this purpose, it is useful to report the percentage weight loss curve and its derivative, representing the rate of weight loss, over time. By examining these curves, it is possible to infer the possible presence of certain components in the sample analyzed.

6.3.5 Ultimate analysis

Ultimate analysis expresses the composition of biomass in terms of percentages of carbon (C), hydrogen (H), nitrogen (N), and oxygen (O) in the elemental form [98]. These elements, to which sulphur and chlorine content is often added to integrate the analytical information, constitute the organic fraction of the sample. On a dry basis, the oxygen content is generally calculated by difference, subtracting the overall percentage of the other elements of organic origin therein and the ash content (determined in the proximate analysis) to 100%.

The information that can be acquired from the elementary analysis is multiple: it is essentially based on the percentage ratio between the main elements and, even if not exhaustive, it helps to identify the most correct use of biomass. The elemental analysis is also valuable when assessing the quality of a biomass from an energy point of view. As a general trend, high carbon and hydrogen contents correspond to high calorific values; high concentrations of oxygen and nitrogen have the opposite effect. The carbon content, moreover, in the context of gasification, helps in estimating the amount of syngas obtainable.

Finally, nitrogen, sulfur and chlorine are particularly significant in relation to polluting emissions and plant reliability and related issues, with particular reference to corrosive phenomena. Chlorine, in particular, in addition to being a precursor for the formation of dioxins during combustion, also plays a primary role in the formation of particularly aggressive ashes.

In general, devices for elemental analysis can be distinguished into two categories: instruments for microanalysis, often used for the determination of the brute formula of unknown organic compounds, which analyze samples up to about 2 mg, and instruments for macroanalysis used for quality control, especially in the industrial field, which operate with higher quantities (up to about 1 g), and therefore more representative of non-homogeneous mixtures or materials.

The methods used for the elemental analysis, albeit multiple, exploit a high temperature combustion process in the presence of pure oxygen (*Dumas combustion method*) followed by the quantitative determination of the reaction products. In general, it is possible to distinguish the instrumentation for elemental analysis in two categories: instruments for microanalysis, often used for the determination of the brute formula of unknown organic compounds, which analyze samples up to about 2 mg, and instruments for macroanalysis used for quality control, especially in the industrial field, which operate with higher quantities (up to about 1 g), and therefore more representative of non-homogeneous mixtures or materials.

CHNS microanalytical instruments commonly involve a dynamic *flash* combustion inside a furnace, followed by a reduction in a catalytic reactor, a chromatographic separation of the combustion product gas and a final detection with katharometer (TCD).

For the macroanalysis, the LECO TruSpec CHN elemental analyzer was used (Figure 6.11).

Devoted to the elemental analysis of organic samples, the instrument operates through a resistance combustion furnace (divided into primary and secondary) at a temperature of about 1000 ° C in an oxygen flow, and is equipped with four detectors, each dedicated to a specific element. The detection principle is infrared (IR) absorption for carbon and hydrogen and thermal conductivity for nitrogen; the fourth detector is used for combustion control. The instrument is expandable for sulfur analysis with an optional Add-on module.

The analysis times are very short: a determination typically takes about 4 minutes, and the analysis of macro samples up to about 1 g is allowed.

The measuring range and accuracy are as follows:

- Measuring range (*)

Carbon	0.005% ÷ 50%
Hydrogen	0.02% ÷ 50%
Nitrogen	0.008% ÷ 100%

- Accuracy (*)

Carbon	0.5% RSD
Hydrogen	1% RSD
Nitrogen	0.5% RSD

(*) for a sample of 500 mg

Figure 6.11 - Elemental analyzer LECO TruSpec CHN

The operating principle of this instrument provides for fast combustion of the sample inside a furnace, at a temperature of 950 °C in excess of oxygen.

Figure 6.12 shows the U-shaped combustion tube. Sample combustion takes place in the primary side of the tube (on the right side of the figure), while in the secondary branch the resulting products are post-burned at 850 °C to ensure their complete oxidation. The porous crucibles collect the ash formed during the test.

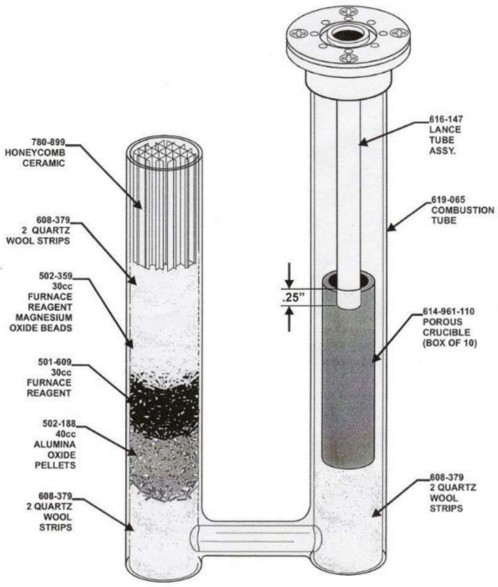


Figure 6.12 - Leco analyzer combustion tube

The evolved gases (carbon dioxide, water and nitrogen oxides) are then collected in a container, called a ballast, with a volume of 4.5 liters, inside which they are homogenized and sent to the infrared absorption detectors for the measurement of carbon dioxide and water; in fact, carbon is measured in the form of CO_2 and hydrogen in the form of H2O. An aliquot of the combustion gases (equal to 3 cc), transported by a constant helium flow, passes through a hot copper catalyst (650 °C) for the removal of the oxygen and the reduction of the NOx to elemental nitrogen and through further filters for the removal of carbon dioxide and water. Finally, a thermal conductivity detector performs the determination of the nitrogen content.

The gases the equipment needs are helium, oxygen, and nitrogen. Helium (purity 99.99%) is the carrier gas of the combustion products, oxygen (purity 99.99%) acts as a comburent while the air (dry and oil-free) has a pneumatic function.

Based on the calibration data obtained with standard reference materials of known composition (ethylenediaminetetraacetic acid or ETDA is commonly used), the instrument provides the percentage by weight of the various elements present in the sample.

The LECO TruSpec CHN analyzer is fully compliant with the reference standard for the elemental analysis of biomass, ASTM D 5373.

The procedural steps adopted for the proper functioning of the CHN analyzer are listed below:

1. prepare the instrument for operation, as indicated in the vendor instruction manual,
2. set the chosen method,
3. perform cold Testing,
4. calibrate with EDTA,

5. grind and dry the sample to be analyzed, as described in paragraphs 6.1.2 and 6.1.3,
6. prepare a sample weighing about 0.10-0.15 g and place it in a suitable tin foil cup (Figure 6.13a),
7. close the cup by folding the upper edges of the foil, making sure that no loss of material from the weighed sample occurs.
8. enter the sample weight and identification in the data acquisition program.
9. place the sample in the proper position of the autoloader and proceed with the analysis,
10. replicate the test at least twice for each sample.

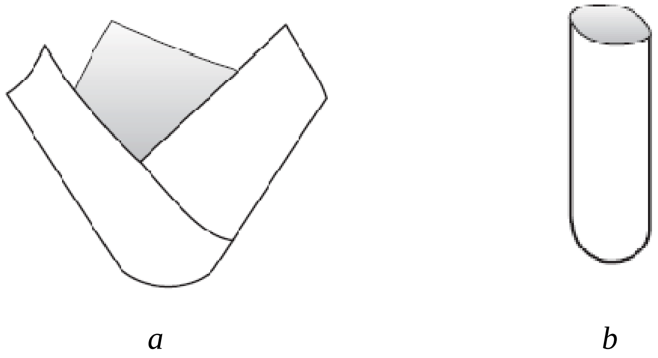


Figure 6.13 - Tin Foil Cup. b: Tin Capsule

The combustion thermal program used during the experiments is shown in Table 6.2. The combustion profile has been optimized by adjusting the oxygen flow.

Table 6.2 – Combustion profile for the biomass method and the sludge method.

Methods	Hold Time (s)	Oxygen Flow
Biomass	40	high
	30	medium
	30	high
Sludge	100	high

Figure 6.14 shows a typical window of the TruSpec software user interface. The application provides for each sample under test the percentages of nitrogen, carbon and hydrogen, together with the relative graph.

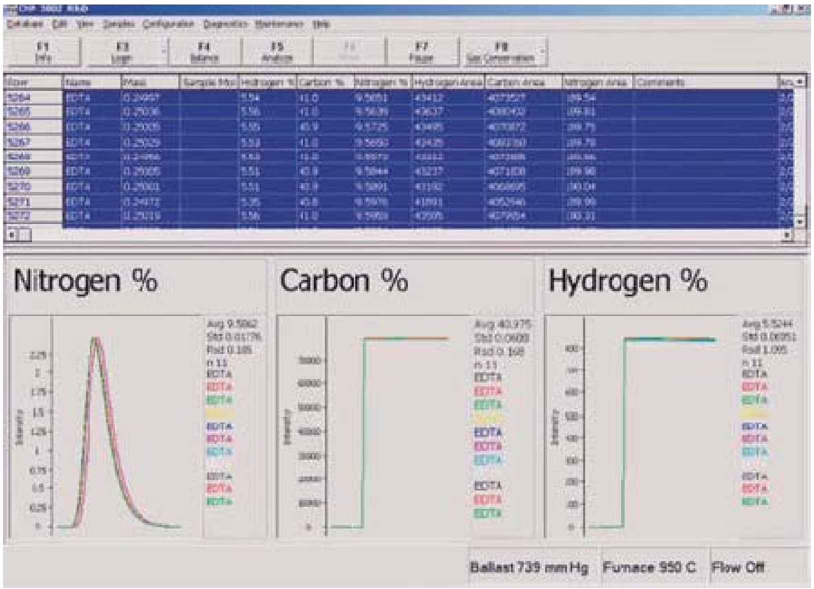


Figure 6.14 - TruSpec operating software user interface

6.3.6 Calorific value

The *heating value* (or *calorific value*) represents the total energy released as heat by a specified quantity of a substance when it undergoes complete combustion with oxygen under standard conditions. A knowledge of this value is essential when considering the thermal efficiency of equipment for producing either power or heat. It is typically measured in units of energy per unit of mass or volume, such as kcal/kg or MJ/kg for solids, kcal/l or MJ/l for liquids and kcal/Nm^3 or MJ/Nm^3 for gases.

There are two types of the enthalpy of combustion, called high(er) and low(er) heat(ing) value, depending on whether the water formed in the reaction is considered in liquid state (condensed), as occurs in calorimetric determinations, or in vapor state.

The higher heating value (HHV; *gross energy, upper heating value, gross calorific value GCV*, or *higher calorific value*; HCV) indicates the upper limit of the available thermal energy produced by the complete combustion of a compound in its standard state. It is determined by bringing all the products of reaction back to the original pre-combustion temperature, and in particular by condensing any vapor produced. It therefore includes the heat of condensation of the water contained in the fuel or formed during combustion.

The lower heating value (LHV; *net calorific value; NCV*, or *lower calorific value; LCV*) is another measure of the available thermal energy produced. In contrast to the HHV, it considers energy losses such as the energy used to vaporize water which is not released as heat of combustion.

Usually, the calorific values are referred to dry material, that is, with a moisture content equal zero; if a little moisture is present, the calorific value must be proportionally decreased.

The determination of the higher heating value is carried out by direct methods, based on experimental calorimetric test or by indirect methods, which employ empirical formulas based on the fuel chemical composition as it results from its ultimate analysis. Low heat values are calculated by subtracting the heat of vaporization of the water from the high heat values.

Among the direct ones, the Berthelot-Mahler method is universally adopted for its accuracy and practicality. It makes use of a constant-volume calorimeter to measure the heat transferred to a given volume of water by a known quantity of fuel, burnt in an oxygen atmosphere in a special metal container called "calorimetric bomb" (Mahler's bomb). The conditions in the bomb are such that, at the end of the test, the water present in the fuel or formed during combustion is in liquid state.

The calorimeter consists of an insulating double-walled jacket filled with water maintained at a controlled constant temperature and an internal vessel (bucket) for holding the bomb in a measured quantity of water together with a stirring mechanism, included to promote rapid thermal equilibrium. A crucible, containing a weighed mass of a reactant sample (typically 0.5–1 g) and a small, fixed amount of water (to saturate the internal atmosphere, thus ensuring that all water produced is liquid, and removing the need to include enthalpy of vaporization in calculations), is placed in the stainless-steel bomb.

A screw cap seals the bomb which is pressurized up to 25-30 atm with excess pure oxygen introduced through a tube with a needle valve. The bomb forms a closed system - no gases escape during the reaction. Residual gases are released through the valve at the conclusion of a test.

The fuel sample to be analyzed is ignited by a fuse wire which in turn is ignited by passing electric current through a firing wire located nearby but not in direct contact of the sample itself.

The bomb is then submerged in the calorimeter bucket, already filled with a certain volume of water. When the water temperature of the calorimetric vessel has reached equilibrium, the electrical circuit closes causing the ignition of the fuel. Energy is released by the combustion and the resulting heat flows through the stainless-steel wall, thereby raising the temperature of the bomb, its contents, and the surrounding water jacket. The temperature change in the water is then accurately measured with a thermometer and recorded.

This reading, along with a bomb factor (which is dependent on the heat capacity of the metal bomb parts), is used to calculate the energy given out by the sample burn. A small correction is made to account for the electrical energy input, the burning fuse, and acid production (by titration of the residual liquid). After the temperature rise has been measured, the excess pressure in the bomb is released.

For the calculation of the gross calorific value the energy equivalent (effective heat capacity) of the calorimeter must be taken into account, i.e. the quantity of heat absorbed by the calorimeter itself to raise its temperature by 1°C. It is determined by performing calibrations on compounds with known heat of combustion; benzoic acid (H_c=6318 cal/g) is commonly used as reference material for this purpose.

The calorimetric determination of the gross calorific value (at constant volume) is the only laboratory test capable of providing a measure of the intrinsic energy value and quality of a substance. The heat of combustion is computed from temperature readings before, during, and after combustion, with proper allowance for thermochemical and heat transfer corrections, by using the following equation:

$$HHV = \frac{W \cdot t - e_1 - e_2 - e_3 - e_4}{1000 \cdot g}$$

where:

HHV = gross heat of combustion, at constant volume expressed as MJ/kg,

W = energy equivalent of calorimeter (MJ/°C),

t = corrected temperature rise (°C), evaluated as shown below

e_1 = correction for heat of formation of nitric acid (MJ),

e_2 = correction for the enthalpy of formation of sulfuric acid (MJ),

e_3 = correction for the heat of combustion of fuse wire (MJ),

e_4 = correction for heat of ignition (MJ),

g = weight of the sample (g).

The corrected temperature rise t (Figure 6.15), which takes into account the heat exchange with the surroundings, is given by the formula

$$t = t_c - t_a - r_1(b - a) - r_2(c - b)$$

where:

a = time of firing,

b = time (to nearest 0.1 min) when the temperature rise reaches 60 % of total,

c = time at beginning of period in which the rate of temperature change with time has become constant (after combustion),

t_a = temperature at the time of ignition,

t_c = temperature at time c,

r_1 = rate of change in temperature during the period before ignition,

r_2 = rate of change in temperature after time c.

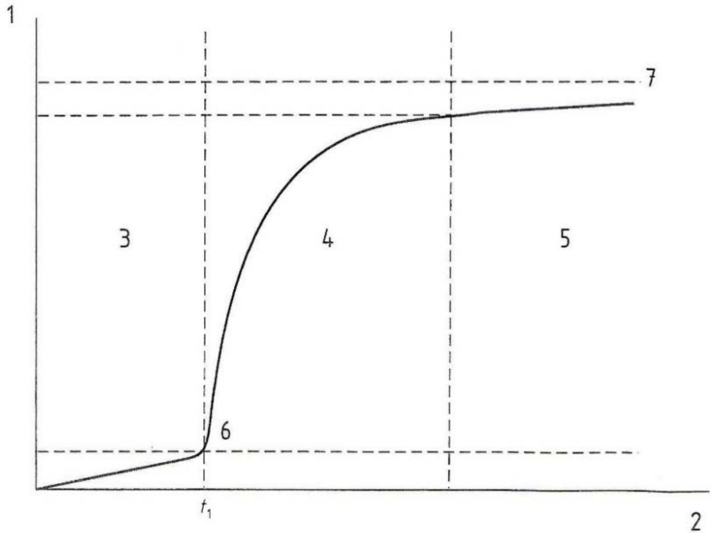


Figure 6.15 - Schematic representation of a typical temperature–time curve:
1) Temperature/°C; 2) Time/min; 3) Preliminary period;
4) Main period; 5) Final period; 6) Ignition; 7) Jacket temperature

In the main period, the chemical or physical process under investigation occurs; the initial and final periods are ideally governed by the energy exchange between the calorimetric system and its surroundings only. The correction terms, that take into account the heat exchanges with the surroundings, are null in the case of adiabatic calorimeters; in the case of automatic equipment, these corrections are calculated automatically.

In practice, the energy efficiency of a thermochemical conversion plant is evaluated with reference to the lower calorific value (LHV) since the exhaust gases are typically at temperatures not allowing the water present to condense.

Once the hydrogen content of a fuel sample is known, its net calorific value can be calculated directly from the HHV, assuming that all the moisture already present and the water formed in the combustion reaction remains in the vapor state.

The LHV at constant volume is obtained by subtracting the latent heat of condensation of water from the higher calorific value, according to the following equation.

$$LHV = HHV - 206.0 \cdot H_{tot} \qquad (6.1)$$

where:

HHV is the gross calorific value in kJ/kg,

LHV is the net calorific value in kJ/kg,

H_{tot} is the percentage by weight of hydrogen contained in the sample, including that deriving from any moisture present.

The energy of condensation, at constant volume, of water at 25 °C is 41.53 kJ/mol, which corresponds to 23.05 kJ/kg for 1% by weight. By multiplying by the ratio between the molecular weight of water and the atomic weight of hydrogen by the number of hydrogen atoms present in a water molecule, it is possible to relate the vaporization energy to the hydrogen content in the sample. The heat of condensation of water therefore corresponds to 206.0 kJ/kg for 1% by weight of hydrogen in the sample.

As an alternative to the experimental determination, the calorific value can be computed using empirical equations, which are based on the elemental composition of the fuel, such as the following formula:

$$HHV = 2{,}326 \cdot [146{,}58 \cdot C + 568{,}78 \cdot H + 29{,}4 \cdot S - 6{,}58\, A - 51{,}53\, (O + N)]$$

where:

HHV is the gross calorific value in kJ/kg,

C, H, O, S, N are the percentages by weight on a dry basis of these elements in the sample,

A is the ash content in the sample, on a dry basis.

Experimental procedure and instruments

The instrument employed in this research to determine the calorific value of the biomass matrices is the LECO AC-500 calorimeter shown in Figure 6.16. It allows a semi-automatic analysis of the calorific content of a substance by applying an isoperibol method in compliance with ASTM, ISO, DIN, BSI standards.

Figure 6.16 - LECO AC-500 Isoperibol Calorimeter.

Figure 6.17 shows a cross section of the calorimeter depicting the internal arrangement of its different components. The insulating jacket consists of a constant-temperature water filled double-walled container with an adiabatic lid. The calorimeter is equipped with a stirrer driven at constant rotational speed. To avoid heat transfer to and from the calorimeter, the stirrer drive shaft must be equipped with a heat-insulated section in the gasket between the jacket lid and the jacket itself.

The heat obtained from the sample combustion occurring in the moist, high-pressure oxygen environment within a bomb is transmitted to the calorimetric bucket (commonly made with a highly polished outer finish) in which the bomb is held completely submerged in water. The water temperature is measured with an electronic thermometer accurate to 0.0001°C every six seconds. The instrument records and processes the temperature differences between the pre-ignition and post-ignition phases, presenting results that are corrected for the length of the wire or for the sulfur, nitrogen, moisture and ash content of the sample.

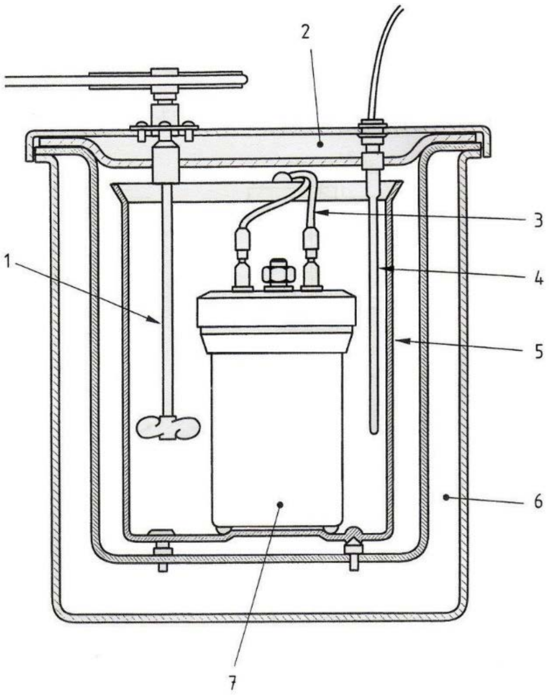


Figure 6.17 - Calorimeter Cross Section: 1. Stirrer; 2. Jacket cover; 3. Ignition wires; 4. Thermometer; 5. Calorimeter bucket; 6. Insulating Jacket; 7. Calorimetric bomb.

In this isoperibol calorimeter a microprocessor monitors and controls the jacket temperature, which is actively kept constant throughout the determination while the bucket temperature is rising; this system allows for continuous analysis and automatic application of the required corrections to compensate for heat leaks within the calorimeter. Higher operating speeds are achieved without the extensive jacket heating and cooling associated with adiabatic mode. The calorimeter also has a closed-circuit water recirculation system.

The corrosion-resistant calorimetric bomb (Mahler Bomb) has a volume of 1 liter and is calibrated to withstand a pressure of 350 bar. The bomb cap is designed to house the crucible and the electric ignition device. The oxygen loading system is equipped with an automatic pressure regulator calibrated at 30 bar.

The combustion gas evacuation system is regulated by a “needle” valve which allows its slow release and, if necessary, its possible "recovery" for the analysis of Chlorine or Sulfur. Figure 6.18 shows the bomb and its components.

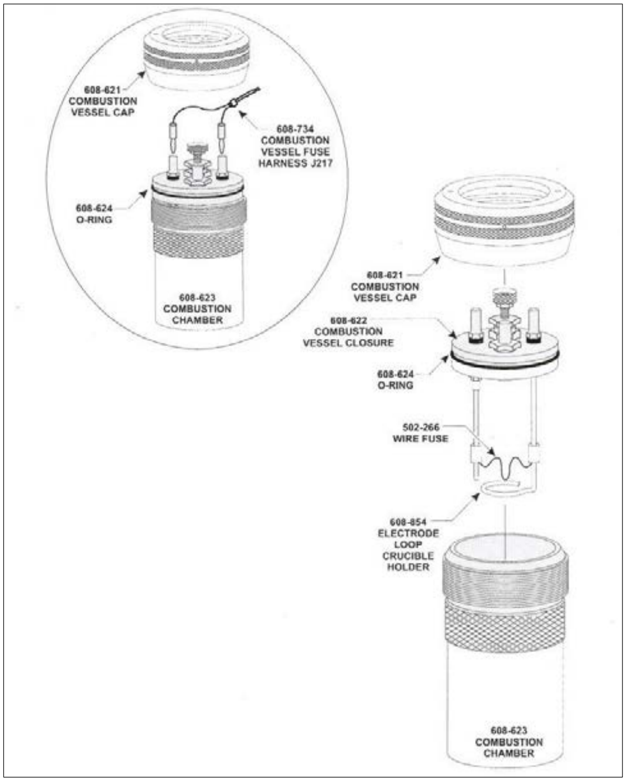


Figure 6.18 - Calorimetric Bomb (Mahler bomb).

The calorimetric unit has the following characteristics:

- Operating range from 6000 to 15000 BTU/lb (per 1 gram of sample).
- Accuracy <0.05% RSD based on benzoic acid analysis, 1 g.
- Resolution 1 BTU/lb or 0.1 cal/g or 0.001 MJ/kg.
- Duration of the analysis:
    - *Regnault-Pfaundler method* - the instrument records and processes the temperature differences between the pre-ignition and post-ignition phases with an evaluation period long enough to ensure adequate accuracy (20 minutes).
    - *High-Precision method* - the high-precision mode employes an algorithm that calculates the heat transferred based on the measurement of the various variables involved. The analysis duration is well optimized to provide maximum accuracy of results (8 minutes).
    - *Predictive method* - uses estimation algorithms to allow the operator to reduce the analysis time (4.5 ÷ 7.5 minutes).
- Resolution of the measured temperature: 0.0001 ° C.

The solid samples, before being analyzed, are ground and dried in an oven at 105 ° C, as described in paragraphs 6.1.2 and 6.1.3. Finely shredded samples are typically compressed by use of a briquette press to increase density and form a pellet. Adequate precautions shall be taken to prevent uptake or loss of moisture by the test sample during mixing and pelletizing, so that the moisture content, previously determined, can be used in further calculations.

The analysis is carried out using the following procedure:

1. Tare the crucible and weigh the sample to be analyzed keeping it in a range of 0.5-1.4 g,
2. Enter the sample weight and its identification code in the data acquisition program,
3. Put the crucible into the specific holder. Connect the ignition wire to the two electrodes, taking care that it does not come into contact with the crucible nor with the sample,
4. Screw the bomb cap down tightly,
5. Screw the needle valve,
6. Connect the bomb to the oxygen loading system and fill in the gas up to a pressure of 25-30 atmospheres,
7. Draw the bucket out of the calorimeter and fill it with distilled or demineralized water, in the quantity set by the automatic measuring system (2 liters),
8. Put the bucket back into the calorimeter compartment and place the bomb inside it;
9. Check that the water completely covers the bomb and that the latter is closed tightly (no bubbles),
10. Connect the ignition wires to the bomb and close the lid,
11. Set one of the three available analysis methods. In our tests the High Precision method was employed because it allows maximum accuracy with relatively short operation times,
12. Start the analysis.

At this point, the calorimeter autonomously yields the higher calorific value of the sample, on the basis of the calibration previously carried out using benzoic acid.

The calorimeter automatically computes the corrections for the heat exchanges with the surroundings and corrections for the heat of combustion of the ignition wire. Thermochemical corrections due to the heat of formation of nitric acid and sulfuric acid can be commonly neglected.

At the end of the analysis remove the bomb from the calorimeter, let it rest for a few minutes and slowly reduce the pressure through the valve. Open the bomb and check that complete combustion has occurred, that is, there are no soot deposits inside the bomb or traces of residual carbon on the sides of the crucible. Finally, rinse and dry the bomb, taking care to remove the combustion ashes from the crucible.

Expression of results

At the end of the test, the software directly provides the higher calorific value of the sample, in cal/g. Each result is obtained as an average of at least two trials.

The lower calorific value is calculated through the formula (6.1), where the hydrogen percentage derives from the ultimate analysis of the fuel from which the sample was extracted.

The measured calorific value has to be expressed on a dry basis (db), since the sample is analyzed after drying.

To report the LHV_{db} on a "as received" basis (ar), the conversion factors of Table 6.1 are used. In this case, it is also necessary to insert a correction that considers the heat of vaporization of the moisture content of the "as received" sample, according to the following formula:

$$LHV_{ar} = LHV_{db} \cdot \frac{100 - M_{ar}}{100} - 23{,}05 \cdot M_{ar}$$

where:

LHV_{ar} is the net calorific value on an as-is basis, in kJ / kg;

LHV_{db} is the net calorific value on a dry basis, in kJ / kg;

M_{ar} is the moisture content of the sample as received.

6.4 Gas Chromatography

6.4.1 Introduction

Gas chromatography (GC) is a widely used analytical technique of separating volatile compounds in a mixture to allow their identification and quantitation in terms of molecular composition.

Separation is accomplished by injecting the mixture to be analyzed into a moving fluid stream, called the mobile phase, and by passing this carrier medium (gas or liquid) over a contiguous sample-free phase, a solid adsorbent material or a suitably supported liquid, that remains fixed or stationary. It is thus possible to carry out the extraction continuously.

The technique exploits the aptitude of a chemical species to distribute itself differently between two distinct phases, according to the diverse affinity it has for them.

The stationary phase absorbs or impedes the various components of the mixture to varying degrees and thus causes them to separate into different layers. The different species are transported at different rates in the direction of fluid flow.

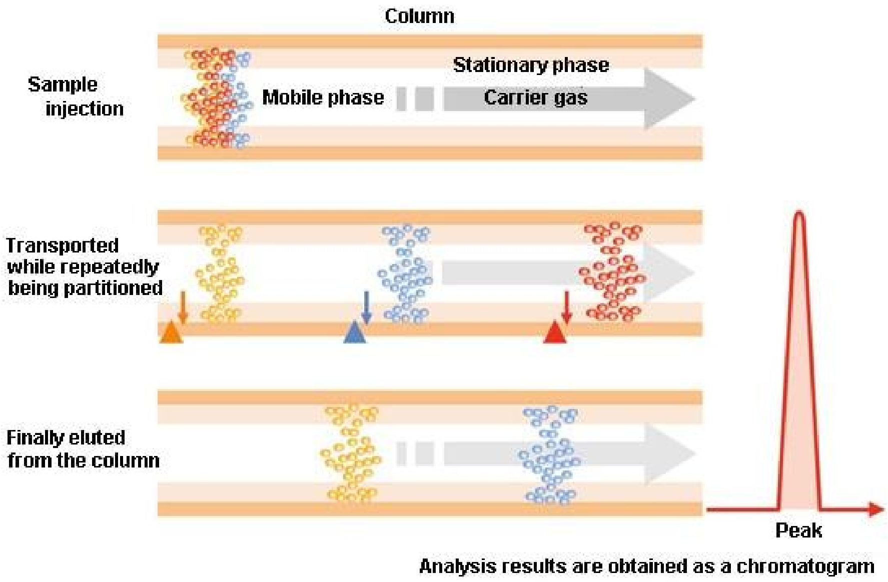


Figure 6.19 - Working principle of gas chromatography.

The basic function scheme of gas chromatograph (Figure 6.19) includes the following steps:

1. Sample injection: The mixture to be analyzed is introduced into the GC system through a sample injector.
2. Sample vaporization: The sample is vaporized and carried by a continuous flow of inert or nonreactive gas (eluent), such as helium or nitrogen, into of a narrow tube, known as the column, filled uniformly with a solid adsorbent material (stationary phase).
3. Separation: As the sample travels through the column, the compounds in the mixture interact differently with the filling adsorbent, moving at different rates and thus separating. The column is typically enclosed within a temperature-controlled oven.
4. Detection: The separated compounds exiting the column are detected by a device, (detector) capable of producing a signal proportional to their concentration. Their presence is recorded as individual peaks on a chromatogram, a two-dimensional plot which correlates the detector response to time, i.e. to elution volume (Figure 6.20).
5. Identification: The peaks on the chromatogram can be identified by comparing them to known standards or by using other techniques such as mass spectrometry.

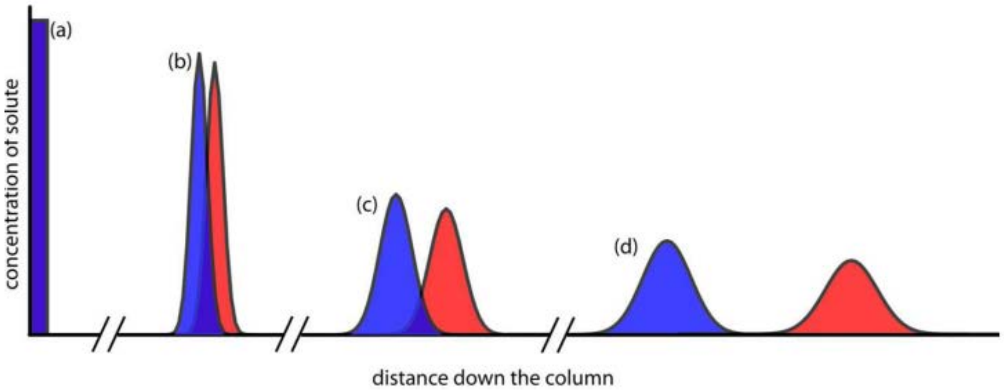


Figure 6.20 - Progress of a chromatographic separation down the column:
a) Sample injection, b) Initial stage, c) intermediate stage, d) final stage.

Given certain analysis conditions, each chemical species passing through the column is characterized by its own retention time t_R, which corresponds to the time elapsed from the introduction of the sample to the time of the compound elution, identified from its maximum signal at the detector. The substances most retained by the stationary phase will have a high retention time and vice versa (Figure 6.20).

The retention time is usually referred to the *dead time* t_0, which is the time a non-retained chemical species needs to elute from the column. This parameter is not related to the retention process and depends on the flow rate and physical characteristics of the column (length, diameter, porosity of stationary phase). The difference between the retention time and the dead time represents the time a given compound is retained on the stationary phase.

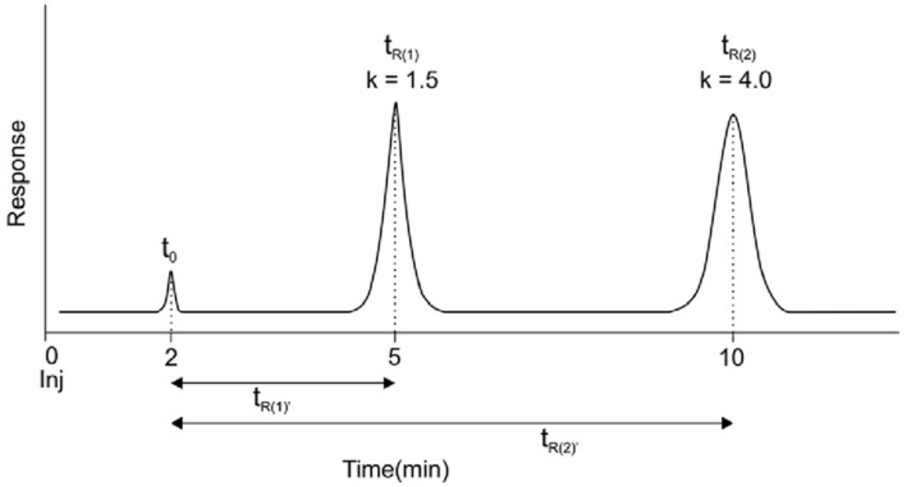


Figure 6.21 - Chromatogram showing the different retention times of the various components in sample

Retention time is an important parameter in GC analysis, as it is directly related to the separation and quantification of compounds in a sample. The retention time can be affected by several factors, including the column type and stationary phase, column temperature and flow rate, and the chemical properties of the compounds. Once all the operating conditions have been set, a certain component comes out at a given retention time which is reproducible; this means that, given the operating conditions, if this component is present in different concentrations and in different mixtures it always comes out at this tR. Retention times for known compounds can be used to identify unknown compounds in a sample.

6.4.2 Distribution coefficient

The distribution coefficient, also known as the partition coefficient, is a measure of the distribution of a compound between two immiscible phases. If we consider a two-phase system in which a compound is introduced, the latter will be selectively partitioned between the two phases according to its chemical and physical properties.

Indicating with C_m and C_s its concentrations respectively in the mobile phase and in the stationary phase, and assuming that the experimental conditions are such that, along the column, successive thermodynamic equilibria are reached of the type:

$$C_m \rightleftharpoons C_s$$

the distribution coefficient can be represented by the equilibrium constant of the reaction i.e. the concentration ratio of the dissolved compound in the two media at equilibrium

$$K = (C_s/C_m)_{equil}$$

A greater affinity for one phase relative to another leads to a higher concentration in that phase. Consequently, a higher distribution coefficient indicates that the compound is more strongly retained in the stationary phase, while a lower distribution coefficient indicates that the compound is more strongly retained in the mobile phase.

The distribution coefficient is affected by several factors, including the polarity of the compound, the polarity of the stationary phase, and the temperature of the column.

The retention time varies with the value of K, in fact, the time that a substance spends in the column depends on the value of C_s with respect to C_m.

The retention time of a compound can be represented by the equation:

$$t_R = K \cdot t_0 + t_0$$

where t_R is the retention time, K is the distribution coefficient and t_0 is the dead time.

Those components with larger partition coefficients are more likely to move into the stationary phase, taking a longer time to pass through the system.

In a graphical representation of the relationship between the concentration of a compound in the stationary phase and the concentration of the same compound in the mobile phase, the equation $K = Cs / C_m$ describes a line of slope K, called the distribution isotherm. It describes the partitioning behavior of the compound between the two phases at a specific temperature.

The distribution isotherm can take on different shapes depending on the properties of the compound and the conditions of the GC analysis. If we plot (Figure 6.22) the relative concentrations of two compound A and B for which Ka <Kb, the distribution isotherm of

the first will be relatively flat, indicating that the compound B is retained (greater affinity) in the stationary phase more strongly than A. If these two substances A and B travel together the column, it happens that A will come out first and the greater the difference in K the better the separation between the two will be.

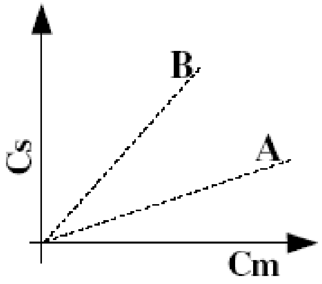


Figure 6.22 - Distribution isotherms for two distinct compounds

In reality, the isotherms are not straight lines with constant slopes (Figure 6.23). At a certain point the fixed phase does not retain the same amount of substance as the mobile phase and approaches saturation, i.e. its solvent capacity can be said to be exhausted. For this reason, the single peak areas of the chromatogram do not have a precise and symmetrical outline.

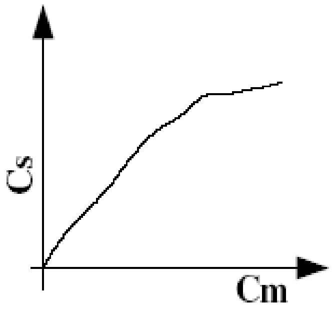


Figure 6.23 - Graphical representation of a real distribution isotherm

6.4.3 Separation modes in Gas chromatography

Chromatographic separation of gases basically relies on two main physico-chemical mechanisms that can be used alone or in combination:

- *Adsorption*: the stationary phase consists of a solid adsorbent, such as activated carbon or silica gel, on whose surface there are active sites capable of establishing secondary bonds (dipole-dipole, hydrogen bridge, Van der Waals) with the different molecules of the mixture to be separated (Figure 6.24). As the gaseous sample flows through the column, its components interact differently with the adsorbent, leading to different retention times for each component. The strength of the interaction between the gas molecule and the adsorbent determines the degree of separation achieved.

We speak of liquid-solid chromatography (LSC) if the mobile phase is a liquid, or gas-solid chromatography (GSC), in the case of a carrier gas.

In general, the molecules most easily fixed are those with polar groups, although the nature of the adsorbent affects the phenomenon. A temperature increase in the column has an adverse effect on the adsorption mechanism as it causes greater thermal agitation.

- *Partitioning*: the stationary phase is a liquid, immiscible with the mobile phase, in which the gas molecules dissolves. The liquid is usually coated on a solid support, such as a glass or metal rod, to form a packed column. As the gaseous sample flows through the column, the different components in the mixture partition between the two phases based on their relative chemical affinities. This mechanism includes absorption (Figure 6.13). The solubility of the gas in the absorbent determines the degree of separation achieved. This mechanism is also known as thermodynamic equilibrium.

  If the mobile phase is a gas we speak of gas-liquid chromatography (GLC), if instead it is a liquid, we speak of liquid-liquid chromatography (LLC).

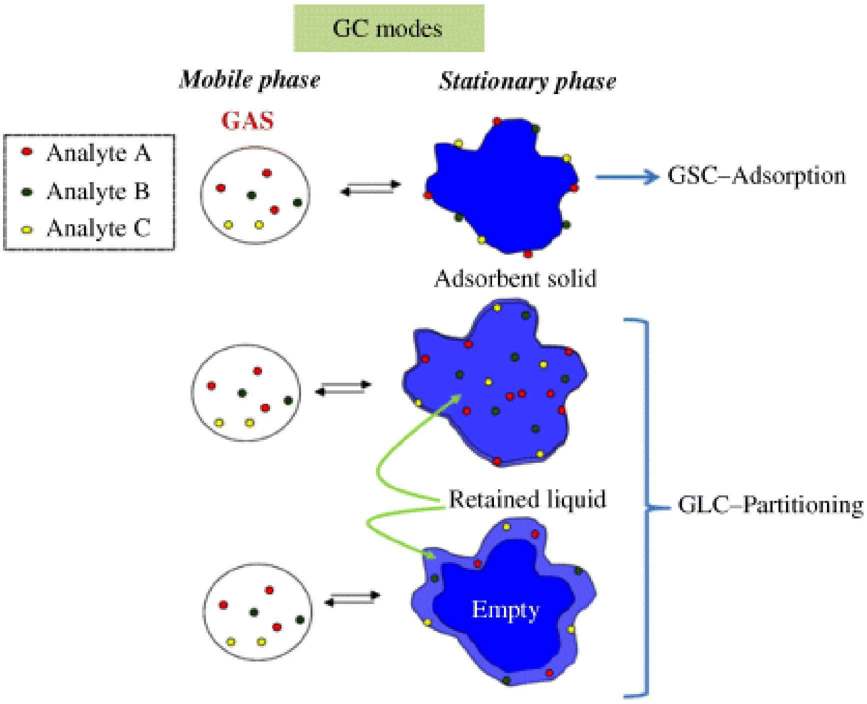


Figure 6.24 - GC separation modes

6.4.4 Basic components of a GC System

A gas chromatographic (GC) system is a complex instrument that consists of several key components that work together to perform a GC analysis.

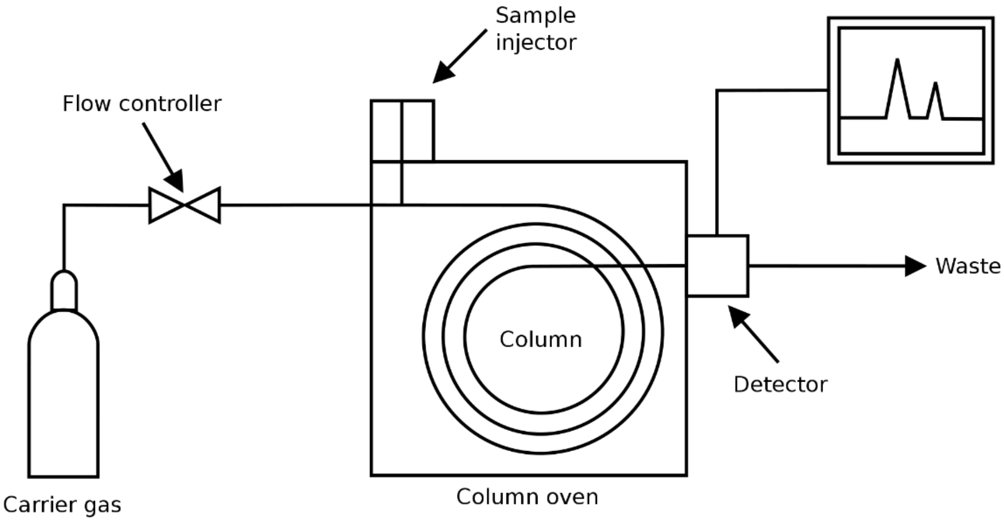


Figure 6.25 - Block diagram of a typical

The basic components of a GC system include:

Sample Injector

The sample injector, also known as the injection chamber, is the first component of a GC system and is responsible for introducing the sample into the GC column. It is a critical component of the GC system as it plays a crucial role in determining the amount of sample introduced as well as the resolution and the sensitivity of the analysis.

It's important to ensure that the sample is properly prepared and that the sample injector is working correctly to ensure accurate and reliable results in GC analysis.

The sample injector typically consists of several components:

1. A sample loop, which is a small volume chamber where the sample is temporarily stored before injection into the inlet of column.
2. A sample injection valve, which is used to introduce the sample from the sample loop into the column.
3. A septum, which is a seal that prevents the sample from leaking out of the sample loop and prevents impurities from entering the sample loop.
4. A thermal control system, which is used to maintain a constant temperature for the sample loop to prevent thermal degradation of the sample.

There are different types of sample injectors available, depending on the sample type and the level of sensitivity required for the analysis. Some common types of sample injectors are:

- Manual syringe injectors: where the sample is manually injected into the column using a syringe.
- Automated liquid injection systems: where the sample is automatically injected into the column using a syringe pump.
- Gas sampling valves: where the sample is injected into the column in the form of a gaseous stream.

Since with the use of capillary columns the amount of liquid sample to be injected is of the order of nanoliters, and measuring these quantities with syringes is practically impossible, special injection techniques have been developed, which allow only a part of the injected liquid to enter the column.

In a gas chromatography (GC) system, the vaporization of the liquid sample in the injection chamber is a critical step that occurs before the sample can be introduced into the column for separation. The sample is heated to a high temperature, typically between 200-450 °C, in order to vaporize it, and it is then introduced into the column as a gas. The temperature of the injection chamber must be carefully controlled to ensure efficient vaporization without decomposition of the sample. There are several methods to vaporize liquid sample in the injection chamber of a GC system, including hot-injection, split/splitless injection, programmed temperature vaporization (PTV) and on-column injection.

Each method has its own advantages and disadvantages, and choosing the right method depends on the nature of the sample, the required sensitivity and the desired analysis conditions.

GC Column

The GC column is the heart of the GC system and is responsible for the separation of the compounds in the sample. It is a long, narrow tube that is packed with a stationary phase that determines the selectivity and resolution of the separation. The column is typically made of stainless steel or glass and is coated with a liquid or solid stationary phase.

Some of the most common types of columns used in GC include:

1. Packed columns: This is a lesser used, and older column type. These columns use a stainless steel or glass tube with a 2 - 4 mm inner diameter, 1 - 4 m in length, filled with an inert solid support, such as diatomaceous earth or glass beads, and are used for lower resolution separations. They are used for medium to high polarity compounds. The separation process and consequently the accuracy of the measurement is limited by the slow elution of the sample molecules along the column. Although an old technology, packed columns have some features that may sometimes be advantageous in that they can accept high sample loading and can give a greater analytical dynamic range.
2. Capillary columns: These columns made of a thin, open tube made of flexible fused silica represent an important innovation for their speed of elution and for their high-resolution separations. They are much longer (10-100 m) than packed columns with a much smaller internal diameter (0.1-0.8 mm) and therefore contain less stationary

phase requiring minimal amount of sample to be injected. This type of column is typically used for low to medium polarity compounds.

3. Monolithic columns: These columns are made of a single piece of material, such as silica or polymeric beads, with a large surface area and high porosity. Monolithic columns allow for faster and more efficient separations.
4. Microbore columns: These columns are similar to capillary columns, but with a smaller internal diameter (typically around 0.05 mm) and are used for trace analysis and sample concentration prior to injection.

Column Oven

The column oven is the component of the GC system that controls the temperature of the column, keeping it constant for the entire duration of the analysis (isotherm) or making it to vary (programmed). It is typically made of a thermostatic metal box that is insulated to maintain a stable temperature. The column oven is critical for the GC analysis, as it determines the speed at which the compounds elute from the column and the resolution of the separation.

Carrier Gas supply system

The carrier gas supply system is responsible for providing the carrier gas as well ensuring the necessary pressure to push the sample through the GC column at a controlled flow rate. The carrier medium typically consists of a high-purity gas, such as nitrogen, helium, argon, and sometimes hydrogen. Due to its easy availability and economic convenience, nitrogen is generally preferred. Before introducing the carrier into the column, it is important to remove any traces of oxygen and carbon dioxide to prevent oxidation of the sample and/or the column, as well as the formation of carbonates, which can cause clogging of the column. These impurities can also interfere with the separation process and cause a decrease in the column's lifetime. Furthermore, it is necessary to dry the carrier, since the presence of water can affect the accuracy of the analysis and cause, in the case of adsorption gas chromatography, a deactivation of the active sites of the stationary phase.

The carrier gas supply system typically consists of several components:

1. A gas cylinder or a liquid nitrogen tank that stores the carrier gas.
2. A pressure regulator that controls the pressure of the carrier gas.
3. A gas flow controller that controls the flow rate of the carrier gas.
4. A gas filter that removes impurities, such as moisture and oxygen, from the carrier gas.
5. A gas line that connects the components of the carrier gas supply system and delivers the carrier gas to the inlet of the GC column.

The carrier gas supply system may also include additional components, such as a gas purifier or a gas dryer, to further remove impurities from the carrier gas.

It's important to ensure that the supply system is functioning properly, and that the carrier gas is free of impurities to ensure accurate and reliable results in GC analysis. It is also important to ensure that the carrier gas flow is constant and stable throughout the analysis, as variations in carrier gas flow can affect the separation of the sample's components.

Detector

The detector is the component of the GC system that detects the compounds as they elute from the column. A variety of detectors are available. In general, each detector takes advantage of a unique characteristic of a molecule and uses that characteristic to generate a measurable electrical signal. The choice of detector depends on the type of compounds being analyzed and the sensitivity required for the analysis.

The different types of devices that can be categorized into universal and selective. The former allows to identify all the components in a mixture, the latter reveal only particular categories of compounds.

Among the most frequently used detectors in GC, the following can be highlight:

Flame Ionization Detector (FID): it is a universal but destructive detector since the samples are burned to obtain their transformation into gas-phase ions (Figure 6.26). The FID works by ionizing the volatile organic compounds (VOCs) in the sample exiting the GC column, as they flow through a stainless-steel jet and pass through a hydrogen flame, which in turn causes the carbon-hydrogen bonds to break. The resulting positive ionized molecules are then attracted to a negatively charged electrode, creating an electrical current, that can be amplified and measured by an electronic detector. The current intensity is directly proportional to the concentration of VOCs in the sample.

The FID is highly sensitive and selective, making it a useful tool for detecting and measuring trace amounts of VOCs in a variety of samples.

The FID has some limitations, mainly its sensitivity to water and CO_2, which can interfere with the accuracy of the measurement. Additionally, the FID is not suitable for the detection of non-volatile compounds, and it requires regular maintenance to ensure optimal performance.

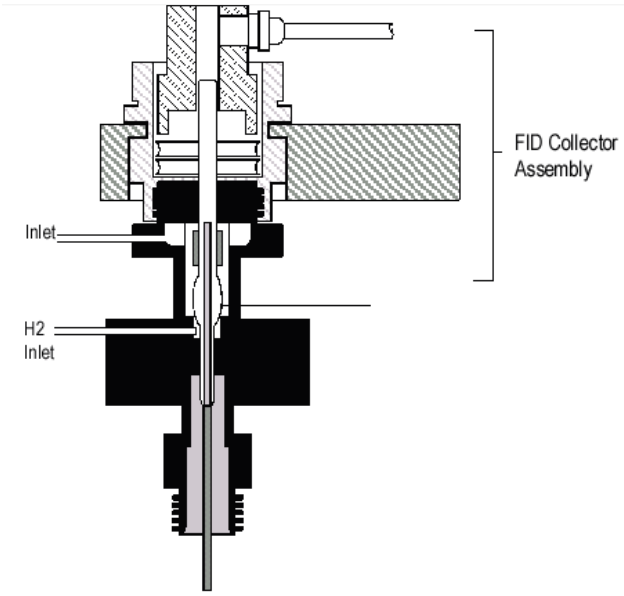


Figure 6.26 - Flame Ionization Detector (FID)

Electron Capture Detector (ECD): it is a selective and non-destructive detector (Figure 6.27) that is used to identify and measure the concentration of halogenated compounds in a sample. It works by capturing electrons from the halogenated compounds, which results in a decrease in the current flowing through the detector.

It consists of a of a sealed stainless-steel cylinder (detector cell), which contains a radioactive source, typically 63Ni, that emits beta particles (primary electrons). These beta particles, accelerated by the electric field generated by a high voltage power supply, collide with the carrier gas molecules ionizing them in the process. A stable cloud of free electrons thus forms in the ECD cell. When an electronegative molecule such as a halogenated molecule enters the cell, it immediately combines with one of the free electrons temporarily reducing their total number. This results in a decrease in the current flowing through the detector, which is directly proportional to the concentration of the halogenated compound in the sample.

The ECD is highly selective for halogenated compounds, such as chlorinated and brominated compounds, making it a useful tool for detecting and measuring trace amounts of these compounds in a variety of samples.

However, it is also important to consider its limitations, such as its sensitivity to matrix effects, meaning the presence of other compounds in the sample can interfere with the accuracy of the measurement. Additionally, the ECD is not suitable for the detection of non-halogenated compounds and it requires regular maintenance to ensure optimal performance.

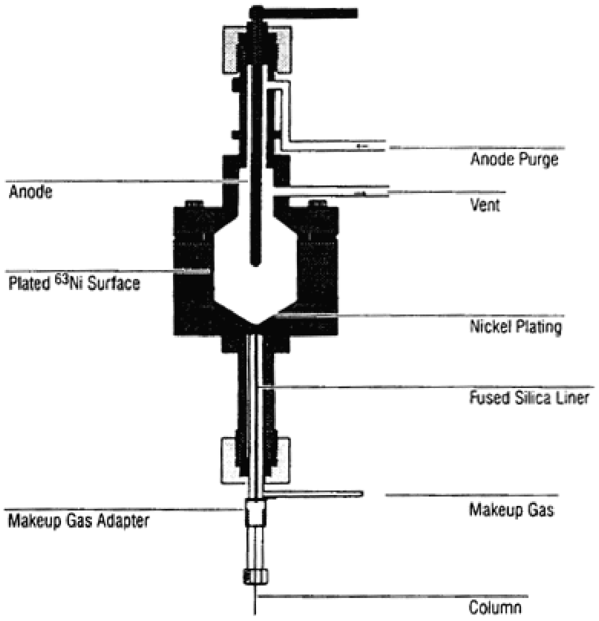


Figure 6.27 - Electron Capture Detector (ECD)

Thermal conductivity detector (TCD): it is a universal and non-destructive detector, that measures the change in thermal conductivity of a gas when a sample is introduced.

The TCD consists of a filament, a reference cell, a detector cell, and a temperature control system (Figure 6.28).

1. The filament, typically made of a metal such as tungsten or platinum, is used as the heat source for the detector.
2. The reference cell is used to measure the thermal conductivity of the carrier gas.
3. The detector cell is where the sample is introduced, and the change in thermal conductivity is measured.
4. The temperature control system is used to maintain the temperature of the filament, the reference and detector cells.

The TCD works by heating the filament. The gas flow carries away excess heat, and the filaments equilibrate. When a sample is introduced into the detector cell, it causes a change in the thermal conductivity of the gas flowing around the filaments, as a result of which the heat flow through the reference cell and the detector cell is different. The TCD can then measure this difference in heat flow and use it to determine the concentration of the sample in the gas.

The sensitivity of this detector is not high and also forces the use of more expensive carriers (eg helium and argon).

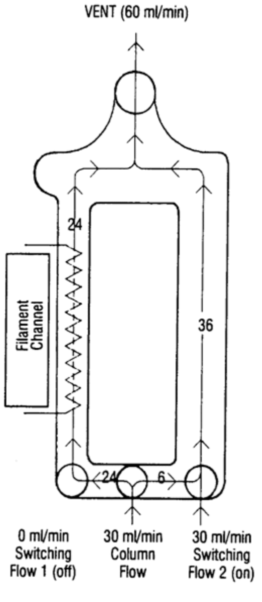


Figure 6.28 - Thermal conductivity detector (TCD)

Mass spectrometry detector: it allows the identification and characterization of the individual components of a mixture based on their mass-to-charge ratio (m/z).

A sample is first ionized, typically by electron impact or chemical ionization. The resulting ions are separated, according to their m/z ratio, by using an electric or magnetic field.

A mass analyzer is employed, which can be of different types such as quadrupole, ion trap, time-of-flight (TOF), and Fourier-transform ion cyclotron resonance (FT-ICR). The separated ions are then detected, and the resulting data is processed and interpreted to identify and quantify the individual components of the sample. The results are presented as a mass spectrum, a plot of the signal intensity of detected ions as a function of the mass-to-charge ratio.

Compounds identification is done by correlating their experimental mass spectrum against a library of known or by performing software assisted interpretation of characteristic fragmentation pattern.

This process is very sensitive and selective, making it useful for identifying and quantifying trace amounts of chemicals in complex samples.

Data Acquisition System

The data acquisition system is the component of the GC system that records the signals produced by the detector and generates a chromatographic trace (chromatogram). It usually has two basic components. The first component amplifies and converts the analog signal from the instrument's detector into digital data. The second component that receives the digitized signal is generally a computer, loaded with a suitable software program, that is used to control the GC system and analyze the data. The data acquisition system is responsible for collecting and processing the data, and it is critical for the accuracy and reproducibility of the GC analysis.

Modern instruments are also equipped with an integrator that allows the automatic calculation of the areas of the peaks, an essential operation for carrying out quantitative analyzes.

6.4.5 Chromatogram

A chromatogram is the graphical representation of the detector response, such as a signal intensity or peak area, as a function of time, or more commonly the retention time of the compounds. It is a very useful tool for visualizing the separation of compounds in a sample and identifying the different components.

Each substance coming out of the column generates a signal that will be recorded in the form of a “peak”. The chromatogram is typically composed of a succession of several peaks, each corresponding to a different compound leaving the column.

Chromatographic peaks are characterized by:

- peak height (PH): it is the perpendicular distance between the maximum of the peak and its base.
- peak width (W): is the segment delimited by the intersection points of the tangents to the inflection points of both sides with the time axis (Figure 6.29).

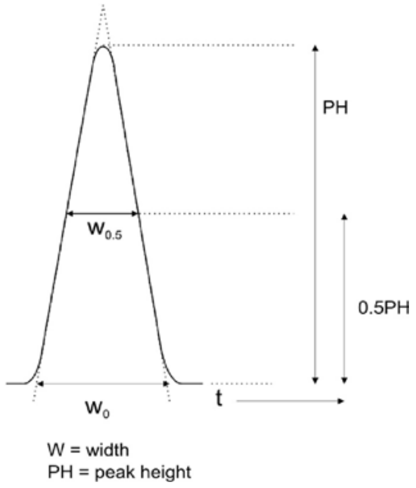


Figure 6.29 - Representation of a peak

The position of the peak on the chromatogram depends on the retention time of the compound. The height of the peak is determined by the detector response, which is directly proportional to the concentration of the compound in the sample. The peak width, instead, gives an estimation of the purity of the sample. The shape, size and position of the peaks can be used to identify the compounds and the relative amount of each compound present in the sample. The baseline of the chromatogram represents the noise level, which can be used to determine the minimum detection limit of the method.

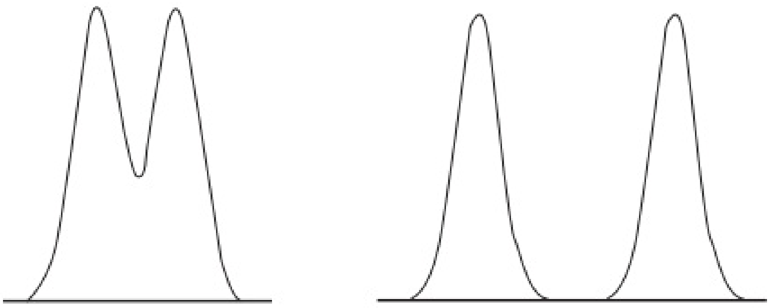
Apart from peaks height and width, two other primary parameters can be determined from the graph:

- *Retention time (RT)*: is time interval between sample injection and the maximum of the peak. This can be used to identify the compound. It depends not only on the specific molecule being detected, but also on factors such as the nature of the mobile and stationary phases, the chromatographic column type and dimensions, the analysis conditions. The RT is an essential parameter for qualitative analyzes.
- *Peak area*: the area under a peak to its baseline is *proportional to the concentration of the corresponding compound. I*t depends on the detector characteristics and it is fundamental for quantitative analyzes.

From the analysis of the chromatogram, some fundamental parameters relating to the quality of the column separation can be obtained.

1. *Selectivity*: refers to the ability of the chromatography column to separate different compounds in a sample by eluding them with different speeds. A column with high selectivity will produce well-resolved peaks for the different compounds in the sample, while a column with low selectivity will produce overlapping peaks, making it difficult to identify and quantify the individual compounds. Factors affecting selectivity in GC, include the nature of stationary phase, column length and diameter, temperature program and injection technique. For capillary columns it is not

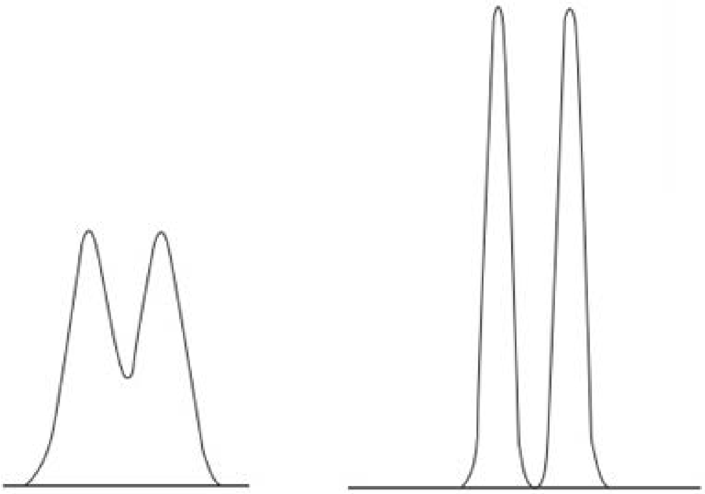
necessary to require high selectivity as their high efficiency can compensate for a lower value of this parameter. Figure 6.30 shows a two-compound mixture chromatogram, obtained by using two different stationary phases: a higher selectivity is obtained in the right graph.



a) Low Selectivity b) High Selectivity

Figure 6.30 - Improvement in column selectivity

2. *Efficiency*: it is the ability of a chromatographic system to keep the elution band of a substance compact along its entire path through the column. It provides a quantitative measure of the extent of band broadening. It refers to ability to elute all molecules of a given chemical species with the same speed. A column with high efficiency will be able to separate components more effectively, resulting in narrow peaks taking up less space. This parameter is of great importance, because even if two substances had very close retention times, a good resolution ensure that they could equally be separated. Figure 6.31 shows the chromatogram of a two-compound mixture obtained with different columns; in both cases there is the same selectivity, but in the second case there is greater efficiency.



a) Low Efficiency b) High Efficiency

Figure 6.31 - Improvement in column efficiency

Efficiency is affected by a number of factors, including column length and diameter, Column packing material, temperature, carrier gas flow rate, column condition.

3. *Resolution*: it is a measure of separation between two adjacent peaks. This parameter takes into account both selectivity and efficiency and indicates the degree of effective separation obtained, in a chromatographic process, for two substances with similar characteristics.
From a numerical point of view, it is expressed as a ratio of the distance between the peaks to the average width of the peaks. The most commonly used formula for its computation id the following [100]:

$$R = \frac{t_r^B - t_r^A}{w_A/2 + w_B/2}$$

Generally, a resolution of greater than 0.8 is considered acceptable for most chromatographic separations. To understand the meaning of this relationship, consider the example shown in Figure 6.32.

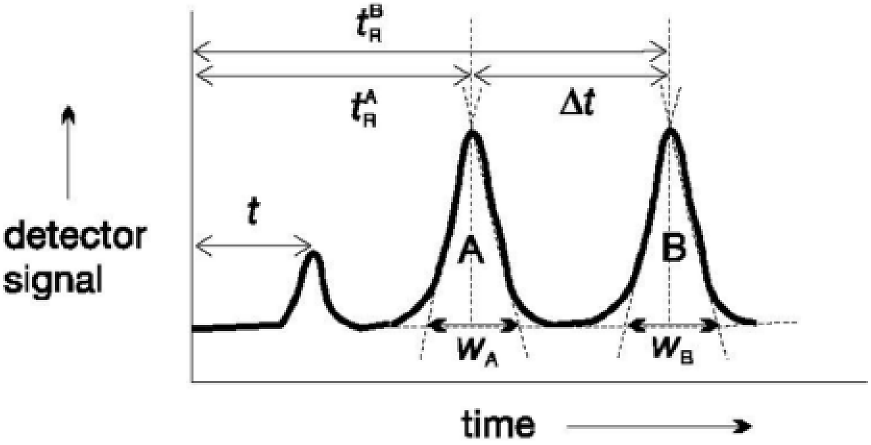


Figure 6.32 - Parameters underlying chromatographic resolution [100]

Factors such as column length, temperature, and carrier gas flow rate also play an important role in determining the final resolution of a chromatographic separation.

6.4.6 Analytical applications

Gas chromatography (GC) can be used for both qualitative and quantitative analyses [99].

Qualitative analysis

Qualitative analysis refers to the process of identifying the presence and/or absence of specific compounds in a sample.

There are several techniques that can be used for qualitative analysis:

1. Retention time comparison: This technique involves comparing the retention time of the peaks in the mixture under examination to those of known standards. Compounds with similar chemical and physical properties will have similar retention times.
2. Mass Spectrometry (MS) detection: This technique involves using a mass spectrometer in conjunction with a GC. The mass spectrum produced, which is unique for a certain chemical species, can be used to identify the compound based on its molecular weight and fragmentation pattern.
3. Library search: This technique involves comparing the retention time and mass spectrum of the peaks in the sample to a library of known compounds. The library can be a software program or a physical reference collection.
4. Enrichment: this technique works by increasing the concentration of specific compounds in a sample before analysis, making them easier to detect. When a certain peak is believed to correspond to a known substance, a certain amount of pure substance is added to the mixture. If another peak appears, we are sure that the known species is not present in the mixture if one of the peaks is higher, the compound under investigation may be present. The latter occurrence requires further analyses to be carried out under different operating conditions.
5. Auxiliary tools. The gas leaving a non-destructive detector can be bubbled in suitable solvents and the solution investigated with other instrumental methods.

The choice of technique will depend on the sample, the compound of interest, and the instrumentation available.

Quantitative analysis

Quantitative analysis refers to the process of measuring the concentration of specific compounds in a sample. This can be done considering that in a GC chromatogram, the peak area is proportional to the amount of the corresponding component reaching the detector. A known reference standard is commonly required for this analysis.

There are several methods for quantitative analysis in GC, that, proceeding from most simple and least accurate to more complex and more accurate, include:

1. *<u>Area Normalization</u>*

   Area normalization is a calculation of area percent that is assumed to be equal to weight percent. If the detector response is the same for all the components and if these are all represented in the chromatogram by distinct and resolved peaks, the ratio between the peak area (S) and the concentration (C) of the component is the same for all peaks (A,B,C,…).

$$\frac{S_A}{C_A} = \frac{S_B}{C_B} = \frac{S_C}{C_C} = \cdots$$

In this case, the mass percentage of each component is obtained by dividing the area of the respective peak by the sum of the areas of all the peaks.

The method uses the area of the target component peak as a proportion of the total area of all detected peaks to analyze quantity.

For this method to be accurate, the following criteria must be met: (i) All analytes must be eluted. (ii) All analytes must be detected. (iii) All analytes must have the same sensitivity (response/mass).

These three conditions are rarely met, but this method is simple (no standard sample is used) and is often useful to determine changes in concentration of a known sample mixture, or to determine an approximate concentration.

2. *Area Normalization with Response Factors*

   This method is used to correct for variations in peak area due to differences in detector sensitivity or column efficiency. Response factors are determined by measuring the peak area of a series of known concentrations of a compound and comparing it to the peak area of an internal standard, which is typically a compound with similar chemical properties. The response factor is then used to normalize the peak area of the unknown sample to the internal standard. This method helps to ensure accurate and consistent quantification of compounds across different runs or samples.

3. *External Standard*

   This method is usually performed graphically and is included in the software of most data systems. It involves preparing a series of standard solutions with known concentrations of the compound of interest. These solutions are then injected into the GC and the peak area of the compound is measured. A calibration curve is then generated by plotting the peak area of the compound against its known concentration. The equation of the data fitting line is determined by linear regression analysis.

   The concentration of the compound in an unknown sample can then be determined by measuring the peak area of the compound and comparing it to the calibration curve. The concentration of the compound in the sample can be determined by substituting the measured peak area into the equation of the line.

   The external standard method is generally considered to be the most straightforward method for quantitative analysis in GC. The considerable advantage of this method is that it does not require working on all the components of the mixture. It does not require the use of internal standards or the addition of standards to the sample, making it a convenient and efficient method. However, it does require that the sample and the standards be similar in chemical and physical properties, and that the sample not contain any interfering compounds.

4. *Internal standard method*

   This method involves adding a known amount of a standard compound to the sample that is similar in chemical and physical properties to the compound of interest. The peak area of the compound of interest is then divided by the peak area of the internal standard, and the ratio is used to calculate the concentration of the compound in the sample.

5. *Standard addition*

   This method involves adding a known amount of a standard compound to a series of samples of varying concentrations. The peak area of the compound of interest is then plotted against the added concentration of the standard, and a linear regression line is calculated. The concentration of the compound in the unknown sample can be determined by extrapolating the linear regression line.

6.4.7 Experimental procedure and instruments

During experimental tests, the syngas composition was monitored on-site at regular intervals of 5 min, right at sampling point, using an on-line micro-gas chromatograph (micro-GC).

The instrument used is the Agilent 3000 micro-GC (Figure 14) which can simultaneously analyze samples on several independent channels; each channel (or module) consists of a sample injector, a high-resolution capillary column and a thermal conductivity detector (TCD).

The Agilent 3000 Micro-GC employed is equipped with two analytical channels. The first channel consists of a molecular sieve column Molsieve 5A (10 m x 0.32 mm x 12 micron), suitable for the separation of He, H2, O2, N2, CH4, CO by using argon (Ar) as carrier gas. This channel features a heated backflush injector, i.e. an injection system complete with a pre-column for the programmed cutting of unwanted compounds. The second channel is a PLOT U column (8 m x 0.32 mm x 30 micron) for the separation of CO_2, C2H4, C2H6, C2H2 and uses helium (He) as a carrier gas. Each analytical channel consists of a plug-and-play module that integrates the following main parts:

- a heated micro-injector equipped with a variable sample volume control from 1 to 10 μL or fixed volume from 1 μL,
- an analytical column and a high efficiency capillary reference column, both inserted in a thermostated compartment at constant temperature (maximum temperature 180 °C),
- a universal micro-detector "Solid State Detector" with internal volume of 240 μL,
- a micro-EPC (Electronic Pressure Control) for the electronic control and programming of the pressure at the head of the column,
- an electronic control and acquisition board.

The 3000 micro-GC also includes:

a sampling pump for the analysis of unpressurized mixtures in the gaseous phase,

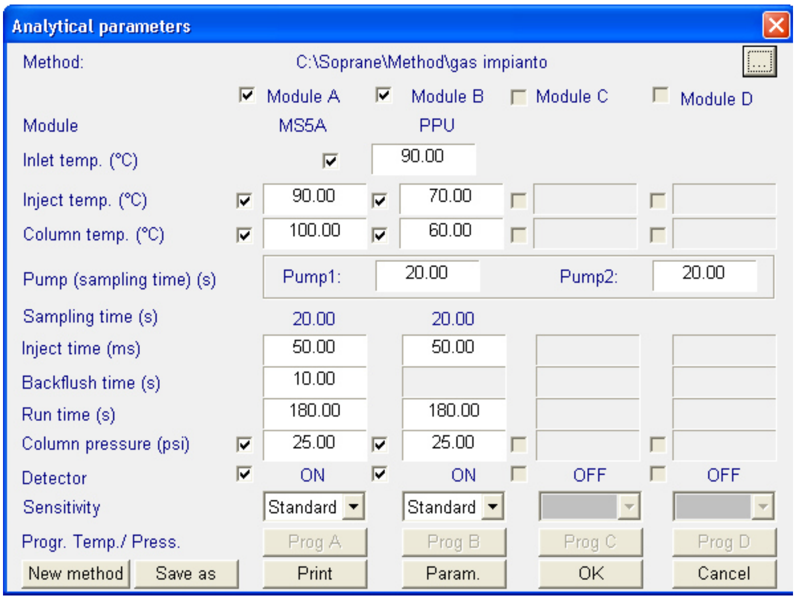
- a 5 μm membrane filter,
- 1/16” sample introduction lines,

- a LAN interface for instrument control.

Figure 6.33 - Picture of the micro-gas chromatograph used.

The SRA Soprane Networked Data System software controls all micro-GC functions (such as activating valves, setting column temperatures, sample inlets and lines transfer, management of detector signals, electronic pneumatics), performs calculations and archive the results. The Soprane software controls the micro-GC from an external PC using the standard LAN communication card via protocol (TCP/IP).

It is possible to create and modify methods and from the analysis obtain chromatograms, in which each peak, having a characteristic retention time, corresponds to a separate component in the column. Figure 6.34 shows the parameters of the method (called "plant gas") used for the analysis of the syngas.

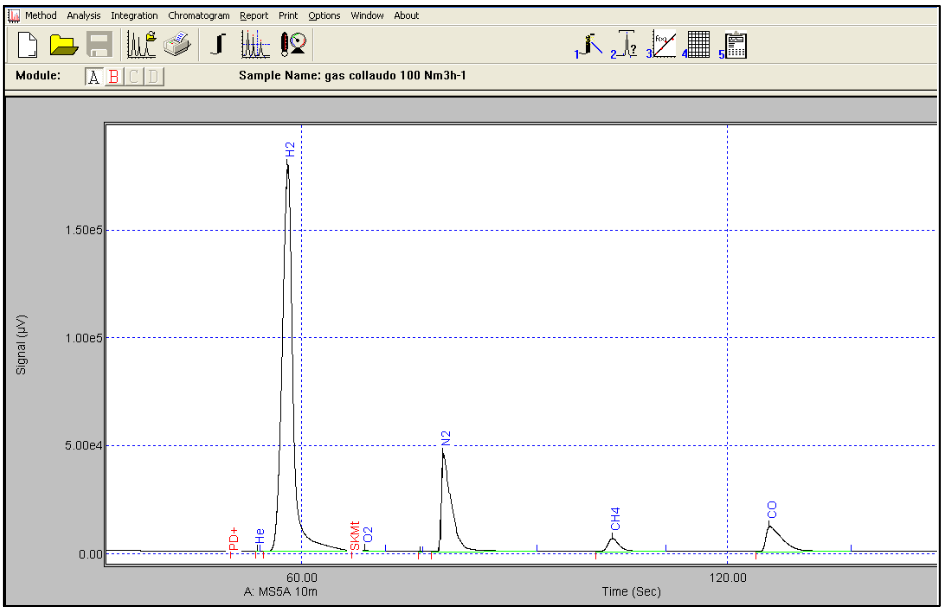


Method: C:\Soprane\Method\gas impianto

	☑ Module A	☑ Module B	☐ Module C	☐ Module D
Module	MS5A	PPU		
Inlet temp. (°C)	☑	90.00		
Inject temp. (°C)	☑ 90.00	☑ 70.00	☐	☐
Column temp. (°C)	☑ 100.00	☑ 60.00	☐	☐
Pump (sampling time) (s)	Pump1: 20.00		Pump2: 20.00	
Sampling time (s)	20.00	20.00		
Inject time (ms)	50.00	50.00		
Backflush time (s)	10.00			
Run time (s)	180.00	180.00		
Column pressure (psi)	☑ 25.00	☑ 25.00	☐	☐
Detector	☑ ON	☑ ON	☐ OFF	☐ OFF
Sensitivity	Standard	Standard		
Progr. Temp./ Press.				

Figure 6.34 - Parameters of the method used for the analysis of the syngas.

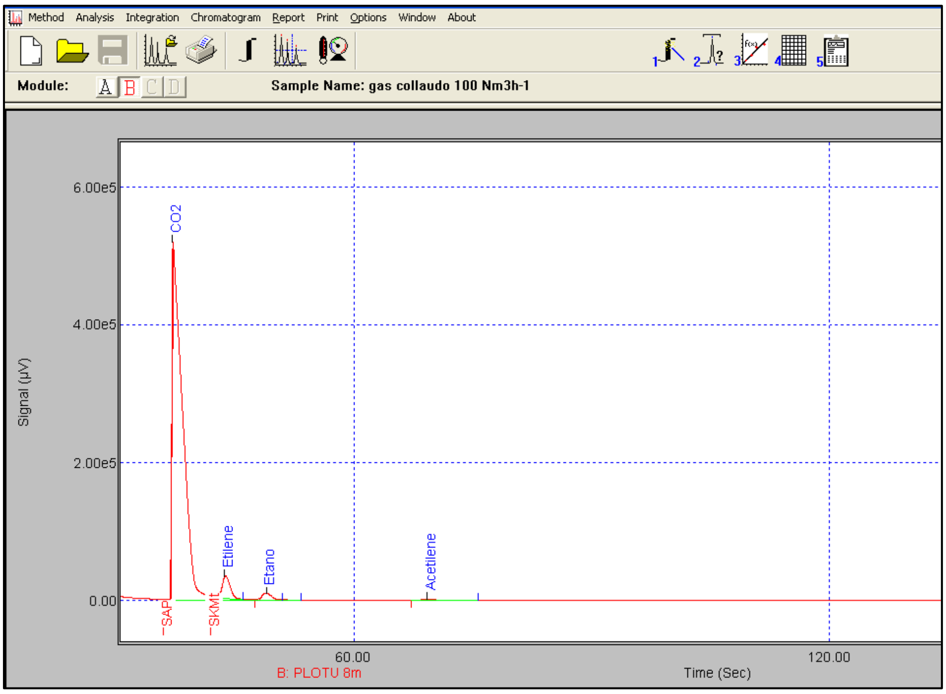
Figure 6.35 and Figure 6.36 show two typical chromatograms obtained respectively for the module A (molecular sieve column) and for the module B (PLOT U column) from the analysis of a sample of syngas.



Module: A

Sample Name: gas collaudo 100 Nm3h-1

Figure 6.35 - Example of chromatogram obtained for module A.



Module: B

Sample Name: gas collaudo 100 Nm3h-1

Figure 6.36 - Example of chromatogram obtained for module B.

The moisture present in the gas is not detected. The steam entering the instrumentation could damage the chromatography columns, therefore, there is a 5 µm membrane filter to remove both water and particulate matter from the sampled gas stream before the injection system.

Calibration of the GC analyzer was required to determine the concentrations of the species of interest in the gaseous mixture produced. Considering the main compounds present in the syngas with their expected concentrations, four different reference gaseous mixtures, having the following compositions, were employed:

- Mixture 1: O2: 0.50 vol %; CH4: 2.99 vol %; CO_2: 14.99 vol%; C2H2: 0.10 vol%; C2H4: 0.50
- vol%; N2 the remaining 80.92 vol%.
- Mixture 2: H2: 15.06 vol%; CO: 24.99 vol%; C2H6: 0.10 vol%; N2 the remaining 59.85 vol%.
- Mixture 3: CO 0.995 vol %, in nitrogen.
- Mixture 4: CO_2 0.999 vol%, in nitrogen.

The reference mixtures were analysed by gas chromatography to obtain, for each component, a calibration curve expressed as the detected peak area as a function of the concentration (external standardization method). Using these calibration curves the actual concentration of each component in the sampled syngas was then calculated.

6.5 Tar analysis

Tar is an undesired by-product of biomass gasification made-up of a complex mixture of condensable organic compounds. Tar formation is a major issue in biomass gasification. Once condensed it can clog gasifiers and gas cleaning equipment, reducing the efficiency of the process and increasing maintenance costs. Furthermore, the higher the tar content, the fewer the possibilities of using the syngas. Indeed above 5000 mg/Nm^3, syngas cleaning is quite complex and therefore possible tar generated deposits, fouling, or clogging, can easily plug the equipment downstream of the gasifier leading to unavailability or even failure.

For this reason, it is very important to characterize the syngas in terms of its tar content (expressed in mg/Nm^3).

6.5.1 Tar Sampling

The tar sampling procedure is standardized in the Technical Specification “*Biomass Gasification - Tar and Particles in Producer Gases - Sampling and Analysis*” [101], also known as "Tar Protocol", which was prepared by a collaboration of 17 partners from Europe and North America under CEN (European Committee for Standardization) starting from April 2000. The “Tar Protocol” aims at developing a general and widely accepted method (Guideline) for sampling and analysis of organic contaminants (tars and particles) in biomass producer gases. The “Tar Protocol” continues and formalizes the earlier work initiated by IEA, DoE and EU in 1998, describing instruments and methodologies for the analysis of tar generated by different gasifier types (updraft, downdraft and fluidized bed) in a wide range of operating conditions and concentrations.

The “Tar Protocol” has been currently implemented by the UNI CEN/TS 15439 standard of January 2006 [102], which refers to the Technical Report "*Sampling and analysis of tar and particles in biomass producer gases*” [103] written in support of the “Tar Protocol”.

Conventional tar analysis uses the condensation method, which is essentially based on a continuous sampling, through a heated probe, of a syngas stream which, after being filtered, is sent to a series of glass bottles, kept at a low temperature (from ambient temperature down to -20°C) in a cold bath. The cooling action of the gas in the bottles determines the condensation of the tar which are thus collected and weighed. The separation efficiency can be improved by increasing the contact surface, so filling materials such as glass tubes or spheres, silica gel, glass wool are usually inserted inside the bottles.

Compared to conventional techniques, the "Tar Protocol" adopts a condensation and absorption sampling method in order to bring the separation efficiency of the tar from the sampled gas to 100%.

In this case the bottles consist of glass impingers partially filled with a solvent, usually isopropanol, to facilitate tar absorption. Tar Protocol provides for a sampling train system (Figure 6.37) consisting of the following 4 module:

1. Module 1: gas pre-conditioning module consisting of an electrically heated sampling probe and a sealing system (shut-off valve) for safely mount and remove the probe during operation,
2. Module 2: heated particle filtration system consisting of a thimble filter operating at high temperatures, generally above 350°C, in order to prevent tar condensation,
3. Module 3: tar collection (sampling) section consisting of a series of 6 glass bubblers (100 ml or 250 ml volume),
4. Module 4: gas suction and volume metering section, consisting of a diaphragm pump equipped with a flowmeter and volumetric counter for measuring the sampled gas volume flow.

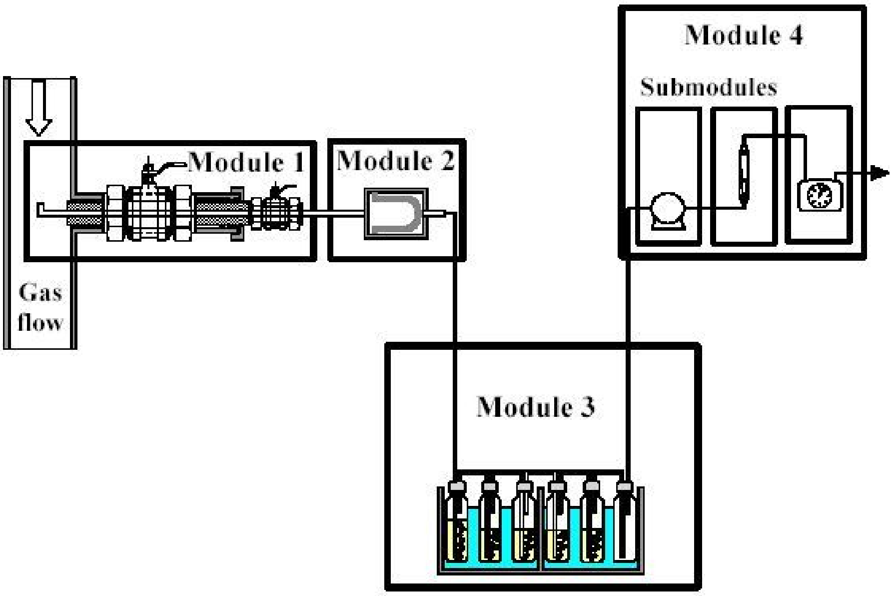


Figure 6.37 - Sampling train system

The sampling section has two differentially tempered sections, the first at 35° ÷ 40°C and the second at -15° ÷ -20°C, each of which houses three bubblers. Some bubblers are equipped with porous septa to favor the formation of small bubbles.

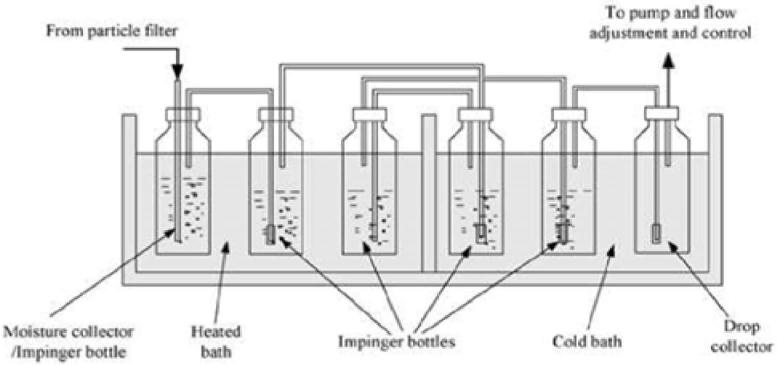


Figure 6.38 - Condensation sampling method.

Impingers 1, 2, 3, 4, 5 contain about 50 ml of isopropanol, while bottle 6 is left empty and acts as a drop separator.

The protocol provides for two possible impinger set-ups (Figure 6.39):

- standard set-up
- alternative set-up

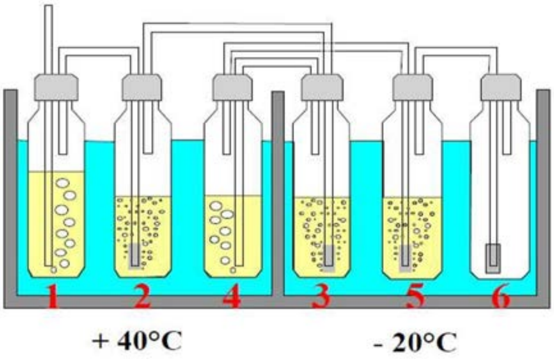


Figure 6.39 - Possible sampling set-ups.

In the standard set-up, impingers 2, 3, 5, 6 must be provided with porous septa with porosity degree G3 (largest pore diameter between 17 and 40 μm), or alternatively G2 (largest pore diameter between 41 and 100 μm) if the pressure drops are excessive. Furthermore, the temperature of bubblers 1, 2, 4 is between 35 ÷ 40 °C, while that of bubblers 3, 5, 6 is between -15 ÷ -20 °C.

In the alternative set-up the impingers 1, 5, 6 contain 6 mm diameter glass spheres in place of the porous septa. The temperature of the impingers 1, 2, 3, 4 is between 35 ÷ 40 °C, while that of the impingers 5, 6 is between -15 ÷ -20 °C.

Both condensation and condensation and absorption methods provide quantitative data by gravimetric analysis (weighing) of the tar collected in the bubblers or in the residue remaining after solvent evaporation (if a solvent has been used for tar absorption). The tar content in the syngas (expressed in mg/m^3 or in mg/Nm^3) is then obtained by dividing the mass of the tar determined by gravimetric analysis by the volume of gas aspirated during sampling.

6.5.2 Adopted TAR sampling system.

In the experimental tests the standard set-up was adopted since it allows greater separation efficiencies. From previous experiences of the UNIPI research team, it has been found that the use of four impingers filled with isopropanol, the first of which without a porous septum, combined with a fifth bubbler for drop separation, is more than sufficient to ensure high tar sampling efficiencies. The ice-water bath is kept a few degrees below freezing by the addition of NaCl.

The experimental apparatus was prepared as follows:

1. a high temperature sampling probe was mounted in the pipe section between the gasifier outlet and the syngas suction fan, where the gas temperature was around 450-550°C. The L-shaped probe was positioned on the pipe axis at a distance of at least 5 hydraulic diameters from the upstream discontinuity and at least 2 hydraulic diameters from the downstream one. A weld tee fitting was added in the syngas outlet pipe to attach the probe. The seal between the latter and the fitting was ensured by a suitable layer of high temperature silicone. The sampling probe (Figure 6.40), consisting of an AISI 316 L-shaped tube in contact with six heating resistance thermometers, is suitably insulated and inserted into a stainless-steel tube. Heating guarantees the probe is maintained above the tar condensing temperature, to prevent any condensation in it. Downstream of the tube there is a heated filter holder containing a quartz filter thimble to remove the particulate from the sample gas. After the filter, a shut-off valve enables flow interruption at any time. Type J thermocouples are installed along the probe for temperature measurements in several points.

Figure 6.40 - Probe equipped with filter holder, shut-off valve and junction box.

The resistances activation is done via an electrical panel (Figure 6.41), through which the user can set the desired temperature of the probe and the filter holder. A PID thermoregulator power the thermoresistances accordingly.

Figure 6.41 - Sampling probe drive panel.

Sampling was performed under isokinetic conditions. Isokinetic sampling means that the velocity, in the sample probe inlet nozzle, must equal the free stream velocity of the gas being sampled. As shown in Figure 6.42, non-isokinetic sampling could result in a reduction or increase in the particulate content of the sample taken, due to the inertial phenomena to which the particles are subject. At each sampling, the flow rate of the aspirated gas was therefore adjusted to obtain isokinetic conditions. For this purpose, velocity measurements were carried out each time using a special Pitot tube.

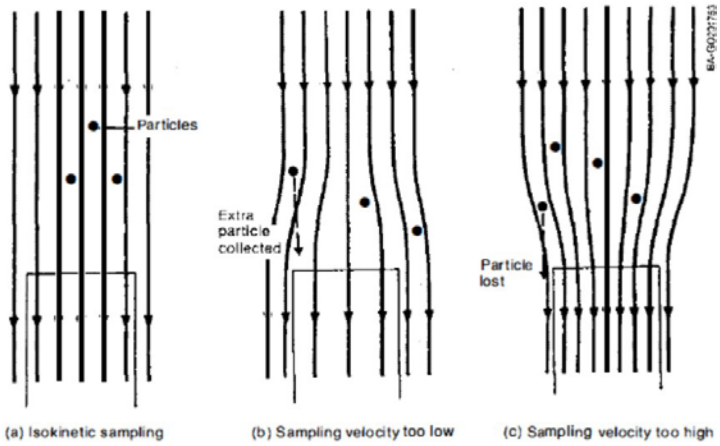


Figure 6.42 - Isokinetic sampling.

2. Moisture and tar collection was performed in a series of 4 impingers bottles, placed inside a thermos flask in an ice-water bath at about -5°C (Figure 6.43). All the bubblers, one of which has no frit, were filled with 50 mL of isopropyl alcohol. A droplet separator has been provided downstream (Figure 6.44). The connection between the particle filter and the glassware was made with HT silicone tubing.

Figure 6.43 - Thermos with ice bath containing four bubblers

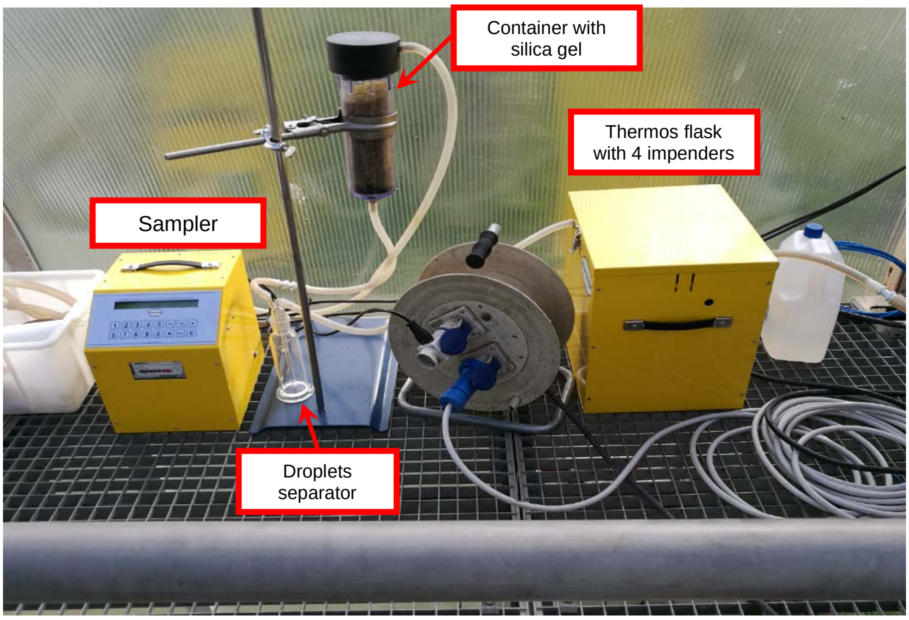


Figure 6.44 - Tar sampling system

3. The syngas flow is ensured by a sampler (compliant with UNI EN 12919), consisting of a diaphragm pump with an automatic pressure drops compensation to keep the flow rate constant for the entire duration of the isokinetic sampling (Figure 6.44). The

sampler is preceded by a container filled with silica gel for moisture removal to protect its diaphragm pump.

4. The sampler is equipped with a flowmeter and a volumetric counter for controlling the flowrate set point and measuring the overall volume of gas sampled during the test. In this way it is possible to trace the concentrations of TAR and particulate in the syngas.
5. The syngas leaving the sampler is released into the atmosphere.
6. Syngas sampling for subsequent laboratory analyses is performed downstream of the sampler using transparent 1-liter Tedlar bags (Figure 6.45) which are inflated thanks to the syngas pressure.

Figure 6.45 - Syngas sampling bag.

Figure 6.46 shows a synthetic scheme of the system.

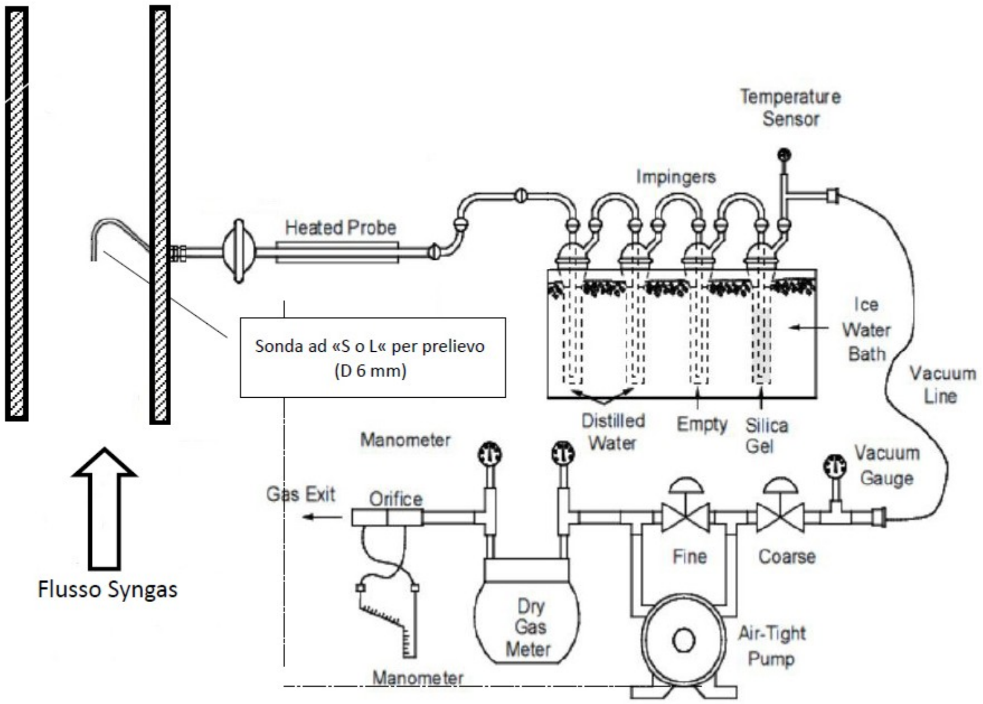


Figure 6.46 - Syngas isokinetic sampling system.

Chapter 7
Process modeling

For a better understanding of the gasification process, applied to a non-traditional biomass such as sludge from the treatment of domestic wastewater, on which a small number of scientific studies are present in the literature, it was believed appropriate to develop two mathematical models aimed at simulating the behaviour of the LIFE AUGIA downdraft gasifier fuelled with sewage sludge and steam-oxygen as gasifying agent.

Due to the current unavailability of the LIFE AUGIA demonstration plant, the validation of the model has been carried out using some previous experimental data, made available by the LIFE AUGIA collaboration, obtained with an existing full-scale gasifier, similar to that envisaged by the project, fed with biomass and air as gasifying agent.

These numerical models, developed with Aspen Plus®, have been used to perform an extensive simulation analysis of the operative behaviour of the oxy-gasification plant under construction. They made also possible the definition of its optimal design point.

In this chapter both models and the main results obtained from their simulation are presented. Once the experimental phase on the demonstrative plant and the consequent data analysis will be completed and consolidated the results obtained will be used to tune again the models and assess their goodness

7.1 Biomass gasification models

Biomass gasification is a complex process involving interrelated chemical and physical phenomena, including fast pyrolysis, partial oxidation of pyrolysis products, gasification of the resulting char, conversion of tar and lower hydrocarbons, and the water–gas shift reaction.

In addition to experimental tests, simulation models are commonly used to fully understand these complicated processes and their underlying mechanisms and relationships. These models are mathematical representations of the gasification process that are based on the fundamental principles of thermodynamics, kinetics, and transport phenomena. They can provide detailed information about the process at different scales, from the molecular level to the entire reactor.

The main objectives of these models are to study the thermochemical processes involved in the gasification of the biomass, to evaluate the influence of various operating conditions and feedstock properties on the process performance (syngas yield, composition and energy content) and to predict the behavior of the plant under different scenarios.

Some models only consider the final composition of chemical equilibrium while others take into account the different processes happening along the gasifier with their specific kinetics. In this perspective, models can be divided into kinetic rate models and thermodynamic equilibrium models. Modelling can be done using process simulation software package such as Aspen Plus®.

7.1.1 Kinetic rate models

Kinetic models provide essential information on kinetic mechanisms and gasifier geometry to describe the conversion during biomass gasification, which is crucial in designing, evaluating and improving gasifiers. These rate models are accurate and detailed but are computationally intensive. They describe the combustion and char reduction process using kinetic rate expressions obtained from experiments and allow better simulation of the experimental data as they can reliably implement the impact of the actual geometry of the reactor. Their approach ensures a better prediction of the overall efficiency of the gasification process.

7.1.2 Thermodynamic equilibrium models

Thermodynamic models use equilibrium calculations, which are independent of gasifier design, making them more suitable for process studies on the influence of the most important fuel process parameters. At chemical equilibrium, a reacting system is at its most stable composition, a condition achieved when the entropy of the system is maximised while its Gibbs free energy is minimized. However, thermodynamic equilibrium may not be achieved, mainly in case of relatively low operation temperatures.

Equilibrium models have two general approaches: stoichiometric and non-stoichiometric. The stoichiometric approach requires a clearly defined reaction mechanism that incorporates all chemical reactions and species involved. In the non-stoichiometric approach is based on minimising Gibbs free energy in the system without specifying the possible reactions taking place. The only inputs needed to specify is the feed elemental composition, which can be readily obtained from ultimate analysis data, and the expected syngas composition (selecting those species that are typically present in the largest amounts)

Equilibrium models assume that the reaction rates are fast enough to reach the equilibrium state. The reactor is implicitly considered to be zero-dimensional, assuring perfect mixing and uniform temperature.

Due to these assumptions, they yield great disagreements under some circumstances. Typical pitfalls at relatively low gasification temperatures are the overestimation of H_2 and CO yields and the underestimation of CO_2, methane, tars and char. For this reason, several authors have modified and corrected the equilibrium model or used the quasi-equilibrium temperature (QET) approach. QET is the temperature at which the chemical reaction is considered to have reached equilibrium, rather than the actual temperature of the gasifier. In order to evaluate the QET, a Data-Fit made by experimental data can be used.

7.1.3 Aspen Plus gasification models

Some authors, trying to avoid complex processes and build the simplest possible model that incorporates the principal gasification reactions and the gross physical characteristics of the reactor, have developed model using the process simulator Advanced System for Process Engineering (Aspen) Plus.

Developed by Massachusetts Institute of Technology (MIT), Aspen Plus is a chemical engineering process optimization software that utilizes unit operation blocks, such as reactors, pumps, columns, heat exchangers, etc. Each unit block is linked to another by material and energy streams to create a flow sheet for the whole process. The program is based on a sub-sequential modular approach, and the simulation calculations use the in-built physical properties database.

It is used to facilitate the calculation of physical, clinical and biological processes as it can successfully describe processes involving solids in addition to vapour and liquid streams. Aspen Plus makes model creation and updating easier, since small sections of complex and integrated systems can be created and tested as separate modules before they are integrated.

This process simulator is equipped with a large property data bank containing the various streams in a gasification plant, with an allowance for the addition of in-house property data. Where more sophisticated block abilities are required, they can be developed as FORTRAN subroutines.

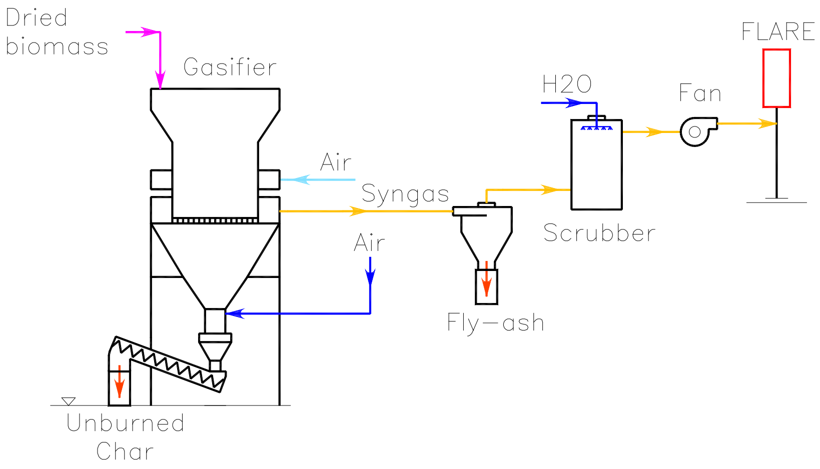
The process flow diagram (PFD) for biomass gasification is almost standard. It is assumed that the gasifier consists of four zones with different physical and chemical processes taking place: (i) Biomass/coal preheating and drying, (ii) Pyrolysis (decomposition), (iii) Gasification and (iv) Combustion, followed a gas cleaning, in which, a cyclone and a flash separator facilitate ash and water removal, respectively.

7.2 Modelling of the LIFE-AUGIA oxy-gasification plant

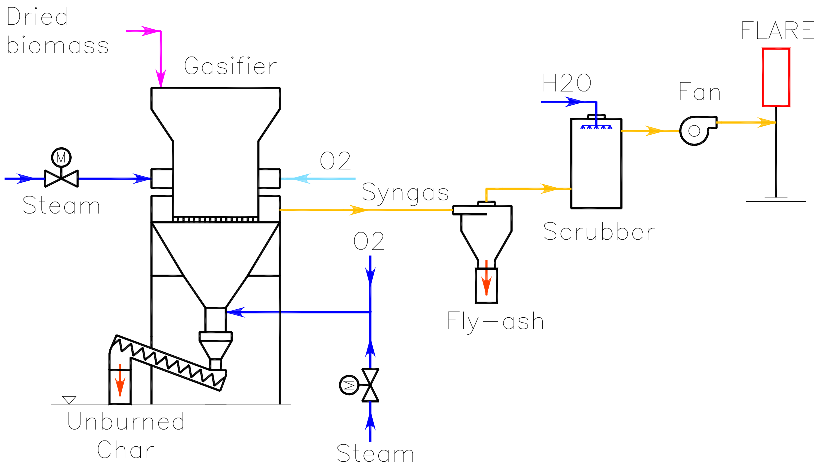
The design of the LIFE AUGIA experimental oxygen gasification plant involved several steps, one of which was performing the mass and energy balances of the system to select the optimal design point for process plant equipment. To this purpose, numerical simulation models of the gasification plant have been developed using Aspen Plus V11® software, with two different approaches, namely an equilibrium model and a kinetic model. Due to the current unavailability of the LIFE AUGIA demonstration plant, the validation of the model was carried out using some previous experimental data, made available by the LIFE AUGIA collaboration, obtained with an existing full-scale gasifier, similar to that envisaged by the project, fed with biomass and air as gasifying agent. The following paragraphs provide more details about this modelling development activity.

7.2.4 Plant layout

The gasifier, that has been taken into consideration as reference for the development of the simulation models and for the design of the novel reactor, is located in Maso del Gusto (TN, Italy) (Figure 7.1). The current gasifier exploits atmospheric air as gasifying agent (Figure 7.1a). As reported above, some experimental data obtained with biomass and air have been used for the calibration of the model. After that the simulations with pure oxygen and steam as gasifying agents have been carried out using this validated model (Figure 7.1b).



(a) air as gasifying agent



(b) pure oxygen and steam as gasifying agents

Figure 7.1 - Scheme of the gasification plant.

The reactor is designed in a downdraft configuration, with most of the air entering at the mid-height located throat. A secondary flow of air is injected from the bottom to facilitate the complete chemical conversion of the char and to raise the reaction temperature for cracking and oxidizing the tar present in the syngas. The syngas is extracted below the throat. The feedstock is charged in an intermittent way from the reactor top when its level inside the gasifier reaches a specified value. So, the gasifier has a concurrent configuration in the upper part and a counter current one in the bottom section. In particular, biomass and gasifying agent flow downward from the entry point in the upper part of the reactor to the syngas exit which is located just below the throat. The secondary air flows upward from the bottom to the syngas exit and the char goes downward to the ash discharge, which is located at the gasifier bottom. When the gasifying agent is changed, a mixture of pure oxygen and saturated steam is used instead of air. It is also possible to keep a lower amount of air and supplement it with a mixture of oxygen and steam. By doing this, the gasifier works with enriched air as gasifying agent.

7.2.5 Quasi-equilibrium model of the gasification process

Based on the plant layout depicted in Figure 7.1, a simulation model was developed under the assumption of ideal thermodynamic equilibrium conditions. To accomplish this task, a brief review of the relevant existing literature on biomass downdraft gasification modelling with Aspen Plus was conducted [104 -110].

The model, whose flowsheet is displayed in Figure 7.2, provided with the biomass composition and feeding rate, as well as the amount and thermodynamic condition of the air injected, allows to calculate the composition of the outgoing syngas, its pressure, and temperature. This model follows those reported in the scientific articles [111] and [112], which have demonstrated its experimental validity.

The fundamental thermochemical processes (drying, pyrolysis, combustion and gasification) taking place inside the reactor, from the biomass inlet down to the ash grate, have been modelled in three linked stages through a series of unit operation blocks.

The first stage simulates the drying process by reducing the moisture content of the fuel to a predefined value before feeding it to the reactor. Then, the feedstock undergoes decomposition into volatile components and char. The yield distribution for this devolatilization step is specified by using a FORTRAN statement in the calculator block. In the third stage the partial oxidation and gasification processes are modelled using a non-stoichiometric approach, based on minimization of the Gibbs free energy. This approach offers the advantage of not having to consider and specify the individual chemical reactions supposed to take place.

This kinetic-free model allows to predict the syngas composition based on the assumption of that the reactions occur in a fully mixed condition for an infinite time, thus reaching a state of chemical equilibrium [105]. This simplified hypothesis offers the benefit of a robust and simple simulation model that is independent of the gasifier design. However, it has a limitation in that the actual conditions inside the reactor may not necessarily lead to chemical equilibrium. Therefore, the results obtained from this approach should be considered as a target value for the plant performances. It is important to note, however, that the cold gas efficiency of the process is well estimated in any case.

An upgrade of the latter non-stoichiometric equilibrium model is the quasi-equilibrium approach. It is a compromise between equilibrium thermodynamic models and experimental ones and does not require specific information on the dimensions, capacity and structure of the reactor. Also implemented in the present study, this approach provides a more accurate description of the syngas composition and is considered one of the most effective ways to simulate the performance of a gasifier [106]. The first one to introduce the quasi-equilibrium model was Gumz [113], who proposed to use the QET (Quasi-Equilibrium Temperature), that is, the temperature at which the chemical reaction is considered to have reached equilibrium, rather than the actual temperature inside the gasifier. The appropriate QET to be used in the model is determined by fitting experimental data.

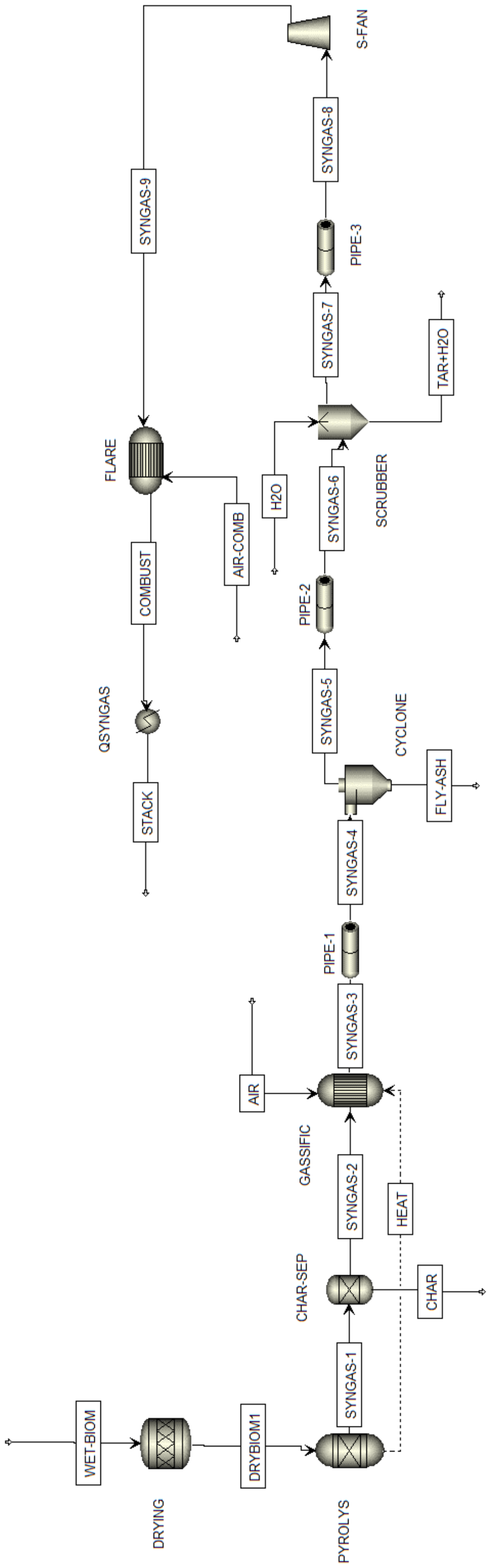


Figure 7.2 - Aspen Plus® equilibrium model: flowsheet of the gasification plant

Assumptions

Some simplified assumptions have been made which marginally affect the simulation accuracy:

- Process is steady state and isothermal [118]. The gasification temperature, which is one of the most representative process parameters, does not oscillate largely during the process due to the large inertia of the system. Some small fluctuations can occur only when new fresh feedstock is suddenly added to the reactor. Also, the ash discharge could theoretically induce a sudden variation of the pressure profile inside the reactor. If the extraction is frequently carried out, this disturb can be considered negligible. So, the steady state hypothesis can be considered largely acceptable.
- Zero-dimensional model. Gasification chemistry alone is modelled without taking into account the geometry of the reactor.
- Drying and pyrolysis occur instantaneously [114].
- Char is 100% carbon (graphite). [119];
- All of the sulphur reacts to form H_2S [115].
- No nitrogen compounds are formed during oxy-gasification [115]. Nitrogen within the feedstock is considered practically inert. The production of nitrogen oxides (NOX) and ammonia (NH3) is generally so low that this simplification does not significantly affect the chemical equilibrium or energy balance of the process. Therefore, the final macro composition of the syngas can be reliably estimated regardless.
- 2% carbon loss in ash [116].
- the production of TAR and other long chain hydrocarbon components have not been simulated because their low production does not affect the energy balance of the reactor and its chemical equilibrium.

Physical property method

Peng-Robinson equation of state with *Boston-Mathias* alpha function (PR-BM) [120] has been used to estimate all physical properties of the conventional components. The alpha parameter alpha in this property package is temperature dependent variable and improves the correlation of pure component vapor pressure when temperature is very high, making this model suitable for gasification process where temperatures are fairly high. To avoid overburdening the discussion, we will not describe this model in detail here. For further information, please refer to reference [122].

HCOALGEN and DCOALGEN models are selected for the evaluation of the enthalpy and density of both biomass and ash, which are non-conventional components [121].

Gasifier model description

Figure 7.2 shows the ASPEN Plus flow diagram of the plant under study, while Figure 7.3 describes the corresponding calculation procedure. The dashed streams are heat streams; the continuous streams are material streams.

Four ASPEN Plus blocks have been used to simulate the gasifier (see Table 7.1).

Table 7.1 – Quasi-equilibrium Model: Function of Each Block

Block	**Model**	**Function**
DRYING	RStoic	Reduces the moisture content of the feedstock to a predefined value
PYROLYS	RYield	Converts the non-conventional feedstock stream into its conventional components by using a FORTRAN statement
GASSIFIC	RGibbs	Calculates syngas composition by minimizing Gibbs free energy. Simulates partial oxidation and gasification and restricts chemical equilibrium of the specified reactions by specifying a temperature approach
CHAR-SEP	Sep2	Separates gases from ash by specifying split fractions

The feedstock is considered as an unconventional solid component, whose chemical composition is expressed considering the ultimate and proximate analysis from laboratory testing (Table 7.2).

Table 7.2 - Ultimate and proximate of feedstocks.

(a) Virgin biomass

Proximate Analysis		**Ultimate Analysis**	
Moisture, wt % ar	10.5	Carbon, wt % daf	50.2
Fixed carbon, wt % dry	16.6	Hydrogen, wt % daf	6.0
Volatile matter wt % dry	82.1	Nitrogen, wt % daf	0.1
Ash, wt % dry	1.3	Oxygen, wt % daf	43.7

(b) Sewage sludge

Proximate Analysis		**Ultimate Analysis**	
Moisture, wt % ar	10	Carbon, wt % daf	45.5
Fixed carbon, wt % dry	2.7	Hydrogen, wt % daf	5.7
Volatile matter wt % dry	46.4	Nitrogen, wt % daf	7.5
Ash, wt % dry	50.9	Oxygen, wt % daf	40.7
		Chlorine, wt % daf	0.3
		Sulphur, wt % daf	0.3

The material stream WET_BIOM represents the feed mixture of biomass and sewage sludge. Its component attributes are calculated using an Excel spreadsheet as a weighted average of the ultimate and proximate analyses of the two components, based on their desired percentage concentration. The thermodynamic conditions and mass flow rate are also specified and entered.

A first operation block DRYING models the drying process. The initial moisture content of the feedstock, as resulting from its proximate analysis, is reduced to a predefined value, generally set at 10%, according to the project data. Although drying is not normally considered a chemical reaction, this is done by means of a *RStoic* reactor block, controlled by a FORTRAN statement in the calculator block, which convert a portion of the biomass to form water according to a given *extent of reaction*. The following equation is used:

$$\text{Biomass (wet)} \rightarrow 0.0555084\ H_2O$$

Aspen Plus treats all nonconventional components as if they have a molecular weight of 1.0. The reaction indicates that 1 mole of biomass reacts to form 0.0555084 mole of water. An optional SEP block can be inserted to separate the excess water from the dryer outlet stream.

The gasification and partial oxidation of the fed mixture is simulated using an *RGibbs* reactor. This type of reactor models chemical equilibrium by minimizing Gibbs free energy. However, the Gibbs free energy of the biomass and sludge mixture cannot be calculated directly because it is a non-conventional component. Therefore, prior to be fed into the *RGibbs* block GASSIFIC, the dried material (DRYBIOM1) is decomposed it into its primary constituent elements (C, H, O, N, S, etc.). This is done by means of the *RYield* block, PYROLYSIS which simulates a reactor with a known yield and does not require reaction stoichiometry and kinetics.

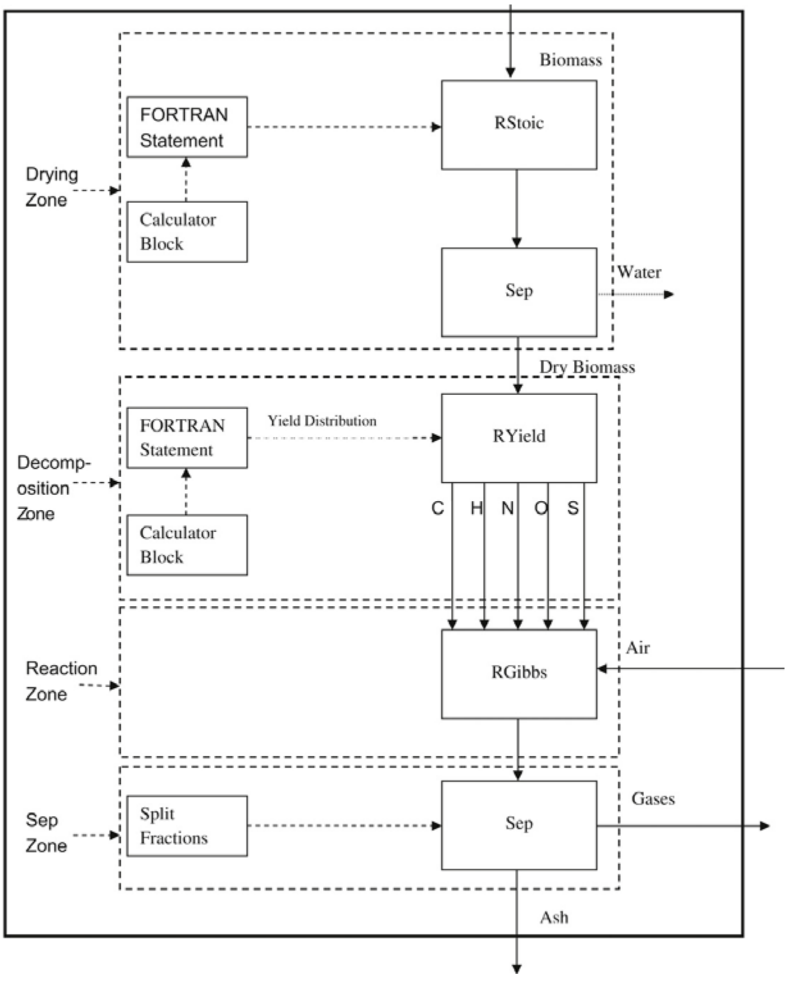


Figure 7.3 - Calculation procedure used in the quasi-equilibrium Aspen Plus model.

The yield distribution of the decomposed matter into its components is determined according to the component attributes of the feed stream to the *RYield* model. Calculations are performed by a Fortran routine in a calculation block, which specifies the mass flow rates of each element in the outlet stream based on the moisture content and chemical composition obtained from the proximate and ultimate analysis of the parent fuel (expressed on a daf basis).

The chemical elements resulting from the feedstock decomposition and the associated heat of reaction are used as input streams for the block GASSIFIC, where the designated gasifying agent (air or a mixture of oxygen and steam) is also introduced to model gasification reactions.

Based on specified split fractions, the block CHAR-SEP (model Sep) separates ash and a given percentage of char (2%) from the outlet stream of the devolatilization step. This unit operation lock simulates the extraction of ash and unreacted char from the bottom of the reactor. It is worth noting that in the Maso del Gusto reactor, which served as reference for validating the simulation model, the amount of unburnt char measured experimentally was practically negligible.

Other equipment of the gasification plant

In order to accurately simulate the operative behaviour of the gasification system and predict its performance under various conditions once the model was verified and validated with experimental data, the features of the plant equipment were introduced in the model. In particular:

- the cyclone for the removal of the fly ash
- the scrubbing of the syngas for its quenching and removal of tar
- the complete oxidation of the syngas occurs in the flare, which is modelled using a block Gibbs (Flare in Figure 7.2). The chemical power which corresponds to the complete oxidation of the syngas from the gasifier is calculated using a heater (QSYNGAS in Figure 7.2). The flue gas at the outlet of the flare is cooled to dew point temperature.

In the first version of the experimental gasification plant the scrubber will not be present and only a syngas cooling to about 350 °C will be carried out by means of a gas-to-air heat exchanger.

The control logics of the experimental plant have been implemented in the simulation model using the Design Specs tool of Aspen Plus. In this way it is possible to find the value of one or more control variables, such as, for example, the motor speed of the syngas fan, in order to iteratively reach a specified goal, such as the syngas mass flow.

Model validation

The simulation model has been validated using available data from air-based biomass and sludge gasification experimental trials carried out in a full-scale downdraft gasifier located in Maso del Gusto (TN, Italy).

It may be observed that the model results are in good agreement with the experimental results. The parity plot of the molar composition between the simulated values and the experimental ones, reported in Figure 7.4, allows to assess the prediction accuracy of the simulation model. The average differences between the measured LHV of the syngas and the simulated values and between the experimental CGE and the simulated ones as well are about 7% and 5%, respectively.

The average differences between the measured LHV of the syngas and the simulated values and between the experimental CGE and the simulated ones as well are about 7% and 5%, respectively.

Moreover, the average difference between the simulated values of the syngas temperature at the outlet of the gasifier and the experimental values is lower than 7%. On the basis of these negligible differences, the Aspen simulation model can be considered particularly accurate for the estimation of the most important energy performance indicators and operative data of the experimental facility. The most relevant difference between the experimental and simulated results concern the mass and molar concentration of H_2, that is overestimated, and CH_4, that is underestimated.

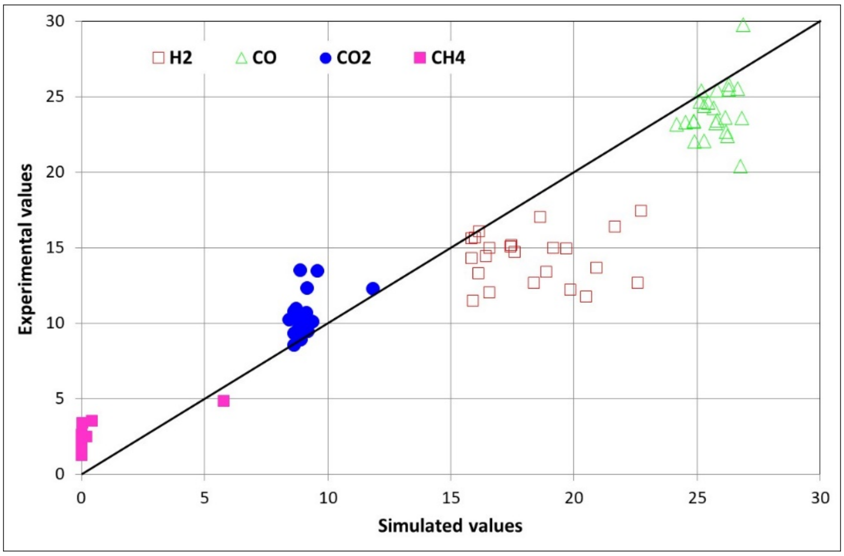


Figure 7.4 - Parity plot for the molar composition of the syngas for the comparison between experimental and simulated data.

Using the equilibrium hypothesis in the simulation model, the conversion of the methane into hydrogen, which depends on the actual crossing time of the gasification bed, is overestimated.

Indeed, the methane that is produced during the pyrolysis is progressively converted along the gasifying bed into H_2 and CO in accordance with the steam reforming reaction. Using the hypothesis of equilibrium, the steam reforming reaction is completed shifted toward the products, as reported also by other authors [106, 107]. This condition is hardly confirmed in real situations. However, it is important to note that the differences are lower with higher values of ER, when the hypothesis of equilibrium is more respected...

7.2.6 Kinetic model of the gasification process

Besides the basic quasi-equilibrium model, a more detailed and accurate description of the gasification process has been developed which makes use of a pseudo-kinetic approach [123]. This enhanced numerical model, also implemented through the Aspen Plus® software package, accounts for the kinetics of both the homogeneous gaseous reactions and heterogeneous gas-solid reactions, thus enabling to calculate the concentration and temperature profiles along the reactor.

The modelling activity involved additional features and assumptions, which will be described in the following paragraphs.

Gasification model description

We supposed that the geometric characteristics of the throated downdraft gasifier, to be constructed within the LIFE AUGIA project, are the same as the reactor, owned by BIOSYN, located at Maso del Gusto (TN). On the basis of the actual geometry of the latter gasifier, six different zones were identified (Figure 7.5), each corresponding to a specific chemical process and modelled separately:

1. Drying-pyrolysis section,
2. Gasifying agent inlet,
3. Throat and first zone under the throat,
4. Syngas outlet,
5. Under throat,
6. Post combustion air inlet and ash discharge.

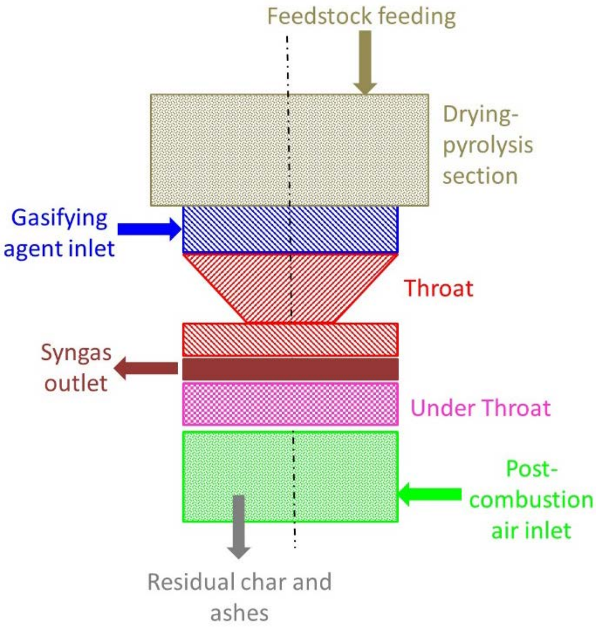


Figure 7.5 - Simulation model of the gasifier: block scheme of the reactor

Hobbs et al. [124] found that, in a gasifier, the axial length required for drying and pyrolysis is much shorter than that for char gasification and combustion. Therefore, these two processes are assumed to occur instantaneously at the top of the gasifier.

In the drying process, the moisture that is physically bound in the mixture being fed is released into the gas phase. The dried stream which results is referred to as DRY-COAL in the model. The amount of vaporized water is determined based on the moisture content in the proximate analysis of the feedstock, because the temperature within the gasifier is typically high enough to vaporize all the bound water.

During pyrolysis the dried mixture is thermally cracked into a solid residue (char), that will be the reactant in the following gasification reactions, and volatile matter consisting of a condensable organic product (tar) and various gaseous species (CO, H_2, CO_2, H_2O, H_2S, N_2, CH_4). In the model, tar is represented by benzene (C_6H_6), which numerous studies in the literature have confirmed to constitute 60-80% of the total tar [104]

No conventional block can represent this step in any commercial codes. In the model, pyrolysis was considered as a one-step global reaction and was expressed as follows:

$$C_{\alpha}H_{\beta}O_{\gamma}N_{\delta}S_{\varepsilon} \rightarrow n_{Char}\cdot Char + n_{H2}\cdot H_2 + n_{CH4}\cdot CH_4 + n_{CO}\cdot CO + n_{H2}\cdot H_2O \ldots$$

$$+ n_{CO2}\cdot CO_2 + n_{H2S}\cdot H_2S + n_{N2}\cdot N_2 + n_{tar}\cdot C_6H_6$$

where the subscripts α, β, γ, δ, ε represent the mole fractions of the components C, H, O, N, S of the dry ashless fuel, as derived from its elemental analysis, while n is the number of moles of the respective pyrolysis product species.

There are two approaches that have been employed in literature to determine the amount of each pyrolysis product. The first method involves conducting pyrolysis experiments outside of the gasifier [125,126]. The second method is based on a theoretical approach, such as utilizing a functional group model [124]. Given the inherent complexity of biomass composition, the theoretical method is often very intricate and challenging to apply in practical settings. In comparison, the experimental method is simpler and more feasible but not always applicable to the various types of feedstock. In this thesis, an empirical model [127] was preferred to predict the outcomes of pyrolysis, which combines a theoretical setting with assumption based on experimental results.

According to Radmanesh et al. [128], primary tar accounts for 60% of the primary pyrolysis products. However, after its formation, primary tar simultaneously undergoes secondary pyrolysis to yield secondary volatile products like CO, CO2, H2, some hydrocarbons like C2H2, C2H4, and C3H6, and inert tar [129, 130]. Experimental investigation by Rath and Staudinger [131] shows that only 78% of the initial tar is cracked, while 22% remains unchanged. In the model, higher aliphatic compounds produced during secondary tar cracking are lumped into methane formation.

The process of secondary tar cracking was not modeled separately in the model, as it is complex. Rather, the total moles of the individual gases released was estimated based on the assumption that the moles of the individual gases, including char formed during primary and secondary pyrolysis reactions, make up the total moles of the individual gases in the pyrolysis zone.

The pyrolysis products yields were estimated by forming a set of simultaneous equations, with the final mole of char and the six volatile matter species as unknowns. The first five equations are the elemental balance equations for C, H, O, S and N. Pyrolysis yields information based on experimental measurements were considered for the other species [136] [128, 137].

Predicting the tar species formed in pyrolysis process is challenging due complexity of the chemical reactions involved. Tar yield varies with biomass composition and temperature. In downdraft biomass gasification, maximum tar yield is negligible and does not vary significantly with temperature [40]. Hence for simplicity tar was considered as an input variable with a constant yield value of 4.5% by mass based< on experimental results on tar measurement [133, 134, 135].

The eight simultaneous equations were solved using an Aspen Plus built-in EXCEL subroutine to obtain the moles of the formed pyrolysis product species n_j (n_{Char}, n_{H2}, n_{CH4}, n_{CO}, n_{H2}, n_{CO2}, n_{H2S}, n_{N2}).

Other simplifying assumptions include the following:

- During de-volatilization, all elemental hydrogen and oxygen in the fuel are released, and thus, the resulting char is modelled as pure carbon [138, 139].
- Char yield is insensitive to temperatures encountered in the pyrolysis zone [138, 139]
- Temperature of the volatiles is assumed to be the same as the char temperature at every point in the gasifier (i.e., heat transfer between gas and solid is instantaneous) [139].
- The nitrogen content of the feedstock (if any) is presumed to form inert nitrogen gas and the thermal formation of nitrogenous compounds such as HCN and NH3 is disregarded.

Table 7.3 - Kinetic Model: Main gasification reactions.

Heterogeneous reactions		
R_1	$C_{(s)} + (\alpha+2)/(2\alpha+2)\ O_{2(g)} \rightarrow \alpha/(\alpha+1)\ CO_{(g)} + 1/(\alpha+1)\ CO_{2(g)} + (110.53\ \alpha + 393.5)/(\alpha+1)$ kJ/mol	*Char combustion*
R_2	$C_{(s)} + CO_{2(g)} \rightarrow 2\ CO_{(g)} - 172$ kJ/mol	*Boudouard*
R_3	$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)} - 131$ kJ/mol	*Water-gas*
R_4	$C_{(s)} + 2\ H_{2(g)} \rightarrow CH_{4(g)} + 75$ kJ/mol	*Methanation*
Homogeneous reactions		
R_5	$CO_{(g)} + 0.5\ O_{2(g)} \rightarrow CO_{2(g)} + 283$ kJ/mol	*CO combustion*
R_6	$H_{2(g)} + 0.5\ O_{2(g)} \rightarrow H_2O_{(g)} + 242$ kJ/mol	*H_2 combustion*
R_7	$CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_{2(g)} + 41$ kJ/mol	*Water gas shift*
R_8	$CH_{4(g)} + H_2O_{(g)} \leftrightarrow CO_{(g)} + 3\ H_{2(g)} - 206$ kJ/mol	*Steam-methane reforming*
R_9	$CH_{4(g)} + 1.5\ O_{2(g)} \rightarrow CO_{(g)} + 2\ H_2O_{(v)} + 517$ kJ/mol	*Methane partial oxidation*
R_{10}	$C_6H_{6(g)} + 7.5\ O_{2(g)} \rightarrow 6\ CO_{2(g)} + 3\ H_2O_{(g)} + 3169$ kJ/mol	*Oxidation of benzene*
R_{11}	$CH_{4(g)} + 2\ O_{2(g)} \rightarrow CO_{2(g)} + 2\ H_2O_{(g)} + 804$ kJ/mol	*Methane oxidation*

Chemical reactions

In all zones but the drying-pyrolysis section the chemical processes of gasification-oxidation were modelled using a pseudo kinetic approach, whose main reactions are reported in Table

7.3 [123]. To this purpose, a specific user-defined routine, compiled in Fortran, has been used within the Aspen Plus model for the assessment of the chemical reaction yield.

In reaction (**R₁**), the parameter α is defined as $\alpha = [CO]/[CO_2] = 2500 \exp(-6249/T)$, where $[CO]$ and $[CO_2]$ are the mean concentrations of CO and CO_2, respectively; and T is temperature in Kelvin (K) units [143].

Reaction kinetics

The complete description of the calculation approach for the reaction rate (r_i) of each reaction is reported below.

Heterogeneous reactions sub-model

The reactions (1-4) are solid-gas reactions that can be classified as either volumetric or surface reactions. In the volumetric reactions, gas can quickly diffuse into the particles and reaction takes place throughout of the interior of particle. In surface reactions, on the other hand, the gas remains confined to the surface of the unreacted solid shrinking core, with no penetration into the particle. Volumetric reactions tend to occur when the chemical reaction is slower compared to diffusion, while surface reactions happen when the chemical reaction is very fast and diffusion is the rate-limiting step. Reaction (1) is typically fast relative to the diffusion rate of reactants, and therefore occurs as a surface reaction. Reactions (2-4), instead, tend to be rather slow due to the low operating temperature in the gasifier, which is typically below 1000ºC. Thus, they are classified as volumetric reactions.

Based on the above statements, the unreacted core shrinking model is applied to describe the reaction rate of reaction (1) [139]:

$$r_1 = \rho_1 \cdot \frac{P_{O_2}}{\frac{1}{k_{film\_O2}} + \frac{1}{Y^2 k_{r\_O2}} + \frac{1}{k_{ash\_O2}}} \cdot 6 \cdot \frac{(1-\varepsilon)}{d_{p,0}}$$

$k_{film\_O2} = 1.24 \, (T/1800)^{1.75} / (d_{p,0} \, T)$
$k_{ash\_O2} = k_{film\_O2} \, \varepsilon_p^{2.5} \, Y/(1-Y)$
$k_{r\_O2} = 2.3 \, T \exp(-11100/T)$
$Y = d_{core} / d_{p,0}$

The rates of reactions (2-4) are expressed in Table 7.4.

Table 7.4 – Kinetic Model: Reaction rates of heterogeneous reactions (2-4)

Reaction rate	**Comment**	**Unit**	**Source**
$r_2 = \rho_2 e^{\frac{-22650}{T}} \left(P_{CO_2} - k_{r\_CO_2}\right) \frac{n_C}{V_{react}}$	$k_{r\_CO_2} = P_{CO}^2 \cdot e^{\left(20.92 - \frac{20280}{T}\right)}$	kmol/s m^3_{bed}	[139]
$r_3 = \rho_3 e^{\frac{-22650}{T}} \left(P_{H_2O} - k_{r\_H_2O}\right) \frac{n_C}{V_{react}}$	$k_{r\_H_2O} = P_{H_2} P_{CO} \cdot e^{\left(17.29 - \frac{16330}{T}\right)}$	kmol/s m^3_{bed}	[139]
$r_4 = \rho_4 e^{\left(-7.087 - \frac{8078}{T}\right)} \left(P_{H_2} - k_{r\_H_2}\right) \frac{n_C}{V_{react}}$	$k_{r_{H_2}} = \left(\frac{P_{CH_4}}{e^{13.43 - \frac{10100}{T}}}\right)^{0.5}$	kmol/s m^3_{bed}	[139]

where:

r_j = reaction rate of the j-th reaction [kmol/s m^3_{bed}]

ρ_j = tuning multiplying coefficient of the reaction rates.

P_i = partial pressure of i-th component [atm]

k_{film_i} = mass transfer coefficient of the i-th component through the gaseous film [m/s]

k_{ash_i} = mass transfer coefficient of i-th component through ash [m/s]

k_{r_j} = chemical reaction constant of j-th reaction [m/s]

d_{core} and $d_{p,0}$ = the diameter of the unreacted core and of the fed particle size, respectively [m]

T = temperature [K]

ε = bed porosity [-]

ε_p = ash layer porosity, supposed equal to 0.75 [-]

n_c = molar flow rate of carbon C [kmol C / s]

V_{react} = volume of the reactor [m^3]

Homogeneous reactions sub-model:

The kinetic expressions proposed in the literature for the gas-phase reactions (5-11), considered in the present model, are illustrated in Table 7.5.

Table 7.5 - Kinetic Model: Reaction rates of the homogeneous reactions (5-11)

Reaction rate	Comment	Unit	Source
$r_5 = \rho_5 \cdot \varepsilon \cdot k_{g5} C_{H_2O} C_{O_2}^{0.5} C_{H_2O}^{0.5}$	$k_{g5} = e^{\frac{-15105}{T}}$	kmol/s m^3_{bed}	[74]
$r_6 = \rho_6 \cdot \varepsilon \cdot k_{g6} C_{H_2} C_{O_2}$	$k_{g6} = e^{\frac{-12005}{T}}$	kmol/s m^3_{bed}	[140]
$r_7 = \rho_7 \cdot \varepsilon \cdot k_{wg} \left(C_{CO} C_{H_2O} - \frac{C_{H_2} C_{CO_2}}{K_{wg,eq}} \right)$	$k_{wg} = e^{\frac{-1513}{T}}$ $K_{wg,eq} = 0.0265 \cdot e^{\frac{3966}{T}}$	kmol/s m^3_{bed}	[141]
$r_8 = \rho_8 \cdot \varepsilon \cdot k_{g8} C_{CH_4} C_{H_2O} \left(C_{CH_4} C_{H_2O} - \frac{C_{H_2}^3 C_{CO}}{K_{g8,eq}} \right)$	$k_{g8} = e^{\frac{-4350}{T}}$ $K_{g8,eq} = e^{\left(30.42 - \frac{27106}{T}\right)}$	kmol/s m^3_{bed}	[141]
$r_9 = \rho_9 \cdot \varepsilon \cdot k_{g9} \cdot T \cdot C_{CH_4} C_{O_2}$	$k_{g9} = e^{\frac{-9650}{T}}$	kmol/s m^3_{bed}	[141]
$r_{10} = \rho_{10} \cdot \varepsilon \cdot k_{g10} \cdot T \cdot C_{C_6H_6}^{0.5} C_{O_2}$	$k_{g10} = e^{\frac{-12200}{T}}$	kmol/s m^3_{bed}	[142]
$r_{11} = \rho_{11} \cdot \varepsilon \cdot k_{g11} \cdot C_{CH_4} C_{O_2}$	$k_{g11} = e^{\frac{-11196}{T}}$	kmol/s m^3_{bed}	[141]

where, ε indicates the reaction bed porosity, Ci are the molar concentration of the generic component i and ρi is a tuning multiplying coefficient of the reaction rates.

Table 7.6 - Customized multiplying coefficients of the reaction rates in the pseudo-kinetic approach.

	Woodchips	**Woodchips – Sewage Sludge**
ρ_1	$1.663\ 10^{-1}$	$3.900\ 10^{-1}$
ρ_2	$2.790\ 10^{12}$	$5.580\ 10^{16}$
ρ_3	$5.580\ 10^{5}$	$3.906\ 10^{5}$
ρ_4	1.094	$5.000\ 10^{-1}$
ρ_5	$1.778\ 10^{10}$	$1.685\ 10^{9}$
ρ_6	1.325	8.830
ρ_7	$4.170\ 10^{3}$	$2.780\ 10^{2}$
ρ_8	$1.460\ 10^{3}$	$1.314\ 10^{5}$
ρ_9	4.600	4.600
ρ_{10}	$1.891\ 10^{5}$	$1.891\ 10^{5}$
ρ_{11}	$5.206\ 10^{8}$	$6.508\ 10^{4}$

For each specific mixture of feedstocks, the multiplying coefficients (ρ_i) (Table 7.6) of the reaction rate of each kinetic reaction were tuned to minimize the overall percentage error between the experimental data and the simulated ones. To this purpose, H_2, CO, CH_4 and CO_2 molar concentration in the syngas composition were used as reference for the model tuning as reported in Figure 7.4. For each experimental condition the actual values of the syngas composition and the corresponding measured ER were known, and they were compared with those calculated with the simulation model. In this way the customized set of multiplying coefficients ρ_i for the reaction rates of each chemical reactions were obtained. This approach was adopted for the operation with biomass and biomass added with sewage sludge as feedstocks. In this way it is possible to reliably simulate the operative behaviour of the gasifier when it is fed with the mixtures here considered.

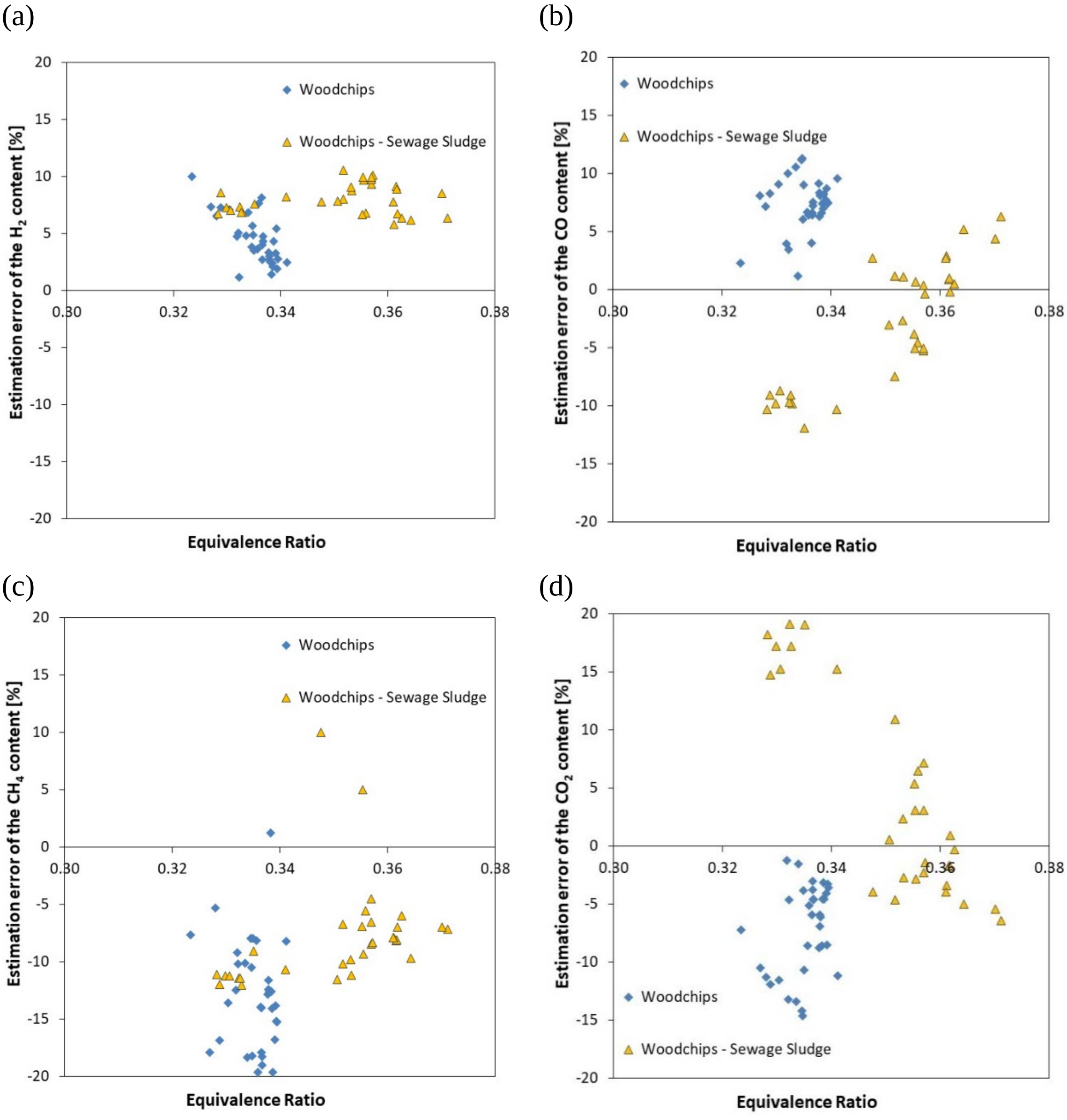


Figure 7.6 - Percentage error of the simulation model estimates of the molar syngas concentration (dry basis) with different feedstocks: a) H2; b) CO; c) CH4; d) CO2 using the pseudo-kinetic approach.

The maximum estimated absolute percentage error is around 15-20% for each component (Figure 7.6**.**) and can be considered quite satisfying. The amount of the gasifying air used as post combustion air in the bottom part of the reactor was estimated using the experimental data, too. It resulted equal to about 11.5% of the overall amount.

Other hypotheses

Further hypotheses of the simulation model are:

- since the gasifier is well insulated with a large thickness of ceramic fiber, the heat losses of each block into the environment are assumed negligible,
- the thermodynamic behaviour of the gas and solid phase is predicted using the Equation of State (EoS) of Redlich Kwong Soave [144]. HCOALGEN and DCOALIGT models are used to calculate the enthalpy and density of non-conventional components, respectively,
- for the characterization of the char and ash generated in feedstock conversion, the same methodology as above is applied and the same models are used to calculate their enthalpy and density. The results of proximate, ultimate, and sulfur analyses for the char and ash are determined from the analysis data of original mixture and the amount of gaseous product in terms of mass balance,
- spherical particles all having the same size,
- constant bed porosity along the reactor,
- constant total pressure along the reactor,
- the ambient gasifying air is not preheated and its inlet temperature in the reactor is 15°C,
- the feedstock temperature at the reactor inlet is equal to ambient value.

For the description of the various phenomena that occur in the reactor, the model foresees two phases: a solid phase and a gaseous phase. The following table lists the chemical species present in the process.

Table 7.7 - Components Used in the kinetic model

ID	Type	Name	Formula
O2	CONV	OXYGEN	O2
CO	CONV	CARBON-MONOXIDE	CO
H2	CONV	HYDROGEN	H2
CO2	CONV	CARBON-DIOXIDE	CO2
H2O	CONV	WATER	H2O
CH4	CONV	METHANE	CH4
N2	CONV	NITROGEN	N2
H2S	CONV	HYDROGEN-SULFIDE	H2S
C6H6*	CONV	BENZENE	C6H6
C	SOLID	CARBON-GRAPHITE	C
S	SOLID	SULFUR	S
COAL	NC	------	------
DRY-COAL*	NC	------	------
CHAR	NC	------	------
ASH	NC	------	------

Simulation Approach

The drying, pyrolysis, combustion, gasification and post-combustion phases within the different zones of the reactor are simulated separately with various blocks. Figure 7.7 shows the simulation diagram of Aspen Plus model. The function of each block is described in Table 7.8.

Table 7.8 – Kinetic Model: Function of Each Block

Block	Model	Function
DRYING	RYield	Simulate coal drying based on the water content value in proximate analysis of feedstock
PYROLYS	RYield	Simulate coal pyrolysis based on the results of pyrolysis model
GASIF-1···18	RCSTR	Simulate char gasification and combustion
CHAR-DEC	RStoic	Decompose char into C, H_2, O_2, N_2, S, and ash in order to easily deal with solid reaction in the simulation of char gasification and combustion
SEP-1···3	Sep2	Separate the gas and solid
MX-GASIN	Mixer	Mix the various gasifying agents according to the desired blend
MX-EXCH	Mixer	Mix the vapor gas and provide the heat for coal drying and pyrolysis

Drying and pyrolysis section

The drying is simulated using a RYield (DRYING) and a Sep (SEP-1) blocks where, under assumption that the physically bound water is vaporized completely in this process, the moisture content (H2O) of the feedstock is extracted, mixed with the gas streams from pyrolysis (PYRO-GAS) and conveyed to the oxidation zone, The separated dried mixture (DRY-COAL) goes on to the next block for the pyrolysis process. In the simulation diagram, there is a heat stream called Q-DRYING which represents the heat duty in the drying process.

The pyrolysis is modelled using three different blocks: a RYield (PYROLYS) reactor and a Sep (SEP-2) block for the conversion of the non-conventional component into volatile components and char and their separation in two streams. The yield of each component is specified according to the results of the pyrolysis model. The heat required in the pyrolysis process originates is represented by the heat stream Q-PYROLYS in the model The solid char from SEP-2 flows to a RStoic unit which operates its separation into C and ash, according with the composition of the feedstock. The gaseous stream is mixed with water vapor from drying and sent to the gasifying agent inlet section.

The thermal power required for the endothermic drying and pyrolysis processes is provided by the heat flux transferred from the combustion zone, where the higher oxygen concentration ensures the combustion of a portion of the dried feedstock.

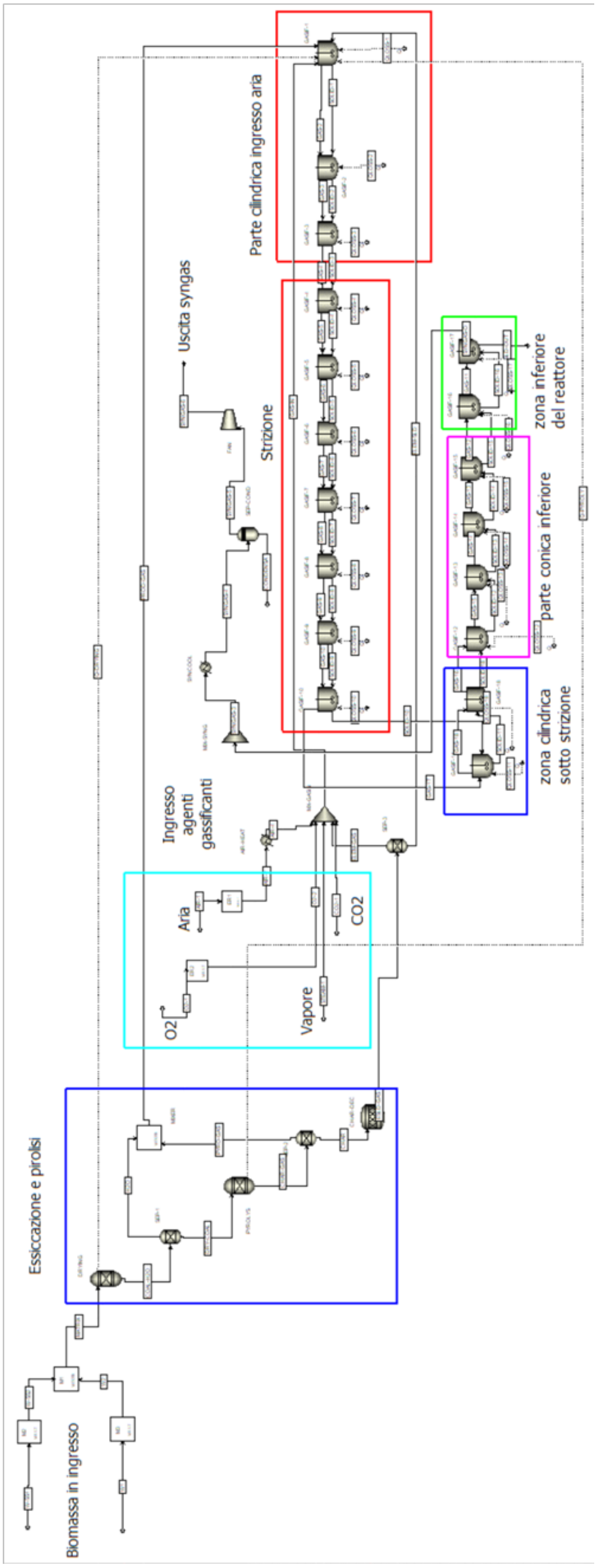


Figure 7.7 - Simulation diagram for the gasifier: (Aspen Plus® model).

Char gasification and combustion section

In the model, drying and pyrolysis are assumed to happen instantaneously at the top of gasifier, as described in the previous sections. This indicates that the length available for char gasification and combustion is equal to the total length of gasifier.

The downdraft throated gasifier is a co-current reactor. However, Aspen Plus does not have a built-in reactor model to deal with this type of gasifier, so, from the viewpoint of directly using the built-in algorithm in Aspen Plus and then simplifying the problem, the gasifier was discretized into a series of cells of volume V equal to the product of the reactor section by the height Δz of the given cell. Each cell is treated as a Continuous Stirred Tank Reactor (RCSTR). As suggested above, the simulation for char gasification and combustion processes is performed in detail by a series of 18 RCSTRs where the solid and volatile phases are present at the same time. According to this reactor model the state variables (composition and temperature) and the solid and gas velocities in the cell are those of the material streams coming out of the cell itself. Each RCSTR implements the chemical reactions of Table 7.3 with the relevant reaction kinetics written in external Fortran code.

In order to easily deal with the solid-gas reactions in this process, a *RStoic* block, CHAR-DEC, is set up before the series of RCSTRs. In this block, char is decomposed into the elements C, H_2, O_2, N_2, S, and ash. The stoichiometric coefficients of these elements are determined according to the ultimate analysis of char, which is automatically done by a calculator block. In the char decomposition, the heat duty is specified as 0 in the specification sheet of *RStoic* in order to maintain the heat balance inside the gasifier. The products leaving from CHAR-DEC enter a solid and gas separator, SEP-3. The separated gases including H_2, O_2, and N_2 are introduced into the bottom of the gasifier together with the feedstock O2 and H2O. The separated solid components, including C, S, and ash, go to a series of RCSTRs to take part in the gasification and combustion reactions.

The char gasification and combustion section can be further divide into 5 different zones:

1) *Gasifying agent inlet*: the reactor section where the air enters is simulated using 3 RCSTR blocks, which rigorously simulate the configuration of continuous stirred tank reactor. The idea is to divide the reactor in some horizontal slices with the axis aligned with the main vertical axis of the gasifier. In the first one, volatile components, char, ash and moisture from the drying and pyrolysis are mixed together with the gasifying agent. In each RCSTR block, volatile and solid phase are present at the same time. The volume of the tank is inserted as input in accordance with the real size of the reactor slice.
2) *Throat and first zone under the throat*: this zone is divided into 8 RCSTR reactors, whose volume is inserted as input. The high number of reactors make it possible to simulate in a reliable way the reaction evolution along the conical throat, which is the most important zone of the gasifier in terms of the outlet composition of the syngas.
3) *Syngas outlet*: a single RCSTR reactor with the right volume is used for the simulation of the zone where the syngas is extracted from the gasifier. The syngas extraction is performed using a lateral grid which has small holes to avoid the drag of char particles.

4) *Under throat*: similarly, to the throat, the zone under the syngas extraction (Under throat in Figure 7.7) is simulated with 4 RCSTR reactors, whose volume is equal to the corresponding value of the reactor part.

5) *Post combustion air inlet*: the bottom part of the reactor, which is dedicated to the inlet of the post-combustion air, is simulated using 2 RCSTR blocks with the right volume. As reported above, the use of the post combustion air assures the local increase of the temperature and the complete reaction of the remaining carbon within the char. In this way, it is possible also to significantly decrease the tar content within the syngas.

   The number of RCSTR blocks used for the simulation of each gasifier zone was selected in order to accurately model the geometry of the reactor and discretize the spatial progress of the chemical reactions along the reactor in a reliable way, considering at the same time a compromise with the computational effort.

The heat loss between the bed and wall is represented by the heat stream. Each heat stream is bound with a Calculator and its value is determined by the corresponding Calculator. The Calculator automatically retrieves the reactor temperature in the flowsheet iteration and then updates the value of heat stream based on the following equation:

$$Q_{loss} = -U \cdot A \cdot (T_{reactor} - T_{wall})$$

where U is the heat transfer coefficient and A is the surface area of the reactor.

In Figure 7.7, the direction of each heat stream is flowing into the RCSTRs. So, the negative term before the heat transfer coefficient U is to correct the direction of heat stream to make it flow out of the RCSTRs.

7.3 Simulation of the operative behaviour (results)

Once the simulation model of the oxy-steam gasifier to be designed has been developed with Aspen Plus V11® and validated against experimental data from a similar gasifier cited earlier, we present the results of the extensive simulation analysis which was performed. The purpose of the analysis is to assess the gasification performances, to investigate the impact of the operative variables and to highlight the nominal design conditions of the gasification plant, whose layout is reported in Figure 7.1 (b).

Two sections related to the equilibrium and kinetic models are reported, respectively.

7.3.7 Simulation results of the equilibrium model

Simulation assumptions

The simulations with the chemical equilibrium assumption have been carried out considering the following data:

1. Gasifier at thermochemical equilibrium.
2. Two feedstocks have been considered: 1) 100% biomass; 2) 70% of biomass + 30% sewage sludge.
3. LHV of the feedstock at the inlet of the gasifier:
    a. Mixture 1: 16.41 MJ/kg
    b. Mixture 2: 12.58 MJ/kg
4. Feedstock mass flow: 100 kg/h (this value has been used as a reference and, when the mass flow is different, the results related to all extensive variables can be obtained using a simple scale factor which is equal to the ratio between this actual value and the reference one).
5. Stoichiometric oxygen mass flow:
    a. Mixture 1: 1.223 kg O_2/kg feedstock
    b. Mixture 2: 0.966 kg O_2/kg feedstock
6. Feeding conditions of pure oxygen: 50°C and 200 bar (pure oxygen is extracted from pressurized gas cylinders using a pressure reducer to the feeding pressure and then heated to 50 °C after the cooling due to the throttling).
7. Gasifier pressure: 1.013 bar.
8. Feeding conditions of steam: 3 bar at saturation conditions.
9. The syngas temperature at the gasifier outlet is fixed equal to 650 °C, 750 °C and 850 °C.
10. The steam mass flow is calculated by the software in such a way the syngas temperature is equal to the specified value. Indeed, the steam is used both as gasifying agent and as mitigating fluid of the syngas temperature.
11. The simulations have been carried out varying the Equivalent Ratio (ER), as defined below: ER = Actual O_2 mass flow / Stoichiometric O_2 mass flow

Simulation results

Mixture 1

In this section we report the simulation results when the mixture 1 is used as feedstock. In Figure 7.8 the steam mass flow which is necessary to obtain a fixed syngas temperature is reported in function of ER for mixture 1. When the ER is low, it is not necessary to adopt steam as mitigating agent and its mass flow is null and the temperature does not reach the assigned value. The increasing of O_2 promotes the corresponding increase of the syngas temperature because the oxidation reactions are promoted. The amount of steam evidently decreases with the syngas temperature because it is requested a lower mitigating effect.

The mole flows of the main chemical components of the syngas are described in Figure 7.9. The points where the trend slopes change suddenly occur when the steam injection starts. So, the first parts of the trend are related to the gasification with pure oxygen (low values of ER). The addition of steam promotes the hydrogen production which has a maximum. The hydrogen mole flow is lowered by the presence of oxygen which induces its oxidation and consumption. The methane yield becomes practically null when the oxygen is high. This kind of results does not be confirmed by the experimental experience, where the amount of methane is not so negligible. This is an important limit of the equilibrium simulation approach. Indeed, the actual presence of methane in the syngas can be considered a symptom of the process distance from the real equilibrium conditions.

The injection of steam promotes the CO shift reaction ($CO + H_2O \leftrightarrow H2 + CO_2$). So, the CO is progressively consumed to produce more H_2 and CO_2.

Finally, an important aspect which must be considered is the syngas volume flow at the gasifier outlet. The reactor design is carried out selecting a specific value, which impacts on the size of the flow sections and, consequently, on its overall size. So, the trend of the syngas volume flow at the thermodynamic conditions at the outlet of the gasifier is reported in Figure 7.8. Obviously, using more steam as mitigating agent promotes the increase of the syngas volume flow. In Figure 7.9, the amount of steam at the outlet of the reactor is reported. We can note that an important part of the injected steam does not react and remains at the outlet of the reactor increasing consequently the syngas volume flow. In the operation of real gasification plants this large amount of steam can be recovered as water in the quench of the syngas just upstream its exploitation in internal combustion engine or in plants for the production of chemicals.

Mixture 2

The trends of the results related to mixture 2 (from Figure 7.12 to Figure 7.15) are very similar to those already reported above for mixture 1. The only relevant difference is due to the lower amount of steam that is required to mitigate the syngas temperature. Indeed, the mixture 2 has a lower LHV than that of mixture 1 and, consequently, the spontaneous temperature increase due to the chemical gasification process is quite lower. So, we can note that each curve of the results reported below is lower than the corresponding one of mixture 1. Also, the molar production of the most important chemical components of the syngas (Figure 7.13) results quite lower with respect to those of mixture 1 (Figure 7.9). So, the same comments reported in the previous sub-section can be used for this case.

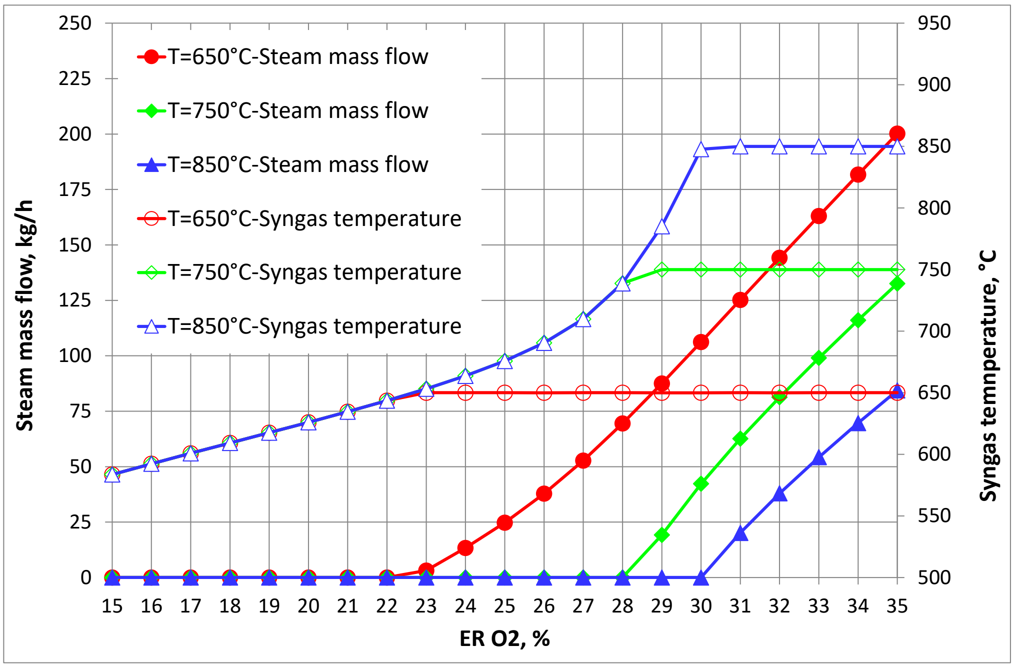


Figure 7.8 - Steam mass flow and syngas temperature at the gasifier outlet Vs ER of pure oxygen (mixture 1)

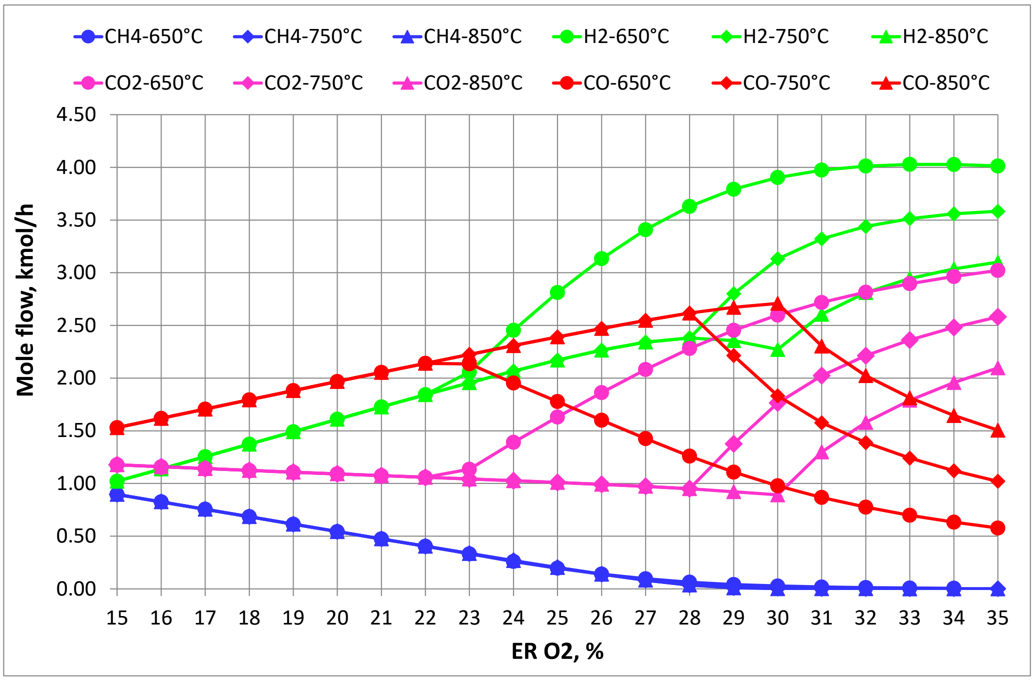


Figure 7.9 - Component mole flow of syngas Vs ER of pure oxygen (mixture 1).

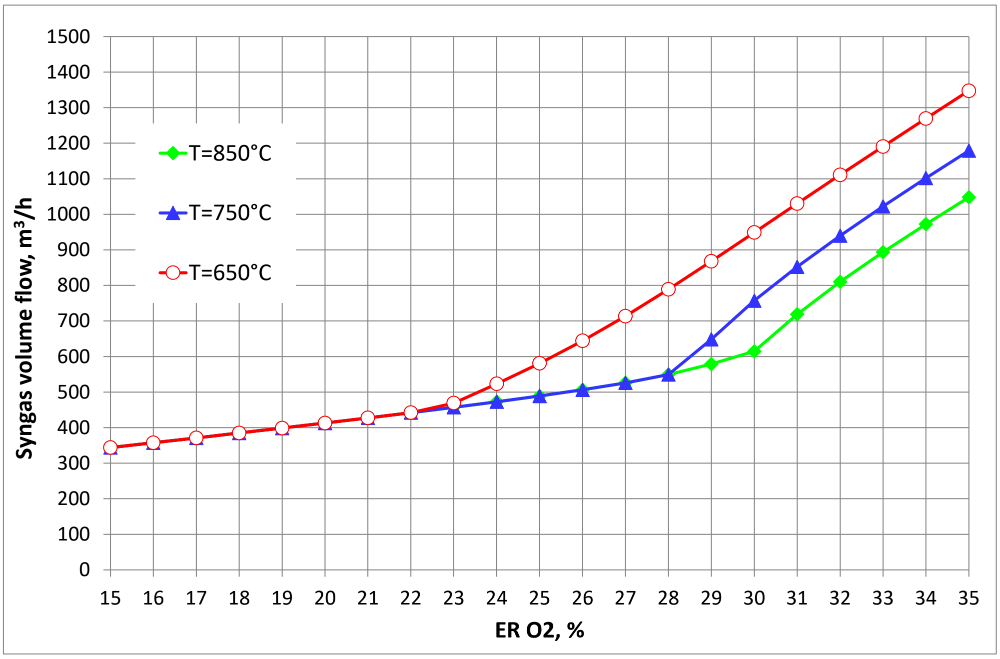


Figure 7.10 - Syngas volume flow at the outlet of the gasifier Vs ER of pure oxygen (mixture 1).

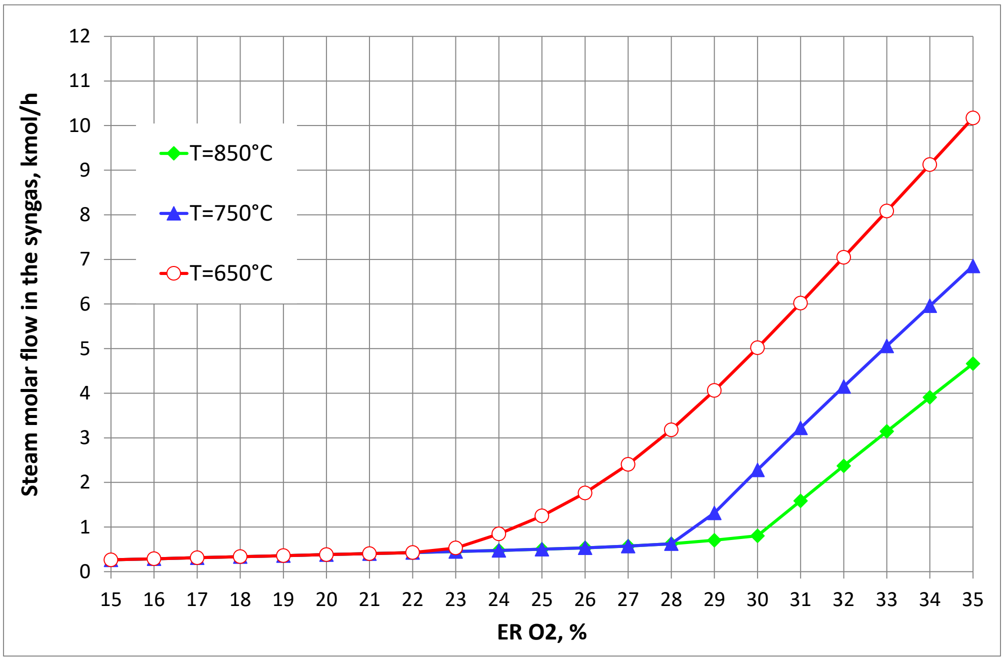


Figure 7.11 - Steam molar flow at the outlet of the gasifier Vs ER of pure oxygen (mixture 1).

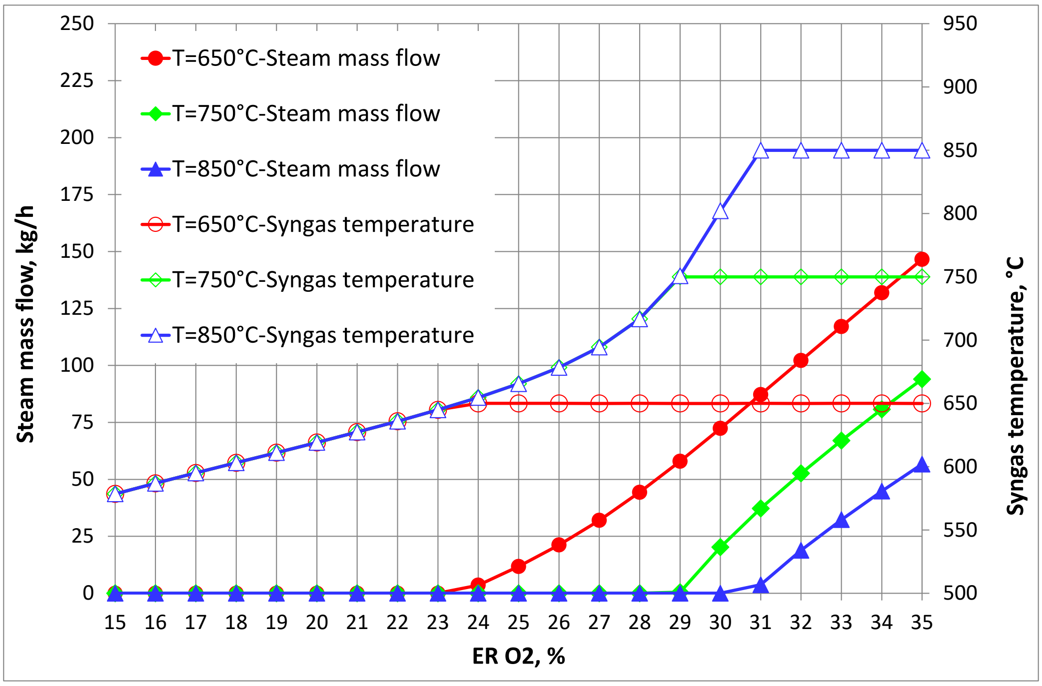


Figure 7.12 - Steam mass flow and syngas temperature at the gasifier outlet Vs ER of pure oxygen (mixture 2).

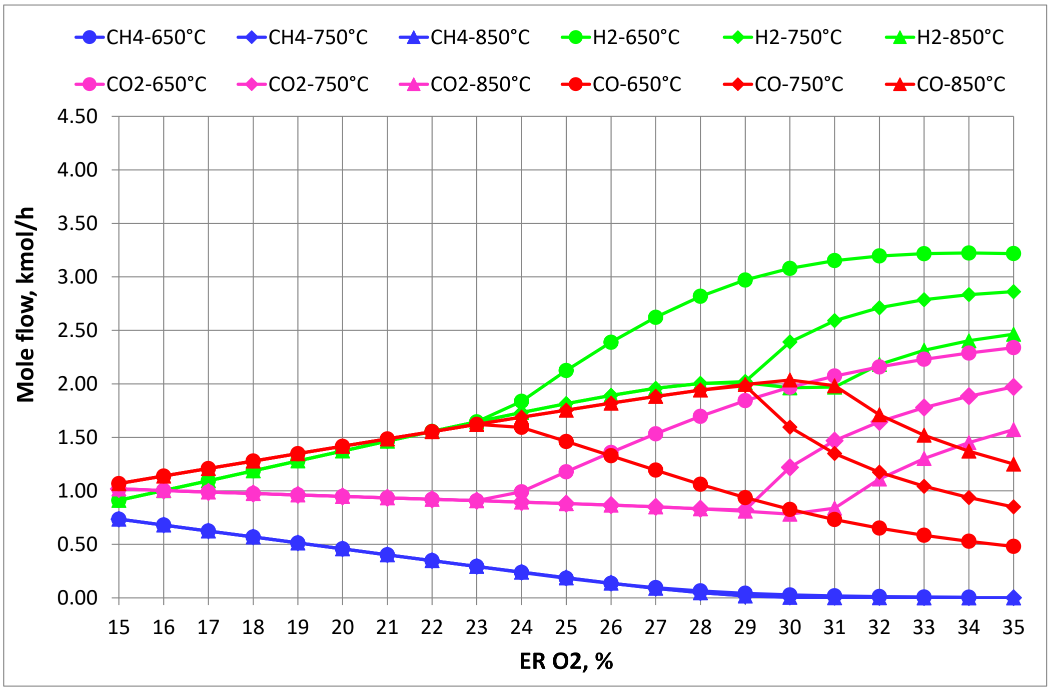


Figure 7.13 - Component mole flow of syngas Vs ER of pure oxygen (mixture 2).

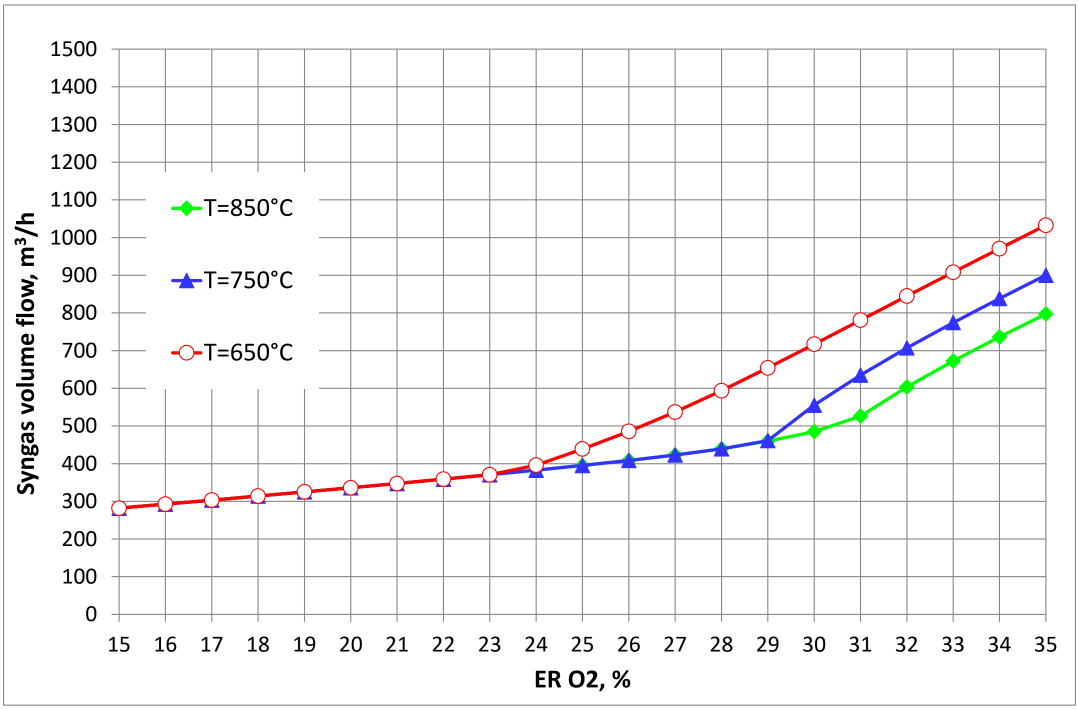


Figure 7.14 - Syngas volume flow at the outlet of the gasifier Vs ER of pure oxygen (mixture 2).

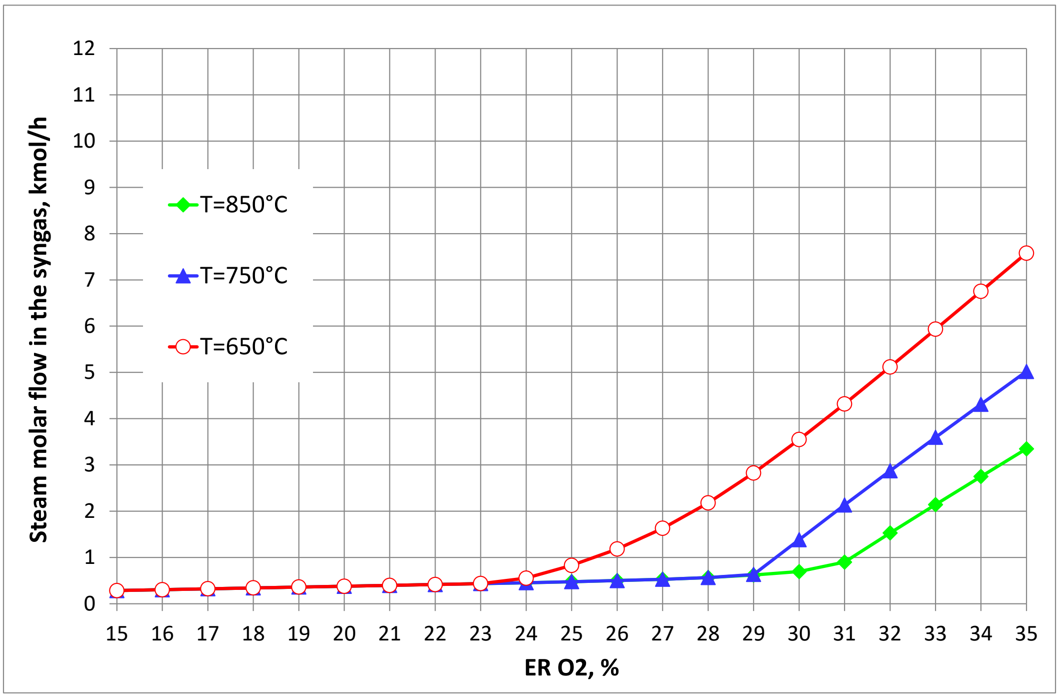


Figure 7.15 - Steam molar flow at the outlet of the gasifier Vs ER of pure oxygen (mixture 2).

7.3.8 Simulation results of the pseudo-kinetic model

Simulation assumptions

The simulations with the pseudo-kinetic approach have been carried out considering the following data:

12. Each reaction yield is calculated considering its specific kinetic mechanism.
13. Two feedstocks have been considered: 1) 100% biomass; 2) 70% of biomass + 30% sewage sludge.
14. LHV of the feedstock at the inlet of the gasifier:
    a. Mixture 1: 16.41 MJ/kg
    b. Mixture 2: 12.58 MJ/kg
15. Feedstock mass flow: from 200 kg/h to 275 kg/h (these values are the actual ones which will be tested during the experimental campaign of the project AUGIA).
16. Stoichiometric oxygen mass flow:
    a. Mixture 1: 1.223 kg O_2/kg feedstock
    b. Mixture 2: 0.966 kg O_2/kg feedstock
17. Feeding conditions of pure oxygen: 50°C and 200 bar (pure oxygen is extracted from pressurized gas cylinders using a pressure reducer to the feeding pressure and then heated to 50 °C after the cooling due to the throttling).
18. Gasifier pressure: 0.8 bar, 1.013 bar, 1.2 bar (in this way the performance difference between a suction configuration and a blowing one is assessed).
19. Feeding conditions of steam: 3 bar at saturation conditions.
20. The syngas temperature at the gasifier outlet is not fixed as an input variable and it is a result of the simulations.
21. The steam mass flow is fixed as an input variable from 50 kg/h to 150 kg/h.
22. The simulations have been carried out varying the Equivalent Ratio, as defined above.
23. The secondary flow of the gasifying agents is equal to 11.5 %, as obtained during the calibration of the simulation model.

Simulation results

Mixture 1

In this section we report and comment the most meaningful simulation results when the mixture 1 is used as feedstock (Table 7.9, Table 7.10 and Table 7.11, where the results are reported for 1.013 bar, 0.8 bar and 1.2 bar, respectively) Comparing the results with those obtained with the equilibrium approach, it is possible to note that the syngas temperature is quite lower with similar ratios of steam / feedstock and ER. Using the pseudo-kinetic approach, it is possible to get three important advantages which improve the reliability of the simulation:

1) the mole flow of unburnt char which is extracted from the gasifier is calculated by the model and it is not supposed as in the equilibrium model. If the gasification of the char is not carried out correctly, the presence of carbon within the unburnt char can induce a strong lowering of the overall CGE of the process (CGE is the ratio between the power related to the syngas lower heating value and that corresponding to the feedstock at the reactor inlet);
2) the model makes it possible to estimate the presence of some oxygen in the syngas at the gasifier outlet. The oxygen content is a strong source of detriment of the performances of the following process plant for chemicals production. For example, oxygen induces the methane oxidation within the methanation process with a lower methane yield;
3) since the equilibrium conditions are not reached, the methane concentration does not result null as experimentally tested. Higher is the methane mole flow, higher is the distance of the process from the equilibrium.

It is possible to obtain a syngas with a LHV which is higher than 8 MJ/Nm^3 with CGE higher than 80%. The gasification performances are slightly lowered when the pressure inside the reactor decreases, because the gasification of char is not promoted. Hence, the plant configuration with the syngas blower located downstream the gasifier does not appear appealing. If the amount of steam is excessive (#4 in Table 7.11), the gasification performances decrease strongly. The best mass ratio between steam and feedstock is around 40-50%.

Mixture 2

In this section we report the best simulation results (Table 7.12 e Table 7.13, which are related to 1.013 bar and 0.8 bar, respectively) when the mixture 2 is used as feedstock. The quality of syngas in terms of LHV and mass flow results quite lower with respect to mixture 1. Moreover, the conversion of char is less effective. Notwithstanding these facts, the CGE appears higher. In this section, only satisfying operative conditions are reported.

Table 7.9 - Some simulation results when the gasifier pressure is 1.013 bar (mixture 1).

	#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**
Feedstock mass flow, [kg/h]	200	225	250	200	225	250	275
ER, [%]	30	30	30	30	30	30	30
Steam mass flow, [kg/h]	100	100	100	150	150	150	100
Pressure, [bar]	1.013	1.013	1.013	1.013	1.013	1.013	1.013
Syngas temperature at the gasifier outlet, [°C]	611	621	628	592	602	611	635
Syngas mass flow at the quench outlet, [kg/h]	293.9	325.2	356.9	290.5	320.9	350.7	387.6
Oxygen mass flow, [kg/h]	73.4	82.6	91.7	73.4	82.6	91.7	100.9
CGE, [%]	81.4	81.4	81.5	77.7	77.5	77.4	81.6
Syngas LHV, [MJ/Nm^3]	8.53	8.71	8.85	8.37	8.53	8.69	8.99
Syngas volume flow at the gasifier outlet, [m^3/h]	1359	1495	1630	1513	1638	1778	1764
Syngas volume flow at the quench outlet, [Nm^3/h]	318	351	384	309	341	372	416
CO molar flow, [kmol/h]	3.10	3.76	4.39	2.63	3.21	3.83	5.08
H_2 molar flow, [kmol/h]	6.17	6.65	7.15	5.98	6.45	6.88	7.60
CO_2 molar flow, [kmol/h]	3.84	4.06	4.29	4.04	4.27	4.46	4.48
CH_4 molar flow, [kmol/h]	0.38	0.42	0.46	0.45	0.49	0.54	0.51
O_2 molar flow, [kmol/h]	0.47	0.51	0.55	0.48	0.54	0.60	0.59
Char molar flow at the gasifier outlet, [kmol/h]	0.00	0.00	0.00	0.20	0.26	0.32	0.00

Table 7.10 - Some simulation results when the gasifier pressure is 0.8 bar (mixture 1).

	#1	**#2**	**#3**	**#4**	**#5**	**#6**
Feedstock mass flow, [kg/h]	200	225	250	200	225	250
ER, [%]	30	30	30	30	30	30
Steam mass flow, [kg/h]	100	100	100	150	150	150
Pressure, [bar]	0.8	0.8	0.8	0.8	0.8	0.8
Syngas temperature at the gasifier outlet, [°C]	619	626	633	592	600	607
Syngas mass flow at the quench outlet, [kg/h]	275.9	303.4	330.7	258.6	285.0	311.2
Oxygen mass flow, [kg/h]	73.4	82.6	91.7	73.4	82.6	91.7
CGE, [%]	78.6	77.6	77.1	68.5	67.7	67.4
Syngas LHV, [MJ/Nm^3]	9.02	9.16	9.30	8.63	8.74	8.88
Syngas volume flow at the gasifier outlet, [m^3/h]	1710	1868	2028	1844	1993	2147
Syngas volume flow at the quench outlet, [Nm^3/h]	292	320	347	266	292	318
CO molar flow, [kmol/h]	3.49	4.07	4.70	2.60	3.07	3.58
H_2 molar flow, [kmol/h]	5.17	5.51	5.84	4.62	4.95	5.27
CO_2 molar flow, [kmol/h]	3.20	3.35	3.47	3.25	3.44	3.58
CH_4 molar flow, [kmol/h]	0.43	0.47	0.52	0.49	0.54	0.59
O_2 molar flow, [kmol/h]	0.47	0.55	0.62	0.65	0.75	0.85
Char molar flow at the gasifier outlet, [kmol/h]	0.21	0.34	0.46	0.98	1.19	1.39

Table 7.11 - Some simulation results when the gasifier pressure is 1.2 bar (mixture 1).

	#1	**#2**	**#3**	**#4**	**#5**	**#6**
Feedstock mass flow, [kg/h]	200	225	250	200	225	250
ER, [%]	25	25	25	25	30	30
Steam mass flow, [kg/h]	100	100	100	150	150	150
Pressure, [bar]	1.2	1.2	1.2	1.2	1.2	1.2
Syngas temperature at the gasifier outlet, [°C]	594	609	618	571	595	604
Syngas mass flow at the quench outlet, [kg/h]	294.4	321.8	351.8	278.5	340.2	372.7
Oxygen mass flow, [kg/h]	61.2	68.8	76.4	61.2	82.6	91.7
CGE, [%]	80.9	81.1	81.1	73.5	80.6	80.7
Syngas LHV, [MJ/Nm^3]	8.28	8.55	8.71	8.10	8.18	8.32
Syngas volume flow at the gasifier outlet, [m^3/h]	1106	1219	1330	1204	1392	1507
Syngas volume flow at the quench outlet, [Nm^3/h]	325	355	387	302	369	403
CO molar flow, [kmol/h]	2.42	3.11	3.73	1.85	2.89	3.48
H_2 molar flow, [kmol/h]	6.83	7.26	7.77	6.27	7.47	8.03
CO_2 molar flow, [kmol/h]	4.48	4.61	4.84	4.39	4.91	5.19
CH_4 molar flow, [kmol/h]	0.40	0.44	0.49	0.46	0.44	0.48
O_2 molar flow, [kmol/h]	0.17	0.18	0.19	0.31	0.52	0.57
Char molar flow at the gasifier outlet, [kmol/h]	0.00	0.07	0.09	0.62	0.00	0.00

Table 7.12 - Some simulation results when the gasifier pressure is 1.013 bar (mixture 2).

	#1	**#2**	**#3**
Feedstock mass flow, [kg/h]	200	225	250
ER, [%]	25	25	25
Steam mass flow, [kg/h]	150	150	150
Pressure, [bar]	1.013	1.013	1.013
Syngas temperature at the gasifier outlet, [°C]	575.3	586.3	595.9
Syngas mass flow at the quench outlet, [kg/h]	271.1	300.2	328.6
Oxygen mass flow, [kg/h]	52.6	59.2	65.8
CGE, [%]	90.2	90.3	90.4
Syngas LHV, [MJ/Nm^3]	8.4	8.5	8.7
Syngas volume flow at the gasifier outlet, [m^3/h]	1425	1551	1677
Syngas volume flow at the quench outlet, [Nm^3/h]	303	335	366
CO molar flow, [kmol/h]	2.05	2.56	3.10
H_2 molar flow, [kmol/h]	6.39	6.95	7.48
CO_2 molar flow, [kmol/h]	4.07	4.33	4.56
CH_4 molar flow, [kmol/h]	0.46	0.51	0.55
O_2 molar flow, [kmol/h]	0.31	0.34	0.37
Char molar flow at the gasifier outlet, [kmol/h]	0.73	0.83	0.94

Table 7.13 - Some simulation results when the gasifier pressure is 0.8 bar (mixture 2).

	#1	**#2**	**#3**
Feedstock mass flow, [kg/h]	200	225	250
ER, [%]	30	30	30
Steam mass flow, [kg/h]	150	150	150
Pressure, [bar]	0.8	0.8	0.8
Syngas temperature at the gasifier outlet, [°C]	593	604	612
Syngas mass flow at the quench outlet, [kg/h]	269.9	298.9	327.3
Oxygen mass flow, [kg/h]	63.1	71.0	78.9
CGE, [%]	90.6	91.0	90.9
Syngas LHV, [MJ/Nm^3]	8.7	8.9	9.0
Syngas volume flow at the gasifier outlet, [m^3/h]	1870	2035	2196
Syngas volume flow at the quench outlet, [Nm^3/h]	294	325	355
CO molar flow, [kmol/h]	2.75	3.35	3.94
H_2 molar flow, [kmol/h]	5.63	6.09	6.55
CO_2 molar flow, [kmol/h]	3.46	3.63	3.81
CH_4 molar flow, [kmol/h]	0.46	0.51	0.56
O_2 molar flow, [kmol/h]	0.52	0.59	0.65
Char molar flow at the gasifier outlet, [kmol/h]	0.65	0.74	0.84

7.3.9 Design point

Once analyzed the simulation results, the design point of the gasifier when it operates in oxy-steam gasification configuration is selected. One important operative constraint of the gasifier, which must be respected in the selection of the design point, is the maximum allowable value of syngas volume flow at the outlet of the reactor. This flow must be not higher than 1700 m^3/h. If the flow is higher, there could be important problems due to the conveying of solid unreacted material and fly ashes at the outlet of the reactor in the syngas. So, the operative point which is considered as referenced for the design is #2 inTable 7.9**.** with the possibility to operate the reactor also at the condition #3 in Table 7.9. So, the design operative conditions are:

- Feedstock mass flow: 225 kg/h
- ER: 30%
- Steam mass flow: 100 kg/h

In this way, the process values of syngas mass flow, composition and temperature are highlighted, and they can be used for the design of the gasification plant equipment, such as piping, feedstock loading system.

Chapter 8
Experimental Activity

The demonstration prototype of the LIFE AUGIA research project, being still under construction and behind schedule, is not available for the conduction of sludge and biomass gasification tests.

Therefore, the LIFE AUGIA research team decided to start a preliminary experimental activity to analyse the effectiveness of the oxy-gasification approach, utilising a small-scale, fixed bed (downdraft) gasification plant, already located in the research area of the University of Pisa. This small gasifier, that has a thermal power of roughly 100 kW (1/10 of the AUGIA gasifier), is very similar, even if on a reduced scale, to that envisaged by the LIFE AUGIA project so it can be in any case considered representative of the overall process (the two reactors are both of the type fixed-bed throathed downdraft). In this perspective, information and data collected with it can be effectively utilised to improve the understanding of the oxygen-based gasification process and verify the versatility and reliability of associated numerical models, implemented in Aspen Plus®, even on small-scale plants.

The experimental activities carried out in the DESTEC department of the University of Pisa (UNIPI) have been managed in collaboration with qualified personnel from UNIPI and BioSyn srl, partner of the AUGIA project.

The pilot gasification plant, already exploited for previous research activities with only biomass and air as gasifying agent, was properly modified for the AUGIA project needs. In particular, the conventional air-gasification approach has been replaced by oxy-CO_2 gasification technology. The decision to start with oxy-CO_2, instead of oxy-steam as planned in the AUGIA project, is due to the fact that the availability of CO_2 was already present at the UNIPI experimental area. The steam use requires the presence of a boiler, which will be adopted in a second time.

In the next future the experimental campaign focused on oxy-steam gasification technology will start, as the main topic of the AUGIA project, but also mixtures of them (O_2/steam/CO_2) will be analised. It is known that this strategy gives the possibility of obtaining a nitrogen-free syngas, mainly composed by elemental chemical species (CO, H_2, CO_2, CH_4), which can be used for the synthesis of several bio-fuels like methanol or synthetic natural gas (SNG). Moreover, carbon dioxide and steam are utilized as gasifying agents with oxygen, in order to mitigate its reactivity, which can lead to excessive reaction temperatures; at the same time, they also take part to the gasification process, promoting the main reactions versus the secondary ones.

8.1 Description of the gasification plant modification

The original plant, a small All power labs Gek gasifier, was conceived for air gasification and had to be adapted for the oxy-gasification experimental activities, also in the attempt to overcome problems and shortcomings of the existing system and to simplify its operation optimizing at the same time its performance. Within the limits of the available budget, steps were taken to identify which equipment needed to be kept, which removed and what instead needed to be modified or added.

The original process flow diagram of the gasifier subject to modification envisaged (Figure 8.1):

- A biomass loading system consisting of a main storage tank from which the biomass is discharged by gravity into a hopper, with an external jacket through which the syngas produced is circulated to preheat the biomass contained therein. An auger moves the biomass towards the reactor,
- the gasification reactor itself, a multi-stage Imbert downdraft, equipped with 5 radially arranged air inlet nozzles in correspondence with the throat section, a system of pipes wound in a spiral around the central stage for the air preheating so as to increase the combustion temperature, an automated moving grate to support the char reduction bed, an ash and unburned collection bin, a level sensor that control the loaded biomass, 3 K-type thermocouples located along the reactor and two pressure ports astride the reaction bed,
- a syngas cleaning system, consisting of three cyclones in series, for the abatement of the solid particulate, followed by a three-layer biomass biofilter (on which a K thermocouple was also mounted),
- the inverter fan, placed downstream of the biofilter, for the suction and regulation of the incoming air, which keeps the whole process under slight depression,
- the torch for the combustion of the syngas before its emission into the atmosphere.

Some technical/mechanical modifications were made in terms of feeding system layout, piping and gasifying agents distribution system inside the gasifier, this last to obtain more homogeneous conditions of reaction. Particular attention has been dedicated to properly seal the gasifier in order to prevent air infiltration during the oxy-gasification activity and also considering the higher temperature that can be reached during the oxy-gasification process. Therefore, the original gasifier sealing gaskets have been changed and replaced with high temperature ones. In addition, the research team decided to implement the small gasifier with new instruments (flow meters and temperature/pressure sensors) in order to monitor the process conditions during experimentation.

Figure 8.2. shows the PFD (*Process Flow Diagram*) of the new plant configuration, which clearly represented the layout, the equipments and all the intrumentations utilised.

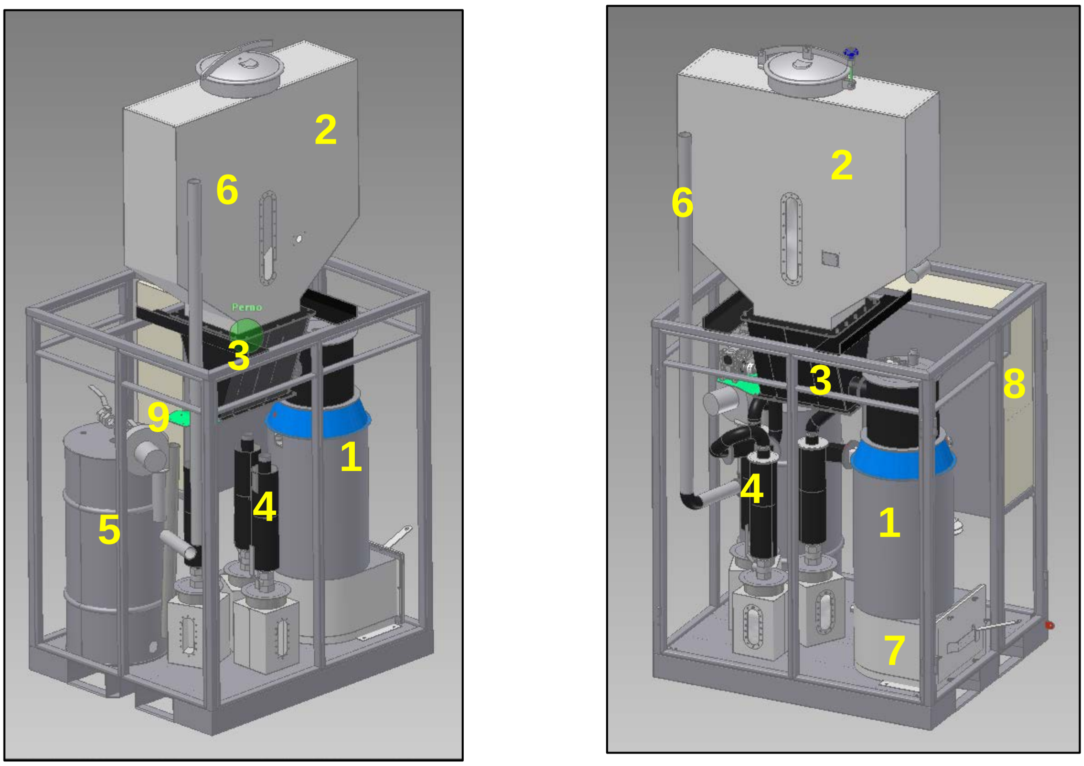
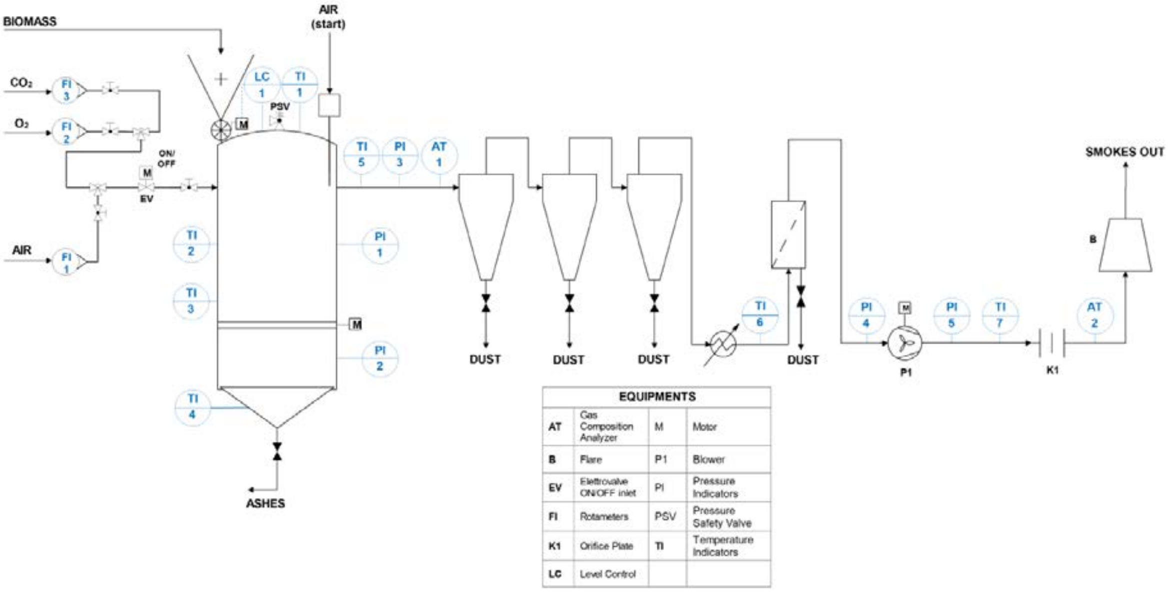


Figure 8.1 - 3D model of the original gasification plant

1. Multi-stage Imbert downdraft reactor; 2. Biomass hopper; 3. Preheated loading hopper; 4. Cyclone filters; 5. 3-layer biomass filter; 6. Flare; 7. Ash pit; 8. Electrical panel; 9. Inverter fan.



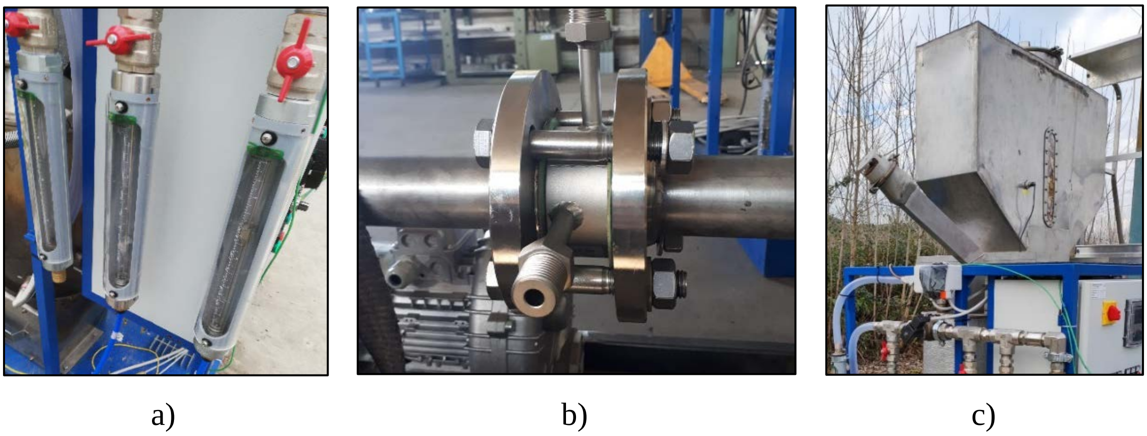
EQUIPMENTS			
AT	Gas Composition Analyzer	M	Motor
B	Flare	P1	Blower
EV	Elettrovalve ON/OFF inlet	PI	Pressure Indicators
FI	Rotameters	PSV	Pressure Safety Valve
K1	Orifice Plate	TI	Temperature Indicators
LC	Level Control		

Figure 8.2 - Process Flow Diagram (PFD), of the new plant configuration

The gasifier (Figure 8) is characterized by a gross thermal power of roughly 100 kW at maximum load, corresponding to a biomass consumption of about 20 kg/h with a moisture content of 10-15 wt%.

Figure 8.3 - The experimental gasifier

The gasification plant operates in a semi-batch mode: the biomass is stored in a sealed hopper with batch loading which allows roughly 8 hours of autonomy and from here, thanks to a level sensor, is intermittently loaded into the downdraft gasifier, while the producer gas flows continuously downstream.



a) b) c)

Figure 8.4 - Flow meters of a) the inlet gasifying agents air/O2/CO_2 and b) the output syngas; c) maximum pressure safety valve.

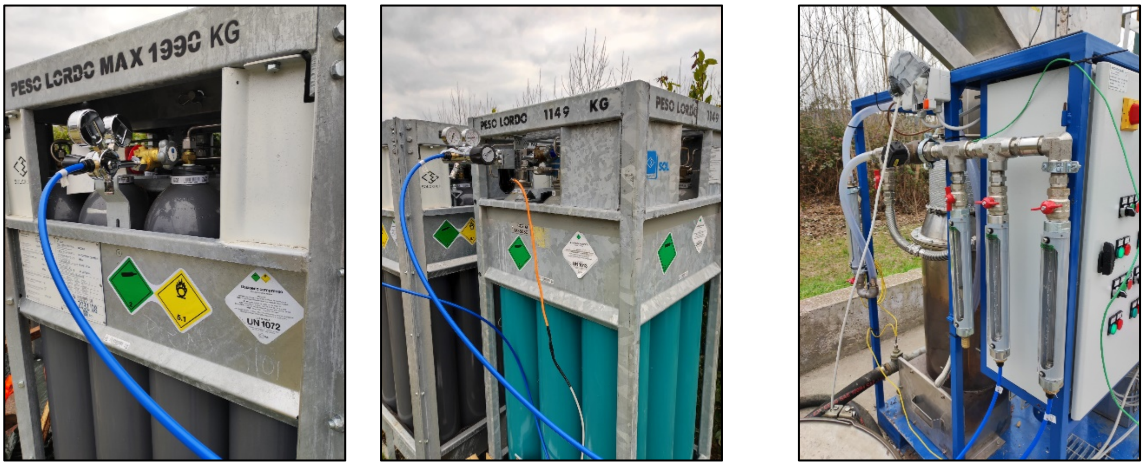
The gasifier was instrumented with air/O2/CO2 and syngas flow meters (Figure 8.4.a-b) and pressure/temperature sensors. A special temperature probe (K type), with a maximum operating temperature of 1150 °C, has been adopted to measure the temperature in the reaction zone (throat position). A safety pressure valve has been located on the top of the gasifier to prevent problems related to excessive pressure conditions inside the reactor or in the process line (Figure 8.4.c).

Three cyclones, connected in line, are located at the exit of the gasifier and dedicated to collect coarse dust (Figure 8.5.a). Besides, upstream the blower, a biomass-fabric filter is emplyed to refine the separation (Figure 8.5.b).

a) b)

Figure 8.5 - Gas/solid separation system: a) three cyclones and b) a biomass-fabric filter.

The pure gasifying agents were stored at high pressure in dedicated gas cylinders and then fed to the gasifier after a pressure reduction (Figure 8.6).



a) b) c)

Figure 8.6 - Storage gas cylinders of the pure inlet gasifying agents: a) O2 and b) CO_2 with a heating element; c) piping connections to the inlet gas flow meters.

After ignition, achieved with a removable external heater, the gasification process becomes completely autothermal as the partial combustion of the biomass generates sufficient heat to sustain the overall gasification process. As the feedstock moves downward due to gravity, the gasifying agent is introduced inside the reactor, forced by a downstream blower (Figure 8.7.c). The bed reaction is sustained by a grate that vibrates at regular intervals, driven by an electric motor, to maintain a continuous downward movement of the feedstock inside the gasifier. This prevents channeling and bridging through the bed and facilitates the discharge of char and ash.

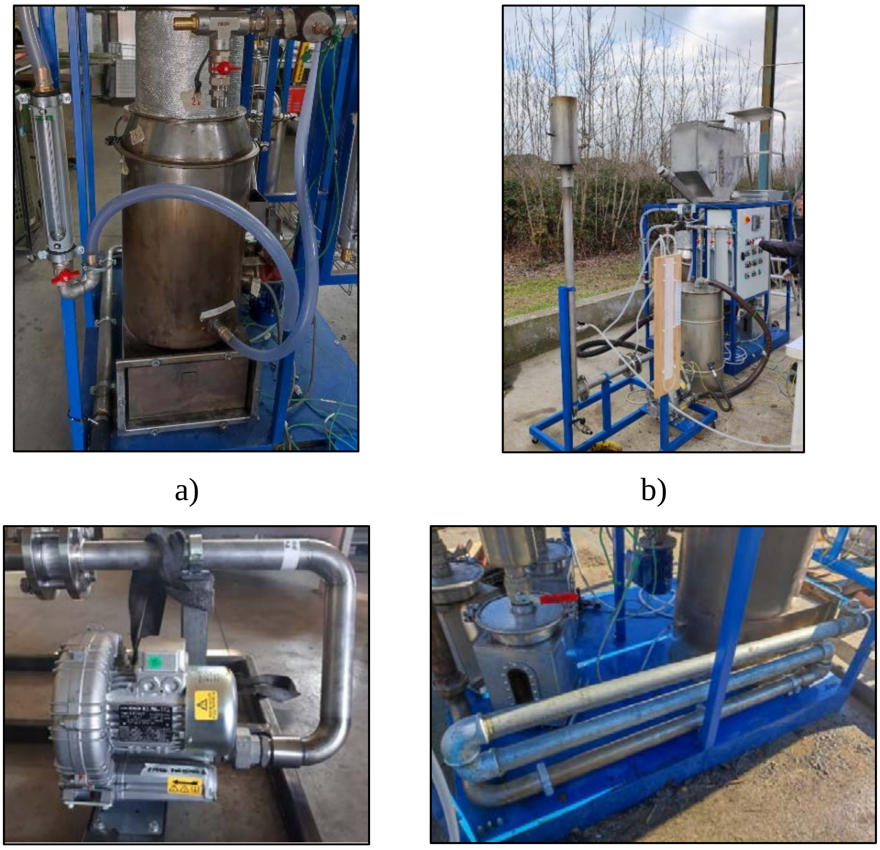

a) b) c) d)

Figure 8.7 - Some equipment present on the process line: a) The gasification reactor with the detail of the ash collector; b) flare on the output syngas flow; c) blower; d) tube coil heat exchanger.

In the present experimental activity, ashes were extracted from the bottom of the gasifier and discharged into a sealed tank (Figure 8.7.a); the syngas produced was flared into the atmosphere with a torch (Figure 8.7.b) located downstream the blower. Upstream the blower, a metal tube air-cooled coil with three rows has been realised to cool down the syngas temperature and protect the blower itself (Figure 8.7.d).

a) b) c)

Figure 8.8 - a) Micro-GC to analyse the composition of the output syngas; b) sampling point for syngas Tar and solid dust analysis; c) sampling equipment as required by Technical Specification CEN/TS 15439:2006.

A syngas sampling probe has been located after the blower in order to monitor the syngas composition using an Agilent 3000 micro-gas chromatograph (micro-GC, Figure 8.8.a). Thanks to this instrumentation, it is possible to continuously evaluate the gasification performances (for example the syngas Lower Heating Value, LHV) varying the operating conditions. Besides, another sampling point has been located at the exit of the gasifier (Figure 8.8.b) for tar and solid dust analysis. Tar analysis was executed following the provisions of the Technical Specification CEN/TS 15439:2006 (Figure 8.8.b-c).

The small gasification plant was also equipped with an electronic data acquisition system (Figure 8.9), which allow to monitor and to record the main operating variables (temperatures and pressures) of the process, together with a syngas flow meter, located downstream of the blower and constituted of a pressure differential device with orifice plate.

Figure 8.9 - Recording device of the main operating variables.

8.2 Biomass characterization activity

As aforementioned, fir pellets were used as the woody biomass feedstock for the experimental campaign owing to their reproducibility in terms of shape, geometry and composition. These pellets typically have a cylindrical shape with a diameter of approximately 6 mm and a length of 10-40 mm, with a very brittle nature. This choice allowed for the study and characterization of the gasification plant behaviour as well as the feasibility of the oxygen-CO2 approach, without considering the variability of the feedstock. In future studies, the possibility of using more cost-effective and more sustainable feedstocks, such as those coming from waste routes, agricultural processing, food industry, municipal solid waste, etc., will be evaluated.

The main analytical parameters of woody biomass are:

- Proximate analysis: moisture content, volatile matter (VM), fixed carbon (FC) and ash content,
- Ultimate analysis: elemental content of carbon (C), hydrogen (H), oxygen (O) and nitrogen (N);
- Heating Value (HV).

The characterization of fir pellets was performed following the methodologies briefly described herein. The moisture content was evaluated according to the European standard test method EN ISO 18134-2:2017. Other parameters of the proximate analysis were determined with a TA Instruments Q-500 thermobalance, according to UNI EN ISO 22167:2021 test method for thermogravimetric analysis (TGA). Ultimate analysis was carried out with a LECO TruSpec CHN Elemental Analyzer, according to EN ISO 16948:2015 test method and the oxygen content was evaluated by difference. A LECO AC-500 Calorimeter was used for heating value determination, according to EN ISO 18125:2017 test method. The results obtained from the material characterization are reported in Table 8.1.

Table 8.1 - Proximate analysis, ultimate analysis and heating value of the feedstocks (ar: as received).

FEEDSTOCKS	Proximate Analysis				Ultimate Analysis				LHV
	M (wt %, ar)	VM (wt %, dry)	FC (wt %, dry)	Ash (wt %, dry)	C (wt %, dry)	H (wt %, dry)	N (wt %, dry)	O (wt %, dry)	LHV (MJ/kg, dry)
Fir pellet	6.83	84.14	15.38	0.47	49.88	6.05	0.07	43.53	18.78

Besides, other parameters have been investigated for the woody biomass. In particular, the characteristic temperatures of the biomass' ashes (sintering, softening, hemispherical and melting) have been determined by a certified laboratory with an optical dilatometer/heating microscope ODLT HSML 1600°C, according to a standardized internal methodology. Furthermore, the quantification of the elemental content of heavy metals, micro- and macro-elements have been carried out with the inductively coupled plasma optical emission spectrometry (ICP-OES) technique, according to UNI EN 15411:2011 + UNI EN ISO 11885:2009. Lastly, fluorides, sulphates and chlorides have been recovered from the post-combustion condenses of the biomass and analysed according to UNI EN 15408:2011 + UNI

EN ISO 10304-1:2009, in order to obtain a more accurate measure of the biomass heating value. The results of this more specific biomass characterization are reported in Table 8.2.

Table 8.2 - Other parameters that characterize the feedstock used in the present investigation.

Feedstock	**Ash Analysis**				**Condense Analysis**		
	Sintering Temperature [°C]	Softening temperature [°C]	Hemispherical temperature [°C]	Melting temperature [°C]	Fluorides [mg/kg]	Sulphates [mg/kg]	Chlorides [mg/kg]
Fir pellet	1054	1056	1110	1180	5.09	224	300
	Heavy metals content Analysis						
	As [mg/kg, dry]	Tl [mg/kg, dry]	Se [mg/kg, dry]	Mo [mg/kg, dry]	Zn [mg/kg, dry]	Sb [mg/kg, dry]	Pb [mg/kg, dry]
	< 0.5	< 0.5	< 1	< 1	10.60	< 1	0.58
	Cd [mg/kg, dry]	Ni [mg/kg, dry]	Co [mg/kg, dry]	Mn [mg/kg, dry]	Fe [mg/kg, dry]	Mg [mg/kg, dry]	Cr [mg/kg, dry]
	< 0.5	1.19	< 0.1	144	204	129	< 5
	V [mg/kg, dry]	Be [mg/kg, dry]	Cu [mg/kg, dry]	Ti [mg/kg, dry]	Ca [mg/kg, dry]	Sr [mg/kg, dry]	Li [mg/kg, dry]
	< 0.05	< 1	1.03	10.79	811	4.21	0.08
	Al [mg/kg, dry]	P [mg/kg, dry]	Sn [mg/kg, dry]	Hg [mg/kg, dry]	Te [mg/kg, dry]	Bi [mg/kg, dry]	Au [mg/kg, dry]
	1317	2908	< 1	< 10	< 5	< 5	< 10
	B [mg/kg, dry]	Si [mg/kg, dry]	Ba [mg/kg, dry]	Na [mg/kg, dry]	K [mg/kg, dry]		
	51.5	5217	120	626	2654		

8.3 Experimental activity

A preliminary step of the experimental activity involved testing both the plant control logic and ensuring the proper functioning of all sensors and devices installed on the process line. Subsequently, cold leak tests were conducted, and the start-up procedure for the small gasification plant was defined.

During this process, important information was gathered and is outlined below:

- The gasifier is ignited in air to ensure a safer and more controlled start-up while avoiding the waste of valuable reactants (O_2/ CO_2)
- Once stable operating conditions are achieved (i.e. when the temperature in the reaction zone is around 800-900 °C), the gasification process is switched from air to oxy-CO_2.
- Switching is a straightforward process, as it only requires stopping the air inlet and gradually opening the O_2 feeding valve until the desired operating temperature is

reached. To avoid excessive temperature in the reaction zone, any further increase of the O2 supply must necessarily take place along with a corresponding CO2 supply increase.

After the successful completion of all the preliminary tests, the oxygen-CO_2 gasification trials were initiated to evaluate the behavior of the system under various operating conditions, in terms of fuel feeding rate, gasifying agent flow rate, CO_2/O_2 ratio, and CO_2/fuel ratio. Once stable operation was achieved, each given set of operating parameters was tested for at least one hour. Pressure and temperature in different sections of the reactor and along the cleaning line were monitored, together with the syngas flow rate and composition. Mean values for all measured parameters were calculated for each operative condition. The operating conditions in terms of gasifying agent flow rate and the corresponding results are reported in Table 8.3, where ER, called equivalent ratio, is the ratio between the actual oxygen supplied to the stoichiometric amount required for complete oxidation of the fuel.

Table 8.3 - Operating conditions and corresponding results of the experimental oxy-CO_2 gasification campaign.

EXPERIMENTAL OXY-CO_2 GASIFICATION CAMPAIGN

CO_2 [Nm^3/h]	**O_2 [Nm^3/h]**	**CO_2/O_2 [Nm^3/Nm^3]**	**CO_2 [kg/h]**	**O_2 [kg/h]**	**CO_2/biomass, [kg/kg]**	**ER [%]**
4.8	4.5	1.07	9.42	6.42	0.52	26.25
4.7	4.6	1.02	9.23	6.57	0.54	28.2
4.7	4.6	1.02	9.23	6.57	0.49	25.9
4.7	4.7	1.00	9.23	6.71	0.51	27.45
4.8	3.5	1.37	9.42	5.00	0.86	33.5
4.7	3.4	1.38	9.23	4.85	0.71	27.45
5.0	3.6	1.39	9.82	5.14	0.80	30.8
5.6	4.0	1.40	10.99	5.71	0.79	30.3
5.5	3.9	1.41	10.80	5.57	0.67	25.55
7.8	4.1	1.90	15.31	5.85	0.78	22.1
7.7	4.2	1.83	15.12	6.00	0.78	22.75
7.9	4.3	1.84	15.51	6.14	0.79	22.95
6.0	3.5	1.71	11.78	5.00	0.78	24.4
5.8	3.05	1.90	11.39	4.35	0.83	23.45
4.9	3.0	1.63	9.62	4.28	0.76	25.0
4.2	3.4	1.24	8.24	4.85	0.71	30.8
5.4	4.1	1.32	10.60	5.85	0.85	34.75
5.3	4.2	1.26	10.40	6.00	0.70	29.9
5.2	3.45	1.51	10.21	4.93	0.79	28.0
5.2	3.45	1.51	10.21	4.93	0.82	29.3
6.7	4.2	1.60	13.15	6.00	0.86	28.8
6.4	4.4	1.45	12.56	6.28	0.83	30.6
3.1	2.8	1.11	6.09	4.00	0.71	34.4
4.1	3.1	1.32	8.05	4.43	0.76	31.0
4.0	3.1	1.29	7.85	4.43	0.86	35.9
7.9	4.1	1.93	15.51	5.85	0.88	24.6

6.5	3.1	2.10	12.76	4.43	1.02	26.2
6.5	3.1	2.10	12.76	4.43	1.06	27.15
5.0	3.1	1.61	9.82	4.43	0.87	28.9
5.8	3.0	1.93	11.39	4.28	0.87	24.0
5.35	4.0	1.34	10.50	5.71	0.94	37.8
5.4	4.05	1.33	10.60	5.78	0.93	37.5
5.4	4.2	1.29	10.60	6.00	0.87	36.4
5.25	3.5	1.50	10.31	5.00	0.98	35.1
5.2	3.6	1.44	10.21	5.14	1.04	38.6
5.2	3.6	1.44	10.21	5.14	1.01	37.5
5.2	3.6	1.44	10.21	5.14	1.07	39.8
6.8	4.4	1.55	13.35	6.28	1.05	36.6
6.6	4.4	1.50	12.96	6.28	1.01	36.2
6.65	4.4	1.51	13.05	6.28	0.99	35.0
6.9	4.5	1.53	13.55	6.42	1.10	38.5
6.7	4.5	1.49	13.15	6.42	1.03	37.1
6.4	4.6	1.39	12.56	6.57	0.99	38.35
4.2	3.05	1.38	8.24	4.35	1.03	40.1
4.15	3.05	1.36	8.15	4.35	0.92	36.2
3.9	3.1	1.26	7.66	4.43	1.03	44.0
4.0	3.1	1.29	7.85	4.43	1.03	43.0
3.95	3.1	1.27	7.75	4.43	0.99	41.7
5.4	2.9	1.86	10.60	4.14	1.25	36.0
5.4	2.9	1.86	10.60	4.14	1.30	37.5
5.7	2.95	1.93	11.19	4.21	1.34	37.4
5.7	3.0	1.90	11.19	4.28	1.31	37.1
6.9	3.5	1.97	13.55	5.00	1.31	35.6
6.7	4.5	1.49	13.15	6.42	1.18	42.6
6.3	3.2	1.97	12.37	4.57	1.46	39.8
6.4	3.2	2.00	12.56	4.57	1.50	40.1
7.0	3.65	1.92	13.74	5.21	1.49	41.7
7.05	3.7	1.91	13.84	5.28	1.55	43.7
7.0	3.5	2.00	13.74	5.00	1.47	39.4
6.9	3.6	1.92	13.55	5.14	1.48	41.5
6.9	3.2	2.16	13.55	4.57	1.66	41.4
6.85	3.2	2.14	13.45	4.57	1.64	41.0
6.8	3.3	2.06	13.35	4.71	1.66	43.1
6.85	3.3	2.08	13.45	4.71	1.71	44.2
6.8	3.3	2.06	13.35	4.71	1.68	43.8
7.0	3.6	1.94	13.74	5.14	1.77	48.8
6.9	3.6	1.92	13.55	5.14	1.62	45.4

8.3.1 Experimental results

As expected, the equivalence ratio (ER) significantly affects the quality of the syngas produced and the performance of the overall gasification process. By varying this ratio, different operating conditions can be obtained, both in terms of oxygen concentration and reaction temperature, which are crucial parameters for the equilibrium of the complex reactions occurring inside the gasifier.

The measured volumetric concentrations of the main components in the dry syngas (CO_2, CO, H_2 and CH_4) are shown in Figure 8.10- 8.13 as a function of the equivalence ratio ER, for different values of the CO_2/Biomass mass flow ratio.

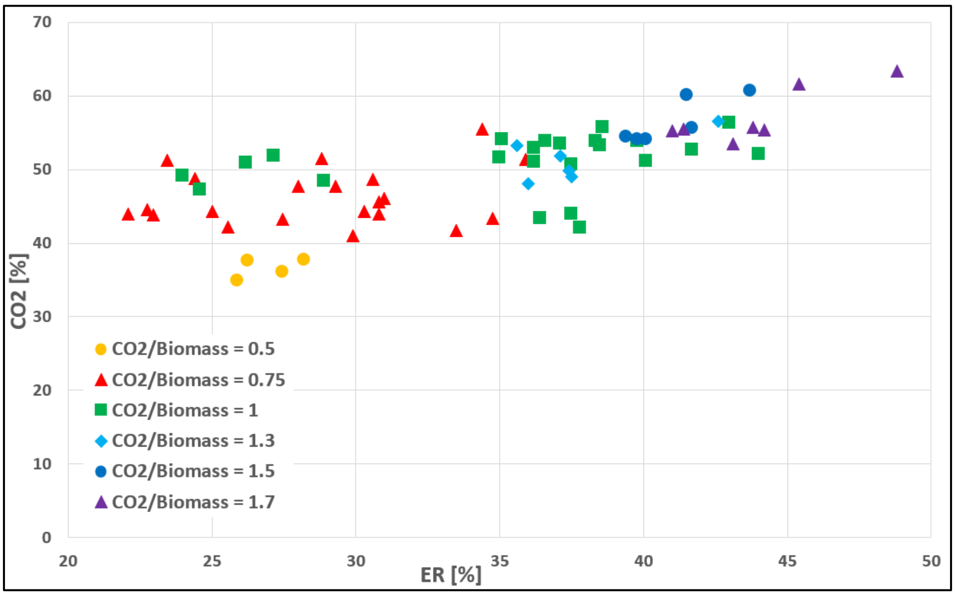


Figure 8.10 - Measured concentration of CO_2 in the syngas in function of ER for different values of the CO_2/Biomass mass flow ratio.

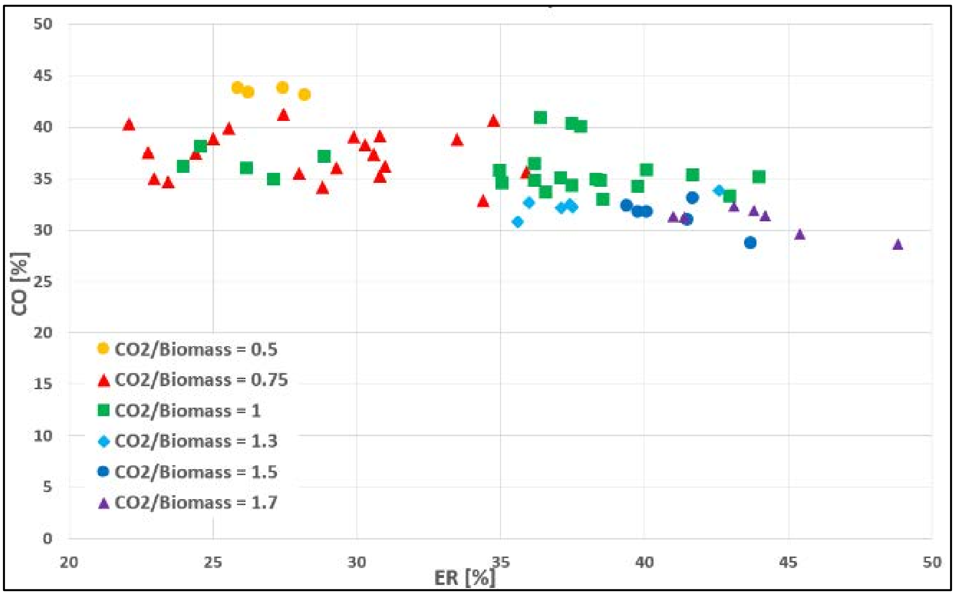


Figure 8.11 - Measured concentration of CO in the syngas in function of ER for different values of the CO_2/Biomass mass flow ratio.

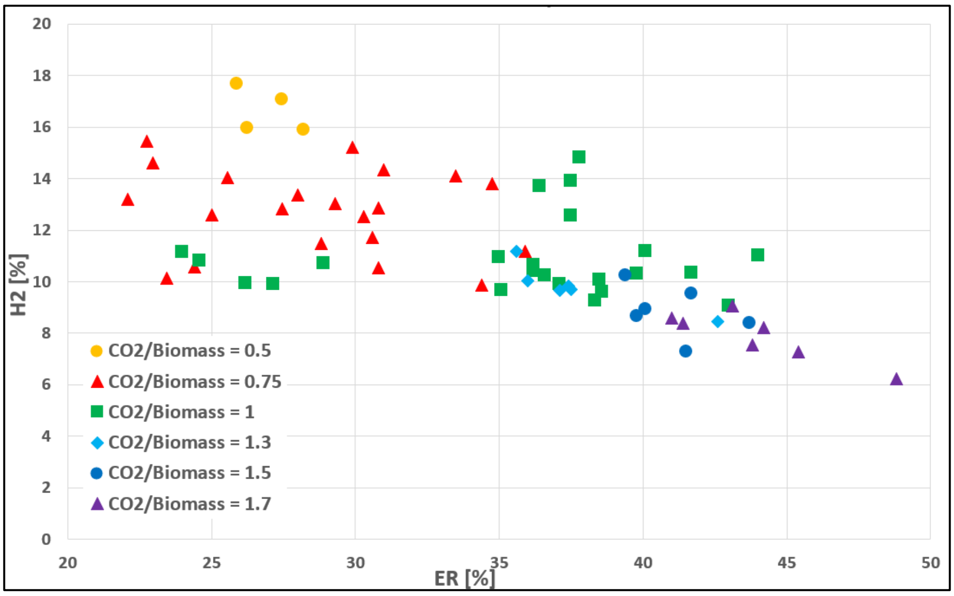


Figure 8.12 - Measured concentration of H_2 in the syngas in function of ER for different values of the CO_2/Biomass mass flow ratio.

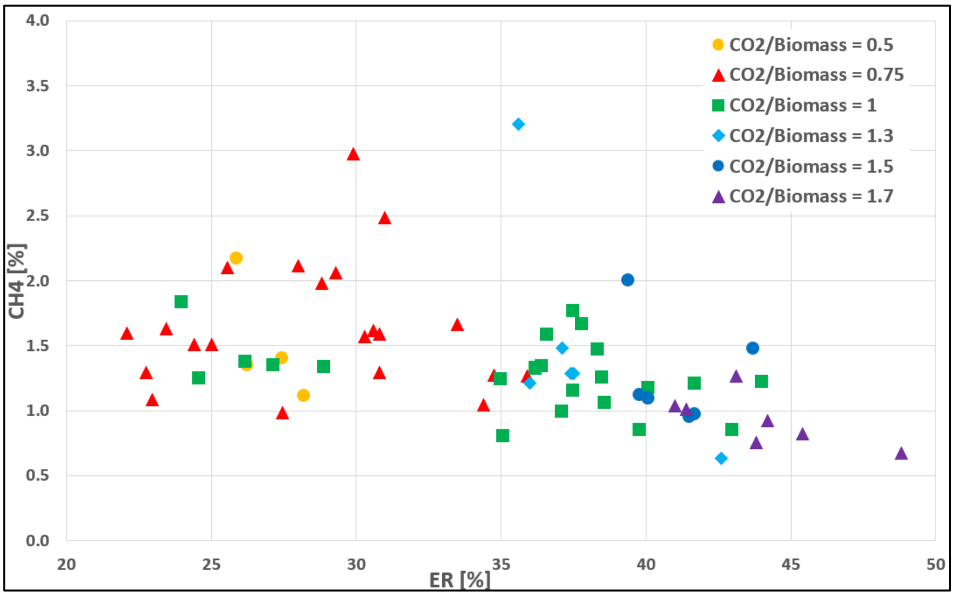


Figure 8.13 - Measured concentrations of CH_4 in the syngas in function of ER for different values of the CO_2/Biomass mass flow ratio.

Specifically, increasing the equivalence ratio (ER) has a positive impact on the volumetric fraction of carbon dioxide, as indicated by an increasing trend (Figure 8.10). Conversely, carbon monoxide (Figure 8.11), hydrogen (Figure 8.12) and methane (Figure 8.13) exhibit a decreasing trend with increasing ER. This is because an increase in ER and consequently of oxygen concentration within the gasifier promotes the oxidation of volatile combustible species.

Syngas obtained during the experimentation showed a significantly higher concentration of CO (ranging from 29 to 43 vol.%) compared to that obtained from conventional air-gasification [145]. Notably, substituting air with an oxygen-CO2 mixture substantially increased the fraction of CO and H2 in the syngas, resulting in a higher quality product.

The influence of ER on the low heating value (LHV) of the product gas is illustrated in Figure 8.14. As ER increases the LHV decreases, indicating the convenience of operating the gasifier with lower ER values. LHV is directly related to the composition of the syngas and can be calculated as:

$$LHV_{syn} = LHV_i \cdot y_i \qquad (1)$$

where LHV_i represents the lower heating value of each species and y_i is the concentration of the i-th combustible species in the syngas flow, expressed in volumetric fraction. CO, H2, CH4 are the important components for determining LHV. The observed LHV trend is consistent with the syngas composition trends. Furthermore, this correlation between syngas LHV and ER has a good agreement with previous findings reported in the literature. For instance, Barontini et al. [145] noted a decreasing trend of LHV as ER increases during their experimental campaign focused on the co-gasification of woody biomass with organic and waste matrices in a downdraft gasifier using only air as gasifying agent. Likewise, in their air-based gasification experimental activity carried out on a demonstrative scale downdraft gasifier fed with different organic waste matrices (including corn cobs, vine pruning, and rice husks), Biagini et al. [146, 147] also observed a similar decreasing trend.

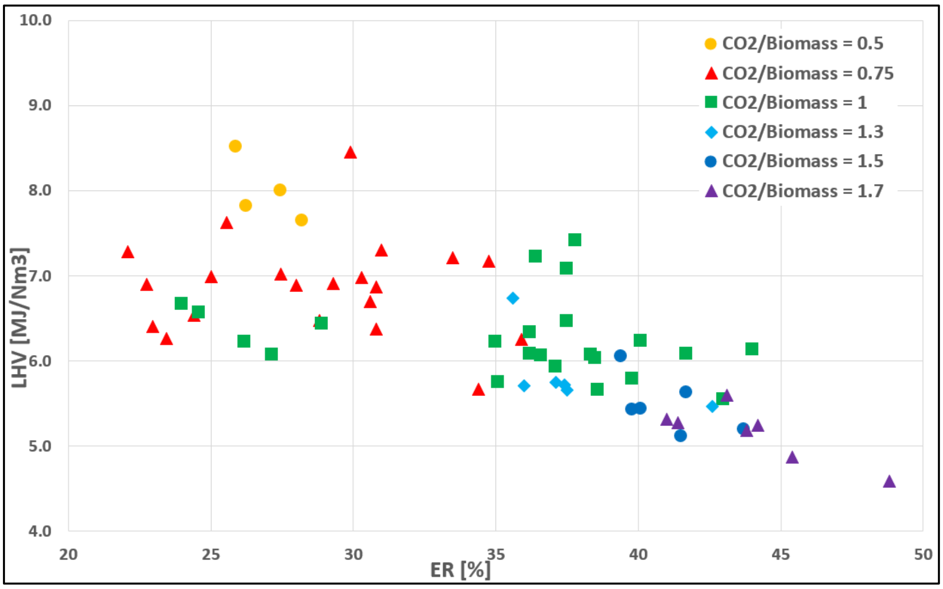


Figure 8.14 - Syngas LHV in function of ER for different values of the CO_2/Biomass mass flow ratio.

The gasification performance was evaluated studying different indices: cold gas efficiency (CGE), biomass mass consumption, syngas volumetric flow rate and syngas yield.

Cold gas efficiency (CGE), defined as the ratio of the thermal power of the produced syngas to the thermal power of the feedstock. was calculated from the following equation:

$$CGE_{syn} = \frac{syngas\ flow\ rate \cdot LHV_{syn}}{fuel\ feeding\ rate \cdot LHV_{fuel}} \qquad (2)$$

As Figure 8.15 shows**,** the relationship between CGE and ER is not very clear due to scattered experimental results under different operative conditions. Anyway, higher CGE values, ranging from 50% to 70%, were obtained with lower equivalence ratios (0,2 ÷ 0,3)

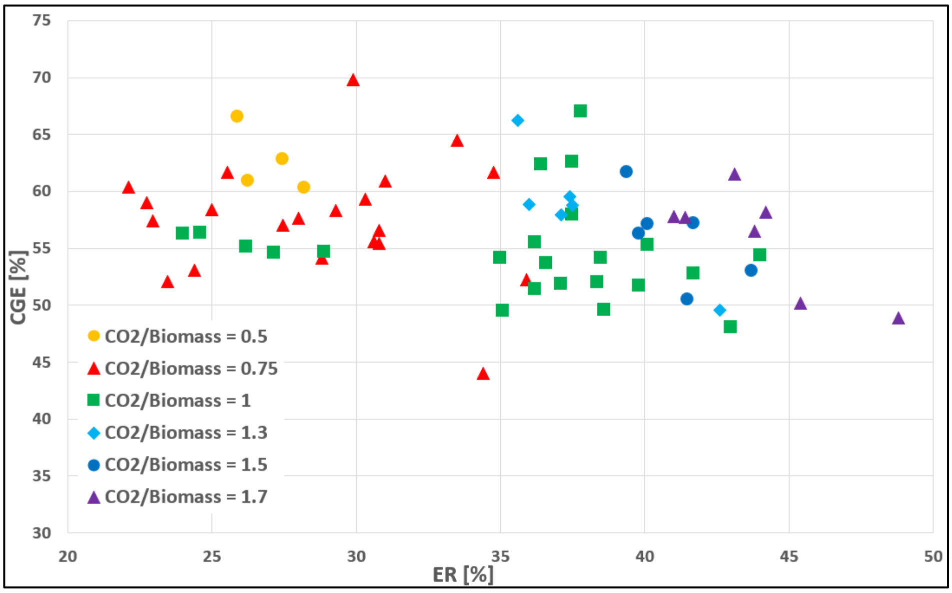


Figure 8.15 - CGE in function of ER for different values of the CO_2/Biomass mass flow ratio.

Furthermore, it is illustrated the effect of ER on the biomass consumption rate (Figure 8.16) and on the syngas volumetric flow rate (Figure 8.17). Both graphs exhibit a decreasing trend as ER increases. This behavior depends on the fact that at higher equivalence ratios, the excess oxygen promotes the oxidation reactions. As a result, the gas composition shifts towards species of higher molecular weight, such as carbon dioxide and water vapor, while monoxide of carbon and hydrogen decrease in concentration.

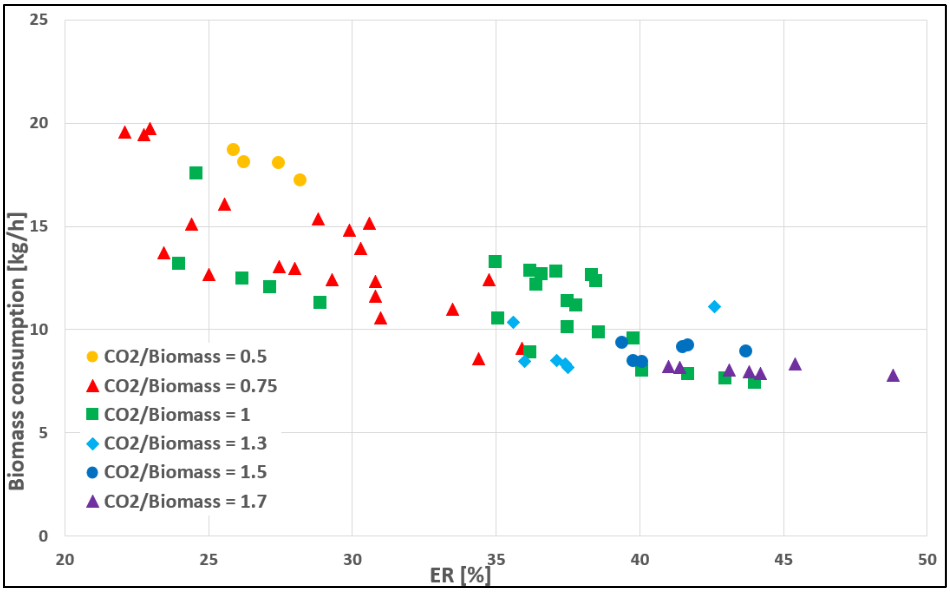


Figure 8.16 - Biomass consumption in function of ER for different values of the CO_2/Biomass mass flow ratio.

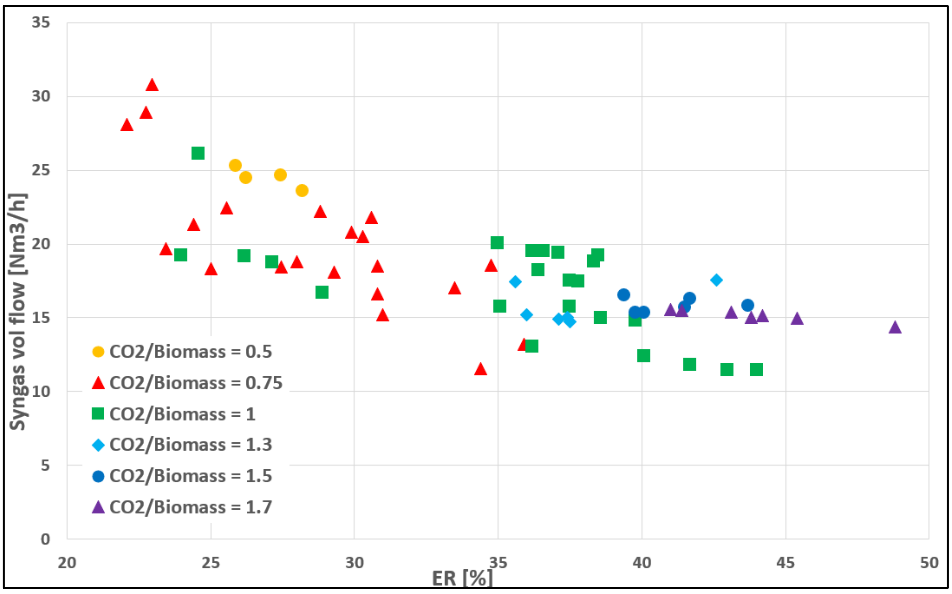


Figure 8.17 - Syngas volumetric flow rate in function of ER for different values of the CO_2/Biomass mass flow ratio.

Finally, Figure 8.18 illustrates the correlation between syngas yield and ER. Syngas yield, defined as the ratio of the syngas volumetric flow rate to the biomass mass consumption at the inlet, shows an increasing trend as the ER increases and it is characterized by values in the range of 1.4÷1.9 Nm^3/kg. Barontini et al. [145] noted the same experimental trend, even if the specific values were higher than the ones showed in the figure below.

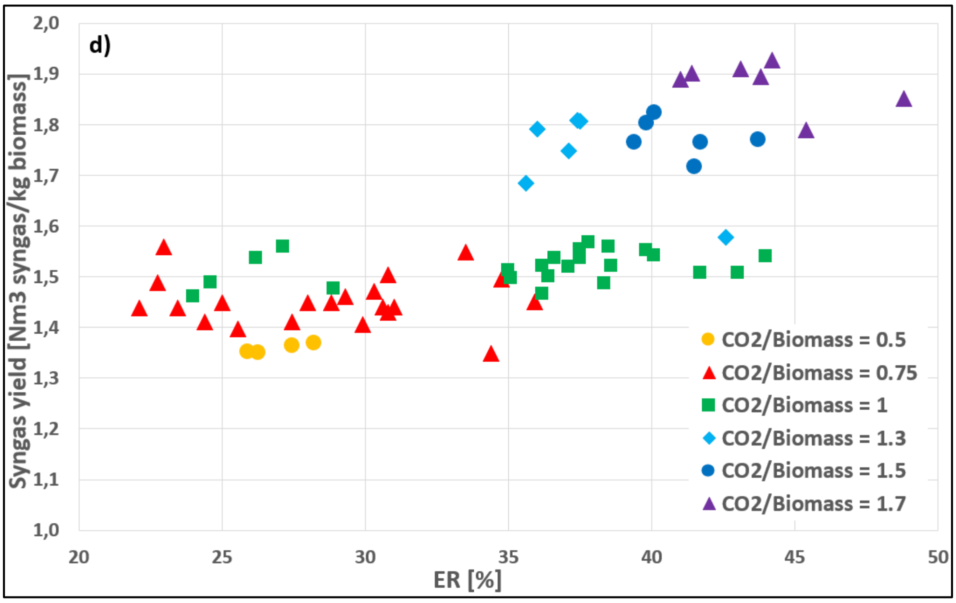


Figure 8.18 - Syngas yield in function of ER for different values of the CO_2/Biomass mass flow ratio.

The temperature of the syngas along the process is also an important parameter to assess the gasifier operation, i.e. the degree of conversion of the reactants; these temperatures were measured thanks to the use of special type K thermocouples, located in specific zones and wired to the recording device. For example, the trends of the syngas temperature in the core of the reaction chamber (Imbert throat) and at the outlet of the gasifier are represented in Figure 8.19 and in Figure 8.20, respectively. The amount of CO_2 supplied largely affects the dilution and temperature of the syngas. During the experimental oxygen-CO_2 wood pellet gasification campaign, throat temperatures varied from approximately 900 °C to 1100 °C (Figure 8.19) while outlet temperatures ranged from 400 °C to 550 °C (Figure 8.20). Higher amounts of CO2 are required as the ER increases to achieve these temperature ranges. This aspect is important for determining the feasibility of a specific operating condition, given the structural limit of the materials used.

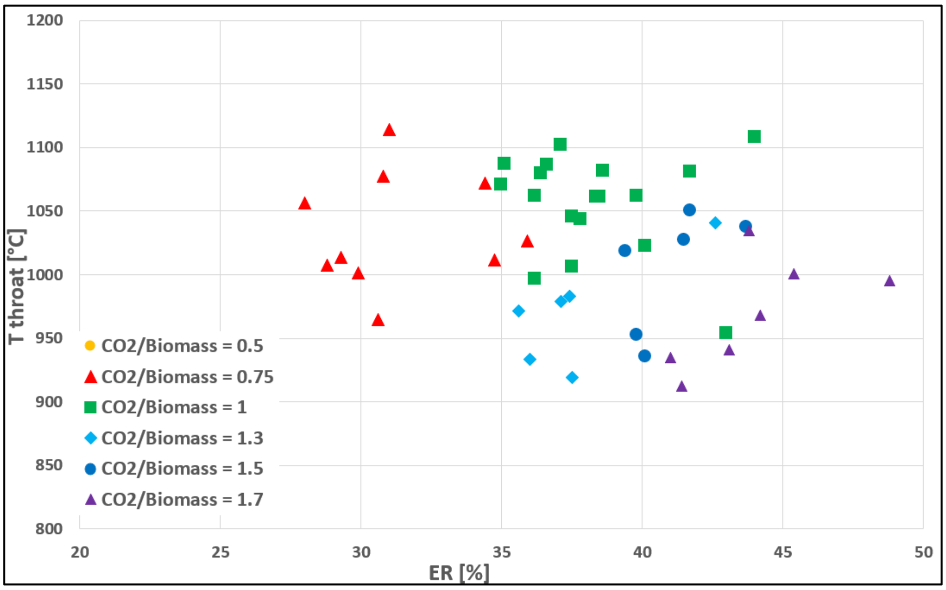


Figure 8.19 - Temperature in the throat of the reactor in function of ER
for different values of the CO_2/Biomass mass flow ratio.

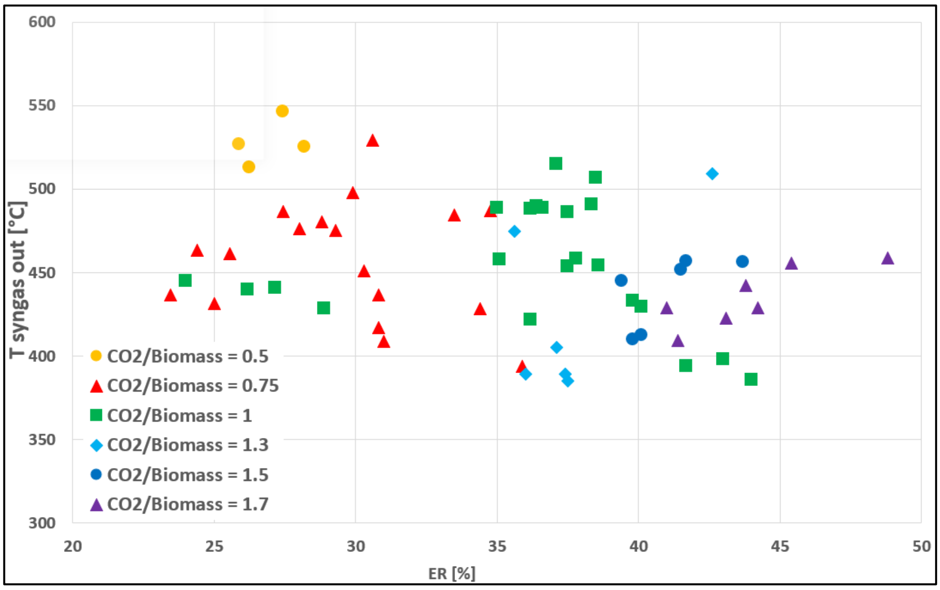


Figure 8.20 – Temperature of the syngas at the outlet of the gasifier in function of ER
for different values of the CO2/Biomass mass flow ratio.

In addition, the produced syngas flow at the gasifier outlet was tested for tar and dust content. These common byproducts of the process can significantly limit the usability of the syngas itself. Reducing tar content is a technically challenging issue in biomass gasification.

As previously mentioned, tar and particulate matter in the syngas were sampled and analyzed according to Technical Specification CEN/TS 15439:2006 [102]. The results, summarized in Table 8.4, are satisfactory when compared to values from literature related to conventional air-based gasification.

In fact, the analysis shows that amount of both tar and particulate matter is very low, depending on the substitution of air with the O_2/CO_2 mixture which lead to higher operating temperature of reactions and so promotes the char conversion and cracking of high hydrocarbons, due to the endothermic nature of some of the main reactions that are favoured at high temperatures.

The low amount of tar and particulates found in the analysis is due to the replacement of air with the O_2/CO_2 mixture, which lead to higher reaction temperature, promoting char conversion and cracking of high molecular weight hydrocarbons.

This effect has been supported in the literature by Han and Kim [148], who found that tar content in the syngas decreases with increasing temperature due to thermal cracking, and Li et al. [116], who reported a significant decrease in tar content from 15 to 0.54 g/Nm^3 in a circulating fluidized-bed gasifier with an increase in temperature from about 700 °C to 820 °C."

Table 8.4 - TAR and dust content in the syngas flow at the outlet of the gasifier.

SAMPLES	OPERATIVE CONDITIONS			ANALYSIS	
	CO_2 [Nm^3/h]	O_2 [Nm^3/h]	CO_2/O_2 [Nm^3/Nm^3]	Tar content [mg/Nm^3]	Dust content [g/Nm^3]
1	6.8	3.3	2.06	134	1.09
2	6.7	4.5	1.49	103	1.27

Air-based biomass gasification in downdraft reactors typically results in higher syngas tar content, as reported in the literature. For instance, Gai and Dong [150] measured tar concentrations ranging from 4.6 to 7.2 g/Nm3 for the gasification of non-woody biomass like corn straw, with tar content decreasing as ER increases from 18% to 41%. Dogru et al. [73] studied the gasification of sewage sludge and found a tar content of 5.5-8.4 g/Nm3 in the syngas flow at the gasifier outlet; they developed a cleanup system consisting of a water scrubber and a filter box, reducing tar content to 1.4-2 g/Nm3. Gautam et al. [150] observed tar concentrations ranging from 0.34-0.68 g/Nm^3 in pelletized biomass gasification."

On the contrary, Barontini et al. [145] reported a very low tar content in the syngas produced during their experimental air co-gasification activity. This may depend on the innovative and sophisticated internal air distribution system, named "double fire," which is covered by a patent and used by the gasifier itself. Their results, ranging from 0.06 to 0.12 g/Nm3, are comparable to the corresponding values obtained with the Oxygen-CO2 gasification approach and shown in Table 8.4. Susastriawan et al. [151], analyzing the performance of many small-scale downdraft gasifiers, found that the design of the gasifiers is as important a parameter in gasification as the properties of the biomass feedstock and process operating parameters.

8.4 Numerical model validation activity

Data collected during experimentation were used to validate the numerical simulation model of the oxy-CO_2 gasification process already developed and implemented in Aspen Plus® environment (Chapter 7). It is important to remind that two different approaches have been developed: an equilibrium model and a pseudo-kinetic one.

In respect to the original model, the pseudo-kinetic one needed some changes to take into account the differences in terms of geometry and layout of the small gasifier in respect of the AUGIA gasifier, and also to take into consideration all the other equipment present in the small gasification plant.

In previous deliverables, the original models had been validated with experimental gasification data obtained with woody biomass and air as gasifying agent; in this new numerical activity, the validation has been carried out using the results of the oxy-CO_2 experimental campaign.

Referring only to the pseudo-kinetic model, using two experimental conditions, a tuning of it has been carried out, in order to limit its estimation error of the molar flow of the main syngas components (H_2, CO, CO_2 and CH_4). As reported in Figure 8.21, the fitting can be considered satisfying with percentage errors not higher than 10%.

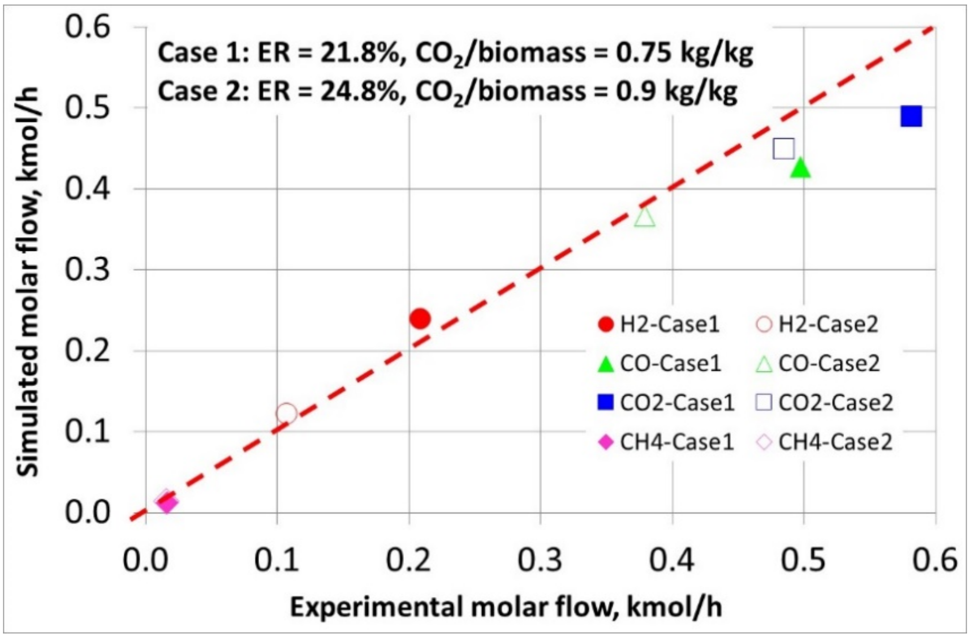


Figure 8.21 - Comparison between experimental and simulated molar flows of main syngas components.

Using the calibrated simulation model, a set of curves has been constructed, in order to assess the behaviour of the existing gasification system. In particular, the best performances of the gasifier can be obtained when a lower amount of CO_2 is used (Figure 8.22). The maximum of the CGE is reached for higher values of ER increasing the CO_2. The quantity of CO_2

largely affects the dilution of the syngas and therefore its temperature (Figure 8.23). This last is important for the actual feasibility of a specific operative condition considering the structural limits of the materials. The syngas from the outlet of the reaction zones to the exit from the reactor reduces its temperature due to some heat exchange with the incoming mixture of O_2/CO_2 and losses towards the environment (Figure 8.23).

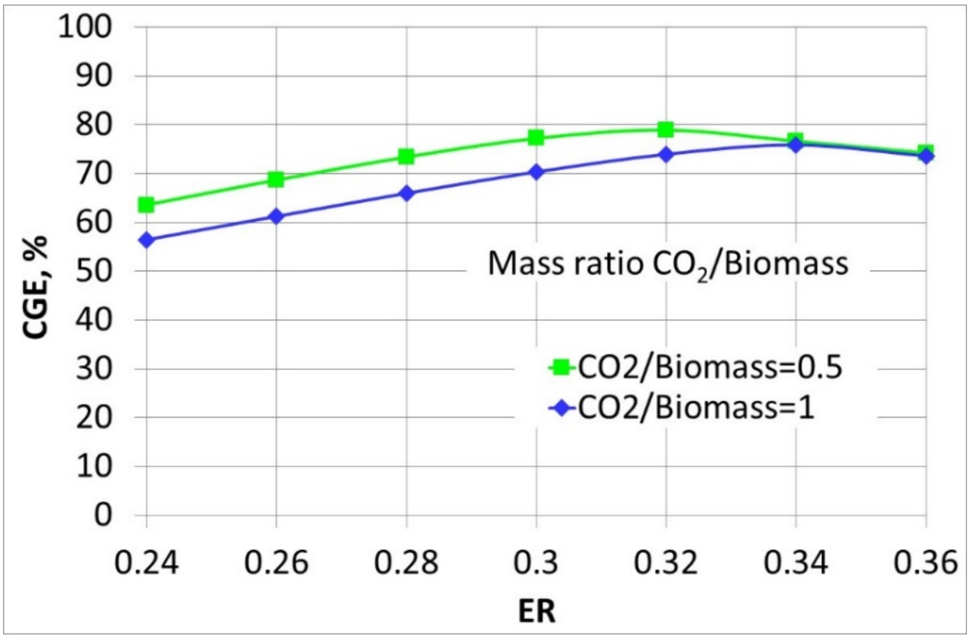


Figure 8.22 - Cold gas efficiency in function of ER for two values of the CO_2/biomass mass flow ratio.

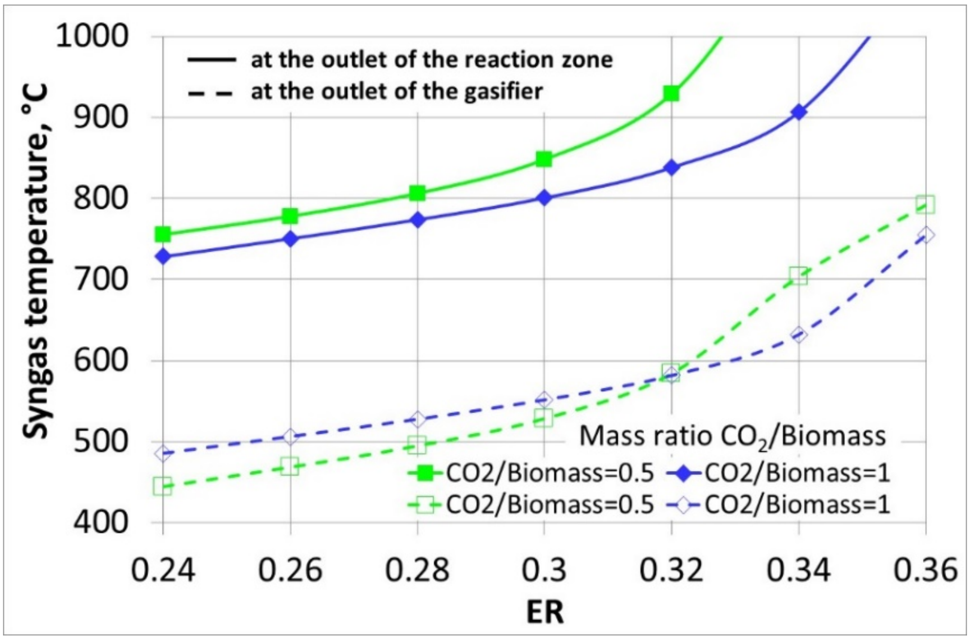


Figure 8.23 - Syngas outlet temp. in function of ER for two values of the CO_2/biomass mass flow ratio.

8.5 Conclusions

The preliminary experimental activity, which was carried out at the laboratories of the University of Pisa, demonstrated the feasibility of the O_2-CO_2 biomass gasification approach and satisfying values of the gasification process have been obtained, with a maximum CGE of about 70% and a syngas LHV of roughly 8 MJ/Nm^3. Useful information was also acquired concerning the correct procedures for the oxy-gasification process start up and normal running.

The gasifier simulation model, which was tuned using some experimental data, showed that it is possible to get high performances when the CO_2 amount is lowered with the drawback of increasing the reaction temperature. So, the CO_2 shall be reduced at most in accordance with the temperature limits due to the structural integrity of the equipment. In accordance with the numerical results, it seems that the optimal condition can be obtained using an intermediate amount of oxygen (ER ≈ 0.32%), in order to have a good compromise between the temperature of the syngas and the efficiency of the gasification process; in fact, the performances decrease with high values of ER, where the oxidation reactions take place largely. Moreover, the value of the CO_2/Biomass mass flow ratio should be around 0.75, ensuring a compromise between the conversion of biomass to syngas and the temperatures of the syngas itself.

The results of this preliminary experimental activity carried out using the small gasifier and focused on the oxy-CO_2 gasification approach are described in detail in a scientific paper entitled "*Biomass oxy-CO_2 gasification process for bio-methane production: an experimental and numerical activity*", which will be presented at the 77th ATI National Congress in Bari on the 12-14th of September 2022. These activities can be included in action D1.2 "Technical dissemination activities" of project AUGIA, because can contribute to raise the global interest on this scientific research area.

Figure 8.24 - New steam electrical boiler for next experimental activities, using an oxy-steam gasification approach.

Future activities will concern the execution of experimental tests using steam as gasifying agent substituting partially or completely the CO_2 in the oxy-gasification approach. To start this second part of experimental activities, the UNIPI research team has just decided to purchase a small steam electrical boiler (Figure 8.24) and the proper piping system, in order to feed steam into the gasification reactor.

The technical data and size of the boiler selected (Table 8.5) satisfy the requests of steam to feed to the process, based on the preliminary material balances which have been already carried out with the numerical model developed on Aspen Plus® environment.

Table 8.5 - Technical data and size of the steam electrical boiler selected for next experimental activities, using an oxy-steam gasification approach.

TECHNICAL DATA		
Power supply (resistance)	kW	6.5
Voltage	V	380
Poles	Nb.	5
Max steam flow output	kg/h	8.7
	°C	130 - 140
	bar	3.5 - 4
Water tank volume	L	8
Steam valve size	“	½” GAS m

Chapter 9

Conclusions and Recommendations for Future Work

9.1 Conclusions

The experimental activity on the lab-scale plant available as well as the numerical simulations performed both on the LIFE AUGIA full-scale plant configuration and on the experimental gasifier made it possible to verify the use of the oxygen-based gasification for the thermochemical treatment of sludge from civil sewage, mixed with woody biomass.

From the study and analyses carried out, the following conclusions can be drawn:

- Experimental tests with wood pellets have shown how the system, supplied with oxygen added with CO_2, is able to produce a syngas with better composition than those found in the literature. The substitution of air with an oxy- CO_2 mixture increases considerably, the fraction of CO and H2 in the syngas, allowing a higher quality syngas. Also, from the point of view of plant management, the experimentation has given satisfactory results.
- The changes and improvements made to the pilot plant, in resolution of problems and shortcomings of the existing system, have optimize its performance and allowed a better management of process and more accurate monitoring of operating parameters.
- A simulation based preliminary study has been performed for sludge and biomass gasification research using a high-performance software such as ASPEN PLUS. Two simulation models have been developed for the simulation of the oxy-steam gasification of biomass and biomass+sewage sludge mixture as feedstocks. Providing important information for understanding the sludge gasification process in downdraft reactors, the models represent a high potential tool for predicting the behaviour of the system under varying operating conditions.
- The equilibrium model makes it possible to easily highlight the macro dependence of the performances on the most important process parameters (ER, reaction temperature, steam mass flow). The injection of steam has proven very effective to limit the syngas temperature and to promote the hydrogen yield.
- Thanks to the kinetic model, which is more complicate and accurate, we were able to estimate reliably the syngas temperature and the unburnt char which can reach values of about 1 kmol/h. The kinetic model can consistently simulate the impact of the actual geometry of the reactor. In particular, the effect of the position of the secondary inlet

of gasifying agent and the shape of the throat are well taken into account in the simulation of the chemical reactions. Using the results of the kinetic model, an effective design point for the gasifier has been selected. This point assures satisfying syngas temperatures and the required volume flow.

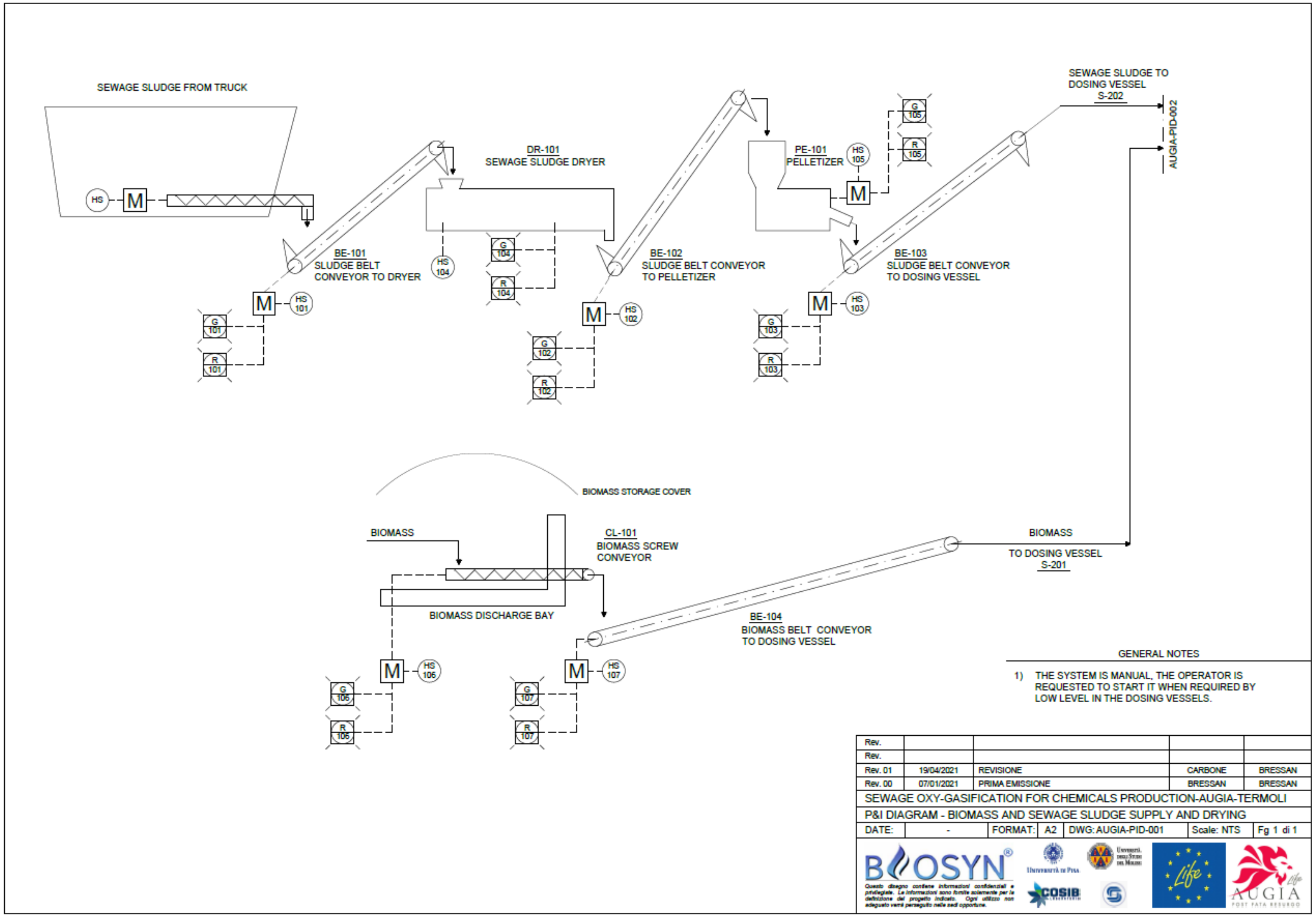
- The numerical simulations made it possible to verify the technical feasibility of the co-gasification of sewage sludge with woody biomass. In particular, in order to minimize operational problems such as the melting of ashes, the formation of clinker and the consequent difficulty in disposing of the residue solid, and increase the performance of the process, the sludge content should be, with the current system configuration, 30% by weight.
- A parametric analysis was conducted regarding the influence of equivalence ratio ER. The optimal operating conditions were obtained for an equivalence ratio in the range 0.25÷0,30. This result was also found true in the experimental trials with oxygen and CO_2 conducted on the small-scale gasifier.

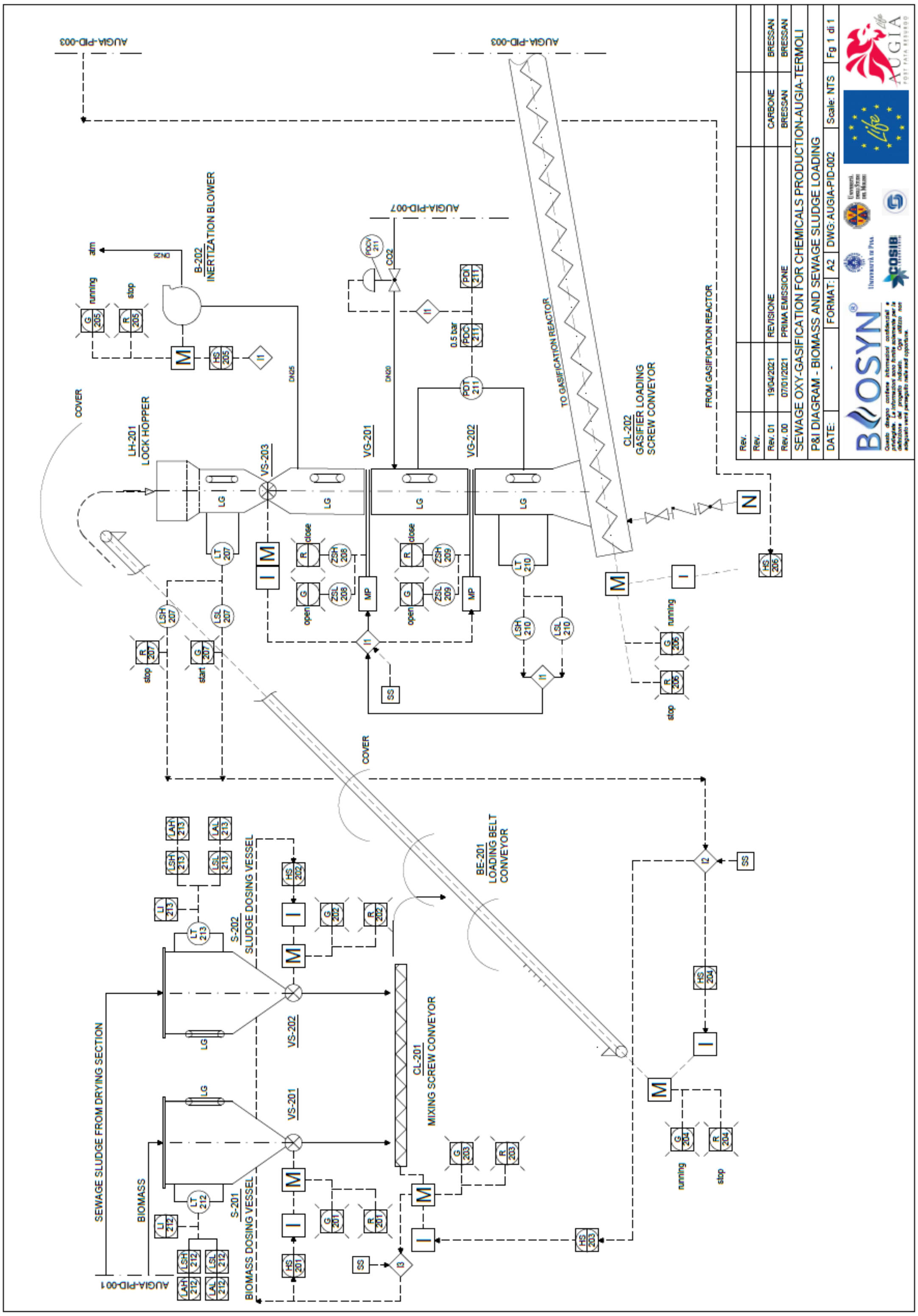
9.2 Recommendations for Future work

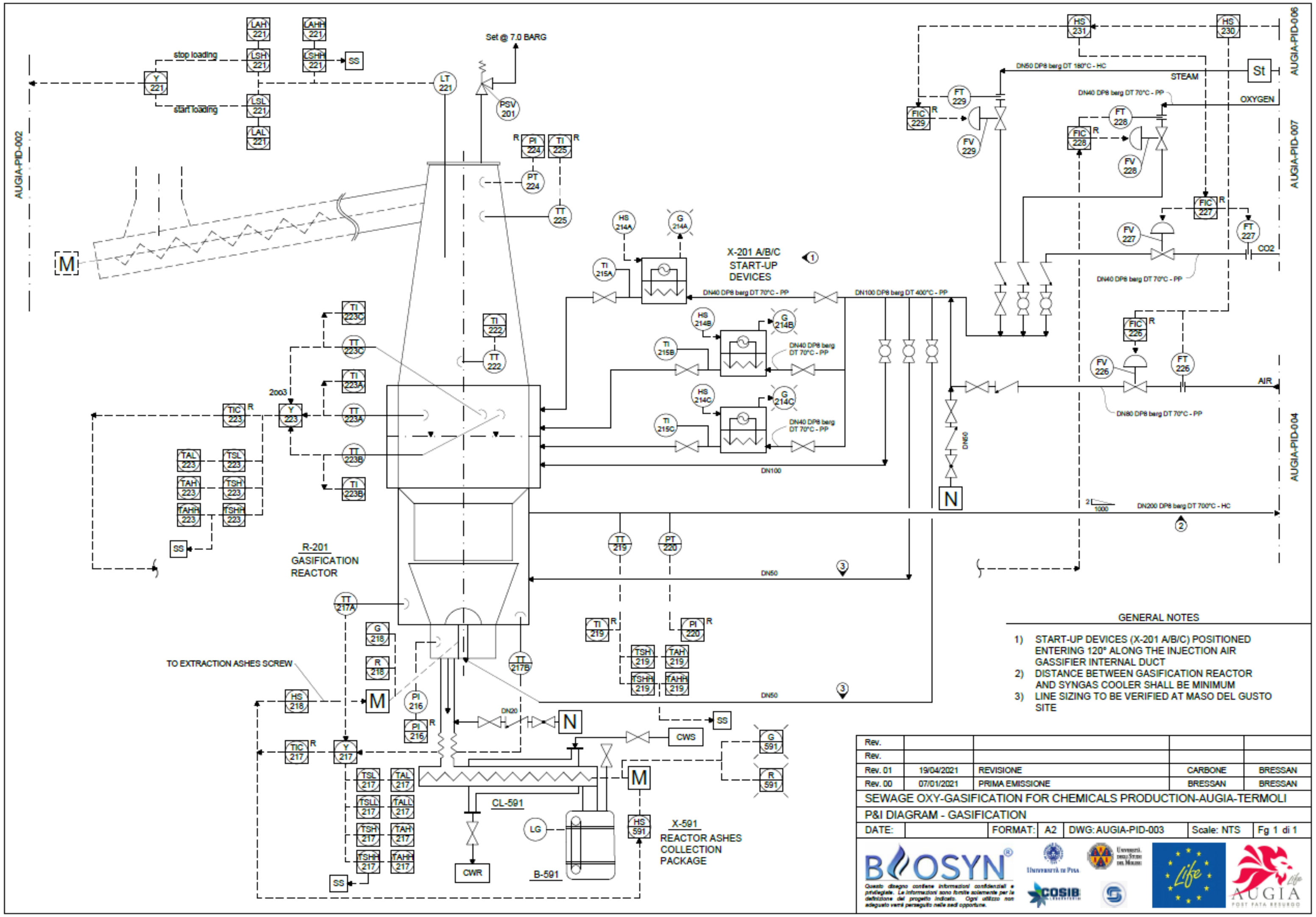
The following are the number of possible future studies that can be done within this study:

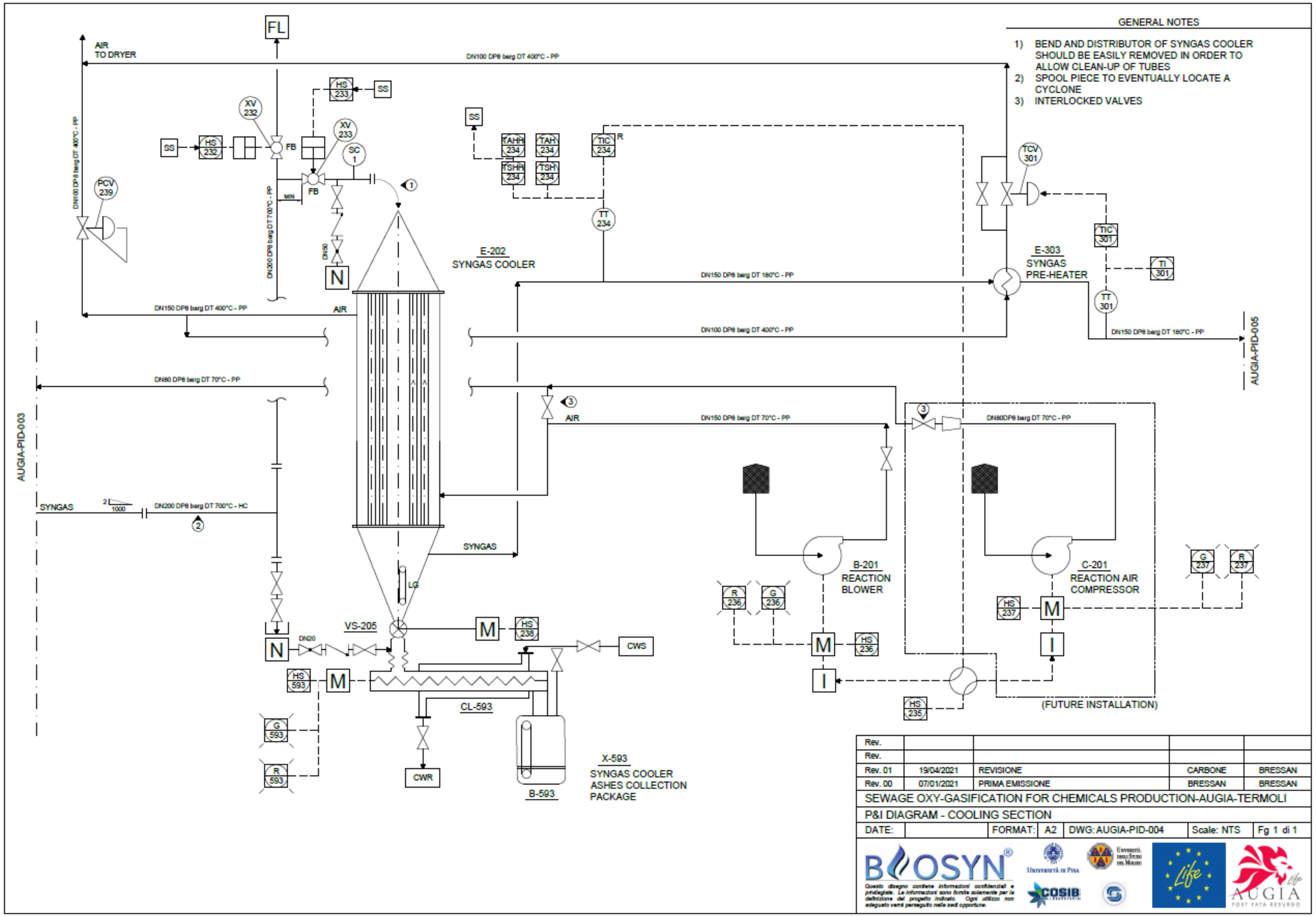
- Perform and extensive experimental campaign to study the performance of the full-scale LIFE AUGIA downdraft gasifier, fed by varying sludge and biomass mixtures, within a broad range of operating parameters. to optimize its gasification process.
- The reliability of simulation models for studying co-gasification of biomass and sewage sludge should be confirmed by the experimental data of the LIFE AUGIA once they will be available. If necessary, an improvement of the models will be carried out in order to obtain a robust tool of performance prediction.
- Test the operation and performance of the laboratory-scale pilot gasifier with different mixtures of woody biomass and waste materials such as plastics and livestock manure.
- Modify the laboratory-scale downdraft gasifier to use steam as gasifying agent substituting partially or completely the CO_2 in the oxygen-based gasification approach.
- A research study should be conducted to examine the catalyst effect of the ash on the char reduction reactions. In addition, another interesting research to counduct the investigation of the effect of other gas agents such as CO_2 on the produced gas tar content.
- Perform a future throughout characterization of the sludge gasification resulting tar to get useful information to improve the structure and management of the LIFE AUGIA plant.
- Carry out the analysis of the ashes to confirme that they contain almost all of the heavy metals originally present in the starting feedstock and that they are below the limits for non-hazardous waste. This test is a necessary, although not a criterion still sufficient, for the admission of non-hazardous waste to landfills.

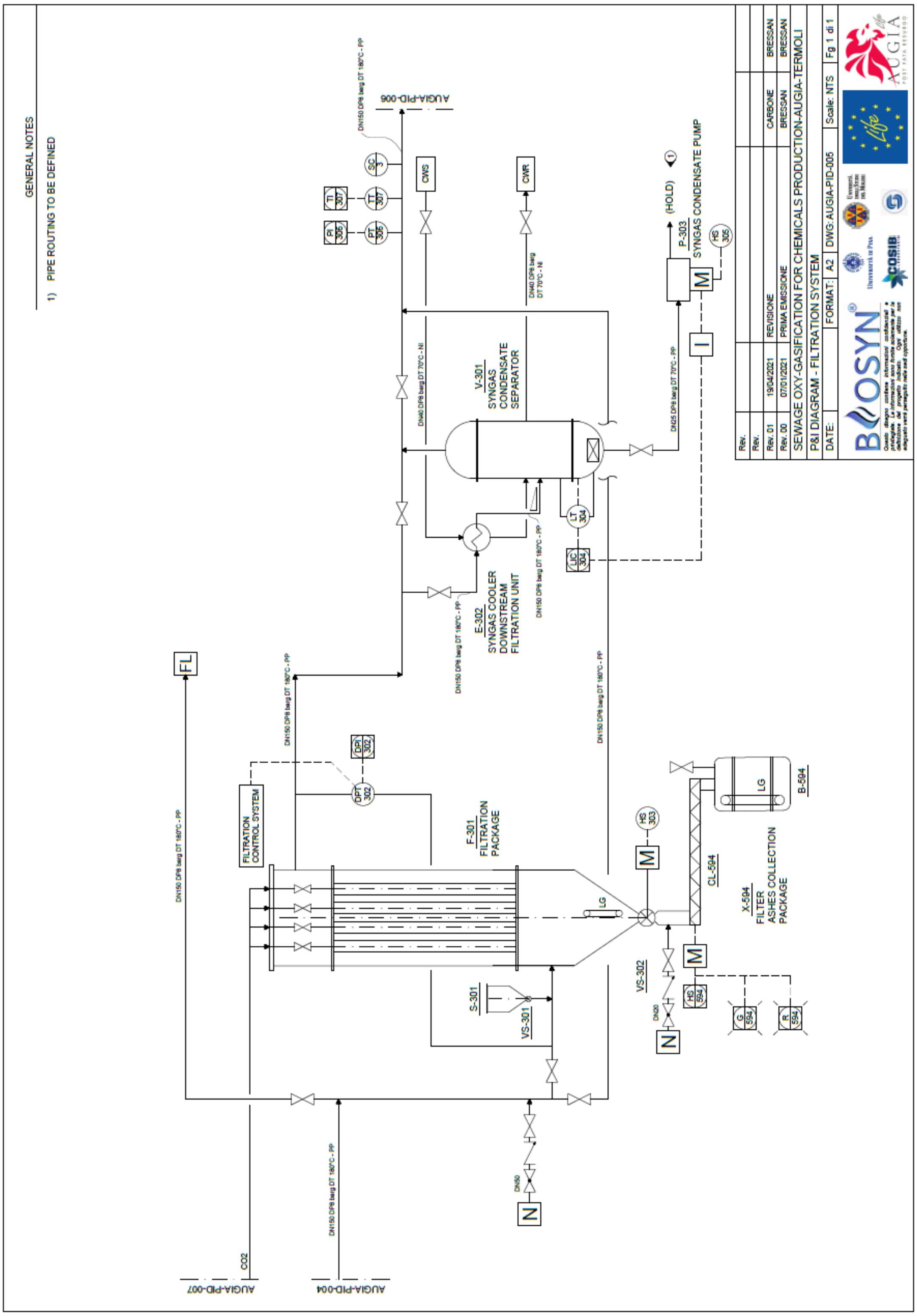
Appendix A

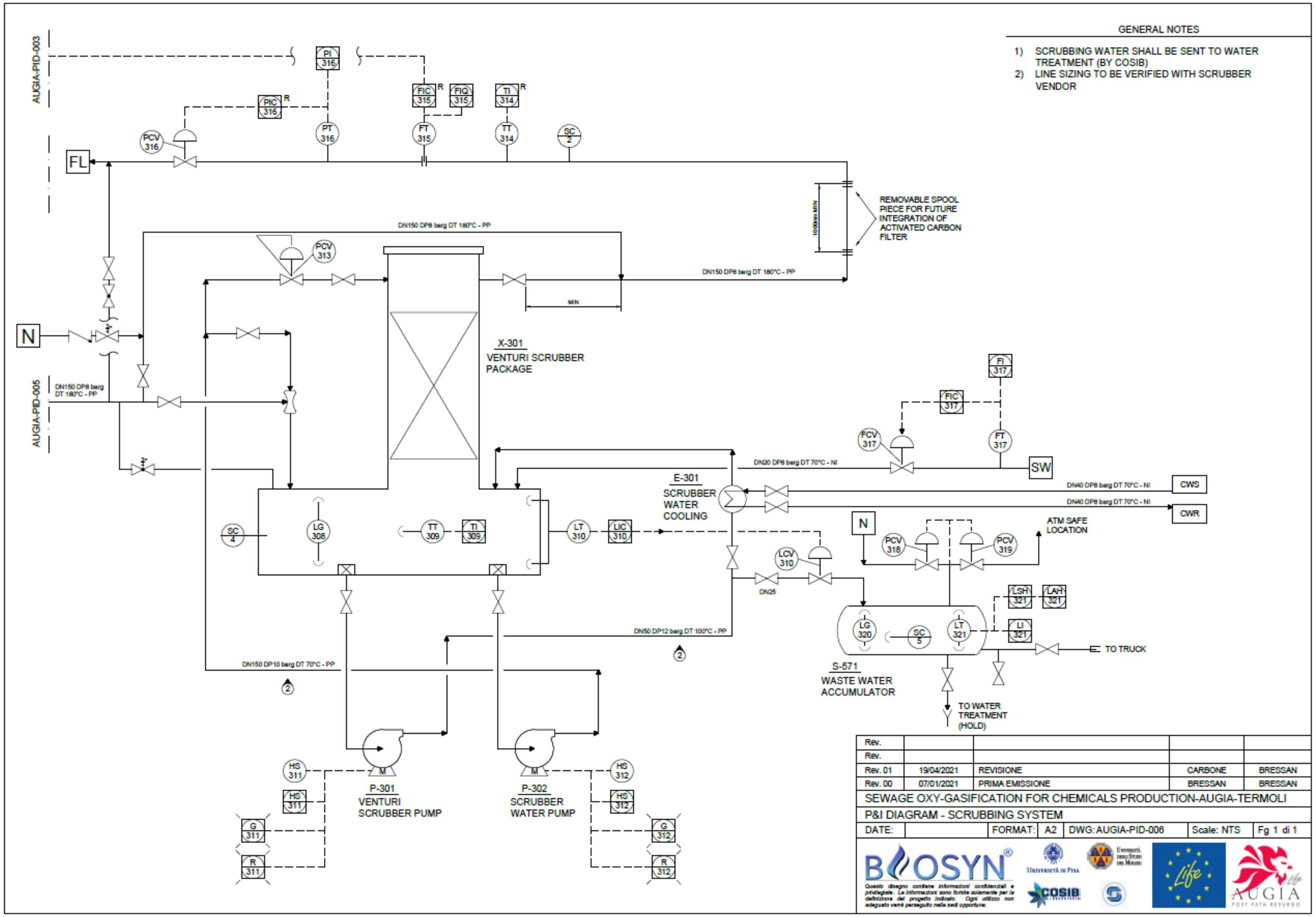

SEWAGE SLUDGE FROM TRUCK
HS
M
BE-101
SLUDGE BELT
CONVEYOR TO DRYER
HS 101
G 101
R 101
DR-101
SEWAGE SLUDGE DRYER
HS 104
G 104
R 104
BE-102
SLUDGE BELT CONVEYOR
TO PELLETIZER
HS 102
G 102
R 102
PE-101
PELLETIZER
HS 105
G 105
R 105
BE-103
SLUDGE BELT CONVEYOR
TO DOSING VESSEL
HS 103
G 103
R 103
SEWAGE SLUDGE TO
DOSING VESSEL
S-202
AUGIA-PID-002
BIOMASS STORAGE COVER
BIOMASS
CL-101
BIOMASS SCREW
CONVEYOR
BIOMASS DISCHARGE BAY
HS 106
G 106
R 106
BE-104
BIOMASS BELT CONVEYOR
TO DOSING VESSEL
HS 107
G 107
R 107
BIOMASS
TO DOSING VESSEL
S-201
GENERAL NOTES
1) THE SYSTEM IS MANUAL, THE OPERATOR IS REQUESTED TO START IT WHEN REQUIRED BY LOW LEVEL IN THE DOSING VESSELS.
Rev.
Rev.
Rev. 01 19/04/2021 REVISIONE CARBONE BRESSAN
Rev. 00 07/01/2021 PRIMA EMISSIONE BRESSAN BRESSAN
SEWAGE OXY-GASIFICATION FOR CHEMICALS PRODUCTION-AUGIA-TERMOLI
P&I DIAGRAM - BIOMASS AND SEWAGE SLUDGE SUPPLY AND DRYING
DATE: -
FORMAT: A2
DWG: AUGIA-PID-001
Scale: NTS
Fg 1 di 1
BIOSYN
Università di Pisa
COSIB
Life
AUGIA

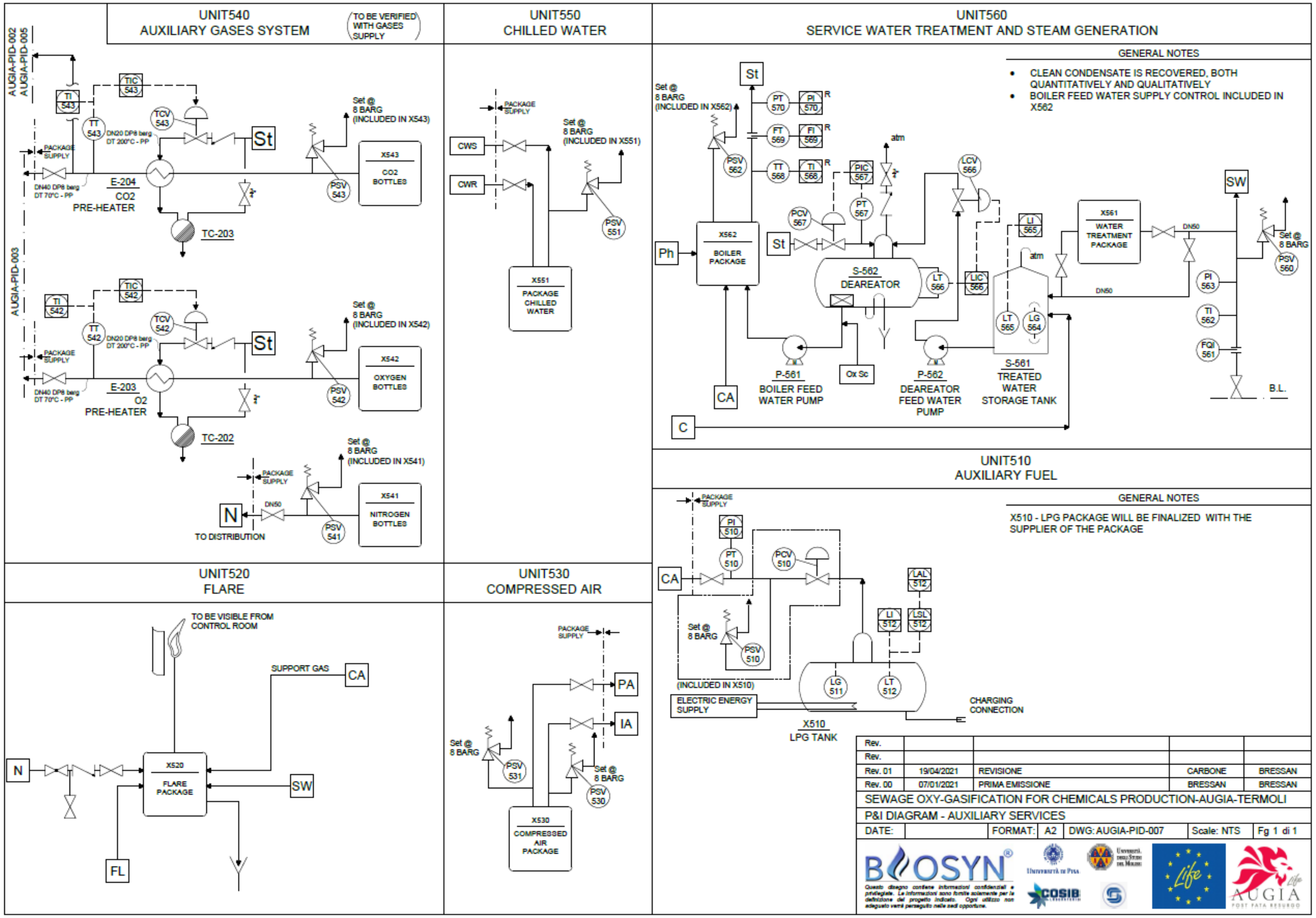

SEWAGE OXY-GASIFICATION FOR CHEMICALS PRODUCTION-AUGIA-TERMOLI
P&I DIAGRAM - BIOMASS AND SEWAGE SLUDGE LOADING
DATE: -
FORMAT: A2
DWG: AUGIA-PID-002
Scale: NTS
Fg 1 di 1
Rev.
Rev. 01
Rev. 00
19/04/2021
07/01/2021
REVISIONE
PRIMA EMISSIONE
CARBONE
BRESSAN
BRESSAN
BRESSAN
BIOSYN
COSIB
AUGIA
Life
AUGIA-PID-001
AUGIA-PID-003
AUGIA-PID-003
AUGIA-PID-007
SEWAGE SLUDGE FROM DRYING SECTION
BIOMASS
S-201
BIOMASS DOSING VESSEL
S-202
SLUDGE DOSING VESSEL
VS-201
VS-202
CL-201
MIXING SCREW CONVEYOR
BE-201
LOADING BELT CONVEYOR
COVER
COVER
LH-201
LOCK HOPPER
VS-203
VG-201
VG-202
CL-202
GASIFIER LOADING SCREW CONVEYOR
TO GASIFICATION REACTOR
FROM GASIFICATION REACTOR
B-202
INERTIZATION BLOWER
atm
DN25
DN25
DN20
CO2
0.5 bar
N
LG
LT 207
LT 210
LT 212
LT 213
LI 212
LI 213
LSH 207
LSL 207
LSH 210
LSL 210
LAH 212
LSH 212
LSL 212
LAL 212
LAH 213
LSH 213
LSL 213
LAL 213
ZSH 208
ZSL 208
ZSH 209
ZSL 209
PDT 211
PDC 211
PDI 211
PDCV 211
HS 201
HS 202
HS 203
HS 204
HS 205
HS 206
G 201
R 201
G 202
R 202
G 203
R 203
G 204
R 204
G 205
R 205
G 206
R 206
G 207
R 207
MP
M
I
I1
I2
I3
SS
open
close
running
stop
start

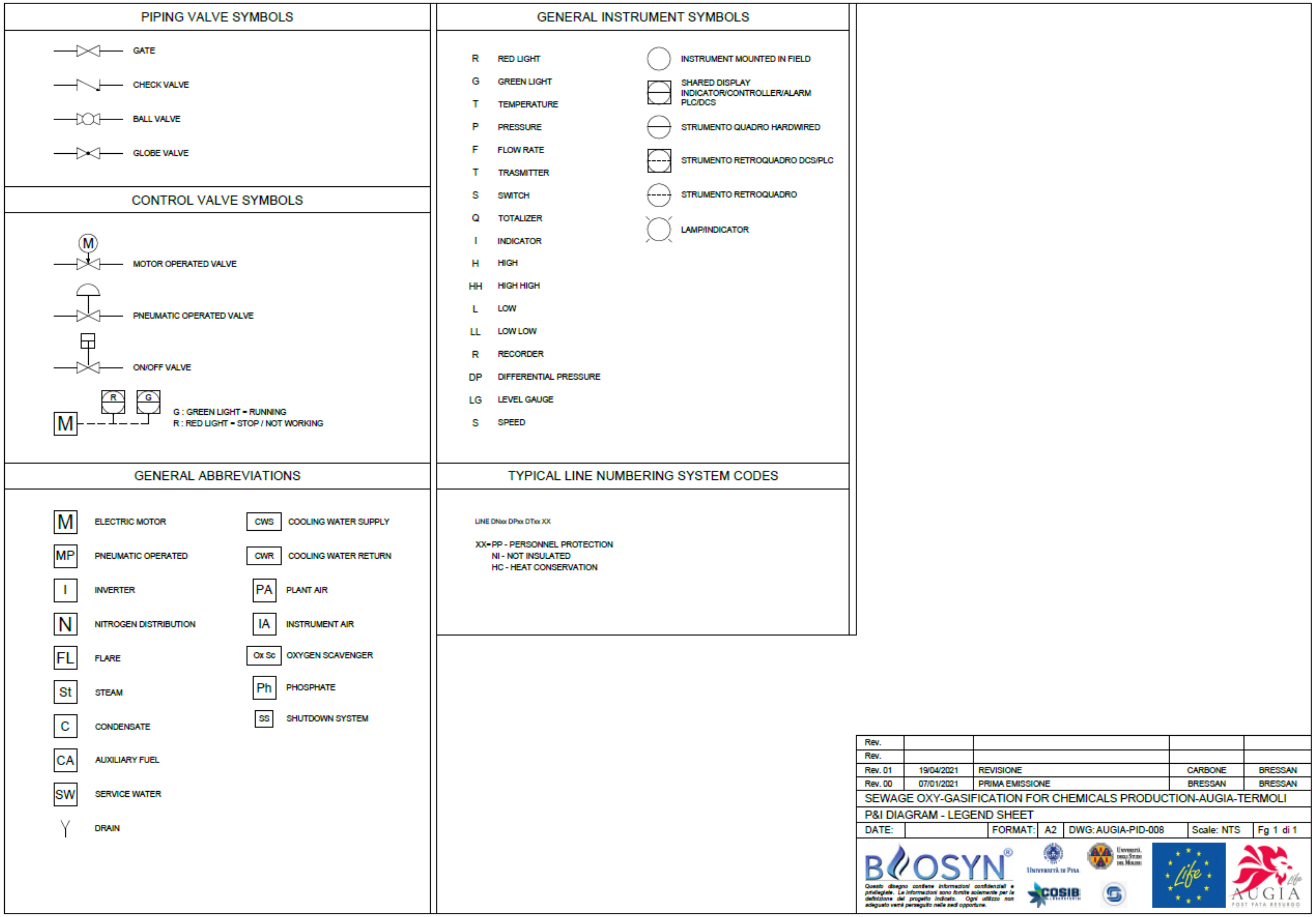

AUGIA-PID-002
AUGIA-PID-006
AUGIA-PID-007
AUGIA-PID-004
Set @ 7.0 BARG
PSV 201
LT 221
stop loading
start loading
LAH 221
LAHH 221
LSH 221
LSHH 221
LSL 221
LAL 221
Y 221
SS
STEAM
OXYGEN
CO2
AIR
St
DN50 DP8 barg DT 180°C - HC
DN40 DP8 barg DT 70°C - PP
DN80 DP8 barg DT 70°C - PP
DN100 DP8 barg DT 400°C - PP
DN200 DP8 barg DT 700°C - HC
DN100
DN50
DN60
DN20
X-201 A/B/C
START-UP
DEVICES
R-201
GASIFICATION
REACTOR
TO EXTRACTION ASHES SCREW
CL-591
B-591
CWS
CWR
LG
X-591
REACTOR ASHES
COLLECTION
PACKAGE
2oo3
GENERAL NOTES
1) START-UP DEVICES (X-201 A/B/C) POSITIONED ENTERING 120° ALONG THE INJECTION AIR GASSIFIER INTERNAL DUCT
2) DISTANCE BETWEEN GASIFICATION REACTOR AND SYNGAS COOLER SHALL BE MINIMUM
3) LINE SIZING TO BE VERIFIED AT MASO DEL GUSTO SITE
Rev.
Rev. 01 19/04/2021 REVISIONE CARBONE BRESSAN
Rev. 00 07/01/2021 PRIMA EMISSIONE BRESSAN BRESSAN
SEWAGE OXY-GASIFICATION FOR CHEMICALS PRODUCTION-AUGIA-TERMOLI
P&I DIAGRAM - GASIFICATION
DATE: FORMAT: A2 DWG: AUGIA-PID-003 Scale: NTS Fg 1 di 1
BIOSYN
COSIB
AUGIA


GENERAL NOTES
1) BEND AND DISTRIBUTOR OF SYNGAS COOLER SHOULD BE EASILY REMOVED IN ORDER TO ALLOW CLEAN-UP OF TUBES
2) SPOOL PIECE TO EVENTUALLY LOCATE A CYCLONE
3) INTERLOCKED VALVES
AIR TO DRYER
FL
DN100 DP8 barg DT 400°C - PP
HS 233
SS
XV 232
XV 233
SC 1
FB
MIN
HS 232
PCV 239
DN200 DP8 barg DT 700°C - PP
DN50
N
E-202
SYNGAS COOLER
SS
TAHH 234
TAH 234
TSHH 234
TSH 234
TIC 234
R
TT 234
TCV 301
TIC 301
TI 301
TT 301
E-303
SYNGAS PRE-HEATER
DN150 DP8 barg DT 180°C - PP
DN150 DP8 barg DT 400°C - PP
AIR
DN100 DP8 barg DT 400°C - PP
DN150 DP8 barg DT 180°C - PP
AUGIA-PID-005
DN80 DP8 barg DT 70°C - PP
AUGIA-PID-003
AIR
DN150 DP8 barg DT 70°C - PP
DN80DP8 barg DT 70°C - PP
SYNGAS
2 1000
DN200 DP8 barg DT 700°C - HC
SYNGAS
LG
VS-205
DN20
N
M
HS 238
CWS
HS 593
M
CL-593
G 593
R 593
CWR
B-593
X-593
SYNGAS COOLER ASHES COLLECTION PACKAGE
B-201
REACTION BLOWER
R 236
G 236
M
HS 236
I
HS 235
C-201
REACTION AIR COMPRESSOR
HS 237
M
I
G 237
R 237
(FUTURE INSTALLATION)
Rev.
Rev.
Rev. 01 | 19/04/2021 | REVISIONE | CARBONE | BRESSAN
Rev. 00 | 07/01/2021 | PRIMA EMISSIONE | BRESSAN | BRESSAN
SEWAGE OXY-GASIFICATION FOR CHEMICALS PRODUCTION-AUGIA-TERMOLI
P&I DIAGRAM - COOLING SECTION
DATE: | FORMAT: A2 | DWG: AUGIA-PID-004 | Scale: NTS | Fg 1 di 1
BIOSYN®
Questo disegno contiene informazioni confidenziali e privilegiate. Le informazioni sono fornite solamente per la definizione del progetto indicato. Ogni utilizzo non adeguato verrà perseguito nelle sedi opportune.
Università di Pisa
Università degli Studi del Molise
COSIB
Life
AUGIA Life
POST FATA RESURGO


GENERAL NOTES
1) PIPE ROUTING TO BE DEFINED
AUGIA-PID-006
DN150 DP8 barg DT 180°C - PP
SC 3
PI 305
PT 305
TI 307
TT 307
CWS
CWR
DN40 DP8 barg DT 70°C - NI
V-301 SYNGAS CONDENSATE SEPARATOR
(HOLD) ①
P-303 SYNGAS CONDENSATE PUMP
HS 305
M
I
DN25 DP8 barg DT 70°C - PP
LT 304
LIC 304
E-302 SYNGAS COOLER DOWNSTREAM FILTRATION UNIT
FL
FILTRATION CONTROL SYSTEM
DPI 302
DPT 302
F-301 FILTRATION PACKAGE
LG
HS 303
B-594
CL-594
X-594 FILTER ASHES COLLECTION PACKAGE
S-301
VS-301
VS-302
DN20
DN50
N
HS 594
G 594
R 594
CO2
AUGIA-PID-007
AUGIA-PID-004
Rev.
Rev. 01 19/04/2021 REVISIONE CARBONE BRESSAN
Rev. 00 07/01/2021 PRIMA EMISSIONE BRESSAN BRESSAN
SEWAGE OXY-GASIFICATION FOR CHEMICALS PRODUCTION-AUGIA-TERMOLI
P&I DIAGRAM - FILTRATION SYSTEM
DATE:
FORMAT: A2
DWG: AUGIA-PID-005
Scale: NTS
Fg 1 di 1
BIOSYN


GENERAL NOTES
1) SCRUBBING WATER SHALL BE SENT TO WATER TREATMENT (BY COSIB)
2) LINE SIZING TO BE VERIFIED WITH SCRUBBER VENDOR
AUGIA-PID-003
AUGIA-PID-005
FL
N
PI 316
PIC 316
PCV 316
PT 316
FIC 315
FIQ 315
FT 315
TI 314
TT 314
SC 2
R
REMOVABLE SPOOL PIECE FOR FUTURE INTEGRATION OF ACTIVATED CARBON FILTER
1000mm MIN
DN150 DP8 barg DT 180°C - PP
MIN
PCV 313
X-301
VENTURI SCRUBBER PACKAGE
DN150 DP8 barg DT 180°C - PP
SC 4
LG 308
TT 309
TI 309
LT 310
LIC 310
E-301
SCRUBBER WATER COOLING
DN20 DP8 barg DT 70°C - NI
DN40 DP8 barg DT 70°C - NI
DN40 DP8 barg DT 70°C - NI
SW
CWS
CWR
FI 317
FIC 317
FCV 317
FT 317
N
PCV 318
PCV 319
ATM SAFE LOCATION
LCV 310
DN25
LSH 321
LAH 321
LI 321
LG 320
SC 5
LT 321
TO TRUCK
S-571
WASTE WATER ACCUMULATOR
TO WATER TREATMENT (HOLD)
DN50 DP12 barg DT 100°C - PP
DN150 DP10 barg DT 70°C - PP
2
P-301
VENTURI SCRUBBER PUMP
P-302
SCRUBBER WATER PUMP
M
HS 311
HS 311
G 311
R 311
HS 312
HS 312
G 312
R 312
Rev.
Rev.
Rev. 01 | 19/04/2021 | REVISIONE | CARBONE | BRESSAN
Rev. 00 | 07/01/2021 | PRIMA EMISSIONE | BRESSAN | BRESSAN
SEWAGE OXY-GASIFICATION FOR CHEMICALS PRODUCTION-AUGIA-TERMOLI
P&I DIAGRAM - SCRUBBING SYSTEM
DATE: | FORMAT: A2 | DWG: AUGIA-PID-006 | Scale: NTS | Fg 1 di 1
BIOSYN
Questo disegno contiene informazioni confidenziali e privilegiate. Le informazioni sono fornite solamente per la definizione del progetto indicato. Ogni utilizzo non adeguato verrà perseguito nelle sedi opportune.
Università di Pisa
COSIB
AUGIA
POST FATA RESURGO


UNIT540
AUXILIARY GASES SYSTEM
TO BE VERIFIED WITH GASES SUPPLY
AUGIA-PID-002
AUGIA-PID-005
AUGIA-PID-003
TIC 543
TI 543
TT 543
TCV 543
DN20 DP8 barg DT 200°C - PP
St
Set @ 8 BARG (INCLUDED IN X543)
X543
CO2 BOTTLES
PSV 543
PACKAGE SUPPLY
DN40 DP8 barg DT 70°C - PP
E-204
CO2
PRE-HEATER
TC-203
TIC 542
TI 542
TT 542
TCV 542
DN20 DP8 barg DT 200°C - PP
Set @ 8 BARG (INCLUDED IN X542)
X542
OXYGEN BOTTLES
PSV 542
E-203
O2
PRE-HEATER
TC-202
Set @ 8 BARG (INCLUDED IN X541)
X541
NITROGEN BOTTLES
PSV 541
DN50
N
TO DISTRIBUTION
UNIT550
CHILLED WATER
CWS
CWR
Set @ 8 BARG (INCLUDED IN X551)
PSV 551
X551
PACKAGE CHILLED WATER
UNIT560
SERVICE WATER TREATMENT AND STEAM GENERATION
GENERAL NOTES
• CLEAN CONDENSATE IS RECOVERED, BOTH QUANTITATIVELY AND QUALITATIVELY
• BOILER FEED WATER SUPPLY CONTROL INCLUDED IN X562
Set @ 8 BARG (INCLUDED IN X562)
PSV 562
PT 570
PI 570
FT 569
FI 569
TT 568
TI 568
R
PIC 567
PT 567
PCV 567
atm
LCV 566
LI 565
LIC 566
LT 566
LT 565
LG 564
Ph
X562
BOILER PACKAGE
S-562
DEAREATOR
P-561
BOILER FEED WATER PUMP
Ox Sc
P-562
DEAREATOR FEED WATER PUMP
S-561
TREATED WATER STORAGE TANK
X561
WATER TREATMENT PACKAGE
DN50
SW
PI 563
TI 562
FQI 561
Set @ 8 BARG
PSV 560
B.L.
CA
C
UNIT510
AUXILIARY FUEL
GENERAL NOTES
X510 - LPG PACKAGE WILL BE FINALIZED WITH THE SUPPLIER OF THE PACKAGE
PACKAGE SUPPLY
PI 510
PT 510
PCV 510
Set @ 8 BARG
PSV 510
(INCLUDED IN X510)
ELECTRIC ENERGY SUPPLY
LAL 512
LI 512
LSL 512
LG 511
LT 512
X510
LPG TANK
CHARGING CONNECTION
UNIT520
FLARE
TO BE VISIBLE FROM CONTROL ROOM
SUPPORT GAS
X520
FLARE PACKAGE
FL
UNIT530
COMPRESSED AIR
PA
IA
Set @ 8 BARG
PSV 531
PSV 530
X530
COMPRESSED AIR PACKAGE
Rev.
Rev.
Rev. 01 | 19/04/2021 | REVISIONE | CARBONE | BRESSAN
Rev. 00 | 07/01/2021 | PRIMA EMISSIONE | BRESSAN | BRESSAN
SEWAGE OXY-GASIFICATION FOR CHEMICALS PRODUCTION-AUGIA-TERMOLI
P&I DIAGRAM - AUXILIARY SERVICES
DATE:
FORMAT: A2
DWG: AUGIA-PID-007
Scale: NTS
Fg 1 di 1
Questo disegno contiene informazioni confidenziali e privilegiate. Le informazioni sono fornite solamente per la definizione del progetto indicato. Ogni utilizzo non adeguato verrà perseguito nelle sedi opportune.



Rev.				
Rev.				
Rev. 01	19/04/2021	REVISIONE	CARBONE	BRESSAN
Rev. 00	07/01/2021	PRIMA EMISSIONE	BRESSAN	BRESSAN

SEWAGE OXY-GASIFICATION FOR CHEMICALS PRODUCTION-AUGIA-TERMOLI
P&I DIAGRAM - LEGEND SHEET

DATE:		FORMAT:	A2	DWG: AUGIA-PID-008	Scale: NTS	Fg 1 di 1

Acronyms

AF ratio	Air to fuel ratio (Nm3 air/kg fuel)
Ash	Ash content in biomass (wt % d.b.)
BFB	Bubbling Fluidised Bed
C	Carbon mass fraction in biomass (wt % d.b.)
CCE	Carbon conversion efficiency (%)
CFB	Circulating Fluidised Bed
CGE	Cold gas efficiency (%)
COSIB	Consortium for Industrial Development of the Biferno valley
Cp	Specific heat capacity (kJ/ kg·K)
CRF	Char reactivity factor
CV	Calorific Value
DESTeC	Department of Energy, Systems, Territory and Construction Engineering
DFB	Dual Fluidised Bed
EM	Equilibrium Model
ER	Equivalence ratio (-)
FC	Fixed carbon content of biomass (% wt d.b.)
FM	Fluidization Models
GC	Gas Chromatography
H	Hydrogen mass fraction in biomass (%)
HGE	Hot gas efficiency (%)
HHV	Higher Heating Value (MJ/kg or MJ/Nm3)
LHV	Lower Heating Value (MJ/kg or MJ/Nm3)
m	Mass flow rate (kg/h or kg/s)
MC	Biomass relative moisture content (wt % w.b.)
MSW	Municipal Solid Waste
N	Nitrogen mass fraction in biomass (wt % d.b.)
O	Oxygen mass fraction in biomass (wt % d.b.)
P	Pressure (kPa)
Q	Heat flux (kW)
QET	Quasi-equilibrium Temperature
RES	Renewable Energy Sources
RMSE	Root Mean Square Error
S	Sulphur mass fraction of biomass (wt % d.b.)
SS	Sewage Sludge

T	Temperature
TGA	Thermogravimetric analysis
UNIMOL	University of Molise
UNIPI	University of Pisa
VM	Volatile mater content of biomass (% wt d.b.)
W	Power output (kW)
WWTP	Wastewater treatment plant
ΔG	Standard Gibbs energy (kJ/kmol)

Bibliography

1. Milieu Ltd; WRc, RPA and DG Environment (2008). *Environmental, Economic and Social Impacts of the Use of Sewage Sludge on Land*, Final report for the European Commission, DG Environment, European Commission.
2. Pérez-Elvira, S. I., Nieto Diez, P., & Fdz-Polanco, F. (2006). *Sludge minimisation technologies*. Reviews in Environmental Science and Bio/Technology, 5(4), 375–398. https://doi.org/10.1007/s11157-005-5728-
3. Greater Vacouver Regional District (GVRD) (2005). *Review of Alternative Technologies for Biosolids Management*, Policy and Planning Department
4. *La valorizzazione energetica dei fanghi di depurazione* (2006) – Quaderni del Dipartimento di Ingegneria Ambientale Università di Trento
5. Livka, R., Chinn, M., Grunden, A., (2011). "*Gasification and synthesis gas fermentation: An alternative route to biofuel production*". Biofuels. 2. 405-419. 10.4155/bfs.11.108.
6. Government of Italy. Ministry of the Environment and Land Protection. *Definition of the admissibility criteria for landfill waste*. Legislative Decree No 3 August 2005, GU n. 201 del 30-8-2005
7. Government of Italy. *Implementation of Directive 86/278/EEC on the Protection of the Environment, and in Particular of the Soil, when Sewage Sludge is Used in Agriculture*. Legislative Decree No. 99, 27 January 1992, GU n.38 del 15-02-1992
8. Basu, P. (2010). "*Biomass Gasification and Pyrolysis. Practical Design*", Academic Press. ISBN 978-0-12-374988-8
9. Lancia, A., Karatza, D., Musmarra, D., & Pepe, F. (1996). *Adsorption of Mercuric Chloride from Simulated Incinerator Exhaust Gas by Means of Sorbalit^{TM} Particles*. Journal Of Chemical Engineering of Japan, 29(6), 939–946. https://doi.org/10.1252/jcej.29.939
10. Karatza, D., Lancia, A., Musmarra, D., Pepe, F., & Volpicelli, G. (1996). *Removal of Mercuric Chloride from Flue Gas by Sulfur Impregnated Activated Carbon*. Hazardous Waste and Hazardous Materials, 13(1), 95–105. https://doi.org/10.1089/hwm.1996.13.95
11. Lancia, A., & Musmarra, D. (1999). *Calcium Bisulfite Oxidation Rate in the Wet Limestone−Gypsum Flue Gas Desulfurization Process*. Environmental Science & Technology, 33(11), 1931–1935. https://doi.org/10.1021/es9805425

12. Mohd Salleh, M. A., Kisiki, N. H., Yusuf, H. M., & Ab Karim Ghani, W. A. W. (2010). *Gasification of Biochar from Empty Fruit Bunch in a Fluidized Bed Reactor*. Energies, 3(7), 1344–1352. https://doi.org/10.3390/en3071344Mohd.

13. James, A., Thring, R., Helle, S., & Ghuman, H. (2012). *Ash Management Review - Applications of Biomass Bottom Ash*. Energies, 5(10), 3856–3873. https://doi.org/10.3390/en5103856.

14. Faaij, A. (2006). *Modern Biomass Conversion Technologies*. Mitigation and Adaptation Strategies for Global Change, 11(2), 343–375. https://doi.org/10.1007/s11027-005-9004-7

15. Kumar, A., Jones, D., & Hanna, M. (2009). *Thermochemical Biomass Gasification: A Review of the Current Status of the Technology*. Energies, 2(3), 556–581. https://doi.org/10.3390/en20300556.

16. Giddey, S., Badwal, S. P. S., Kulkarni, A., & Munnings, C. (2012). *A comprehensive review of direct carbon fuel cell technology*. Progress in Energy and Combustion Science, 38(3), 360–399. https://doi.org/10.1016/j.pecs.2012.01.003.

17. McKendry, P. (2002). *Energy production from biomass (part 1): Overview of biomass.* Bioresource Technology, 83(1), 37–46. https://doi.org/10.1016/S0960-8524(01)00118-3.

18. McKendry, P. (2002). *Energy production from biomass (part 2): Conversion technologies.* Bioresource Technology, 83(1), 47–54. https://doi.org/10.1016/S0960-8524(01)00119-5.

19. Kishore, V. V. N., & Energy and Resources Institute (A c. Di). (2008). *Renewable energy engineering and technology: A knowledge compendium*. The Energy and Resources Institute. ISBN 10: 8179930939

20. Liu, K., Cui, Z., Fletcher, T.H. (2009). *Coal gasification.* In: Hydrogen and Syngas Production and Purification Technologies. John Wiley & Sons, Inc., pp. 156-218.

21. Breault, Ronald W. (2010). *Gasification Processes Old and New: A Basic Review of the Major Technologies*. Energies. 3 (2): 216–240. https://doi:10.3390/en3020216.

22. Warnatz, J., Maas, U., & Dibble, R. W. (2006). *Combustion: Physical and chemical fundamentals, modeling and simulation, experiments, pollutant formation* (4th ed). Springer. ISBN 978-3-540-25992-3

23. Arena, U. (2012). *Process and technological aspects of municipal solid waste gasification. A review*. Waste Management, 32(4), 625–639. https://doi.org/10.1016/j.wasman.2011.09.025

24. Blasi, C.D. (2009). *Combustion and gasification rates of lignocellulosic chars*. Progress in Energy and Combustion Science, 35, 121-140. https://doi.org/10.1016/J.PECS.2008.08.001

25. Barrio, M., Gøbel, B., Risnes, H., Henriksen, U., Hustad, J. E., & Sørensen, L. H. (2001). *Steam gasification of wood char and the effect of hydrogen inhibition on the chemical kinetics*. Progress in thermochemical biomass conversion, 1, 32-46.

26. Reed, T. B. (2002). *Kinetics of char gasification reactions above 500 C* (Chapter 7). Encyclopedia of Biomass Thermal Conversion. Biomass Energy Foundation Press, p. II–289.

27. Devi, L., Ptasinski, K. J., & Janssen, F. J. (2003). *A review of the primary measures for tar elimination in biomass gasification processes*. Biomass and bioenergy, 24(2), 125–140. https://doi.org/10.1016/S0961-9534(02)00102-2

28. Arena, U., Zaccariello, L., & Mastellone, M. L. (2010). *Fluidized bed gasification of waste-derived fuels.* Waste Management, 30(7), 1212–1219. https://doi.org/10.1016/j.wasman.2010.01.038

29. Smoot, L. D., & Smith, P. J. (1985). *Coal Combustion and Gasification*. Springer US. https://doi.org/10.1007/978-1-4757-9721-3.

30. Knoef, H., (2005). *Practical aspects of biomass gasification,* chapter 3 in Handbook Biomass Gasification edited by H. Knoef. BTG-Biomass Technology Group (BTG), ISBN: 90–810068-1–9. Enschede, The Netherlands.

31. Schwager, J., Whiting, K., & Heermann, C. (2001). *Pyrolysis and Gasification of Waste: A Worldwide Business & Technology Review*. Juniper Consultancy Services Ltd.

32. Gagliano, A., Nocera, F., & Bruno, M. (2018). *Simulation models of biomass thermochemical conversion processes, gasification and pyrolysis, for the prediction of the energetic potential*. In Advances in renewable energies and power technologies (pp. 39-85). Elsevier. ISBN 9780128131855,

33. Milne, T. A., Evans, R. J., & Abatzoglou, N. (1998). *Biomass gasifier 'tars': their nature, formation, and conversion,* NREL Technical Report (NREL/TP-570–25357), National Energy Laboratory. Golden, Colorado, USA.

34. Basu, P. (2013) *Biomass gasification, pyrolysis and torrefaction: practical design and theory*, 2nd ed.; Elsevier: London; 3, 199−313.

35. Rauch, R. (2003). *Biomass gasification to produce synthesis gas for fuels and chemicals*, report made for IEA Bioenergy Agreement., Task 33, Thermal Gasification of Biomass.

36. Rampling, T. W., & Gill, P. J. (1994). *Fundamental research on the thermal treatment of wastes and biomass*. Harwell Laboratory, Energy Technology Support Unit: Vol. 208 ETSU-B/T-1/00208/REP/2

37. Lucas, C. (2005). *High temperature air/steam gasification of biomass in an updraft fixed bed batch type gasifier*. Doctoral thesis. Stockholm (Sweden): KTH, School of Industrial Engineering and Management, Energy Furnace and Technology.

38. Reed, T. B., & Das, A. (1988). *Handbook of biomass downdraft gasifier engine systems*. Biomass Energy Foundation

39. Knoef, H. A. M. (2000). *Inventory of Biomass Gasifier Manufacturers and Installations: Final Report to European Commission*. Contract DIS/1734/98-NL. Biomass Tecnology Group BV.

40. Pedroso, D. T., Machín, E. B., Silveira, J. L., & Nemoto, Y. (2013). *Experimental study of bottom feed updraft gasifier*. Renewable energy, 57, 311-316. https://doi.org/10.1016/j.renene.2013.01.056

41. Bermudez, J. M., & Fidalgo, B. (2016). *Production of bio-syngas and bio-hydrogen via gasification*. Handbook of biofuels production (2nd Edition), 15, 431-494, Woodhead Publishing, , ISBN 9780081004555

42. Ugwuodo, C. B., Ugwuoke, E. C., Owabor, C. N., & Ogbeide, S. E. (2020). *Fundamental Review and Analysis of Gasifier Performance and Gasification Model*. International journal of Engineering, Business and Management (IJEBM), 4(1), 12-20.

43. Yamazaki, T., Kozu, H., Yamagata, S., Murao, N., Ohta, S., Shiya, S., & Ohba, T. (2005). *Effect of superficial velocity on tar from downdraft gasification of biomass*. Energy & Fuels, 19(3), 1186-1191. https://doi.org/10.1021/ef0497210

44. Narvaez, I., Orio, A., Aznar, M. P., & Corella, J. (1996). *Biomass gasification with air in an atmospheric bubbling fluidized bed. Effect of six operational variables on the quality of the produced raw gas*. Industrial & Engineering Chemistry Research, 35(7), 2110-2120. https://doi.org/10.1021/ie9507540

45. Lv, P. M., Xiong, Z. H., Chang, J., Wu, C. Z., Chen, Y., & Zhu, J. X. (2004). *An experimental study on biomass air–steam gasification in a fluidized bed*. Bioresource technology, 95(1), 95-101. https://doi.org/10.1016 /j.biortech.2004.02.003

46. Wang, Y., Yoshikawa, K., Namioka, T., & Hashimoto, Y. (2007). *Performance optimization of two-staged gasification system for woody biomass*. Fuel Processing Technology, 88(3), 243-250. https://doi.org/10.1016 /j.fuproc.2006.10.002

47. Kumar, A., Eskridge, K., Jones, D. D., & Hanna, M. A. (2009). *Steam–air fluidized bed gasification of distillers grains: Effects of steam to biomass ratio, equivalence ratio and gasification temperature*. Bioresource Technology, 100(6), 2062-2068. https://doi.org/10.1016/j.biortech.2008.10.011

48. Grimshaw, A. J., & Lago, A. (2010, November). *Small Scale Energos Gasification Technology*. 3rd Int. In Symposium on Energy from Biomass and Waste (pp. 8-11). CISA Publisher, Italy. ISBN 978-88-6265-008-3.

49. Hankalin, V., Helanti, V., & Isaksson, J. (2011, October). *High efficiency power production by gasification*. In Thirteenth International Waste Management and Landfill Symposium (pp. 3-7)., S. Margherita di Pula, Cagliari, Italy. CISA Publisher, Italy. ISBN 978-88-6265-000-7.

50. Kaupp, A., & Goss, J. R. (1981). *State-of-the-art report for small scale (to 50 kw) gas producer-engine systems* (No. PB-85-102002/XAD). California Univ., Davis (USA). Dept. of Agricultural Engineering.

51. Maschio, G., Lucchesi, A., & Stoppato, G. (1994). *Production of syngas from biomass*. Bioresource Technology, 48(2), 119-126. https://doi.org/10.1016/0960-8524(94)90198-8

52. Lucas, C., Szewczyk, D., Blasiak, W., & Mochida, S. (2004). *High-temperature air and steam gasification of densified biofuels*. Biomass and bioenergy, 27(6), 563-575. https://doi.org/10.1016/j.biombioe.2003.08.015

53. Trocchi M., *La gassificazione di biomasse lignocellulosiche per l'elettrogenerazione in impianti di piccola potenzialità*, Università degli studi di Roma "La Sapienza".

54. Neeft, J., Knoef, H. A., & Onaji, P. (1999). Behaviour of tar in biomass gasification systems. Tar related problems and their solutions. Novem Report No. 9919. Energy from Waste and Biomass (EWAB), Netherlands.

55. Herguido, J., Corella, J., & Gonzalez-Saiz, J. (1992). *Steam gasification of lignocellulosic residues in a fluidized bed at a small pilot scale. Effect of the type of feedstock*. Industrial & engineering chemistry research, 31(5), 1274-1282. https://doi.org/10.1021/ie00005a006

56. Gil, J., Corella, J., Aznar, M. P., & Caballero, M. A. (1999). *Biomass gasification in atmospheric and bubbling fluidized bed: effect of the type of gasifying agent on the product distribution*. Biomass and bioenergy, 17(5), 389-403. https://doi.org/10.1016/S0961-9534(99)00055-0

57. Kinoshita, C. M., Wang, Y., & Zhou, J. (1994). *Tar formation under different biomass gasification conditions*. Journal of Analytical and Applied Pyrolysis, 29(2), 169-181. https://doi.org/10.1016/0165-2370(94)00796-9

58. Yamazaki, T., Kozu, H., Yamagata, S., Murao, N., Ohta, S., Shiya, S., & Ohba, T. (2005). *Effect of superficial velocity on tar from downdraft gasification of biomass*. Energy & Fuels, 19(3), 1186-1191. https://doi.org/10.1021/ef0497210

59. Walawender, W. P., Hoveland, D. A., & Fan, L. T. (1985). *Steam Gasification of Aplha Cellulose in a Fluid Bed Reactor*. Fundamentals of thermochemical biomass conversion, 897-910. https://doi.org/10.1007/978-94-009-4932-4_49

60. Walawender, W. P., Ganesan, S., & Fan, L. T. (1981). *Steam gasification of manure in a fluid bed. Influence of limestone as a bed additive*. In Symposium Papers. Energy from biomass and wastes V. Lake Buena Vista, Florida, January 26-30, 1981 (pp. 517-527). Institute of Gas Technology.

61. Corella, J., Aznar, M. P., Gil, J., & Caballero, M. A. (1999*). Biomass gasification in fluidized bed: where to locate the dolomite to improve gasification?*. Energy & Fuels, 13(6), 1122-1127. https://doi.org/10.1021/ef990019r

62. Rapagnà, S., Jand, N., Kiennemann, A., & Foscolo, P. U. (2000). *Steam-gasification of biomass in a fluidised-bed of olivine particles*. Biomass and bioenergy, 19(3), 187-197. https://doi.org/10.1016/S0961-9534(00)00031-3

63. Bergman, P. C., Van Paasen, S. V., & Boerrigter, H. (2002). *The novel "OLGA" technology for complete tar removal from biomass producer gas*. In Pyrolysis and gasification of biomass and waste. Expert meeting, Strasbourg, France.

64. Bhattacharya, S. C., Siddique, A. M. M. R., & Pham, H. L. (1999). *A study on wood gasification for low-tar gas production*. Energy, 24(4), 285-296. https://doi.org/10.1016/S0360-5442(98)00091-7

65. Elliott, D. C., & Baker, E. G. (1986). *The effect of catalysis on wood-gasification tar composition.* Biomass, 9(3), 195-203. https://doi.org/10.1016/0144-4565(86)90089-2

66. Pan, Y. G., Roca, X., Velo, E., & Puigjaner, L. (1999). Removal of tar by secondary air in fluidised bed gasification of residual biomass and coal. Fuel, 78(14), 1703-1709. https://doi.org/10.1016/S0016-2361(99)00118-0

67. Ekström, C., Lindman, N., & Pettersson, R. (1985). *Catalytic conversion of tars, carbon black and methane from pyrolysis/gasification of biomass*. Fundamentals of thermochemical biomass conversion, 601-618. https://doi.org/10.1007/978-94-009-4932-4_34

68. Huber, G. W., Iborra, S., & Corma, A. (2006). *Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering*. Chemical reviews, 106(9), 4044-4098. https://doi.org/10.1021/cr068360d

69. Han, J., & Kim, H. (2008). *The reduction and control technology of tar during biomass gasification/pyrolysis: an overview*. Renewable and sustainable energy reviews, 12(2), 397-416. https://doi.org/10.1016/j.rser.2006.07.015

70. Abu El-Rub, Z., Bramer, E. A., & Brem, G. (2004). *Review of catalysts for tar elimination in biomass gasification processes*. Industrial & engineering chemistry research, 43(22), 6911-6919. https://doi.org/10.1021/ie0498403

71. Baggio P., Baratieri M., Grigiante M., Ragazzi M. (2006) *Gassificazione Di Fanghi Di Depurazione*, Quaderni del Dipartimento SAN 5: “La Valorizzazione Energetica Dei Fanghi Di Depurazione” a cura Rada E.C., Ragazzi M., Ziglio G. Dipartimento di Ingegneria Civile e Ambientale – Università degli Studi di Trento,

72. Manya, J. J., Sánchez, J. L., Abrego, J., Gonzalo, A., & Arauzo, J. (2006). *Influence of gas residence time and air ratio on the air gasification of dried sewage sludge in a bubbling fluidised bed*. Fuel, 85(14-15), 2027-2033.

73. Dogru, M., Midilli, A., & Howarth, C. R. (2002). *Gasification of sewage sludge using a throated downdraft gasifier and uncertainty analysis*. Fuel Processing Technology, 75(1), 55-82. https://doi.org/10.1016/S0378-3820(01)00234-X

74. Petersen, I., & Werther, J. (2005). *Experimental investigation and modeling of gasification of sewage sludge in the circulating fluidized bed*. Chemical Engineering and Processing: Process Intensification, 44(7), 717-736.

75. Phuphuakrat, T., Nipattummakul, N., Namioka, T., Kerdsuwan, S., & Yoshikawa, K. (2010). *Characterization of tar content in the syngas produced in a downdraft type fixed bed gasification system from dried sewage sludge*. Fuel, 89(9), 2278-2284. https://doi.org/10.1016/j.fuel.2010.01.015

76. Paterson, N., Reed, G. P., Dugwell, D. R., & Kandiyoti, R. (2002, January). *Gasification tests with sewage sludge and coal/sewage sludge mixtures in a pilot scale, air blown, spouted bed gasifier*. In Turbo Expo: Power for Land, Sea, and Air (Vol. 36061, pp. 197-202).

77. Pinto, F., Lopes, H., André, R. N., Dias, M., Gulyurtlu, I., & Cabrita, I. (2007). *Effect of experimental conditions on gas quality and solids produced by sewage*

sludge co-gasification. 1. Sewage sludge mixed with coal. Energy & Fuels, 21(5), 2737-2745.

78. Pinto, F., André, R. N., Lopes, H., Dias, M., Gulyurtlu, I., & Cabrita, I. (2008). *Effect of experimental conditions on gas quality and solids produced by sewage sludge co-gasification. 2. Sewage sludge mixed with biomass*. Energy & fuels, 22(4), 2314-2325.

79. Rauch, R., Hrbek, J., & Hofbauer, H. (2014). *Biomass gasification for synthesis gas production and applications of the syngas*. Wiley Interdisciplinary Reviews: Energy and Environment, 3(4), 343-362. https://doi.org/10.1002/wene.97

80. Ren, J., Liu, Y. L., Zhao, X. Y., & Cao, J. P. (2020). *Methanation of syngas from biomass gasification: An overview*. International Journal of Hydrogen Energy, 45(7), 4223-4243. https://doi.org/10.1016/j.ijhydene.2019.12.023

81. Wang, S., Bi, X., & Wang, S. (2015). *Thermodynamic analysis of biomass gasification for biomethane production*. Energy, 90, 1207-1218.

82. Cao, Y., Wang, Q., Du, J., & Chen, J. (2019). *Oxygen-enriched air gasification of biomass materials for high-quality syngas production*. Energy conversion and management, 199, 111628. https://doi.org/10.1016/j.enconman.2019.05.054

83. Pettinau, A. (2008). *Valutazione del processo di gassificazione con miscele di ossigeno e CO2*, report RSE/2009/15, ENEA

84. Billaud, J., Valin, S., Peyrot, M., & Salvador, S. (2016). *Influence of H2O, CO2 and O2 addition on biomass gasification in entrained flow reactor conditions: Experiments and modelling*. Fuel, 166, 166-178.

85. Xiang, Y., Cai, L., Guan, Y., Liu, W., Cheng, Z., & Liu, Z. (2020). *Study on the effect of gasification agents on the integrated system of biomass gasification combined cycle and oxy-fuel combustion*. Energy, 206, 118131. https://doi.org/10.1016/j.energy.2020.118131

86. Kajitani, S., Suzuki, N., Ashizawa, M., & Hara, S. (2006). CO2 gasification rate analysis of coal char in entrained flow coal gasifier. Fuel, 85(2), 163-169. https://doi.org/10.1016/j.fuel.2005.07.024

87. Zheng, C., & Liu, Z. (Eds.). (2018). *Oxy-fuel combustion: fundamentals, theory and practice*. Elsvier. ISBN 978-0-12-812135-0

88. Broer, K. M., Woolcock, P. J., Johnston, P. A., & Brown, R. C. (2015). *Steam/oxygen gasification system for the production of clean syngas from switchgrass*. Fuel, 140, 282-292. https://doi.org/10.1016/j.fuel.2014.09.078

89. Kurkela, E., Kurkela, M., & Hiltunen, I. (2016). *Steam–oxygen gasification of forest residues and bark followed by hot gas filtration and catalytic reforming of tars: Results of an extended time test*. Fuel Processing Technology, 141, 148-158. https://doi.org/10.1016/j.fuproc.2015.06.005

90. Liu, L., Huang, Y., Cao, J., Liu, C., Dong, L., Xu, L., & Zha, J. (2018). *Experimental study of biomass gasification with oxygen-enriched air in fluidized bed gasifier*. Science of the Total Environment, 626, 423-433.

91. Sandeep, K., & Dasappa, S. (2014). *Oxy–steam gasification of biomass for hydrogen rich syngas production using downdraft reactor configuration*. International journal of energy research, 38(2), 174-188.

92. Sandeep, K., & Dasappa, S. (2014). *First and second law thermodynamic analysis of air and oxy-steam biomass gasification*. International Journal of Hydrogen Energy, 39(34), 19474-19484. https://doi.org/10.1016/j.ijhydene.2014.09.134

93. Shayan, E., Zare, V., & Mirzaee, I. J. E. C. (2018). *Hydrogen production from biomass gasification; a theoretical comparison of using different gasification agents*. Energy Conversion and management, 159, 30-41,

94. Jaganathan, V. M., Mohan, O., & Varunkumar, S. (2019). *Intrinsic hydrogen yield from gasification of biomass with oxy-steam mixtures*. International journal of hydrogen energy, 44(33), 17781-17791.

95. Dudyński, M. (2019). *Novel oxygen-steam gasification process for high quality gas from biomass*. Detritus-Multidisciplinary Journal for Waste Resources and Residues, 6, 68-76.

96. Jaganathan, V. M., & Varunkumar, S. (2019). *Net carbon-di-oxide conversion and other novel features of packed bed biomass gasification with O2/CO2 mixtures*. Fuel, 244, 545-558. https://doi.org/10.1016/j.fuel.2019.01.171

97. International Organization for Standardization (2016). *Solid biofuels - Conversion of analytical results from one basis to another* (ISO Standard No. 16993:2016). https://www.iso.org/standard/70098.html

98. Pinelli, G., & Zerlia, T. (2005). *The energetic and commercial characterization of vegetable biomass*. La Rivista dei Combustibili, 59, (1), 23-37.

99. Grob, R. L., & Barry, E. F. (Eds.). (2004). *Modern practice of gas chromatography. John Wiley & Sons*. ISBN 0-471-22983-0

100. Mermet, J.-M., Otto, M., & Valcárcel Cases, M. (A c. Di). (2004). *Analytical chemistry: A modern approach to analytical science* (2nd ed). Wiley-VCH. ISBN 978-3-527-30590-2.

101. The European Committee for Standardization (2005). *Biomass Gasification - Tar and Particles in Producer Gases - Sampling and Analysis* prepared by CEN task force BT/TF 143 WI CSC 03002.4TC

102. The European Committee for Standardization (2006). *Biomass gasification - Tar and particles in product gases - Sampling and analysis* (CEN/TS 15439:2006)

103. The European Committee for Standardization (2005) *Sampling and analysis of tar and particles in biomass producer gases*. Technical Report prepared under CEN BT/TF 143 “Organic contamination (“tar”) in biomass producer gases”.

104. Damartzis, T., Michailos, S., & Zabaniotou, A. (2012). *Energetic assessment of a combined heat and power integrated biomass gasification–internal combustion engine system by using Aspen Plus®*. Fuel processing technology, 95, 37-44. https://doi.org/10.1016/j.fuproc.2011.11.010

105. Baruah, D., & Baruah, D. C. (2014). *Modeling of biomass gasification: A review*. Renewable and Sustainable Energy Reviews, 39, 806-815. https://doi.org/10.1016/j.rser.2014.07.129

106. Patra, T. K., & Sheth, P. N. (2015). *Biomass gasification models for downdraft gasifier: A state-of-the-art review*. Renewable and Sustainable Energy Reviews, 50, 583-593. https://doi.org/10.1016/j.rser.2015.05.012

107. Safarian, S., Unnþórsson, R., & Richter, C. (2019). *A review of biomass gasification modelling*. Renewable and Sustainable Energy Reviews, 110, 378-391. https://doi.org/10.1016/j.rser.2019.05.003

108. Han, J., Liang, Y., Hu, J., Qin, L., Street, J., Lu, Y., & Yu, F. (2017). *Modeling downdraft biomass gasification process by restricting chemical reaction equilibrium with Aspen Plus*. Energy conversion and management, 153, 641-648. https://doi.org/10.1016/j.enconman.2017.10.030

109. Zainal, Z. A., Ali, R., Lean, C. H., & Seetharamu, K. N. (2001). *Prediction of performance of a downdraft gasifier using equilibrium modeling for different biomass materials*. Energy conversion and management, 42(12), 1499-1515. https://doi.org/10.1016/S0196-8904(00)00078-9

110. Formica, M., Frigo, S., & Gabbrielli, R. (2016). *Development of a new steady state zero-dimensional simulation model for woody biomass gasification in a full-scale plant*. Energy conversion and management, 120, 358-369.

111. Fu, Z., Zhang, Y., Liu, H., Zhang, B., & Li, B. (2013). *Simulation analysis of biomass gasification in an autothermal gasifier using Aspen Plus*. In Cleaner combustion and sustainable world (pp. 479-483). Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-642-30445-3_66

112. Ramzan, N., Ashraf, A., Naveed, S., & Malik, A. (2011). *Simulation of hybrid biomass gasification using Aspen plus: A comparative performance analysis for food, municipal solid and poultry waste*. Biomass and bioenergy, 35(9), 3962-3969. https://doi.org/10.1016/j.biombioe.2011.06.005

113. Gumz, W. (1950). *Gas producers and blast furnaces: theory and methods of calculation*. Wiley: Hoboken, NJ, USA.

114. Zanzi, R., Sjöström, K., & Björnbom, E. (2002). *Rapid pyrolysis of agricultural residues at high temperature*. Biomass and Bioenergy, 23(5), 357-366. https://doi.org/10.1016/S0961-9534(02)00061-2

115. Schuster, G., Löffler, G., Weigl, K., & Hofbauer, H. (2001). *Biomass steam gasification–an extensive parametric modelling study*. Bioresource technology, 77(1), 71-79. https://doi.org/10.1016/S0960-8524(00)00115-2

116. Li, X. T., Grace, J. R., Lim, C. J., Watkinson, A. P., Chen, H. P., & Kim, J. R. (2004). *Biomass gasification in a circulating fluidized bed*. Biomass and bioenergy, 26(2), 171-193. https://doi.org/10.1016/S0961-9534(03)00084-9

117. Donolo G, Simon GD, Fermeglia M. *Steady state simulation of energy production from biomass by molten carbonate fuel cells*. J Power Sources. 2006;158(2):1282–9. https://doi.org/10.1016/S0961-9534(03)00084-9

118. Ye, G., Xie, D., Qiao, W., Grace, J. R., & Lim, C. J. (2009). *Modeling of fluidized bed membrane reactors for hydrogen production from steam methane reforming with Aspen Plus*. International journal of hydrogen energy, 34(11), 4755-4762. https://doi.org/10.1016/j.ijhydene.2009.03.047

119. Demirbaş, A. (2001). *Carbonization ranking of selected biomass for charcoal, liquid and gaseous products*. Energy Conversion and Management, 42(10), 1229-1238. https://doi.org/10.1016/S0196-8904(00)00110-2

120. Peng, D. Y., & Robinson, D. B. (1976). *A new two-constant equation of state*. Industrial & Engineering Chemistry Fundamentals, 15(1), 59-64. https://doi.org/10.1021/i160057a011

121. Aspen Plus (2001). *Aspen Plus Physical Property: Physical Property Methods and Models*. Aspen Technology, Inc., Cambridge, MA

122. Aspen Plus (2000). *Aspen Plus User Guide* Aspen Technology, Inc., Cambridge, MA

123. Frigo, S., Gabbrielli, R., & Seggiani, M. (2017). *Comparison between equilibrium and kinetic models with aspen plus for a full-scale biomass downdraft gasifier*. In Proceedings of 25th European Biomass Conference & Exhibition EUBCE, 12-15 June 2017, Stockholm, Sweden.

124. Hobbs, M. L., Radulovic, P. T., & Smoot, L. D. (1992). *Modeling fixed-bed coal gasifiers*. AIChE Journal, 38(5), 681-702. https://doi.org/10.1002/aic.690380506

125. Suuberg, E. M., Peters, W. A., & Howard, J. B. (1978). *Product composition and kinetics of lignite pyrolysis*. Industrial & Engineering Chemistry Process Design and Development, 17(1), 37-46. https://doi.org/10.1021/i260065a008

126. Shao, J., Yan, R., Chen, H., Wang, B., Lee, D. H., & Liang, D. T. (2008). *Pyrolysis characteristics and kinetics of sewage sludge by thermogravimetry Fourier transform infrared analysis*. Energy & Fuels, 22(1), 38-45.

127. Diyoke, C., Gao, N., Aneke, M., Wang, M., & Wu, C. (2018). *Modelling of down-draft gasification of biomass–An integrated pyrolysis, combustion and reduction process*. Applied Thermal Engineering, 142, 444-456.

128. Ratnadhariya, J. K., & Channiwala, S. A. (2009). *Three zone equilibrium and kinetic free modeling of biomass gasifier–a novel approach*. Renewable energy, 34(4), 1050-1058. https://doi.org/10.1016/j.renene.2008.08.001

129. Ngo, S. I., Nguyen, T. D., Lim, Y. I., Song, B. H., Lee, U. D., Choi, Y. T., & Song, J. H. (2011). *Performance evaluation for dual circulating fluidized-bed steam gasifier of biomass using quasi-equilibrium three-stage gasification model*. Applied Energy, 88(12), 5208-5220.

130. Wurzenberger, J. C., Wallner, S., Raupenstrauch, H., & Khinast, J. G. (2002). *Thermal conversion of biomass: Comprehensive reactor and particle modeling*. AIChE Journal, 48(10), 2398-2411. https://doi.org/10.1002/aic.690481029

131. Rath, J., & Staudinger, G. (2001). *Cracking reactions of tar from pyrolysis of spruce wood*. Fuel, 80(10), 1379-1389. https://doi.org/10.1016/S0016-2361(01)00016-3

132. Kaushal, P., Abedi, J., & Mahinpey, N. (2010). *A comprehensive mathematical model for biomass gasification in a bubbling fluidized bed reactor*. Fuel, 89(12), 3650-3661. https://doi.org/10.1016/j.fuel.2010.07.036

133. Radmanesh, R., Chaouki, J., & Guy, C. (2006). *Biomass gasification in a bubbling fluidized bed reactor: experiments and modeling*. AIChE Journal, 52(12), 4258-4272. https://doi.org/10.1002/aic.11020

134. Tinaut, F. V., Melgar, A., Perez, J. F., & Horrillo, A. (2008). *Effect of biomass particle size and air superficial velocity on the gasification process in a downdraft fixed bed gasifier. An experimental and modelling study*. Fuel processing technology, 89(11), 1076-1089. https://doi.org/10.1016/j.fuproc.2008.04.010

135. Barman, N. S., Ghosh, S., & De, S. (2012). Gasification of biomass in a fixed bed downdraft gasifier–A realistic model including tar. Bioresource technology, 107, 505-511. https://doi.org/10.1016/j.biortech.2011.12.124

136. Merrick, D. (1983). *Mathematical models of the thermal decomposition of coal: 1. The evolution of volatile matter*. Fuel, 62(5), 534-539.

137. Mott, R. A., & Spooner, C. E. (1940). *The calorific value of carbon in coal: the Dulong relationship*. Fuel, 19(226-231), 242-251.

138. Sharma, A. K. (2011). *Modeling and simulation of a downdraft biomass gasifier 1. Model development and validation*. Energy Conversion and Management, 52(2), 1386-1396. https://doi.org/10.1016/j.enconman.2010.10.001

139. Wen, C. Y., Chen, H., & Onozaki, M. (1982). User's manual for computer simulation and design of the moving-bed coal gasifier. Final report (No. DOE/MC/16474-1390). West Virginia Univ., Morgantown (USA). Dept. of Chemical Engineering. https://doi.org/10.2172/6422177

140. Mandl, C., Biedermann, F., & Obernberger, I. (2009). *Updraft fixed-bed gasification of softwood pellets: mathematical modelling and comparison with experimental data*. In Proceedings of the 17th European Biomass Conference and Exhibition (pp. 750-758).

141. Di Blasi, C. (2004). *Modeling wood gasification in a countercurrent fixed-bed reactor*. AIChE journal, 50(9), 2306-2319. https://doi.org/10.1002/aic.10189

142. Yang, W., Ponzio, A., Lucas, C., & Blasiak, W. (2006). *Performance analysis of a fixed-bed biomass gasifier using high-temperature air*. Fuel processing technology, 87(3), 235-245. https://doi.org/10.1016/j.fuproc.2005.08.004

143. Wen, C. Y., & Chaung, T. Z. (1979). *Entrainment coal gasification modeling*. Industrial & Engineering Chemistry Process Design and Development, 18(4), 684-695. https://doi.org/10.1021/i260072a020

144. Soave, G. (1972). *Equilibrium constants from a modified Redlich-Kwong equation of state*. Chemical engineering science, 27(6), 1197-1203.

145. Barontini, F., Frigo, S., Gabbrielli, R., & Sica, P. (2021). *Co-gasification of woody biomass with organic and waste matrices in a down-draft gasifier: An experimental and modeling approach*. Energy Conversion and Management, 245, 114566.

146. Biagini, E., Barontini, F., & Tognotti, L. (2014). *Gasification of agricultural residues in a demonstrative plant: Corn cobs*. Bioresource technology, 173, 110-116. https://doi.org/10.1016/j.biortech.2014.09.086
147. Biagini, E., Barontini, F., & Tognotti, L. (2015). *Gasification of agricultural residues in a demonstrative plant: Vine pruning and rice husks*. Bioresource technology, 194, 36-42. https://doi.org/10.1016/j.biortech.2015.07.016
148. Han, J., & Kim, H. (2008). *The reduction and control technology of tar during biomass gasification/pyrolysis: an overview*. Renewable and sustainable energy reviews, 12(2), 397-416. https://doi.org/10.1016/j.rser.2006.07.015
149. Gai, C., & Dong, Y. (2012). *Experimental study on non-woody biomass gasification in a downdraft gasifier*. International Journal of hydrogen energy, 37(6), 4935-4944. https://doi.org/10.1016/j.ijhydene.2011.12.031
150. Gautam, G., Adhikari, S., Thangalazhy-Gopakumar, S., Brodbeck, C., Bhavnani, S., & Taylor, S. (2011). *Tar analysis in syngas derived from pelletized biomass in a commercial stratified downdraft gasifier*. BioResources, 6(4), 4653-4661.
151. Susastriawan, A. A. P., & Saptoadi, H. (2017). *Small-scale downdraft gasifiers for biomass gasification: A review*. Renewable and Sustainable Energy Reviews, 76, 989-1003. https://doi.org/10.1016/j.rser.2017.03.112