

École polytechnique de Louvain

Technical requirements for bio-methane production from woody biomass and added value of hydrogen input in the process

Author: **Olivia MAHY**

Supervisor: **Hervé JEANMART**

Readers: **Arnaud ROUANET, Emmanuel DE JAEGER**

Academic year 2021–2022

Master [120] in Mechanical Engineering

Abstract

This master thesis is rooted in the global challenge of renewable energy integration into energy mix. More precisely, it takes part in answering the question "How to overcome the intermittency of renewable energies". To this end, it studies the production of methanation by thermal process and its potential coupling with the production of hydrogen that can be produced thanks to renewable energies.

To do this, a literature review was first carried out in order to collect data and to synthesise the theories of biomass gasification and syngas methanation processes. It was also concluded that the first is already well developed while the second is still in the research stage.

Secondly, a model was developed to model the gasification process and the methanation process separately. These models are based on the equilibrium model. The first model is solved using the stoichiometric method, while the second model is solved using the non-stoichiometric method.

These two models were coupled and used to model the whole process of bio-methane production from biomass, through gasification, methanation and finally to obtain bio-methane. Two cases were analysed. A first case where the gasification is done with oxygen as gasification agent and where a hydrogen supply has to be provided. A second case where the gasification is done with steam as gasification agent.

The addition of hydrogen in the process of bio-methane production with oxygen gasification is well cost effective. The energy input contained in the hydrogen is well used and is largely recovered in the bio-methane. There is little loss of hydrogen and carbon in this case. The model predicts a CO₂ methanation in the pre-methanation reactor for the vapor gasification leading to a large consumption of hydrogen and a small consumption of carbon monoxide. However, an observation of the gas composition before and after the pre-methanation reactor in GoBiGas lets think that in reality, the reactor does not behave like this. A CO methanation take place in the reactor. There are some limits of the model.

Acknowledgements

Firstly, I would like to thank my supervisor, Pr. Hervé Jeanmart. I am grateful for having the opportunity to work on this project. Thank you for the follow-up throughout the year, your availability and your flexibility regarding the constraints of the agenda of my year.

The second person related to the academic framework that I would like to thank is Arnaud Rouanet. Great thanks you for your precious advice and for your enthusiasm. Thank you very much for all the time you spent answering my questions and reflecting with me. Thank you for giving me a tour of the gasifier at UCLouvain to make the subject of my thesis more concrete.

I would also like to thank the team of De Smet Engineers and Contractors for welcoming me for an internship. Thank you for giving me the opportunity (not offered in the frame of my studies) to get a foot in the world of work and business. I learned a lot during this internship.

A special thanks goes to my family who supported me during these long years of study. Thank to my father, my mother, my sister and Phoebe for cheerin me up in the moments of failure and celebrating with me in the moments of success. Thank you for proofreading this thesis.

Finally, thanks to my friends. The ones I knew before I start my studies and the ones I met on the spot. Thank you for making these years more enjoyable. A special thanks to Leila and Marie-Ombeline for being great partners in all the projects we did together.

Content

List of Figures	viii
List of Tables	ix
List of Abbreviations	xi
1 Introduction	1
2 Literature review about production of bio-SNG from woody biomass	5
2.1 Gasification	6
2.1.1 Process	6
2.1.2 Reactors	7
2.1.3 Gasifying agent	11
2.2 Methanation	12
2.2.1 Process	12
2.2.2 Reactors	16
2.2.3 Catalyst	16
2.3 Gas cleaning	17
2.3.1 Syngas quality improvement	18
2.3.2 Thermodynamic state adjustment	18
2.3.3 Hydrogen to dioxide ratio improvement	18
2.4 Overview of current applications	18
3 Process modelisation	25
3.1 Theory of equilibrium modeling	26
3.2 Gasification	26
3.3 Methanation	29
4 Results	31
4.1 Modelisation objectives and strategy	31
4.2 Gasification	31
4.2.1 Oxygen gasification	32
4.2.2 Vapor gasification	34
4.2.3 Cooler 0	36
4.3 Methanation	36
4.3.1 Hydrogen to carbon monoxide ratio adaptation	36
4.3.2 Gas composition through the process	37
4.4 Mass and energy balance	44
4.4.1 Secondary inlet flux	44
4.4.2 Hydrogen and carbon distribution	46

4.4.3	Energy	48
5	Discussion	51
6	Appendix	53
6.1	GoBiGas set-up	54
6.2	Mass balance for oxygen gasification case	55
6.3	Mass balance for vapor gasification case	56

List of Figures

1.1	Wind energy production in Walloon Region on July 16, 2022 [1]	1
1.2	Solar energy production in Walloon Region on July 16, 2022 [1]	2
1.3	Storage Technologies characteristics [2]	2
2.1	General scheme of a bio-methane production process	5
2.2	General scheme of a bio-methane production process with gasification step highlighted	6
2.3	Updraft gasifier	8
2.4	Downdraft gasifier	8
2.5	Bubbling fluidized gasifier	9
2.6	Circulating fluidized gasifier	9
2.7	Top-fed entrained gasifier	10
2.8	Side-fed entrained gasifier	10
2.9	Application range of biomass for each types of gasifier [3]	11
2.10	General scheme of a bio-methane production process with methanation step highlighted	12
2.11	Equilibrium constant values of the reactions involved in methanation [4]	13
2.12	Product composition of CO methanation at equilibrium [4]	14
2.13	Effects of pressure and temperature on CO conversion (a), CH ₄ selectivity (b), CH ₄ yield (c), and carbon yield (d) in the process of CO methanation [4]	15
2.14	General scheme of a bio-methane production process with gas cleaning step highlighted	17
2.15	Maturity of energy storage technologies [5]	19
2.16	Scheme of the complete set-up of the GoBiGas demonstration plant	21
2.17	Scheme of the dual fluidized bed used in GoBiGas	22
2.18	Example of the Topsøe TREMP™ technology [6]	23
3.1	Overall scheme of the process set up modeled in the context of this master thesis	25
3.2	Scheme of the gasification step set up	26
3.3	Equilibrium constants of intermediate gasification reactions	28
3.4	Scheme of the methanation step set up	29
4.1	Scheme of the gasification step set up	31
4.2	ER evolution regarding the air inlet temperature for gasification with oxygen as GA	32
4.3	H ₂ /CO evolution regarding the air inlet temperature for gasification with oxygen as GA	32
4.4	Equilibrium temperature evolution regarding the equivalence ratio for gasification with oxygen as GA	33
4.5	H ₂ /CO Equilibrium temperature evolution regarding the equivalence ratio for gasification with oxygen as GA	33
4.6	Hydrogen to carbon monoxide ratio evolution with ER=0.25 and SBR=1.21	34

4.7	Hydrogen to biomass ratio evolution with SBR and steam inlet temperature . .	35
4.8	Equilibrium temperature evolution with SBR and steam inlet temperature . . .	35
4.9	Scheme of the methanation step set-up	36
4.10	Methan molar fraction at every step of the process where the letters refer to the step in figure 4.9	37
4.11	Methan content and temperature evolution through the methanation stages where the letters refer to the step in figure 4.9	38
4.12	Evolution of mole numbers for individual gase through the methanation stages where the letters refer to the step in figure 4.9	39
4.13	Hydrogen to carbon ratio evolution through the methanation stages where the letters refer to the step in figure 4.9	40
4.14	Syngas mole evolution	42
4.15	Methane fraction evolution	42
4.16	Syngas mole evolution	42
4.17	Methane fraction evolution	42
4.18	Scheme of water electrolysis technology	44
4.19	Sankey diagram of hydrogen flux for the oxygen gasification case	47
4.20	Sankey diagram of hydrogen flux for the vapor gasification case	47
4.21	Sankey diagram of carbon flux for the oxygen gasification case	48
4.22	Sankey diagram of carbon flux for the vapor gasification case	48
4.23	Evolution of the through the process. The purple part is the LHV coming from the hydrogen	49
6.1	Schematic of the process layout for the GoBiGas demonstration unit [7]. 1: Heat generation, 2:Gasification, 3:methanation, 4: compression, 5:Gas cleaning	54

List of Tables

2.1	Biomass characteristics matching with the gasifier the most adapted to it	10
2.2	Syngas quality coming from each type of gasifiers	11
2.3	Recommended size of biomass for each type of gasifier	11
4.1	Composition of the syngas coming out from the gasifier in the case of gasification with oxygen as GA	34
4.2	Composition of the syngas coming out from the gasifier in the case of gasification with vapor as GA	36
4.3	Gas composition in moles percentage for the oxygen and vapor gasification cases at the outlet of the Cooler 0	36
4.4	Gas composition at step C in moles percentage for the oxygen and vapor gasification cases an GoBiGas	37
4.5	GoBiGas dry gas composition of the gas in mole percentages before and after the pre-methanation [8]	43
4.6	GoBiGas dry gas composition in number of moles before and after the pre-methanation for 1 mole of inlet syngas	43
4.7	Additional inlet flux needed for each cases in number of moles for one mole of biomass entering the process	46
4.8	Summarize of the different energy efficiencies for each case	50

List of Abbreviations

CAPEX Capital expenditure.

CGE Cold gas efficiency.

daf dry and ash free.

ER Equivalence ratio.

GA Gasification Agent.

HHV Higher heating value.

IE Intermitent energy.

LHV Lower heating value.

RME rapeseed oil methyl.

SBR Steam to biomass ratio.

SMR Steam methane reforming.

TREMP Topsøe Recycle Energy-efficient Methanation Process.

WGS Water Gas Shift.

Chapter 1

Introduction

Energy has been at the heart of human societies' development. At all times, humankind uses sources of energy from nature. Before the industrial revolution, energy was mainly provided by mechanical forces coming from humans or animals. The energy coming from wood combustion was essentially for domestic uses or for foundry. The later discovery of coal and fuel was the spark for an explosion of technological development. Fossil energy utilisation has evolved from decade to decade since then. The consumption has considerably grown with the society and the technology evolution [9].

Fossil energy is however closely related to three significant problems of our era which are air pollution, global warming, and energy insecurity [10]. To face these problems, the question of energy transition toward a more sustainable system is on the table. In this aim, renewable energies are attracting more interest. The U.S Energy information administration (IEA) defines renewable energy as energy coming from naturally refilling sources but limited in supply. This definition includes biomass, hydro-power, geothermal, wind and solar [11].

Even if renewable energies are key to energy transition, there remains issues to solve. Fossil fuels can give energy at any time and in few seconds while wind and solar energy are more constrained. Wind and solar energies are called intermittent because they can strongly vary and can remain without production for a long time. Wind energy production depends on the wind and can strongly vary during the day such as the wind energy production on the 16th of July 2022 plot in the figure1.1.

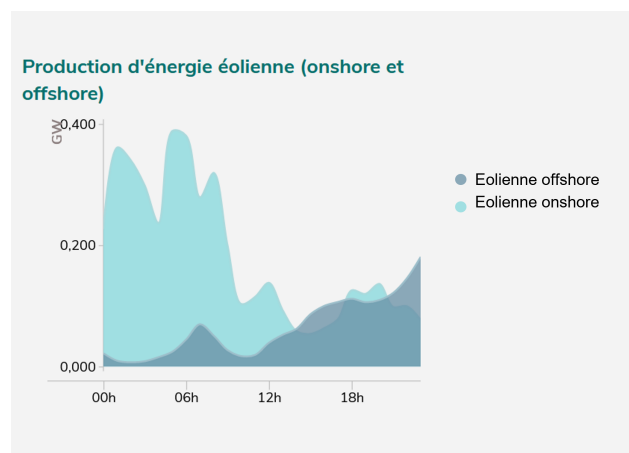


Figure 1.1: Wind energy production in Walloon Region on July 16, 2022 [1]

Solar energy is only produced during the day and depends on the cloudiness of the sky. The passage of a large cloud reduces the energy produced at the time. The energy production on sunny days resembles that of the 16th of July 2022 plot in the figure 1.2.

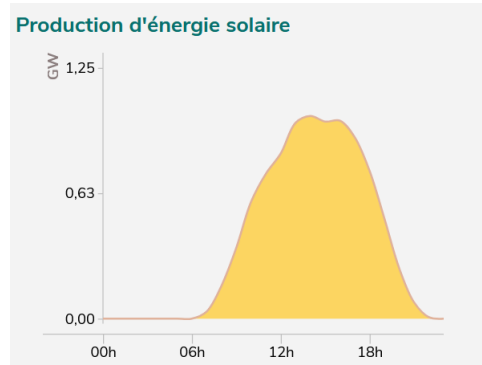


Figure 1.2: Solar energy production in Walloon Region on July 16, 2022 [1]

Unfortunately, it is not possible to align our society with the variable curves of intermittent energy (IE) production. This would imply that energy consumption is only possible when the sun is shining or when the wind is blowing. It is why the integration of renewable energy to the energy system should be combined with energy storage facilities. There are several possible energy storage such as batteries, hydrogen, hydraulic gravity storage, methane and more... Two major characteristics of energy storage are their discharging time and their storage capacity. The graph 1.3 expresses the fact that Power-to-Gas Methane store the more Wh and can have the longer duration time.

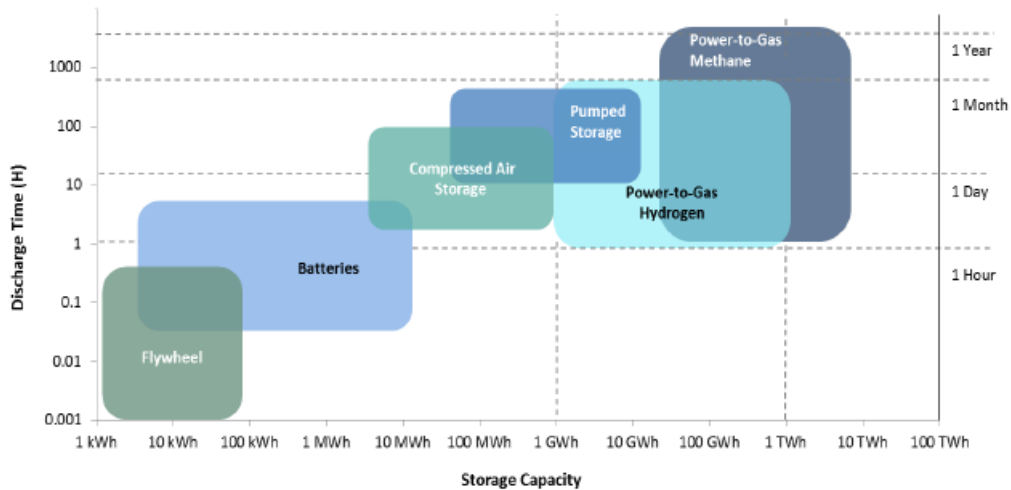


Figure 1.3: Storage Technologies characteristics [2]

Power to gas technologies use electrical power to produce a gaseous fuel (methane for example). The production of bio-methane in particular consists of a synthesis reaction of methane from hydrogen and carbon monoxide or carbon dioxide contents in a syngas. This syngas is coming from the gasification process of biomass.

The methane production may need an hydrogen supply depending on the technology. This hydrogen can come from water electrolysis using intermittent energy. This could be a way to stock intermittent energy.

The aim of this thesis is first to synthesis the theory behind the methanation process, to assess its technical requirements and to draw up an inventory of the technologies available today. To this end, a bibliographical search was carried out and presented in the first chapter.

All this information is then used to model the main technologies used in the bio-methane production process and to create a model of the entire process.

This model allows to study the reactions of the process when changing parameters such as the input biomass, the type of gasification or the addition of hydrogen. The set-up modelled is essentially based on the GoBiGas project presented in chapter 1, with the difference that it uses a downdraft gasifier and not a dual fluidised gasifier.

Finally, the interest of introducing hydrogen into the system was studied. For this purpose, the model was used to study two main cases while keeping the GoBiGas model for comparison. These two cases are :

- Oxygen gasification coupled with the GoBiGas methanation set-up and an additional hydrogen supply.
- Vapor gasification coupled with the GoBiGas methanation set-up

The flux and the gas quality will be compared and an energy balance for the two cases will be made.

Chapter 2

Literature review about production of bio-SNG from woody biomass

The process of biomethane production is a complex process requiring many steps in order to reach the gas quality needed to be allowed to inject the gas into the grid. The procedure can be divided into three main steps : the gasification, the gas cleaning and the methanation.

As shown in the figure 2.1, biomass is first converted into a gas called synthesis gas (also called syngas) during gasification. Subsequently, the syngas is cleaned to avoid chemical deactivation in the methanation stage. During the cleaning process, the syngas has to be compressed because methanation requires higher pressure. To ensure a good ratio of hydrogen and carbon monoxide for the methanation, a step is added. This step adjusts the ratio if necessary. It can be realized with a Water gas shift (WGS) reactor or an addition of hydrogen.

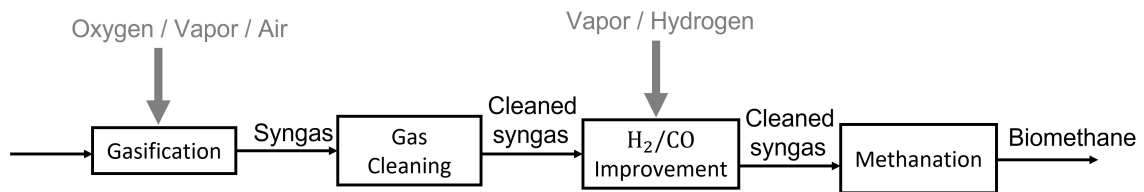


Figure 2.1: General scheme of a bio-methane production process

In addition to the biomass, secondary inputs are needed during the process. The gasification section needs an input of gasifying agent (GA) that can be vapor, oxygen, air or a mixture of them. The step of hydrogen to carbon monoxide improvement may require vapor or hydrogen depending on the technology.

The first point of this chapter explains what happens in a gasifier reactor. The second section explains what happens in a methanation reactor and what are the syngas quality requirements. This section leads to the last point where the gas cleaning process required between gasification and methanation is explained. At the end of this chapter, a state of the art of the current technologies used so far is presented.

2.1 Gasification

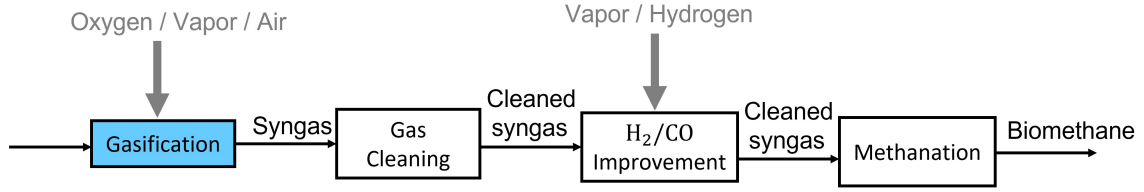


Figure 2.2: General scheme of a bio-methane production process with gasification step highlighted

2.1.1 Process

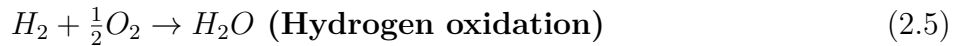
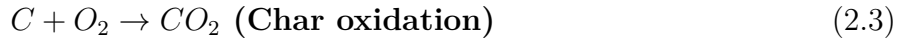
Gasification is the first step in the biomass transformation process. This reaction takes place in a reactor called gasifier and converts carbonaceous material (biomass in this case) into a combustible gas [12].

During gasification, the biomass goes through different stages. Considering a non-dry biomass, the moisture is first removed from the biomass and evaporated into steam. Next, the biomass goes through a thermal decomposition called pyrolysis where the solid material is decomposed into light gases, condensable volatiles (tar) and solid char . This step is endothermic and needs an heat supply. The reaction can be written as followed [13] :



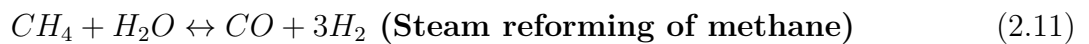
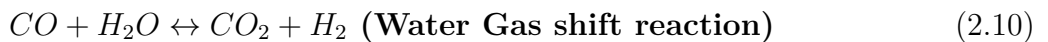
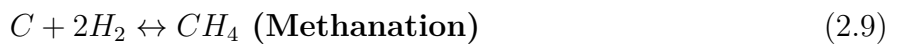
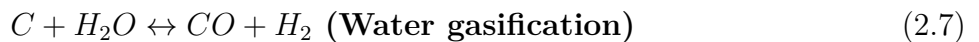
(2.2)

After that, the volatile substances undergo partial oxidation. They are partially oxidized to form carbon monoxide, carbon dioxide and steam. This reaction is exothermic :



(2.6)

In the above equation, the char is assumed to be pure carbon. When oxygen is consumed by the combustion, several reductions occur without oxygen. This last stage is called gasification. The main reactions that take place during the gasification are the following ones [13] :



(2.12)

In the gasification step, the two first and last reactions are endothermic while the other three are exothermic [14] [15]:

Reaction	$\Delta H_{298^{\circ}C}$ kJ/mol
Char reforming	135.8
Boduard reaction	169.8
Methanation	-91.0
Water gas shift (WGS) reaction	-34.0
Complete oxidation of carbon	-395.0
Steam reforming methane	206

2.1.2 Reactors

One of the main parameters of gasification is the type of gasifier. Gasifiers can be classified into three categories depending on how the biomass moves through the gasifier and the way it is in contact with the gasification agent (GA). A distinction is made between fixed bed, fluidised bed and entrained flow gasifiers.

Fixed bed gasifiers can be divided into two types depending on where the GA is introduced.

In updraft gasifier or counter current gasifier, biomass is introduced at the top of the reactor while the air intake is situated at the bottom of the gasifier. The syngas leaves the reactor at the top. In this type of gasifier, the combustion zone is under the pyrolysis zone, meaning that the tar produced by the pyrolysis does not go through the combustion zone. The product syngas of a updraft fixed bed gasifier has a higher tar content. However, the updraft gasifier can deal with higher moisture content fuel. The syngas being collected at the top of the gasifier, it meets the biomass going down. The heat contents in the syngas is available to vaporize the biomass moisture. [16]

In the downdraft gasifier, the biomass is also introduced at the top but the GA intake is at or above the oxidation zone of the gasifier and the syngas is collected on the bottom side. Here, the gas produced by the pyrolysis goes through the oxidation zone reducing the tar content of the syngas.

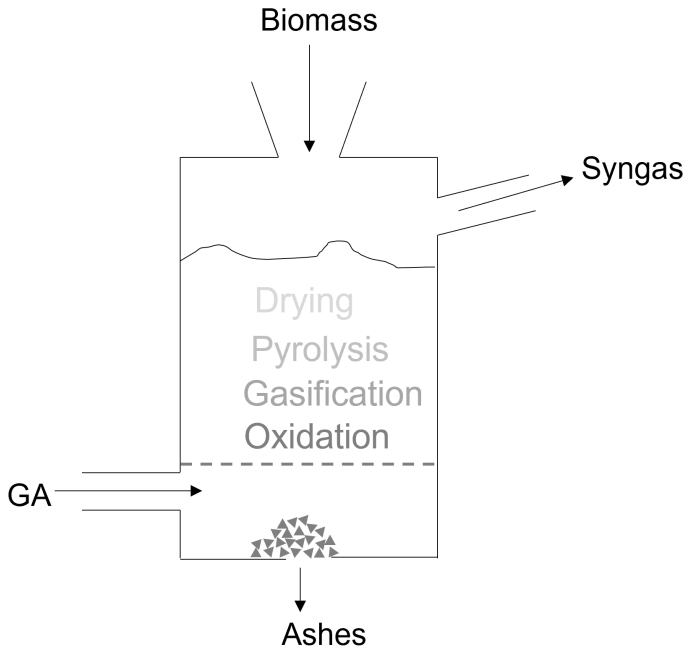


Figure 2.3: Updraft gasifier

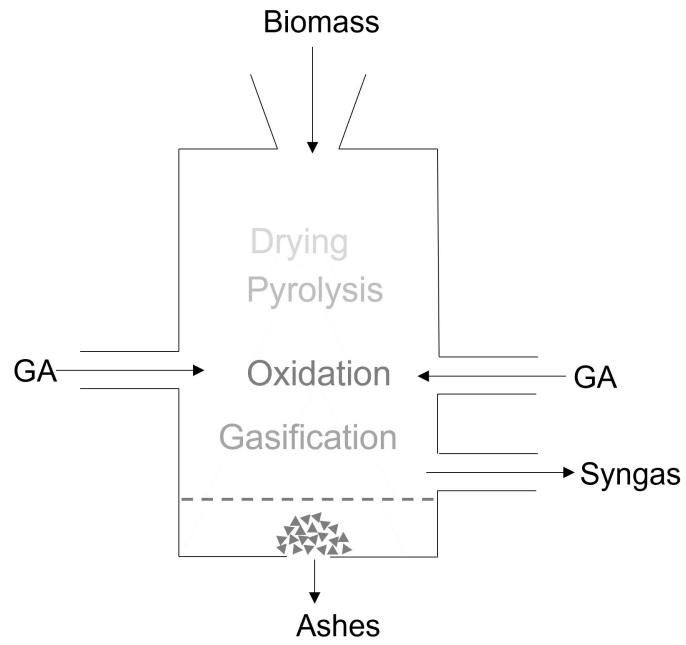


Figure 2.4: Downdraft gasifier

The second type of gasifier is the fluidized bed gasifier. The main principle of fluidized bed gasifier is to introduce the GA at a sufficiently high enough velocity so that the bed particles are in suspension in the reactor [17]. There are two main types of fluidized bed: the bubbling and the circulating fluidized bed reactors.

In the bubbling fluidized bed, the flow rate of the GA is increased beyond the minimum fluidization condition. The minimum fluidization condition occurs when the gas velocity is high enough to reach a situation where the particles are just suspended in the upward flowing gas. In the bubbling gasifier, the velocity is higher and reaches the point where large instabilities with channel and bubbling of the gas occur and when there are vigorous movements of solids. However, the bed does not expand much more than its initial volume [17]. In this type of gasifier, the char and syngas are produced through pyrolysis in the bed reactor. The syngas goes up to the middle of the reactor where reforming reactions take place while the char is consumed in the bed material [14]).

In the circulating fluidized bed, the velocity of the GA is higher and exceeds the bubbling fluidized bed regime. The bed expands beyond its initial volume and will be distributed in the entire reactor volume such that bed particles are leaving the reactor with the gas. They are then separated with a cyclon and recirculated in the gasifier. Before entering the reactor, the GA is heating up in an heat exchanger where the hot fluid is the bed material coming from the cyclon [16]. The pyrolysis occurs at the level of the GA intake and the syngas reacts upper in the reactor [14].

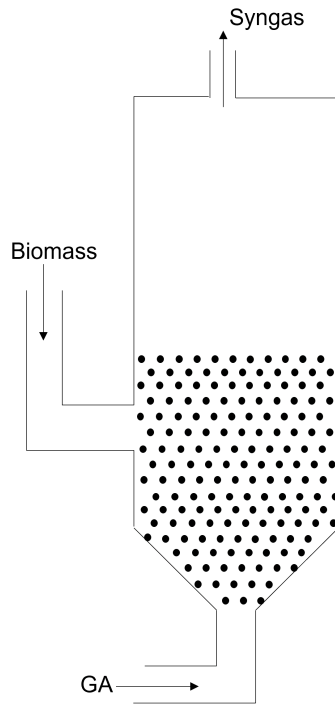


Figure 2.5: Bubbling fluidized gasifier

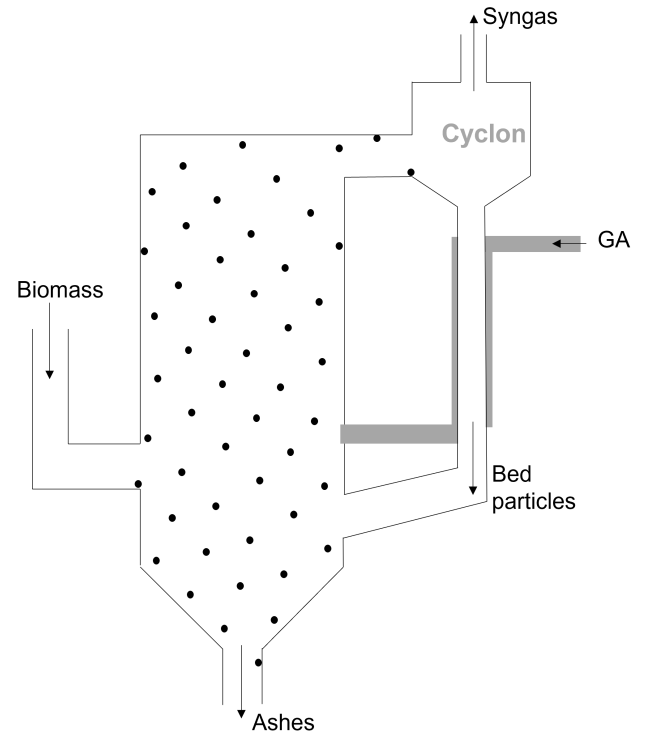


Figure 2.6: Circulating fluidized gasifier

The last type is the entrained flow gasifier. This reactor is fed with fine particles pulverized at high velocity in the form of a jet and co-currently with the GA [13]. The high velocity of the jet forms a re-circulation zone in the admission zone. As the particles are very small, they heat up rapidly due to the radiative heat transfer from the hot walls of the reactor and from the hot gases downstream. They begin to burn with a lack of oxygen consuming almost all the oxygen. The residual char of the reaction goes through CO_2 and H_2O gasification downstream of this combustion zone.

There are two different families of entrained flow gasifiers depending on the way they are fed.

In the top-fed gasifier the reactor is fed from the top with a jet of biomass and GA, while the syngas is taken from the lower side.

In the side-fed reactor, the fuel is injected through horizontal nozzles located in the lower section of the reactor and placed opposing each other and the syngas is collected in the top of the reactor. The syngas is produced in the first stage gasifier. In the second stage feed it is devolatilized and gasified using the heat content in the syngas coming from the first stage [12].

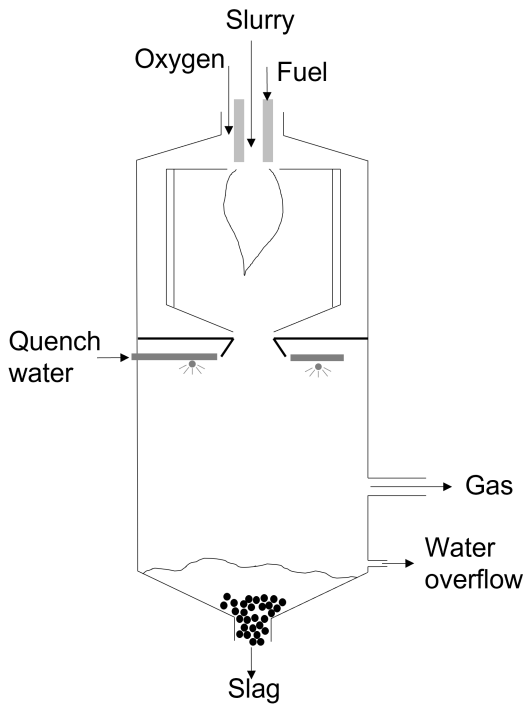


Figure 2.7: Top-fed entrained gasifier

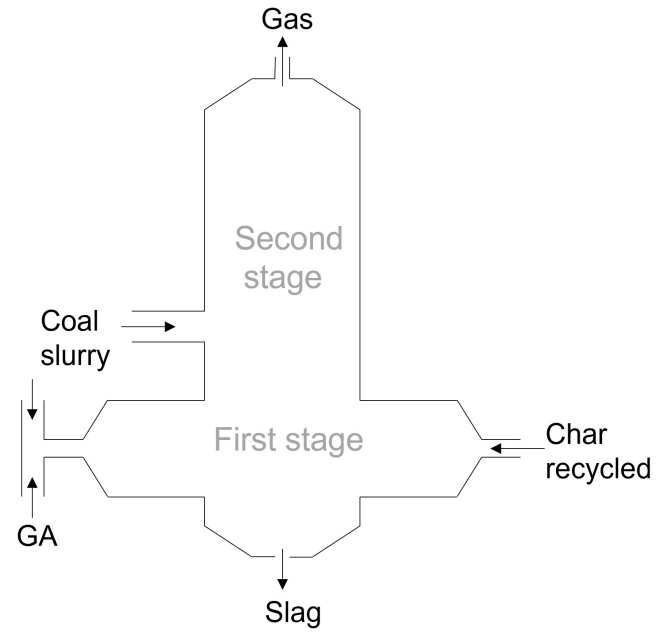


Figure 2.8: Side-fed entrained gasifier

There are several criteria to consider when choosing a gasifier. The choice of reactor depends on the available feedstock (quality and particle size of the feedstock), the desired syngas quality, and the size of the plant.

It has already been explained why the updraft gasifier is the most suitable for biomass with high moisture content. Other biomass characteristics and gasifier being able to deal with them can be found in the table 2.1 [16].

Type of gasifier	Quality of the feedstock
Updraft fixed bed	High moisture content
Dowdraft fixed bed	
Bubbling fluidized bed	High volatile matter content
Circulating fluidized bed	
Top fed entrained flow	Any type of coal
Side fed entrained flow	

Table 2.1: Biomass characteristics matching with the gasifier the most adapted to it

Depending on the purpose of the gasification, the syngas needs to reach some quality requirements. For example, for bio-SNG production, it is preferable to have a syngas with low tar and high hydrogen content. The principal characteristics of the syngas coming from each type of reactors are summarize in the table 2.2

Type of gasifier	Syngas quality
Updraft fixed bed	High tar content
Downdraft fixed bed	Less tar content
Bubbling fluidized bed	High CO_2 , H_2O and hydrocarures content
Circulating fluidized bed	
Top fed entrained flow	Clean, tar-free
Side fed entrained flow	

Table 2.2: Syngas quality coming from each type of gasifiers

Each type of gasifiers is able to deal with a size of particle. The fixed bed gasifier being the more flexible. Since the biomass needs to be pulverized in the entrained flow gasifier, the particles matter have to be really small. The table 2.3 gives an order of magnitude of the particles size needed for each gasifier [3].

Gasifier type	Particles size
Fixed bed	Large (< 51 mm)
Fluidized	Smalle (< 0.6 mm)
Entrained bed	Fine paricle (< 0.15 mm)

Table 2.3: Recommended size of biomass for each type of gasifier

Downdraft fixed bed gasifiers are more suitable for small scale plants while the entrained flow gasifiers are more suitable for large scale plants The figure 2.9 resumes and quantifies the range of application of each reactor.

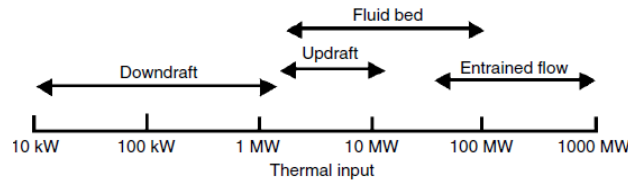


Figure 2.9: Application range of biomass for each types of gasifier [3]

2.1.3 Gasifying agent

The gasification process requires an oxidant called a gasifying agent (GA) which is normally a gas such as oxygen, air, steam or a combination of these. The choice of the GA will have an impact on the quality of the syngas and its calorific value. Depending on the application, one will be chosen over another.

Air gasification for example will be cheaper because the air is "free" as it does not have to be produced. The drawback is that air contains nitrogen which is not converted. This leads to dilution of the syngas with nitrogen, which reduces its calorific value and the overall energy efficiency of the gasification process.

This problem does not occur when oxygen or steam are used as GA. Oxygen gasification produces a syngas with a higher calorific value. However, the operating cost is high due to the high energy cost for the O_2 production.

Steam seems to be a good compromise. It increases the calorific value of the syngas and the hydrogen content in the syngas is high (which is a good point for applications requiring hydrogen as hydrogen engines or for syngas methanation). However, the need in energy to produce vapor is more important than the energy cost to make oxygen purification. It is important to note that gasification with vapor as the only agent is not possible with a fixed bed reactor.

2.2 Methanation

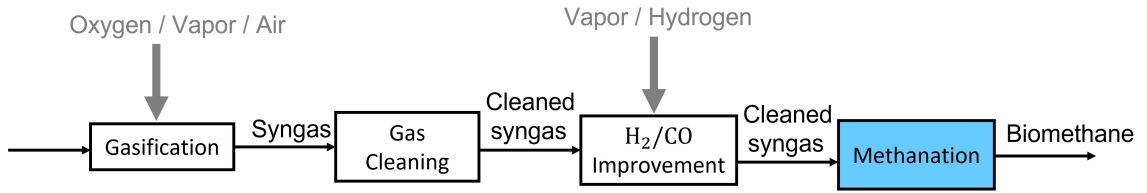


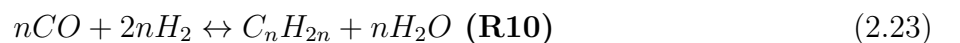
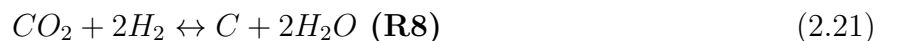
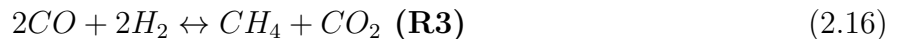
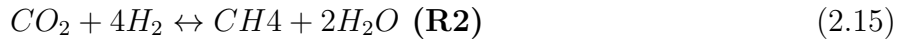
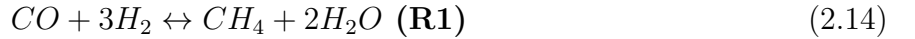
Figure 2.10: General scheme of a bio-methane production process with methanation step highlighted

2.2.1 Process

Methanation is a catalytic reaction leading to the formation of methane and water from carbon oxides and hydrogen. In the case of biomass to fuel conversion, the reaction is carbon monoxide methanation. The equation of methane formation is an exothermic reaction producing 206 [kJ/mol] at 298K:



The stoichiometric H_2/CO ratio is three. The equation above is the main and most important reaction in the methanation reactor. In reality there are much more reactions involved [4] :



The catalyst does not appear in the equations because its involvement is implicit. The catalyst provides an alternative way of reaction with lower activation energy but is not consumed or modified during the reaction. All these reactions occur at the same time. Depending on the conditions in the reactor, some are more important than others.

2.2.1.1 Theoretical effect of pressure and temperature

The thermodynamics conditions inside the reactor have a great impact on reactions. The article [4] studied the impact of temperature and pressure assuming a reactor proceeding at chemical equilibrium.

To study the effects of temperature and pressure, the article uses the Gibbs free energy minimization method to find the typical products fraction at equilibrium. The change in the Gibbs free energy corresponds to the maximum work which can be extracted from a closed system at constant temperature and pressure, excluding the work used for volume change. For a chemical reaction to progress, the Gibbs free energy of the reaction system has to decrease. When the free energy reaches a minimum, the system is at equilibrium [18].

One way to interpret the results is to analyse the evolution of the equilibrium constant of the reactions with the change in temperature.

The equilibrium constant (K) of a reaction is the relative amount of product and reactants present in a reaction mixture at chemical equilibrium. If the equilibrium constant of a reaction is higher than 1 (or its logarithm is bigger than 0), this reaction will take place in the forward direction. If it is lower than 1 (its logarithm being lower than 0), the reaction will proceed in the backward direction. The figure 2.11 shows the constants of the methanation reaction (2.14 to 2.23). For temperatures lower than 650°C, all the reactions proceed in the forward direction except the reaction 2.21.

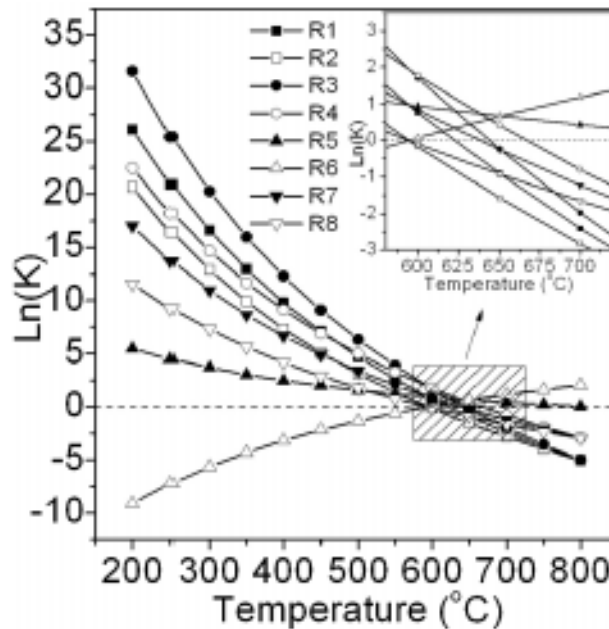


Figure 2.11: Equilibrium constant values of the reactions involved in methanation [4]

The article makes a first analysis of the effect of temperature on the typical product fraction at equilibrium at 1 atm (figure 2.12). The input gas is a mixture of H_2 and CO with a stoichiometric H_2/CO ratio of three.

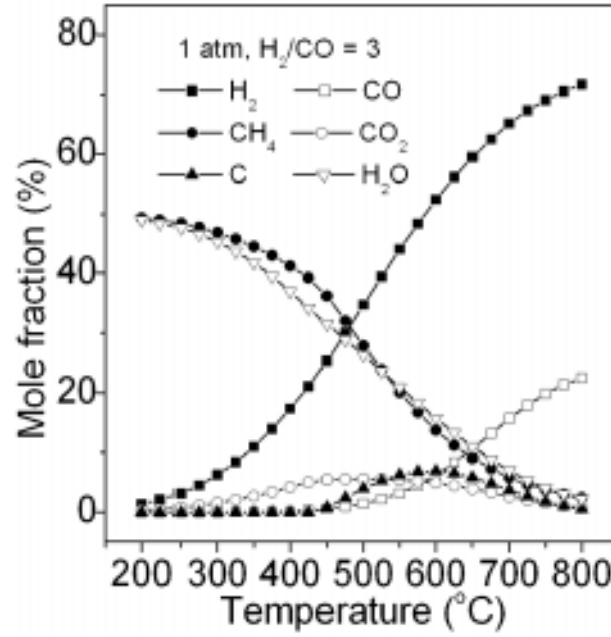


Figure 2.12: Product composition of CO methanation at equilibrium [4]

The result presented in the figure 2.12 shows that the product contains more CH_4 and H_2O and less CO_2 for lower temperatures. Low temperatures favour the production of methane and theoretically minimise the carbon deposits. Furthermore at such temperatures, there is no carbon deposit. The figure 2.11 shows that the reaction R1, R2, R3, R4 and R7 have high constant equilibrium for small temperatures. Which can explain the high CH_4 product concentration for temperature around 200-300°C.

The second analysis presented in the article is the study of the impact of temperature and pressure simultaneously. The CO conversion, CH_4 selectivity, CH_4 yield and carbon yield are studied.

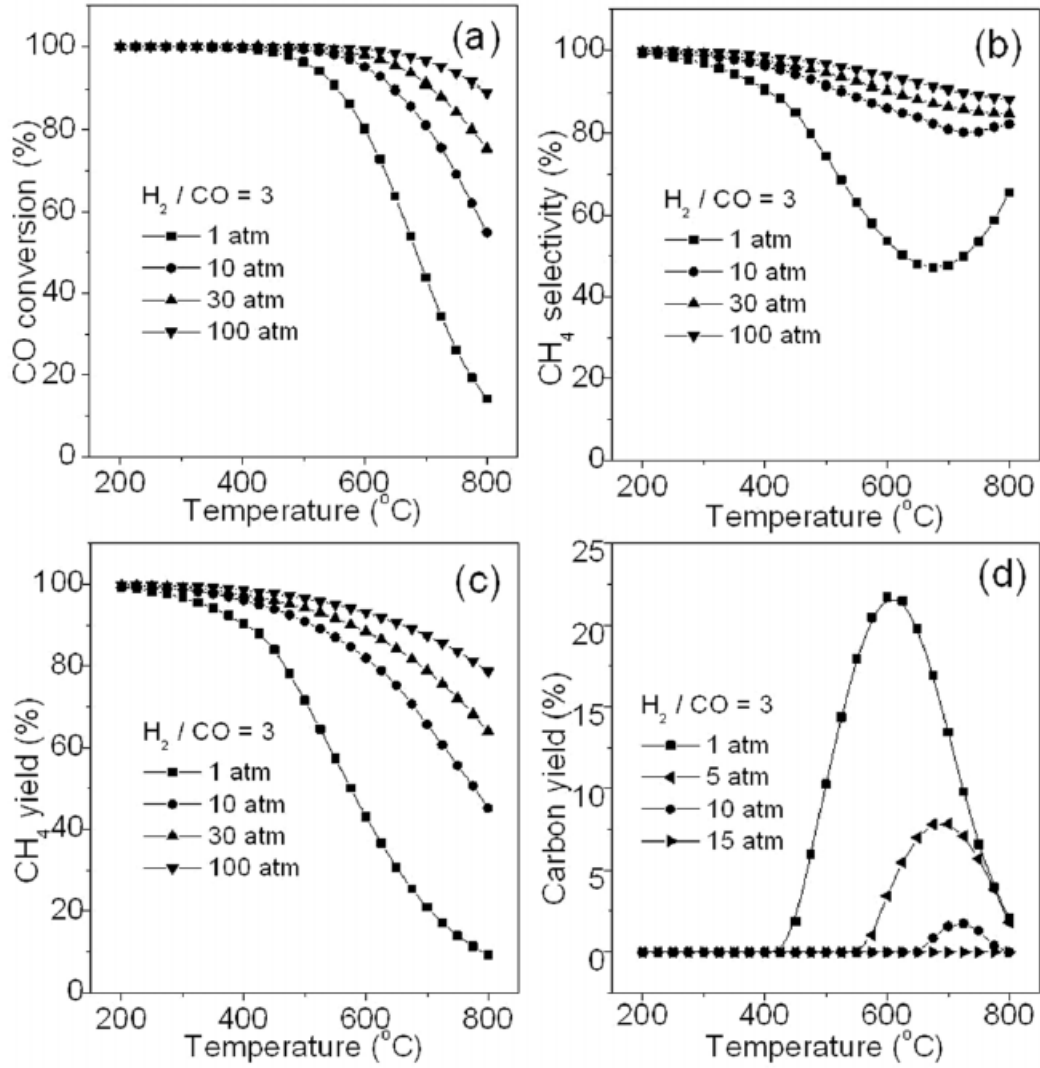


Figure 2.13: Effects of pressure and temperature on CO conversion (a), CH₄ selectivity (b), CH₄ yield (c), and carbon yield (d) in the process of CO methanation [4]

Graph (a) in figure 2.13 shows that there is a greater conversion of CO for a higher pressure at the same temperature. This can be explained by *Le Chatelier* principle. Equation (2.14) is a volume reduction reaction. If we increase the pressure, this equation will shift towards the products [4].

The graph (b) demonstrates that for high pressures and relatively low temperatures, high CH₄ selectivity can be achieved. This can be explained by the fact that at high temperature and low pressure, reactions 2.16 and 2.17 convert partially the CO into by-product such as CO₂ [4].

In the graph (c) the CH₄ yield is shown. It can be observed that at low temperatures (mainly below 250°C), a CH₄ near 100 is reached. It confirms that CO methanation is favoured at low temperature and high pressure.

The last graph reveals that there is no carbon deposition observed for a methanation carried out at a pressure higher than 15 atm [4].

2.2.2 Reactors

The methanation reactors can be distinguished primarily by the number of phases they contain. They can be two-phases reactors (gas and solid) or three-phases reactors (gas, liquid and solid). These two types of reactors can be sub-divided according to their reactor structure. The two phases reactor can be fixed bed reactor, fluidized bed reactor or structured catalyst reactor.

The three phases reactor can be fluidized bed reactor or slurry reactor.

2.2.3 Catalyst

The catalyst is a substance added to the process to increase the rate of the chemical reaction. The catalyst offers other pathways of reactions than the uncatalyzed one. These pathways have lower activation reaction which is the minimum amount of energy needed to result in a chemical reaction. The catalyst does not change and is not consumed during the reaction [19].

The choice of catalyst is crucial for methanation and has a direct impact on the efficiency of methane production. Many metals from the 8th to the 10th group of the periodic table are suitable for methanation catalysis.

A catalyst can be evaluated for its selectivity, activity and price. It has been shown that nickel catalyst is the most selective methanation catalyst. In addition, it has a high activity and a comparatively lower price [20].

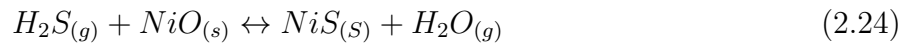
The catalyst is a key element in methanation. Over time or under certain conditions it can lose its activity and selectivity. This phenomenon is called catalyst deactivation. It is important to avoid this by ensuring good conditions for the catalyst inside the reactor. There are three types of catalyst deactivation : mechanical, chemical and thermal.

Thermal deactivation

Thermal deactivation also known as catalyst sintering occurs when the catalyst is exposed to a too high temperature. It leads to a shrinkage of the active surfaces due to growth of catalyst crystals and a decrease in catalyst dispersion. [8]. The loss of surface area reduces the activity of the catalyst. High temperature resistant catalysts are available for methanisation between 600 and 700 °C [20].

Chemical deactivation

In Nickel-based methanation catalysts the main chemical deactivation is poisoning. It is due to the fact that catalysts are sensitive to gas impurities. Gas impurities are chlorine compounds, tars, particles, ammonia but the more problematic is the sulfur. The hydrogen sulfide reacts with nickel oxide. The nickel sulfide resulting has less activity for methanation :



It is necessary to keep the sulfur content in the range of several parts per billion in order to keep the catalyst active for over hundred of hours[20]. Some biomass content sulfur which has the impact of contaminate the syngas. It is why in the gas cleaning section, a H_2S removal is necessary.

Mechanical deactivation

There are three main mechanical deactivations that must be avoided during methanation. The first one is fouling. This occurs when some species pass from gas phase to deposit on the catalyst active material. Due to the Boudouard reaction (reaction 2.17), carbon deposits are formed. As steam and hydrogen react with carbon, resulting in the inhibition of stable carbon formation, steam can be added or the hydrogen to carbon molar ratio increased to avoid fouling [4]. In the other hand, coke deposition comes from higher hydrocarbons at high temperatures (between 500 and 600 °C)

Attrition is another type of mechanical deactivation. It is a loss of catalytic material due to abrasion. It is more specially a problem in fluidized bed reactor where the particles are subjected to attrition via collisions among particles and against the walls of reactor.

The last one is crushing. It occurs in the presence of thermal or mechanical stress and results in the breakage of the catalytic particles.

2.3 Gas cleaning

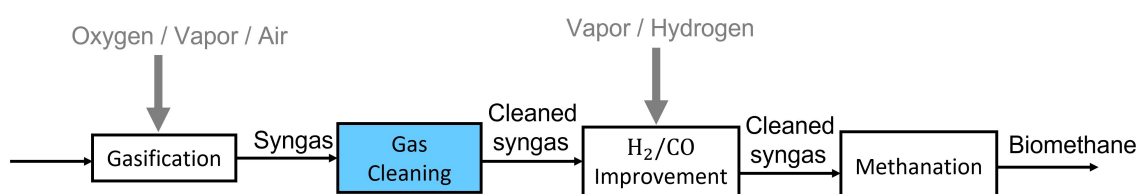


Figure 2.14: General scheme of a bio-methane production process with gas cleaning step highlighted

2.3.1 Syngas quality improvement

At the outlet of the gasifier, the syngas contains undesired components. Some of them as sulfur or tar should be removed from the syngas to avoid catalytic deactivation.

The hydrogen sulfur in the syngas causing a decline in catalyst activity (see 2.24) can be removed by a H_2S scrubber.

Large tar components such as 3-rings aromatic hydrocarbons, Biphenyl, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Crysene [7] can be totally removed with a rapeseed oil methyl (RME) scrubber. Lighter tar components (mainly benzene and the remaining part of naphthalene) can be removed with an adsorption bed.

2.3.2 Thermodynamic state adjustment

In the section 2.2.1.1, the thermodynamics conditions of the inlet syngas in the methanation have been studied. The methanation presents better results for high pressure and low temperature. However the syngas coming from the gasifier is really hot (around 700°C-800°C) and is at low pressure (around atmospheric pressure) [21]. It is why a cooler and a compressor are needed between the gasifier and the methanation.

It is preferable to install a cooler (with water condensation and removal) right after the gasifier to prevent the other cleaning station from degradation due to high temperature. Furthermore, the compressor should be placed after the cooler to avoid to compress the water contained in the syngas leaving the gasifier.

2.3.3 Hydrogen to dioxide ratio improvement

As mentioned before, the hydrogen to carbon dioxide ratio should be equal to 3 while the syngas enters the methanation. To do so, two technologies are possible.

In one hand, the gas can go through a Water gas shifts reactor (WGS). The WGS reaction occurring in the catalytic reactor shifts a part of the carbon monoxide and water into carbon dioxide and additional hydrogen. It is the same reaction as the reaction 2.10 occurring in the gasifier.

The other possibility is to add pure hydrogen to the system. This hydrogen could come from water electrolysis which will be explained later in this document.

It is not always necessary to have a hydrogen to monoxide ratio improvement step. For vapor gasification with optimal conditions, the ratio could reach the value of three. In this case, the hydrogen to carbon monoxide does not need to be improved.

2.4 Overview of current applications

The interest of scientists in the gasification process is not new. The first attempt to obtain carbonated hydrogen dates back to the 17th century. The first commercial-scale gasifier appeared in the mid-19th century. The development of the technology was paused after the second World War because of oil abundance. Researches have increased in recent years to develop the gasification of biomass and organic waste.

Unlike the gasification process, bio-methane production by thermal process is at its beginning. Unfortunately it is still only available on a demonstration or pilot scale [22]. As it can be seen in the figure 2.15, the synthetic natural gas technology is still at its early stage.

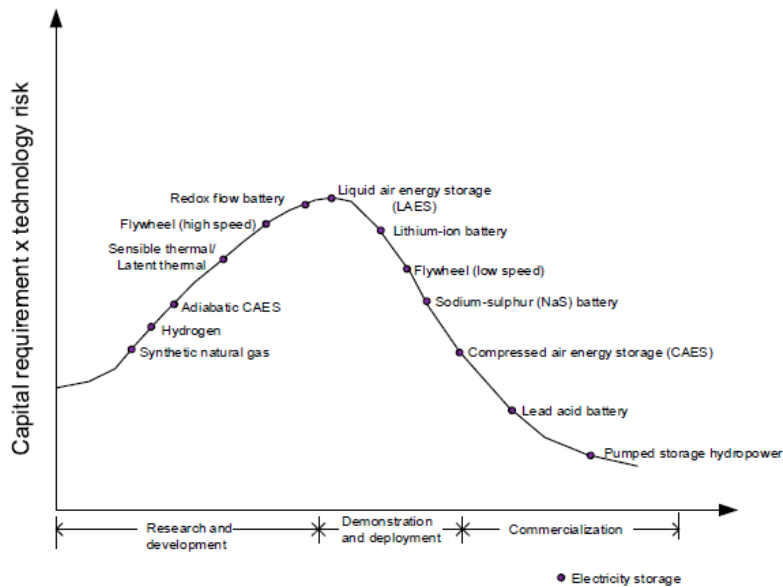


Figure 2.15: Maturity of energy storage technologies [5]

There is currently no commercial-scale production of biomethane surveyed. The project that seems the closest to be implemented on a commercial scale is the Gaya project. If the Gaya project is advanced and could lead to a real commercial project, other projects have not gone beyond the demonstration stage. This chapter summarises what is known about some of the technologies and projects that exist or have existed to this day. For more information about biomass conversion around the world, the reader is invited to look at the Global database of biomass conversion facilities developed by IEA Bioenergy ¹.

Gaya project

Launched in 2010, this project aims to validate the technological possibilities that can be used in the production of biomethane using a thermal process. To this end, a pilot project was launched in 2013 in Saint-Fons, south of Lyon. This demonstration plant uses a pyro-gasification unit coupled with a methanation unit. The plant was inaugurated in 2017 and benefited from its first injection of forest biomass in 2018. In 2019 Engie celebrated its first cubic metre of methane production. One year later a new milestone was reached when the platform produced its first cubic metre of biomethane from Solid Recovered Fuel (made from waste wood, paper etc.). Data about the results of this pilot project are not available but in a press release Engie announces a brand new project. Engie plans to open a commercial bio-methanation unit in 2023, projecting a consumption of 70,000 tonnes of non-recyclable waste by 2026 [23].

¹<https://www.ieabioenergy.com/installations/>

Woodroll technology

The Woodroll technology is a thermal gasification converting wet solid biomass into clean syngas using a dryer, a pyrolysis reactor, and a steam gasifier. All the gasification process is auto-thermal. The pyrolysis gases are burned, and the heat supplies the gasifier and the dryer. In 2012 a pilot plant has been taken into operation to test the three stages Woodroll gasification. From 2015, further developments of the pilot plant were made to study the coupling of woodroll technology and SNG production. Even if positive results have been related, no datas were published yet [24].

Bio2G project

In 2007, the German electric utility company became interested in gasification with the ultimate goal of producing bio-methane. After several studies, a complete technical design of a 300 MW biomass power plant producing 200MW of bio-methane and more than 50MW of district heat was carried out. The expected thermal efficiency of this power plant (excluding oxygen production) was evaluated in the range of 60-65% in bio-methane. The plant was designed with the following technologies: a gasification system based on pressurised oxygen blown gasification in a fluidized bed, a hot gas cleaning (tar reforming, HAT filter), cold gas cleaning (water scrubber, acid gas removal), a compression, a WGS reactor and a methane production unit. The plant launch was scheduled for early 2022.

GoBiGas project

This project is particularly interesting in the framework of this master thesis. The technologies used are most similar to what is studied here. Moreover, unlike some projects where the datas are kept secret, many reports and results on the GoBiGas project are published. It will be explained in the following chapters how the study presented in this document is based on the process used in the GoBiGas project.

The Gothenburg Biogas Gasification project also called GoBiGas was a demonstration plant for the production of 20MW of biomethane. In early 2014 the demonstration plant was officially inaugurated and biomethane was produced by the end of the year. It was planned that the plant would transit from demonstration to commercial installation. However in 2018, the project was stopped at the demonstration stage after 1800 hours of continuous operation (it had reached 100% of its designed capacity) for economical reasons [21] [25]. The main reason for justifying the shut down is that the sales value of the bio-methane did not followed the predictions such that the plant was running with direct operating net loss [24].

The GoBiGas plant consists of the three stages explained in the previous chapter : Gasification, Gas cleaning and Methanation. In the figure 2.16 the detailed process is represented. For even more detailed scheme, see the figure 6.1 in the Appendix.

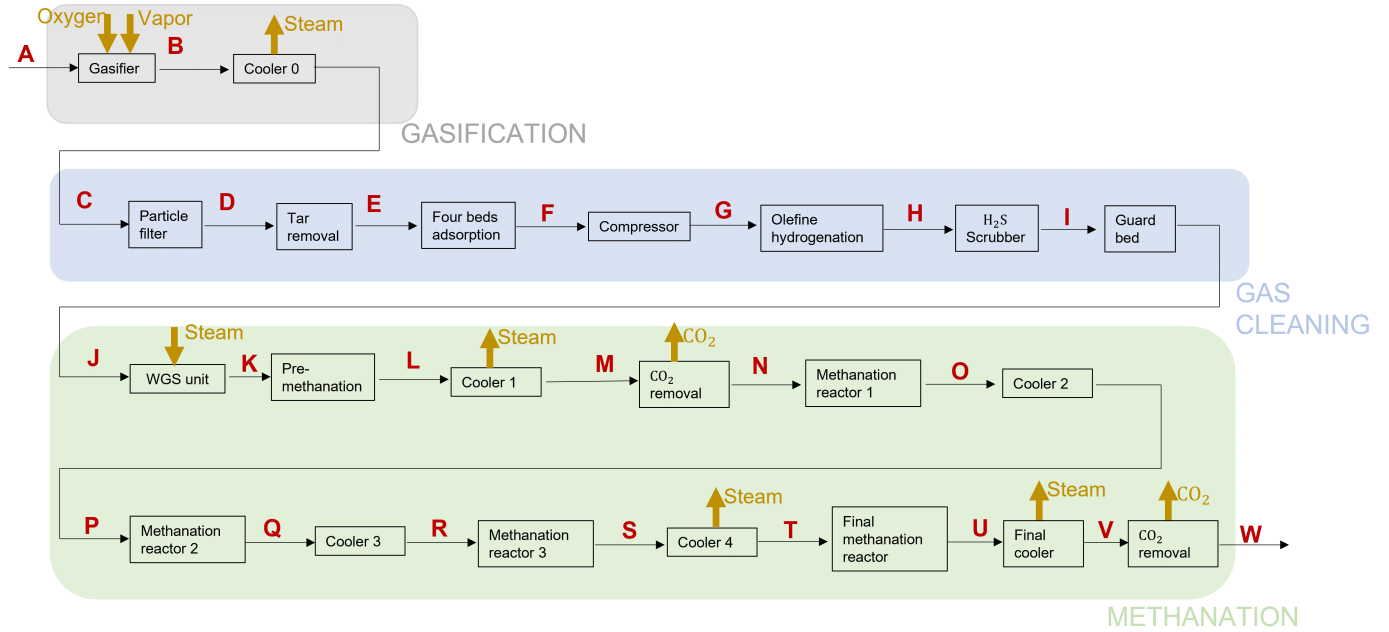


Figure 2.16: Scheme of the complete set-up of the GoBiGas demonstration plant

In the GoBiGas process, the gasifier and the combustion chamber are linked. The gasifier is a fast internally circulating fluidized bed connected to the combustion chamber via a connecting tube. In this configuration, heat and bed material circulate between the combustion chamber and the gasifier. The unconverted tar and bed materials from the gasifier feed the combustion chamber through the connecting tube.

After combustion, the bed material must be recovered to feed again the gasifier. This is done by the cyclone located after the combustion chamber. It removes bed material and particles from combustion flue gas and feeds the gasifier. As the combustion takes place with air it is necessary to prevent nitrogen from passing from the flue gas to the gasifier to avoid nitrogen dilution in the gasifier. A loop seal allows the bed material and the heat to go from the cyclone to the gasifier without allowing the nitrogen to pass [13][26].

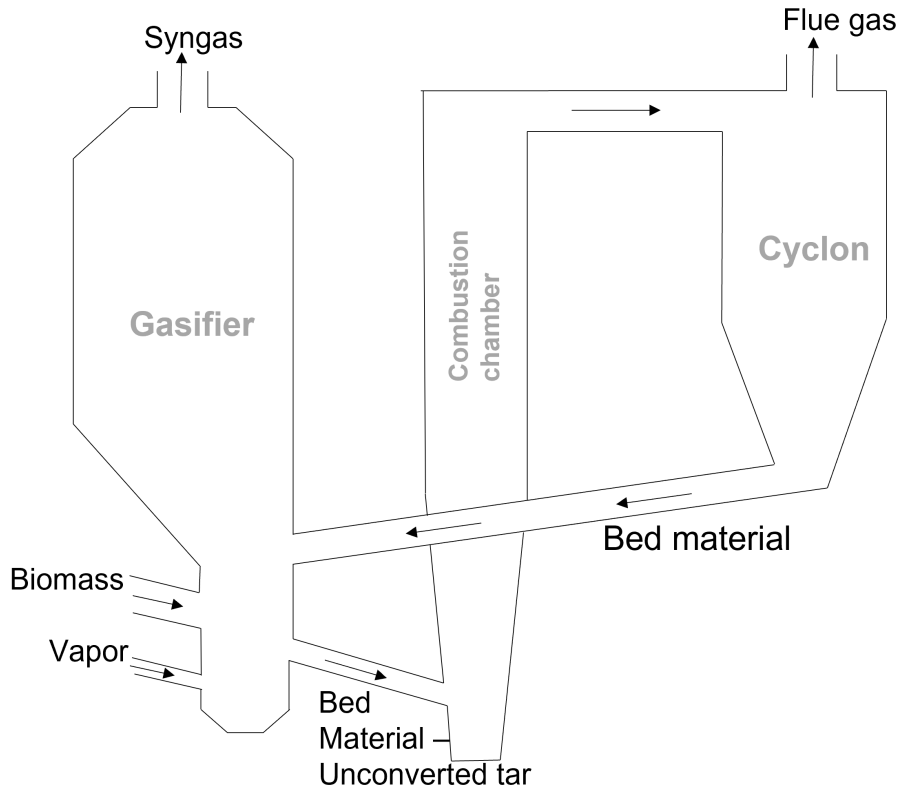


Figure 2.17: Scheme of the dual fluidized bed used in GoBiGas

In the GoBiGas gasifier, the active bed material is olivine [21][7] which is a magnesium iron silicate. The olivine has to be artificially catalytically activated. For this purpose potassium in the form of K_2CO_3 diluted into water is added in the combustion chamber. The potassium flows through the gasifier via the seal loop with the bed material. This addition of potassium has two disadvantages :

- Presence of silicate in the gasifier would lead to the formation of K-Si making potassium inactive and sticky [21]. The silicate content of biomass and bed material must therefore be limited.
- The increase of potassium in the combustion chamber leads to a dwindling CO-burnout. This issue can be solved by adding sulfur in the combustion chamber.

The gasifier works at ambient pressure [26]. The operational temperature needs to be less than 830°C to simplify potassium activation [21].

The cooler 0 is tubular heat exchanger using water at 160°C to cool down the syngas. At the outlet of the Cooler 0, the syngas has reached temperature between 140 to 200°C [21].

The syngas goes through some cleaning steps to reach the degree of purity and composition needed for the methanation stage. After the cooler, it goes through a textile-bag filter where particles are removed. Then large tar are removed in a scrubber using RME as scrubber. The lighter tar are subsequently removed thanks to the four bed adsorption.

Then compression step compresses the gas from atmospheric pressure to 16 bars thanks to a six-stages inter-cooled compressor. The pressure will decrease in the next cleaning steps before

entering in the methanation step.

The H_2S scrubber and the guard bed are there to ensure that as little hydrogen sulfide as possible enters the reactor and therefore avoids catalytic deactivation.

Before entering the methanation, the gas also needs to improve its hydrogen to carbon monoxide ratio. To do so, the cleaned, compressed syngas go through a WGS reactor before entering the pre-methanation. The WGS reactor needs a steam supply.

The methanation step is a modified version of the '*Topsøe Recycle Energy-efficient*' (TREMPE) methanation Process.

The classical TREMPE reactors set-up is a succession of three adiabatic fixed bed reactors with recycle loops allowing to control the temperature rise in the first reactor. The exit gas of the first reactor is cooled and super-heated steam is created. The exits gas of the other reactors are cooled. The figure 2.18 shows an example of TREMPE configuration with three reactors. The number of reactors and their configuration are editable depending on the application.

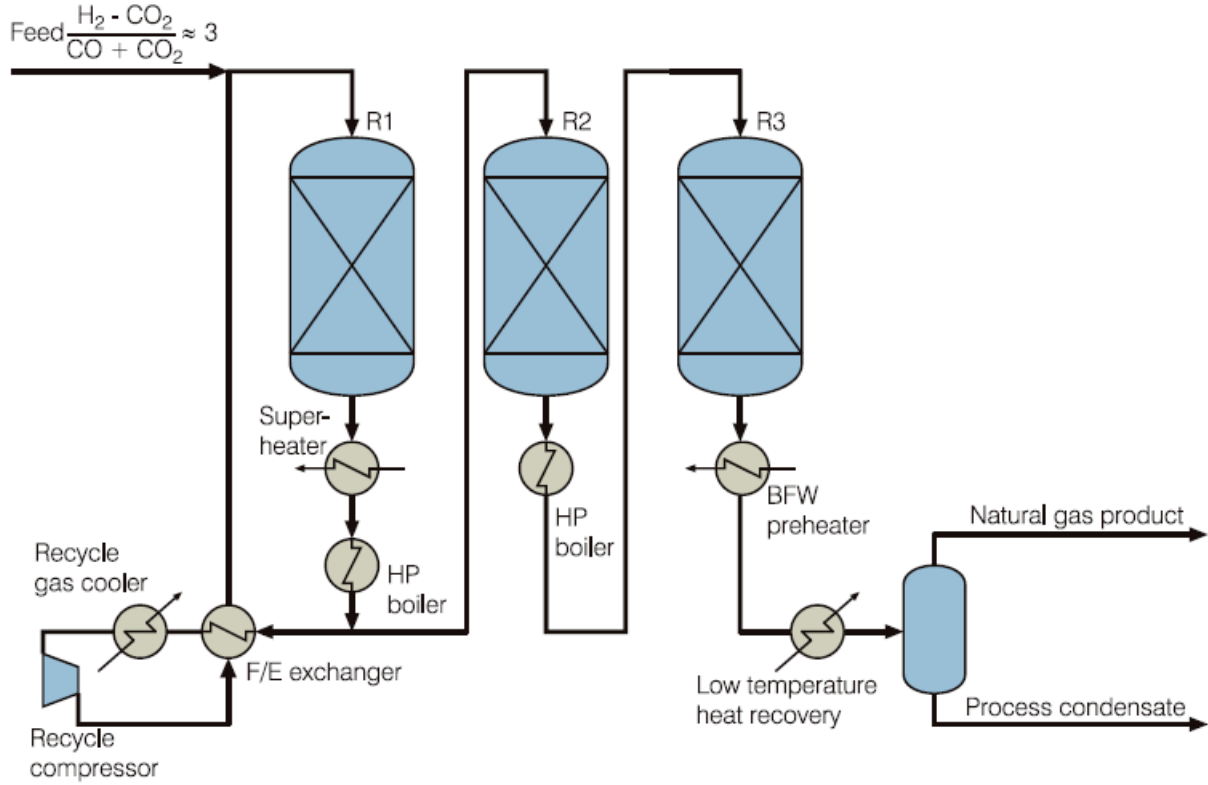


Figure 2.18: Example of the Topsøe TREMPE™ technology [6]

The set-up of the methanation section in the GoBiGas is slightly modified from the basic TREMPE as shown in the figure 2.16. It counts in total five methanation reactors, one for pre-methanation and four for methanation. The GoBiGas set-up does not use recycling to limit the temperature but uses the ballast gases.

The first methanation reactor is used to perform a pre-methanation before the next cooler and carbon dioxide scrubber to use steam and CO_2 as ballast to damp the temperature in the reactor. Some of the carbon monoxide and carbon dioxide are converted to methane but the

main objective of pre-methanation is to crack ethane. There are then four methanation reactors with intermediate intercooling. In the four reactors, the amount of methane is sufficiently high to limit together with the produced steam the temperature. Only the Cooler 4 condenses the steam. This condensation shifts the equilibrium curve, so higher methane yields are achievable at relatively high temperatures.

After passing through all the methanation stages, the final syngas has its pressure reduced to 6 bars. The gas must therefore be compressed to 30 bars in order to supply the network.

Chapter 3

Process modelisation

For this master thesis, the gasification step and the methanation step were modeled separately like two boxes linked together by the syngas coming out from the gasification step and entering in the methanation step. The two models modeling respectively the two stages are based on reactors assumed to be at equilibrium. The entire set-up was inspired by the GoBiGas process. The blocks diagram is recalled in the figure 3.1.

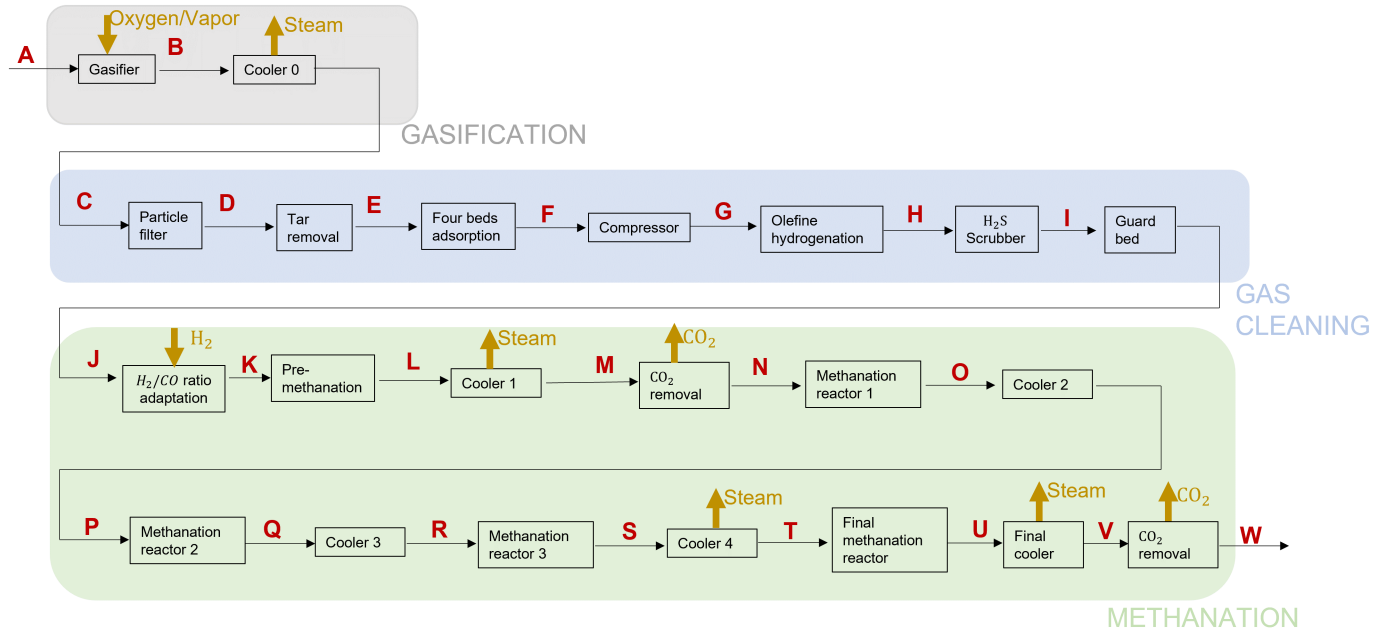


Figure 3.1: Overall scheme of the process set up modeled in the context of this master thesis

The first section of this chapter explains the concept of equilibrium while the two next explain the resolution used for each model. The set-up of the process stage will be recalled in each section with the corresponding part of the overall process scheme.

3.1 Theory of equilibrium modeling

A reactor is at its equilibrium when all the reactions have reached the equilibrium. The chemical equilibrium of a reaction is the state where the forward and reverse reactions take place at the same rate so that there is no change in the concentrations of the reactants and products anymore [27]. An equilibrium model considers that the reactions that occur are fast or have enough time to reach the equilibrium.

There are two methods to model and predict the equilibrium composition of a chemical system : the stoichiometric and the non-stoichiometric methods. They are both based on the minimization of Gibbs energy but in different ways.

The stoichiometric method needs the set of the R independent chemical reactions happening in the reactor and the initial concentrations of the chemical species. It solves the extent of each reaction (ξ_i) by using the equilibrium constant explained in the previous chapter and a molecular mole balance of every species [28].

The non-stoichiometric method does not require the reactions but needs all the chemical species of reactants and possible products. The method uses the initial concentration of all the species and computes the number of moles of each element present initially in the system. Then all the possible distribution of the atoms between all the possible species (reactants and products) are computed. The distribution minimizing the overall Gibbs energy of the system is the distribution of the system at equilibrium. This method requires the set of the N chemical species [28]

3.2 Gasification

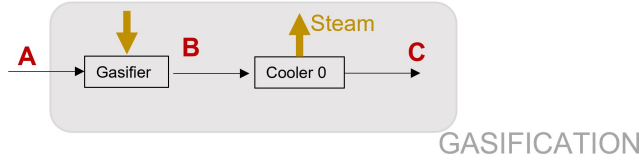
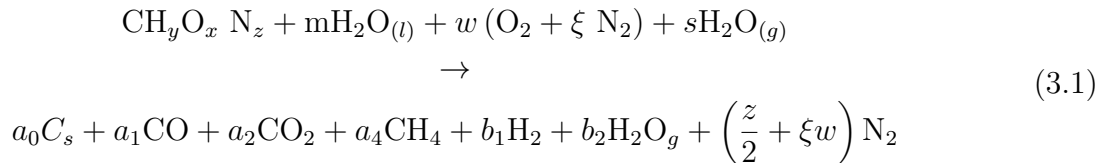


Figure 3.2: Scheme of the gasification step set up

The composition of the syngas at the outlet of the gasifier is studied using an existing equilibrium model described and explained in this section. The unknowns are the molar concentrations : x_{CO} , x_{CO_2} , x_{CH_4} , x_{H_2} , $x_{H_2O_g}$, x_{N_2} and n_{C_s} of the syngas. To find the composition, the stoichiometry of the main reaction needs to be determined :



The coefficients m , w , s , h and c in 3.1 are set according to the type of gasification. For exemple, a gasification with pure oxygen as GA will take $m = 0$, $s = 0$, $h = 0$, $c = 0$ and $\xi = 0$.

The following chapter will explain the different cases studied in this master thesis. There are 6 unknown coefficients ($a_0, a_1, a_2, a_4, b_1, b_2$) related to the syngas composition .

The present model uses a combination of the global stoichiometric reaction (equation 3.1) and the intermediate reactions given in the previous chapter (see equation 2.7 to 2.11). These reactions are assumed to be at equilibrium. The model determines the composition of the gas by applying the conservation of mass and chemical equilibrium equations to these reactions. Since there are 6 unknowns to find, 6 equations are needed to determine the composition of the gas. The conservation equations of carbon, hydrogen and oxygen are used in this model :

$$(x_{CO} + x_{CO_2} + x_{CH_4}) \frac{n_{N_2}}{x_{N_2}} = (1 - n_{C_s}) \text{ (Carbon conservation)} \quad (3.2)$$

$$(4x_{CH_4} + 2x_{H_2} + 2x_{H_2O_g}) \frac{n_{N_2}}{x_{N_2}} = (y + 2m + 2s) \text{ (Hydrogen conservation)} \quad (3.3)$$

$$(x_{CO} + 2x_{CO_2} + x_{H_2O_g}) \frac{n_{N_2}}{x_{N_2}} = (x + m + s + 2w) \text{ (Oxygen conservation)} \quad (3.4)$$

$$x_{CO} + x_{CO_2} + x_{CH_4} + x_{H_2} + x_{H_2O_g} + x_{N_2} = 1 \quad (3.5)$$

The equation 3.5 was added to ensure the gas concentrations sum to be equal to 1.

To complete the system, three equilibrium equations of independent reactions are required. In this model, the chosen combination was WGS, SMR and Boudouard.

$$\log \left[\frac{x_{CO_2} x_{H_2}}{x_{CO} x_{H_2O_g}} \right] = \log K_{WGS} \text{ (WGS equilibrium)} \quad (3.6)$$

$$\log \left[\frac{x_{CO} x_{H_2}^3}{x_{CH_4} x_{H_2O_g}} \left(\frac{p}{p^f} \right)^2 \right] = \log K_{SMR} \text{ (SMR equilibrium)} \quad (3.7)$$

$$\log \left[\frac{x_{CO}^2 p}{x_{CO_2} p^f} \right] = \log K_{Boudouard} \text{ (Boudouard equilibrium)} \quad (3.8)$$

Where n_i is the absolute quantity of the species i and $x_i = \frac{n_i}{n_{gas}}$ is the molar fraction of the species i in the syngas. The equation 3.1 tells that $n_{N_2} = \frac{z}{2} + \xi w$

The terms K_{SMR} , K_{WGS} and $K_{Boudouard}$ are the equilibrium constants. For each reaction, the equilibrium constant depends on the equilibrium temperature T_{eq} as shown in the figure 3.3.

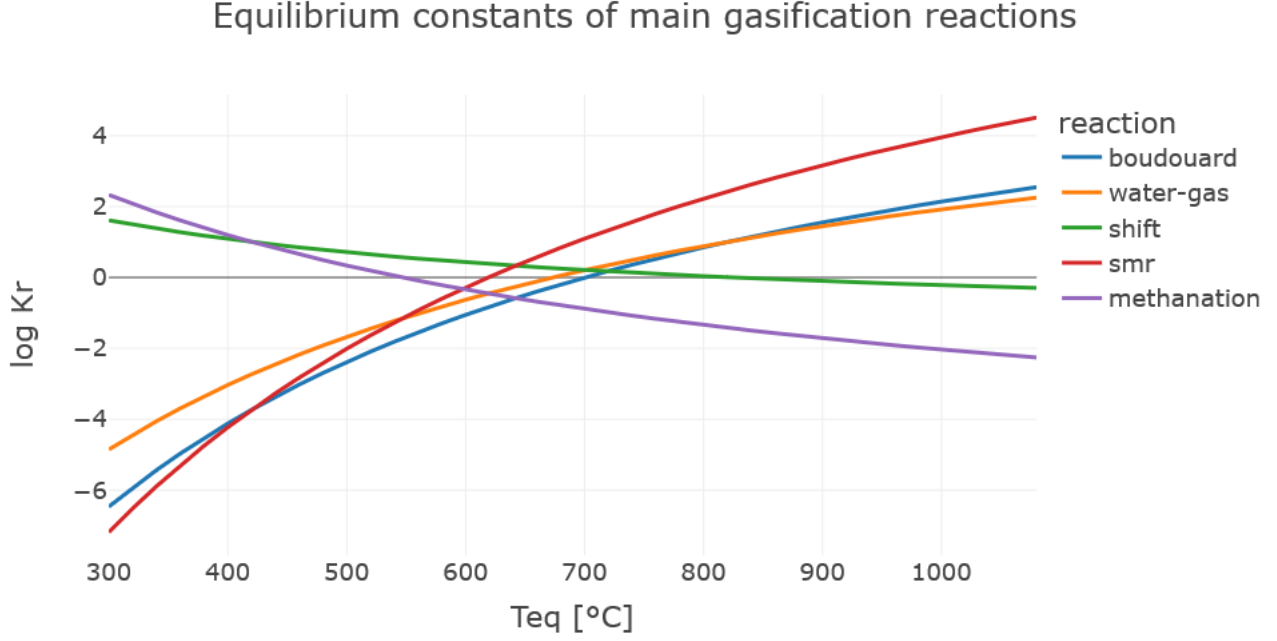


Figure 3.3: Equilibrium constants of intermediate gasification reactions

The equilibrium temperature is an additional unknown determined by combining the above equations with the energy conservation :

$$\sum_{i \in P} n_i H_i^\circ(T_{eq}) + A H_A(T_{eq}) = \sum_{i \in R} n_i H_i^\circ(T_{in}) - Q_{\text{loss}} \quad (3.9)$$

where:

- $H_i^\circ(T) = \Delta_f H_i^\circ + \int_{T^\circ}^T c_{p,i} dT$
- A is the mass of Ash per mol of biomass dry and ash free (daf) [$kg/mol_{\text{biomass}_{\text{daf}}}$]
- $H_A(T_{eq})$ is the sensible enthalpy of ash [kJ/kg]
- Q_{loss} is an exogenous heat loss [$kJ/mol_{\text{biomass}_{\text{daf}}}$]

The model takes the informations about enthalpy, enthalpy of formation and equilibrium constant from the *NIST-JANAF* database. The JANAF tables contain these informations for a large number of molecules, at various temperatures, considering a standard state pressure $p^\circ = 1$ bar and a reference temperature $T_r = 298.1$ K.

One important parameter is the equivalence ratio ($ER = \lambda$). It represents the actual oxygen to biomass mass ratio used in the gasification divided by the stoichiometric oxygen to biomass mass ratio for biomass combustion. This definition is expressed as a formula in the equation 3.10

$$ER = \frac{m_{\text{oxygen}}}{m_{\text{biomass}}} \cdot \frac{1}{ma_1} \quad (3.10)$$

Where ma_1 is the stoichiometric mass ratio between oxygen and biomass during biomass combustion.

The ER has an optimum value for each set of gasification parameters. This optimum corresponds

to the case where all the carbon is converted (no solid carbon remains). It happens when the Cold gas efficiency (CGE) is maximized. The CGE corresponds to the energy content of the dry and cold syngas, relative to the energy content in the biomass entering the gasifier.

$$CGE = \frac{n_{CO} \cdot LHV_{CO} + n_{H_2} \cdot LHV_{H_2} + n_{CH_4} \cdot LHV_{CH_4}}{LHV_{biomass}} \quad (3.11)$$

The model proposes an option called *ER optimization*. When this option is activated, it will iterate by varying the parameter until the maximum CGE is obtained

3.3 Methanation

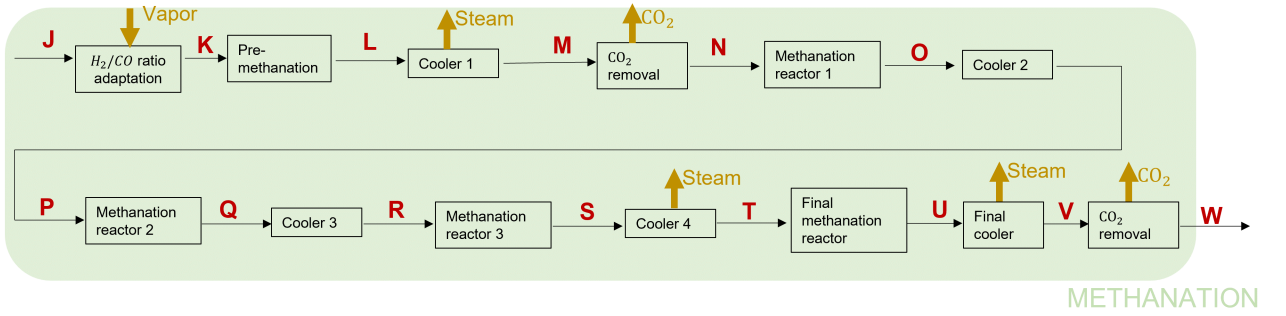


Figure 3.4: Scheme of the methanation step set up

The methanation stage is based on the set-up of the GoBiGas process. Like GoBiGas, it contains five adiabatic reactors and five intercoolers interspersed between the reactors. Two carbon dioxide purges are included: one after the methanation reactor and one at the end of the process before feeding the gas into the grid. Three intercoolers condense the steam: cooler 1 after the pre-methanation, cooler 4 just before the final methanation and at the end of the process.

Before entering the pre-methanation reactor, the gas enters the hydrogen to carbon monoxide ratio adaptation stage. In the model presented in this master thesis, if this ratio needs to be increased, a pure hydrogen supply is modelled.

The whole process is represented in the scheme 3.1 where the methanation is in the green box. The figure 3.4 shows the block diagram of the part that interests us in this section. The model takes as input the syngas coming from the gasification model.

For the methanation reactor, the open-source *Cantera* was used. *Cantera* offers a suite of tools for solving problems involving chemical kinetics, thermodynamics and transport processes [29].

Firstly, *Cantera* allows to use the *Solution* class. This class gives representation of a substance that has thermodynamic and chemical kinetic properties. The gas entering the process can be created as a *Solution* object designating the gas mixture. *Solution* object has a temperature,

pressure, moles of species, mass fractions, enthalpy etc. The state of the gas can be easily modified to suit the syngas entering the methanation.

Once the input gas is created, the reactions in the methanation reactor are modelled using the function *Equilibrate*. This function sets the state of the gas inlet *Solution* object to the state of chemical equilibrium by holding two state variables fixed. The function *Equilibrate* used the non-stoichiometric method presented in the section 3.1.

In the model computed in this master thesis, the reactors are modeled as adiabatic and isobar reactors by defining the two constant variables as enthalpy and pressure.

The inter-coolers were considered as isobar inter-coolers. To model these inter-coolers, a new gas with the same property but the target temperature is created.

The CO_2 scrubbers are ideal and are modeled as they remove all the CO_2 .

Chapter 4

Results

The purpose of this section is to propose the main results of the analysis. First the objectives of the master thesis will be recalled. Then results of the gasification models are presented for the oxygen and the vapor gasification cases separately. The methanation section will compare the results of both cases.

Additional mass and energy balance calculations have also been performed and are presented. All the calculation are made for one mole of biomass entering the process.

4.1 Modelisation objectives and strategy

The aim of this master thesis is to study the production of methane by thermal process and its potential coupling with the production of hydrogen.

The previous section presented the two models developed to model the gasification process and the methanation process separately. Then the two models were coupled and used to model the whole process of bio-methane production from biomass, through gasification, methanation and finally to obtain bio-methane.

This overall model was used to study two cases. A first case where the gasification is done with oxygen as gasification agent and where a hydrogen supply has to be provided. A second case where the gasification is done with steam as gasification agent.

To assess the interest of the methanation with oxygen gasification and hydrogen addition, the overall model was used to compute a range of data such as the syngas composition, the hydrogen and carbon flux and the energy content of the syngas at some critical points. They were then analysed to draw conclusions.

4.2 Gasification

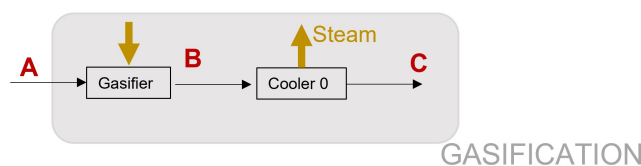


Figure 4.1: Scheme of the gasification step set up

4.2.1 Oxygen gasification

In the modelisation of gasification with oxygen as GA, two parameters need to be defined. They are the temperature of the oxygen entering the gasifier and the ER.

The graphs 4.2 and 4.3 are plotted using the ER optimization function. They show that oxygen temperature impacts merely the optimal equivalence ratio and the hydrogen to carbon monoxide ratio.

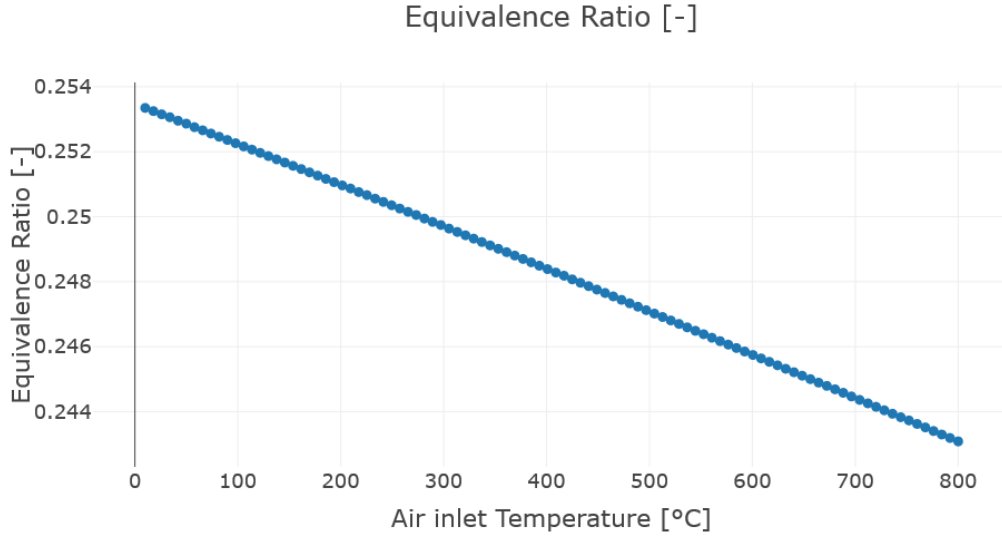


Figure 4.2: ER evolution regarding the air inlet temperature for gasification with oxygen as GA

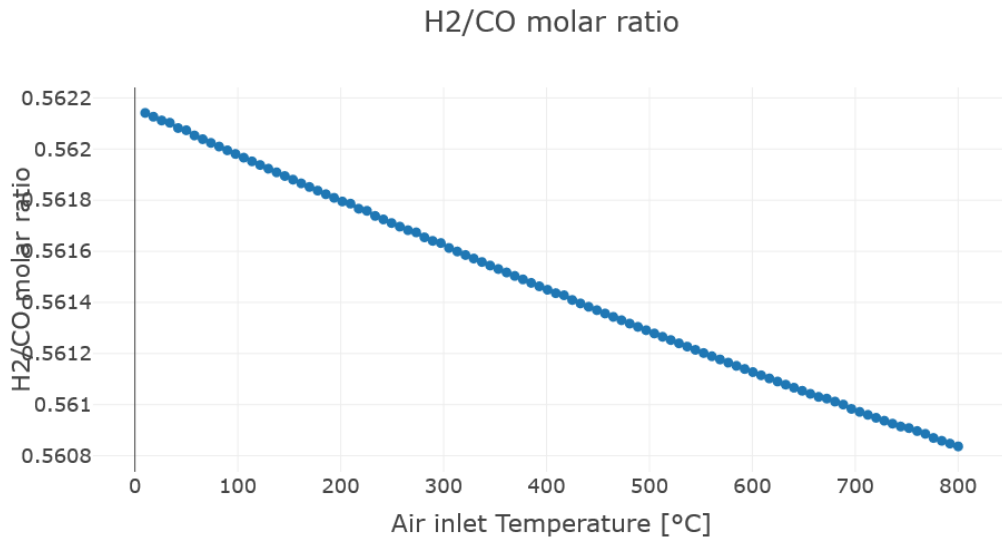


Figure 4.3: H_2/CO evolution regarding the air inlet temperature for gasification with oxygen as GA

Since the ER given by the model, when the ER optimization is activated, ranges from 0,245 to 0,255 it seems judicious to choose and ER around 0,25. The graph 4.4 shows that for an ER higher than 0,25, the temperature begins to increase more. The chosen ER for this modelling is therefore 0,25.

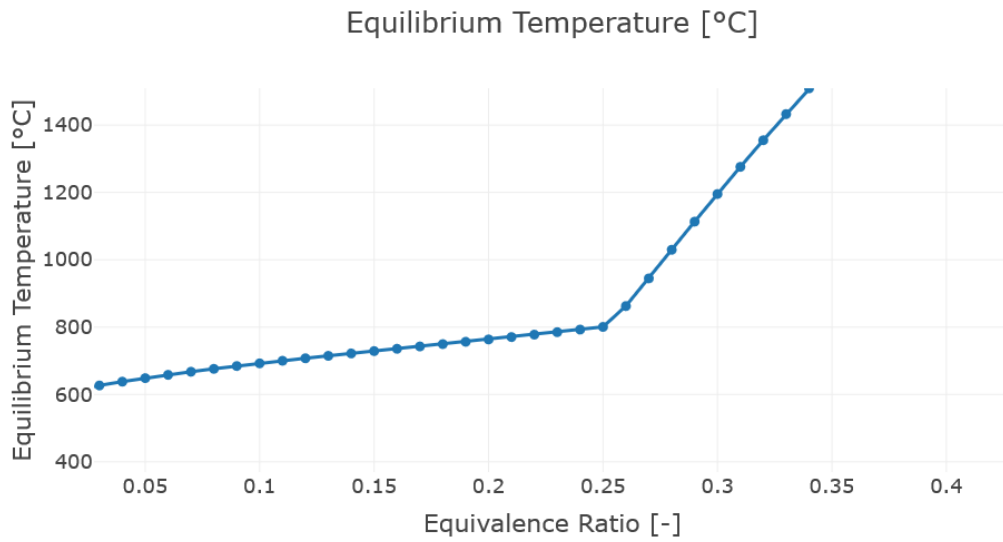


Figure 4.4: Equilibrium temperature evolution regarding the equivalence ratio for gasification with oxygen as GA

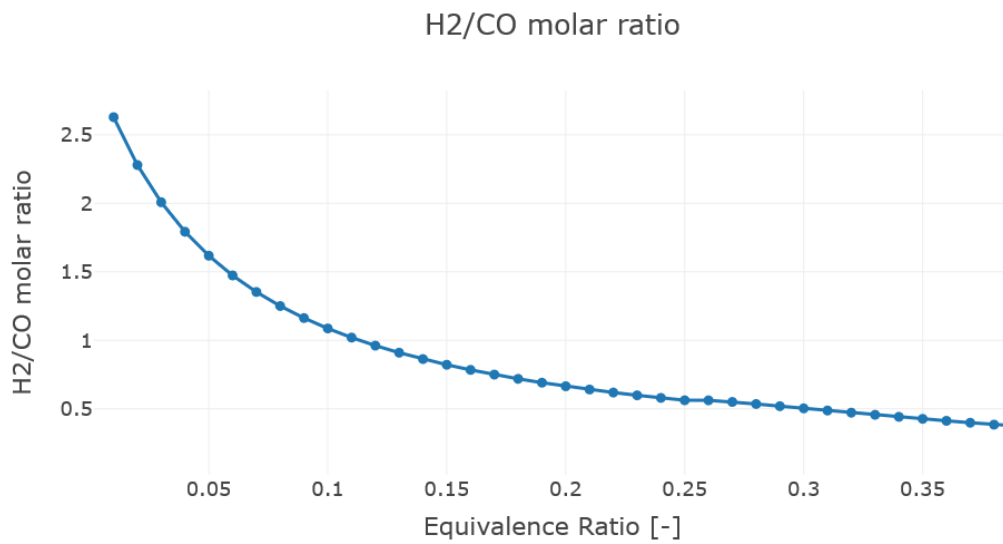


Figure 4.5: H_2/CO Equilibrium temperature evolution regarding the equivalence ratio for gasification with oxygen as GA

For an $ER = 0.25$ the equilibrium temperature is equal to 800°C and the outlet hydrogen to carbon monoxide ratio is equal to 0.56. The syngas composition is resumed in the table 4.1.

Syngas components	Number of mole for one mole of biomass	Mole percentage
CO	0.92	58.7
CO_2	0.075	4.8
CH_4	0.0077	0.5
H_2	0.51	32.9
H_2O_g	0.039	2.5
N_2	0.0075	0.48

Table 4.1: Composition of the syngas coming out from the gasifier in the case of gasification with oxygen as GA

The model also predicts a production of 0.00014 moles of char.

4.2.2 Vapor gasification

For the vapor gasification, there are three customizable parameters.

The first one is the equivalence ratio (ER) which is arbitrarily set at 0.25 (as the optimal ER for oxygen gasification).

The second one is the temperature of the steam entering the reactor. The production of steam requires a lot of energy and equipment allows to have steam around $300\text{-}400^{\circ}\text{C}$. At this range of temperatures, the hydrogen to carbon monoxide ratio does not change that much with the steam inlet temperature and the ER fixed (see figure 4.6). The inlet vapor temperature was therefore chosen at 250°C for safety.

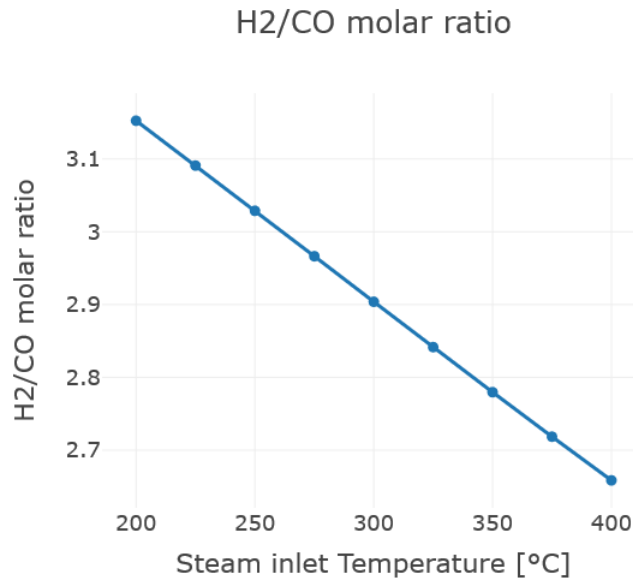


Figure 4.6: Hydrogen to carbon monoxide ratio evolution with $ER=0.25$ and $SBR=1.21$

The last parameter to define is the steam to biomass mass ratio SBR. Since it is possible to obtain hydrogen to carbon monoxide ratio of 3 with vapor gasification, the SBR is chosen such

that the ratio reaches this value. The figure 4.7 shows the evolution of the hydrogen to carbon monoxide ratio regarding the evolution of the SBR and the steam inlet temperature. For a steam inlet temperature of 250°C, the hydrogen to carbon monoxide ratio reaches 3 for a SBR of 1.21. The value of the SBR is therefore set at 1.21.

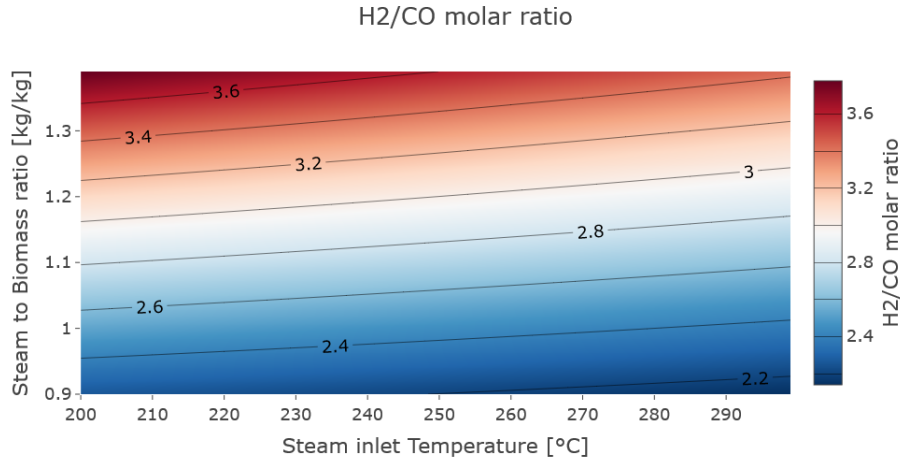


Figure 4.7: Hydrogen to biomass ratio evolution with SBR and steam inlet temperature

For a SBR = 1.121, a steam inlet temperature of 250°C, the equilibrium temperature reaches 665°C (see 4.8).

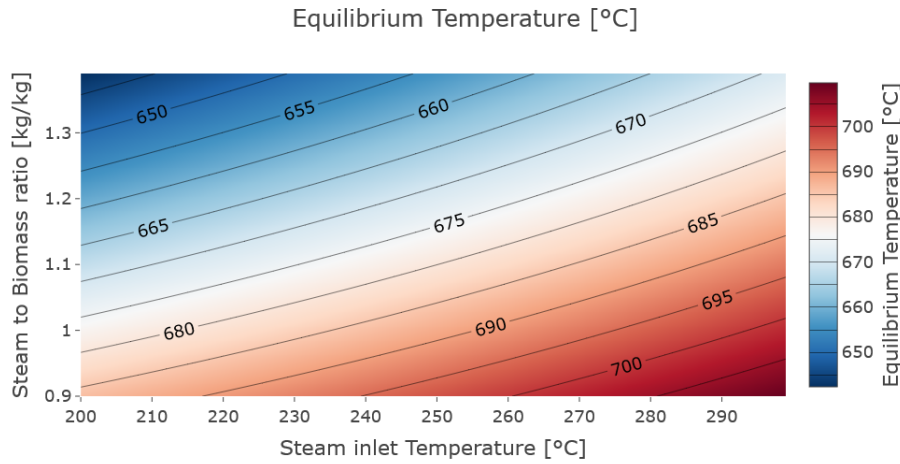


Figure 4.8: Equilibrium temperature evolution with SBR and steam inlet temperature

The table 4.2 resumes the composition of the syngas at the outlet of the gasifier for SBR = 1.121, ER=0.25 and a steam inlet temperature of 250°C.

Syngas components	Number of moles for one mole of biomass	Mole percentag
CO	0.35	11.4
CO ₂	0.64	20.39
CH ₄	0.0083	0.27
H ₂	1.07	34.4
H ₂ O _g	1.04	33.3
N ₂	0.0074	0.24

Table 4.2: Composition of the syngas coming out from the gasifier in the case of gasification with vapor as GA

4.2.3 Cooler 0

After the gasifier, the syngas goes through a cooler. The cooler 0 decreases the syngas temperature to 300°C, condenses and purges the vapor. The syngas composition after the Cooler 0 for each model is summarized in the table 4.3.

Gas components	Oxygen gasification	Vapor gasification
CO	60.2	17
CO ₂	4.9	30.5
CH ₄	0,508	0.4
H ₂	33.83	51.6
H ₂ O	0	0
N ₂	0.49	0.36

Table 4.3: Gas composition in moles percentage for the oxygen and vapor gasification cases at the outlet of the Cooler 0

4.3 Methanation

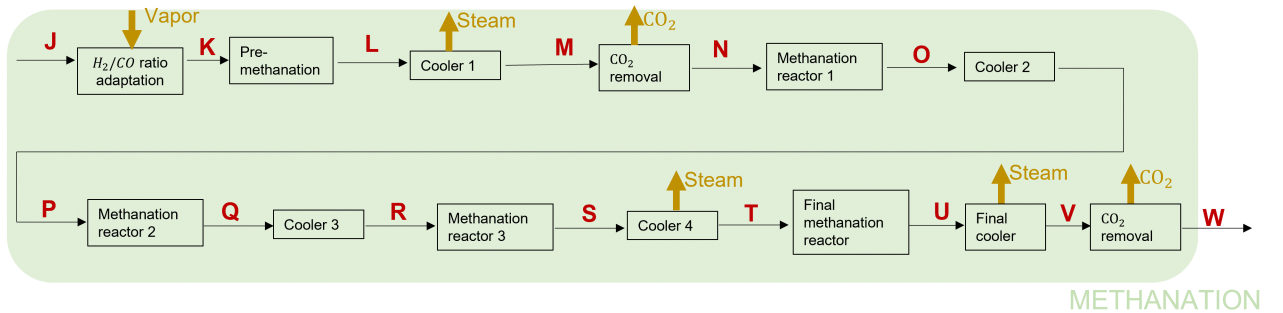


Figure 4.9: Scheme of the methanation step set-up

4.3.1 Hydrogen to carbon monoxide ratio adaptation

As discussed in the section 2.2.1, monoxide methanation requires an hydrogen to carbon monoxide molar ratio equal to three. This is already the case for the syngas coming from the vapor gasification since the number of moles of hydrogen is equal to 0.35 and the number of

moles of carbon monoxide is equal to 1.074 given $\frac{H_2}{CO} = 0.33$.

The syngas coming from oxygen methanation needs a supply of hydrogen to reach the hydrogen to carbon monoxide molar ratio of 3. The number of moles of CO in the syngas at the outlet of the gasification is equal to 0,9166. The number of moles of hydrogen should therefore reach the value of $0.92 \cdot 3 = 2.75$.

The table 4.4 resumes the composition of the gas after this step (at the inlet of the pre-methanation reactor) for each cases.

Gas components	Oxygen gasification	Vapor gasification	GoBiGas
CO	24.7	17	16.5
CO ₂	2	30.5	20.2
CH ₄	0.2	0.4	8.3
H ₂	73.2	51.6	52.8
H ₂ O	0	0	0
N ₂	0.2	0.36	0

Table 4.4: Gas composition at step C in moles percentage for the oxygen and vapor gasification cases an GoBiGas

4.3.2 Gas composition through the process

The figure 4.10 shows the evolution of the methane molar fraction computed with the models. The letters correspond to the flux presented in the figure 4.9.

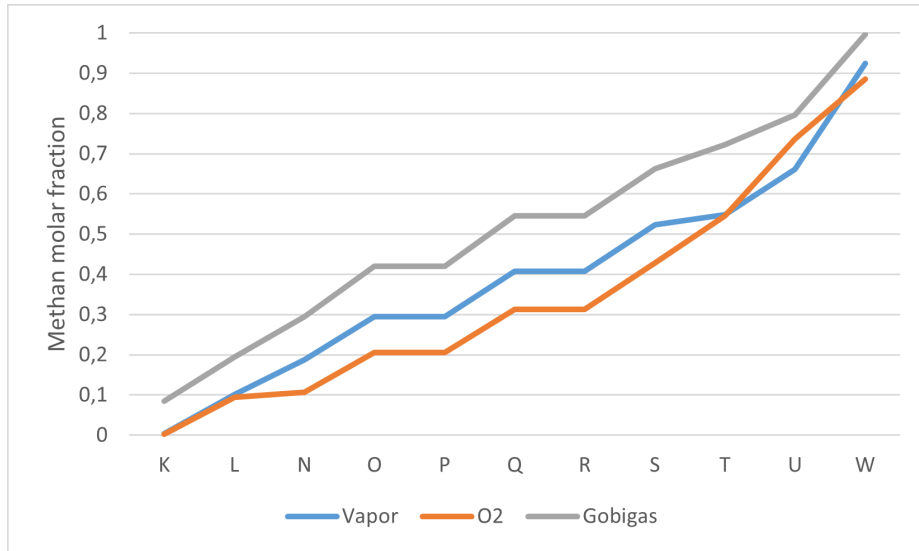
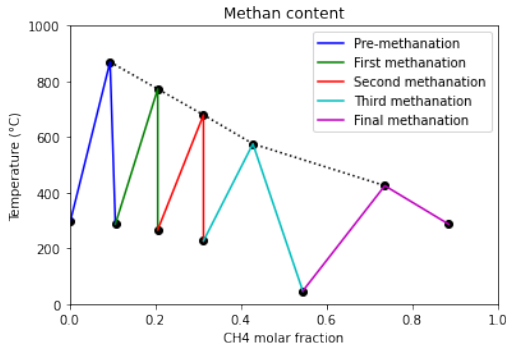


Figure 4.10: Methan molar fraction at every step of the process where the letters refer to the step in figure 4.9

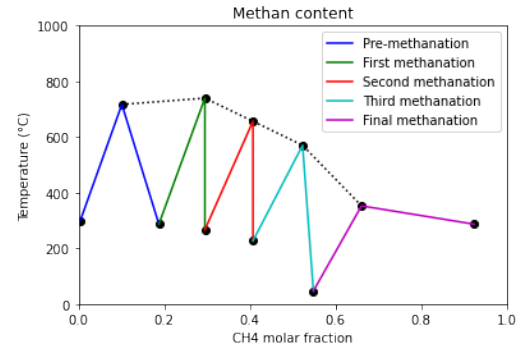
The stages can be distinguished by the methane content. The positives slopes are either methanation reactors in which methane is produced through the consumption of other compounds, or purge stages in which the composition of some elements (vapor and/or carbon monoxide) drops. The null slope represent non-purging cooling stages where the composition of the gas does not change.

The inlet composition of the gas has a big impact on the methane component. In the GoBiGas case, the syngas at the inlet of the pre-methanor is significantly higher than in the two other cases. Therefore, in graph 4.10, the curve for the GoBiGas case is shifted slightly upwards compared to the other two cases.

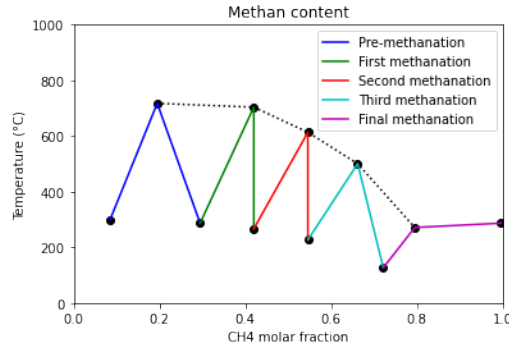
The same statement can be done in with a graph representing the evolution of the methane content and the gas temperature in the figure 4.11.



Oxygen gasification case



Vapor gasification case

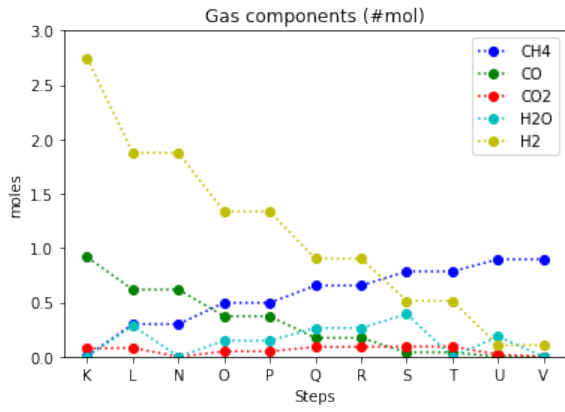


GoBiGas

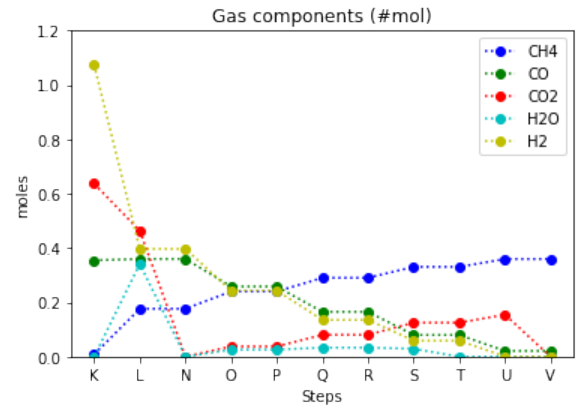
Figure 4.11: Methan content and temperature evolution through the methanation stages where the letters refer to the step in figure 4.9

It is also interesting to see how the pre-methanation reactor temperature is impacted by the composition of the syngas. In the vapor gasification and GoBiGas cases, the syngas contains much more carbon dioxide which is a ballast gas. It is why the pre-methanation reaches an higher temperature in the oxygen gasification case for the pre-methanation. The first methanation has the same temperatures for both cases since the ballast gas was removed during the passage in the Cooler1 and in the CO₂ scrubber.

To understand the differences between the vapor gasification and oxygen gasification cases, it is interesting to study the evolution of each species during the process. The graph 4.12 shows the evolution of the mole number of each species.



Oxygen gasification case



Vapor gasification case

Figure 4.12: Evolution of mole numbers for individual gas through the methanation stages where the letters refer to the step in figure 4.9

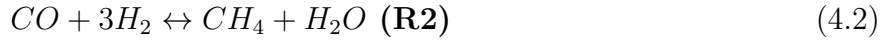
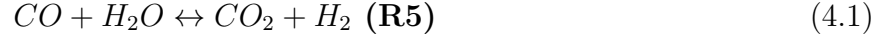
Please note that the calculations were made for one mole of biomass entering the whole process. Since the gasification does not give the same gas for oxygen or vapor as GA and since it was necessary to add hydrogen for the oxygen gasification case, the total amount of moles of gas entering the methanation is not the same. It is therefore not convenient to compare the number of moles of each species among the different species. However, it is interesting to compare the number of moles of two species in each case. Also note that for readability reasons, the two graphs are not at the same scale.

During the pre-methanation step, the number of moles of carbon monoxide decreases in the oxygen gasification case while it stays constant in the vapor gasification case. The only difference in this step between the two cases is the composition of the syngas entering the reactor. The major difference is in the carbon dioxide content. The pre-methanation in vapor gasification case receives a syngas with a higher carbon dioxide fraction. The way the dioxide carbon decreases a lot during the pre-methanation while the carbon monoxide remains the same lets think that the pre-methanation is a carbon dioxide methanation. This is correlated with the fact that carbon dioxide methanation is favored at higher temperature than carbon monoxide methanation since it is more exothermic.

The pre-methanation will have an impact on the rest of the process. Since the pre-methanation is a dioxide carbon methanation in the vapor gasification case, the carbon dioxide and the hydrogen are consumed while the carbon monoxide is not consumed. In the oxygen gasification case, the pre-methanation is a carbon dioxide methanation consuming hydrogen and carbon monoxide. At the end of the pre-methanation, the ratio hydrogen to carbon monoxide is equal to $\frac{1.87}{0.61} = 3.04$ for the oxygen gasification case and equal to $\frac{0.396}{0.359} = 1.1$ for the vapor gasification case.

The chains of methanation reactor will begin with a lack of hydrogen in the vapor gasification case. In the following methanation reactors, the system does not have enough hydrogen to make carbon methanation. There are also no carbon dioxide anymore because of the carbon dioxide removal between the steps L and N (see figure 3.1). So the reaction 2.14 and 2.15 cannot happen. Instead, a WGS reaction takes place producing carbon dioxide and hydrogen. This

hydrogen is then produced in carbon monoxide methanation reaction :

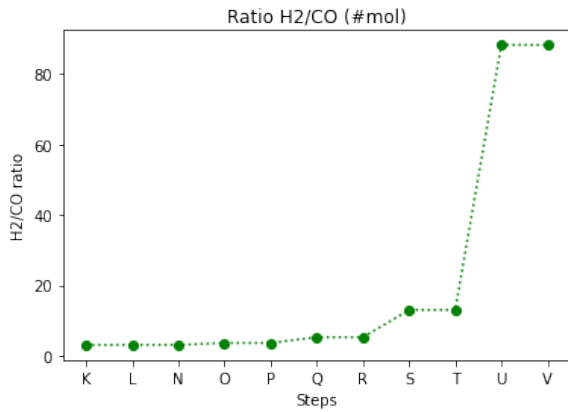


Each time a mole of methane is produced, a mole of carbon dioxide is produced. It is why the increase of carbon dioxide follows the one of methane in the graph displaying 'Vapor gasification case' in figure 4.12.

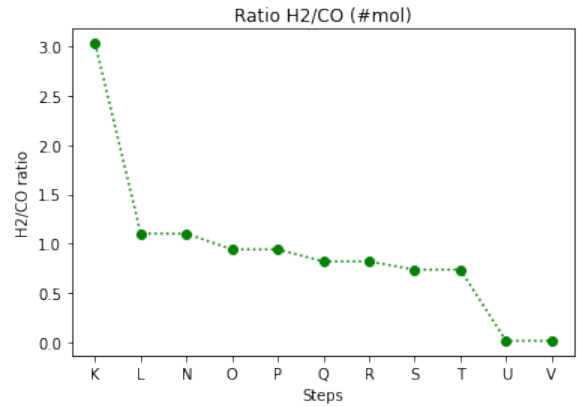
The amount of vapor does not increase that much as compared to the oxygen gasification case. It is because one mole of vapor is consumed and one mole of water is created for one mole of methane created (see the equation 4.3).

These equations also explained why the amount of hydrogen and carbon monoxide follows each other while in the oxygen gasification case, the amount of hydrogen decreases faster than the amount of carbon monoxide (which is an expected result since in theory, the carbon monoxide methanation consume three time less carbon monoxide than hydrogen).

The figure 4.13 expresses well this difference in the hydrogen to carbon dioxide ratio for the two cases. The left graph shows a constant ratio of three during the process (except in the last methanation where nearly all the carbon monoxide is consumed). This ratio is conserved because each time a carbon monoxide is consumed, three hydrogens are also consumed. On the other hand, the right graph shows a drop in the hydrogen to carbon monoxide ratio and then constant ratio of one.



Oxygen gasification case



Vapor gasification case

Figure 4.13: Hydrogen to carbon ratio evolution through the methanation stages where the letters refer to the step in figure 4.9

Seeing the hydrogen deficiency after pre-methanation, it is tempting to consider an adaptation of the hydrogen to carbon monoxide ratio in the case of steam gasification too. This adaptation would aim to increase the amount of hydrogen in the syngas sufficiently to always have an hydrogen to carbon monoxide ratio of three after pre-methanation.

This hydrogen supply could be done in two places:

- First improvement: Adding hydrogen before the first methanation reactor so that the hydrogen to carbon monoxide ratio is equal to three.
- Second improvement : Adding hydrogen before the pre-methanator reactor to boost the hydrogen content. If there is not enough hydrogen added, the system will just consume more CO_2 and not consume any CO. It is needed to add enough hydrogen for both methanations to occur. Hydrogen must be added so that the $\frac{H_2}{3CO+4CO_2}$ ratio is equal to 1.

Since, one of the goal of this master thesis is to study the interest of the introduction of hydrogen in the process, these two alternative cases are interesting to study. They were tested with the models and presented in the following box.

First improvement

The addition of hydrogen after the pre-methanator instantly boosts the hydrogen to carbon ratio to reach the value of three.

The graph 4.14 shows that the number of moles of methane produced is equal to 0.47 when the classic case produces only 0.36 moles (see 4.12). Even if the amount of moles is higher, it is far from reaching the amount of moles of methane produced by the oxygen gasification case. This is due to the fact that this improvement does not change the amount of carbon removed from the system in the first carbon dioxide scrubber. Since a lot of carbon were purged, the quantity of methane that can be produced is limited.

Since a lot of hydrogen (9.8%_{molar}) remains in the gas at the end of the methanation, the methane content is weaker than in the classic case

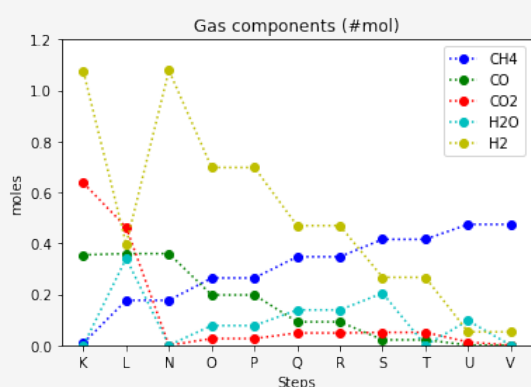


Figure 4.14: Syngas mole evolution

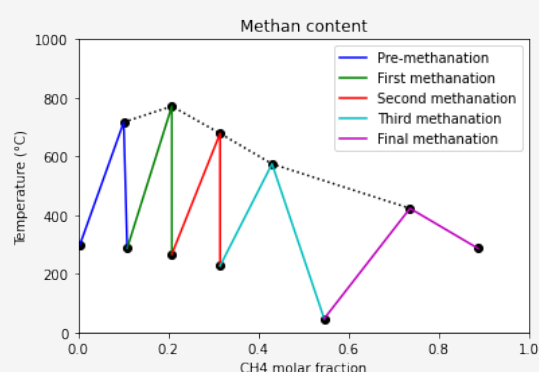


Figure 4.15: Methane fraction evolution

Second improvement

The model does not give expected results. Much more dioxide carbon was consumed but the amount of carbon monoxide does not decrease. On the contrary, since there is a large amount of carbon dioxide and hydrogen, the reverse reaction 2.18 seems to be encouraged. This could explain the slight increase of carbon monoxide and the big increase of water. The methanation chain begins with an hydrogen to carbon monoxide ratio of 4.93. All the carbon monoxide is consumed after the third methanation reactor.

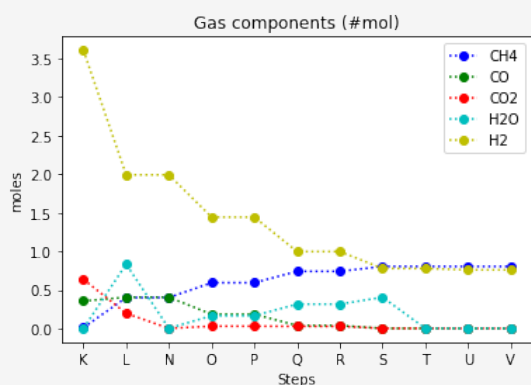


Figure 4.16: Syngas mole evolution

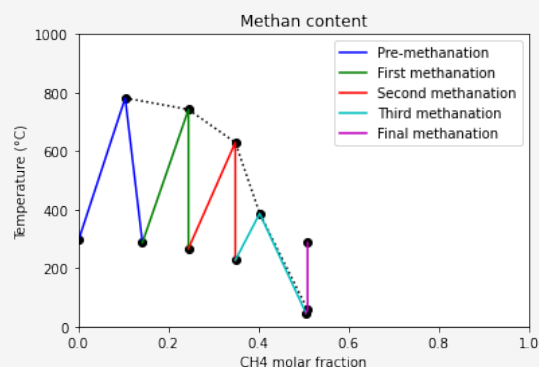


Figure 4.17: Methane fraction evolution

The theoretical analysis of the two alternatives leads to the conclusion that they do not provide a real improvement compared to the classic case under study.

Moreover, nowhere in the GoBiGas set-up was an additional hydrogen addition step planned. It is therefore tempting to ask why no hydrogen addition is planned. The energy cost of the hydrogen could be an explanation.

Another reason can lead in the results of the models used in this master thesis. It is important to remember that the data presented in this chapter are the result of theoretical models. It is therefore advisable to make a quick analysis of the gas entering and leaving the pre-methanation reactor and compare it to the assumptions mentioned above. In the literature, only the molar compositions of dry gas of certain stages are given (see table 4.5).

Components	Before pre-methanation	After pre-methanation
CO	16.5	11.5
CO ₂	20.2	26.5
CH ₄	8.3	26.8
H ₂	52.8	35.8
C ₂ H ₆	2.2	0

Table 4.5: GoBiGas dry gas composition of the gas in mole percentages before and after the pre-methanation [8]

It is already interesting to see that the hydrogen to carbon monoxide ratio is equal to three after the pre-methanation. However, it is more interesting to look in amount of moles. Unfortunately, the literature only gives the dry gas composition of the syngas in mole percents. In order to transform this into mole numbers, the total number of moles of syngas entering pre-methanation is first assumed to be equal to 1. To transform that in number of moles, the fact that the moles number of carbon is conserved during pre-methanation is used. The result is presented in the table 4.6

Components	Before pre-methanation	After pre-methanation
CO	0.16	0.084
CO ₂	0.2	0.19
CH ₄	0.083	0.2
H ₂	0.53	0.26
C ₂ H ₆	0.22	0

Table 4.6: GoBiGas dry gas composition in number of moles before and after the pre-methanation for 1 mole of inlet syngas

The amount of carbon monoxide decreases by half during pre-methanation while the amount of carbon dioxide decreases slightly. This result suggests that in reality, carbon monoxide methanation is still dominant even though the amount of carbon dioxide at the inlet is greater. So the idea of boosting the amount of hydrogen before the pre-methanation does not seem to be the best choice in practice.

4.4 Mass and energy balance

The evolution of the syngas composition through all the stages for both cases is presented in the section 6.2 and 6.3 of the Appendix.

4.4.1 Secondary inlet flux

The process is fed by biomass feedstock but also by secondary flux such as GA and hydrogen. This section will summarize all the inlet secondary flux.

Addition of hydrogen

The supply of hydrogen needed to upgrade the syngas coming from oxygen methanation is calculated by subtracting the number of moles to reach (2.23 see sub-section 4.3.1) and the actual number of moles in the syngas before the hydrogen addition (0.51). The H_2/CO adaptation step in the diagram 4.1 need therefore to add $2.75 - 0.51 = 2.23$ mole of pure hydrogen .

The hydrogen can be produced by water electrolysis. This process uses electricity to decompose water into oxygen and hydrogen. The set-up is represented in the figure 4.18. Two tanks full of water are separated by a membrane allowing the passage of the protons, blocking the passage of the reactants and blocking an electronic pathways from one tank to the other. There are two electrodes, each immersed in a pool and connected by a DC electrical power.

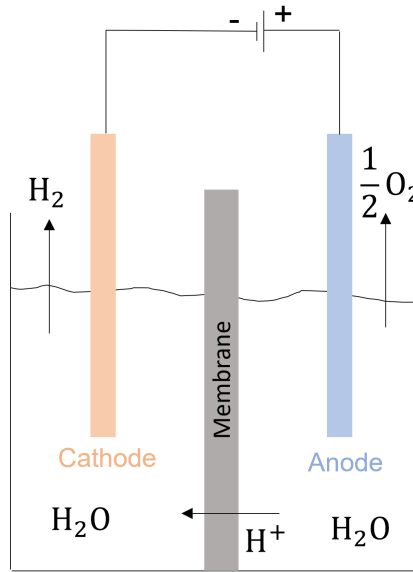
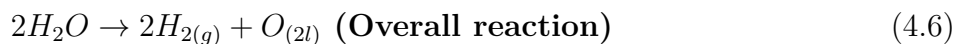
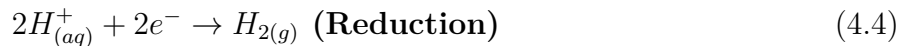


Figure 4.18: Scheme of water electrolysis technology

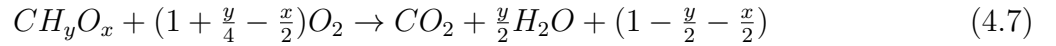
In the cathode, the hydrogen cations are reduced to form hydrogen gas (eq 4.4) while in the anode an oxidation reaction occurs forming oxygen gas (eq 4.5).



Oxygen

The oxygen gasification case and vapor gasification case have the same ER. Since the calculation is made for one mole of biomass for the two cases, the amount of oxygen entering the reactor is the same for both cases.

The definition of the ER 3.10 allows to compute the number of moles of oxygen needed for one mole of biomass. Given that the gasification runs for one mole of biomass, the mass of biomass $m_{biomass}$ is equal to the molar mass of biomass $Mm_{biomass}$ which is equal to 0.023 [kg/mol].



The coefficient ma_1 can be computed regarding the combustion equation of biomass with oxygen 4.7, the coefficients being $y=1,139$ and $x=0,619$.

$$\begin{aligned} ma_1 &= \left(\frac{m_{O_2}}{m_{biomass}} \right)_{st} \\ &= \frac{(1 + \frac{y}{4} - \frac{x}{2}) \cdot Mm_{O_2}}{1 \cdot Mm_{biomass}} = 1.34 \end{aligned} \quad (4.8)$$

The equation 3.10 can be transformed into the equations 4.9 to find the number of moles of oxygen needed.

$$\begin{aligned} m_{oxygen} &= \frac{Mm_{biomass} \cdot ma_1}{ER} \cdot ma_1 = 0.0078 \text{ kg} \\ n_{oxygen} &= \frac{m_{oxygen}}{0.036} = 0.24 \text{ mol} \end{aligned} \quad (4.9)$$

The oxygen can be produced in the same time than hydrogen with electrolysis gasification. If no hydrogen supply is needed, less energy-demanding process are available such as air separation.

The vapor gasification case needs also vapor as GA. It is possible to compute the quantity of vapor needed using the SBR. The equation 4.10 uses the definition of the SBR, the molar mass of biomass $Mm_{biomass} = 0.023$ [kg/mol] and the molar mass of steam $Mm_{steam} = 0.018$ [kg/mol].

$$\begin{aligned} SBR &= \frac{m_{steam}}{m_{biomass}} \\ \rightarrow n_{steam} &= \frac{SBR \cdot Mm_{biomass}}{Mm_{steam}} = 1,56 \text{ mol} \end{aligned} \quad (4.10)$$

Summary

The table 4.7 summarises the secondary flux needed along the process like the oxygen and/or vapor and the additional hydrogen.

Additional flux (in moles)	Oxygen gasification	Vapor gasification
Oxygen	0.24	0.24
Steam	0	1.56
Hydrogen	2.23	0

Table 4.7: Additional inlet flux needed for each cases in number of moles for one mole of biomass entering the process

The oxygen gasification case needs about ten times more hydrogen than oxygen. With the water electrolysis, when one mole of hydrogen is produced, half a mole of oxygen is produced (see equation 4.6).

The water electrolysis can therefore be sufficient to supply the process with hydrogen and oxygen without additional oxygen production.

The vapor gasification case will need to produce vapor and oxygen independently. However, the oxygen can be provided by technology less energy-consuming than water electrolysis such as air separation.

In the case of a dual fluidized bed such as GoBiGas, it is not necessary to produce oxygen with an external process. The oxygen required for gasification comes from the combustion chamber (see section 2.4).

4.4.2 Hydrogen and carbon distribution

The hydrogen in the final bio-methane comes from the biomass and the additional hydrogen or vapor GA depending on the case. Not all the hydrogen introduced into the system is in the bio-methane, some of it is lost in the water purges. The figures 4.19 and 4.20 give the distribution of hydrogen sources and use for the oxygen gasification and vapor gasification case respectively.

A large proportion of hydrogen is found in bio-methane for the oxygen gasification case. In the other case, a lot of hydrogen is purged in the Cooler O. It is due to the fact that the vapor gasification produces a large fraction of vapor.

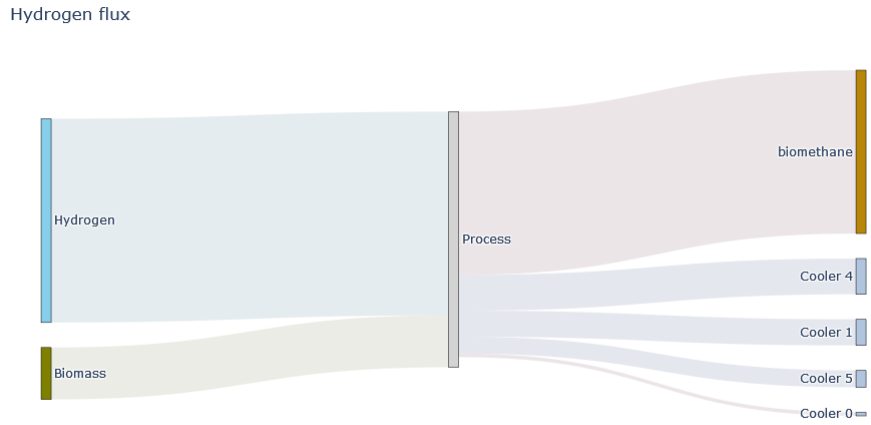


Figure 4.19: Sankey diagram of hydrogen flux for the oxygen gasification case

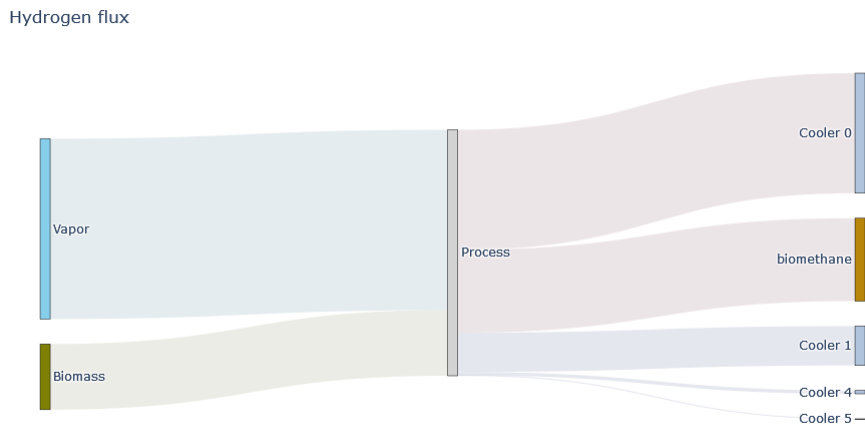


Figure 4.20: Sankey diagram of hydrogen flux for the vapor gasification case

The figures 4.21 and 4.22 give the distribution of carbon sources and uses for the oxygen gasification and vapor gasification case respectively. The only source of carbon is the biomass. A part is converted in the bio-methane while the other part is lost in the carbon dioxide collected by the CO_2 scrubbers. Only a small part of carbon exits the process in the carbon dioxide form for the oxygen gasification case.

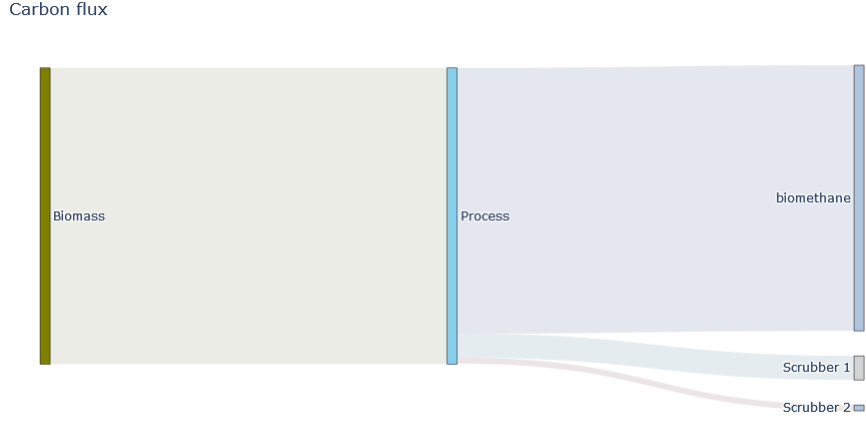


Figure 4.21: Sankey diagram of carbon flux for the oxygen gasification case

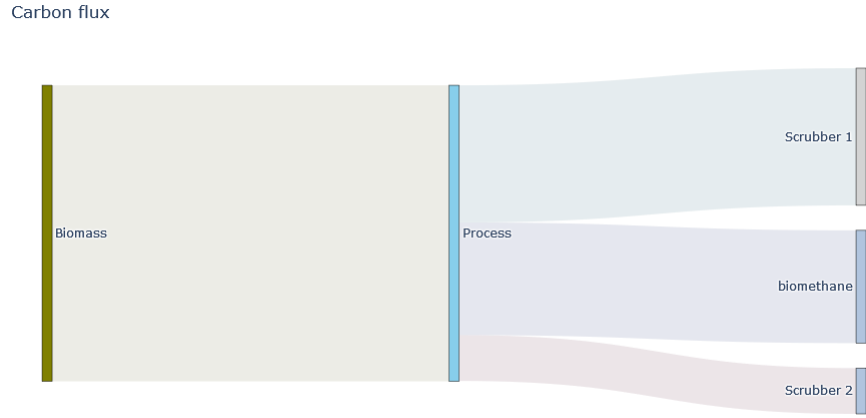


Figure 4.22: Sankey diagram of carbon flux for the vapor gasification case

4.4.3 Energy

One way of tracing the energy content through the stages is to calculate the Lower heating value (LHV). The lower heating value of a fuel is defined as the amount of heat released when fully burnt. The LHV takes into account the heat of evaporation of the water formed from the hydrogen in the material and the moisture.

The amount of heat released when burnt, without considering the heat of evaporation of the water formed from the hydrogen in the material and the moisture, is the higher heating value (HHV). The LHV and HHV can be related by the mass of water content in the fuel

$$LHV = HHV - \frac{m_{H_2O}}{m_{biomass}} \cdot 2.5 \quad (4.11)$$

Many scientists have been working on defining a relationship between HHV and fuel composition. Several mathematical relationships based on experiments have been published. In this thesis, the relationship of Channiwala and Parikh was used (see 4.12) [30].

$$HHV = 0.3491 \cdot (C) + 1.1778 \cdot (H) - 0.1034 \cdot (O) - 0.00151 \cdot (N) \text{ [MJ/kg]} \quad (4.12)$$

Four steps are most interesting to evaluate, they are represented in the figure 4.23.

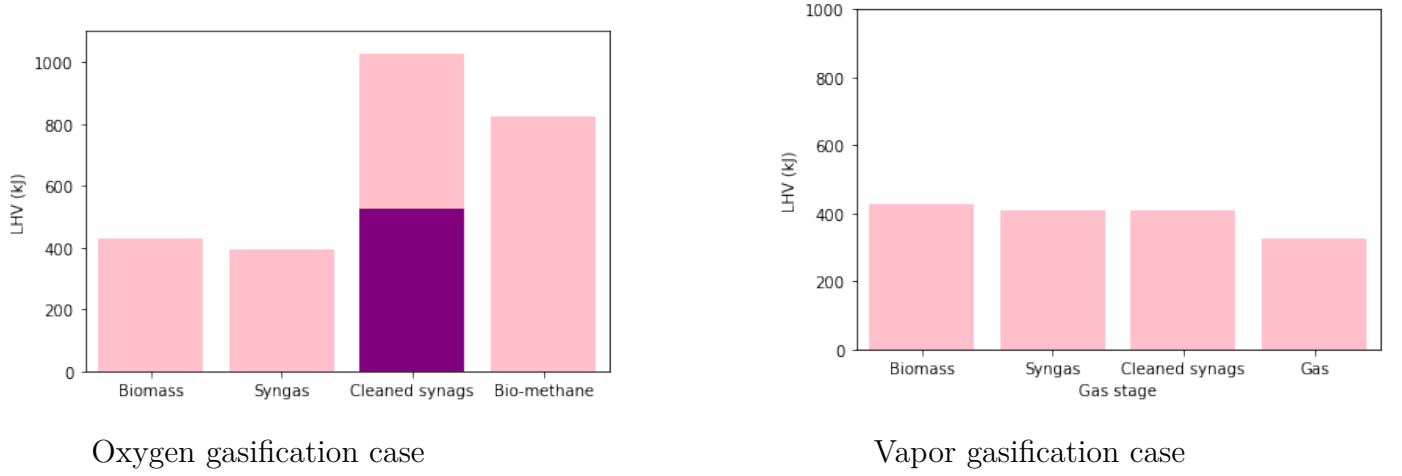


Figure 4.23: Evolution of the LHV through the process. The purple part is the LHV coming from the hydrogen

The graph about the oxygen gasification case on the figure 4.23 demonstrates that from an energy perspective, the hydrogen is well valued in the bio-methane.

It is understandable to have much more energy content in the bio-methane in the oxygen gasification case since there is an LHV input with the hydrogen addition. The amount of LHV in the produced SNG for both cases can not really be compared. To compare both cases, efficiencies can be computed.

The energy efficiency can be computed by comparing what is recovered in the bio-methane (the useful energy) and the energy invested in the step under interest.

Because inputs are not the same for oxygen gasification and vapor gasification cases, the definition of the overall energy efficiency will be different :

Oxygen gasification case :

$$\eta_{LHV-overall} = \frac{LHV_{bio-methane}}{LHV_{biomass} + LHV_{H_2}} \quad (4.13)$$

Vapor gasification case

$$\eta_{LHV-overall} = \frac{LHV_{bio-methane}}{LHV_{biomass}} \quad (4.14)$$

On the other hand, gasification energy efficiency and methanation energy efficiency have the same definition for both cases :

$$\eta_{LHV-gasification} = \frac{LHV_{syngas}}{LHV_{biomass}} \quad (4.15)$$

$$\eta_{LHV-methanation} = \frac{LHV_{Bio-methane}}{LHV_{Cleanedsyngas}} \quad (4.16)$$

The table 4.8 summarize the above efficiencies for both cases.

η_{LHV}	Oxygen gasification	Vapor gasification
Overall	86.4	76.6
Gasification	92	95.7
Methanation	80.2	80

Table 4.8: Summarize of the different energy efficiencies for each case

While the gasification and the methanation efficiencies are pretty similar, the overall efficiency is much higher in the oxygen gasification. When the objective is only to produce the most energy-content syngas from gasification, the vapor gasification case seems to be the best approach. In the energy content point of view, the oxygen gasification case is more interesting for an overall methanation process.

Chapter 5

Discussion

With the results presented in previous section, we can bring new insights on the integration of hydrogen supply in the methanation process using an oxygen downdraft gasifier. The hydrogen added is well used since a large part of hydrogen is found in the final bio-methane and few is lost in the purges. We can do the same observation with the carbon. The energy content in the syngas is well improved and the energy added with the hydrogen is well used.

However, there is no obvious conclusion about the choice of technology. Advantages and disadvantages of both oxygen gasification and steam gasification are apparent and their impact on the methanation production process is different. The introduction of hydrogen has some advantages even if the difference is not huge. These results should be read with the application in mind for which the technology will be used.

For example, let us say we have a source of biomass (sawmill waste, forestry waste etc.) and we want to exploit it by producing bio-methane. We also have the possibility to have electrolyzer and to exploit the production of hydrogen. The goal in the stockage here is to store the maximum amount of energy coming from the biomass and the hydrogen. We have demonstrated that the oxygen gasification with hydrogen supply does the job properly.

In other hand, we can imagine that we have an energy supply and we want to stock this energy. Since energy is poorly stored in the form of hydrogen, we would like to store it in the form of methane. In this case, the objective will be to transform biomass into bio-methane with as little carbon loss as possible during the process. In this case, the vapor gasification case is not the most optimal. Even if the energy efficiency is still high, the production of a syngas with high carbon dioxide content generates losses of carbon in the CO_2 scrubber.

The present master thesis is based on theoretical models for which hypothesis are made. These hypothesis do not always reflect the reality. It is why the results always need to be put into perspective.

First, the model does not take into account the practical limits. The biggest assumption the model makes is to work at system equilibrium. In practice, the reactor is potentially not at equilibrium since the catalyst increases the speed of the reactions.

Then, the model does not take into account instantaneous loss of pressure. Since the reactors are modeled as adiabatic and isobare reactors. However, there are pressure losses during the process. This is why, the pre-methanator reactor works at 13 bar while the next methanation reactors work are 6bar.

In practice, the CO_2 scrubber does not remove totally the carbon dioxide. Like the ideal equilibrium state, the CO_2 scrubber is also idealized. In the model, the CO_2 is therefore totally removed.

This area of study is really large and this master thesis covers only a small part. A lot of further studies could be interesting. For example, only the energy costs were studied here. However, the economical scope is an important parameter for political and financial reasons. First, the Capital expenditure (CAPEX) should be calculated. Then the operational cost needs to be assessed.

In addition, one of the reasons for studying the value of adding hydrogen to the process is to be able to couple the production of bio-methane to the energy supplied by IE. The research in this thesis can therefore be extended to the study of the operational flexibility of the process to compensate for the intermittence of renewable energy. Is it possible to stop and restart the production of bio-methane depending on the hydrogen supply? Will it be necessary to use a generator to compensate for the low production of IE? Is it possible to temporarily store hydrogen to ensure a constant supply to the process?

Chapter 6

Appendix

6.1 GoBiGas set-up

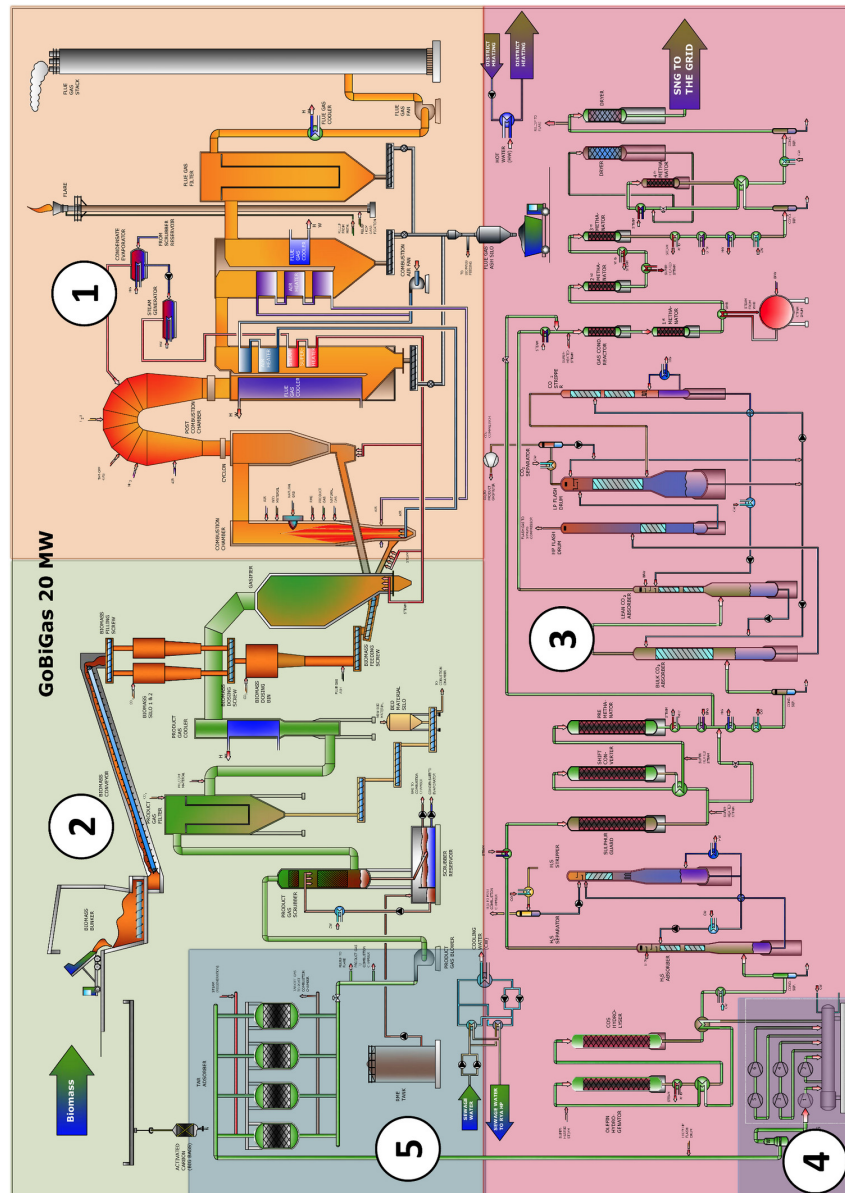


Figure 6.1: Schematic of the process layout for the GoBiGas demonstration unit [7]. 1: Heat generation, 2: Gasification, 3: methanation, 4: compression, 5: Gas cleaning

6.2 Mass balance for oxygen gasification case

Gasification				Methanation										
moles	B	C		K	L	N	O	P	Q	R	S	T	U	Final
CO	0.9166	0.9166		0.9166	0.618612732	0.618612732	0.369586417	0.369586417	0.171763304	0.171763304	0.03942576	0.03942576	0.001200846	0.001200846
CO2	0.0754	0.0754		0.0754	0.081174254	0.081174254	0.048846257	0.048846257	0.089374247	0.089374247	0.092508325	0.092508325	0.019913063	0
CH4	0.00774	0.00774		0.00774	0.300616481	0.300616481	0.493907445	0.493907445	0.651571605	0.651571605	0.781111538	0.781111538	0.891994956	0.891994956
H2	0.5149522	0.5149522		2.7498	1.878001413	1.878001413	1.326519893	1.326519893	0.895249851	0.895249851	0.510845806	0.510845806	0.105965734	0.105965734
H2O	0.03907	0		0	0.286830918	0.286830918	0.146360185	0.146360185	0.263065598	0.263065598	0.38904782	0.38904782	0.183315852	0
N2	0.007475	0.007475		0.007475	0.000138428	0.000138428	0.007338683	0.007338683	0.007325815	0.007325815	0.007313317	0.007313317	0.007339855	0.007339855
Tot	1.5612372	1.5221672		3.757015	3.164924225	2.79736053	2.39255888	2.39255888	2.07850419	2.07850419	1.82099529	1.82099529	1.20973006	1.006501391
H2/CO	0.561806895	0.561806895		3	3.03582729	3.03582729	3.589200878	3.589200878	5.21211359	5.21211359	12.95715799	12.95715799	88.24255261	88.24255261
Mm														
masse (gr)														
28 CO	25.6648	25.6648		25.6648	17.32115648	17.32115648	10.34811968	10.34811968	4.809372509	4.809372509	1.103821291	1.103821291	0.033623693	0.033623693
44 CO2	3.3176	3.3176		3.3176	3.571667157	3.571667157	2.149235322	2.149235322	3.932466872	3.932466872	4.07036631	4.07036631	0.876174766	0
16 CH4	0.12384	0.12384		0.12384	4.809636396	4.809636396	7.902519117	7.902519117	10.42514568	10.42514568	12.4977846	12.4977846	14.27191029	14.27191029
2 H2	1.038143635	1.038143635		5.5435968	3.780508048	3.780508048	2.674264104	2.674264104	1.804823699	1.804823699	1.029865146	1.029865146	0.213626919	0.213626919
18 H2O	0.70384605	0		0.2093	5.159152246	5.159152246	2.63667873	2.63667873	4.739126743	4.739126743	7.009542492	7.009542492	3.302435078	0
28 N2	0.2093	0.2093		34.8591368	0.103875987	0.103875987	0.205483123	0.205483123	0.205122822	0.205122822	0.204772889	0.204772889	0.20551594	0.20551594
Tot	31.05752969	30.35368364		34.8591368	25.92094702	25.92094702	25.92094702	25.92094702	25.92094702	25.92094702	25.92094702	18.90671024	18.90671024	14.72468584
%massique														
CO	0.826563212	0.845525054		0.73624813	0.49689	0.668230079	0.39923	0.39923	0.18554	0.18554	0.042588	0.042588	0.0017784	0.002283481
CO2	0.106821117	0.10298102		0.095171605	0.10246	0	0.082915	0.082915	0.15171	0.15171	0.15703	0.15703	0.046342	0
CH4	0.003987439	0.00407799		0.003552584	0.13798	0.185558949	0.30487	0.30487	0.40219	0.40219	0.48215	0.48215	0.75488	0.968251191
H2	0.033426472	0.03420157		0.159028516	0.10861	0.14606144	0.10317	0.10317	0.069628	0.069628	3.97E-02	0.05447088	0.011299	0.01450808
H2O	0.022662654	0		0	0.148	0	0.10172	0.10172	0.18283	0.18283	0.27042	0.27042	0.17467	0
N2	0.006739106	0.006895374		0.006004165	0.00011119	0.000149531	0.0079273	0.0079273	0.0079134	0.0079134	0.0078989	0.010830699	0.01087	0.013957238
Tot	1	1		1	0.99405119	1	0.99986323	0.99986323	0.9998114	0.9998114	0.9998189	1	0.9998194	1
%molaire														
CO	58.70984883	60.21677513		0.24397028	0.195458939	0.221140908	0.15447328	0.15447328	0.082644054	0.082644054	0.021658941	0.027547254	0.000992856	0.001193089
CO2	4.829503166	4.953463719		0.020069124	0.025648088	0	0.0200415905	0.0200415905	0.043002492	0.043002492	0.050803386	0.064636681	0.016460746	0
CH4	0.49576067	0.508485533		0.002060146	0.099883785	0.107464005	0.206434813	0.206434813	0.313504209	0.313504209	0.439111542	0.545772042	0.73735026	0.886233208
H2	32.98559788	33.83019947		0.731910859	0.593379582	0.671345603	0.554435631	0.554435631	0.430750196	0.430750196	0.280688323	0.35695412	0.08759451	0.105281259
H2O	2.502502503	0		0	0.090485869	0.061173075	0.061173075	0.061173075	0.126574227	0.126574227	0.213753163	0.213753163	0.15153448	0
N2	0.478786952	0.491076145		0.001989611	4.37382E-05	4.94851E-05	0.003067295	0.003067295	0.003524822	0.003524822	0.004017645	0.005109903	0.006067348	0.007292444
Tot	100	100		1	1	1	1	1	1	1	1	1	1	1

6.3 Mass balance for vapor gasification case

	Gasification					Methanation									
	moles	B	C	K	L	N	O	P	Q	R	S	T	U	Final	
mm	CO	0.3548609	0.3548609	0.35988647	0.35988647	0.35988647	0.254727584	0.254727584	0.162823697	0.162823697	0.162823697	0.078897188	0.078897188	0.020959414	
	H2	0.6368379	0.6368379	0.463619782	0.463619782	0.463619782	0.037090664	0.037090664	0.037090664	0.037090664	0.037090664	0.123500425	0.123500425	0.135312721	
	CH4	0.008301455	0.008301455	0.17692455	0.17692455	0.17692455	0.237121283	0.237121283	0.286826854	0.286826854	0.286826854	0.32671986	0.32671986	0.355154391	
	H2	1.074809	1.074809	0.396710449	0.396710449	0.396710449	0.239903516	0.239903516	0.133459594	0.133459594	0.133459594	0.058187757	0.058187757	0.000360253	
	H2O	0	0	0.341337765	0.341337765	0.341337765	0.025643464	0.025643464	0.032932111	0.032932111	0.032932111	0.028627882	0.028627882	0.000127354	
	N2	0.007475	0.007475	0.000160693	0.000160693	0.000160693	0.007343202	0.007343202	0.007343202	0.007343202	0.007343202	0.007353976	0.007353976	0.00736501	
	Tot	2.082284255	2.082284255	1.73863971	1.73863971	1.73863971	0.80182969	0.80182969	0.80182969	0.702778545	0.702778545	0.623287087	0.594659205	0.536337693	
	H2/CO	3.028817771	3.028817771	1.02321099	1.02321099	1.02321099	0.541804231	0.541804231	0.541804231	0.819657066	0.819657066	0.737513707	0.737513707	0.017188125	
		CO	9.9361052	9.9361052	10.07682116	10.07682116	10.07682116	7.132372353	7.132372353	4.559063526	4.559063526	2.209121251	2.209121251	0.586863584	
		H2	28.0208676	28.0208676	20.39927041	20.39927041	20.39927041	1.631988153	1.631988153	3.493101848	3.493101848	5.434018694	5.434018694	6.70433592	
CH4		0.13282328	0.13282328	2.830792806	2.830792806	2.830792806	0.793940531	0.793940531	4.589296666	4.589296666	5.227517756	5.227517756	5.682470259		
H2		2.166814944	2.166814944	0.799769265	0.799769265	0.799769265	0.483645489	0.483645489	0.269064542	0.269064542	0.117306519	0.117306519	0.00072627		
H2O		0	0	6.149199839	6.149199839	6.149199839	0.461967004	0.461967004	0.593271983	0.593271983	0.205911327	0.205911327	0.206220275		
N2		0.2093	0.2093	0.004499405	0.004499405	0.004499405	0.205609665	0.205609665	0.205733072	0.205733072	0.056313292	0.056313292	0.000294288		
Tot		40.46591102	40.46591102	13.71188164	13.71188164	13.71188164	13.71188164	13.71188164	13.71188164	13.71188164	13.71188164	13.19387555	13.19387555	6.476280388	
		%massique													
		CO	0.167776925	0.245542605	0.24902	0.24902	0.24902	0.52016	0.52016	0.33249	0.33249	0.16111	0.167435356	0.04448	0.090617384
		CO2	0.473148673	0.692456117	0.50411	0.50411	0.50411	0.11902	0.11902	0.25475	0.25475	0.3963	0.411859175	0.50814	0
	CH4	0.002382328	0.00328235	0.069955	0.069955	0.069955	0.27669	0.27669	0.33469	0.33469	0.38124	0.396207903	0.43069	0.877428079	
	H2	0.036587933	0.053546674	0.191764	0.191764	0.191764	0.058326661	0.058326661	0.19622	0.19622	8.56E-03	0.008899883	5.50E-05	0.000112143	
	H2O	0.316709518	0	0.15196	0.15196	0.15196	0.033691	0.033691	0.043267	0.043267	0.037612	0.00017389	0.000112143	0	
	N2	0.003534152	0.005172255	0.000328139	0.000328139	0.000328139	0.014595	0.014595	0.015004	0.015004	0.015017	0.015606584	0.01563	0.031842394	
	Tot	1	1	1	1	1	0.999828	0.999828	0.999828	0.999828	0.999828	0.9998341	1	0.999168936	1
		%molaire													
		CO	11.36126304	17.04190478	0.206993127	0.206993127	0.206993127	0.317682904	0.317682904	0.231685641	0.231685641	0.126582419	0.132676307	0.039078763	0.054064091
CO2		20.38906765	30.58361981	0.266656616	0.266656616	0.266656616	0.046257504	0.046257504	0.112964004	0.112964004	0.198143724	0.207688692	0.284085772	0.284085772	
CH4		0.265780236	0.398670594	0.10176033	0.10176033	0.189491197	0.295725247	0.295725247	0.408132628	0.408132628	0.524188398	0.549423698	0.662184284	0.932526902	
H2		34.4111954	51.682404	0.228172891	0.228172891	0.228172891	0.299195103	0.299195103	0.189902772	0.189902772	0.093556269	0.097850595	0.00671691	0.000938552	
H2O		33.3333733	0	0.196324611	0.196324611	0.196324611	0.031981185	0.031981185	0.04685987	0.04685987	0.045930491	0.000237451	0.000237451	0	
N2		0.239320368	0.358980767	9.24246E-05	9.24246E-05	9.24246E-05	0.009158057	0.009158057	0.010455085	0.010455085	0.011796968	0.012366707	0.013732038	0.019187755	
Tot*		100	100	1	1	1	1	1	1	1	1	1	1	1	1

Bibliography

- [1] Wallonie service public SPW. Production d'électricité à partir d'énergies renouvelables en wallonie. <https://zealous-nobel-aa39f4.netlify.app/>. [Online; accessed 10-august-2022].
- [2] Jason Moore and Bahman Shabani. A critical study of stationary energy storage policies in australia in an international context: The role of hydrogen and battery technologies, 2016.
- [3] Prabir Basu. Design of biomass gasifiers, 2010.
- [4] Jiajian Gao, Yingli Wang, Yuan Ping, Dacheng Hu, Guangwen Xu, Fangna Gu, and Fabing Su. A thermodynamic analysis of methanation reactions of carbon oxides for the production of synthetic natural gas. RSC Advances, 2:2358–2368, 3 2012.
- [5] Muhammed Y. Worku. Recent advances in energy storage systems for renewable source grid integration: A comprehensive review, 5 2022.
- [6] From solid fuels to substitute natural gas (sng) using trempTM topsøe recycle energy-efficient methanation process.
- [7] Henrik Thunman, Martin Seemann, Teresa Berdugo Vilches, Jelena Maric, David Pallares, Henrik Ström, Göran Berndes, Pavleta Knutsson, Anton Larsson, Claes Breitholtz, and Olga Santos. Advanced biofuel production via gasification – lessons learned from 200 man-years of research activity with chalmers' research gasifier and the gobigas demonstration plant. Energy Science and Engineering, 6:6–34, 2 2018.
- [8] Martin Seemann and Henrik Thunman. Methane synthesis, 1 2019.
- [9] Léon Freris and Infield David. Les énergies renouvelables pour la production d'électricité. Dunod, 2009.
- [10] Mark Z.Jacobson. 100 % clean renewable energy and storage for everything. Cambridge university press, 2021.
- [11] EIA contributor. Renewable energy explained. <https://www.eia.gov/energyexplained/renewable-sources/>. [Online; accessed 10-february-2022].
- [12] Bruce G. Miller and David A. Tillman. Combustion Engineering Issues for Solid Fuel Systems. 2008.
- [13] Kristian Stangeland, Dori Kalai, Hailong Li, and Zhixin Yu. Co2 methanation: The effect of catalysts and reaction conditions. volume 105, pages 2022–2027. Elsevier Ltd, 2017.
- [14] Antonio Molino, Massimo Migliori, Vincenzo Larocca, Tiziana Marino, Alberto Figoli, Patrizia Casella, Pierpaolo Iovane, Antonietta Cerbone, Jury Rimauro, and Antonio Donatelli. Power production by biomass gasification technologies, 1 2018.

- [15] Wikipedia contributor. https://en.wikipedia.org/wiki/Steam_reforming. [Online; accessed 03-august-2022].
- [16] A. Dutta and B. Acharya. Production of bio-syngas and biohydrogen via gasification, 2011.
- [17] Chanchal Loha, Sai Gu, Juray De Wilde, Pinakeswar Mahanta, and Pradip K. Chatterjee. Advances in mathematical modeling of fluidized bed gasification, 2014.
- [18] Wikipedia contributor. https://fr.wikipedia.org/wiki/Enthalpie_libre. [Online; accessed 26-july-2022].
- [19] Wikipedia contributor. <https://en.wikipedia.org/wiki/Catalysis>. [Online; accessed 30-july-2022].
- [20] Stefan Rönsch, Jens Schneider, Steffi Matthischke, Michael Schlüter, Manuel Götz, Jonathan Lefebvre, Praseeth Prabhakaran, and Siegfried Bajohr. Review on methanation - from fundamentals to current projects. *Fuel*, 166:276–296, 2 2016.
- [21] Anton Larsson, Ingemar Gunnarsson, and Freddy Tengberg. The gobigas project demonstration of the production of biomethane from biomass via gasification.
- [22] Sacha Alberici, Marissa Moultak, Jaap Peters, and (Guidehouse. The future role of biomethane gas for climate / the future role of biomethane imprint, 2021.
- [23] In a world first, engie produces renewable gas from solid non-recyclable waste.
- [24] Jitka Hrbek. Status report on thermal gasification of biomass and waste 2019 IEA Bioenergy Task 33 special report Status report on thermal gasification of biomass and waste IEA Bioenergy Task 33 special report. 2015.
- [25] Henrik Thunman and Martin Seemann. The gobigas plant, 1 2019.
- [26] Der Technischen Fakultät and Michael Franz Walter Neubert. Catalytic methanation for small-and mid-scale sng production katalytische methanisierung für die sng erzeugung in kleinen bis mittleren anlagengrößen.
- [27] Álvaro L. De Bortoli, Greice S.L. Andreis, and Felipe N. Pereira. Chemical equilibrium, 2015.
- [28] Sahar Safarian, Runar Unnthorsson, and Christiaan Richter. The equivalence of stoichiometric and non-stoichiometric methods for modeling gasification and other reaction equilibria, 10 2020.
- [29] Cantera contributor. <https://cantera.org/>. [Online; accessed 26-july-2022].
- [30] Ayhan Demirbas, Namık Ak, Avni Aslan, and Nejdett Sen. Calculation of higher heating values of hydrocarbon compounds and fatty acids. *Petroleum Science and Technology*, 36:712–717, 6 2018.

UNIVERSITÉ CATHOLIQUE DE LOUVAIN
École polytechnique de Louvain

Rue Archimède, 1 bte L6.11.01, 1348 Louvain-la-Neuve, Belgique | www.uclouvain.be/epl