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Multiscale Design, Integration & Optimization of Biorefineries for the Production of Liquid Fuels

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Acknowledgements

To mommy, daddy, all the ingratas and gino.

To my neguileja.

To my old friends that I see every often but are always in my heart: Borbeto, Vitam, Ribas, Netam and Giulia.

To my new friends that have supported me in this journey: Paulo, Pergunto, Baby E and Baby V.

To my SuPER colleagues: Myke, AleX Rose, Davyde, Bax, Frank, Dany P, Alejandro, Angela and Bisotten. To my SuPERvisor Flavio Manenti.

To my Masters and friends from Capuera. Viva Agostinho. Viva Baixinho. Viva Pintado & Marcolino. Viva Grupo Ginga e Viva Grupo ICA.

I would like to acknowledge the financial support from the following institutions: the National Council of Scientific and Technological Development (CNPq) of Brazil (grant number 205843/2014-0); the CARIPLO foundation.

Abstract

Biorefineries have been conceptualized to substitute the traditional oil refineries, producing heat, electricity and chemicals (among which, liquid fuels) from biomass. In this work, these processes were studied from a multiscale perspective using computer simulations. Four different software were used: commercial process simulator Aspen HYSYS; energy integration software Aspen Energy Analyzer; GasDS, a gasification / pyrolysis simulator and the MATLAB programming environment.

Lignocellulosic biomass gasification was described with the aid of a detailed phenomenological model. In this model, biomass is considered a mixture of cellulose, hemicellulose and three surrogate compounds that account for the most abundant monomers in lignin. Biomass composition was determined from an innovative data fitting method based on Lagrange multipliers. The calculated biomass composition produces lower heating values (LHVs) that are consistent with experimental observations. The relative LHV error was not bigger than 10% for any of the biomasses studied. The developed method represents an improvement from the previous 'triangle model', especially because it uses experimental information in a more systematic approach to quantify biomass composition.

An entrained flow gasifier was simulated using a detailed, phenomenological model, implemented in the GasDS program. The model considered a kinetic mechanism based on the above mentioned results on biomass composition to successfully predict biomass conversion and syngas yield for a given oxygen consumption. Almond shells and olive pits were the two biomasses with the biggest syngas yield per oxygen input, with a value of 314 mol syngas / mol O_2^{in} . Biomass conversion values compared well with experimental values and were close to chemical equilibrium. The simulator displayed numerical instabilities during the unsteady state operation, due to the strategy used to increase the step size. This effect is not present during steady state operation and, therefore, does not influence these results.

The coproduction of heat, electricity and chemicals from second-generation biomass was assessed. Two different scale sizes were considered, with biomass lower heating value inputs of 1 and 100 MW, respectively. These scales are representative of decentralized and centralized production concepts, each of which with its own characteristic transformation pathways.

For the centralized concept, biomass gasification was considered. Two final uses for syngas were considered: production of methanol and production of Fischer-Tropsch (FT) fuels. The FT product distribution model considered olefin readsorption and it was solved using an innovative power series solution. Methanol production is the superior process, both in economic and in terms of final conversion to liquid fuels. The economics of the Fischer-Tropsch process suffers due to the low energetic yield of the reaction in terms of high valued liquid products. It remains to be confirmed (1) whether if the correlations used are adequate to represent the FT reaction system and (2) if further income could be expected if the other reaction products could be sold as high value products. Both processes are economically unfeasible, with product costs that range (approximately) from 60 to 90 €/MWh (MeOH) and 80 to 210 €/MWh (FT). Even so, methanol production is an interesting alternative to current biogas concepts. The minimum subsidy cost of this process ranges from half to one third of current biogas subsidy costs.

The decentralized utilization concept considers the anaerobic digestion of biomass for the production of biogas. Three biogas processes were assessed: HPC (biogas to methanol), BioCH4 (biogas to biomethane) and CHP (biogas to heat & electricity). The last two processes are already used commercially with the aid of subsidy policies. The economic analysis indicates that, without these policies, none of these attain self-sustainability due to high overall manufacturing costs; the estimated minimum support cost (MSCs) were 108, 62 and 110 \in /MWh for the HPC, BioCH4 and CHP processes, respectively. The model could explain currently practised government subsidies in Italy and Germany. It was seen that the newly proposed HPC process is economically comparable to the traditional CHP process. Therefore, the HPC process is a possible alternative to biogas usage. A subsidy policy was proposed: 50, 66, 158 and 148 \in /MWh for available heat, methane, electricity and methanol (respectively). The proposed policy results in a 10% OpEx rate of return for any of the processes, thus avoiding a disparity in the production of different products.

Table of Contents

A	cknov	wledgements	i
A	bstra	ct	iii
Ta	able o	of Contents	v
Li	st of	Figures	ix
Li	st of	Tables	xi
1	Ene	rgy Security, Biomass & Biorefineries	1
	1.1	Thermochemical and Biochemical Conversion of Biomass	1
	1.2	Biorefineries	3
	1.3	Objectives & Methods	5
2	Ligr	nocellulosic Biomass Gasification	7
	2.1	Lignocellulosic Biomass	7
	2.2	Biomass Gasification	9
	2.3	Conclusion	14
	2.A	Biomass Molecular Composition	17

	3.1	Introduction	1
	3.2	Materials and Methods	3
		3.2.1 Air Separation Unit (ASU)	24
		3.2.2 Biomass Gasification	5
		3.2.3 Quenching	7
		3.2.4 The Water-Gas Shift (WGS) Section	7
		3.2.5 Gas Sweetening	8
		3.2.6 Methanol Synthesis 2	8
		3.2.7 The Fischer-Tropsch (FT) Synthesis	ig.
		3.2.8 Distillation	1
		3.2.0 Distinction $3.2.0$ Dever Concretion $3.2.0$	1 19
		2.2.9 Tower Generation $2.2.9$ Tower Generation $2.2.9$	12 10
	<u>?</u> ?	3.2.10 Economic Assessment	
	3.3		.4
		3.3.1 Separation Columns	G.
		3.3.2 Reaction Sections	0
		3.3.3 Power Generation	1
		3.3.4 Economic Assessment	8
	3.4	Conclusion	:0
	3.A	Fischer-Tropsch Synthesis Stoichiometry - Olefin Readsorption Model	2
		3.A.1 Component Lumping	2
		3.A.2 Power series hypothesis 4	3
		3.A.3 Hydrocarbon Formation Rates	:4
		3.A.4 Recurrence Relationship	5
		3.A.5 Non Hydrocarbon Formation Rates	6
		3.A.6 Infinite series	8
		3.A.7 Experimental correlations	0
		3.A.8 Calculation algorithm	1
		3.A.9 Supplementary Material on Power Series	3
	3.B	MATLAB Codes	6
	0	3.B.1 GetSheet 55	6
		3.B.2 Importables 55	7
		3 B 3 Exportables 5	ġ
			0
4	Bio	gas Beyond CHP: The HPC ('Heat Power and Chemicals') Process 6	1
	4.1	Introduction	2
		4.1.1 The HPC Concept	5
	4.2	Methodology	7
		4.2.1 Pressurized Water Scrubbing (PWS)	7
		4.2.2 Methane Reforming 6	8
		4.2.3 Methanol Synthesis 7	'n
		$4.2.0$ Methanor Synthesis \dots 7	о И
		4.2.4 Distillation 7	0 /1
		4.2.5 For β and β as a second state of γ and γ	1 /1
	19	4.2.0 Economic Assessment	ים ניי
	4.0	A 2 1 DWC 7	2 0
		4.3.1 PW5	2 29
		4.3.2 Reforming Section	3
		4.3.3 Methanol Synthesis	6
		4.3.4 Distillation section	6
		4.3.5 Power Generation	7
		4.3.6 Economic Assessment	9
	4.4	Conclusion	2
-	a		0
5	Gen	eral Conclusions & Future Work 8	3
A	ppen	dices 8	5
	G	-law automs Mataulal	-
Α	Sup	Mein simulation promotion	1
	A.I	Main simulation parameters	1
	A.2	Simulation sections specifications	1
	A.3	Economic Assessment: PCI evaluation	5
	A.4	Data from other authors	4

Bibliography

List of Figures

1.1	World oil demand by sector. Historic data and forecast (years in bold, on the top). Total values in million oil barrels per day. Reproduced from IEA [53]	2
1.2	Scheme depicting biomass pyrolysis and gasification reactions, with the associated secondary gas-phase reactions (reproduced from Corbetta et al [18])	2
1.3	Scheme depicting biomass biochemical conversion route	3
1.4	Biorefinery superstructure scheme depicting possible conversion pathways	4
2.1	Scheme representing the problem posed by Equations 2.1 to 2.3. (a): The polygon repre- sents the set of the atomic compositions deriving from a convex combination of the biomass components. (b): Multiple solutions may arise when number of biomass components is bigger than the number of atomic elements. (c) The 'triangle method', from Ranzi et al [78]. (d) triangles represent the atomic composition (\mathbb{C}_j) of the biomass species analysed in this work	9
2.2	Scheme detailing the different scales of the GasDS simulator model (from Ranzi et al [78]).	12
2.3	Gas- and solid-phase mass and energy balances for the GasDS model (from Corbetta et al [18])	13
2.4	Steady state profiles of main system variables	15
2.5	Unsteady state simulation results for the start up procedure. (a): Temperature profiles for different reactor layers. (b): Temperature profiles for different time values. (c): Accumulated time-steps profile.	16

3.1	Projections for energy statistics in the European Union. Consumption data was taken from the report by IEA [53] while biomass supply was obtained from the BEE Project	
	report [80]	22
3.2	Methanol production cost from fossil and renewable sources. Adapted from the report by	
	IEA & IRENA [54]. Second generation (residual) biomass was considered in this techno-	
	economic assessment.	23
3.3	Scheme depicting the transformation pathway and the task assignment of each software.	
	Numbers with percentages indicate mass flow values.	24
3.4	Aspen HYSYS simulation used in the process assessment. Top lane represents the FT	
	fuel production process while the bottom lane is associated to methanol production. The	
	'OUE' stream is copied into 'OUE*' using a specific simulator unit (not shown).	24
3.5	HYSYS flowsheet depicting the Air Separation Unit (ASU).	25
3.6	Detail of the HYSYS gasification flowsheet. MATLAB is used to write the GasDS output	
	into the HYSYS spreadsheet ('GAS SS'). In the sequence, the spreadsheet assigns these	
	values to the streams 'Gas [*] ' and 'Ashes', effectively connecting the gasification simulator	
	with HYSYS.	26
3.7	Connection scheme between the different programs using an ActiveX interface: MATLAB	-
	was used to import /export data to HYSYS with Excel serving as a data storage medium.	26
3.8	HYSYS flowsheet depicting the quenching section.	27
3.9	HYSYS flowsheet depicting the WGS section.	28
3.10	HYSYS flowsheet depicting the 'gas sweetening' section for the FT fuels production.	$\frac{1}{29}$
3.11	HYSYS flowsheet depicting the methanol synthesis section.	30
3.12	HYSYS flowsheet depicting the FT synthesis section.	30
3.13	HYSYS flowsheet depicting the distillation section.	31
3.14	HYSYS flowsheet depicting the power generation section.	32
3.15	Mass and molar fraction profiles inside the FT reactor. Paraffins and olefins were grouped	-
0.10	and are represented by letters 'P' and 'O', respectively	37
3.16	Composite curves for biomass gasification processes obtained through pinch analysis using	
0.10	the Energy Analyzer software.	38
3.17	Production costs of biomass gasification processes as a function of biomass LHV input.	41
0.11	rioduction costs of sionass gasheddion processes as a randoton of sionass phiv input.	11
4.1	Graphical abstract depicting the result of the techno-economic assessment	61
4.2	Schematic representation of the current BioCH4 concept of biogas utilization. On the	
	bottom is the percentage of the carbon initially present in biogas that remains in the	
	process intermediates / final products.	64
4.3	Schematic representation of the HPC concept. On the bottom is the percentage of the	
	carbon initially present in biogas that remains in the methanol product.	65
4.4	Scheme of the investigated biogas utilization concepts.	67
4.5	Aspen HYSYS flowsheet of the investigated biogas utilization concepts; the top, middle	
	and bottom lane represent the CHP, BioCH4 and the HPC processes, respectively	68
4.6	HYSYS flowsheet of the PWS section for the BioCH4 process; the gas recycle (stream	
	'CO2*') is absent in the HPC concept (further details on the Supplementary Material).	68
4.7	HYSYS flowsheet of the methane reforming process	69
4.8	HYSYS flowsheet of the methanol synthesis step.	70
4.9	HYSYS flowsheet of methanol distillation.	71
4.10	Contour lines of functions of the previously introduced parameters R_1 and R_2 : (A) fraction	
	of inlet CH_4 that goes into the reformer; (B) CH_4 conversion in the reformer; (C) and	
	(D): Reforming step MY and EY; (E) and (F): S_1 and S_2 of syngas.	75
4.11	Contour lines of functions of parameters S_1 and S_2 : (A) R_1 ; (B) R_2 ; (C) & (D) MY of the	
	reforming and synthesis section (respectively)	77
4.12	Sensitivity analysis of functions of parameter D_1 : (A) Distillation MY; (B) Distillation	
	EY; other simulation parameters are those of the base conditions	78
4.13	Sensitivity analysis of the net electricity production; non-changing parameters assume	
	values from the base conditions: $(R_1, R_2, D_1) = (175\%, 30\%, 85\%)$.	78
4.14	Figure 14: Sensitivity analysis of the net OpEx of the HPC process; non-changing param-	
	eters assume values from the base conditions.	79
4.15	Sensitivity analysis of the MSC for the different processes; analyzed parameters: PCI and	
	cost/selling price of consumables/products.	81

List of Tables

2.1	Components used for describing lignocellulosic biomasses; atomic composition and lower heating value (LHV). All of the values are for DAF (dry, ash-free) biomass	8
2.2	Results for the composition analysis of lignocellulosic biomasses. Top: biomass atomic composition C; Middle: biomass composition for the new approach. Bottom: biomass composition for the triangle method. Except when noted otherwise, all of the values refer to DAF (dry, ash-free) biomass	10
2.3	Parameters used in the simulations.	12
2.4	Results of the simulation of corn stover gasification with GasDS.	14
2.5	Comparison of carbon conversion from different references	14
2.6	Comparison of the (steady state) gasification simulation results for different biomasses	14
3.1	Summary of the processing steps according to their order and function.	24
3.2	Main parameters used in the ASU section	25
3.3	Main parameters used in the WGS section.	28
3.4	Parameters used in the SWT section	29
3.5	Methanol synthesis reactions	29
3.6	Parameters used in the distillation section	31
3.7	Summary of OpEx evaluation methodology	32
3.8	Cost (selling prices) of consumables (products) pertinent of the biomass gasification process.	34
3.9	Biomass gasification process mass balance: mass flow values of the main streams and MY.	34
3.10	Biomass gasification process energy balance: energy flow values (columns 2 to 8, values in MW) and EY; values refer to the output of each process section.	35
3.11	Yearly amount of consumables/products for biomass gasification processes. \ldots	35
3.12	Column dimensions resulting from the assumptions used in this work. 'HP' and 'LP' indicate the high and low pressure columns in each section	36
3.13	Calculated process parameters for each separation section	36
3.14	Comparison between different references for electricity consumption in cryogenic air separation.	36
3.15	Comparison between the different reaction sections in the biomass gasification process	37
3.16	Energy balance for the power generation section for biomass gasification processes	38
3.17	PCI details of biomass gasification processes; values are in $M \in \dots \dots \dots \dots \dots \dots$	39
3.18	OpEx details of biomass gasification processes; values are in M \in /y	40
3.19	MSC for biomass gasification processes.	40

4.1	Biogas composition ranges; molar fraction values (in %) by Ryckebosch et al [84]	63
4.2	Biogas yields by feedstock [74].	63
4.3	Main Italian standards for supplied gas quality [90]; braces indicate molar fractions; the	
	asterisk indicates properties measured at 1 atmosphere and 15 °C.	64
4.4	Comparison of different biogas-to-biomethane upgrading technologies [41]	64
4.5	Reforming section reactions [39]; *: $kJ/(mol CO_2)$, in the last reaction.	69
4.6	Cost (selling prices) of consumables (products) pertinent of the process.	72
4.7	Biogas processes mass balance: mass flow values of the main streams and MY	73
4.8	Biogas processes energy balance: energy flow values (columns 2 to 8, values in kW) and	
	EY; values refer to the output of each process section.	73
4.9	Yearly amount of consumables/products for biogas processes	73
4.10	Operative parameters for the PWS section.	74
4.11	Operative parameters for the reforming section	76
4.12	Operative parameters for the synthesis section.	77
4.13	Operative parameters and performance indexes for the distillation section	78
4.14	Energy balance for the power generation section for biogas processes	79
4.15	PCI details for biogas processes; values are in $k \in \ldots \ldots \ldots \ldots \ldots \ldots \ldots$	80
4.16	OpEx details for biogas processes; values are in $k \in /y$.	80
4.17	MSC for each biogas process and comparison with data from other authors	80
4.18	MSC by product for each process; values on the top portion of the table are in \in /MWh.	
	The net OpEx values on the bottom part of the table already include revenues from the	
	support policy.	81

Chapter 1

Energy Security, Biomass & Biorefineries

In the last decades, world energy demand is constantly increasing as a consequence of population growth and economic development. According to the International Energy Agency (IEA), total primary energy supply is increasing [55]. The contribution of fossil fuels is still high thanks to recent developments of extraction technologies for new reserves [71]. On the other hand, there is urgent need to reduce such dependency due to the well-known drawbacks of petroleum: (1) its finite supply (2) emissions of green house gases(GHGs) and global warming and (3) increasing price and unexpected fluctuations [44].

Energy security and climate change mitigation are core elements in current European energy policy. The EU countries are mandated to meet by 2030 the following targets: 40% reduction in GHG emissions (from 1990 levels), 32% of renewable energy share and 32.5% improvement in energy efficiency [33]. Among different renewable sources, photovoltaics, wind and biogas have shown the biggest increase in the latest years [56], mostly due to tax incentives.

Figure 1.1 shows the world oil demand by sector, reproduced from the 'World Energy Outlook' report by IEA [53]. It is clear that the majority of the oil is used for energy applications with only a minor share being directed to the petrochemical sector. A similar behaviour is also observed for natural gas and coal [53]. These numbers suggest that the actions targeting GHG reduction should focus on the substitution of fossil energy sources.

Wind and solar are the renewables with the highest rate of growth in terms of installed units and power. However, these sources are characterised by high variability, unpredictability and uncontrollability. On account of these drawbacks, several researchers are reconsidering the role of biomass in future energy scenario [8]. Biomass energy truly constitutes an opportunity to boost local development because it (1) can improve energy security, reducing the dependency on foreign energy importations (2) has stable and programmable production, which does not suffer of variability, unpredictability and uncontrollability (3) develops local markets, promoting economic growth and reducing poverty (4) supports extra-regional development without any increase in GHG emissions and (5) is available in enormous quantities worldwide.

1.1 Thermochemical and Biochemical Conversion of Biomass

Among the different biomass conversion processes, thermochemical and biochemical processes in particular have been thoroughly studied and developed in the last years.

At the core of biomass thermochemical transformation processes are biomass pyrolysis and gasification reactions. Pyrolysis is the fundamental chemical reaction process that is the precursor of both the gasification and combustion of solid fuels. It is defined as the chemical changes that occur when heat is applied to a material in the absence of oxygen. In pyrolysis the feedstock decomposes and fragments itself into smaller molecules. At the same time, these fragments, which are unstable and reactive, repolymerize into different compounds through homogeneous reactions in the gas phase.

Conventional pyrolysis is pyrolysis which occurs under a slow heating rate. Conventional slow pyrolysis has been applied for thousands of years and has been mainly used for the production of charcoal.Slow pyrolysis of biomass is associated with high charcoal continent, fast pyrolysis is associated with tar, at low temperatures (675-775 K), and/or gas, at high temperatures. At present, the preferred technology is fast or flash pyrolysis at high temperatures with very short residence times. Fast pyrolysis is a process in which a material, such as biomass, is rapidly heated to high temperatures in the absence of oxygen. For biomass this yields liquids (almost 75% of the mass), char and non-condensable gases. Biomass pyrolysis





Figure 1.1: World oil demand by sector. Historic data and forecast (years in bold, on the top). Total values in million oil barrels per day. Reproduced from IEA [53].

is attractive because the liquid products have advantages in transport, storage, combustion, retrofitting and flexibility in production and marketing.

Gasification of biomass for use in internal combustion engines for power generation provides an important alternate renewable energy resource. The gasification of biomass is a thermal treatment, which results in a high production of gaseous products and small quantities of char and ash. Gasification is carried out at high temperatures in order to optimize the gas production, using air, pure oxygen or even water and carbon dioxide as oxidants. The resulting gas is a mixture of CO, CO_2 , H_2O , H_2 , CH_4 , other gaseous hydrocarbons, tars, char, inorganic constituents, and ash. The first step of lignocellulosic biomass gasification is the thermochemical decomposition (pyrolysis) of the cellulose, hemicelluloses and lignin compounds with production of char and volatiles. Figure 1.2 presents a scheme depicting such processes and the associated products.



Figure 1.2: Scheme depicting biomass pyrolysis and gasification reactions, with the associated secondary gas-phase reactions (reproduced from Corbetta et al [18]).

Biochemical conversion proceeds at lower temperatures and lower reaction rates and can offer high selectivity for products. For lignocellulosic biomass, these processes require pretreatment by chemical, physical, or biological means to depolymerize biomass into simple sugars. This set of pretreatments is often referred to as hydrolysis. The resulting sugars can then be fermented by the yeast and bacteria employed in the process. Feedstocks high in starch and sugar are most easily hydrolyzed. Lignocellulosic feedstocks (which includes the major fraction of organics in municipal solid waste) are more difficult to hydrolyze, requiring more extensive pretreatment.

Fermentation is generally used industrially to convert substrates such as glucose to ethanol for use in beverage, fuel, and chemical applications and to other chemicals (e.g. lactic acid used in producing renewable plastics) and products (e.g. enzymes for detergents). Strictly speaking, fermentation is an enzymatically controlled anaerobic process although the term is sometimes more loosely applied to include aerobic processing as well [36].

Bioethanol is an important renewable liquid fuel for motor vehicles which can reduce both the consumption of crude oil and environmental pollution. For lignocellulosic ethanol production, researchers have focused on a process model of dilute acid hydrolysis of hemicelluloses followed by enzymatic hydrolysis of cellulose. Another important product deriving from the fermentation of biomass is biogas, which has gained much attention in recent years. Biogas can be burned directly in situ in a combined cycle to generate electricity, or purified and upgraded to biomethane to be subsequently injected in the gas grid. With the aid of government subsidies, biogas numbers in Europe have grown at an elevated pace until recently, when a reduction in the same incentives discouraged its commercialization [8]. A scheme summarizing the pertinent steps for biochemical processes is seen in Figure 1.3.



Figure 1.3: Scheme depicting biomass biochemical conversion route.

1.2 Biorefineries

Biomass has been classified into different types ('generations') according to its origin and composition. First generation biomass (FGB) is the typical designation of vegetable food crops that are rich in starch, sugars and oil. The production of fuels from FGBs (such as sugarcane ethanol in Brazil, corn ethanol in the US, rapeseed biodiesel in Germany, and palm oil biodiesel in Malaysia) is characterized by mature commercial markets and well understood technologies [36]. Future targets and investment plans suggest strong growth will continue in the near future. Second generation biomass is residual, abundant vegetable material that is typically used in low-value applications (e.g. as animal fodder). Examples of such input are non-food crops, agro-industrial residues (sugarcane bagasse, cereal straw and leaves, corn cob), municipal waste, pruning/forestry residues, etc [36].

The replacement of fossil fuels and petroleum derivatives with renewables is the basis of what is called a bio-economy. Second-generation biorefineries are particularly important in this scenario because of their economic, environmental and social role. Second-generation biorefineries use second-generation biomass as input and do not compete with other industry sectors for the use of sugar/starchy materials. Dahunsi et al have demonstrated the techno-economic potential of using papaya peels (a second-generation biomass) to coproduce biogas and fertilizer, thus avoiding fossil fuel emissions while adding value to a sustainable production chain [23]. Hagman et al have studied how biogas is an important player inside a biorefinery, its presence adding flexibility to the plant design, while allowing for the valorization of waste streams. In fact, process integration is a crucial, fundamental concept that is inherent to the sustainability of the biorefinery concept as much as circularity is fundamental to the concept of bio-economy [45].

Different biofuels have been exploited world-wide, like wood, biogas, biomethane, bioethanol, biodiesel, vegetable oil, etc [8]. Different conversion routes are foreseen for obtaining each of these products, among which are biological, physical, chemical and thermochemical pathways. These routes can be systematically represented using a superstructure. Superstructures are models used in optimal process design. They represent all the possible interconnections between the sub-processes inside the main process, together with their equations and constraints [99]. Corbetta et al used such concepts in order to select the most economical design for the distillation of complex bio-chemicals [19].

While the selection of the optimal design is usually done with optimization techniques, the construction of the superstructure model is a matter of describing each step by choosing an appropriate set of equations. A qualitative description of a biorefinery superstructure was introduced on a previous work by the author [4]. Such a scheme is presented on Figure 1.4, showing the different processes and their possible connections. The top box on each block represents the operation while the boxes below represent products; blue (colored) boxes represent final products, white boxes are intermediate products. Plus/minus signs are 'decisional mixers/splitters'; the first one means different inputs may be offered for a process (e.g. the conditioning operation may receive two types of input: biogas or producer gas); the second one means the same input can be directed to different processes (e.g. syngas may become one of two products). Following the scheme of Figure 1.4, computer simulations can be performed in order to develop the mass and energy balances pertinent to each process. Those balances are necessary to assess the economics of each transformation pathway. Such indices, in their turn, enable determining the level of maturity of the corresponding technology and how close it is to commercial implementation.



Figure 1.4: Biorefinery superstructure scheme depicting possible conversion pathways.

Figure 1.4 collects different biomass conversion processes which take as input a generic second generation (lignocellulosic) biomass. Among these are biochemical processes (hydrolysis, fermentation), chemical processes (dehydration, synthesis), thermochemical (gasification and pyrolysis) and physical (hydrogen purification). All of these products are commodities, consumed globally in massive scales, with varying levels of sophistication. γ -valerolactone (as much as methanol) is a precursor of different types of products, such as polymers, solvents, fuel additives and biofuels [3]. This scheme supports the huge versatility associated with biomass conversion into chemicals. It is a thriving field, especially for sugar-derived products. Many of such products have reached or are close to reaching commercial implementation [25]. This is a very interesting feature, especially from the point-of-view of biomass valorization. On the other hand, this aspect alone has a limited potential to contribute to GHGs reduction. Alternatively, a biorefinery production model can focus on energy applications. The issue with bioenergy is its high manufacturing costs and low market prices, especially if compared to the other previously mentioned bioproducts. This factor combination usually produces economically unfeasible processes. Some recent attempts at improved process economics include increasing boiler pressure in biomass-fired turbines. Alternatively, this scenario could be changed by associating bioenergy production to other high-value commodity chemicals. In a properly structured process, it may well be that the income from selling valuable bioproducts compensates for the lesser value of bioenergy. This might be a good solution to promote the diffusion of biomass energy and lastly meet the sought-after environmental targets.

Energy production from biomass has been proposed and re-proposed over the years in different processes. For some processes (as is the case of gasification) different sources have presented conflicting values for production costs. This may originate from a lack agreement in the typical size these plants would adopt at a commercial implementation of the process. Alternatively, differences in product cost may result from an overly simplified process assessment. In some new processes (as is the case of biogas), different process designs may result in more economic configurations. As it will be made clear throughout this work, the potential reach of this technology is still not well understood. Maybe for this reason, biomass usage for energy production is an active area of research.

1.3 Objectives & Methods

The aim of this work is to elevate the description of biomass conversion processes for the production of chemicals, heat and electricity. In this work, these processes were studied from a multiscale perspective using computer simulations. Four different software were used: commercial process simulator Aspen HYSYS; energy integration software Aspen Energy Analyzer; GasDS, a gasification / pyrolysis simulator and the MATLAB programming environment. The results of such assessments provide effective means of comparing different transformation pathways, while gaining insight in the state-of-art and providing guidelines to close the gap between research and commercial application on the topic.

On Chapter 2, lignocellulosic biomass gasification was described with the aid of a detailed phenomenological model. Biomass composition was determined from an innovative data fitting method based on Lagrange multipliers. An entrained flow gasifier was simulated using a detailed, phenomenological model, implemented in the GasDS program.

The coproduction of heat, electricity and chemicals from second-generation biomass was assessed. Two different scale sizes were considered, with biomass lower heating value inputs of 1 and 100 MW, respectively. These scales are representative of decentralized and centralized production concepts, each of which with its own characteristic transformation pathways. Chapter 3 describes the centralized concept, in which biomass gasification was considered. Two final uses for syngas were considered: production of methanol and production of Fischer-Tropsch (FT) fuels. Chapter 4 presents the decentralized utilization concept, which considers the anaerobic digestion of biomass for the production of biogas. Three biogas processes were assessed: HPC (biogas to methanol), BioCH4 (biogas to biomethane) and CHP (biogas to heat & electricity). The last two processes are already used commercially with the aid of subsidy policies.

This work presents an updated overview on the production of heat, electricity and biofuels from biomass. Among its main contributions are, in the first place, innovative, robust methods for performing the energy/mass balances in different process sections. Among such methods are those for the determination of biomass composition (Chapter 2) and for the product distribution model of Fischer-Tropsch synthesis (Chapter 3). Secondly, the critical discussion of the techno-economic assessment methodology brings more accurate values on the cost of production of bioenergy (Chapters 3 and 4). The calculated cost of energy compares well with the estimates given by other authors and are supported by the reported values of the governmental subsidy offered by different countries. In the third place, the economic assessments presented here indicate either more economic ways of producing bioenergy (by increasing the scale-size) or logistically interesting, comparable alternatives to the actual schemes (such as with liquid biofuels).

Chapter 2

Lignocellulosic Biomass Gasification

Abstract

Lignocellulosic biomass gasification was described with the aid of a detailed phenomenological model. In this model, biomass was considered a mixture of cellulose, hemicellulose and three surrogate compounds that account for the most abundant monomers in lignin. Biomass composition was determined from an innovative data fitting method based on Lagrange multipliers. The calculated biomass composition produces lower heating values (LHV) that are consistent with experimental observations. The relative LHV error was not bigger than 10% for any of the biomasses studied. The developed method represents an improvement from the previous 'triangle model', especially because it uses experimental information in a more systematic approach to quantify biomass composition.

An entrained flow gasifier was simulated using a detailed, phenomenological model, implemented in the GasDS program. The model considered a kinetic mechanism based on the above mentioned results on biomass composition to successfully predict biomass conversion and syngas yield for a given oxygen consumption. Almond shells and olive pits were the two biomasses with the biggest syngas yield per oxygen input, with a value of 314 mol syngas / mol O_2^{in} . Biomass conversion values compared well with experimental values and were close to chemical equilibrium. The simulator displayed numerical instabilities during the unsteady state operation, due to the strategy used to increase the step size. This effect is not present during steady state operation and, therefore, does not influence these results.

2.1 Lignocellulosic Biomass

"Biomass is biological material derived from living, or recently living organisms. In the context of biomass for energy this is often used to mean plant based material, but biomass can equally apply to both animal and vegetable derived material" [10]. Lignocellulosic biomass is vegetable derived material which is a mixture of the following components: cellulose, hemicellulose, lignin, extractives, ashes, sugars and starch [88].

For what concerns the kinetic modeling of pyrolysis and combustion of biomass, among the main components considered are cellulose, hemicellulose and lignin. Following such guidelines a method was defined for determining biomass composition in terms of these species. For this analysis, cellulose and hemicellulose are considered pure components, in opposition to lignin, which is further divided in three subtypes. These lignin subtypes are surrogate compounds that account for the most abundant monomers that compose lignin chains. Information on these components is summarized on Table 2.1 below, while further details are given on the work of Ranzi et al [79].

Problem statement: given a biomass atomic composition \mathbb{C} (determined experimentally) and given the biomass components' atomic composition \mathbb{C}_j (seen on Table 2.1 above), find the mass fractions (\mathbb{k}_j) of the biomass components that solves the following atomic mass balance (AMB):

$$\mathbb{C} = \sum \mathbb{C}_j \mathbb{k}_j \tag{2.1}$$

$$0 \le \mathbb{k}_j \le 1 \tag{2.2}$$

$$\sum k_j = 1 \tag{2.3}$$

The problem description is represented graphically in Figure 2.1, where the \mathbb{C}_j are plotted (blue squares). The enclosed region in Figure 2.1(a) shows the locus of \mathbb{C} for any given convex combination of the single species (i.e., a combination that satisfies Equations 2.2 and 2.3). When considering the inverse

Component	\rightarrow	CELL	HCELL	LIGC	LIGH	LIGO
Element		Numbe	er of atoms	s in the b	piomass s	species
C		6	5	15	22	20
Η		10	8	14	28	22
Ο		5	4	4	9	10
Element			Atomic m	ass fracti	ions $(\%)$	
C		44.4	45.5	69.8	60.6	56.9
Η		6.17	6.06	5.43	6.42	5.21
О		49.4	48.5	24.8	33	37.9
LHV (MJ/kg)		16.2	16.7	26.8	24.2	20.8

Table 2.1: Components used for describing lignocellulosic biomasses; atomic composition and lower heating value (LHV). All of the values are for DAF (dry, ash-free) biomass.

situation, it may be that different convex combinations of the \mathbb{C}_j produce the same \mathbb{C} . This multiplicity is due to the system being overdetermined, i.e., there are more biomass components (variables) than the number of atomic elements characterizing the system (equations). This is seen in Figure 2.1(b), in which the hypothetical biomass falls inside two different triangles (LIGO-CELL-LIGH and LIGC-CELL-LIGH). A past approach to deal with this issue was the 'triangle method', represented in Figure 2.1(c) [78]. In this approach a determined proportion is assumed between the mass fractions (\mathbb{k}_j) of certain biomass species. This effectively increases the number of equations so that the system becomes determined. An equivalent representation of the system resulting from this approach is the substitution of the original species by the 'equivalent species', labeled ES1-ES3 in Figure 2.1(c). The \mathbb{C}_j of each ES is calculated through a linear combination of two of the original species by considering the predetermined proportion between them. A positive aspect of this method is that the calculated atomic composition (\mathbb{C}) matches exactly the experimental value. The negative aspect of it is essentially the need to reliably estimate the ratios between biomass components.

In this work an alternative procedure is proposed in order to tackle the difficulties presented by the triangle method. The problem is initially tended in the same manner: the number of variables is reduced from five to three. This is done so by using the experimental mass fractions (\mathbb{k}_j) of cellulose and hemicellulose. Even for this new AMB, the previously established bounds usually prevent an exact solution to be found, i.e., the biomass \mathbb{C} cannot be matched exactly by a convex combination of the \mathbb{C}_j . It is possible, though, to estimate a solution which is the closest possible to the experimental values through an optimization process. The criterion chosen for evaluating the goodness of the solution is the SSRR (sum of the squared relative residues) of the AMB; this choice avoids high relative errors on the estimation of the hydrogen massive content, which is much lower than oxygen and carbon. For the mathematical details on the solution of the AMB the reader is referred to Appendix 2.A.

Different biomasses were analysed in order to test determine their composition in terms of the 5 previously mentioned components. Both the new and the triangle method were used to determine biomass composition. Biomass parameters were taken from the Phillys2 database [27]; their \mathbb{C}_j can be seen on Figure 2.1(d). Two entries from the database were used when any single entry could not provide all the required information. For each biomass type, the predicted composition was used to calculate the lower heating value (LHV), which was compared to the experimental values. For the triangle method the proportion between biomass components are those used by Ranzi et al [78]:

- ES1: 60% CELL and 40% HCELL
- ES2: 80% LIGH and 20% LIGC
- ES3: 80% LIGO and 20% LIGC

These proportions generate the ES seen in Figure 2.1. The results for the composition analysis are shown on Table 2.2. The Table is divided into three parts; in the top part there is biomass information from the Phillys2 database [27]. The middle part displays the results for the new method. In the bottom part the results for the triangle method are shown.

Not all of the biomass types have been successfully processed by the triangle method. Clearly this could be tended by choosing a more appropriate set of ES. For the new approach, none of the biomasses' atomic composition (\mathbb{C}) could be matched exactly. It is interesting to notice that there is no direct connection between the SSRR and the LHV relative deviation. In terms of the calculated LHV the new approach performed slightly better than the triangle model, which overly predicts wheat straw LHV by 14%. Biomass predicted composition differs greatly between the two methods, not only quantitatively



Figure 2.1: Scheme representing the problem posed by Equations 2.1 to 2.3. (a): The polygon represents the set of the atomic compositions deriving from a convex combination of the biomass components. (b): Multiple solutions may arise when number of biomass components is bigger than the number of atomic elements. (c) The 'triangle method', from Ranzi et al [78]. (d) triangles represent the atomic composition (\mathbb{C}_i) of the biomass species analysed in this work.

but also qualitatively. For every biomass, the new approach predicts that one of the lignin components (the least similar to \mathbb{C}) is absent from biomass composition. Contrarily, the triangle method predicts a biomass composition that is distributed between all of the components. Without making use of the experimental information on the values of either cellulose or hemicellulose, the triangle method presents a considerable deviation for at least one of these components in each case.

It is clear that the application of the triangle method is considerably simpler than the newly proposed method. The former requires much more information than the previous. On the other hand, the triangle method has an associated lower accuracy, since it does not use information on cellulose and hemicellulose composition. The newly proposed method is somewhat more general in the sense that it does not depend on estimating the compositions of the ES. The new method gives an unambiguous answer to the posed problem while the triangle model may give different compositions for a different choice of ES.

The main implications of these stunning differences arise when considering the different reactivity of biomass components during biomass pyrolysis and gasification. Among the biomass components, hemicellulose is the most reactive, followed by cellulose and lastly by the lignin components.

The above findings point in favor of the proposed biomass composition analysis method, even though real biomass composition is significantly more complex. It is important to realize that the results presented here depend strongly on the methods used to determine cellulose and hemicellulose composition. The most recent analytical methods for determining these components quantify them directly and produce much more exact values than the older ones, which determine these quantities indirectly (e.g., by sugar analysis, for instance).

2.2 Biomass Gasification

Gasification is a process that converts carbonaceous materials into a mixture of gases by reacting the material with a controlled amount of a gasifying agent, which can be oxygen, steam or carbon dioxide.

Table 2.2: Res	ults for the compos	ition analysis of lig	nocellulosic biom	nasses. Top: h	biomass atomic	com-
position \mathbb{C} ; Mi	ddle: biomass com	position for the new	v approach. Bot	tom: biomass	composition for	r the
triangle metho	d. Except when not	ed otherwise, all of	the values refer	to DAF (dry,	ash-free) bioma	ss.

Biomass type	Corn	Wheat	Switch	Sugarcane	Almond	Olive	Birch
	stover	straw	grass	bagasse	shells	pits	wood
Phillys2 #	889	977	2436	2342 /	2314	1978 /	2066
v n				2806		2290	
Ash (Dry wt%)	7.4	13.5	5.4	1.6	3.3	3	0.2
$C \exp(wt\%)$	50.6	53.7	50.6	49.9	50.2	48.3	48.3
$H \exp(wt\%)$	6.32	6.03	5.7	6.04	6.28	6.11	6.02
$O \exp (wt\%)$	43.1	40.3	43.7	44.1	43.6	45.6	45.7
C calc (wt%)	50.3	50.3	50.4	49.8	49.2	49.4	49.8
H calc $(wt\%)$	6.2	5.96	5.94	6.01	6.01	5.99	5.85
O calc $(wt\%)$	43.5	43.7	43.7	44.2	44.8	44.6	44.3
SSRR $(\%^2)$	5	113	18	0	30	14	27
Cellulose (wt%)	39.7	33.3	40.7	43.1	52.4	29	35.8
Hemicellulose (wt%)	27.4	45.2	34.8	35.9	29.9	38.4	25.2
Lignin C (wt $\%$)	2.6	21.5	19.5	17.6	17.7	0	0
Lignin H (wt%)	30.3	0	0	3.4	0	14.1	6.7
Lignin O $(wt\%)$	0	0	5	0	0	18.6	32.4
LHV calc (MJ/kg)	19.1	18.7	18.7	18.5	18.2	18.4	18.4
$\Delta rel LHV (\%)$	-0.4	1.9	7.6	3.1	0.9	5.7	5.6
ES1 (wt%)	70.2	46.8	58.9	69.1	71.9	79.5	78.4
ES2 (wt%)	46.2	37.4	-7.4	18.4	40.9	16.5	8.4
ES3 (wt%)	-16.5	15.8	48.5	12.5	-12.8	4	13.3
Cellulose (wt%)	-	28.1	-	41.5	-	47.7	47
Hemicellulose (wt%)	-	18.7	-	27.6	-	31.8	31.4
Lignin C (wt $\%$)	-	10.6	-	6.2	-	4.1	4.3
Lignin H $(wt\%)$	-	29.9	-	14.7	-	13.2	6.7
Lignin O $(wt\%)$	-	12.7	-	10	-	3.2	10.6
LHV calc (MJ/kg)	-	21	-	19	-	18.2	18.1
$\Delta rel LHV (\%)$	-	14.2	-	5.6	-	4.8	4.2

The main reactions for a generic biomass gasification are presented on Equation 2.4, with the gasifying agent being identified as species G:

$C_x H_y C$	$D_z + a G \longleftrightarrow b C C$	$O + c H_2$	(2.4)
G	a	b	С
O_2	(x-z)/2	x	y/2
H_2O	x-z	x	x+y/2-z
CO_2	x-z	2x-z	y/2

The main output of the gasification process is called producer gas, which is a mixture of methane, light hydrocarbons, carbon monoxide, carbon dioxide, hydrogen, water, and volatile organic compounds [89]. The producer gas can then be upgraded to syngas through a series of operations called conditioning operations. Syngas is a CO/H_2 -rich mixture that can be processed to synthesize chemicals (such as methanol) or liquid fuels (such as diesel and gasoline). From the process point of view, gasification is a very flexible process: (1) it is capable of processing inputs with differing qualities; (2) the process output, syngas is also extremely flexible in terms of process design; (3) almost every organic molecule can be produced from syngas.

Gasification is a mature technology, it has been used commercially for many years in oil refineries to obtain syngas from heavy oil residues [7]. In recent years it has been considered in applications with biomass. In fact, biomass gasification could be used as a valorization process that is organic with the current energetic scenario, especially in developing countries where input is abundant and cheap. There are still unresolved issues, especially regarding scale sizes and the feeding of biomass in pressurized vessels. In any case, biomass gasification has been deemed as a promising, evolving technology, with a huge field of application [35].

The gasification of biomass was simulated by considering an 'entrained flow' gasifier. The entrained flow configuration is the most diffused gasification technology in the world [62]. In this arrangement the fuel follows concurrently with the input gas stream (which is usually rich in oxygen). The operation is carried out at high pressures which promotes high temperatures and fast reactions. The combined effect of these features is the production of low-tar syngas at high output capacities and with high fuel conversion. This technology is currently applied in the gasification of coal feedstock [9]. Application of such a process with biomass feedstocks could have a strong potential for the valorization of such feedstock.

Different entrained flow gasifier models have been proposed. Kunze & Spliethoff [62] have considered a 'thermodynamic approach', in which the operation output was correctly predicted by considering chemical equilibrium; coal gasification with 85% pure oxygen in considered (among others). Billaud et al [9] considered the steady state atmospheric gasification of biomass using a 'kinetic approach'. These authors considered a detailed gas-phase kinetic mechanism for the gas-phase reactions but considered a lumped, single step mechanism for the biomass. Chen et al [16] have considered describing such system using a CFD simulation. The higher degree of refinement in terms of the description of the velocity patterns inside the reactor was compensated by a simplification on the kinetic schemes. Coal was used as fuel and the system was considered in steady state.

A good compromise must be established between the levels of description of the model as it becomes more sophisticated. In this work the gasification reactor is simulated with two different approaches in order to predict output composition and temperature. For the first approach, simulations were performed with the biomass gasification / pyrolysis simulator GasDS. Among the main features of the model are the unsteady operation of the equipment with detailed kinetic schemes both for the solid and gas-phase reactions. For the second approach, gasification output is determined by letting the GasDS output attain adiabatic chemical equilibrium through minimization of Gibbs energy. The 'Gibbs reactor' unit, inside the HYSYS process simulator, is used to perform the calculations.

Figure 2.2 presents the a scheme for the reactor model simulated in the GasDS software. This program is an implementation of a phenomenological model that can simulate pyrolysis and gasification of coal and biomass. The reactor model is divided into layers, which are considered a series of perfectly mixed reactors. Biomass particles are discretized in spherical concentric shells, thus representing the intra-particle temperature and composition gradients. A detailed mechanism is used for the gas-phase reactions while the solid-phase kinetics are based on the biomass composition model presented on the previous section (cellulose, hemicellulose and 3 types of lignin). The unsteady operation of the equipment is described by a system of differential equations, which is presented in Figure 2.3. The system is solved using a smart implementation of the Adams-Moulton and the Gear methods using the BzzMath, a sophisticated and performant numerical library written in C++ which exploits the features of object-oriented programming [14]. This simulator has been extensively validated on both coal and biomass feedstocks [20, 18, 78]. Further details of the GasDS simulator are presented in Cabianca et al [15]. For the simulation of entrained flow gasifier, biomass and the oxidizing gaseous stream enter the equipment from the top while the product streams exit from the bottom. The reaction occurs at high pressures (approximately 40 bar) and no heat loss is considered.

Table 2.3 details the parameters used in the simulations. The considered biomass LHV input is reached by assuming an 'year-effective' value of 100 MW. This is the lower bound of the values suggested on the report by IRENA for this gasification technology [57]. The value of 111 MW is attained by considering the previous power input distributed over 90% of the days in the year (i.e. the plant availability). The oxygen input was estimated at 230% of the stoichiometric value for the partial oxidation of biomass (the first reaction of Equations 2.4). This value was reached by taking the reported input values for coal gasification and correcting the value for biomass reactivity. Since biomass is more reactive than coal, it can be converted at a lower temperature, which reduces the amount of oxygen required. Kunze & Spliethoff [62] report of an industrial gasifier running on coal with $O_2/C = 45\%$ (inlet molar ratio). In this work, the reported stoichiometric ratio of 230% produces $O_2/C = 40\%$ for corn stover and similar values for different biomasses, as it will be seen ahead. The equipment size (diameter and height) was estimated arbitrarily since no previous literature reference could be found for those parameters.

The steady state results are presented on Table 2.4 for the case of corn stover. Almost all of the DAF portion biomass is consumed, the remaining part being completely composed of char, which is the less reactive solid component. Calculated output temperatures are around 1400 °C, which is in agreement with the values of 1500 °C reported by Kunze & Spliethoff. Its worth reminding that these authors report not only a bigger output temperature but also a bigger oxygen input.

On Table 2.5 the value obtained for the carbon conversion is compared between different references. The carbon conversion for the GasDS output and the equilibrium calculation match each other closely. It is clear that the values calculated by the gasifier model are very close to equilibrium. This is expected

REACTOR SCALE



Figure 2.2: Scheme detailing the different scales of the GasDS simulator model (from Ranzi et al [78]).

Parameter	Value
LHV biomass input (MW)	111
O_2 Stoich. Ratio (%)	230
Outlet pressure (bar)	42
Diameter (m)	2
Height (m)	6
Simulated reactor layers	10
Simulated particle layers	1
Particle size (μm)	200

Table 2.3: Parameters used in the simulations.

since the reactions proceed fast at high temperatures. Additionally, the use of high pressures promotes an equilibrium shift towards volume reduction, which is usually associated to exothermic reactions. Among such reactions are the methanation and the inverse Boudouard reaction, which are particular cases of Equation 2.4. Kunze & Spliethoff report a similar value for a industrial unit running with coal, which is much less reactive than biomass. Billaud et al report a slightly smaller value for biomass gasification at much less severe conditions (atmospheric pressure and only steam as oxidant). Therefore a good agreement is seen between experiment and the model.

The steady state profiles of the main system variables are seen on Figure 2.4. The reactor position is measured from the top of the reactor and increases in the same sense of the gas / solid movement shown in Figure 2.2. The profiles quickly reach values that are very close to the outlet values, which is indicative of how fast the reactions are progressing. The slow descent on the temperature profile after the initial combustion is characteristic of the endothermic char gasification reactions (with steam or carbon dioxide). Char is much less reactive than biomass and the downstream portion of the reactor is depleted of oxygen. For any reactor position the added mass / molar fraction of components O_2 , H_2 , H_2O , COand CO_2 (i.e., the five components whose profiles are shown in Figure 2.4) is always more than 99.5%.

Figure 2.5 shows the results of the unsteady state operation of the simulator representing the start up procedure for the gasifier. In such a procedure, a stream containing fuel provides heat to the equipment so that it can achieve a temperature configuration in which the gasification is self-sustained (a.k.a. 'autothermal'). For this simulation the inlet gas stream was provided at a temperature of 2000 K and was diluted with combustion products (methane was the considered fuel). Biomass input was 30% of the steady state value seen in Table 2.3 while the oxygen input (after methane combustion) followed the same proportion (to the stoichiometric ratio) used in the steady state simulation. Figure 2.5(a) shows the temperature profile for the different reactor layers. Steady state is reached after about 3000 seconds (50 minutes). The temperature at the first stage presents a sharp rise at t = 500 s, when it reaches a temper-



Figure 2.3: Gas- and solid-phase mass and energy balances for the GasDS model (from Corbetta et al [18]).

ature of about 600 K (330 °C). At this point the biomass on that layer has been completely pyrolyzed. The pyrolysis process are endothermic; their interruption makes the temperature rise by heat transfer from the gas. With the temperature increase the volatiles and char are rapidly oxidized, which raises even further the temperature. The other stages follow the same pattern of the first stage but at a slower rate since the gas is cooled down and oxygen is consumed through the reactor. Figure 2.5(b) reverses the disposition of time and axial coordinates to show the reactor temperature profiles for different time values. An important observation must be made at this point. Qualitatively, the heating of such an equipment should follow a pattern of a 'break-through' curve. Such a curve possess a single concavity inflexion along its profile, which is in direct contrast to the multiple inflexions seen at the temperature profiles for $600 \, s \le t \le 1100 \, s$. The cause for such a behaviour could reside in an inadequate solution strategy of the ODE solver, which would cause numerical instabilities and produce non-physical oscillations. The ODE solver adjusts the step size with the predicted error. As the derivatives become less steep the step size becomes bigger, eventually violating stability constraints. This hypothesis is supported by Figure 2.5(c), which shows the accumulated time-steps taken by the solver for the integration of the differential equation system. 35% of the time-steps are used up to $t = 500 \, s$, which can be attributed to biomass pyrolysis. At t = 600 s, another 45% of the computational effort was spent in calculating the oxidation of volatiles and char. At this point the time step increases considerably, at the same time that oscillations begin to appear. Even if these perturbations may add numerical errors to the unsteady state profiles, it should be noticed that they eventually fade away, and that the results of the steady state simulations are not influenced by this phenomenon.

A comparative analysis was carried out by performing the gasification simulation with the biomasses seen on the previous chapter. The same conditions seen on Table 2.3 were used for every biomass and the operation is considered at the steady state. The results are seen in Table 2.6. After a visual inspection the biomasses were grouped according to their characteristics. The biomasses from group D had the highest syngas-to-oxygen ratio. A striking remark is that, for the biomasses from groups B, C and D, an increase in the amount of oxygen did not produce extra syngas, but only converted more carbon. Corn stover gave the highest amount of syngas for slightly less oxygen than Group B, but with the same carbon

Parameter	Inlet	Outlet
Gas mass flow (kg/h)	11325	33431
Syngas mole flow (kmol/h)	-	1110
H_2/CO molar ratio (%)	-	57
Solid mass flow (kg/h)	23850	1744
Solid mass flow - DAF (kg/h)	20992	78
Carbon mass flow (kg/h)	10549	78
Gas temperature (°C)	27	1402
Solid temperature (°C)	27	1402
Pressure (bar)	46	42
Porosity (%)	87	100

Table 2.4: Results of the simulation of corn stover gasification with GasDS.

Table 2.5: Comparison of carbon conversion from different references.

Reference	GasDS	Equilibrium	Kunze & Spliethoff [62]	Billaud et al [9]
Carbon conversion (%)	99.3	98.4	98.5	95.0

conversion. In any case it seems that such a system could be optimized in terms of the trade-off between oxygen consumption and syngas yield. This is, of course, an economic consideration, not a physical one.

Table 2.6: Comparison of the (steady state) gasification simulation results for different biomasses.

Biomass type	Corn stover	Wheat straw	Switch grass	Sugarcane bagasse	Almond shells	Olive pits	Birch wood
Syngas produced (kmol/h)	1110	1067	1071	1070	1071	1084	1071
O_2 input (kmol/h)	354	360	361	345	329	332	345
Syngas / O_2^{in} molar ratio (%)	314	297	297	310	326	326	310
O_2/C inlet molar ratio (%)	40	40	40	39	37	37	38
Carbon conversion $(\%)$	99	99	99	97	96	95	96
H_2/CO outlet molar ratio (%)	57	55	54	56	60	60	55
Biomass Group	А	В	В	\mathbf{C}	D	D	\mathbf{C}

2.3 Conclusion

Lignocellulosic biomass gasification was described with the aid of a detailed phenomenological model. Biomass composition was determined from an innovative data fitting method. The developed method represents an improvement from the previous 'triangle model', especially because it uses experimental information in a more systematic approach to quantify biomass composition. A further extension of such model could use the LHV information to establish an additional relationship involving biomass composition. Eventually, this problem could effectively be transmuted into the data reconciliation problem. In this case, cellulose and hemicellulose compositions would also be variables in the fitting process but penalty parameters would be introduced to take into account their deviation from the experimental measurements.

An entrained flow gasifier was simulated using a detailed, phenomenological model, implemented in the GasDS program. The model displayed good accuracy for the assessments performed at steady state and compared well to experimental observations. Numerical instabilities were seen during the unsteady state operation due to the step size adjustment procedure. The component description of the model is very rich while its spatial resolution is still fairly poor. It seems that better compromise between the levels of description of the model would yield more insightful results. If the the gas-phase kinetics could be effectively shrinked a CFD reelaboration of the model would enable the investigation of innovative aspects of biomass gasification. Among such aspects are the unsteady state operation of the gasifier, the modeling of the slag flow, the quantification of the temperature profile along the reactor walls, etc, all of which considered at the high spatial resolution of a CFD simulation.



Figure 2.4: Steady state profiles of main system variables.



Figure 2.5: Unsteady state simulation results for the start up procedure. (a): Temperature profiles for different reactor layers. (b): Temperature profiles for different time values. (c): Accumulated time-steps profile.

2.A Biomass Molecular Composition

This section clarifies the method used to determine biomass composition in terms of its molecular components. For this analysis, cellulose and hemicellulose are considered pure components, in opposition to lignin, which is further divided in three subtypes. All of the components are considered on a dry, ash-free (DAF) basis. Problem statement: for a given biomass atomic composition \mathbb{C} (determined experimentally) and given biomass components' atomic composition \mathbb{C}_j (from the model by Ranzi et al [79]), find the biomass components mass fraction k_j that solves the following atomic mass balance (AMB):

$$C = \sum C_j k_j$$

$$0 \le k_j \le 1$$

$$\sum k_j = 1$$
(2.5)

The vectors and their elements on the equation above are the following:

$$\mathbb{C}^{T} = [x, y, z]
\mathbb{C}^{T}_{j} = [x_{j}, y_{j}, z_{j}]$$
(2.6)

which x, y, z are the normalized carbon, hydrogen and oxygen mass fractions in the biomass; x_j, y_j, z_j refer to the same mass fractions of species j. To solve Equation 2.5, it is instructive first to consider a simpler case in which no constraints are imposed. Any combination of three different molecular components form a linearly independent basis (LIB); since any LIB is able to span \mathbb{R}^3 , this means that at least one solution should be found for every LIB. As a consequence, the linear system above may have multiple solutions even if the constraints are imposed (it will definitely have multiple solutions for the no constraint case). The problem can be tended by reducing the number of independent variables to three, by using the experimentally determined composition of cellulose and hemicellulose. If these two quantities are respectively denominated as α and β , the problem can be redefined in the following form:

$$\mathbb{C} - \alpha \mathbb{C}_{\alpha} - \beta \mathbb{C}_{\beta} = \sum \mathbb{C}_{j} \mathbb{k}_{j}$$

$$0 \leq \mathbb{k}_{j} \leq 1 - \alpha - \beta$$

$$\sum \mathbb{k}_{j} = 1 - \alpha - \beta$$
(2.7)

For this new AMB, k_j represents the DAF mass fractions of the three lignin compounds. Such a system is well defined, for it has the same number of equations and variables (three). Even so, the previously established bounds usually prevent an exact solution to be found, i.e., the atomic experimental composition cannot be matched exactly by a convex combination of the \mathbb{C}_j . It is possible, though, to estimate a solution which is the closest possible to the observed values of the AMB through an optimization process. The criterion chosen for evaluating the goodness of the solution is the SSRR (sum of the squared relative residues) of the AMB; this choice avoids high relative errors on the estimation of the hydrogen massive content, which is much lower than oxygen and carbon. The AMB can now be rewritten with the following definitions:

$$\mathbb{C} = \sum \mathbb{C}_{j} \mathbb{k}_{j} + R$$

$$\mathbb{C}_{j}^{T} = \left[\frac{x_{j}}{x}, \frac{y_{j}}{y}, \frac{z_{j}}{z}\right] = [X_{j}, Y_{j}, Z_{j}]$$

$$\mathbb{C}^{T} = [1, 1, 1] - \alpha \mathbb{C}_{\alpha}^{T} - \beta \mathbb{C}_{\beta}^{T}$$
(2.8)

Other than the vector of residuals it is interesting to notice that the system was rescaled with the x, y, z parameters and, therefore, X, Y, Z do not sum up to 1. This rescaling is useful to produce the desired relative values for the optimization process. For the vector of residuals it can be seen that

$$R = \mathbb{C} - \sum \mathbb{C}_{j} \mathbb{k}_{j}$$

$$R_{i} = 1 - \sum i_{j} \mathbb{k}_{j}$$

$$\frac{\partial R_{i}}{\partial \mathbb{k}_{j}} = -i_{j}$$

$$i = X, Y, Z$$
(2.9)

and the sought-after cost function (the SSRR) and its partial derivatives are written as

$$f = \sum R_i^2$$

$$\frac{\partial f}{\partial k_j} = \sum_i 2R_i \frac{\partial R_i}{\partial k_j}$$

$$= -2\sum_i R_i i_j = -2\mathbb{L}_j$$

$$\mathbb{L}_j = R \cdot \mathbb{C}_j$$
(2.10)

Since this is a problem of constrained quadratic programming, the method of the Lagrange multipliers can be used in order to find the solution. The constraints are used to write terms that compose the Lagrangian:

• $\sum k_j = 1 - \alpha - \beta$: $h = \sum k_j - 1 + \alpha + \beta$ (2.11) • $k_j > 0$:

$$g_j = -\mathbf{k}_j \tag{2.12}$$

The last constraint $(k_j < 1)$ is automatically satisfied if these two constraints are enforced. The Lagrangian can be written as

$$L = f + \lambda h + \sum \mu_j g_j$$

$$L = f + \lambda (\sum k_j - 1 + \alpha + \beta) - \sum \mu_j k_j$$
(2.13)

From the optimality conditions (OCs) the following expressions can be derived:

$$\frac{\partial L}{\partial \mathbf{k}_j} = -2\mathbb{L}_j + \lambda - \mu_j = 0$$

$$\sum \mathbf{k}_j = 1 - \alpha - \beta$$

$$\mu_j, \mathbf{k}_j \ge 0$$

$$\mu_j \mathbf{k}_j = 0$$

(2.14)

By using the last OC, μ_j is eliminated from the first OC:

$$2\mathbb{L}_{j} - \lambda + \mu_{j} = 0$$

$$(2\mathbb{L}_{j} - \lambda + \mu_{j})\mathbb{k}_{j} = 0$$

$$\left(\mathbb{L}_{j} - \frac{\lambda}{2}\right)\mathbb{k}_{j} = 0$$

$$(2.15)$$

By summing the last expression over all the j and using the second OC, the value of λ is found:

$$\mathbb{L}_{j}\mathbb{k}_{j} = \frac{\lambda}{2}\mathbb{k}_{j}$$

$$\sum \mathbb{L}_{j}\mathbb{k}_{j} = \frac{\lambda}{2}(1 - \alpha - \beta)$$
(2.16)

As it will be seen further ahead, this last step is not necessary in obtaining a solution. For the sake of having a cleaner notation the previous expression is maintained

$$\left(\mathbb{L}_j - \frac{\lambda}{2}\right) \mathbb{k}_j = 0 \tag{2.17}$$

For such an expression to be valid, either k_j or the term between parentheses will be zero.

Hypothesis 1 (H1): no k_j is zero

We allow the term between parentheses to vanish. It is interesting to note that this implies $\mu_i = 0$ since

$$\frac{\mu_j}{2} = \mathbb{L}_j - \frac{\lambda}{2} \tag{2.18}$$

The system of equations deriving from H1 is the same as if no inequality constraints were adopted; this means that the solutions deriving from this hypothesis will not always be able to respect the inequality constraints. With the current system of equations it is now clear why it is not necessary to calculate the value of λ : since all $\mathbb{L}_j = \frac{\lambda}{2}$, the constant can be cancelled out by shifting indexes and subtracting two consecutive expressions

$$\mathbb{L}_{j} = \frac{\lambda}{2}$$

$$\mathbb{L}_{j} - \mathbb{L}_{j+1} = 0$$
(2.19)

The downside of that strategy is that the number of independent equations fall by one, which leaves the system undetermined; this can be promptly compensated by use of the much simpler equality constraint

$$\sum \mathbf{k}_j = 1 - \alpha - \beta \tag{2.20}$$

The definition of \mathbb{L}_j is plugged in Equation 2.19 to yield

$$R \cdot (\mathbb{C}_j - \mathbb{C}_{j+1}) = 0 \tag{2.21}$$

The resulting system of equations can be written in a more concise vector form

$$AR = 0$$

$$A^{T} = \mathcal{D}_{3} - \mathcal{D}_{1}$$

$$\mathcal{D} = [\mathbb{C}_{1}, \mathbb{C}_{2}, \mathbb{C}_{3}]$$

(2.22)

In the equation above, \mathcal{D} is the matrix that has vectors \mathbb{C}_k as columns; subscripts 1 to 3 in \mathbb{C}_k refer to each of the three lignin compounds; \mathcal{D}_k is the matrix that results from removing k-th column of matrix \mathcal{D} . Plugging in the definition for the residual the following expression is obtained:

$$0 = A \left(\mathbb{C} - \mathcal{D} \mathbb{k} \right)$$

$$A \mathcal{D} \mathbb{k} = A \mathbb{C}$$
(2.23)

Lastly, since

$$\sum \mathbf{k}_j = c^T \mathbf{k} = 1 - \alpha - \beta$$

$$c^T = [1, 1, 1]$$
(2.24)

the following constitutes a system of equations with equal number of variables and equations

$$B\mathbb{k} = b$$

$$B^{T} = \left[(A\mathcal{D})^{T}, c \right] = \left[\mathcal{D}^{T} A^{T}, c \right]$$

$$b^{T} = \left[(A\mathbb{C})^{T}, 1 - \alpha - \beta \right] = \left[\mathbb{C}^{T} A^{T}, 1 - \alpha - \beta \right]$$

(2.25)

in which the square parethesis and comma denotes the concatenation of the elements of different vectors into one single array. The calculation algorithm is summarized below. Some terms were redefined to

reduce the number of passages. Start by defining and calculating auxiliary terms in the following order:

F

$$\mathbb{C}_{j}^{T} = \left[\frac{x_{j}}{x}, \frac{y_{j}}{y}, \frac{z_{j}}{z}\right]$$

$$\mathbb{C}^{T} = [1, 1, 1] - \alpha \mathbb{C}_{\alpha}^{T} - \beta \mathbb{C}_{\beta}^{T}$$

$$\mathcal{D} = [\mathbb{C}_{1}, \mathbb{C}_{2}, \mathbb{C}_{3}]$$

$$c^{T} = [1, 1, 1]$$

$$A = \mathcal{D}_{n} - \mathcal{D}_{1}$$

$$B^{T} = [\mathcal{D}^{T} A, c]$$

$$b^{T} = [\mathbb{C}^{T} A, 1 - \alpha - \beta]$$
(2.26)

Calculate the mass fractions of each component by solving the linear system

$$Bk = b \tag{2.27}$$

Hypothesis 2 (H2): some of the k_j are zero

This will be the case if, after solving the system using H1, some of the compositions are negative. In this case, the smallest composition is set to zero and the system is redefined to remove that variable and the system is solved again with H1. Supposing lignin 2 must be set to zero, the procedure to solve such system is basically the same. Start by calculating the following auxiliary terms:

$$\mathbb{C}_{j}^{T} = \left[\frac{x_{j}}{x}, \frac{y_{j}}{y}, \frac{z_{j}}{z}\right]$$

$$\mathbb{C}^{T} = [1, 1, 1] - \alpha \mathbb{C}_{\alpha}^{T} - \beta \mathbb{C}_{\beta}^{T}$$

$$\mathcal{D} = [\mathbb{C}_{1}, \mathbb{C}_{3}]$$

$$c^{T} = [1, 1]$$

$$A = \mathcal{D}_{n} - \mathcal{D}_{1}$$

$$B^{T} = [\mathcal{D}^{T} A, c]$$

$$b^{T} = [\mathbb{C} A, 1 - \alpha - \beta]$$
(2.28)

Again, calculate the mass fractions of the remaining components by solving the following linear system:

$$Bk = b \tag{2.29}$$

Chapter 3

Biomass Gasification for the Production of Methanol and Fischer-Tropsch Fuels

Abstract

Two processes were considered for the coproduction of heat, electricity and chemicals. Both of these involve biomass gasification for the production of syngas, which can then be used to produce methanol (MeOH) or Fischer-Tropsch (FT) fuels. The transformation pathways are described through a rigorous techno-economic assessment which uses a combination of four different softwares: commercial process simulator Aspen HYSYS; energy integration software Aspen Energy Analyzer; GasDS, a gasification / pyrolysis simulator and the MATLAB programming environment. The FT product distribution model considered olefin readsorption and it was solved using an innovative power series solution.

Methanol production is the superior process, both in economic and in terms of final conversion to liquid fuels. The economics of the Fischer-Tropsch process suffers due to the low energetic yield of the reaction in terms of high valued liquid products. It remains to be confirmed (1) whether if the correlations used are adequate to represent the FT reaction system and (2) if further income could be expected if the other reaction products could be sold as high value products.

Both processes are economically unfeasible, with product costs that range (approximately) from 60 to $90 \in /MWh$ (MeOH) and 80 to $210 \in /MWh$ (FT). Even so, methanol production is an interesting alternative to current biogas concepts. The minimum subsidy cost of this process ranges from half to one third of current biogas subsidy costs.

3.1 Introduction

Methanol is a key compound widely employed as building block for producing intermediates or synthetic hydrocarbons, solvent, energy storage medium, and fuel [12]. The catalytic synthesis of methanol from syngas is a well-established process, with multiple commercial technologies developed by different companies [89]. Methanol production from biomass gasification has been proposed by different authors as a sustainable alternative to fossil fuels [89, 47]. A similar alternative to methanol are Fischer-Tropsch (FT) fuels. FT synthesis is one of the most developed strategies for producing liquid fuels from syngas [11]. However, its economic feasibility is strongly connected to production in large, centralized facilities with syngas being produced from fossil fuels [11]. The same is true for methanol production, the majority of which comes from the steam reforming of natural gas in plants with capacities on the order of 1 Mt of methanol per year [22] (around 1 GW lower heating value methanol output).

It should be made clear that biomass availability is not an issue, even in Europe. This is seen in Figure 3.1, which brings projections for energy statistics in the European Union. It is seen biomass supply greatly surpasses its consumption, which is indicative of the greater costs associated with bioenergy. Transportation costs, in special, might have a significant impact on process economics. In the US, the nominal mill size for pulp processing receives a black liquor input of around 400 MW (lower heating value, LHV) [28]. It must be noted that, for such an enterprise, dedicated wood crops are used. In a similar fashion, the average Brazilian sugar cane mill generates around 200 MW LHV of residues [24]. For this process, the sugar cane is transported in trucks that travel an average of 20 km. This scale corresponds to the current scenario at the Sao Paulo state, which alone produces over 60% of the total Brazilian sugar



Figure 3.1: Projections for energy statistics in the European Union. Consumption data was taken from the report by IEA [53] while biomass supply was obtained from the BEE Project report [80].

cane harvest.

If current sustainability and social directives are to be followed, biorefineries will most likely receive residual lignocellulosic biomass that is collected from sparse sources. Given the above numbers for agroindustrial processes, it seems reasonable to think that the typical scale of such plants should lie between 100 and 500 MW biomass (LHV) input. If the process energy yield in terms of biofuels can be estimated at 50%, even at 500 MW biomass LHV input the biofuel production capacity is virtually one order of magnitude below that of the fossil fuel industry. In any case this gives a reasonable estimate to work with. Accordingly, if the same 50% energy yield is assumed, process output in terms of biofuels should lie between 50 and 250 MW.

Several references report results on the production of biofuels with models having different levels of detail. Anex et al [5] did an assessment on the production of different biofuels. Only superficial results are shown for the technical assessment, with almost no detail on the considerations taken at each step. The economic assessment has good premises but uses at its core a methodology which is dubious with parameters that are chosen arbitrarily. The discussion is very poor and the only comparison made with other literature works is purely qualitative.

Hamelinck & Faaij [47, 46] present authoritative assessments on the production of commodity chemicals from biomass gasification. Innovative technologies have been investigated, with a high level of detail in their models. The authors analysed scales ranging from 80 to 2000 MW LHV input, the upper bound being far out of the previously estimated limit of 500 MW. Unfortunately, the gasification technology chosen by the authors does not correspond to that which is most adequate to this scale (entrained flow). Evidence of this is the need to reform the resulting syngas, which contains reasonable quantities of tars. Lastly, methanol production costs are too low, even for the shortest possible scale. This can be largely attributed to the low biomass costs assumed ($2 \in /\text{GJ LHV}$).

In this work we propose a detailed techno-economic assessment concerning the production of chemicals from the gasification of second-generation biomass. Four different software were used together in order to obtain a rigorous description of the process. Every transformation step is evaluated with rigorous phenomenological models, either by using thermodynamic equilibrium or through kinetic models. Updated prices of raw materials and coherent correlations between equipment parameters and their cost were used in the economic evaluation step. This allows for the accurate estimation of process economic indicators, such as the cost of production of final products.

Figure 3.2 summarizes information on methanol production costs from the report by IEA & IRENA [54] together with calculated values from this work. Second generation (residual) biomass was considered in this techno-economic assessment. It is seen that the production cost of methanol remains high compared to fossil sources, even at great output quantities. In any case, these values represent an advantageous opportunity compared to current renewable energy concepts, as it will be shown ahead. The economic indicators calculated in this work point strongly in favor of a production model that obeys sustainability, environmental and social standards.


Figure 3.2: Methanol production cost from fossil and renewable sources. Adapted from the report by IEA & IRENA [54]. Second generation (residual) biomass was considered in this techno-economic assessment.

3.2 Materials and Methods

The simulations studied in this chapter, except when noted otherwise, used the same considerations from Section 2.2: corn stover was the considered biomass with an input value of 100 MW (in terms of LHV), if 365 work days per year are considered. Plant availability (ratio between working days and total days of the year) was 90%. A scheme representing the process considered in this work is presented on Figure 3.3. Numbers with percentages indicate mass flow values. Biomass is gasified to yield 'producer gas', which is syngas contaminated with different impurities. Conditioning operations are required to convert the producer gas into syngas, especially because the former contains several impurities which may cause problems in downstream operations [21]. Finally, syngas may be used to produce FT fuels or it can be converted to methanol. The previously introduced GasDS simulator (Section 2.2) was used to predict biomass gasification output. Commercial process simulator Aspen HYSYS was used in order to perform mass and energy balances on the gas conditioning operations that adjust syngas parameters. The FT section was modeled using both HYSYS and the MATLAB programming environment. MATLAB was used as a support interface to connect the different softwares. Further information on the connection of the programs is given on Section 3.2.2. Lastly, an energy integration (a.k.a. 'Pinch Analysis') of the simulation was performed using the Aspen Energy Analyzer software.

Further details on the HYSYS simulation are given on Figure 3.4. Each one of the gray squares with a 'T' inside represent a process section while 'SFSs' is a HYSYS spreadsheet used for connection with the external programs. The two lanes seen represent the operations used for the production of the FT fuels (top lane) and methanol (bottom). Table 3.1 below summarizes the operations performed in each process section. The operations are presented in the order they are executed in HYSYS; they are given a tag with which they will be identified in later sections. Up to the quenching operation, both processes use the same steps, and therefore only the bottom lane is simulated. The quenching operation output is copied for the top lane using a specific simulator unit ('virtual stream', not shown in Figure 3.4).

Throughout this work two important indexes will be used to evaluate the performance of the process steps: the mass yield (MY) and the energy yield (EY); the MY is the ratio between mass flow values of products leaving and reactants entering a process section; the EY is the equivalent of the MY for the total energy entering and leaving each section; in order to compute the EY it is important to consider (i.e., to sum) all of the different types of energy: that stored in material streams (in the form of chemical energy, translated by the LHV of such streams) and that in energy streams (as electricity or heat). Whenever heat or electricity is consumed in a process section, that energy amount is subtracted from the current energy balance to determine the total energy balance at the end of each section (conversely, if energy is produced, that amount is summed to the energy balance). As a last remark on Figure 3.4, when multiple streams leave a process section, they are summed to determine the EY (e.g. the 'MEOH' stream the and the 'Purge1' after the synthesis section).



Figure 3.3: Scheme depicting the transformation pathway and the task assignment of each software. Numbers with percentages indicate mass flow values.



Figure 3.4: Aspen HYSYS simulation used in the process assessment. Top lane represents the FT fuel production process while the bottom lane is associated to methanol production. The 'QUE' stream is copied into 'QUE*' using a specific simulator unit (not shown).

Table 3.1: Summary of the processing steps according to their order and function.

Section Tag	Section Name	Description
ASU	Air separation unit	Produces pure oxygen to be used in the gasifier
GAS	Gasification	Partially oxidizes biomass to generate producer gas
QUE	Quenching	Cools gas with a cold gas recycle + residual tar removal
WGS	Water-gas-shift reaction	Adjusts the H_2/CO ratio of the syngas stream
SWT	Gas sweetening	Removes CO and H_2S from the syngas
MEOH	MeOH synthesis	Produces MeOH from syngas
FTS	Fischer-Tropsch synthesis	Produces long-chain alkanes and 1-alkenes from syngas
DIST	Distillation	Removes water and dissolved gases from the raw product
PWR	Power generation	Generation of heat and electricity in a combined cycle

3.2.1 Air Separation Unit (ASU)

The ASU model is partially based on a Linde brochure [65], among other references [26, 73]. Figure 3.5 details the model used. The air stream is compressed in a battery of compressors, after which it is

refrigerated to cryogenic temperatures (heat exchangers C4a and C4b) and then throttled to the operative pressure of the first column. In this column, nitrogen is partially separated from from air (stream 9a), which is then used as reflux in the second column. Stream 12b is liquid oxygen, which is pressurized to the working pressure for biomass gasification (around 42 bar). The temperature of the streams that exchange energy were set to consider a 'cold' loss of around 10%, i.e., the heat donated by hot streams represented 90% of the value absorbed by cold streams, representing process inefficiency. The Souders and Brown equation was used to estimate D^* , the column critical diameter (in meters), i.e, that below which flooding occurs:

$$D^* = \sqrt{\frac{4F}{\pi\rho_v u_v^*}}$$

$$u_v^* = (-0.17h^2 + 0.27h - 0.047)\sqrt{\frac{\rho_l}{\rho_v} - 1}$$
(3.1)

in which F is the vapor mass flow rate (kg/s), u_v^* is the critical vapor velocity (m/s), h is the plate spacing (m), and ρ is the density (kg/m³) of either liquid or vapor. The column diameter was taken as the biggest D^* value between the first and last column stage and was increased by 50%. Table 3.2 summarizes the main parameters used in this section.



Figure 3.5: HYSYS flowsheet depicting the Air Separation Unit (ASU).

Column	High Pressure	Low Pressure
Pressure (kPa)	668	132
Number of stages	50	60
Inlet stage top	1	1
Inlet stage bottom	50	5
Column plate spacing (cm)	60	60
Stage efficiency $(\%)$	60	15
Reflux fraction $(\%)$	80	-

Table 3.2: Main parameters used in the ASU section.

3.2.2 Biomass Gasification

Biomass gasification was simulated with the GasDS program. The same configuration used in the previous chapter is assumed (entrained-flow gasification), together with pertinent parameters (see Table 2.3). The gasification output (which is written in .txt files) was imported into Excel and then transferred into HYSYS. The HYSYS units used in this process section are those needed to import the GasDS output. This is shown in Figure 3.6, in which the HYSYS spreadsheet ('GAS_SS') is used by MATLAB to write the gasification output. 10% of the ashes in biomass are considered to leave the equipment together with the gas stream.



Figure 3.6: Detail of the HYSYS gasification flowsheet. MATLAB is used to write the GasDS output into the HYSYS spreadsheet ('GAS_SS'). In the sequence, the spreadsheet assigns these values to the streams 'Gas*' and 'Ashes', effectively connecting the gasification simulator with HYSYS.

The different programs were interconnected using an ActiveX interface. Figure 3.7 presents a scheme detailing this operation. In this Figure it can be seen that data is transferred between spreadsheets, from Excel to HYSYS (and back, from HYSYS to Excel) in an operation that is mediated by MATLAB. The use of spreadsheets enables ease manipulation of the data. In HYSYS the imported data was assigned to streams or units, while in Excel the exported data was used to construct tables and graphs. The MATLAB codes used to import and export data are presented on Appendix 3.B.

	A	В	С	D	E					
37	EXPORTABLES									
38	Temperature	1402	С							
39	Pressure	4236	kPa			А	В	С	D	
40	mass flow - CH4	0.9501	kg/h		1	Subfs	Parameter	Value	Unit	
41	mass flow - H2O	5600	kg/h		18	ASU	LP - D	3.533072	m	
42	mass flow - CO	1.975e+004	kg/h		19	ASU	LP - P	132	kPa	
43	mass flow - CO2	7237	kg/h		20	GAS	Temperature	1402.341	С	
44	mass flow - H2	815.1	kg/h		21	GAS	Pressure	4235.964	kPa	
45	mass flow - C	244.4	kg/h		22	GAS	mass flow - CH4	0.950065	kg/h	
46	mass flow - Tar	27.88	kg/h		23	GAS	mass flow - H2C	5599.616	kg/h	
47	mass flow - O2	1.693e-007	kg/h		•	· · · · · ·	Exportables 🕂	: •	Þ]
48	Mass Flow Inlet	3.351e+004	kg/h							
49	Mass Flow Outlet	3.368e+004	kg/h						Ŧ	
50	C Mass Flow Inlet	1.053e+004	kg/h					X	ΞŦ	ł
51	C Mass Flow Outlet	1.070e+004	kg/h							1
52	LHV inlet	83.43	MW		ivc	vc				
53	LHV outlet	84.94	MW		113	13	IVIATLA		CEI	
54	EXPORTABLES_end					Δ	В	C	D	
55				1	Su	hfs	Parameter	Value	Unit	1
56	IMPORTABLES				A		radificient of the second se	11225	ka/h	-
57	Temperature	1402	С	2				4226	kDa	
58	Pressure	4236	kPa	3	A		ressure	4230	кра	
59	mass flow - CH4	0.9501	kg/h	4	G	AS 10	emperature	1402		
60	mass flow - H2O	5600	kg/h	5	G	AS PI	ressure	4236	кРа	
61	mass flow - CO	1.975e+004	kg/h	6	G	AS m	hass flow - CH4	9.50E-01	kg/h	
62	mass flow - CO2	7237	kg/h	7	G	AS m	nass flow - H2O	5600	kg/h	•
63	mass flow - H2	815.1	kg/h		•	Imp	ortables Export: 🕀		Þ	

Figure 3.7: Connection scheme between the different programs using an ActiveX interface: MATLAB was used to import/export data to HYSYS with Excel serving as a data storage medium.

3.2.3 Quenching

The output gas coming from the gasifier contains hot ashes which are sticky and must be cooled down and removed before entering any downstream equipment. The HYSYS flowsheet for the quenching section is reported in Figure 3.8. The entering gas is cooled down by direct mixing with a cold gas recycle. The amount of gas from the recycle was such that the resulting stream attained a temperature of 900 °C. The cooled gas enters a cyclone in which 99% of the solid is removed considering 0.1 mm particles with a density of 170 kg/m³. The remaining particles are removed through filtration with candle filters. Filtration velocities of 5 cm/s were considered, with negligible pressure drop [95]; cartridge superficial area was obtained from a supplier on the Alibaba.com website [2]. The ash-free gas is then led through a 'tar-polisher', an adiabatic reformer in which residual tar is converted. In the real system, the gas flows through a catalytic bed containing nickel oxide catalyst, which promotes tar reforming and the water gas shift (WGS) reaction:

$$C_x H_y O_z + (x - z) H_2 O \longleftrightarrow x CO + (x + y/2 - z) H_2$$

$$(3.2)$$

$$H_2O + CO \longleftrightarrow H_2 + CO_2 \tag{3.3}$$

This helps bring tar concentration down to a few ppm, increasing downstream catalyst life-span. A high inlet temperature (in this case, 900 °C) is important in this context because of two aspects: (1) it helps shifting equilibrium of Reaction 3.2 towards the production of syngas; (2) in the real system, high temperatures prevent sulphur and coke deposition on the catalyst [48]. In this simulation the operation was modelled by considering that the reacting stream attains chemical equilibrium, which is calculated with the 'Gibbs reactor' unit in HYSYS. For purposes of sizing the reactor, a residence time of 10 seconds was considered with 40% porosity. After the tar polisher, the reformed stream is then cooled to the operating temperature required at the the next sections. Part of the stream is recycled while another part follows further downstream of the process.



Figure 3.8: HYSYS flowsheet depicting the quenching section.

3.2.4 The Water-Gas Shift (WGS) Section

The WGS reaction, as seen in Equation 3.3, is a heterogeneous-phase, exothermic reaction that can be used to adjust the H_2/CO ratio of the syngas. This is desirable since specific values of such ratio are necessary for each type of synthesis operation. Many different types of catalysts are active for the WGS reaction but in order to displace equilibrium towards the formation of hydrogen the reaction temperature must be lowered. Iron-supported, chromium oxide catalysts are specially suited for operation from 300 to 400 °C.

The HYSYS flowsheet used in this section is shown in Figure 3.9. The inlet gas stream is mixed with hot steam and directed to the reactor, which was modelled as a multi-tube plug flow reactor (MTPFR). The steam provided in this section is saturated steam extracted from the steam turbine cycle (at 294 °C and 80 bar) as it will be seen further ahead in the power generation section. The reaction system was considered isothermal and the rate equations, catalyst properties and other parameters were taken from the case-study presented in the work of Turton et al [94]. The main parameters used for the section are summarized in Table 3.3.

For the TEA of this work, the energy released from the reaction was accounted for at pinch analysis calculations.



Figure 3.9: HYSYS flowsheet depicting the WGS section.

Parameter	Unit	Value
H_2/CO (outlet)	molar ratio $(\%)$	190
H_2O/CO (inlet)	molar ratio $(\%)$	100
Reactor P drop	kPa	200
Cooling jacket ΔT	$^{\circ}\mathrm{C}$	50
Tube length	m	10
Tube diameter	cm	5
Catalyst apparent density	$ m kg/m^3$	1121

Table 3.3: Main parameters used in the WGS section.

A glitch in the HYSYS software prevents the 'cWGS*' energy stream to be imported when performing pinch calculations (explained in Section 3.2.9). This is seen as the Energy Analyzer software is called and the corresponding energy stream presents an error status. For such a case, it is then observed that the enthalpy value of the stream is not accounted for, without which the available process heat is underestimated. The lower block containing names with asterisks mimics the original heat flow values and compensates the missing value. In line with this representation, streams '1*' and '2*' are saturated liquid water and saturated water steam, respectively and represent the fluids in the cooling jacket. From these streams the cooling jacket pressure is obtained, which is an important parameter affecting the reactor PCI.

3.2.5 Gas Sweetening

In the gas sweetening section, acid gases $(CO_2 \text{ and } H_2S)$ are removed from syngas in an absorption column. This step is important because CO_2 dilutes syngas, which lowers yields during the syntesis step. In the real system, this step is also important because it removes residual H_2S from the gas stream, which poisons synthesis catalysts. The HYSYS flowsheet for this section is represented in Figure 3.10 for the case of FT fuels production. The gases from the quench section are further cooled before entering the absorber, in which syngas is contacted by a (60:40) stream of water/MDEA (methyldiethanolamine). The molar flow ratio (a.k.a. the 'loading') between CO_2 (in syngas) and MDEA (in the solvent) was 90%. The spent solvent is regenerated in a low pressure stripping column, releasing CO_2 and producing fresh solvent that can be recycled. Table 3.4 collects other parameters used in this section. Stage efficiency values refer to CO_2 only and are calculated by internal simulator correlations, specific for acid gas systems (the 'DBR Amine Fluid Package'). For the production of methanol a similar flowsheet configuration is used, with the only difference that the syngas stream is already cold and enters the absorption column directly. The same procedure used to size the columns in Section 3.2.1 is used in this section.

3.2.6 Methanol Synthesis

Methanol synthesis from syngas is a heterogeneous phase reaction typically catalyzed by copper/zinc oxides on alumina supports [12]. Typical reaction conditions include high temperatures $(200 - 300 \,^{\circ}\text{C})$ and pressures (50 - 100 bar). This section was simulated using the kinetic model proposed by Graaf et al [43], one of the most widespread and authoritative in the literature. The model, which is based on a commercial catalyst, considers three reactions and uses the SRK equation of state to calculate gas



Figure 3.10: HYSYS flowsheet depicting the 'gas sweetening' section for the FT fuels production.

Column	Absorber	Regenerator
Pressure (kPa)	3827	105
Number of stages	40	20
Inlet stage top	1	1
Inlet stage bottom	40	-
Column plate spacing (cm)	50	60
Stage efficiency $(\%)$	7	3
Condenser T ($^{\circ}C$)	-	70
Condenser duty (MW)	-	0.1

Table 3.4: Parameters used in the SWT section.

fugacities. The reactions involved in the process are reported on Table 3.5. Only two of these reactions are (linearly) independent.

Table 3.5: Methanol synthesis reactions.

Reaction	Stoichiometry	$\Delta H_{298K} \; (\text{kJ/mol} \; CO_x)$	Reaction number
CO to $MeOH$	$CO + 2H_2 \longleftrightarrow CH_3OH$	-91	(3.4)
CO_2 to $MeOH$	$CO_2 + 3H_2 \longleftrightarrow CH_3OH + H_2O$	-49	(3.5)
Water-gas shift	$CO_2 + H_2 \longleftrightarrow CO + H_2O$	41	(3.6)

A liquid-phase methanol reactor was considered in which the catalyst is suspended in an oil bath. This configuration has high processing capacities and extremely desirable heat control properties (as seen in Hamelinck & Faaij [47]). In HYSYS such a reactor is modelled as a CSTR, considering isothermal operation and the absence of diffusion limitations (in line with the used kinetic scheme); pressure and temperature were set to 7300 kPa and 240 °C. The slurry volume was considered as 50% of the reactor volume and a residence time of 10 seconds was assumed.

The HYSYS flowsheet of the methanol synthesis step is reported in Figure 3.11. Syngas is brought to the operating pressure by compression with intermediate cooling and water removal; after mixing with the recycle stream, syngas is brought to the operating temperature and enters the reactor. The outlet stream of the reactor, after being cooled down, is composed by liquids (water and methanol) and unreacted syngas. A condenser ('C1') was used to separate the unreacted syngas from liquid water and methanol; the unreacted syngas is split into two streams, with most of it being recycled in the reaction loop while a small fraction is purged and burned at the gas turbine.

3.2.7 The Fischer-Tropsch (FT) Synthesis

The FT synthesis is a heterogeneous-phase, exothermic reaction in which syngas reacts to produce a distribution of long-chain alkanes ('paraffins', $P_j : C_j H_{2j+2}$) and 1-alkenes ('olefins', $O_j : C_j H_{2j}$). Equation



Figure 3.11: HYSYS flowsheet depicting the methanol synthesis section.

3.7 is a schematic representation of this reaction:

$$CO + \nu H_2 \rightarrow \sum_{j=1}^{j=\infty} (\nu_j P_j + \mu_j O_j) + H_2 O$$
 (3.7)

In this work the FT section is modelled using both MATLAB and HYSYS. Figure 3.12 shows the HYSYS flowsheet used in this section. The gas coming from the sweetening section is mixed with unreacted recycled gases and, optionally, some steam before entering a MTPFR. The reactor unit in HYSYS is included for illustrative reasons. The differential equation system representing the reactor (Equations 3.49) was implemented and solved in MATLAB using the ODE45 routine and passed back to HYSYS, which calculates product distribution in the 3-phase separator. The gas recycle mass balance is solved iteratively. The composition of the entering stream is checked between two iterations; if the SSRR of the mass fractions is above a certain tolerance, the reactor system is solved once more, and the recycle composition is updated. In this manner, the gas recycle mass balance is solved with a few number of iterations (usually less than 10).

In the same fashion of the previous Sections 3.2.4 and 3.2.6, the block containing streams with an asterisk is used to represent the cooling jacket and to take into account the energy released by the reaction. Final product upgrading was not considered and, therefore, the output of this operation is sometimes referred to as 'FT crude fuel'.



Figure 3.12: HYSYS flowsheet depicting the FT synthesis section.

Two main issues arise for the simulation of such a system due to the (theoretically) infinite number of product species. The first of which is the calculation of specific terms in the mass balance equations, which are infinite series arising from the the FT reaction stoichiometry. In the second place, the differential equation system must have as many equations as there are species. Therefore, an adequate strategy must be adopted to properly reduce the number of equations (i.e. species) of the reaction system.

In this work, an iron-silicon oxide catalyst is considered, following sustainability and economic directives. For such a catalyst, the FT kinetic mechanism must include olefin readsorption reactions, which further complicates the arising system of equations. The product distribution model considered here was solved using an innovative power series solution. The number of components on the FT product distribution was reduced according to the following strategy: individual components were considered for carbon numbers 1 to 10 and two lumped components from 11+. The formation of the two lump components preserves the average molecular weight of the original distribution. Further details on the derivation of the solution are given on the Appendix 3.A.

For this process section the following process parameters were considered: pressure at the entrance of the reactor was 31 bar and temperature was constant at 250 °C. Catalyst porosity and apparent density were estimated from the work of Jianmin et al [60]. Thermodynamic and physical properties of the lumps were estimated according to the works of Marano & Holder [67, 68, 69, 66].

3.2.8 Distillation

Final product purification is necessary to attain market specifications (99.85 % mass fraction). Methanol distillation is performed on two columns: a high pressure one, in which soluble gases are removed, and a low pressure column for water removal. The stream 'VENT' from the first column contains dissolved gases from the entering raw MeOH stream (mostly CO_2) but it is also rich in methanol. This stream is directed to the power generation section to be burned in the gas turbine (this is seen in Figure 3.4). The HYSYS flowsheet of the distillation step is reported in Figure 3.13.

The relief valve allows the fluid to depressurize (a.k.a. 'flash') from around 7000 to 500 kPa before entering the distillation column. While the presence of such a valve does not alter the final numerical result, it seems to have a positive influence on the convergence properties of the tower calculation routine. The cause of this effect may lie on the uncoupling of the flash and the tower balance equations. Flash equations are widely known for their complexity and difficult convergence [76].

Table 3.4 collects the parameters used in this section. The same procedure used to size the columns in Section 3.2.1 is used in this section.



Figure 3.13: HYSYS flowsheet depicting the distillation section.

Column	High Pressure	Low Pressure
Pressure (kPa)	470	130
Number of stages	30	20
Inlet stage	15	10
Column plate spacing (cm)	60	60
Stage efficiency $(\%)$	60	60
Methanol mass fraction $(\%)$	-	99.85
Methanol recovery $(\%)$	99	99.9
Boiler duty (MW)	1	-

Table 3.6: Parameters used in the distillation section.

3.2.9 Power Generation

In this section heat and electricity are produced in a combined cycle; the electricity can be used in these processes to move pumps and compressors (among others) with the excess being sold at the power grid. The HYSYS flowsheet for the methanol process is seen on Figure 3.14: the streams/units on the left represent a gas turbine (GT), while the loop on the right represents a Rankine cycle in which energy is recovered at a steam turbine (ST). For the FT process, the stream 'Fuel' is substituted with a different fuel stream (see Figure 3.4).



Figure 3.14: HYSYS flowsheet depicting the power generation section.

The amount of electricity produced in the ST is estimated through a simplifying assumption: the energy input of the Rankine cycle (represented by the red energy stream 'h1') is the maximum available process heat that can be delivered to such cycle by process heat integration. This is implemented by iteratively increasing the value of the heat flow delivered to the cycle at stream 'h1' while ensuring that no hot utilities are consumed in the process. Hot utilities are calculated using Pinch Analysis with the Aspen Energy Analyzer software, which can be called directly from inside Aspen HYSYS. The iterative process was done manually with an error tolerance of 0.5 MW on hot utilities and a minimum approach temperature of 20 °C. Lastly, the available heat that can be sold as district heating is calculated from the amount of cold utilities in the integrated system. This is, again, obtained from pinch analysis.

3.2.10 Economic Assessment

In this work, the production of methanol and FT fuels from biomass gasification is assessed economically. The operational expenses (OpEx, i.e., the manufacturing costs) are evaluated according to the methodology presented in the book by Turton et al [94] and are summarized in Table 3.7. Further information will be given ahead with respect to the quantities defined as YCA (yearly capital amortization) and PCI (present cost of investment).

Tag	Name	Value
А	Raw materials	Calculated
В	Utilities	Calculated
С	Operating labor	Calculated
D	Supervisory & clerical labor	$18\% \mathrm{C}$
Ε	Maintenance & repairs	6% PCI
F	Supplies	15% E
G	Laboratory	15% C
Η	Patents	3% OpEx
Ι	Taxes & insurance	3.2% PCI
J	Overhead	60% (C+D+E)
Κ	Administration	15% (C+D+E)
\mathbf{L}	Distribution & selling	11% OpEx
Μ	Research & development	5% OpEx
Ν	YCA	9% PCI

Table 3.7: Summary of OpEx evaluation methodology.

Summing all of the entries in Table 3.7 and solving for the OpEx produces the following expressions:

$$OpEx = A + B + 222\%C + 23\%PCI + 19\%OpEx$$

$$OpEx = 123\%(A + B) + 273\%C + 29\%PCI$$
(3.8)

The YCA is obtained from the conversion of the total PCI (present cost of investment) to an equivalent series of yearly instalments. The equation below, a known result from power series, allows calculating the YCA from a given PCI, considering m years of construction, m years of operation and i yearly interest rate:

$$YCA = \beta \cdot PCI$$

$$\beta = \frac{\mathbf{i}(1+\mathbf{i})^{m+n}}{(1+\mathbf{i})^n - 1}$$
(3.9)

For this work, (m, n, i) = (2 years, 20 years, 5%); using these parameters yields $\beta = 9\%$, which is the value seen on Table 3.7. The estimation of the PCI was performed using two different methodologies. The first case is according to the work of Turton et al [94]. First, the base cost of each single equipment ('C') is calculated through correlations based on the equipment 'size' or its capacity parameter 'A' (volume for reactors, area for heat exchangers, power for pumps and compressors, etc):

$$C = K_0 + K_1 \log A + K_2 (\log A)^2 A_{min} < A < A_{max}$$
(3.10)

in which the K are constants that depend on the equipment type and the subscripts min and max denote the minimum and maximum capacity values for which the cost correlation is valid. The base cost is changed through a multiplying factor that takes into consideration custom design specifications, such as the operating pressure or the construction material. The heat exchanger network PCI was considered to be worth 15% of the total PCI; this cost was distributed through each of the sections with a multiplying factor.

If the capacity parameter value is below or above the lower limit value of the correlation, the base cost is calculated by scaling the extremum value with a 0.6 exponent, for example:

$$C = C_{min} (A/A_{min})^{0.6}$$

$$A < A_{min}$$

$$C_{min} = K_0 + K_1 \log A_{min} + K_2 (\log A_{min})^2$$
(3.11)

The 0.6 exponent is a typical value used for in scaling equipment cost if no information is know a priori about the behaviour of the cost function [94]. The usefulness of such approach is that the extrapolated values (the equipment cost whenever the scale parameter is out of the correlation range) have a qualitative behaviour that is coherent with the expected behaviour for such cost functions. Additionally, this procedure avoids obtaining negative numbers for the equipment cost, which may be produced for specific values of the scale parameter with the original correlations.

The correlations in the works of Hamelinck et al [47, 46] were used in the second approach for estimating the PCI, and are similar to the functional form seen in Equation 3.11:

$$C = F \cdot C_0 (A/A_0)^k \tag{3.12}$$

In Equation 3.12, F is the 'overall installation factor', which is specific for each equipment and takes into account peripheral costs with hardware and other project costs. Such correlations are already in the exponential form and already possess the expected qualitative behaviour.

Costs with raw materials comprise biomass, filter cartridges and catalysts. Revenues are composed by sales of electricity, available heat and chemicals. For the sale of heat, only 7 (cold) months of the year are considered. Operating labor cost is estimated as 45 k \in /y, correspondent to the yearly salary (plus associated costs) of one engineer; the availability (ratio between working days and total days of the year) was 90%; the considered life-time of catalysts was 1 year. Table 3.8 presents the cost (selling price) for the consumables (products) considered in this work.

The minimum support cost (MSC) accounts for the capital that must be provided for the process to run without profits/expenses; it is a measure of the process economic self-sufficiency. It is calculated as

$$MSC\left[\notin/MWh\right] = -\frac{\text{net OpEx}}{\text{net energy output}}$$
(3.13)

with the net OpEx being calculated as revenues minus expenses; the net energy output corresponds to the energy associated to products minus that consumed with electricity; the minus sign in front of the expression accounts for the (usually) negative net OpEx value.

Consumables	Basis	$\mathrm{Cost}~({\Subset})$	Reference
Biomass	MWh	14	[85]
Filter catridges	Filter units	40	[2]
Catalyst - reforming	\mathbf{t}	2000	[2]
Catalyst - WGS	\mathbf{t}	10000	[2]
Catalyst - MeOH synthesis	\mathbf{t}	5000	[2]
Catalyst - FT synthesis	\mathbf{t}	10000	[2]
Consumed electricity	MWh	114	[34]
Products	Basis	Selling price $({\ensuremath{\in}})$	Reference
Available Heat	MWh	12	estimated
Produced electricity	MWh	38	[32]
Methanol	MWh	56	[70]
FT liquids	MWh	49	[75]

Table 3.8: Cost (selling prices) of consumables (products) pertinent of the biomass gasification process.

3.3 Results

In this section the technical assessment is presented first, followed by the economic one. The results obtained were compared to those of other authors, especially concerning the modelling of the ASU section, the modelling of the synthesis sections and the economic evaluation. All of the mass / energy flow values have been normalized to a yearly basis, after multiplication by the plant availability value of 90%.

Table 3.9 presents the mass balances of the processes, showing the mass flow values of the main streams seen in Figure 3.4 and the MY for each stage and the accumulated MY ('Acc. MY'). The MeOH process retains more carbon and more mass in the final product than the FT process.

Tab	le 3.9 :	Biomass	gasification	process	${\rm mass}$	balance:	mass :	flow va	lues o	of th	ie main	streams	and	MY
-----	------------	---------	--------------	---------	--------------	----------	--------	---------	--------	-------	---------	---------	-----	----

Process	Stream	Mass flow (kg/h)	Stage MY (%)	Acc. MY (%)	Carbon flow (kg/h)	Stage CY (%)	Acc. CY (%)
MeOH	Biomass	21465	_	100	9494	_	100
MeOH	GAS	30308	141	141	9630	101	101
MeOH	QUE	30063	99	140	9400	98	99
MeOH	WGS	30069	100	140	9400	100	99
MeOH	SWT1	12488	42	58	4601	49	48
MeOH	MeOH	9824	79	46	3499	76	37
MeOH	DIST	8623	88	40	3227	92	34
FTS	Biomass	21465	-	100	9494	-	100
\mathbf{FTS}	GAS	30308	141	141	9630	101	101
\mathbf{FTS}	QUE	30063	99	140	9400	98	99
\mathbf{FTS}	SWT2	18250	61	85	7295	78	77
\mathbf{FTS}	FTS	2949	16	14	2441	33	26

Table 3.10 reports the process energy balance after each process section considering optimal conditions; except when otherwise indicated, values are in kW. Column 2 presents the energy stored in the material streams as LHV; column 3 presents the net heat absorbed (negative) or released (positive) by process streams; column 4 presents the accumulated net heat (sum of column 2 values up to the pertinent stage); column 5 presents the net electricity produced (positive) or consumed (negative) in a process section; column 6 presents the net accumulated electricity (sum of column 4 values up to the pertinent stage); column 7 presents the accumulated 'noble' energy: the sum of heat and electricity (columns 2 and 6) for the same stage, heat excluded; column 8 presents the total accumulated energy (sum of columns 2, 5 and 6 for the same stage); columns 9 and 10 present the EY by stage (considering all forms of energy) and the accumulated EY.

If all the forms of energy are considered (column 8), the FT process has a slightly bigger EY value than the methanol process. The opposite is true if only chemicals and electricity are considered (column 7). In some sections the stage EY is bigger than one due to the transfer of sensible heat, which is not tracked in the analysis.

0	1	2	3	4	5	6	7	8	9	10
Process	Process	Streams	ΔQ	ΣQ	ΔE	ΣE	LHV	LHV +	Stage	Acc.
	Section	LHV	-				$+ \Sigma E$	$\Sigma(E+Q)$	EY (%)	EY $(\%)$
MeOH	Biomass	100	0	0	0	0	100	100	-	100
MeOH	GAS	76	0	0	0	0	76	76	76	76
MeOH	QUE	72	18	18	0	0	72	90	118	90
MeOH	WGS	70	6	24	0	0	69	94	104	94
MeOH	SWT1	70	-3	21	0	0	69	90	96	90
MeOH	MeOH	60	11	32	-1	-2	58	90	100	90
MeOH	DIST	60	0	32	0	-2	58	90	100	90
MeOH	PWR1	48	1	33	10	8	56	89	99	89
MeOH	ASU	48	0	33	-7	1	49	82	92	82
FTS	Biomass	100	0	0	0	0	100	100	-	100
FTS	GAS	76	0	0	0	0	76	76	76	76
\mathbf{FTS}	QUE	72	18	18	0	0	72	90	118	90
FTS	SWT2	72	6	23	0	0	72	95	106	95
FTS	FTS	41	14	37	0	0	41	78	82	78
FTS	PWR2	17	2	39	22	22	39	78	99	78
\mathbf{FTS}	ASU	17	0	39	-7	15	32	71	91	71

Table 3.10: Biomass gasification process energy balance: energy flow values (columns 2 to 8, values in MW) and EY; values refer to the output of each process section.

Table 3.11 below summarizes the yearly amount of consumables / products calculated for each process.

Table 3.11: Yearly amount of consumables/products for biomass gasification processes.

Consumables	Basis	MeOH	FTS
Biomass	GWh	876	876
Filter catridges	Filter units	108	108
Catalyst - reforming	\mathbf{t}	48	48
Catalyst - WGS	\mathbf{t}	15	0
Catalyst - MeOH synthesis	\mathbf{t}	35	0
Catalyst - FT synthesis	\mathbf{t}	0	14
Consumed electricity	GWh	0	0
Products	Basis	MeOH	FTS
Available Heat	GWh	186	222
Produced electricity	GWh	12	131
Methanol	GWh	417	0
FT liquids	GWh	0	149

3.3.1 Separation Columns

This section groups the results for the separation columns seen in this work. Table 3.12 presents the results on the columns dimensions as estimated through the Souders and Brown equation (3.1) and the other previously stated assumptions. 'HP' and 'LP' indicate the high and low pressure columns in each section. It is seen that none of the L/D ratios is above 15. This is in agreement with heuristics that determine that such parameter should not be above 20 lest a special column design be required [94]. In special, the SWT1 section is bigger in size than the SWT2 due to the entering syngas having more CO_2 that is produced in the WGS section.

Table 3.13 summarizes the different process parameters calculated for each separation section. For the sweetening sections, it is seen that, while a great amount of water evaporates, almost no MDEA is lost. Except for the ASU, great amounts of heat are required from the columns in each case, and above all, at relatively high boiler temperatures (around 100 °C.) This puts an important constraint on heat integration of the system. In any case, the specific heat consumption agrees with literature values; Rolker & Seiler report a value of 33 kWh/kmol CO_2 [82].

Table 3.12: Column dimensions resulting from the assumptions used in this work. 'HP' and 'LP' indicate the high and low pressure columns in each section.

	AS	SU	SW	T1	SW	T2	DI	ST
Column	HP	LP	ΗP	LP	ΗP	LP	ΗP	LP
Diameter (m) Length (m) L / D ratio Volume (m ³)	$2.5 \\ 30 \\ 12 \\ 145$	$3.5 \\ 36 \\ 10 \\ 353$	1.9 20 11 54	$3.5 \\ 12 \\ 3 \\ 116$	$1.7 \\ 20 \\ 12 \\ 44$	$2.4 \\ 12 \\ 5 \\ 56$	1.4 18 13 27	$2.9 \\ 12 \\ 4 \\ 81$

Table 3.13: Calculated process parameters for each separation section.

Section	Parameter	Unit	Value
ASU	Electricity consumption	MW	6.9
ASU	Air mass flow	$\rm kg/s$	19.1
ASU	O_2 recovery	%	71
ASU	O_2 mass fraction	%	99.97
SWT1	Water make up	$\rm kg/h$	4949
SWT1	MDEA make up	$\rm kg/h$	0.045
SWT1	Boiler duty	MW	12.7
STW1	Boiler T	$^{\circ}\mathrm{C}$	103
STW1	CO_2 removal	$\rm kmol/h$	442
STW1	CO_2 specific duty	$\rm kWh/kmol$	29
SWT2	Water make up	$\rm kg/h$	1584
SWT2	MDEA make up	$\rm kg/h$	0.049
SWT2	Boiler duty	MW	6.1
SWT2	Boiler T	$^{\circ}\mathrm{C}$	103
SWT2	CO_2 removal	$\rm kmol/h$	197
SWT2	CO_2 specific duty	kWh/kmol	31
DIST	LP boiler duty	MW	5
DIST	LP boiler T	$^{\circ}\mathrm{C}$	107

Table 3.13 shows a comparison of the results on the electricity consumption for this process and that of other authors. The value calculated in this work is more than twice the value of the smaller estimate. It seems that overly conservative assumptions might have been taken into consideration in the model. Nevertheless, the other references do not present their assumptions.

Table 3.14: Comparison between different references for electricity consumption in cryogenic air separation.

Reference	This work	[47]	[61]	[81]
Electricity consumption (kWh / t O_2)	673	350	327	480

3.3.2 Reaction Sections

The main results obtained for the reaction sections are summarized in Table 3.15. The reaction sections are ordered according to the amount of heat released in each reaction system. All of these systems promote the WGS reaction and only one of them promotes it without catalyzing other parallel reactions (i.e., the WGS section itself). The sections are also ordered in a decreasing order of temperature, which is intuitive from the perspective of an energetic integration. Conversely, the systems at lower temperatures release more heat than those at higher temperatures. The reasoning behind this observation is, first of all, thermodynamic. The temperature decrease between two sections results in an equilibrium displacement in the sense that promotes chemical energy release. In the second place are the specific chemical reactions in each section. Heat control is particularly critical for the FT section, being the one with the highest heat release. Another critical aspect is the high pressure on the jacket side (Table 3.15 shows reactor pressure for the MEOH section). In this aspect, the QUE section is the least critical (no external jacket is considered) while the WGS is the most.



Figure 3.15: Mass and molar fraction profiles inside the FT reactor. Paraffins and olefins were grouped and are represented by letters 'P' and 'O', respectively.

The FT reactor mass and molar fraction profiles are seen in Figure 3.15. Paraffins and olefins were grouped and are represented by letters 'P' and 'O', respectively. The rising CO_2 profile is related to the WGS reaction, which regenerates CO consumed by the FT reaction. Above all, it is seen that the qualitative behaviour of olefin readsorption is respected by the model. This is clear from the downward inflection in the olefin mass fraction profile at the end of the reactor. The numerical error on the sum of mass fractions at any point inside the reactor was below 1E-14, which indicates that the stoichiometric relationships are respected.

Table 3.15: Comparison between the different reaction sections in the biomass gasification process.

Section	QUE	WGS	MEOH	FTS
Bed / slurry volume (m^3)	51	14	24	12
Vessel volume (m^3)	51	68	47	39
Number of tubes	-	689	-	600
Heat exchange area (m^2)	-	1082	-	942
Cooling jacket T ($^{\circ}C$)	-	275	-	220
Cooling jacket P (kPa)	-	5844	7300	2317
Heat release (MW)	0	3	8	15

3.3.3 Power Generation

The energy balance for the power generation section is presented on Table 3.16, detailing electricity production in the GT and ST. Rankine cycle heat input and the total available heat were determined through pinch analysis, as explained previously in Section 3.2.9.

Heat and electricity production is much bigger for the FT process due to the great amount of heat released in the respective synthesis section when compared to the MEOH process. This implies that the FT process is economically more competitive when the sales of electricity and heat provide advantageous income when compared to chemicals. It is worth remembering that the selling price of liquid fuels is usually much higher than that of heat and electricity (as seen in Table 3.8). In any case, the product distribution trade-off between the different process outputs should be optimized. In this way, bigger electricity gains compensate for a smaller yield in chemicals.

		MEG	Η	FΤ	\mathbf{S}
Process unit	Parameter	Value (MW)	EY (%)	Value (MW)	EY (%)
GT GT	Inlet streams LHV Gross electricity production	$\begin{array}{c} 12 \\ 5 \end{array}$	$\begin{array}{c} 100\\ 38 \end{array}$	$\begin{array}{c} 24 \\ 10 \end{array}$	$\begin{array}{c} 100\\ 43 \end{array}$
ST ST	Rankine cycle heat input Gross electricity production	$\begin{array}{c} 20 \\ 5 \end{array}$	$\begin{array}{c} 100 \\ 27 \end{array}$	$\begin{array}{c} 38\\12\end{array}$	$\begin{array}{c} 100\\ 31 \end{array}$
$\overline{\mathrm{GT}} + \mathrm{ST}$	Gross electricity production Available heat	10 33	-	22 39	-

Table 3.16: Energy balance for the power generation section for biomass gasification processes.

Figure 3.16 shows the hot and cold composite curves for both processes. The curves were obtained through pinch analysis using the Energy Analyzer software. It is clear that both processes produce much more heat than they consume: for both case the red curve (top) is bigger than the blue curve (bottom). In any case the biggest temperature a cold stream attains is 500 °C, which refers to the rankine cycle at the power generation section. Qualitatively, the two diagrams present relevant differences. The pinch point for the methanol process is located around 100 °C, which is indicative of the heat consumption at the SWT and DIST sections (refer to Table 3.13). For the FT process the pinch point is located around 250 °C. This is clearly connected to the high amount of heat donated at this temperature (in the synthesis section), combined with a much smaller duty at the SWT section.



Figure 3.16: Composite curves for biomass gasification processes obtained through pinch analysis using the Energy Analyzer software.

3.3.4 Economic Assessment

Table 3.17 details the calculated PCI for the different process sections and with the two sets of correlations. In general, the values are very close between the two processes (for the same set of correlations), which is expected since the processes are very similar. In the works of Hamelinck et al, the PCI is increased by multiplying terms (the 'overall installation factor', seen in Equation 3.12) that anticipate different OpEx entries that are considered later in this work. As a result, their original PCI is bigger, while the OpEx is a 'weaker' function of the PCI. The values reported in Table 3.17 are corrected for such disparity by

taking the ratio between the PCI multipliers from their respective OpEx function (refer to Equation 3.8):

$$OpEx = x (A + B) + y C + z PCI$$

$$PCI_1 = \frac{z_2}{z_1} PCI_2$$
(3.14)

Most of the values evaluated for the correlations presented by Turton et al [94] match those of Hamelinck et al [47, 46]. Among the sections which present disparities among such correlations are (1) the methanol synthesis, (2) the distillation and (3) the power generation section. The correlations presented by Hamelinck et al for (1) are originally based on the economic assessment from the report produced for the Clean Coal Technology Program of the United States Department of Energy [51]. In fact, the original values presented on such report, if scaled to match the size of the methanol loop in this work (with Equation 3.12) yield a PCI of 9 M \in . It is then reasonable to think that the PCI obtained with the Turton correlation is a good compromise between the Hamelinck correlation and the original value. Not only it better reproduces the original value but also slightly reduces it, which is in line with the much smaller PCI of the other reacting sections. For (3), there is an excellent PCI matching for the steam turbine, but poor agreement for the gas turbine. The gas turbine value by the Hamelinck correlations are too high and seem inadequate here. Again, the values by Turton et al seem more reasonable. Lastly, for (2), further studies are needed to assess the adequacy of each correlation set.

It is interesting to notice the agreement not only between the PCI (seen in Table 3.17) but also on the economic assessment methodology. Hamelinck et al use (F, z) = (1.9, 16%) (Equations 3.12 and 3.14). Taking the product between these two quantities yields 30%, which agrees well with the value used in this work (29% of the PCI, Equation 3.8).

In Table 3.18 the OpEx is presented; values are in $M \in /y$ with expenses being negative while income is positive. For both processes, the cost with materials other than biomass (catalysts and candle filters) is minimal. The 'others' entry accumulates the rounding error and other OpEx entries that produced very small values. Economic sustainability is not attained for any of the processes due to the overall high manufacturing costs.

The MSC cost was calculated and is shown in Table 3.19. The values found for the methanol process are much smaller than the ones seen for the FT process, mostly due to the much bigger amount of chemicals produced by the former. The MSC for methanol is, respectively, less than half and one third of current government biomethane subsidies in Germany and Italy [83, 58]. This indicates a great potential for such a process to meet environmental goals at a much reduced cost than current policies.

Figure 3.17 presents the production costs of both processes as a function of biomass input. The obtained results match those reported by other authors, as seen on Figure 3.2 at the end of Section 3.1. For the FT process, the cost of chemicals is much higher that the gross energy cost since much of the output energy is under the form of heat and electricity. Increasing biomass input up until 200 MW has a significant impact on MSC, after which the decrease is much less pronounced. Economic feasibility is not attained for any of the processes. This is clear since the MSC never reaches zero. Lastly, such findings are supported by the fact that demonstration and commercial scale bio-methanol production facilities have been proposed (and some constructed) in Canada and Europe, with production capacities that are similar to the ones obtained in this work [54].

Process	Μ	IEOH]	FTS
Correlations from	Turton et al [94]	$\begin{array}{c} \text{Hamelinck} \\ \text{et al} \left[47, 46 \right] \end{array}$	Turton et al [94]	Hamelinck et al [47, 46]
ASU	15	17	15	17
GAS	31	29	31	29
QUE	1	1	1	1
WGS	2	2	-	-
SWT	4	4	2	2
MEOH	6	1	-	-
DIST	2	5	-	-
FTS	-	-	1	1
PWR	10	12	14	21
Total	70	72	65	72

Table 3.17: PCI details of biomass gasification processes; values are in $M \in$.

Process	MeOH	FTS
Biomass	-13	-13
Operating labor	-1	-1
Maintenance & repairs	-4	-4
Supplies	-1	-1
Patents	-1	-1
Taxes and insurance	-2	-2
Overhead	-4	-3
Administration	-1	-1
Distribution and selling	-4	-4
Research and development	-2	-2
YCA	-6	-6
Others	-1	0
Total OpEx	-40	-38
Available Heat	2	3
Produced electricity	0	5
Methanol	24	0
FT liquids	0	7
Net OpEx	-14	-24

Table 3.18: OpEx details of biomass gasification processes; values are in $M \in /y$.

Table 3.19: MSC for biomass gasification processes.

Process	MeOH	\mathbf{FTS}
Total OpEx $(M \in /y)$	40	38
Energy output (GWh/y)	616	501
Gross energy cost (\in/MWh)	65	77
Non chemicals revenues $(M \in /y)$	3	8
Net OpEx - w/o chemicals $(M \in /y)$	37	31
Chemicals output (GWh/y)	417	149
Cost of chemicals (\in /MWh)	90	207
$MSC \ ({ { \in / MWh}})$	33	159

3.4 Conclusion

The coproduction of heat, electricity and chemicals from second-generation biomass gasification was described. It is clear that methanol production is the superior process, both in economic and in terms of final conversion to liquid fuels. The economics of the Fischer-Tropsch process suffers due to the low energetic yield of the reaction in terms of high valued liquid products. It remains to be confirmed (1) whether if the correlations used are adequate to represent the FT reaction system and (2) if further income could be expected if the other reaction products could be sold as high value products. It can be further expected that, by diversifying and optimizing the product portfolio, the process economic output can be maximized.

While both processes are economically unfeasible without subsidies, methanol production is an interesting alternative to current biogas concepts. The minimum support cost of this process ranges from half to one third of current biogas support costs. This kind of technology is being tested on demonstration level in Europe and Canada and is expected to reach commercial scale on the following years. It is still unclear how big is the issue of the transportation logistics of biomass but, whenever there is biomass availability and the investment budget allows it, the bigger size plants are to be preferred. Such plants have increased resilience to market price fluctuations, bigger ability to generate income and, consequently, smaller payback times.

Biomass valorization is not only a matter of meeting the obvious environmental goals but it is also linked with energy security and strategic sovereignty. Considering the projections on biomass supply and demand and the economic competitiveness of bioenergy, it is safe to say that these processes are to play a fundamental role for mankind development in the near and long-term future.



Figure 3.17: Production costs of biomass gasification processes as a function of biomass LHV input.

3.A Fischer-Tropsch Synthesis Stoichiometry - Olefin Readsorption Model

In this section the development of the Fischer-Tropsch synthesis (FTS) stoichiometry calculation routine is presented. A steady state, plug-flow reactor (PFR) is considered. The following is based on the kinetic mechanism and correlations found on the works of van der Laan & Beenackers [96, 97]. The FTS reaction is represented by

$$CO + nH_2 \rightarrow \sum_{j=1}^{\infty} \left(\nu_j C_j H_{2j+2} + \mu_j C_j H_{2j} \right) + H_2 O$$
 (3.15)

The products and reactants generation rates are connected through the reaction stoichiometry. The following expressions are obtained from molar balances on carbon and hydrogen

$$-R_{CO} = \sum_{j=1}^{\infty} j \left(R_P^{(j)} + R_O^{(j)} \right)$$

$$-R_{H_2} = \sum_{j=1}^{\infty} \left[(j+1) R_P^{(j)} + j R_O^{(j)} \right] + R_{H_2O}$$

(3.16)

The infinite series can be solved by using recursive relationships deriving from the proposed kinetic mechanism:

$$R_{P}^{(i)} = f\left(R_{P}^{(i-1)}\right)$$

$$R_{O}^{(i)} = g\left(R_{P}^{(i)}, y_{O}^{(i)}\right)$$
(3.17)

with the model parameters that are calculated from correlations obtained with data fitting:

$$-R_{CO} = \frac{a_1 P_{CO} P_{H_2}}{\left(1 + a_2 P_{CO} + a_3 P_{H_2O}\right)^2}$$
(3.18)

3.A.1 Component Lumping

To deal with the infinite number of products generated in the FTS, the components over a certain carbon number N are lumped together:

$$y^{[N,\infty]} = \sum_{k=N}^{k=\infty} y^{(k)} \qquad w^{[N,\infty]} = \sum_{k=N}^{k=\infty} w^{(k)}$$
(3.19)

Due to the different nature of paraffins and olefins, these are grouped separately. The connection between the mass and molar fractions of a component is given by the equation below:

$$y^{(k)}M^{(k)} = w^{(k)}M (3.20)$$

The average molar mass of the lump is one of its defining parameters; it is calculated by solving the previous equation, using either mass or molar fractions

$$y^{[N,\infty]}M^{[N,\infty]} = w^{[N,\infty]}M$$
(3.21)

$$M^{[N,\infty]} = \frac{w^{[N,\infty]}M}{y^{[N,\infty]}} \qquad M^{[N,\infty]} = \frac{w^{[N,\infty]}}{y^{[N,\infty]}/M}$$

$$= \frac{\sum_{k=N}^{k=\infty} w^{(k)}M}{y^{[N,\infty]}} \qquad = \frac{w^{[N,\infty]}}{\sum_{k=N}^{k=\infty} y^{(k)}/M}$$

$$= \frac{\sum_{k=N}^{k=\infty} y^{(k)}M^{(k)}}{y^{[N,\infty]}} \qquad = \frac{w^{[N,\infty]}}{\sum_{k=N}^{k=\infty} w^{(k)}/M^{(k)}}$$

$$= \frac{y^{[N,\infty]}}{y^{[N,\infty]}} \qquad = \frac{w^{[N,\infty]}}{w^{[N,\infty]}}$$

$$(3.22)$$

with the following definitions being introduced:

$$\mathbb{y}^{[N,\infty]} = \sum_{k=N}^{k=\infty} y^{(k)} M^{(k)} \qquad \mathbb{w}^{[N,\infty]} = \sum_{k=N}^{k=\infty} w^{(k)} M^{(k)}$$
(3.23)

In a plug-flow reactor, the steady state component mass balance results in a set of ordinary differential equations. Together with the previously introduced variables, the following balances are obtained

$$\frac{dw^{(j)}}{dz} = \frac{A\rho_c}{\dot{m}} M^{(j)} R^{(j)}$$

$$\frac{dw^{[N,\infty]}}{dz} = \frac{A\rho_c}{\dot{m}} \left(\sum_{j=N}^{j=\infty} M^{(j)} R^{(j)} \right)$$

$$\frac{dw^{[N,\infty]}}{dz} = \frac{A\rho_c}{\dot{m}} \left(\sum_{j=N}^{j=\infty} R^{(j)} \right)$$
(3.24)

The infinite series on the mass balances are written in the following manner for both lump types:

Lump type	Paraffin	Olefin
Molar mass	$M_{\rm P}^{(k)} = 14k + 2$	$M_0^{(k)} = 14k$
Infinite series	$\sum_{j=N}^{j=\infty} M_{\rm P}^{(j)} R_{\rm P}^{(j)} = 14 \mathbb{R}_{\rm P}^{[N,\infty]} + 2 R_{\rm P}^{[N,\infty]}$	$\sum_{j=N}^{j=\infty} M_O^{(j)} R_O^{(j)} = 14 \mathbb{R}_O^{[N,\infty]}$

With the following definitions being introduced:

$$R^{[k,\infty]} = \sum_{j=k}^{j=\infty} R^{(j)} \qquad \mathbb{R}^{[k,\infty]} = \sum_{j=k}^{j=\infty} j R^{(j)}$$
(3.25)

3.A.2 Power series hypothesis

It is known (both from experiment and theory) that olefin and paraffin formation rates fall with an increase in the carbon numbers [38]. A simplification that will enable the solution of the system of equations is the following hypothesis: the concentration of the olefin components inside the lump is represented by a decaying geometric sequence. This can be translated into molar fractions as

$$y_o^{(k)} = \gamma^k \frac{y_o^{(N)}}{\gamma^N} \qquad k \ge N \tag{3.26}$$

With this hypothesis the following is calculated:

Define
$$y_0^{[j,\infty]}$$
 and $y_0^{[j,\infty]}$ $y_0^{[j,\infty]} = \sum_{k=j}^{k=\infty} y_0^{(k)}$ $y_0^{[j,\infty]} = \sum_{k=j}^{k=\infty} y_0^{(k)} M_0^{(k)}$
For $j = N$, substitute the expression for $y_0^{(k)}$ $y_0^{[N,\infty]} = \frac{y_0^{(N)}}{\gamma^N} \sum_{k=N}^{k=\infty} \gamma^k$ $y_0^{[N,\infty]} = \frac{y_0^{(N)}}{\gamma^N} \left\{ 14 \sum_{k=N}^{k=\infty} k \gamma^k \right\}$
Plug in classic infinite $y_0^{[N,\infty]} = \frac{y_0^{(N)}}{\gamma^N} \frac{\gamma^N}{1-\gamma}$ $y_0^{[N,\infty]} = \frac{y_0^{(N)}}{\gamma^N} \left\{ 14 \frac{\gamma^N}{1-\gamma} \frac{[N-\gamma(N-1)]}{1-\gamma} \right\}$
Simplify the expression $y_0^{[N,\infty]} = \frac{y_0^{(N)}}{1-\gamma}$ $y_0^{[N,\infty]} = \frac{14y_0^{[N,\infty]}[N-\gamma(N-1)]}{1-\gamma}$

The last expression on the first column can be solved in terms of $y_o^{(N)}$:

$$y_o^{(N)} = y_o^{[N,\infty]} (1-\gamma)$$
(3.27)

An expression for γ can be found if the results above are used to calculate the olefin molar mass. From the definitions of the previous sections

$$\frac{y_o^{[N,\infty]}}{y_o^{[N,\infty]}} = M_o^{[N,\infty]} = \frac{14[N - \gamma(N-1)]}{1 - \gamma}$$

$$\gamma = \frac{M_o^{[N,\infty]} - 14N}{M_o^{[N,\infty]} - 14(N-1)}$$
(3.28)

The geometric sequence hypothesis allows calculating another two infinite series that will be useful later:

Define
$$B^{[j,\infty]}$$
 and $\mathbb{B}^{[j,\infty]}$ $B^{[j,\infty]} = \sum_{k=j}^{k=\infty} e^{ck} y_0^{(k)}$
For $j = N$, substitute
the expression for $y_0^{(k)}$ $B^{[N,\infty]} = \frac{y_0^{[N,\infty]}(1-\gamma)}{\gamma^N} \sum_{k=N}^{k=\infty} (e^c \gamma)^k$ $\mathbb{B}^{[N,\infty]} = \frac{y_0^{[N,\infty]}(1-\gamma)}{\gamma^N} \sum_{k=N}^{k=\infty} k(e^c \gamma)^k$
Plug in classic infinite
series result $B^{[N,\infty]} = \frac{y_0^{[N,\infty]}(1-\gamma)}{\gamma^N} \frac{(e^c \gamma)^N}{1-e^c \gamma}$ $\mathbb{B}^{[N,\infty]} = \frac{y_0^{[N,\infty]}(1-\gamma)}{\gamma^N} \frac{(e^c \gamma)^N [N-e^c \gamma(N-1)]}{(1-e^c \gamma)^2}$
Simplify the expression $B^{[N,\infty]} = \frac{y_0^{[N,\infty]}(1-\gamma)e^{cN}}{1-e^c \gamma}$ $\mathbb{B}^{[N,\infty]} = \frac{B^{[N,\infty]}[N-e^c \gamma(N-1)]}{1-e^c \gamma}$

3.A.3 Hydrocarbon Formation Rates

The reaction mechanism here considered is the same as seen from the work of van der Laan & Beenackers [96]. The molar rates of formation are given as

i	Paraffin	Olefin	Methylene
1	$R_P^{(1)} = k_{t,P}^{(1)} \theta_H \theta_1$	$R_{O}^{(1)}=0$	$R_M^{(1)} = k_p \theta_M \theta_1$
2	$R_P^{(2)} = k_{t,P}^{(2)} \theta_H \theta_2$	$R_{0}^{(2)} = k_{t,0}^{(2)} \theta_{v} \theta_{2} - k_{R}^{(2)} \theta_{v} \theta_{H} e^{c2} \mathbb{C}_{0}^{(2)}$	$R_M^{(2)}=k_p\theta_M\theta_2$
≥ 3	$R_{P}^{(i)}=k_{t,P}\theta_{H}\theta_{i}$	$R_{O}^{(i)} = k_{t,O}\theta_{v}\theta_{i} - k_{R}\theta_{v}\theta_{H}e^{ci}\mathbb{C}_{O}^{(i)}$	$R_M^{(i)} = k_p \theta_M \theta_i$

For C1 and C2 there is a marked deviation from the classic Anderson-Schulz-Flory (ASF) theory: methane and ethane are produced in bigger quantity than it foresees. In the same fashion, the correspondent C1 olefin is not produced at all and ethene is in pronounced defect with respect to the ASF prediction. It is now useful to rewrite the previously presented expressions by introducing the following variables (for which correlations are presented in the work of van der Laan & Beenackers [96]:

$\mathcal{R}^{(i)} = k_{t,P} \theta_{H} \theta_{i}$	$t_{\rm P}^{(1)} = k_{t,\rm P}^{(1)}/k_{t,\rm P}$	$p = \frac{k_p \theta_M}{k_{t,P} \theta_H}$	$\Bbbk = \mathbb{C}k_R\theta_v\theta_H$
$\mathbb{C} = \mathbb{P}/\mathbb{R}\mathbb{T}$	$t_{P}^{(2)}=k_{t,P}^{(2)}/k_{t,P}$	$t_{0} = \frac{k_{t,0}\theta_{v}}{k_{t,P}\theta_{H}} = \frac{k_{t,0}^{(2)}\theta_{v}}{k_{t,P}\theta_{H}}$	$b\Bbbk = \mathbb{C}k_R^{(2)}\theta_v\theta_H$

With these definitions the previous system of equations is rewritten as

i	Paraffin	Olefin	Methylene
1	$R_{P}^{(1)}=t_{P}^{(1)}\mathcal{R}^{(1)}$	$R_{O}^{(1)}=O$	$R_{M}^{(1)} = p\mathcal{R}^{(1)}$
2	$R_{P}^{(2)}=t_{P}^{(2)}\mathcal{R}^{(2)}$	$R_0^{(2)} = t_0 \mathcal{R}^{(2)} - b \Bbbk e^{c2} y_0^{(2)}$	$R_{M}^{(2)} = p\mathcal{R}^{(2)}$
≥ 3	$R_{P}^{(i)} = \mathcal{R}^{(i)}$	$\mathbf{R}_{O}^{(i)} = \mathbf{t}_{O} \mathcal{R}^{(i)} - \mathbb{k} \mathbf{e}^{ci} \mathbf{y}_{O}^{(i)}$	$R_{M}^{(i)} = p\mathcal{R}^{(i)}$

If a more intuitive pattern had been observed, the following definitions/expressions would have been expected

$$t_{0}^{(2)} = \frac{k_{t,0}^{(2)}\theta_{v}}{k_{t,P}\theta_{H}} \qquad \Bbbk^{(2)} = \mathbb{C}k_{R}^{(2)}\theta_{v}\theta_{H} \qquad R_{0}^{(2)} = t_{0}^{(2)}\mathcal{R}^{(2)} - \Bbbk^{(2)}e^{c2}y_{0}^{(2)}$$

Instead the authors chose the definitions seen on the other table, probably to avoid problems with collinearity (as they have mentioned in some parts of the article) as well as to adjust to the already mentioned theory deviations.

3.A.4 Recurrence Relationship

The stoichiometric relationship between the methylene, paraffin and olefin species (equation 1 on the article by van der Laan & Beenackers [96] is the following:

$$R_M^{(i-1)} = R_P^{(i)} + R_M^{(i)} + R_O^{(i)}$$
(3.29)

Plugging in the results from the previous section on the expression above yields the following:

For the original $R_{M}^{(1)} = R_{P}^{(2)} + R_{M}^{(2)} + R_{O}^{(2)}$ $R_{M}^{(i-1)} = R_{P}^{(i)} + R_{M}^{(i)} + R_{O}^{(i)}$ stoichiometric relationship Substitute the previously $p\mathcal{R}^{(1)} = \big(t_p^{(2)} + p + t_0\big)\mathcal{R}^{(2)} - b\Bbbk e^{c2}y_0^{(2)}$ $p\mathcal{R}^{(i-1)} = (1 + p + t_0)\mathcal{R}^{(i)} - \Bbbk e^{ci} y_0^{(i)}$ introduced variables $\mathcal{R}^{(2)} = \frac{p\mathcal{R}^{(1)} + b k e^{c2} y_0^{(2)}}{t_p^{(2)} + p + t_0}$ $\mathcal{R}^{(i)} = \frac{p\mathcal{R}^{(i-1)} + \Bbbk e^{ci} y_{O}^{(i)}}{1 + p + t_{O}}$ Solve for $\mathcal{R}^{(i)}$ Rewrite the relationships $\mathcal{R}^{(2)} = \alpha^{(2)} \mathcal{R}^{(1)} + \beta^{(2)} e^{c_2} y_0^{(2)}$ $\mathcal{R}^{(i)} = \alpha \mathcal{R}^{(i-1)} + \beta e^{ci} y_0^{(i)}$ with new definitions With the following definitions being introduced $\alpha^{(2)} = ---p$ $\alpha =$ p

$$\begin{aligned}
\alpha &= \frac{1}{t_P^{(2)} + p + t_O} & \alpha &= \frac{1}{1 + p + t_O} \\
\beta^{(2)} &= \frac{bk}{t_P^{(2)} + p + t_O} & \beta &= \frac{k}{1 + p + t_O}
\end{aligned}$$
(3.30)

The recursion relationship can be used to write any sequence element in terms of an arbitrary previous term

$$\begin{split} \mathcal{R}^{(i)} &= \alpha \mathcal{R}^{(i-1)} + \beta e^{ci} y_0^{(i)} \\ \mathcal{R}^{(i)} &= \alpha^2 \mathcal{R}^{(i-2)} + \alpha \beta e^{c(i-1)} y_0^{(i-1)} + \beta e^{ci} y_0^{(i)} \\ \mathcal{R}^{(i)} &= \alpha^3 \mathcal{R}^{(i-3)} + \alpha^2 \beta e^{c(i-2)} y_0^{(i-2)} + \alpha \beta e^{c(i-1)} y_0^{(i-1)} + \beta e^{ci} y_0^{(i)} \\ \mathcal{R}^{(i)} &= \alpha^{i-K+1} \mathcal{R}^{(K-1)} + \beta \sum_{k=K}^{k=i} \alpha^{i-k} e^{ck} y_0^{(k)} \\ &= \alpha^i \left[\frac{\mathcal{R}^{(K-1)}}{\alpha^{K-1}} + \beta \sum_{k=K}^{k=i} \left(\frac{e^c}{\alpha} \right)^k y_0^{(k)} \right] \end{split}$$

Thus, the following pattern is observed

With the previous result it is possible to represent any term of the series as a function of $\mathcal{R}^{(1)}$ and $y_Q^{(i)}$:

For K = 3

$$\mathcal{R}^{(i)} = \alpha^{i} \left[\frac{\mathcal{R}^{(2)}}{\alpha^{2}} + \beta \sum_{k=3}^{k=i} \left(\frac{e^{c}}{\alpha} \right)^{k} y_{0}^{(k)} \right]$$
Plug in the recursive expression for $\mathcal{R}^{(2)}$ to find
$$\mathcal{R}^{(i)} = \alpha^{i} \left[\frac{\alpha^{(2)} \mathcal{R}^{(1)} + \beta^{(2)} e^{c^{2}} y_{0}^{(2)}}{\alpha^{2}} + \beta \sum_{k=3}^{k=i} \left(\frac{e^{c}}{\alpha} \right)^{k} y_{0}^{(k)} \right]$$

3.A.5 Non Hydrocarbon Formation Rates

The formation rates of carbon monoxide, hydrogen and water can be related the paraffin/olefin rates through the FTS stoichiometry. For CO the following relationship holds:

$$-R_{CO} = \sum_{j=1}^{\infty} j \left(R_P^{(j)} + R_O^{(j)} \right)$$
(3.31)

The previously presented recurrence relationship can be used develop the last expression:

$$R_{P}^{(j)} + R_{O}^{(j)}$$

$$= R_{M}^{(j-1)} - R_{M}^{(j)}$$

$$= p \left(\mathcal{R}^{(j-1)} - \mathcal{R}^{(j)} \right)$$
(3.32)

Plugging back this result in the CO rate expression yields

$$-R_{CO} = \sum_{j=1}^{\infty} j \left(R_P^{(j)} + R_O^{(j)} \right)$$

= $R_P^{(1)} + R_O^{(1)} + \sum_{j=2}^{\infty} j \left(R_P^{(j)} + R_O^{(j)} \right)$
= $t_P^{(1)} \mathcal{R}^{(1)} + 0 + p \sum_{j=2}^{\infty} j \left(\mathcal{R}^{(j-1)} - \mathcal{R}^{(j)} \right)$ (3.33)

The summation can be worked out to yield a simpler expression:

$$\begin{split} \sum_{j=2}^{\infty} j \left(\mathcal{R}^{(j-1)} - \mathcal{R}^{(j)} \right) &= \\ &= \sum_{j=2}^{\infty} j \mathcal{R}^{(j-1)} - \sum_{j=2}^{\infty} j \mathcal{R}^{(j)} \\ &= \sum_{j=1}^{\infty} (j+1) \mathcal{R}^{(j)} - \sum_{j=2}^{\infty} j \mathcal{R}^{(j)} \\ &= 2 \mathcal{R}^{(1)} + \sum_{j=2}^{\infty} (j+1) \mathcal{R}^{(j)} - \sum_{j=2}^{\infty} j \mathcal{R}^{(j)} \\ &= 2 \mathcal{R}^{(1)} + \sum_{j=2}^{\infty} \mathcal{R}^{(j)} \\ &= \mathcal{R}^{(1)} + \mathcal{R}^{[1,\infty]} \end{split}$$
(3.34)

The CO rate expression then becomes

$$-R_{CO} = \left(t_P^{(1)} + p\right) \mathcal{R}^{(1)} + p\mathcal{R}^{[1,\infty]}$$
(3.35)

Water and carbon monoxide generation rates are directly connected since these are the only considered species that contain oxygen

$$R_{H_2O} = -R_{CO} (3.36)$$

The formation rate of hydrogen is related to the rate of the products in the following way:

$$R_{H_2} = -\sum_{j=1}^{\infty} \left[(j+1) R_P^{(j)} + j R_O^{(j)} \right] - R_{H_2O}, \qquad R_{H_2O} = R_{CO}$$
$$= -\sum_{j=1}^{\infty} R_P^{(j)} - \sum_{j=1}^{\infty} j \left(R_P^{(j)} + R_O^{(j)} \right) + R_{CO}, \qquad \sum_{j=1}^{\infty} j \left(R_P^{(j)} + R_O^{(j)} \right) = -R_{CO}$$
(3.37)
$$= -R_P^{[1,\infty]} + 2R_{CO}$$

3.A.6 Infinite series

With the previous results it is possible to determine the value of the infinite series that appear on the mass balances. To do so, it is best to start by calculating the first series on $R^{(i)}$:

$$\begin{array}{ll} \text{Define the infinite series} \qquad & \mathcal{R}^{[K,\infty]} = \sum_{j=K}^{j=\infty} \mathcal{R}^{(j)} \\ \\ \text{Substitute the expression} \\ \text{for } \mathcal{R}^{(j)} \qquad & \mathcal{R}^{[K,\infty]} = \frac{\mathcal{R}^{(K-1)}}{\alpha^{K-1}} \sum_{j=K}^{j=\infty} \alpha^{j} + \beta \sum_{j=K}^{j=\infty} \left[\alpha^{j} \sum_{k=K}^{k=j} \left(\frac{e^{c}}{\alpha} \right)^{k} y_{0}^{(k)} \right] \\ \\ \text{Reverse the summation} \\ \text{order on the term on the} \\ \text{right (see Appendix 1)} \qquad & \mathcal{R}^{[K,\infty]} = \frac{\mathcal{R}^{(K-1)}}{\alpha^{K-1}} \sum_{j=K}^{j=\infty} \alpha^{j} + \beta \sum_{k=K}^{k=\infty} \left[\left(\frac{e^{c}}{\alpha} \right)^{k} y_{0}^{(k)} \sum_{j=K}^{j=\infty} \alpha^{j} \right] \\ \\ \\ \text{Plug in classic geometric} \\ \text{series result} \qquad & \mathcal{R}^{[K,\infty]} = \frac{\mathcal{R}^{(K-1)}}{\alpha^{K-1}} \frac{\alpha^{K}}{1-\alpha} + \beta \sum_{k=K}^{k=\infty} \left[\left(\frac{e^{c}}{\alpha} \right)^{k} y_{0}^{(k)} \frac{\alpha^{k}}{1-\alpha} \right] \\ \\ \\ \\ \\ \\ \\ \\ \text{Simplify the expression;} \\ \\ \\ \text{use the definition of } B^{[K,\infty]} \qquad & \mathcal{R}^{[K,\infty]} = \frac{\alpha \mathcal{R}^{(K-1)} + \beta B^{[K,\infty]}}{1-\alpha} \end{array}$$

With the previous result the complete series is calculated:

Decompose it in the following manner	$\mathcal{R}^{[1,\infty]} = \mathcal{R}^{(1)} + \mathcal{R}^{(2)} + \mathcal{R}^{[3,\infty]}$
Plug in the expression for $\mathcal{R}^{[K,\infty]}$	$\mathcal{R}^{[1,\infty]} = \mathcal{R}^{(1)} + \mathcal{R}^{(2)} + \frac{\alpha \mathcal{R}^{(2)} + \beta B^{[3,\infty]}}{1 - \alpha}$
Collect terms	$\mathcal{R}^{[1,\infty]} = \mathcal{R}^{(1)} + \frac{\mathcal{R}^{(2)} + \beta B^{[3,\infty]}}{1 - \alpha}$
Plug in the expression for $\mathcal{R}^{(2)}$	$\mathcal{R}^{[1,\infty]} = \mathcal{R}^{(1)} + \frac{\alpha^{(2)}\mathcal{R}^{(1)} + \beta^{(2)}e^{c2}y_0^{(2)} + \beta B^{[3,\infty]}}{1 - \alpha}$
Collect terms	$\mathcal{R}^{[1,\infty]} = \mathcal{R}^{(1)} \left(1 + \frac{\alpha^{(2)}}{1-\alpha} \right) + \frac{\beta^{(2)} e^{c2} y_0^{(2)} + \beta B^{[3,\infty]}}{1-\alpha}$

Similarly, the infinite series on ${\cal R}_P^{(i)}$ can be calculated:

Define the infinite series

Decompose it in the following manner

Substitute previously obtained results

$$R_{\mathrm{p}}^{[1,\infty]} = R_{\mathrm{p}}^{[1,N-1]} + \mathcal{R}^{[N,\infty]}$$

 $R_{\rm p}^{[1,\infty]} = R_{\rm p}^{[1,N-1]} + R_{\rm p}^{[N,\infty]}$

 $R_{\mathrm{p}}^{[i,j]} = \sum_{k=i}^{k=j} R_{\mathrm{p}}^{(k)}$

The second $R^{(i)}$ series can also be calculated:

j=∞

Define the infinite seri

order on the term on

for $\mathcal{R}^{(j)}$

result

Define the infinite series
$$\mathbb{R}_{p}^{[N,\infty]} = \sum_{j=N} j\mathcal{R}^{(j)}$$
Substitute the expression for $\mathcal{R}^{(j)}$

$$\mathbb{R}_{p}^{[N,\infty]} = \frac{\mathcal{R}^{(N-1)}}{\alpha^{N-1}} \sum_{j=N}^{j=\infty} j\alpha^{j} + \beta \sum_{j=N}^{j=\infty} \left[j\alpha^{j} \sum_{k=N}^{k=j} \left(\frac{e^{c}}{\alpha} \right)^{k} y_{0}^{(k)} \right]$$
Reverse the summation order on the term on the right (see Appendix 1)
$$\mathbb{R}_{p}^{[N,\infty]} = \frac{\mathcal{R}^{(N-1)}}{\alpha^{N-1}} \sum_{j=N}^{j=\infty} j\alpha^{j} + \beta \left[\sum_{k=N}^{k=\infty} \left(\frac{e^{c}}{\alpha} \right)^{k} y_{0}^{(k)} \left(\sum_{j=k}^{j=\infty} j\alpha^{j} \right) \right]$$
Use classic infinite series result
$$\mathbb{R}_{p}^{[N,\infty]} = \frac{\mathcal{R}^{(N-1)}}{\alpha^{N-1}} \left[\frac{\alpha^{N}(\alpha+N-\alpha N)}{(1-\alpha)^{2}} \right] + \beta \sum_{k=N}^{k=\infty} \left(\frac{e^{c}}{\alpha} \right)^{k} y_{0}^{(k)} \left[\frac{\alpha^{k}(\alpha+k-\alpha k)}{(1-\alpha)^{2}} \right]$$

The last term can be worked out:

$$\begin{array}{lll} \text{Define W} & W = \displaystyle\sum_{k=N}^{k=\infty} \left(\frac{e^c}{\alpha}\right)^k y_0^{(k)} \left[\frac{\alpha^k (\alpha + k - \alpha k)}{(1 - \alpha)^2}\right] \\ \\ \text{Simplify the} & equation & W = \displaystyle\sum_{k=N}^{k=\infty} e^{ck} y_0^{(k)} \frac{\alpha + k - \alpha k}{(1 - \alpha)^2} \\ \\ \text{Divide the} & W = \displaystyle\frac{\alpha}{(1 - \alpha)^2} \displaystyle\sum_{k=N}^{k=\infty} e^{ck} y_0^{(k)} + \displaystyle\frac{1}{1 - \alpha} \displaystyle\sum_{k=N}^{k=\infty} ke^{ck} y_0^{(k)} \\ \\ \\ \text{Identify B}^{[N,\infty]} & W = \displaystyle\frac{\alpha B^{[N,\infty]} + (1 - \alpha) \mathbb{B}^{[N,\infty]}}{(1 - \alpha)^2} \end{array}$$

Plug in the last result on the previous expression for $\mathbb{R}_P^{[N,\infty]}$ to obtain

$$\mathbb{R}_{P}^{[N,\infty]} = \frac{\alpha \left(\alpha + N - \alpha N\right) \mathcal{R}^{(N-1)} + \beta \left[\alpha B^{[N,\infty]} + (1-\alpha) \mathbb{B}^{[N,\infty]}\right]}{\left(1-\alpha\right)^{2}}$$
(3.38)

The above results allows the calculation of the olefin series:

$$\begin{array}{ll} \text{Define the infinite series} & R_{0}^{[N,\infty]} = \sum\limits_{j=N}^{j=\infty} R_{0}^{(j)} & \\ \mathbb{R}_{0}^{[N,\infty]} = \sum\limits_{j=N}^{j=\infty} j R_{0}^{(j)} \\ \\ \text{Substitute the expression} \\ \text{for } R_{0}^{(j)} & \\ R_{0}^{[N,\infty]} = t_{0} \sum\limits_{j=N}^{j=\infty} \mathcal{R}^{(j)} - \Bbbk \sum\limits_{j=N}^{j=\infty} e^{cj} y_{0}^{(j)} & \\ \mathbb{R}_{0}^{[N,\infty]} = t_{0} \sum\limits_{j=N}^{j=\infty} j \mathcal{R}^{(j)} - \Bbbk \sum\limits_{j=N}^{j=\infty} j e^{cj} y_{0}^{(j)} \\ \\ \\ \text{Identify previously} \\ \text{obtained results} & \\ R_{0}^{[N,\infty]} = t_{0} \mathcal{R}^{[N,\infty]} - \Bbbk \mathbb{B}^{[N,\infty]} & \\ \end{array} \\ \begin{array}{l} \mathbb{R}_{0}^{[N,\infty]} = t_{0} \mathbb{R}_{P}^{[N,\infty]} - \Bbbk \mathbb{B}^{[N,\infty]} \\ \\ \end{array}$$

The value of $\mathcal{R}^{(1)}$ can be obtained by using the formation rate of carbon monoxide and the results above:

$$-R_{CO} = \left(t_P^{(1)} + p\right) \mathcal{R}^{(1)} + p\mathcal{R}^{[1,\infty]}$$

$$= \mathcal{R}^{(1)} \left[t_P^{(1)} + p\left(2 + \frac{\alpha^{(2)}}{1 - \alpha}\right)\right] + \frac{p\left(\beta^{(2)}e^{c^2}y_O^{(2)} + \beta B^{[3,\infty]}\right)}{1 - \alpha}$$

$$\mathcal{R}^{(1)} = -\frac{(1 - \alpha)R_{CO} + p\left(\beta^{(2)}e^{c^2}y_O^{(2)} + \beta B^{[3,\infty]}\right)}{(1 - \alpha)t_P^{(1)} + p\left[2(1 - \alpha) + \alpha^{(2)}\right]}$$
(3.39)

3.A.7 Experimental correlations

A spinning basket reactor was used to perform the experiments with which the correlations below were developed [1,2]. The experiments were performed at a constant temperature of 523 K. The mass balance for this equipment considering zero inflow of olefin is

$$WR_O^{(i)} = \Phi \mathbb{C} y_O^{(i)} \tag{3.40}$$

The previous equation can be rearranged to yield

$$y_O^{(i)} = \frac{W}{\Phi \mathbb{C}} R_O^{(i)}$$

$$\mathbb{k} e^{ci} y_O^{(i)} = \mathbb{k}^* e^{ci} R_O^{(i)}$$

$$(3.41)$$

with the following definition being introduced

$$k^* = k \frac{W}{\Phi \mathbb{C}} \tag{3.42}$$

Plugging the above expression into the olefin formation rate and manipulating the resulting expression yields the following:

$$R_{o}^{(i)} = t_{o} \mathcal{R}^{(i)} - \Bbbk e^{ci} y_{o}^{(i)}$$

$$R_{o}^{(i)} = t_{o} \mathcal{R}^{(i)} - \Bbbk^{*} e^{ci} R_{o}^{(i)}$$

$$R_{o}^{(i)} (1 + \Bbbk^{*} e^{ci}) = t_{o} \mathcal{R}^{(i)}$$

$$\frac{R_{o}^{(i)}}{\mathcal{R}^{(i)}} = \frac{t_{o}}{1 + \Bbbk^{*} e^{ci}}$$
(3.43)

The authors used

$$k^* = k^{\dagger} \frac{W}{\Phi_0}$$

$$k^{\dagger} = 3.32 \cdot 10^{-4} \{H_2\}^{1.4} \{CO\}^{-0.49}$$
(3.44)

By combining the previous expressions it can be found that

$$\begin{aligned} &\mathbb{k} = \mathbb{k}^{\dagger} \frac{\Phi \mathbb{C}}{\Phi_0} \\ &= \mathbb{k}^{\dagger} \mathbb{C}_0 \end{aligned} \tag{3.45}$$

A few observations can be made at this point:

- From the expressions above it becomes clear that k^* is dimensionless.
- The expression for k^{\dagger} is a correlation in which the input terms are provided at specific units;
- From the olefin rate of formation it can be seen that k has the same units of the rates, given in kmol/(kg catalyst*s). If W has dimensions of kg, then $\Phi \mathbb{C}$ must have dimensions of kmol/s;
- To maintain a coherent set of units, since Φ_0 has the units of m^3/s , \mathbb{C}_0 must be given in kmol/m³.

The correlations for the FTS kinetic parameters are (with partial pressures in MPa)

$$k^{\dagger} = 3.32 \cdot 10^{-4} \{H_2\}^{1.4} \{CO\}^{-0.49}$$

$$t_o = 6.1686 \{H_2\}^{-0.5}$$

$$p = 13.8 \{H_2\}^{-0.47} \{CO\}^{0.43}$$

(3.46)

The kinetics for the FTS and WGS are represented by models FT-III3 and WGS-I5, respectively:

$$R_{FTS} = \frac{a_1 \{CO\} \{H_2\}}{(1 + a_2 \{CO\} + a_3 \{H_2O\})^2} \qquad a_1 = 0.0556 \cdot 10^{-3} \quad a_2 = 0.125 \quad a_3 = 7.00$$

$$R_{WGS} = \frac{a_4 (\{CO\} \{H_2O\} - \{CO_2\} \{H_2\}/K)}{(1 + a_5 \{CO\} + a_6 \{H_2O\})^2} \quad a_4 = 1.77 \cdot 10^{-3} \qquad a_5 = 2.10 \qquad a_6 = 24.19 \qquad (3.47)$$

$$K = 10^{(2073/T - 2.029)}$$

Partial pressures are in MPa and the reaction rates are given in kmol/(kg catalyst*s).

3.A.8 Calculation algorithm

The calculation algorithm is presented below.

Define constant value parameters

Input reactor parameters, molar masses, enthalpy correlations and kinetic parameters:

$$a_1 = 0.0556*10^{-3}$$
 $a_2 = 0.125$ $a_3 = 7.00$
 $a_4 = 1.77*10^{-3}$ $a_5 = 2.10$ $a_6 = 24.19$ $K = 10^{(2073/T - 2.029)}$ (3.48)
 $t_P^{(1)} = 6.62$ $t_P^{(2)} = 1.59$ $b = 12.58$ $c = 0.29$

Calculate terms of the ODE system

First, calculate auxiliary terms; use partial pressures in MPa

$y_i = \frac{w_i/M_i}{\sum w_j/M_j}$	$\gamma = \frac{w_{O}^{[N,\infty]} - 14Nw_{O}^{[N,\infty]}}{w_{O}^{[N,\infty]} - 14(N-1)w_{O}^{[N,\infty]}}$
$B^{[N,\infty]} = \frac{y_0^{[N,\infty]}(1-\gamma)e^{cN}}{1-e^c\gamma}$	$\mathbb{B}^{[N,\infty]} = \frac{B^{[N,\infty]}[N - e^c \gamma (N-1)]}{1 - e^c \gamma}$
$\mathbb{k} = \frac{P_0}{RT_0} a_7 P_{H_2}^{1.4} P_{CO}^{-0.49}$	$t_0 = a_8 P_{H_2}^{-0.5}$
$p = a_9 \ P_{H_2}^{-0.47} \ P_{CO}^{0.43}$	$R_{CO} = -\frac{a_1 P_{CO} P_{H_2}}{\left(1 + a_2 P_{CO} + a_3 P_{H_2O}\right)^2}$
$\alpha^{(2)} = \frac{p}{t_{\rm P}^{(2)} + p + t_0}$	$\beta^{(2)} = \frac{b \Bbbk}{t_p^{(2)} + p + t_0}$
$\alpha = \frac{p}{1 + p + t_0}$	$\beta = \frac{lk}{1 + p + t_0}$

Then, calculate molar rates of formation:

Г

$\mathcal{R}^{(1)} = -\left\{(1-\alpha)R_{CO} + p\left(\beta^{(2)}e^{c2}y_{O}^{(2)} + \beta B^{[3,\infty]}\right)\right\} / \left\{(1-\alpha)t_{P}^{(1)} + p\left[2(1-\alpha) + \alpha^{(2)}\right]\right\}$					
$\mathcal{R}^{(2)} = \alpha^{(2)} \mathcal{R}^{(1)} + \beta^{(2)} e^{c^2} y_0^{(2)}$	$R_0^{(2)} = t_0 \mathcal{R}^{(2)} - b \mathbb{k} e^{c_2} y_0^{(2)}$				
$\boldsymbol{\mathcal{R}}^{(i)} = \alpha \boldsymbol{\mathcal{R}}^{(i-1)} + \beta e^{ci} \boldsymbol{y}_0^{(i)}$	$\mathbf{R}_{0}^{(i)} = \mathbf{t}_{0} \boldsymbol{\mathcal{R}}^{(i)} - \mathbf{k} \mathbf{e}^{\mathbf{c} i} \mathbf{y}_{0}^{(i)}$				
$R_{p}^{(1)} = t_{p}^{(1)} \mathcal{R}^{(1)}$	$R_{p}^{(2)} = t_{p}^{(2)} \mathcal{R}^{(2)}$				
$\mathrm{R}_\mathrm{P}^{(\mathrm{i})} = \mathcal{R}^{(\mathrm{i})}$	$3 \le i \le N - 1$				
$R_{P}^{[N,\infty]} = \frac{\alpha \mathcal{R}^{(N-1)} + \beta B^{[N,\infty]}}{1-\alpha} \qquad \qquad \mathbb{R}_{P}^{[N,\infty]}$	$=\frac{\mathcal{R}^{(N-1)}\alpha(\alpha+N-\alpha N)+\beta[\alpha B^{[N,\infty]}+(1-\alpha)\mathbb{B}^{[N,\infty]}]}{(1-\alpha)^2}$				
$\mathbf{R}_{0}^{[\mathbf{N},\infty]} = \mathbf{t}_{0} \mathbf{R}_{\mathbf{P}}^{[\mathbf{N},\infty]} - \mathbf{k} \mathbf{B}^{[\mathbf{N},\infty]}$	$\mathbb{R}_{O}^{[N,\infty]} = t_{O} \mathbb{R}_{P}^{[N,\infty]} - \mathbb{k} \mathbb{B}^{[N,\infty]}$				
$\sum_{j=N}^{j=\infty} M_p^{(j)} R_p^{(j)} = 14 \mathbb{R}_p^{[N,\infty]} + 2 R_p^{[N,\infty]}$	$\sum_{j=N}^{j=\infty} M_0^{(j)} R_0^{(j)} = 14 \mathbb{R}_0^{[N,\infty]}$				
$R_{H_2} = -(R_P^{[1,N-1]} + R_P^{[N,\infty]}) + 2R_{CO}$	$R_{H_2O} = -R_{CO}$				

and, finally, calculate derivatives:

$$\frac{dw^{(j)}}{dz} = \frac{A\rho_c}{\dot{m}} M^{(j)} R^{(j)}$$

$$\frac{dw^{[N,\infty]}}{dz} = \frac{A\rho_c}{\dot{m}} \sum_{j=N}^{j=\infty} M^{(j)} R^{(j)}$$

$$\frac{dw^{[N,\infty]}}{dz} = \frac{A\rho_c}{\dot{m}} R^{[N,\infty]}$$
(3.49)

3.A.9 Supplementary Material on Power Series

The following presents further information on the results from the series theory used in the previous sections.

Sum order reversion

The following double sum

$$F = \sum_{j=L}^{j=\infty} \left[a_j \sum_{k=M}^{k=j} b_k \right] \quad M < L \tag{3.50}$$

can be written in the following way by changing the sum order

$$F = \sum_{k=M}^{k=L-1} \left[b_k \sum_{j=L}^{j=\infty} a_j \right] + \sum_{k=L}^{k=\infty} \left[b_k \sum_{j=k}^{j=\infty} a_j \right]$$
(3.51)

For the special case when L = M

$$F = \sum_{k=M}^{k=\infty} \left[b_k \sum_{j=k}^{j=\infty} a_j \right]$$
(3.52)

Proof: The table below gives a scheme for the terms of the double sum. The highlighted terms are the ones involved in the sum.

L + 2		a _{L+2} b _M	a _{L+2} b _{M+1}	a _{L+2} b _{M+2}	<mark></mark>	a _{L+2} b _L	a _{L+2} b _{L+1}	a _{L+2} b _{L+2}
L + 1		a _{L+1} b _M	a _{L+1} b _{M+1}	a _{L+1} b _{M+2}	<mark></mark>	a _{L+1} b _L	a _{L+1} b _{L+1}	-
L		a _L b _M	a _L b _{M+1}	a _L b _{M+2}	<mark></mark>	a _L b _L	-	-
:		:	:	:	1	:	:	:
M + 2		a _{M+2} b _M	a _{M+2} b _{M+1}	a _{M+2} b _{M+2}		-	-	-
M + 1		a _{M+1} b _M	$a_{M+1}b_{M+1}$	_		-	-	-
М		a _M b _M	_	_		_	-	-
j↑	k →	М	M + 1	M + 2		L	L + 1	L + 2

The sum of the terms of line j is given by

$$\mathcal{L}_j = a_j \sum_{k=M}^{k=j} b_k \tag{3.53}$$

The sum of all the lines gives back the original series

$$F = \sum_{j=L}^{j=\infty} \mathcal{L}_j = \sum_{j=L}^{j=\infty} \left[a_j \sum_{k=M}^{k=j} b_k \right]$$
(3.54)

The sum of the terms of column k is given by

$$C_{k} = b_{k} \sum_{\substack{j=L\\ j=\infty}}^{j=\infty} a_{j} \quad k \le L$$

$$C_{k} = b_{k} \sum_{\substack{j=k\\ j=k}}^{j=\infty} a_{j} \quad k > L$$
(3.55)

The sum of all the columns gives back the original series

$$F = \sum_{k=M}^{k=\infty} C_k = \sum_{k=M}^{k=L-1} C_k + \sum_{k=M}^{k=\infty} C_k$$
$$= \sum_{k=M}^{k=L-1} \left[b_k \sum_{j=L}^{j=\infty} a_j \right] + \sum_{k=L}^{k=\infty} \left[b_k \sum_{j=k}^{j=\infty} a_j \right]$$
(3.56)

For the special case when L = M the first double sum on the equation above disappears, yielding Equation 3.52.

Geometric series

The closed form solution of the geometric series is presented. Let the sum of its first j terms be

$$r_j = \sum_{k=1}^{k=j} \alpha^{k-1} = 1 + \sum_{k=2}^{k=j} \alpha^{k-1} = 1 + \sum_{k=1}^{k=j-1} \alpha^k$$
(3.57)

Multiply by α the above equation and rearrange the result to find a closed form expression for r_j :

$$\alpha r_j = \sum_{k=1}^{k=j} \alpha^k = \sum_{k=1}^{k=j-1} \alpha^k + \alpha^j$$

$$r_j - \alpha r_j = 1 - \alpha^j$$

$$r_j = \frac{1 - \alpha^j}{1 - \alpha}$$
(3.58)

The sum of elements i to j of the preceding series can now be calculated as

$$R_{[i,j]} = \sum_{k=i}^{k=j} \alpha^{k-1} = r_j - r_{i-1} = \frac{\alpha^{i-1} - \alpha^j}{1 - \alpha}$$
(3.59)

For $|\alpha| < 1$

$$R_{[i,\infty]} = \frac{\alpha^{i-1}}{1-\alpha} \tag{3.60}$$

'Gabriel's staircase' series

The closed form solution of the 'Gabriel's staircase' series is presented. Let the sum of its first j terms be

$$s_j = \sum_{k=1}^{k=j} k \alpha^{k-1} = 1 + \sum_{k=2}^{k=j} k \alpha^{k-1} = 1 + \sum_{k=1}^{k=j-1} (k+1) \alpha^k$$
(3.61)

Multiply by α the above equation and rearrange the result to find a closed form expression for s_j

$$\alpha s_{j} = \sum_{k=1}^{k=j} k \alpha^{k} = \sum_{k=1}^{k=j-1} k \alpha^{k} + j \alpha^{j}$$

$$s_{j} - \alpha s_{j} = 1 + \sum_{k=1}^{k=j-1} (k+1)\alpha^{k} - \sum_{k=1}^{k=j-1} k \alpha^{k} - j \alpha^{j}$$

$$(1-\alpha)s_{j} = 1 + \sum_{k=1}^{k=j-1} \alpha^{k} - j \alpha^{j} = 1 + \frac{\alpha - \alpha^{j}}{1 - \alpha} - j \alpha^{j}$$

$$s_{j} = \frac{1}{1 - \alpha} \left(\frac{1 - \alpha^{j}}{1 - \alpha} - j \alpha^{j} \right)$$
(3.62)

The sum of elements i to j of the preceding series can now be calculated as

$$S_{[i,j]} = \sum_{k=i}^{k=j} k\alpha^{k-1} = s_j - s_{i-1} = \frac{1}{1-\alpha} \left(\frac{\alpha^{i-1} - \alpha^j}{1-\alpha} + (i-1)\alpha^{i-1} - j\alpha^j \right)$$
(3.63)

For $|\alpha| < 1$

$$S_{[i,\infty]} = \frac{\alpha^{i-1}[i-\alpha(i-1)]}{(1-\alpha)^2} = \frac{R_{[i,\infty]}[i-\alpha(i-1)]}{1-\alpha}$$
(3.64)

3.B MATLAB Codes

This section presents the MATLAB codes used to transfer data between Excel and HYSYS spreadsheets. The operations require that both Excel and HYSYS be running at the same time. The first code is used to get a handle for a given tab inside an Excel spreadsheet. The second and third codes can be used to import/export data to HYSYS from Excel and vice-versa (respectively). For the second and third codes, each variable has 3 parameters: name, value and units.

```
function f = GetSheet(SheetName)
% Gets handle to the specified MS Excel sheet
% connecting with Excel
exServer = actxGetRunningServer( 'excel.Application');
% check each sheet in Excel to find the correct one
k = 0;
         % start the counter
tf = 0;
         % start the flag
while tf == 0
    k = k + 1;
                 % pass onto the next sheet
    f = exServer.Sheets.Item(k).name;
                                        % get its name
    tf = strcmp(SheetName,f); % check if the current is <
the correct sheet
end
f = exServer.Sheets.Item(k); % select the correct sheet
```

end

```
function Importables
% Reads values from Excel and writes them in HYSYS.
% Each variable has 3 parameters: name, value and unit.
% Get the handle to the specified MS Excel sheet
ExcelSheet = GetSheet( 'Importables');
% Set the Excel range containing the variables to be 🖌
imported. In this example, 10 variables are copied.
Importables = ExcelSheet.get( 'Range', 'A1:C10').value;
% Clear connection with Excel
delete(ExcelSheet);
% Connect with HYSYS
HyServer = actxGetRunningServer( 'hysys.Application');
% Pause the solver
HyServer.Activedocument.Solver.CanSolve = 0;
🖇 Define the subflowsheet/spreadsheet in HYSYS inside which 🖌
the data will be written.
SFS = 'MySubflowsheet';
SS = 'MySpreadsheet';
\% Define the starting line in the HYSYS spreadsheet where \checkmark
the data will be written:
StartLineHYSYS = 1;
% define number of imported variables
[NumVars,~] = size(Importables);
\% define the line indexes that will be accessed in the \checkmark
HYSYS spreadsheet
idx = StartLineHYSYS:(StartLineHYSYS + NumVars - 1);
% Get the handle for the HYSYS spreadsheet
g = HyServer.ActiveDocument.Flowsheet.Flowsheets.Item(SFS).
Operations.Item(SS);
```

```
57
```

```
% Write each variable in the HYSYS spreadsheet
for k = 1:NumVars
K = num2str(idx(k));
g.Cell(['A' K]).CellText = Importables{k,1};
g.Cell(['B' K]).CellValue = Importables{k,2};
g.Cell(['C' K]).CellText = Importables{k,3};
```

end

% Restore solver
HyServer.Activedocument.Solver.CanSolve = 1;

% Clear connection with HYSYS
delete(HyServer);

end
```
function Exportables
% Reads values from HYSYS and writes them in Excel.
% Each variable has 3 parameters: name, value and unit.
% connect with HYSYS and Excel
HyServer = actxGetRunningServer( 'hysys.Application');
ExcelSheet = GetSheet( 'Exportables');
% Define the spreadsheet/subflowsheet in HYSYS from which 
the data will exported.
SFS = 'MySubflowsheet';
SS = 'MySpreadsheet';
% HYSYS spreadsheet: define the lines with the variables to ✔
be exported.
StartLineHYSYS = 1;
EndLineHYSYS = 10;
\% Calculate number of variables and define the indexes that \checkmark
will be accessed in the HYSYS spreadsheet
NumVars = EndLineHYSYS - StartLineHYSYS + 1;
idx = StartLineHYSYS:(StartLineHYSYS + NumVars - 1);
% Prelocate an intermediary data structure to store the 
variables
Table = cell(NumVars,3);
% Excel: define the lines where the variables will be 🖌
written;
StartLineExcel = 1;
EndLineExcel = StartLineExcel + NumVars - 1;
% Get the handle for the HYSYS spreadsheet
```

```
g = HyServer.ActiveDocument.Flowsheet.Flowsheets.Item(SFS). <br/> <br/> Operations.Item(SS);
```

```
% Copy each variable from the HYSYS spreadsheet
for k = 1:NumVars
```

```
K = num2str(idx(k));
Table{k,1} = g.Cell([ 'A' K]).CellText;
Table{k,2} = g.Cell([ 'B' K]).CellValue;
Table{k,3} = g.Cell([ 'C' K]).CellText;
```

end

% Clear all the cells on the Excel sheet before writing ExcelSheet.Cells.Clear;

```
% Write range string
Rstr = ['A' num2str(StartLineExcel) ':C' num2str
(EndLineExcel)];
```

```
% Write values to Excel
ExcelSheet.get('Range', Rstr).value = Table;
```

```
% Clear connection with external programs
delete(ExcelSheet)
delete(HyServer)
```

end

Chapter 4

Biogas Beyond CHP: The HPC ('Heat Power and Chemicals') Process

Abstract

The techno-economic feasibility of three biogas utilization processes was assessed through computer simulations on commercial process simulator Aspen HYSYS: HPC (biogas to methanol), BioCH4 (biogas to biomethane) and CHP (biogas to heat & electricity). The last two processes are already used commercially with the aid of subsidy policies. The economic analysis indicates that, without these policies, none of these attain self-sustainability due to high overall manufacturing costs; the estimated minimum support cost (MSCs) were 108, 62 and 110 \in /MWh for the HPC, BioCH4 and CHP processes, respectively. The model could explain currently practised government subsidies in Italy and Germany. It was seen that the newly proposed HPC process is economically comparable to the traditional CHP process. Therefore, the HPC process is a possible alternative to biogas usage. A subsidy policy was proposed: 50, 66, 158 and 148 \in /MWh for available heat, methane, electricity and methanol (respectively). The proposed policy results in a 10% OpEx rate of return for any of the processes, thus avoiding a disparity in the production of different products.



Figure 4.1: Graphical abstract depicting the result of the techno-economic assessment.

Nomenclature

Acronym	Meaning
CHP	Combined heat and power
\mathbf{CS}	Chemical scrubbing
EY	Energy yield
GT	Gas turbine
HHV	Higher heating value
HPC	Heat, power and chemicals
LHV	Lower heating value
MF	Membrane filtration
MSC	Minimum support cost
MY	Mass yield
OpEx	Operative expenses
PCI	Present cost of investment
PSA	Pressure swing adsorption
PWS	Pressurized water scrubbing
RoR	Rate of return
ST	Steam turbine
TEA	Techno-economic assessment
VOCs	Volatile organic compounds
VS	Volatile solid
WGS	Water gas shift
YCA	Yearly capital amortization

Symbol	Description	Units
А	Equipment capacity parameter	-
\mathbf{C}	Equipment base cost	€
D_1	Methanol recovery at the distillation section	-
i	Yearly interest rate	-
K_0, K_1, K_2	Parameters for the equipment base cost correlations	-
MSC_i	Minimum support cost of product i	€/MWh
n	Number of operating years	-
O_i	(Energetic) output of product i	MWh/y
P_1	Parameter related to the operation of the PWS section	-
R_{1}, R_{2}	Parameters related to biogas inlet composition at the reforming section	-
S_{1}, S_{2}	Parameters related to syngas inlet composition at the synthesis section	-
ΔH	Enthalpy of Reaction	$\rm kJ/mol$
min, max	Subscripts related to correlation validity values	-
[i]	Square parenthesis indicate the hourly molar flow of component i	$\rm kmol/h$
δ, Δ	Variation on initial/final molar flow value	kmol/h

4.1 Introduction

In 2015, the European Union produced 181 TWh of biogas energy, mainly in Germany (92 TWh), United Kingdom (27 TWh) and Italy (22 TWh). Biogas potential is high and the production can rise up to 472 TWh by 2030, equivalent to 10% of the European Union's current natural gas consumption [29]. The growth rate is stable; from 2009 to 2015 the number of biogas plants triplicated, reaching 17376 CHP plants (Combined Heat and Power, i.e. heat and electricity production) and 459 biomethane injection plants [30].

From the numbers shown, it is clear that biogas is mainly used in Europe for electricity and heat production in CHP plants while its injection into the natural gas grid (and use as a transportation fuel, consequently) is less common. The reasons behind this disparity, among others, must be due to (i) the stricter purification treatments required for the latter case; (ii) the smaller probability of being in a zone that disposes of a gas grid with respect to a zone that is served by the electrical grid (i.e., it is easier to construct the latter network); (iii) gas prices are lower than electricity prices [32, 31]; (iv) above all, the value of the economic incentives offered in each case.

Biogas is produced by anaerobic digestion (AD) of organic materials and it is mainly constituted by methane (CH_4) and carbon dioxide (CO_2) , among other minor components $(H_2O, H_2S, \text{siloxanes}, NH_3, \text{etc})$ [91]. Its composition varies according to the adopted feedstock, seasonality and operating conditions of fermenters and plants; average values are presented in Table 4.1.

Component	Min	Max	Mean
CH_4	40	70	60
CO_2	15	60	40
H_2O	0	10	2
H_2S	0.005	2	0.7
Siloxanes	0	0.02	0.01
VOCs	0	0.6	0.3
NH_3	0	1	0.3
O_2	0	1	0.4
CO	0	0.6	0.3
N_2	0	2	0.5

Table 4.1: Biogas composition ranges; molar fraction values (in %) by Ryckebosch et al [84].

The adopted feedstock influences not only biogas composition but also the quantity of biogas that can be produced. According to the amount of volatile solids (VS, the biodegradable fraction of the feedstock, usually 70-80% of the total mass) it is possible estimate the obtainable quantity of biogas, as shown on Table 4.2.

Table 4.2: Biogas yields by feedstock [74].

Feedstock	Biogas $[Nm^3/t VS]$
Manure	200 - 500
Cultivation residues	350 - 400
Agro-industrial residues	450 - 800
Butchery organic waste	550 - 1000
Depuration sludge	250 - 350
Organic fraction of municipal waste	400 - 600
Energy crops	550 - 750

In current biogas production concepts, the organic feedstock is fed to a fermenter where specific microorganisms convert the feedstock to biogas in an anaerobic environment. Biogas is then processed according to two routes: biomethane production (henceforth denominated 'Bio CH_4 ' process) or CHP process. In the simpler CHP concept, biogas is burned to generate heat and electricity in a combined cycle; the electricity produced can be sold to the grid while the heat can be sold as district heating. For the Bio CH_4 process, biogas is purified, enhancing its methane content by removing the other components; most importantly is the removal of CO_2 from biogas, the most abundant impurity; after purification, biomethane is pressurized and sold at the gas grid. Table 4.3 presents the main standards for gas injection in the Italian gas network.

Among the main commercial processes used for the purification of biogas to biomethane are pressure swing adsorption (PSA), pressurized water scrubbing (PWS), chemical scrubbing (CS) and membrane filtration (MF) [63]. PSA is a batch process based on the different affinity that impurities have with the adsorbents (e.g. zeolites, alumina or activated carbon). It is an interesting process since it allows removing not only CO_2 , but also other chemicals like H_2S , H_2O , O_2 and N_2 . PWS is based on the difference of CO_2 and CH_4 solubility in water and is one of the most diffused technologies for biogas purification; previous work has been done on the attempt to decrease operating pressures, which is clearly an impacting factor in process cost [77]. CS involves chemical absorption, usually with amines like MDEA. The process can be done at small pressures but high temperatures are required to regenerate the amine solvent. MF is a physical process; biogas is compressed and put in contact with a membrane permeable to CO_2 , thus separating it from CH_4 . The comparison of the different upgrading technologies is reported in Table 4.4.

A scheme for the current BioCH4 concept of biogas utilization is presented in Figure 4.2 together with the accumulated carbon balance relative to the initial quantity of biogas. As a simplification, biogas

Table 4.3: Main Italian standards for supplied gas quality [90]; braces indicate molar fractions; the asterisk indicates properties measured at 1 atmosphere and $15 \,^{\circ}$ C.

Parameter	Unit	Min	Max
HHV*	MJ/m^3	35	45
Density*	$\mathrm{kg/m^{3}}$	0.68	0.98
Water dew point	$^{\circ}\mathrm{C}$	-	-5
Hydrocarbons dew point	$^{\circ}\mathrm{C}$	-	0
Temperature	$^{\circ}\mathrm{C}$	3	50
$\{O_2\}$	%	-	0.6
$\{CO_2\}$	%	-	3.0
$\{H_2\}$	%	-	0.5
$\{CO\}$	%	-	0.1

Table 4.4: Comparison of different biogas-to-biomethane upgrading technologies [41].

PSA	PWS	\mathbf{CS}	MF
Yes	No	Yes	Yes
<3	1 - 2	< 0.1	0.6 - 3
4 - 7	5 - 10	0 - 5	5 - 16
32 - 44	34 - 42	$<\!\!15$	34 - 51
-	-	110 - 160	-
No	No	Yes	No
38	55	55	11
	PSA Yes <3 4 - 7 32 - 44 - No 38	PSA PWS Yes No <3	PSA PWS CS Yes No Yes <3

is considered as a binary mixture containing only carbon dioxide and methane; its CO_2 molar fraction is 40%. After the purification step the biomethane intermediate contains only 60% of the initial carbon, if one assumes the complete separation of carbon dioxide (and its discharge into the atmosphere). At the end of the process, after grid injection, biomethane is burned by the final user; this brings the overall carbon balance to zero since all of the carbon initially present in biogas has been released into the atmosphere. A similar scheme could be drawn for the CHP plant, where the biogas is not purified to biomethane but instead it is directly burned (in situ) to produce heat and electricity.



Figure 4.2: Schematic representation of the current BioCH4 concept of biogas utilization. On the bottom is the percentage of the carbon initially present in biogas that remains in the process intermediates / final products.

Since all of the carbon initially present on biogas was at one point absorbed from the atmosphere as CO_2 , its reemission means that current biogas exploitation models are zero-impact processes (in terms

of carbon emissions). Therefore, even if its economic sustainability depends on incentives [71], biogas contributes significantly to the achievement of European standards on renewable energies.

4.1.1 The HPC Concept

In the HPC concept, biogas is converted into liquid, high-value chemicals. Inserted after the traditional operations in existing biogas plants, the HPC concept is characterized by (i) a reforming section; (ii) a synthesis section; and (iii) a purification section to upgrade the final product to the market specifications. The reforming section consists of a catalytic reformer that allows transforming the biogas in syngas (a mixture of CO and H_2). This section requires medium pressures and temperatures around 900 °C. Biogas reforming is an endothermic operation and requires relevant heat to proceed; energy integration of the whole plant is essential for the successful realization of the concept, as it will be shown.

Main chemicals that can be obtained in the HPC concept are partially oxidized organic molecules such as methanol, dimethyl ether and acetic acid; indeed, it is possible to synthesize every type of organic molecule starting from syngas through well-known procedures, including aldehydes, superior alcohols, ethers, acids, long-chain hydrocarbons (through Fischer-Tropsch synthesis) and other chemicals [86]. This new concept could involve many industrial sectors due to the potential of syngas.

Downstream the synthesis section is the purification section (unnecessary only if chemicals can be produced at market specifications). Whenever purification is performed, the separated byproducts are either recycled back upstream to the reforming section or burned for energy generation, thus promoting effective process integration.

A scheme for such concept is presented in Figure 4.3 together with the accumulated carbon balance relative to the initial quantity of biogas. Negative carbon balance is observed for the process since carbon is retained in the chemical structure of the produced liquid chemicals. Methanol, the main product investigated in this work, is an important component in the production of polymers and textile fibers, i.e., a process which provides a mid to long-term sequestration of CO_2 . The number reported on Figure 2 (41%) is the result found in this work if the corresponding biogas is used (i.e., CO_2 molar fraction equals 40%).

Input Fuel crops Stock farming Organic waste Organic	Anaerobic digestion Biogas: 60% CH ₄ 40% CO ₂ (molar)	Purification	Downstream processes Heat Electricity Chemicals (MeOH)
100%	100%	60%	41%

Figure 4.3: Schematic representation of the HPC concept. On the bottom is the percentage of the carbon initially present in biogas that remains in the methanol product.

The HPC concept is not entirely new: much research has been conducted on a spectrum of processes that range from being almost the same process to those that have only small similarities. Over 20 years ago, Choudhary et al [17] worked with the steam and dry reforming of methane using Ni/Ca catalysts (reactions 4.1 and 4.2, as it will be seen ahead); the use of atmospheric pressure allowed these researchers to benefit from the reforming activity of CaO, which becomes inactive if found in its carbonated or hydrated forms ($CaCO_3$ and $Ca(OH)_2$, respectively), which are the prevailing forms at the standard operating pressures of industrial reformers (between 5 and 25 bar) [64]. These authors already knew that such a reaction system could be used to produce syngas suitable for the production of methanol or Fischer-Tropsch fuels. More recently, other authors have extended the reaction system by investigating the effects of adding pure oxygen to the reforming mixture (the so called tri-reforming of methane) while also using more sophisticated catalysts; Izquierdo et al [59] researched atmospheric pressure tri-reforming for producing syngas from biogas using Ni/NiRh catalysts with either magnesia or modified alumina supports; Vita et al [98] studied the same reaction system with Ni catalysts supported on ceria oxide.

Contrarily to the established industrial practice, it seems that there is a tendency to do experimental research at atmospheric pressures. This is somewhat problematic, mostly because the methane conversion is favored in this condition, which leads to overestimation of this value. Secondly, low pressures foresee high gas volumes, which require bigger equipment (especially the reformer and the heat exchangers), thus affecting investment costs. For what concerns catalyst and reaction system complexity, while the optimum trade-off between cost and activity/stability has not yet been solved, it is clear enough that adding pure oxygen to the reaction system brings additional logistic / capital costs to a specific plant.

Given the above scenario, it is reasonable to think that a near term solution for biogas reforming should lay somewhat close to the traditional methane reforming, with high pressures, the cheapest stable catalyst and no added oxygen. In this work, a TEA of such a process is performed using computer simulation, as many other authors have also produced TEAs of HPC processes. Unfortunately, most of these works are incomplete (or even wrong) and the TEAs they present is insufficient, as it will be shown ahead.

Abdelaziz et al [1] simulated the production of methanol by reducing CO_2 with hydrogen; while the first reactant was obtained from a power plant flue gas stream, the second came from a chlor-alkali plant. The economic analysis was somewhat dubious: no cost was attributed to hydrogen, the proposed concept was not confronted with an alternative (competing) process and equipment and process cost estimation is unrealistic (payback times were around 1 year, with 70% net profit of the present-value investment). In this work, the newly proposed HPC concept (methanol from biogas) is confronted with the already established BioCH4 and CHP processes. We shall demonstrate that, while none of the three processes is economically sustainable, the new process (HPC) possesses a cost that is between that of the CHP (higher) and that of the BioCH4 process (smaller).

Gopaul & Dutta [42] worked on three different biogas dry reforming concepts with varying degrees of complexity and energy self-sufficiency. For the more complex designs, energy was provided either by adding pure oxygen or by separating hydrogen from biogas and burning it (with pure oxygen). Through a sensitivity analysis, an optimal set of operating conditions was defined for each process. The unresolved issue is that, with no economic evaluation whatsoever (or any other means of comparing process performance), it is impossible to rank the different processes.

Gangadharan et al [40] compared two processes for producing syngas from natural gas: (1) steam reforming and (2) a combination of steam and dry reforming. The economic analysis is chaotic; even though capital costs are estimated, the economic analysis does not consider final manufacturing costs (i.e. the unitary cost of syngas), and a final comparison between process performances is left for the reader as an exercise. It must be emphasized, however, that the reformers were priced as packed distillation towers.

For this work, methanol was the considered chemical for the HPC concept. Methanol is one of the most important building blocks of the chemical industry with an annual production of 90 million tons [70]. It is used for the synthesis of several chemicals (MTBE, DME, acetic acid) and end-use products like plastic resins, gasoline additives, olefins, solvents and fuels. Methanol is mainly produced from fossil fuels using process like steam reforming, non-catalytic POX and coal gasification [52].

Santos et al [87] simulated and optimized the methanol production from syngas obtained through dry reforming of different biogas sources; oddly enough, no attention was given to the energy (heat and electricity) requirements of the optimal process. For the production scheme proposed in this work, biogas reforming and methanol synthesis consume approximately 40% of the initial LHV energy input (which is transformed in heat); discounting available heat, the process energy yield is approximately 60%, which means that these two operations are responsible for practically all of the energy loss in the process.

Hernandez & Martin worked on the simulation and optimization of biogas conversion to methanol [49] and Fischer-Tropsch fuels [50]. Despite being one of the most sophisticated TEAs of a such HPC process, the authors still committed gross mistakes: (1) the economic optimization is uncoupled from the final economic assessment, which leads to suboptimal solutions; (2) electricity generation is not considered; the surplus heat dissipated with cooling utilities becomes a cost (3) the reformers are priced as fired heaters, synthesis reactors are not priced at all; among others.

In this work, the HPC concept is compared to the already existing biogas utilization models; the general process scheme is reported in Figure 4.4; in the traditional CHP plant, biogas is sent to a power generation section where it is burned in a combined cycle (gas turbine + steam turbine) for heat and electricity production. In the henceforth denominated 'BioCH4' process, biogas is purified (in this work with PWS), to obtain biomethane. In the proposed HPC process, the PWS section is slightly modified in order to produce two streams; the first stream is rich in methane while the second is rich in CO_2 . In the reforming section, part of the methane stream reacts with a fraction of the CO_2 stream to produce syngas

while the remainder of the methane stream is burned to provide process heat. In the synthesis section, syngas reaction produces a raw methanol stream (methanol, water and dissolved gases) and a stream of purge gases (unreacted syngas plus inerts); the raw methanol stream is processed in a distillation column to produce a high-purity, liquid-methanol stream and a gaseous, methanol-rich stream ('Off gas' on Figure 4.4). Lastly, heat and electricity are produced by burning a fuel stream that combines purge gases from the synthesis section with off gases from the distillation in a power generation section, just like in the CHP process. This chapter is based on the article submitted to the Energy journal, which is currently under revision (October 2019).



Figure 4.4: Scheme of the investigated biogas utilization concepts.

4.2 Methodology

The processes were studied through computer simulations on commercial process simulator Aspen HYSYS. As a simplification, biogas was considered a binary mixture containing only carbon dioxide and methane $(CO_2 \text{ molar fraction was } 40\%)$. Biogas input was equal to 1 MW (in terms of LHV), which equals 204 kg/h if 365 work days per year are considered. The simulation flowsheet is reported in Figure 4.5 with the pertinent sections that were previously introduced together with Figure 4.4. The first lane on the top of Figure 4.5 refers to the CHP process; the second lane pertains to the BioCH4 process (a post compression section is seen after the PWS section); the bottom lane belongs to the assessment realized on the HPC process. In the next sections, some information is given on the design and modeling strategies of each of the subsections (PWS, reforming, synthesis, etc), while a complete description is given on the Supplementary Material. For the sake of brevity, the details on the post compression section are left for the Supplementary Material.

The same criteria seen in the previous chapter are used to quantify process mass and energy yields (MY and EY, introduced in Section 3.2). As a last remark on Figure 4.5, when multiple streams leave a process section, they are summed to determine the EY, i.e.(1) the two streams after the PWS section; i.e.(2) the streams 'raw MeOH' and 'Purge gases' after the synthesis section; i.e.(3) the streams 'Fuel' and 'MeOH' after the distillation section.

4.2.1 Pressurized Water Scrubbing (PWS)

The PWS section was modeled in close relationship to the paper by Rotunno et al [83]; the HYSYS flowsheet of the section is seen on Figure 4.6. Biogas enters the scrubbing tower after being pressurized together with a recycled stream containing residual methane (stream 'CO2*'). The amount of water



Figure 4.5: Aspen HYSYS flowsheet of the investigated biogas utilization concepts; the top, middle and bottom lane represent the CHP, BioCH4 and the HPC processes, respectively.

entering the scrubber tower is such that the carbon dioxide molar fraction of the outlet gas stream ('CH4') is 2%. The liquid stream containing carbon dioxide (stream '4') is regenerated, first by depressurization, which allows recovery (and recycling) of residual methane (stream 'CO2') and, in a second step, by stripping of the dissolved gases by contact with air (in the 'Stripper' column). Figure 4.6 represents the scheme used for the BioCH4 process; for the HPC process a similar configuration is used, except that the stream 'CO2' is not recycled but directed to the reforming step. The Peng-Robinson equation of state is used, together with the NRTL activity model (internal simulator parameters are used for these two models); the estimated stage efficiency was 15%.

Two important parameters are now presented concerning the operation of the PWS section. The first of these is the water make-up, i.e., the mass flow value of water that must be added to the system due to water evaporation at the columns; this parameter is related with process OpEx. The second, hereafter known as P_1 , is the ratio between the mass flow values of water in the liquid stream entering the scrubber column (stream '8*') and the amount of CO_2 in the 'Biogas' stream; bigger values of this parameter indicate that bigger equipment is required, which impacts the YCA.



Figure 4.6: HYSYS flowsheet of the PWS section for the BioCH4 process; the gas recycle (stream 'CO2*') is absent in the HPC concept (further details on the Supplementary Material).

4.2.2 Methane Reforming

Methane reforming is a process that produces syngas (a mixture of H_2 and CO) by reacting methane with water and/or carbon dioxide in the presence of a metallic catalyst (usually nickel supported on aluminum or magnesium oxide). Since it is an endothermic process, heat must be provided to the system, usually by burning part of the methane available at the process; it is usually performed at elevated temperatures

 $(750 - 950 \,^{\circ}\text{C})$ and pressures (5 - 25 bar) [64]. In a steam reforming furnace, the reacting mixture flows through tubes that contain the catalyst; on the outside of the tubes (inside the furnace) methane is burned with air, thus heating the tubes and enabling the reforming reactions to proceed. The main reactions involved in the process are reported on Table 4.5. It is interesting to notice that only two of these reactions are independent.

Table 4.5: Reforming section reactions [39]; *: $kJ/(mol CO_2)$, in the last reaction.

Reaction	Stoichiometry	$\Delta H_{298K} \ (\text{kJ/mol} \ CH_4)^*$	Reaction number
Steam reforming Dry reforming	$CH_4 + H_2O \longleftrightarrow 3H_2 + CO$ $CH_4 + CO_2 \longleftrightarrow 2H_2 + 2CO$	$\frac{206}{247}$	(4.1) (4.2)
Water-gas shift	$CO_2 + H_2 \longleftrightarrow CO + H_2O$	41	(4.3)

The simultaneous occurrence of Reactions 4.1 and 4.2 helps overcoming the difficulties of singlereaction systems; the presence of water steam avoids the deactivation by coke formation while the presence of CO_2 incorporates carbon to the process. By using square parenthesis to indicate molar flows, two important parameters were used to characterize the composition of the reforming inlet stream:

$$R_1 = \frac{[H_2O]}{[CH_4]} \qquad R_2 = \frac{[CO_2]}{[CH_4]} \tag{4.4}$$

It will be seen that these parameters determine outlet syngas yield and composition. For Reaction 4.1 the H_2/CO ratio of the products equals 3; for Reaction 4.2 it equals 1; this suggests that, by using appropriate values of R_1 and R_2 , the H_2/CO ratio in the reformed gas could somehow be adjusted to meet the requirements of the downstream application.



Figure 4.7: HYSYS flowsheet of the methane reforming process

The HYSYS flowsheet for the reforming step is reported in Figure 4.7. The methane- and carbon dioxide-rich streams from the PWS enter this section; a fraction of these is mixed with high temperature steam (stream '4') to react in the reformer and produce syngas. The high temperature steam is provided at the same conditions of the hot steam produced at the Rankine cycle of the power generation section (to be seen in the next sections). Since the reforming reactions are highly endothermic, heat is provided to the process by burning the remaining part of the methane stream. Therefore, the methane splitting was such that the heat provided by the furnace (stream 'h4') equaled the heat required in the tube side (stream 'h3'). The furnace gases exit the equipment at 1000 °C; as a consequence, the heat represented by stream 'h4' was donated at temperatures above this value. The furnace gases are then cooled down to allow for the computation of the sensible heat that can be recovered from this stream when pinch analysis is used; this will be explained in the power generation section. It is interesting to notice that the proposed configuration for the reforming section allows tuning the tube-side inlet composition. This enabled optimizing the operation of this processing step through a sensitivity analysis, thus maximizing the profits. Tube-side composition after reforming is calculated using chemical equilibrium through minimization of Gibbs energy. This was calculated using the polynomials provided by Burcat & Ruscic [13] (a.k.a. 'the NASA polynomials'). The SRK equations of state are used with the default binary

coefficients from the simulator. Pressure and temperature were set to 5 bar and 900 $^{\circ}$ C, as in the typical range of reforming operations [64].

4.2.3 Methanol Synthesis

This section was simulated using the kinetic model proposed by Graaf et al [43], previously introduced in Section 3.2.6. By using square parenthesis to indicate molar flows, two important parameters were used to characterize the composition of the inlet syngas stream:

$$S_1 = \frac{[H_2]}{[CO]} \qquad S_2 = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]}$$
(4.5)

It will be seen that these parameters determine outlet methanol yield. These parameters can be associated to Reactions 3.4 and 3.5 (respectively) and are related to systems without and with CO_2 (respectively). From the stoichiometry of reaction 3.4 it is intuitive to think that the optimal value of S_1 should be near 2 for a system without CO_2 . The reasoning behind the identification of the second parameter is that, if all of the CO_2 of the system were converted to CO through reaction 3.6, the amount of H_2 (and the amount of CO) would have decreased (increased) by the initial amount of CO_2 (thus producing a system which is essentially H_2 and CO as reactants); therefore, one could think that the optimal value of S_2 should be near 2 for a system with CO_2 ; this is verified for the simulations performed in this work.

The HYSYS flowsheet of the methanol synthesis step is reported in Figure 4.8. A close resemblance is seen between this configuration and that used in Section 3.2.6, with the only difference being the type of reactor used. In this case a MTPFR is considered. Since the methanol synthesis is highly exothermic, heat control is of fundamental importance for this system. It was hypothesized that the catalyst tubes are cooled by an external water cooled jacket at 200 °C (a configuration similar to the Lurgi reactors). Therefore, as the reaction heat evaporates the water, temperature control is attained while simultaneously producing steam which can be used to provide heating for other parts of the plant (the distillation section, for instance). The same considerations from Section 3.2.6 regarding heat integration and streams with an asterisk apply here.



Figure 4.8: HYSYS flowsheet of the methanol synthesis step.

4.2.4 Distillation

Methanol distillation is performed on a 80-stage column with reboiler and condenser; the HYSYS flowsheet of the methanol synthesis step is reported in Figure 4.9. A liquid water stream exits from the bottom of the equipment (its methanol concentration was specified as 0) while high-purity liquid methanol is recovered on the condenser (99.85% mass fraction). A gaseous stream also exits the condenser: it contains dissolved gases from the entering 'raw MeOH' stream (mostly CO_2) but it is also rich in methanol. One operative parameter of this section influences the economic feasibility of the process and was object of study: the fraction of methanol that is recovered in the final product; this parameter was identified as D_1 .



Figure 4.9: HYSYS flowsheet of methanol distillation.

4.2.5 Power Generation

The power generation section (considered in the HPC and CHP processes) was modelled in the same way as seen in Section 3.2.9. The HYSYS flowsheet used in any case is exactly the same and is not included here for brevity reasons.

4.2.6 Economic Assessment

In this work, the innovative HPC process is compared to the traditional biogas plants, represented by the BioCH4 process and the CHP plant. The operational expenses (OpEx, i.e., the manufacturing costs) are evaluated according to the methodology presented in the book by Turton et al [94] and have already been summarized in Table 3.7. For these processes the following parameter values were considered: (m, n, i) = (1 year, 20 years, 2%); using these parameters yields $\beta = 6\%$ (see Equation 3.9).

Costs with raw materials comprise biogas production cost (for all processes) and catalysts (for the HPC process). Only the BioCH4 process consumes utilities (electricity) since it does not possess a power generation section. For the CHP plant, revenues are composed by electricity and available heat sales. For the BioCH4 process, revenues come from biomethane production. For the HPC concept, there are revenues with methanol, electricity and available heat. For the sales of available heat, only 7 (cold) months of the year are considered. The heat exchanger network PCI was considered to be worth 15% of the total PCI.

For all of the processes the operating labor cost is estimated as 40 k \in /y, correspondent to the yearly salary (plus associated costs) of one engineer; the availability (ratio between working days and total days of the year) was 95%; the considered life-time of catalysts was 1 year. Table 4.6 presents the cost (selling price) for the main consumables (products) considered in this work; biogas production cost was estimated by taking the smallest value from the work of Thran et al [92] (18 \in /MWh, correspondent to biogas produced with an input that consist of 90% cow manure and 10% maize sillage) and correcting it slightly for inflation; electricity cost is that of retail electricity for industry buyers while the electricity selling price is that of the wholesale market; available heat selling price was estimated as 70% of natural gas (as a simplification) [31]; methanol selling price equals 380 \in /t [70], the conversion to MWh was calculated using the LHV (5.58 MWh/t). From the selling prices of the products one realizes that, for the same amount of energy, methanol is the most valuable product while available heat is the least valuable.

The minimum support cost (MSC, as defined in Equation 3.13) was used to quantify the processes economic self-sufficiency. This index alone is insufficient to rank the processes, since different products are being produced in each case, each product serving a different (energy) need. The MSC by product can be found by solving the following equation:

$$- \text{ net } \text{OpEx} = \sum MSC_i O_i \tag{4.6}$$

in which MSC_i is the MSC of product i (in \in/MWh) and O_i is the output of product *i* (in MWh). The calculation of these quantities is insightful in defining energy policy guidelines regarding an incentive system. For this work, the ratio between market prices and MSC of the products was preserved.

The typical rate of return on the PCI value is not so representative in this analysis; the conversion of the PCI into YEA is equivalent to considering that the initial investment is completely financed (through,

Consumables	$\mathrm{Cost}~({ { \in } })$	Basis	Reference
Biogas (production cost)	$\overline{25}$	MWh	[92]
Catalyst - reforming	2	$_{\mathrm{kg}}$	[2]
Catalyst - synthesis	5	$_{\rm kg}$	[2]
Electricity	114	MWh	[34]
Products	Selling price $({\ensuremath{\in}})$	Basis	Reference
Available heat	12	MWh	estimated
Biomethane	17	MWh	[32]
Electricity	38	MWh	[31]
Methanol	68	MWh	[70]

Table 4.6: Cost (selling prices) of consumables (products) pertinent of the process.

e.g., a bank loan). The rate of return on the OpEx (henceforth RoR OpEx) is considered since it allows for a more fair comparison between the processes:

$$RoR OpEx = -\frac{net OpEx}{OpEx}$$
(4.7)

4.3 Results and Discussion

In this section the technical assessment is presented first, followed by the economic one. The results obtained were compared to those of other authors, especially concerning the modelling of the PWS section, the modelling of the methanol synthesis section and the economic evaluation. All the mass / energy flow values have been normalized to a yearly basis, after multiplication by the plant availability value of 95%.

A sensitivity analysis was performed with key variables that were introduced in previous sections: R_1 , R_2 and D_1 . In order to make the presentation of the results more straightforward, two sets of operating conditions are defined:

- base: $(R_1, R_2, D_1) = (175\%, 30\%, 85\%)$
- optimal: $(R_1, R_2, D_1) = (175\%, 30\%, 92\%)$

Base conditions have been used for most of the performed sensitivity analysis while the optimal conditions are those that present highest calculated net OpEx for the HPC process, as it will be shown further ahead. It is worth remembering that the net OpEx is calculated in terms of revenues minus expenses. Table 4.7 presents the mass balances of the processes, showing the mass flow values of the main streams seen in Figure 4.5 and the MY for each stage and the accumulated MY ('Acc. MY'); optimal conditions are used for the HPC process. The final amount of carbon retained in the product stream of the HPC process (around 41% of the initial carbon) is less than the carbon initially present as methane (which equals 60% of the initial carbon).

Table 4.8 reproduces the same analysis seen in the previous chapter for the gasification processes (refer to Table 3.10). If all the forms of energy are considered (heat included), the stage EYs are similar for all processes while the final accumulated EY for the CHP and BioCH4 processes are bigger than for the HPC process. The EY of the synthesis step is bigger than 1 because heat and electricity (from other process sections) are added to the process. If only chemicals and electricity are considered (column 7), the BioCH4 process performs considerably better than the other two processes; for the HPC process, the reforming and the synthesis step are the ones where the biggest amount of energy is lost, coinciding with the biggest chemical transformations for such process.

Table 4.9 below summarizes the yearly amount of consumables / products calculated for each process; optimal conditions are used for the HPC process.

4.3.1 PWS

In Table 4.10 are reported main results for the PWS section; the 'CO2 recovery' entry applies only to the HPC process, where the 'CO2' stream is not recycled but separated and directed to the reforming section (see Figure 4.6 and the Supplementary Material). Due to the presence of the gas recycle, the operation of the PWS section is more energy intensive for the BioCH4 process. Almost half of the electricity produced in the HPC process is consumed at this section (no electricity is produced in the BioCH4 process). The

Process	Stream	Mass flow (kg/h)	Stage MY (%)	Acc. MY (%)	Carbon Balance (%)
HPC	Biogas*	204	-	100	100
HPC	$CH4^* + CO2$	161	79	79	87
HPC	Syngas	127	79	63	46
HPC	raw MeOH	119	94	59	45
HPC	MeOH	97	82	48	41
BioCH4 BioCH4	Biogas BioCH4	204 76	- 37	$\begin{array}{c} 100\\ 37\end{array}$	$\begin{array}{c} 100\\ 60\end{array}$

Table 4.7: Biogas processes mass balance: mass flow values of the main streams and MY.

Table 4.8: Biogas processes energy balance: energy flow values (columns 2 to 8, values in kW) and EY; values refer to the output of each process section.

0	1	2	3	4	5	6	7	8	9	10
Process	Process	Streams	ΔQ	ΣQ	ΔE	ΣE	LHV	LHV +	Stage	Acc.
	Section	LHV					$+ \Sigma E$	$\Sigma(E+Q)$	EY $(\%)$	EY $(\%)$
HPC	Input	1000	0	0	0	0	1000	1000	-	100
HPC	PWS	999	8	8	-43	-43	956	964	96	96
HPC	Reforming	745	196	205	-3	-46	699	904	94	90
HPC	Synthesis	634	155	360	-34	-80	553	913	101	91
HPC	Distillation	634	-61	299	0	-80	553	852	93	85
HPC	Power Gen.	538	-9	290	102	22	560	850	100	85
BioCH4	Input	1000	0	0	0	0	1000	1000	-	100
BioCH4	PWS	987	8	8	-45	-45	942	950	95	95
BioCH4	\mathbf{PC}	987	8	17	-13	-58	929	946	100	95
CHP	Input	1000	0	0	0	0	1000	1000	-	100
CHP	Power Gen.	0	416	416	533	533	533	948	95	95

Table 4.9: Yearly amount of consumables/products for biogas processes.

Consumable	Unit	HPC	BioCH4	CHP
Biogas	MWh	8760	8760	8760
Catalyst - reforming	kg	1821	0	0
Catalyst - synthesis	kg	277	0	0
Electricity	MWh	0	507	0
Product	Unit	HPC	BioCH4	CHP
Available heat	MWh	1561	90	2235
Biomethane	MWh	0	8645	0
Electricity	MWh	190	0	4667
Methanol	MWh	4713	0	0

results obtained compare favorably with the values seen in Table 4.4 and with those of Rotunno et al, who also reported 42 kWh / LHV MWh biogas [83].

4.3.2 Reforming Section

A sensitivity analysis was performed on the composition of the inlet reforming stream, i.e., parameters R_1 and R_2 . The results are shown on the graphs of Figure 4.10, where the contour lines of functions of such parameters are plotted. Figure 4.10(A) shows the amount of methane that is sent for reforming; it can be seen that as the amount of reactants increase (by an increase in R_1 or R_2), the amount of methane diverted to the reformer lowers progressively, due to the bigger amount of heat that needs to be provided for the exothermic reactions (by burning part of the methane). Figure 4.10(B) shows that, by increasing reactants concentrations, the conversion of methane increases (as expected). The effect related to Figure 4.10(A) contributes to decrease the MY of the reforming section while that of Figure 4.10(B) contributes

Table 4.10: Operative parameters for the PWS section.

Parameter	Unit	Value - HPC	Value - BioCH4
Water makeup	kg/h	40	38
P_1	%	179	206
'CH4' stream - CH_4 recovery	%	95	99
'CO2' stream - CO_2 recovery	%	63	-
Electricity consumption	kWh / kg biogas	0.21	0.22
Electricity consumption	kWh / kmol biogas	5.81	6.02
Electricity consumption	kWh / LHV MWh biogas	42	43
Electricity consumption	% of produced electricity	40	-
Stage MY	%	79	37
Stage EY	%	96	95

to increase the MY. At the current ranges of R_1 and R_2 it is clear from Figure 4.10(C) that the first effect is stronger while the MY can only increase with an increase in reactant concentration. The EY of the reforming step is seen of Figure 4.10(D), with the value of the index increasing (slightly) with bigger values of R_2 . Again, this behavior does not suggest the position of the maximum process net OpEx, which is obtained for $(R_1, R_2) = (30\%, 175\%)$, as it will be shown further ahead.

Parameters S_1 and S_2 are plotted in Figure 4.10(E) and Figure 4.10 (F); they are related to syngas composition. As stated previously, an increase in R_1 promotes reaction 4.1 in the direct sense and reaction 4.3 in the reverse sense, both of which contribute to increase S_1 ; a similar reasoning applies to an increase in R_2 , which promotes reactions 4.2 and 4.3, both on the direct sense, which contribute to a decrease in S_1 .

The S_2 parameter has a completely different type of dependence on R_1 and R_2 : while it is almost insensitive to the value of R_1 , it has a negative linear dependence on R_2 . This behavior is connected to the underlying thermodynamics: equilibrium constants of reactions 4.1 and 4.3 are on the order of 1000 and 1, respectively. This means reaction 4.3 governs syngas component distribution when input composition is changed while the influence of reaction 4.1 is minimal. By using the definition of S_2 the above statement on the dependency on R_1 and R_2 can be demonstrated. First, define the following quantity:

$$S_2^0 = S_2(R_1^0, R_2^0) = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]}$$
(4.8)

Let a variation of δ on the initial value of R_1 generate Δ_1 amount of reaction 4.3 on the final values of the involved mole flow values (i.e., by increasing the initial amount of water, the final equilibrium is displaced of a certain amount); considering the stoichiometry of such reaction and plugging in values on the above equation yields the following relationship for S_2 at $R_1 = R_1^0 + \delta$:

$$S_{2}(R_{1}^{0} + \delta, R_{2}^{0}) = \frac{([H_{2}] + \Delta_{1}) - ([CO_{2}] + \Delta_{1})}{([CO] - \Delta_{1}) + ([CO_{2}] + \Delta_{1})}$$

$$= \frac{[H_{2}] - [CO_{2}]}{[CO] + [CO_{2}]} = S_{2}^{0}$$
(4.9)

thus, confirming that S_2 is independent of the value of R_1 under the previously assumed hypothesis. The same can be done for R_2 , with the difference that the δ term appears on the correspondent expression, since the $[CO_2]$ term is present on the relationship for S_2 :

$$S_{2}(R_{1}^{0}, R_{2}^{0} + \delta) = \frac{([H_{2}] - \Delta_{2}) - ([CO_{2}] + \delta - \Delta_{2})}{([CO] + \Delta_{2}) + ([CO_{2}] + \delta - \Delta_{2})}$$

$$= \frac{[H_{2}] - [CO_{2}]}{[CO] + [CO_{2}] + \delta} - \frac{\delta}{[CO] + [CO_{2}] + \delta}$$

$$\approx \frac{[H_{2}] - [CO_{2}]}{[CO] + [CO_{2}]} - \frac{\delta}{[CO] + [CO_{2}]}$$

$$= S_{2}^{0} - \frac{\delta}{[CO] + [CO_{2}]}$$
(4.10)

thus proving the negative linear dependence of S_2 with R_2 .



Figure 4.10: Contour lines of functions of the previously introduced parameters R_1 and R_2 : (A) fraction of inlet CH_4 that goes into the reformer; (B) CH_4 conversion in the reformer; (C) and (D): Reforming step MY and EY; (E) and (F): S_1 and S_2 of syngas.

Table 4.11 below presents a summary of the operative parameters used at the reforming section. As it will be seen further ahead, the chosen (R_1, R_2) pair maximizes the net OpEx of the HPC process; it is interesting to notice that the point that maximizes the OpEx does not coincide with the maximum of any of the functions presented. This is expected, since the OpEx results from the combination of different factors.

Parameter	Unit	Value
R_1	%	175
R_2	%	30
CH_4 in reformer	%	61
CH_4 converted	%	98
Stage MY	%	79
Stage EY	%	94
S_1	%	275
S_2	%	206
Bed volume	m^3	0.77
Catalyst mass	kg	1821

Table 4.11: Operative parameters for the reforming section.

4.3.3 Methanol Synthesis

A sensitivity analysis was performed with the inlet syngas concentration in terms of the previously introduced parameters S_1 and S_2 . The results are shown on the graphs of Figure 4.11, where the contour lines of functions of such parameters are plotted. The (S_1, S_2) pairs used to plot these functions are those obtained from the sensitivity analysis from the previous section for specific (R_1, R_2) pairs and, therefore, they do not cover completely the square shown in each graph; nevertheless, this fact does not affect the analyses here presented. On Figure 4.11(A) and Figure 4.11(B) are presented values of R_1 and R_2 , respectively. This approach is useful for it allows the determination of the (R_1, R_2) pair that produces the desired (S_1, S_2) pair. Figure 4.11(C) and (D) display the MY of the reforming section and the synthesis section (respectively).

A number of works (Refs. [49, 12], among others) cannot properly shed light in the matter of defining the optimal operative values of (S_1, S_2) for the synthesis step other than informing a broad range of values in which the process should be carried out. Other works (Refs. [6, 22], among others) inform a single value with which to work (usually with $S_2 \approx 2$), which is then vaguely identified as the 'ideal' value. The term 'ideal' probably originated as a reference to the hypothetical situation of all of the CO_2 being converted to CO through reaction 3.6 with (subsequent) complete conversion of all of the CO to methanol through reaction 3.4; the problem is that these works (Refs. [6, 22]) identify this value (erroneously) as an optimal operating point for the synthesis step.

If the MY is used as a criteria to assess the efficiency of the processing steps, it is important to understand that a number of factors give rise to the shape of the response surface in Figure 4.11(D) from the amount of inerts to the kinetic properties of the catalyst, the working pressure, temperature, recycle ratio and other system parameters. Accordingly, the location of the synthesis step MY maximum should be a function of all of these factors. Even though the maximum seen in Figure 4.11(D) is indeed located close to $S_2 = 2$ (more precisely at $S_2 = 2.15$), there is no guarantee of verifying this behavior should this step be performed in different conditions. In the second place, it is clear that the MY is also function of S_1 and that the value of S_2 alone is not enough to enforce optimality.

More important than these considerations is to acknowledge the coupling between reforming and synthesis steps. It is seen on Figure 4.11(C) and (D) that the operating optima for MY of the reforming and synthesis steps do not coincide; this is indicative that the optimal process operating point (associated to the optimal (R_1, R_2) or (S_1, S_2) pair) is the best trade-off between the efficiencies of the single stages.

Table 4.12 presents a summary of the operative parameters and performance indices of this section. It should be clear that these parameters are associated with the operating conditions from the reforming section, $(R_1, R_2) = (30\%, 175\%)$, which is the configuration that maximizes the net OpEx of the HPC process. The EY of this process step is bigger than 1 because energy is added to the process, in the form of heat and electricity produced at other process sections.

4.3.4 Distillation section

For the distillation section, a sensitivity analysis was performed in terms of the previously introduced parameter D_1 ; other simulation parameters are those of the optimal conditions; the results are shown on the graphs of Figure 4.12. On Figure 4.12(A) it can be seen that the distillation MY is controlled directly by D_1 , as one would expect from the definition of such parameter. The highest value attainable for D_1 is 93%; as one tries to increase D_1 above this value the boiler duty increases steeply, indicating that the column approaches the condition of infinite reflux. If D_1 is set to 94% the system does not converge, which means no more methanol can be recovered without lowering the purity of the product



Figure 4.11: Contour lines of functions of parameters S_1 and S_2 : (A) R_1 ; (B) R_2 ; (C) & (D) MY of the reforming and synthesis section (respectively).

Table 4.12: Operative parameters for the synthesis section.

Parameter	Unit	Value
S_1	%	275
S_2	%	206
Stage MY	%	94
Stage EY	%	101
Bed volume	m^3	0.18
Catalyst mass	kg	277

stream or changing the number of plates in the column or, in general, by adjusting the system parameters. In Figure 4.12(B) the EY of the process section is seen to change very slowly with D_1 , a consequence of the considerable amount of heat that is spent with the separation process, despite the increase in the recovered chemical energy (associated with methanol). This behavior contributes to the location of optimal OpEx value ($D_1 = 92\%$) not being the maximum attainable value of the variable ($D_1 = 93\%$). Table 4.13 presents a summary of the operative parameters and performance indexes of this section.

4.3.5 Power Generation

Figure 4.13 presents the results of the sensitivity analysis on operating parameters pertinent to the electricity generation section; non-changing parameters assume values from the base conditions: $(R_1, R_2, D_1) =$ (175%, 30%, 85%). The results shown on Figure 4.13 indicate that, the more biogas is converted to methanol and the more methanol is recovered at the distillation section, less is the amount of the (re-



Figure 4.12: Sensitivity analysis of functions of parameter D_1 : (A) Distillation MY; (B) Distillation EY; other simulation parameters are those of the base conditions.

Table 4.13: Operative parameters and performance indexes for the distillation section.

Parameter	Unit	Value
D_1	%	92
Stage MY	%	82
Stage EY	%	93
MeOH mass flow	kg/h	97
MeOH mass flow	t/y	853
Condenser duty	kW	-123
Boiler duty	kW	184
Column diameter	m	0.62

mainder) fuel streams directed to the power generation section, thus lowering the amount of electricity produced.



Figure 4.13: Sensitivity analysis of the net electricity production; non-changing parameters assume values from the base conditions: $(R_1, R_2, D_1) = (175\%, 30\%, 85\%)$.

The energy balance for the power generation section is presented on Table 4.14, detailing electricity production in the GT and ST. Rankine cycle heat input and the total available heat were determined through pinch analysis, as explained previously in Section 3.2.9.

The energy balance for the HPC process was obtained using the optimal conditions presented at the beginning of the Results & Discussion section. It is clear that the electricity production is much bigger for the CHP process, since it is the most important output of such process; this brings important consequences on the size of the equipment and on the PCI of the GT and ST, as it will be seen on the economic assessment.

		HPC		BioCH4		CHP	
Process unit	Parameter	Value (kW)	EY (%)	Value (kW)	EY (%)	Value (kW)	EY $(\%)$
GT	Inlet streams LHV	96	100	-	-	1000	100
GT	Gross electricity production	38	40	-	-	384	38
ST	Rankine cycle heat input	222	100	-	-	518	100
ST	Gross electricity production	64	29	-	-	149	29
GT + ST	Gross electricity production	102	-	0	-	533	-
_	Total available heat	290	-	17	-	416	-

Table 4.14: Energy balance for the power generation section for biogas processes.

4.3.6 Economic Assessment

Figure 4.14 presents the results of the sensitivity analysis on the net OpEx of the HPC process; nonchanging parameters assume values from the base conditions. By examination of Figure 4.14 it becomes clear that the maximum net OpEx is obtained for $(R_1, R_2, D_1) = (175\%, 30\%, 92\%)$, a.k.a., the optimal conditions. The inflexion point on Figure 4.14(B) is created due to the trade-off between methanol yield and electricity production with parameter D_1 . As D_1 increases, more methanol is recovered, at the expense of a higher boiler duty. Therefore, not only less gases are burned on the gas turbine, but also less heat is available for the steam turbine, thus reducing the electricity output. The optimal conditions are used for the HPC process in all of the following analyses.



Figure 4.14: Figure 14: Sensitivity analysis of the net OpEx of the HPC process; non-changing parameters assume values from the base conditions.

Table 4.15 details PCI information; the BioCH4 process is the most economically competitive; in terms of PCI it presents a value that is around one third of the value seen for the HPC or the CHP process (both have similar PCIs); further details on the PCI calculations are given in the Supplementary Material (Section A). In Table 4.16 the OpEx is presented; values are in $k \in /y$ with expenses being negative while income is positive. Economic sustainability is not attained for any of the processes due to the overall high manufacturing costs.

Table 4.17 shows the MSC for each process, together with corresponding values from different literature sources. Again, the BioCH4 process (for this work) is clearly the most interesting, yielding the least expensive MSC. All of the MSC presented by other authors are less conservative than the ones found in this work. The reason for such disparity lies in the use of different parameters than the ones from this work. The data extracted from these works is presented in the Supplementary material Section A),

Process	HPC	BioCH4	CHP
PWS	605	580	-
PC	-	103	-
Reforming	365	-	-
Synthesis	274	-	-
Distillation	306	-	-
Power Gen.	629	-	1923
Heat Exchangers	385	121	339
Total	2565	804	2262

Table 4.15: PCI details for biogas processes; values are in $k \in$.

Table 4.16: OpEx details for biogas processes; values are in $k \in /y$.

Process	HPC	BioCH4	CHP
Biogas	-219	-219	-219
Catalyst - reforming	-4	0	0
Catalyst - synthesis	-1	0	0
Utilities	0	-58	0
Operating labor	-40	-40	-40
Supervisory & clerical labor	-7	-7	-7
Maintenance & repairs	-154	-48	-136
Supplies	-23	-7	-20
Laboratory	-6	-6	-6
Patents	-31	-20	-29
Taxes and insurance	-82	-26	-72
Overhead	-121	-57	-110
Administration	-30	-14	-27
Distribution and selling	-115	-72	-106
Research and development	-52	-33	-48
YCA	-160	-50	-141
OpEx	-1046	-658	-962
Available heat	19	1	27
Biomethane	0	147	0
Electricity	7	0	177
Methanol	321	0	0
Net OpEx	-699	-510	-758

together with comparisons on the values of the main parameters used by these authors and those used in this work. All of these works present problematic hypothesis and, in general, manufacturing costs are too low. Among other problems, Tricase et al [93] considers unreasonably high electricity selling prices $(90 \in /MWh vs 38 \in /MWh$ in this work) while Hernandez and Martin [49] consider a production scale which is one order of magnitude bigger than the one considered here (differently from the current trend in biogas plants), with 50% of the specific costs of electricity and biogas used in this work. The consequence of underestimating the cost of production of these commodities is that these processes are economically challenged, with support policies that may not provide the proper amount of subsidy needed to promote implementation of such processes.

Table 4.17: MSC for each biogas process and comparison with data from other authors.

	HPC		BioCH	4	CHP	
Reference	This work	[49]	This work	[83]	This work	[93]
Net OpEx $(k \in /y)$	-699	-1838	-510	-207	-758	-16
Net energy output (MWh/y)	6464	40694	8229	5400	6903	438
$MSC \ (\in/MWh)$	108	45	62	40	110	36

The values predicted by the model constructed in this work are dependent on many parameters, the

values of which may eventually not correspond to the actual values not only due to poor modeling but due to their change in time for several reasons (e.g. the market price of electricity may oscillate due to variations on its availability/demand). The influence of some economic parameters on the MSC is illustrated on Figure 4.15, in which a 'star diagram' is presented for each of the processes. The MSC value is shown on the vertical axis while the horizontal axis shows the variation of the original parameter value; among the analyzed parameters are the PCI, along with the cost (selling prices) of consumables (products). As expected, the MSI is a strong function of the PCI, the biogas cost, and the selling price of the main product of each process. The BioCH4 is the least sensitive of the processes, which is indicative of a high economic resilience in case of market fluctuations. It is interesting to notice that both the HPC and the CHP processes, having electric self-sufficiency, are not influenced by the cost of this commodity.



Figure 4.15: Sensitivity analysis of the MSC for the different processes; analyzed parameters: PCI and cost/selling price of consumables/products.

A unifying support policy can be proposed, so that no process is economically superior to each other (this avoids having a disparity in the production of different products). The MSC by product is presented on Table 4.18; it is seen that the same products, when produced in different processes, have different MSCs. The fifth column presents a set of estimated support values, all of which are superior to the individual MSC in any case; the values for this support policy were estimated by simple trial and error in such a way that all of the processes have equal RoR OpEx (this is seen on the bottom part of Table 4.18, with the net OpEx values already including revenues from the support policy). In columns 7 and 8 the current governmental subsidy policies offered from Italy and Germany can be seen. The subsidy offered by both countries in terms of electricity are close to the MSC values calculated in this work; the german subsidy is considerably above, which explains the leading position of this country in European biogas energy usage. The agreement between calculated MSC and observed subsidy values is indicative of a good accuracy of the model. It is thus worth to observe that, at the current energy policy scenario, the HPC process is comparable to the CHP process (in terms of MSC). This finding supports the HPC process as a possible alternative to biogas usage.

Table 4.18: MSC by product for each process; values on the top portion of the table are in \in /MWh. The net OpEx values on the bottom part of the table already include revenues from the support policy.

Product	HPC	BioCH4	CHP	This work (proposed)	Italy (current)	Germany (current)
Available heat Biomethane Electricity Methanol	24 - 77 137	41 59 -	44 - 141 -	$50 \\ 66 \\ 158 \\ 148$	75 [83] 160 [72]	105 [58] 130 [37]
OpEx $(k \in /y)$ Net OpEx $(k \in /y)$ RoR OpEx $(\%)$	-1046 107 10	$-658 \\ 65 \\ 10$	-962 91 10			

4.4 Conclusion

In this work the techno-economic feasibility of three biogas utilization processes was assessed, two of which already used commercially (BioCH4 and CHP). The processes were studied through computer simulations on commercial process simulator Aspen HYSYS. Biogas was considered as a binary mixture, i.e., containing only carbon dioxide and methane; CO_2 molar fraction was 40%; biogas input was equal to 1 MW (in terms of LHV). A set of optimal conditions was determined for the innovative HPC process through a sensitivity analysis of the variables R_1 , R_2 and D_1 .

For the HPC process, the coupling between the reforming and synthesis section was examined, with the correct relationship being established between the reforming parameters, syngas output and methanol yield, as well as illustrating a method to analyze and choose optimal operating parameters. A long-standing point concerning the optimal operation of the synthesis section was discussed; such an optimum must be function of multiple parameters and cannot be defined singularly by the parameter S_2 . Process energetic efficiency is highly dependent of the transformations at the reaction sections. The use of new technology, such as a catalytic membrane reactors, could improve the energy yield significantly by effectively integrating the process.

The economic analysis of all of the three processes indicates that none of these attain self-sustainability due to high overall manufacturing costs. It was discovered that the BioCH4 process has the least expensive MSC ($62 \in /MWh$); the MSCs of the CHP and HPC processes are almost twice the value. The model could explain currently practised government subsidies in Italy and Germany. It was seen that the newly proposed HPC process is economically comparable to the traditional CHP process. Therefore, the HPC process is a possible alternative to biogas usage. A support policy was proposed, which results in a constant value of 10% OpEx RoR for any of the processes. This avoids a disparity in the production of different products.

The economic assessment in this work is certainly insightful in revealing the importance of the support policies on the short- and medium-term survival of such processes. Other than the obvious environmental aspect, these processes are fundamentally associated to the valorization of biomass. Process economics could be enhanced if part of the biomass were elaborated into acetic acid or any other high-valued chemical. This could be the missing elements with which to make such processes economically selfsufficient. These measures could effectively enable the establishment of a new productive model, reducing dependence on fossil imports while promoting social and economic development.

Chapter 5

General Conclusions & Future Work

Biomass conversion processes were studied from a multiscale perspective using computer simulations.

An innovative data fitting method was used to determine lignocellulosic biomass composition. The developed method represents an improvement from the previous 'triangle model', especially because it uses further experimental information in a more systematic approach to quantify biomass composition. A further extension of such model could use the LHV information to establish an additional relationship involving biomass composition. Eventually, this problem could effectively be transmuted into the data reconciliation problem. In this case, cellulose and hemicellulose compositions would also be variables in the fitting process but penalty parameters would be introduced to take into account their deviation from the experimental measurements.

An entrained flow gasifier was simulated using a detailed, phenomenological model, implemented in the GasDS program. The model displayed good accuracy for the assessments performed at steady state and compared well to experimental observations. Numerical instabilities were seen during the unsteady state operation due to the step size adjustment procedure. The component description of the model is very rich while its spatial resolution is still fairly poor. It seems that better compromise between the levels of description of the model would yield more insightful results. If the the gas-phase kinetics could be effectively shrinked, a CFD reelaboration of the model would enable the investigation of innovative aspects of biomass gasification. Among such aspects are the unsteady state operation of the gasifier, the modeling of the slag flow, the quantification of the temperature profile along the reactor walls, etc, all of which considered at the high spatial resolution of a CFD simulation.

The coproduction of heat, electricity and chemicals from second-generation biomass was assessed. Two different scale sizes were considered, with biomass lower heating value inputs of 1 and 100 MW, respectively. These scales are representative of decentralized and centralized production concepts, each of which with its own characteristic transformation pathways.

For the centralized concept, biomass gasification was considered. Two final uses for syngas were considered: production of methanol and production of Fischer-Tropsch fuels. It is clear that methanol production is the superior process, both in economic and in terms of final conversion to liquid fuels. The economics of the Fischer-Tropsch process suffers due to the low yield of the reaction in terms of high valued liquid products. It remains to be confirmed (1) whether if the correlations used are adequate to represent the FT reaction system (2) if further income could be expected if the other reaction products could be sold as high value products and (3), if the cost of upgrading FT fuels has a substantial impact on process economics. While both gasification processes are economically unfeasible without subsidies, methanol production is an interesting alternative to current biogas concepts. The MSC of this process ranges from half to one third of current biogas subsidies. This kind of technology is being tested on demonstration level in Europe and Canada and is expected to reach commercial scale on the following years. Compared to current trends, there seems to be a huge potential for cost reduction if the shift towards big scales could be accomplished (above 100 MW LHW biomass input). However, it is still unclear how big is the issue of the transportation logistics of biomass. This parameter is definitively a major driver in such a context and is to be assessed with great priority.

The decentralized utilization concept considers the anaerobic digestion of biomass for the production of biogas. Three biogas processes were assessed, two of which already used commercially (BioCH4 and CHP) and a third one (HPC) in which methanol is produced. The economic analysis of all of the three processes indicates that none of these attain self-sustainability due to high overall manufacturing costs. It was discovered that the BioCH4 process has the least expensive MSC ($62 \in /MWh$); the MSCs of the CHP and HPC processes are almost twice the value. The model could explain currently practised government subsidies in Italy and Germany. It was seen that the newly proposed HPC process is economically comparable to the traditional CHP process. Therefore, the HPC process is a possible alternative to biogas usage. A support policy was proposed, which results in a constant value of 10% OpEx RoR for any of the processes. This avoids a disparity in the production of different products.

For both processes the energy efficiency is highly dependent on the transformations at the reaction sections. The use of new technology, such as catalytic membrane reactors, could improve the energy yield significantly by effectively integrating the process. In biomass gasification, such membrane reactors could be used either for oxygen separation or as fuel cells for the production of electricity. For the biogas process, such membrane reactors could be used in the reforming section, which could increase syngas yield significantly.

The economic assessment in this work is certainly insightful in revealing the importance of the support policies on the short- and medium-term diffusion of bioenergy. Other than the obvious environmental aspect, bioenergy diffusion is fundamentally associated to the economic valorization of biomass.

Process economics could be substantially enhanced if part of the biomass were elaborated into acetic acid or other high-valued chemicals. The use of micro-scale membrane reactors could produce the same effect, not only by promoting process integration but also by considerably equipment size (and the associated costs). This could be the missing elements with which to make such a process economically self-sufficient. Such measures could effectively enable the establishment of a new productive model, reducing dependence on fossil imports while promoting social and economic development.

Appendices

Appendix A

Supplementary Material

This Material contains the following sections

- 1) Main simulation parameters
- 2) Simulation sections specifications
- 3) Economic Assessment: PCI evaluation
- 4) Data from other authors

1. Main simulation parameters

Parameter	Value
Interest rate	2.00%
Number of years	20
beta (as defined in article)	6.116%
Isentropic efficiency of compressors / turbines (%)	80
Electricity Generator efficiency	95%
Chemical Engineering Price Index - year	2017
Chemical Engineering Price Index	567.5
Availability	95%
Construction specifications were taken from Jin et al $[6]$	^{1]} 7
Running months	11.4
Cold months / Running months (%)	61.4

2. Simulation sections specifications

All the parameters here presented, when applicable, refer to optimal HPC conditions. Values in square parenthesis indicate molar fractions; components that were not considered in a process section (i.e., were not included in the component list) have their composition shown as '<hidden>'. The mass / molar flow values presented are those before averaging with the estimated plant availability, i.e., only 95% of the total days of the year.

2.1. Main flowsheet



Stream Name	[CO]	[CO2]	[H2]	[C]	[N2]	[MeOH]	[02]
Biogas 1	0.00E+00	4.00E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Biogas 2	0.00E+00	4.00E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Biogas 3	0.00E+00	4.00E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
CH4	0.00E+00	2.00E-02	0.00E+00	0.00E+00	3.68E-03	0.00E+00	2.02E-03
CH4*	0.00E+00	2.00E-02	0.00E+00	0.00E+00	3.45E-03	0.00E+00	1.91E-03
CO2	0.00E+00	8.75E-01	0.00E+00	0.00E+00	1.21E-27	0.00E+00	1.19E-22
Distillation gases	9.02E-03	1.43E-01	2.21E-02	0.00E+00	2.98E-03	7.62E-01	0.00E+00
Fuel	6.37E-02	6.63E-02	5.14E-01	0.00E+00	1.05E-02	2.28E-01	0.00E+00
High pressure CH4	0.00E+00	2.00E-02	0.00E+00	0.00E+00	3.68E-03	0.00E+00	2.02E-03
MeOH	2.30E-06	9.75E-04	1.98E-06	0.00E+00	1.48E-06	9.99E-01	0.00E+00
Purge gases	8.63E-02	3.47E-02	7.18E-01	0.00E+00	1.36E-02	6.99E-03	0.00E+00
raw MeOH	6.26E-04	1.07E-02	1.53E-03	0.00E+00	2.07E-04	8.79E-01	0.00E+00
Syngas	2.71E-01	3.46E-02	6.59E-01	0.00E+00	8.28E-04	9.21E-09	3.81E-19

2.2. PWS BioCH4

Energy	Heat
stream	Flow (kW)
c1	8.77
w1	10.28
w2	8.05
w3	4.25
wP	7.44



Parameter	Value
Scrubber - Pressure drop (kPa)	20
Stripper - Air / H2O mass ratio	0.15
Both Columns - Number of stages	40
Both Columns - Tray efficiency	15%

Stream Name	Vapor	Temperature	Pressure	Molar	Mass	Liquid	Heat	[CH4]	[H2O]
	fraction	(ºC)	(kPa)	flow	flow	Volume	Flow		
				(kmol/h)	(kg/h)	Flow (m3/h)	(kW)		
0	1	150	370	8	214	0.4208	-432	6.00E-01	0.00E+00
1	1	50	370	8	214	0.4208	-441	6.00E-01	0.00E+00
2	1	50	370	8	214	0.4208	-441	6.00E-01	0.00E+00
3	1	144	1000	8	214	0.4208	-433	6.00E-01	0.00E+00
4	0	11	1000	1382	24973	25.0616	-109836	1.87E-04	9.98E-01
5	0	11	101	1380	24881	24.9409	-109610	3.63E-06	9.99E-01
6	1	18	104	172	4967	5.7418	-10	0.00E+00	0.00E+00
7	0	11	101	1379	24836	24.8858	-109516	7.50E-114	1.00E+00
8	0	11	980	1379	24836	24.8858	-109508	7.50E-114	1.00E+00
8*	0	11	980	1379	24836	24.8858	-109508	7.50E-114	1.00E+00
Air	1	15	101	172	4967	5.7418	-14	0.00E+00	0.00E+00
Biogas 3	1	30	101	8	214	0.4208	-442	6.00E-01	0.00E+00
CH4*	1	11	980	5	76	0.2449	-104	9.73E-01	1.62E-03
CO2	1	11	101	2	93	0.1207	-226	1.11E-01	1.34E-02
Lean water	0	11	101	1376	24793	24.8434	-109329	7.51E-114	1.00E+00
Vented CO2	1	11	101	176	5054	5.8393	-291	2.86E-05	1.32E-02
Water makeup	0	15	101	2	42	0.0424	-186	0.00E+00	1.00E+00

Stream Name	[CO]	[CO2]	[H2]	[C]	[N2]	[MeOH]	[02]
0	0.00E+00	4.00E-01	0.00E+00	<hidden></hidden>	0.00E+00	<hidden></hidden>	0.00E+00
1	0.00E+00	4.00E-01	0.00E+00	<hidden></hidden>	0.00E+00	<hidden></hidden>	0.00E+00
2	0.00E+00	4.00E-01	0.00E+00	<hidden></hidden>	0.00E+00	<hidden></hidden>	0.00E+00
3	0.00E+00	4.00E-01	0.00E+00	<hidden></hidden>	0.00E+00	<hidden></hidden>	0.00E+00
4	0.00E+00	2.21E-03	0.00E+00	<hidden></hidden>	2.02E-30	<hidden></hidden>	2.01E-25
5	0.00E+00	7.66E-04	0.00E+00	<hidden></hidden>	1.74E-32	<hidden></hidden>	3.57E-27
6	0.00E+00	0.00E+00	0.00E+00	<hidden></hidden>	7.90E-01	<hidden></hidden>	2.10E-01
7	0.00E+00	2.05E-56	0.00E+00	<hidden></hidden>	1.15E-05	<hidden></hidden>	6.35E-06
8	0.00E+00	2.05E-56	0.00E+00	<hidden></hidden>	1.15E-05	<hidden></hidden>	6.35E-06
8*	0.00E+00	2.05E-56	0.00E+00	<hidden></hidden>	1.15E-05	<hidden></hidden>	6.35E-06
Air	0.00E+00	0.00E+00	0.00E+00	<hidden></hidden>	7.90E-01	<hidden></hidden>	2.10E-01
Biogas 3	0.00E+00	4.00E-01	0.00E+00	<hidden></hidden>	0.00E+00	<hidden></hidden>	0.00E+00
CH4*	0.00E+00	2.00E-02	0.00E+00	<hidden></hidden>	3.45E-03	<hidden></hidden>	1.91E-03
CO2	0.00E+00	8.75E-01	0.00E+00	<hidden></hidden>	1.21E-27	<hidden></hidden>	1.19E-22
Lean water	0.00E+00	2.06E-56	0.00E+00	<hidden></hidden>	1.15E-05	<hidden></hidden>	6.36E-06
Vented CO2	0.00E+00	6.02E-03	0.00E+00	<hidden></hidden>	7.75E-01	<hidden></hidden>	2.06E-01
Water makeup	0.00E+00	0.00E+00	0.00E+00	<hidden></hidden>	0.00E+00	<hidden></hidden>	0.00E+00

2.3. PWS HPC

Parameter	Value
Scrubber - Pressure drop (kPa)	20
Stripper - Air / H2O mass ratio	0.2
Both Columns - Number of stages	40
Both Columns - Tray efficiency	15%



Flowsheet	Energy	Heat
	stream	Flow (kW)
PWS HPC	c1	8.78
PWS HPC	w1	10.28
PWS HPC	w2	8.61
PWS HPC	w3	3.65
PWS HPC	wP	8.54

Stream Name	Vapor	Temperature	Pressure	Molar	Mass	Liquid	Heat	[CH4]	[H2O]
	fraction	(ºC)	(kPa)	flow	flow	Volume	Flow		
				(kmol/h)	(kg/h)	Flow (m3/h)	(kW)		
0	1	150	370	8	214	0.4208	-432	6.00E-01	0.00E+00
1	1	50	370	8	214	0.4208	-441	6.00E-01	0.00E+00
2	1	47	370	8	236	0.4542	-490	5.81E-01	3.14E-04
3	1	141	1000	8	236	0.4542	-481	5.81E-01	3.14E-04
4	0	13	1000	1584	28620	28.7205	-125832	1.76E-04	9.98E-01
5	0	13	370	1583	28599	28.6871	-125782	3.90E-05	9.98E-01
6	1	18	104	148	4270	4.9356	-9	0.00E+00	0.00E+00
7	0	12	101	1580	28465	28.5221	-125468	1.35E-108	1.00E+00
8	0	12	980	1580	28465	28.5221	-125459	1.35E-108	1.00E+00
8*	0	12	980	1580	28465	28.5221	-125459	1.35E-108	1.00E+00
Air	1	15	101	148	4270	4.9356	-12	0.00E+00	0.00E+00
Biogas 1	1	30	101	8	214	0.4208	-442	6.00E-01	0.00E+00
CH4	1	12	980	5	80	0.2558	-109	9.72E-01	1.80E-03
CO2	1	13	370	1	21	0.0334	-49	3.45E-01	4.25E-03
CO2*	1	13	370	1	21	0.0334	-49	3.45E-01	4.25E-03
Lean water	0	12	101	1578	28425	28.4822	-125292	1.36E-108	1.00E+00
Vented CO2	1	13	101	153	4444	5.1405	-499	4.03E-04	1.44E-02
Water makeup	0	15	101	2	40	0.0399	-175	0.00E+00	1.00E+00

Stream Name	[CO]	[CO2]	[H2]	[C]	[N2]	[MeOH]	[02]
0	0.00E+00	4.00E-01	0.00E+00	<hidden></hidden>	0.00E+00	<hidden></hidden>	0.00E+00
1	0.00E+00	4.00E-01	0.00E+00	<hidden></hidden>	0.00E+00	<hidden></hidden>	0.00E+00
2	0.00E+00	4.19E-01	0.00E+00	<hidden></hidden>	2.23E-28	<hidden></hidden>	1.15E-22
3	0.00E+00	4.19E-01	0.00E+00	<hidden></hidden>	2.23E-28	<hidden></hidden>	1.15E-22
4	0.00E+00	2.18E-03	0.00E+00	<hidden></hidden>	1.35E-30	<hidden></hidden>	7.80E-25
5	0.00E+00	1.93E-03	0.00E+00	<hidden></hidden>	1.53E-31	<hidden></hidden>	1.63E-25
6	0.00E+00	0.00E+00	0.00E+00	<hidden></hidden>	7.90E-01	<hidden></hidden>	2.10E-01
7	0.00E+00	3.45E-30	0.00E+00	<hidden></hidden>	1.11E-05	<hidden></hidden>	6.14E-06
8	0.00E+00	3.45E-30	0.00E+00	<hidden></hidden>	1.11E-05	<hidden></hidden>	6.14E-06
8*	0.00E+00	3.45E-30	0.00E+00	<hidden></hidden>	1.11E-05	<hidden></hidden>	6.14E-06
Air	0.00E+00	0.00E+00	0.00E+00	<hidden></hidden>	7.90E-01	<hidden></hidden>	2.10E-01
Biogas 1	0.00E+00	4.00E-01	0.00E+00	<hidden></hidden>	0.00E+00	<hidden></hidden>	0.00E+00
CH4	0.00E+00	2.00E-02	0.00E+00	<hidden></hidden>	3.68E-03	<hidden></hidden>	2.02E-03
CO2	0.00E+00	6.51E-01	0.00E+00	<hidden></hidden>	3.02E-27	<hidden></hidden>	1.56E-21
CO2*	0.00E+00	6.51E-01	0.00E+00	<hidden></hidden>	3.02E-27	<hidden></hidden>	1.56E-21
Lean water	0.00E+00	3.46E-30	0.00E+00	<hidden></hidden>	1.12E-05	<hidden></hidden>	6.14E-06
Vented CO2	0.00E+00	1.99E-02	0.00E+00	<hidden></hidden>	7.63E-01	<hidden></hidden>	2.03E-01
Water makeup	0.00E+00	0.00E+00	0.00E+00	<hidden></hidden>	0.00E+00	<hidden></hidden>	0.00E+00

2.4. Post compression

Flowsheet	Energy stream	Heat Flow (kW)
Post compression	c1	-5.59
Post compression	c2	-3.30
Post compression	w1	6.84
Post compression	w2	2.19



Stream Name	Vapor	Temperature	Pressure	Molar flow	Mass flow	Liquid Volume	Heat	[CH4]	[H2O]
	fraction	(ºC)	(kPa)	(kmol/h)	(kg/h)	Flow (m3/h)	Flow		
							(kW)		
1a	1	150	4315	5	80	0.2558	-102	9.72E-01	1.80E-03
1b	1	50	4315	5	80	0.2558	-108	9.72E-01	1.80E-03
1c	0	50	4315	0	0	0.0000	0	1.72E-06	1.00E+00
2a	1	97	7000	5	80	0.2558	-105	9.72E-01	1.80E-03
2c	0	40	7000	0	0	0.0000	0	8.03E-07	1.00E+00
BioCH4	1	40	7000	5	80	0.2558	-109	9.73E-01	1.36E-03
CH4	1	12	980	5	80	0.2558	-109	9.72E-01	1.80E-03

Stream Name	[CO]	[CO2]	[H2]	[C]	[N2]	[MeOH]	[02]
1a	0.00E+00	2.00E-02	0.00E+00	0.00E+00	3.68E-03	0.00E+00	2.02E-03
1b	0.00E+00	2.00E-02	0.00E+00	0.00E+00	3.68E-03	0.00E+00	2.02E-03
1c	0.00E+00	3.26E-04	0.00E+00	0.00E+00	1.33E-06	0.00E+00	6.19E-07
2a	0.00E+00	2.00E-02	0.00E+00	0.00E+00	3.68E-03	0.00E+00	2.02E-03
2c	0.00E+00	2.94E-04	0.00E+00	0.00E+00	1.18E-06	0.00E+00	4.15E-07
BioCH4	0.00E+00	2.00E-02	0.00E+00	0.00E+00	3.68E-03	0.00E+00	2.02E-03
CH4	0.00E+00	2.00E-02	0.00E+00	0.00E+00	3.68E-03	0.00E+00	2.02E-03
2.5. Reforming



Parameter	Value	Reference
Gas flow (m ³ /s)	0.0692	Calculated
Reaction time (s)	10	estimated
Void volume (m³)	0.692	-
Porosity (-)	0.4	estimated
Bed volume (m ³)	1.730	-
Catalyst apparent specific mass (kg/m ³)	950	Alibaba.com
Catalyst mass per cycle (kg)	1643	-
Cycles per year	1	estimated
Catalyst mass per year (kg)	1643	-

Stream Name	Vapor	Temperature	Pressure	Molar	Mass	Liquid	Heat	[CH4]	[H2O]
	fraction	(ºC)	(kPa)	flow	flow	Volume	Flow		
				(kmol/h)	(kg/h)	Flow (m3/h)	(kW)		
1	1	162	500	1	37	0.0480	-89	1.11E-01	1.34E-02
2	1	49	500	4	84	0.1982	-152	7.63E-01	4.51E-03
3	0	25	8000	4	64	0.0637	-281	0.00E+00	1.00E+00
4	1	500	8000	4	64	0.0637	-222	0.00E+00	1.00E+00
5	1	235	500	7	147	0.2619	-375	3.91E-01	4.89E-01
6	1	600	500	7	147	0.2619	-340	3.91E-01	4.89E-01
7	1	905	500	13	147	0.3851	-131	8.55E-03	1.00E-01
8	0	905	500	0	0	0.0000	0	8.55E-03	1.00E-01
9	0	50	500	1	18	0.0177	-78	1.13E-09	1.00E+00
10	1	50	101	19	517	0.6235	-437	0.00E+00	1.85E-01
12	0	1000	101	0	0	0.0000	0	0.00E+00	1.85E-01
Air	1	25	101	17	488	0.5640	0	0.00E+00	0.00E+00
CH4	1	11	980	5	76	0.2449	-104	9.73E-01	1.62E-03
CH4 burn	1	11	980	2	30	0.0947	-40	9.73E-01	1.62E-03
CH4 react	1	11	980	3	47	0.1502	-64	9.73E-01	1.62E-03
CO2	1	11	101	2	93	0.1207	-226	1.11E-01	1.34E-02
CO2 react	1	11	101	1	37	0.0480	-90	1.11E-01	1.34E-02
CO2 vent	1	11	101	1	56	0.0727	-136	1.11E-01	1.34E-02
Furnace gases	1	1000	101	19	517	0.6235	-250	0.00E+00	1.85E-01
H2O	0	25	101	4	64	0.0637	-281	0.00E+00	1.00E+00
Syngas	1	50	500	12	130	0.3674	-161	9.27E-03	2.50E-02

Stream Name	[CO]	[CO2]	[H2]	[C]	[N2]	[MeOH]	[02]
1	0.00E+00	8.75E-01	0.00E+00	0.00E+00	1.21E-27	0.00E+00	1.19E-22
2	0.00E+00	2.29E-01	0.00E+00	0.00E+00	2.61E-03	0.00E+00	1.44E-03
3	0.00E+00						
4	0.00E+00						
5	0.00E+00	1.17E-01	0.00E+00	0.00E+00	1.34E-03	0.00E+00	7.40E-04
6	0.00E+00	1.17E-01	0.00E+00	0.00E+00	1.34E-03	0.00E+00	7.40E-04
7	2.50E-01	3.19E-02	6.08E-01	0.00E+00	7.64E-04	1.02E-08	3.52E-19
8	2.50E-01	3.19E-02	6.08E-01	1.00E-45	7.64E-04	1.02E-08	3.52E-19
9	4.56E-06	4.15E-05	1.04E-06	0.00E+00	1.90E-08	2.16E-08	7.55E-24
10	0.00E+00	9.43E-02	0.00E+00	0.00E+00	7.15E-01	0.00E+00	5.55E-03
12	0.00E+00	9.43E-02	0.00E+00	0.00E+00	7.15E-01	0.00E+00	5.55E-03
Air	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.90E-01	0.00E+00	2.10E-01
CH4	0.00E+00	2.00E-02	0.00E+00	0.00E+00	3.45E-03	0.00E+00	1.91E-03
CH4 burn	0.00E+00	2.00E-02	0.00E+00	0.00E+00	3.45E-03	0.00E+00	1.91E-03
CH4 react	0.00E+00	2.00E-02	0.00E+00	0.00E+00	3.45E-03	0.00E+00	1.91E-03
CO2	0.00E+00	8.75E-01	0.00E+00	0.00E+00	1.21E-27	0.00E+00	1.19E-22
CO2 react	0.00E+00	8.75E-01	0.00E+00	0.00E+00	1.21E-27	0.00E+00	1.19E-22
CO2 vent	0.00E+00	8.75E-01	0.00E+00	0.00E+00	1.21E-27	0.00E+00	1.19E-22
Furnace gases	0.00E+00	9.43E-02	0.00E+00	0.00E+00	7.15E-01	0.00E+00	5.55E-03
H2O	0.00E+00						
Syngas	2.71E-01	3.46E-02	6.59E-01	0.00E+00	8.28E-04	9.21E-09	3.81E-19

2.6. MeOH Synthesis



Parameter	Value	Reference
Reactor gas flow (m3/h)	66.5	Calculated
Reaction time (s)	10	estimated
Bed volume (m³)	0.1847	-
Vessel / Bed volume ratio	3	estimated
Vessel volume (m3)	0.5541	-
Vessel H/D ratio	4	estimated
Vessel diameter (m)	0.561	-
Vessel area (m2)	0.247	-
Vessel height (m)	2.243	-
Catalyst apparent specific mass (kg/m3)	1500	Alibaba.com
Catalyst mass per cycle (kg)	277	-
Cycles per year	1	estimated
Catalyst mass per year (kg)	277	-

Stream Name	Vapor fraction	Temperature (ºC)	Pressure (kPa)	Molar flow (kmol/h)	Mass flow (kg/h)	Liquid Volume Flow (m3/h)	Heat Flow (kW)	[CH4]	[H2O]
3	1	149	5000	11	126	0.3633	-137	9.45E-03	5.83E-03
4	1	60	5000	76	661	2.5604	-761	1.20E-01	1.15E-03
5	1	240	5000	76	661	2.5604	-641	1.20E-01	1.15E-03
6	1	239	4800	69	661	2.3691	-733	1.32E-01	6.17E-03
7	1	40	4800	66	541	2.2194	-633	1.40E-01	3.24E-04
8	1	40	4800	65	535	2.1972	-627	1.40E-01	3.24E-04
9	1	44	5000	65	535	2.1972	-624	1.40E-01	3.24E-04
10	1	44	5000	65	535	2.1972	-624	1.40E-01	3.24E-04
1a	1	145	1055	12	130	0.3674	-152	9.27E-03	2.50E-02
1b	1	50	1055	12	127	0.3646	-151	9.39E-03	1.21E-02
1c	0	50	1055	0	3	0.0028	-12	2.41E-09	1.00E+00
2a	1	150	2308	12	127	0.3646	-142	9.39E-03	1.21E-02
2b	1	50	2308	11	126	0.3633	-146	9.45E-03	5.83E-03
2c	0	50	2308	0	1	0.0013	-6	5.21E-09	1.00E+00
5*	0	239	3194	3459	62314	62.4399	-257798	0.00E+00	1.00E+00
6*	0	238	3194	3459	62314	62.4399	-257890	0.00E+00	1.00E+00
Purge gases	1	40	4800	1	5	0.0222	-6	1.40E-01	3.24E-04
raw MeOH	0	40	4800	4	120	0.1498	-268	4.29E-03	1.04E-01
Syngas	1	50	500	12	130	0.3674	-161	9.27E-03	2.50E-02

Stream Name	[CO]	[CO2]	[H2]	[C]	[N2]	[MeOH]	[02]
3	2.76E-01	3.52E-02	6.72E-01	0.00E+00	8.44E-04	8.29E-09	3.89E-19
4	1.15E-01	3.48E-02	7.11E-01	0.00E+00	1.17E-02	5.94E-03	5.85E-20
5	1.15E-01	3.48E-02	7.11E-01	0.00E+00	1.17E-02	5.94E-03	5.85E-20
6	8.15E-02	3.34E-02	6.78E-01	0.00E+00	1.28E-02	5.63E-02	0.00E+00
7	8.63E-02	3.47E-02	7.18E-01	0.00E+00	1.36E-02	6.99E-03	0.00E+00
8	8.63E-02	3.47E-02	7.18E-01	0.00E+00	1.36E-02	6.99E-03	0.00E+00
9	8.63E-02	3.47E-02	7.18E-01	0.00E+00	1.36E-02	6.99E-03	0.00E+00
10	8.63E-02	3.47E-02	7.18E-01	0.00E+00	1.36E-02	6.99E-03	0.00E+00
1a	2.71E-01	3.46E-02	6.59E-01	0.00E+00	8.28E-04	9.21E-09	3.81E-19
1b	2.74E-01	3.50E-02	6.68E-01	0.00E+00	8.39E-04	8.77E-09	3.86E-19
1c	9.71E-06	8.78E-05	2.23E-06	0.00E+00	4.03E-08	4.24E-08	1.61E-23
2a	2.74E-01	3.50E-02	6.68E-01	0.00E+00	8.39E-04	8.77E-09	3.86E-19
2b	2.76E-01	3.52E-02	6.72E-01	0.00E+00	8.44E-04	8.29E-09	3.89E-19
2c	2.11E-05	1.89E-04	4.90E-06	0.00E+00	8.79E-08	8.34E-08	3.50E-23
5*	0.00E+00						
6*	0.00E+00						
Purge gases	8.63E-02	3.47E-02	7.18E-01	0.00E+00	1.36E-02	6.99E-03	0.00E+00
raw MeOH	6.26E-04	1.07E-02	1.53E-03	0.00E+00	2.07E-04	8.79E-01	0.00E+00
Syngas	2.71E-01	3.46E-02	6.59E-01	0.00E+00	8.28E-04	9.21E-09	3.81E-19

2.7. Distillation

Parameter	Value
Pressure drop (kPa)	20
Number of stages	80
Tray efficiency	60%
MeOH recovery	0.94
MeOH mass fraction	0.9985
MeOH in water stream	0.000



Stream Name	Vapor	Temperature	Pressure	Molar flow	Mass flow	Liquid Volume	Heat	[CH4]	[H2O]
	fraction	(ºC)	(kPa)	(kmol/h)	(kg/h)	Flow (m3/h)	Flow (kW)		
1	0	40	130	4	120	0.1498	-268	4.29E-03	1.04E-01
Distillation gases	1	62	110	0	9	0.0116	-16	6.11E-02	7.31E-05
MeOH	0	62	110	3	104	0.1308	-215	7.88E-05	2.10E-04
raw MeOH	0	40	4800	4	120	0.1498	-268	4.29E-03	1.04E-01
Water	0	107	130	0	7	0.0073	-32	1.59E-30	1.00E+00

Stream Name	[CO]	[CO2]	[H2]	[C]	[N2]	[MeOH]	[02]
1	6.26E-04	1.07E-02	1.53E-03	0.00E+00	2.07E-04	8.79E-01	0.00E+00
Distillation gases	9.02E-03	1.43E-01	2.21E-02	0.00E+00	2.98E-03	7.62E-01	0.00E+00
MeOH	2.30E-06	9.75E-04	1.98E-06	0.00E+00	1.48E-06	9.99E-01	0.00E+00
raw MeOH	6.26E-04	1.07E-02	1.53E-03	0.00E+00	2.07E-04	8.79E-01	0.00E+00
Water	6.75E-235	7.82E-148	9.72E-268	0.00E+00	1.78E-223	9.26E-11	0.00E+00

Flowsheet	Energy stream	Heat Flow (kW)
Distillation	c1	139
Distillation	h1	201

2.8. Power generation CHP

Parameter	Value
Air to fuel mass ratio	20.98
(Stoich air)/ (Actual air) mass ratio	2.34
Compressor P in (kPa)	101.325
Compressor P ratio	19.5
Compressor P out (kPa)	1976
Turbine/Compressor P ratio	1
Turbine inlet P (kPa)	1976
Turbine inlet T (ºC)	1371



Stream Name	Vapor	Temperature	Pressure	Molar	Mass	Liquid	Heat	[CH4]	[H2O]
	fraction	(ºC)	(kPa)	flow	flow	Volume	Flow		
				(kmol/h)	(kg/h)	Flow (m3/h)	(kW)		
1	1	486	1976	10	296	0.3425	40	0.00E+00	0.00E+00
2	0	1370	1976	0	0	0.0000	0	0.00E+00	1.01E-01
3	1	1370	1976	11	310	0.3639	18	0.00E+00	1.01E-01
4	1	632	100	11	310	0.3639	-64	0.00E+00	1.01E-01
5	1	60	100	11	310	0.3639	-120	0.00E+00	1.01E-01
6	1	500	8000	14	256	0.2560	-893	0.00E+00	1.00E+00
7	1	51	13	14	256	0.2560	-963	0.00E+00	1.00E+00
8	0	50	13	14	256	0.2560	-1120	0.00E+00	1.00E+00
9	0	50	8000	14	256	0.2560	-1120	0.00E+00	1.00E+00
Air	1	25	101	10	296	0.3425	0	0.00E+00	0.00E+00
Fuel	1	47	110	1	14	0.0338	-22	1.17E-01	2.51E-04

Stream Name	[CO]	[CO2]	[H2]	[C]	[N2]	[MeOH]	[02]
1	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.90E-01	0.00E+00	2.10E-01
2	0.00E+00	3.99E-02	0.00E+00	0.00E+00	7.36E-01	0.00E+00	1.23E-01
3	0.00E+00	3.99E-02	0.00E+00	0.00E+00	7.36E-01	0.00E+00	1.23E-01
4	0.00E+00	3.99E-02	0.00E+00	0.00E+00	7.36E-01	0.00E+00	1.23E-01
5	0.00E+00	3.99E-02	0.00E+00	0.00E+00	7.36E-01	0.00E+00	1.23E-01
6	0.00E+00						
7	0.00E+00						
8	0.00E+00						
9	0.00E+00						
Air	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.90E-01	0.00E+00	2.10E-01
Fuel	6.37E-02	6.63E-02	5.14E-01	0.00E+00	1.05E-02	2.28E-01	0.00E+00

Energy	Heat
stream	Flow (kW)
c0	56.48
c1	157.69
h1	227.00
w1	70.03
wA	40.25
wB	81.32
wP	0.72

2.9. Power generation HPC

For the sake of brevity the figure of the HYSYS scheme is not included since the only change from the 'Power generation CHP' is the name of the stream entering the stage ('Biogas 1' instead of 'Fuel').

Parameter	Value
Air to fuel mass ratio	14.2
(Stoich air)/ (Actual air) mass ratio	2.35
Compressor P in (kPa)	101.325
Compressor P ratio	19.5
Compressor P out (kPa)	1976
Turbine/Compressor P ratio	1
Turbine inlet P (kPa)	1976
Turbine inlet T (ºC)	1370

Energy	Heat
stream	Flow (kW)
c0	594.02
c1	378.59
h1	545.00
w1	168.13
wA	412.98
wB	838.52
wP	1.72

Stream Name	Vapor	Temperature	Pressure	Molar	Mass	Liquid	Heat	[CH4]	[H2O]
	fraction	(ºC)	(kPa)	flow	flow	Volume	Flow		
				(kmol/h)	(kg/h)	Flow (m3/h)	(kW)		
1	1	486	1976	105	3040	3.5144	413	0.00E+00	0.00E+00
2	0	1371	1976	0	0	0.0000	0	0.00E+00	8.34E-02
3	1	1371	1976	113	3254	3.8388	-29	0.00E+00	8.34E-02
4	1	640	100	113	3254	3.8388	-868	0.00E+00	8.34E-02
5	1	60	100	113	3254	3.8388	-1462	0.00E+00	8.34E-02
6	1	500	8000	34	613	0.6147	-2143	0.00E+00	1.00E+00
7	1	51	13	34	613	0.6147	-2311	0.00E+00	1.00E+00
8	0	50	13	34	613	0.6147	-2690	0.00E+00	1.00E+00
9	0	50	8000	34	613	0.6147	-2688	0.00E+00	1.00E+00
Air	1	25	101	105	3040	3.5144	0	0.00E+00	0.00E+00
Biogas 1	1	30	101	8	214	0.4208	-442	6.00E-01	0.00E+00

Stream Name	[CO]	[CO2]	[H2]	[C]	[N2]	[MeOH]	[02]
1	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.90E-01	0.00E+00	2.10E-01
2	0.00E+00	6.95E-02	0.00E+00	0.00E+00	7.35E-01	0.00E+00	1.12E-01
3	0.00E+00	6.95E-02	0.00E+00	0.00E+00	7.35E-01	0.00E+00	1.12E-01
4	0.00E+00	6.95E-02	0.00E+00	0.00E+00	7.35E-01	0.00E+00	1.12E-01
5	0.00E+00	6.95E-02	0.00E+00	0.00E+00	7.35E-01	0.00E+00	1.12E-01
6	0.00E+00						
7	0.00E+00						
8	0.00E+00						
9	0.00E+00						
Air	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.90E-01	0.00E+00	2.10E-01
Biogas 1	0.00E+00	4.00E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

3. Economic Assessment: PCI evaluation

The following presents information regarding the PCI evaluation for Chapter 4. the reader is referred to Turton et al [94] for further clarifications

3.1.	PWRO

Equipment	Tag	2º.ary	Value	Number	А	Α'	A_min	А	log10	K1	K2	КЗ	log10	C0
Туре		Parameter		of units	(Units)				А				C0	(USD)
Turbines (Axial	GT	-	-	1	Power	425.5	100	425.5	2.63	2.7051	1.4398	-0.1776	5.26	183146
gas turbines)					(kW)									
Turbines	ST	-	-	1	Power	168.1	100	168.1	2.23	2.2476	1.4965	-0.1618	4.78	59815
(Radial					(kW)									
gas/liquid														
expanders)														
Pump	Р	Shaft eff.	70%	1	Power	2.5	1	2.5	0.39	3.3892	0.0536	0.1538	3.43	2714
(Centrifugal)					(kW)									
Drive (Eletric -	DP*	-	-	1	Power	2.5	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084
open/drip-					(kW)									
proof)														

Total cost (k€) 1923

Tag	Р	F_P	Material	B1	B2	F_M	F_BM	C_BM	C_TM	F_BM0	C_BM0	C_GR'	C_GR
	(bar)					/ F*		(USD)			(USD)		(Scaled)
GT	-	-	CS	-	-	-	3.5	641,011	756,393	3.5	641,011	1,076,898	1,076,898
ST	-	-	CS	-	-	-	3.5	209,352	247,035	3.5	209,352	351,711	351,711
Р	80	2.23	CS	1.89	1.35	1	4.9	13,319	15,716	3.2	8,794	20,113	20,113
DP*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	10,078

3.2. HENO

Equipment Type	Tag	2º.ary Parameter	Value
HEN*	-	% of PCI is HEN	15%
Total cost (k€)	339		

3.3. PWS0

Equipment	Tag	2º.ary	Value	Number	А	Α'	A_min	А	log10	K1	K2	КЗ	log10	C0
Туре		Parameter		of units	(Units)				А				C0	(USD)
Compressor	К1	Shaft eff.	80%	1	Power	12.9	18	18.0	1.26	5.0355	-1.8002	0.8253	4.08	11918
(Rotary)					(kW)									
Compressor	К2	Shaft eff.	80%	1	Power	10.8	18	18.0	1.26	5.0355	-1.8002	0.8253	4.08	11918
(Rotary)					(kW)									
Compressor	КЗ	Shaft eff.	80%	1	Power	4.6	18	18.0	1.26	5.0355	-1.8002	0.8253	4.08	11918
(Rotary)					(kW)									
Pump	P1	Shaft eff.	70%	1	Power	12.2	1	12.2	1.09	3.3892	0.0536	0.1538	3.63	4255
(Reciprocating)					(kW)									
Drive (Eletric -	D1*	-	-	1	Power	12.9	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084
open/drip-					(kW)									
proof)														
Drive (Eletric -	D2*	-	-	1	Power	10.8	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084
open/drip-					(kW)									
proof)	-													
Drive (Eletric -	D3*	-	-	1	Power	4.6	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084
open/drip-					(kW)									
proof)														
Drive (Eletric -	DP*	-	-	1	Power	12.2	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084
open/drip-					(kW)									
proof)														
Process	Scrubber	Diameter	0.41	1	Volume	1.3	0.3	1.3	0.12	3.4974	0.4485	0.1074	3.55	3568
vessels		(m)			(m3)									
(Vertical)														
Packing	Scrubber	-	-	1	Volume	1.3	0.03	1.3	0.12	2.4493	0.9744	0.0055	2.57	368
_	.				(m3)									
Process	Stripper	Diameter	1.41	1	Volume	34.4	0.3	34.4	1.54	3.4974	0.4485	0.1074	4.44	27521
vessels		(m)			(m3)									
(Vertical)	<u>.</u>						0.00				0.0744	0.0055		
Packing	Stripper	-	-	1	Volume	34.4	0.03	34.4	1.54	2.4493	0.9744	0.0055	3.96	9098
					(m3)				1					

Tag	Р	F_P	Material	B1	B2	F_M	F_BM	C_BM	C_TM	F_BM0	C_BM0	C_GR'	C_GR
	(bar)					/ F*		(USD)			(USD)		(Scaled)
K1	-	-	CS	-	-	-	2.4	28,602	33,751	2.4	28,602	48,052	39,256
К2	-	-	CS	-	-	-	2.4	28,602	33,751	2.4	28,602	48,052	35,300
КЗ	-	-	CS	-	-	-	2.4	28,602	33,751	2.4	28,602	48,052	21,096
P1	9	1.00	CS	1.89	1.35	1	3.2	13,787	16,269	3.2	13,787	23,163	23,163
D1*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	27,180
D2*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	24,441
D3*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	14,607
DP*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	26,345
Scrubber	9	1.00	CS	2.25	1.82	1	4.1	14,524	17,138	4.1	14,524	24,400	24,400
Scrubber	-	-	Polyethylene	-	-	-	1.0	368	434	1.0	368	618	618
Stripper	0	1.00	CS	2.25	1.82	1	4.1	112,011	132,174	4.1	112,011	188,179	188,179
Stripper	-	-	Polyethylene	-	-	-	1.0	9,098	10,735	1.0	9,098	15,284	15,284

3.4. PC

Equipment	Tag	2º.ary	Value	Number	А	Α'	A_min	А	log10	K1	К2	КЗ	log10	C0
Туре		Parameter		of units	(Units)				А				C0	(USD)
Compressor	К1	Shaft eff.	80%	1	Power	8.6	18	18.0	1.26	5.0355	-1.8002	0.8253	4.08	11918
(Rotary)					(kW)									
Compressor	К2	Shaft eff.	80%	1	Power	2.7	18	18.0	1.26	5.0355	-1.8002	0.8253	4.08	11918
(Rotary)					(kW)									
Drive (Eletric -	D1*	-	-	1	Power	8.6	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084
open/drip-					(kW)									
proof)														
Drive (Eletric -	D2*	-	-	1	Power	2.7	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084
open/drip-					(kW)									
proof)														

Tag	P (bar)	F_P	Material	B1	B2	F_M	F_BM	C_BM	C_TM	F_BM0	C_BM0	C_GR'	C_GR
						/ F*		(USD)			(USD)		(Scaled)
K1	-	-	CS	-	-	-	2.4	28,602	33,751	2.4	28,602	48,052	30,745
K2	-	-	CS	-	-	-	2.4	28,602	33,751	2.4	28,602	48,052	15,516
D1*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	21,287
D2*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	10,743

3.5. HEN1

Equipment Type	Tag	2º.ary Parameter	Value
HEN*	-	% of CAPEX is HEN	15%
Total cost (k€)	121		

3.6. PWS1

Equipment	Tag	2º.ary	Value	Number	А	A'	A_min	А	log10	K1	K2	КЗ	log10	C0
Туре		Parameter		of units	(Units)				А				C0	(USD)
Compressor	K1	Shaft eff.	80%	1	Power	12.8	18	18.0	1.26	5.0355	-	0.8253	4.08	11918
(Rotary)					(kW)						1.8002			
Compressor	К2	Shaft eff.	80%	1	Power	10.1	18	18.0	1.26	5.0355	-	0.8253	4.08	11918
(Rotary)					(kW)						1.8002			
Compressor	К3	Shaft eff.	80%	1	Power	5.3	18	18.0	1.26	5.0355	-	0.8253	4.08	11918
(Rotary)					(kW)						1.8002			
Pump	P1	Shaft eff.	70%	1	Power	10.6	1	10.6	1.03	3.3892	0.0536	0.1538	3.61	4039
(Centrifugal)					(kW)									
Drive (Eletric -	D1*	-	-	1	Power	12.8	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084
open/drip-					(kW)									
proof)														
Drive (Eletric -	D2*	-	-	1	Power	10.1	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084
open/drip-					(kW)									
proof)														
Drive (Eletric -	D3*	-	-	1	Power	5.3	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084
open/drip-					(kW)									
proof)														
Drive (Eletric -	DP*	-	-	1	Power	10.6	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084
open/drip-					(kW)									
proof)														
Process	Scrubber	Diameter	0.39	1	Volume	1.2	0.3	1.2	0.08	3.4974	0.4485	0.1074	3.53	3424
vessels		(m)			(m3)									
(Vertical)														
Packing	Scrubber	-	-	1	Volume	1.2	0.03	1.2	0.08	2.4493	0.9744	0.0055	2.53	338
					(m3)									
Process	Stripper	Diameter	1.51	1	Volume	39.2	0.3	39.2	1.59	3.4974	0.4485	0.1074	4.48	30505
vessels		(m)			(m3)									
(Vertical)														
Packing	Stripper	-	-	1	Volume	39.2	0.03	39.2	1.59	2.4493	0.9744	0.0055	4.02	10362
					(m3)									

Tag	Р	F_P	Material	B1	B2	F_M	F_BM	C_BM	C_TM	F_BM0	C_BM0	C_GR'	C_GR
	(bar)					/ F*		(USD)			(USD)		(Scaled)
K1	-	-	CS	-	-	-	2.4	28,602	33,751	2.4	28,602	48,052	39,250
К2	-	-	CS	-	-	-	2.4	28,602	33,751	2.4	28,602	48,052	33,890
КЗ	-	-	CS	-	-	-	2.4	28,602	33,751	2.4	28,602	48,052	23,101
P1	9	1.00	CS	1.89	1.35	1	3.2	13,088	15,444	3.2	13,088	21,988	21,988
D1*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	27,176
D2*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	23,465
D3*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	15,995
DP*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	24,259
Scrubber	9	1.00	CS	2.25	1.82	1	4.1	13,938	16,446	4.1	13,938	23,415	23,415
Scrubber	-	-	Polyethylene	-	-	-	1.0	338	399	1.0	338	567	567
Stripper	0	1.00	CS	2.25	1.82	1	4.1	124,155	146,503	4.1	124,155	208,580	208,580
Stripper	-	-	Polyethylene	-	-	-	1.0	10,362	12,227	1.0	10,362	17,408	17,408

110

3.7. PWR1

Equipment Type	Tag	2º.ary	Value	Number	А	Α'	A_min	А	log10	K1	K2	К3	log10	C0
		Parameter		of units	(Units)				А				C0	(USD)
Turbines (Axial	GT	-	-	1	Power	41	100	100.0	2.00	2.7051	1.4398	-0.1776	4.87	74869
gas turbines)					(KW)									
Turbines (Radial gas/liquid expanders)	ST	-	-	1	Power (kW)	70	100	100.0	2.00	2.2476	1.4965	-0.1618	4.59	39210
Pump (Centrifugal)	Р	Shaft eff.	70%	1	Power (kW)	1	1	1.0	0.01	3.3892	0.0536	0.1538	3.39	2453
Drive (Eletric - open/drip-proof)	DP*	-	-	1	Power (kW)	1	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084
Total cost (k€)	618													

Tag	Р	F_P	Material	B1	B2	F_M	F_BM	C_BM	C_TM	F_BM0	C_BM0	C_GR	C_GR
	(bar)					/ F*		(USD)			(USD)		(Scaled)
GT	-	-	CS	-	-	-	3.5	262,040	309,208	3.5	262,040	440,228	258,122
ST	-	-	CS	-	-	-	3.5	137,236	161,938	3.5	137,236	230,556	186,186
Р	80	2.23	CS	1.89	1.35	1	4.9	12,039	14,206	3.2	7,949	18,181	18,181
DP*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	5,959

3.8. REF

Equipment Type	Tag	2º.ary	Value	Number	А	Α'	A_min	А	log10	K1	K2	КЗ	log10	C0
		Parameter		of units	(Units)				А				C0	(USD)
Compressor	K1	Shaft eff.	80%	1	Power	1.9	18	18.0	1.26	5.0355	-	0.8253	4.08	11918
(Rotary)					(kW)						1.8002			
Pump	Р	Shaft eff.	70%	1	Power	0.2	1	1.0	0.00	3.3892	0.0536	0.1538	3.39	2450
(Centrifugal)					(kW)									
Furnace	Furnace	-	-	1	Power	209.3	1000	1000.0	3.00	3.0680	0.6597	0.0194	5.22	166610
(Reformer					(kW)									
Furnace)														
Drive (Eletric -	D1*	-	-	1	Power	1.9	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084
open/drip-proof)					(kW)									
Drive (Eletric -	DP*	-	-	1	Power	0.2	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084
open/drip-proof)					(kW)									

Tag	Р	F_P	Material	B1	B2	F_M	F_BM	C_BM	C_TM	F_BM0	C_BM0	C_GR'	C_GR
	(bar)					/ F*		(USD)			(USD)		(Scaled)
K1	-	-	CS	-	-	-	2.4	28,602	33,751	2.4	28,602	48,052	12,390
Р	80	2.23	CS	1.89	1.35	1	4.9	12,023	14,187	3.2	7,939	18,157	7,853
Furnace	5	1.00	CS	-	-	1	2.2	366,541	432,518	2.2	366,541	615,789	240,965
D1*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	8,579
DP*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	2,540

3.9. SYNTH

Equipment	Tag	2º.ary	Value	Number	А	Α'	A_min	А	log10	K1	K2	К3	log10	C0	Р
Туре		Parameter		of units	(Units)				А				C0	(USD)	(bar)
Compressor	K1	Shaft eff.	80%	1	Power	3.1	18	18.0	1.26	5.0355	-1.8002	0.8253	4.08	11918	-
(Rotary)					(kW)										
Compressor	К2	Shaft eff.	80%	1	Power	11.9	18	18.0	1.26	5.0355	-1.8002	0.8253	4.08	11918	-
(Rotary)					(kW)										
Compressor	КЗ	Shaft eff.	80%	1	Power	11.8	18	18.0	1.26	5.0355	-1.8002	0.8253	4.08	11918	-
(Rotary)					(kW)										
Compressor	К4	Shaft eff.	80%	1	Power	3.1	18	18.0	1.26	5.0355	-1.8002	0.8253	4.08	11918	-
(Rotary)					(kW)										
Drive (Eletric -	D1*	-	-	1	Power	3.1	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084	-
open/drip-					(kW)										
proof)															
Drive (Eletric -	D2*	-	-	1	Power	11.9	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084	-
open/drip-					(kW)										
proof)															
Drive (Eletric -	D3*	-	-	1	Power	11.8	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084	-
open/drip-					(kW)										
proof)															
Drive (Eletric -	D4*	-	-	1	Power	3.1	75	75.0	1.88	2.9508	1.0688	-0.1315	4.49	31084	-
open/drip-					(kW)										
proof)															
Process	MeOH	Diameter	0.56	1	Volume	0.6	0.3	0.6	-0.26	3.4974	0.4485	0.1074	3.39	2452	32
vessels		(m)			(m3)										
(Vertical)															

Tag	Р	F_P	Material	B1	B2	F_M	F_BM	C_BM	C_TM	F_BM0	C_BM0	C_GR'	C_GR
	(bar)					/ F*		(USD)			(USD)		(Scaled)
K1	-	-	CS	-	-	-	2.4	28,602	33,751	2.4	28,602	48,052	16,680
К2	-	-	CS	-	-	-	2.4	28,602	33,751	2.4	28,602	48,052	37,533
КЗ	-	-	CS	-	-	-	2.4	28,602	33,751	2.4	28,602	48,052	37,320
К4	-	-	CS	-	-	-	2.4	28,602	33,751	2.4	28,602	48,052	16,680
D1*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	11,549
D2*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	25,987
D3*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	25,840
D4*	-	-	CS	-	-	-	1.5	46,625	55,018	1.5	46,625	78,331	11,549
MeOH	32	2.2	CS	2.25	1.82	1	6.3	15,381	18,150	4.1	9,978	23,139	23,139

3.10. DIST

Equipment	Tag	2º.ary	Value	Number	А	Α'	A_min	А	log10	K1	K2	K3	log10	C0
Туре		Parameter		of units	(Units)				А				C0	(USD)
Process	Distillation	Diameter	0.64	1	Volume	9.1	0.3	9.1	0.96	3.4974	0.4485	0.1074	4.03	10600
vessels	Column	(m)			(m3)									
(Vertical)														
Trays (Sieve)	Distillation	-	-	80	Area	0.3	0.1	0.3	-0.49	2.9949	0.4465	0.3961	2.87	59474
	Column				(m2)									

Total cost (k€) 311

Тад	Р	F_P	Material	B1	B2	F_M	F_BM	C_BM	C_TM	F_BM0	C_BM0	C_GR'	C_GR
	(bar)					/ F*		(USD)			(USD)		(Scaled)
Distillation Column	1	1.00	CS	2.25	1.82	1	4.1	43,141	50,907	4.1	43,141	72,478	72,478
Distillation Column	-	-	SS	-	-	1.0	1.9	113,001	133,341	1.0	59,474	163,078	163,078

3.11. HEN2

Equipment Type	Equipment Tag	2º.ary Parameter	Value	Number of units
HEN*	-	% of CAPEX is HEN	15%	10

4. Data from other authors

The following tables summarize the data obtained from other authors.

4.1. Tricase & Lombardi [93]

Entry	Size	Unit	Min cost (€)	Max cost (€)
Digester	460	m3	17000	36000
Post-digestion tank	539	m3	20500	29500
Biogas storage tank	106	m3	3500	8500
Pre-mixing	-	-	25000	25000
Co-substrates tank	-	-	0	10000
Blade pumps	3	kW	3000	3000
Immersion mixers	11	kW	6800	6800
CHP unit	43	kW	27000	73000
Insulation	17.5	m3	6378	10168
Torches	143	kW	0	10000
Heat exchanger for digester	72	kW	15000	15000
Connection to thermal plant	72	kW	5000	5000
Other elements of safety	-	-	7100	11100
Other components (pipes)	-	-	4702	5062
Civil works	-	-	0	15000
????	-	-	3000	13000
Engineering works	-	-	7199	27613
Project management	-	-	5000	15000
Total costs	-	-	156179	318743

Gruouped values			Min	Max	Mean
Digester	-	-	76	119	97
СНР	-	-	33	93	63
HEN	-	-	20	20	20
Others	-	-	27	87	57
Total costs	-	-	156	319	237

'Others' distributed over			Min	Max	Mean	
Digester	-	-	92	163	127	
СНР	-	-	40	128	84	
HEN	-	-	24	27	26	
Total costs	-	-	156	319	237	

Basis	Year	CEPCI
Reference	2009	521
Current	2017	568
Ratio	-	109%

Inflation update			Min	Max	Mean
Digester	-	-	100	178	139
СНР	-	-	44	139	92
HEN	-	-	26	30	28
Total costs	-	-	170	347	259

Parameter	Units	Ref1	Scaled value
Gross electricity production	MWh / y	323	4668
Biogas input	MWh / y	605	8760
Biogas specific cost (from YEA)	€/MWh	14	5
Biogas specific cost (from OpEx)	€/MWh	10	10
Total biogas cost	€/MWh	24	15

Production ratio	14.5
Exp factor	60%
Cost Ratio	5.0

Parameter	Units	Ref. Value	This work	Ratio
Biogas cost	€/MWh	24	25	1.0
Electricity selling price	€/MWh	90	38	0.4
Biogas input	MWh / y	605	8760	14
Net heat production	MWh / y	180	2235	12
Net electricity production	MWh / y	258	4668	18
Net energy output	MWh / y	438	6903	16
Net OpEx cost	k€ / y	-16	-754	48
MSC	€/MWh	36	109	3

4.2. Rotunno et al [83]

Input LHV flow (MWh/y)	5430
Electricity input (MWh/y)	239
Biogas output (MWh/y)	5400
Net energy output (MWh/y)	5161
Process efficiency (%)	95

OpEx entry	Value (k€/y)	Fraction (%)
Operating labor	40	13
Maintenance	19	6
Electricity	45	14
Biogas	164	52
Capital cost	48	15
Total	316	100

CH4 revenues (k€/y)	110
Net OpEx (k€/y)	-207
MSC (€/MWh)	40

BioCH4 cost (€/MWh)	59
Natural gas selling price (€/MWh)	20
BioCH4 support cost (€/MWh)	38

Parameter	€/Nm3	€/MWh	Ratio (%)
BioCH4 cost	0.171	29	100
BioCH4 supported cost	0.740	125	433
BioCH4 support	0.569	96	333

Parameter	Ref. Value	This work	Ratio (%)
Input LHV flow (MWh/y)	5430	8760	62
Net energy output (MWh/y)	5161	8229	63
Process efficiency (%)	95	95	100
Net OpEx (k€/y)	-207	-509	41
MSC (€/MWh)	40	62	65
Biogas cost (€/MWh)	29	25	116
Electricity cost (€/MWh)	188	114	165
Natural gas selling price (€/MWh)	20	17	120

4.3. Hernandez & Martin [49]

Gas flow (Nm3/y)	12080000
CH4 molar fraction (%)	50.1
CH4 flow (Nm3/y)	6052080
Input LHV flow (MWh/y)	59560
MeOH flow (m3/y)	9207
MeOH flow (t/y)	7292
MeOH LHV flow (MWh/y)	40694
Process efficiency (%)	68
Production cost (€/t)	582
MeOH selling price (€/t)	295
MSC (€/t)	287
MSC (€/MWh)	45
Net OpEx (k€/y)	-1838

Natural gas selling price (€)	Nft3	MWh
3.71	1000	0.28
13	3588	1

Parameter	Ref. Value	This work	Ratio (%)
Biogas cost (€/MWh)	13	25	53
Natural gas selling price (€/MWh)	13	17	78
Electricity cost (€/MWh)	60	114	53
MeOH selling price (€/t)	287	380	76
Input LHV flow (MWh/y)	59560	8760	680
Process efficiency (%)	68	85	80
Net OpEx (k€/y)	-1838	-686	268
MeOH LHV flow (MWh/y)	40694	6496	626
MSC (€/MWh)	45	106	43

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