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# Thermodynamic analysis of polygeneration systems based on catalytic hydrolysis for the production of bio-oil and fuels

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## Abstract

Novel polygeneration concepts based on catalytic hydrolysis and hydrodeoxygenation are presented and compared via process simulation and thermodynamic analysis. These systems process and convert biomass into high-quality bio-oil and fuels such as synthetic natural gas (SNG), molecular hydrogen (H<sub>2</sub>) and methanol (MeOH). Twelve system layouts were evaluated and compared with regards to their energy demands and performances. Detailed thermodynamic models were developed, considering the different technological alternatives for the valorisation of bio-char, removal of carbon dioxide, fuel upgrading and water electrolysis, as well as the opportunities for energy integration. The results show that the standard system, which produces only bio-oil, reaches an energy efficiency of 61 % (LHV). This value can be increased by 7 to 28 %-points when co-producing SNG, 10 to 21 %-points when producing H<sub>2</sub>, and 10 to 19 %-points when producing MeOH. The highest values are achieved by co-production of SNG as light hydrocarbons are produced in the hydrolysis, and limited processing is therefore required to reach the desired product quality. High system efficiencies are possible mainly because of the high efficiency of the core hydrolysis process. Carbon conversion efficiencies are highest when generating SNG or MeOH and reach a maximum when electrolysis and char gasification are implemented (98 % and 95 %). The performance of these polygeneration systems is strongly impacted by the type of CO<sub>2</sub>-separation process and electrolyser - these processes have a strong influence on the power and heating demands, as well as on the potential energy savings and waste heat valorisation.

*Keywords:* Biomass, green fuels, hydrolysis, hydrodeoxygenation

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## 1. Introduction

The Danish transport sector emitted about 13.2 mill. tonnes CO<sub>2</sub>-equivalent in 2010, of which 92 % was attributable to road transport (e.g. passenger cars and vans) [1]. The emissions were overall stable since, but are expected to increase in the near-future because of increasing road activity. In this context, the

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## Nomenclature

$\dot{Q}$	Heat rate, W	NRTL	Non-Random Two-Liquids
$\dot{W}$	Power, W	PC	Perturbated Chain
$\dot{m}$	Mass flowrate, kg/s	PSA	Pressure Swing Adsorption
$\bar{c}$	Molar fraction, mol/mol	SAFT	Statistical Associating Fluid Theory
$x$	Mass fraction, kg/kg	SN	Stoichiometric Number
T	Temperature, K or °C	SNG	Synthetic Natural Gas
p	Pressure, Pa	SOEC	Solid Oxide Electrolyser Cell
<i>Abbreviations</i>			
AEC	Alkaline Electrolyser Cell	WGS	Water Gas Shift
DEPG	Dimethyl Ether of Polyethylene Glycol	<i>Greek letters</i>	
DNA	Dynamic Networks Analysis	$\Delta h^0$	Lower heating value, J/kg
EOS	Equation of State	$\Delta h_r^0$	Standard enthalpy of reaction, J/mol
HDO	Hydrodeoxygenation	$\eta$	energy efficiency
LHV	Lower Heating Value	<i>Subscripts</i>	
MEA	Monoethanolamine	system	system
MeOH	Methanol	total	total

5 recent Danish governments had set out a strategy on clean and energy-efficient vehicles. A main goal is to  
 6 substitute transportation fuels derived from petroleum with ones derived from biomass.

7 Biomass can be converted into high-value chemicals, fuels, power and heat by undergoing thermal,  
 8 chemical or biological processing and separation. Several studies in the scientific literature deal with the  
 9 modelling and optimization of pathways from biomass to transportation fuels. For example, Baliban et al.[2]  
 10 focused on the conversion of hardwood biomass to gasoline, diesel and jet fuel, analysing the Fischer-Tropsch  
 11 and methanol synthesis pathways. Niziolek et al.[3] performed a similar analysis, analysing the production  
 12 routes from coal and two types of biomass, optimizing the system topology to minimize the costs. Onel  
 13 et al.[4] reviewed the work on biomass/coal refineries for fuel production, and discussed the advances in  
 14 this field. They argued that polygeneration systems result in lower production costs, and increase the  
 15 competitiveness of biomass-derived fuels.

16 Pyrolysis is a thermal process for converting biomass into a liquid product that can be further upgraded  
 17 into a transportation fuel. It is defined as the thermal decomposition in an oxygen-free environment by

18 heating from approximately 250 to 650 °C. It releases volatile gases, of which a part condenses into a  
19 viscous fluid named bio-oil, as well as solids collected as char. The operating conditions (temperature,  
20 pressure, heating rate and residence time) have a direct effect on the yield and composition of each product.  
21 Flash pyrolysis, i.e. pyrolysis with heating rate of up to  $10^4 \text{ K}\cdot\text{s}^{-1}$ , results in higher liquid yield than slow  
22 pyrolysis [5].

23 The produced bio-oil has undesirable properties: high oxygen and water contents, low heating value,  
24 high acidity, high viscosity, non-miscibility with conventional fossil fuels, and short shelf life. Upgrading  
25 is necessary to reduce the oxygen content, stabilise the bio-oil and produce a diesel- or gasoline-like fuel.  
26 Catalysts are necessary, but their lifetimes are short because of carbon deposition and sulphur poisoning.  
27 A promising route is to combine pyrolysis [6] and hydrodeoxygenation (HDO) in a catalytic hydropyrolysis  
28 process [7]. When performing these reactions in a hydrogen-rich environment at high pressure [8], oxygen  
29 atoms are converted into water, carbon oxides and hydrocarbons before condensation of the bio-oil. Parasite  
30 reactions such as polymerization and coking are then avoided, leading to a high-grade oil product [9].

31 The present work focuses on catalytic hydropyrolysis coupled with deep hydrodeoxygenation in a second  
32 reactor (sometimes referred as ex-situ hydrotreating [8]). Fast hydropyrolysis is carried out in a catalytic  
33 reactor and the produced vapours undergo upgrading in a second unit, usually a catalytic packed bed.  
34 An advantage of having two separate reactors is a better system control and optimization, as the reac-  
35 tors can operate in different conditions. Venkatakrishnan et al.[10] at Purdue University developed the  
36 H2Bioil system, in which fast hydropyrolysis takes place at 480-580 °C and the produced vapours undergo  
37 hydrodeoxygenation reactions in a catalytic bed at 300-375 °C. Experimental studies in parallel [11] show  
38 how the catalyst selection impacts strongly the distribution of hydrocarbons in the liquid yield. GTI de-  
39 veloped the IH2 system, in which fast hydropyrolysis also takes place in presence of a catalyst. Similar  
40 temperature and pressure ranges as in Venkatakrishnan et al.[10] are reported, and tests were performed to  
41 validate the proposed concept.

42 These systems are further detailed in the Purdue [12] and GTI [13] patents. The former suggests the use of  
43 a carbon-free energy source, such as solar energy, to generate hydrogen, heat or electricity to convert biomass  
44 into bio-oil, which is then further upgraded. Synergies with thermo-chemical and biological processes are  
45 discussed to extend the product portfolio to other liquid fuels such as alcohols. The latter focuses specifically  
46 on the hydropyrolysis and hydroconversion route, aiming to develop a self-sustaining process for liquid fuel  
47 production. According to the authors, the economics of such systems depend mainly on the hydrogen and  
48 feedstock prices, as well as on the system capital cost and selling price of the liquid product. Marker et al.[14]  
49 demonstrate the proof-of-concept of their integrated hydropyrolysis and hydroconversion (IH2) system for  
50 the direct production of bio-oil, using experimental data a pilot plant operating on a feed flowrate of 0.45 kg/h  
51 in semi-continuous conditions. In a further work, they present the experimental data from the pilot plant,  
52 operating on 50 kg/day, on a continuous basis (750 h). Tan et al.[15] performed a techno-economic analysis

53 of the standard GTI system. They estimated a total capital investment of M\$ 264 for a processing capacity  
 54 of 2000 dry metric tonnes of woody biomass per day and found that the hydrogen plant, followed by the  
 55 hydropyrolysis section, represented the biggest share of the capital costs. Stummann et al.[16] performed an  
 56 experimental investigation using beach wood, and analysed how changes in temperature (365-511 °C) and  
 57 hydrogen pressure (1.6-3.6 MPa) impact the product yield and organic composition. Their results suggest  
 58 that catalytic hydropyrolysis may be a viable biomass-to-liquid fuels pathway.

59 The few works in this field suggest that the main challenges are to (i) demonstrate and optimize this  
 60 combined hydropyrolysis/hydrodeoxygenation process, (ii) develop the proper catalyst formulations and  
 61 address the possible deactivation by carbon deposition, contamination, and mechanical break-down, (iii)  
 62 and improve the system economics, depending on the system scale and hydrogen source. The present paper  
 63 aims at addressing some of these gaps: it presents the conceptual design and thermodynamic analysis  
 64 of biorefineries based on catalytic hydropyrolysis and hydrodeoxygenation. The presented concepts are all  
 65 characterised by the production of a high-grade bio-oil, together with added-value chemicals such as synthetic  
 66 natural gas, hydrogen and methanol. The impact of various layouts, operating conditions and hydrogen  
 67 source on the system performance is analysed in details. The novelty of this work lies in the systematic  
 68 analysis of polygeneration systems based on hydropyrolysis and hydrodeoxygenation, using process modelling  
 69 tools and advanced thermodynamic methods. It investigates the opportunities for producing other chemical  
 70 fuels such as synthetic natural gas, and how the system layouts actually change. Such systems were not  
 71 assessed before, and only the standard IH2 system was analysed from a technical and economic perspective.

## 72 2. Methods

### 73 2.1. System design

74 The present paper investigates the performance of a polygeneration system (Figure 1) producing bio-  
 75 oil and by-products such as synthetic natural gas (SNG), hydrogen (H<sub>2</sub>) and methanol (CH<sub>3</sub>OH/MeOH).  
 76 Each system layout presents different characteristics with regards to the electricity and heating demand and  
 77 production, generation of bio-oil, hydrogen, chemicals and char.

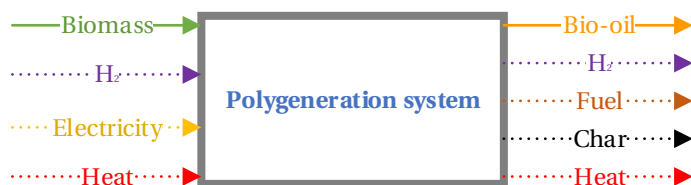


Figure 1: Schematics of the investigated polygeneration system for production of bio-oil and other green fuels through hydropyrolysis and hydrodeoxygenation.

78 Pressurised catalytic hydrolysis and hydrodeoxygenation has attracted interest because of the high  
79 quality of the produced bio-oil and the potentially high efficiency. The following steps are essential: (1)  
80 the feedstock preparation, with pressurisation, (2) the hydrolysis and hydrodeoxygenation, and (3) the  
81 gas-liquids separation. Biomass is fed into a pressurised and catalyst-enhanced fast hydrolysis reactor  
82 in the presence of hydrogen. The reactor is preferably a fluidized bed with hydrogen as fluidising agent,  
83 since biomass should be decomposed under high heating rates with short vapour residence times. Solids are  
84 removed, and the produced vapours are upgraded in a second reaction step. It takes place in another catalytic  
85 stage and at similar pressure levels. Coupling with hydrodeoxygenation results in a low oxygen content, and  
86 the production of hydrocarbons with properties in the boiling ranges of gasoline and diesel. Four phases  
87 are generated and then separated for further upgrading: (i) an organic phase composed of hydrocarbons  
88 ( $C_4^+$ ), which is the target product, (ii) an aqueous phase, (iii) a solid phase, with char and ash, and (iv)  
89 a gaseous mixture consisting of hydrocarbon gases ( $C_1-C_3$ ), carbon monoxide and dioxide ( $CO$  and  $CO_2$ ),  
90 hydrogen and water vapour. The produced hydrocarbons are not soluble in water as conventional pyrolysis  
91 oil, meaning that the two liquid phases are easily separable into a near carbon-free water and gasoline/diesel  
92 fractions.

## 93 *2.2. Process superstructure*

94 Alternative layouts can be designed building on this process concept. The first option, presented in  
95 the Gas Technology Institute (GTI) patent [13], is to ensure that the overall polygeneration system is  
96 self-sustaining, i.e. does not require any external input other than biomass. The second option is to  
97 implement other process units to maximise the gas-liquid yield by valorising the bio-char generated in the  
98 hydrolysis process. The third possibility is to co-produce fuels such as SNG or MeOH. All the possible  
99 process pathways, as well as the different technological options of each step, are assembled and summarised  
100 in a process superstructure (Figure 2).

## 101 *2.3. Process technologies*

### 102 *2.3.1. Hydrogen production*

103 Hydrodeoxygenation is a hydrogenolysis process requiring molecular hydrogen to convert the oxygen  
104 present in the biomass feedstock into water, avoiding the production of an oxygen-rich bio-oil. It may  
105 be produced internally, through conversion of the non-condensable gases, or externally, through water or  
106 steam electrolysis. In the first case, the main steps are: gas cleaning, steam methane reforming, water-gas  
107 shift and  $CO_2$ -removal. As the non-condensable gasses mainly contain hydrogen, it is beneficial to use a  
108 pressure swing adsorption (PSA) unit. It generates a hydrogen-rich stream that can be fed into the  
109 hydrolysis section, by-passing the reforming and water-gas-shift reactors. PSA processes are mature  
110 technologies widely used in the petrochemical industry for producing a hydrogen-rich product stream with

111 a purity exceeding 98 % for a recovery of 70-90 %, depending on the system design, adsorbent and feed gas  
112 pressure. The separation efficiency is enhanced with higher hydrogen partial pressures. The addition of a  
113 PSA unit results in a smaller flowrate into the reforming section.

114 Hydrocarbon reforming is a strongly endothermic process for converting hydrocarbons such as methane,  
115 ethane and propane into hydrogen and carbon monoxide by reaction with steam. Water-gas-shift is a mildly  
116 exothermic reaction, included to increase the hydrogen fraction. This reaction generally takes place in two  
117 reactors operated at two different temperature levels to maximise the conversion of carbon monoxide and  
118 improve the reaction kinetics.

119 The addition of a CO<sub>2</sub>-removal process, through chemical absorption with alkanamines, or physical  
120 absorption with glycols, results in a hydrogen-rich flow that can be used in the hydrolysis. Chemical  
121 absorption processes consist of the removal of carbon dioxide by chemical reactions with amines in an  
122 absorber at low temperatures and pressures.

123 Physical absorption processes typically include an absorber, where the physical solvent dissolves the acid  
124 gas at high pressure, and a succession of flash tanks, with carbon dioxide flashed at decreasing pressure  
125 levels. The preferred solvent in the present work is a mixture of dimethyl ethers of polyethylene glycols  
126 (DEPG), i.e. the Selexol process [17]. Alternatives such as physical absorption with methanol, adsorption  
127 or membrane processes are not considered. The first one requires refrigeration, which is impractical in the  
128 present system. The two last require compression operations both prior and after the separation process to  
129 reach high removal performance and comply with the system requirements.

130 In case that hydrogen is not produced from the non-condensable gases, external generation of hydrogen  
131 can be ensured by electrolysis, either at low temperatures by converting water in alkaline electrolyte cells  
132 (AEC), or at high temperatures by converting steam in solid oxide electrolysis cells (SOEC). The use of  
133 electrolysis results in a higher fuel production, and is claimed to be an efficient and economically promising  
134 option [18]. A main advantage of high-temperature electrolysis is the higher reaction efficiency, and the  
135 heat of evaporation can be supplied as low-temperature heat instead of electricity [19,20]. On the contrary,  
136 low-temperature electrolysis results in the release of energy as waste heat, because the electricity input to the  
137 cell is larger than the enthalpy change of the electrolysis reaction [21]. At present, AECs are commercialised  
138 and mature technologies, while SOECs are available in niche markets, and require further development.

### 139 *2.3.2. Char valorisation*

140 Char is characterised by a high carbon content, and can be valorized in three manners: (1) through  
141 combustion, to produce the heat required in the polygeneration system; (2) through gasification, to increase  
142 the gas yield; (3) through soil incorporation, to improve the soil quality, increase agricultural productivity  
143 and sequester carbon. The first option may be preferred if hydrogen has to be produced internally, since  
144 reforming reactions are highly endothermic and require heat supply at high temperatures. However, it may

Table 1: List of chemical reactions occurring in the polygenation system - hydrolysis and hydrodeoxygenation reactions are not presented here, as they consist of complex reaction schemes involving several intermediate reactions; reactions involving sulphur, chlorine and other organic and inorganic components are neglected.

Process	Reaction	Chemistry	$\Delta h_r^0$ [ $\frac{kJ}{mol}$ ]
Combustion	Oxidation	$C + O_2 \longrightarrow CO_2$	-394
	Partial oxidation	$C + 0.5O_2 \longrightarrow CO_2$	-111
	Partial oxidation	$2CO + O_2 \longrightarrow 2CO_2$	-283
Gasification	Water-gas	$C + H_2O \rightleftharpoons CO + H_2$	131
	Boudouard	$C + CO_2 \rightleftharpoons 2CO$	173
	C-methanation	$C + 2H_2 \rightleftharpoons CH_4$	-75
Reforming	CH <sub>4</sub> -reforming	$CH_4 + H_2O \longrightarrow CO + 3H_2$	206
	C <sub>2</sub> H <sub>6</sub> -reforming	$C_2H_6 + 2H_2O \longrightarrow 2CO + 5H_2$	
	C <sub>3</sub> H <sub>8</sub> -reforming	$C_3H_8 + 3H_2O \longrightarrow 3CO + 7H_2$	
Water-gas-shift	WGS	$CO + H_2O \rightleftharpoons CO_2 + H_2$	-41
CO <sub>2</sub> -removal	MEA	$2H_2O \rightleftharpoons H_3O^+ + OH^-$	
		$CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^-$	
		$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$	
		$MEAH^+ + H_2O \rightleftharpoons MEA + H_3O^+$	
		$MEACOO^- + H_2O \rightleftharpoons MEA + HCO_3^-$	
	TEA	$CO_2 + R_3N + H_2O \rightleftharpoons R_3NH^+ + HCO_3^-$	
SNG synthesis	CO-methanation	$CO + 3H_2 \longrightarrow CH_4 + H_2O$	-206
	Sabatier	$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$	-164
MeOH synthesis	CO-to-MeOH	$CO + 2H_2 \rightleftharpoons CH_3OH$	-90.8
	CO <sub>2</sub> -to-MeOH	$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$	-49.2
Electrolysis	Water electrolysis	$H_2O \longrightarrow H_2 + \frac{1}{2}O_2$	237

145 be challenging to design an efficient combustion system that transfers most of the generated heat to the  
146 high-temperature reactor. The second option results in an increased fuel output, but requires steam and/or  
147 oxygen - the focus in this paper is on steam hydrogasification [22]. Carrying out the gasification process in  
148 a hydrogen-rich environment, without oxygen, leads to smaller CO<sub>2</sub>-removal processes and lower equipment  
149 costs. The addition of steam leads to a higher fraction of both methane and hydrogen in the synthesis gas.  
150 The third option is not analysed further in the present work.

### 151 2.3.3. Fuel synthesis

152 Fuels such as SNG and MeOH can be generated from the produced syngas. The non-condensable gases  
153 contain a significant fraction of light hydrocarbons, implying that only the carbon oxides should be converted



154 into methane to produce a high-quality SNG. The reactions taking place in the methanation process [23] are  
 155 thermodynamically favoured at low temperatures and high pressures. Adiabatic reactors [24] are the simplest  
 156 design option, since no reactor cooling is needed, and moderate amounts of catalyst are required. However,  
 157 the temperature increase may cause catalyst sintering and the resulting equilibrium state is not optimal  
 158 regarding the carbon oxides conversion. On the contrary, isothermal reactors allow for higher methane  
 159 yield, but need continuous heat removal and high amounts of catalyst to compensate for the lower reaction  
 160 rates at moderate temperatures. Methanol is synthesised by exothermal catalytic reactions, involving as well  
 161 carbon oxides and hydrogen [25,26]. As for methanation, adiabatic or quasi-isothermal reactors [27] may be  
 162 implemented, with the same advantages and issues regarding the conversion rate and reaction kinetics.

#### 163 2.4. System layouts

164 All possible system layouts can be grouped into thirteen types (Table 2). B is the standard system  
 165 layout, with bio-oil generation and hydrogen production from reforming of the light gases. The prefixes  
 166 ‘SNG’, ‘H2’ and ‘MeOH’ indicate which fuel is produced in addition to bio-oil. The prefixes ‘R’ and ‘E’  
 167 denote whether the hydrogen required in the pyrolysis process is generated by reforming of the light gases  
 168 or by water electrolysis. The prefixes ‘C’ and ‘G’ stand for combustion and gasification, if char is valorized.

Table 2: List of investigated configurations

Layout	Fuel	H <sub>2</sub> -production	Char use	Upgrading	Reformer heating
B	none	Reforming	-	PSA	Gas combustion
SNG-R	SNG	Reforming	-	PSA	Electrical
SNG-R-C	SNG	Reforming	Combustion	PSA	Char combustion
SNG-R-G	SNG	Reforming	Gasification	PSA	Electrical
SNG-E	SNG	Electrolysis	-	-	-
SNG-E-G	SNG	Electrolysis	Gasification	-	-
H2-R-G	H <sub>2</sub>	Reforming	Gasification	PSA	Electrical
MeOH-R-G	MeOH	Reforming	Gasification	PSA	Electrical
MeOH-E-G	MeOH	Electrolysis	Gasification	PSA	Electrical

169 These thirteen layouts can be further subdivided depending on the technologies used for performing  
 170 specific process operations, such as CO<sub>2</sub>-capture and electrolysis. In the rest of this study, the suffixes  
 171 ‘CA’ and ‘PA’ indicate whether chemical or physical absorption is implemented. The suffixes ‘SE’ and ‘AE’  
 172 stand for solid oxide and alkaline electrolysis. For example, a polygeneration system with SNG production,  
 173 hydrogen production by reforming and char gasification is denoted SNG-R-G. It can either be designed with  
 174 a chemical absorption unit (SNG-R-G-CA) or a physical one (SNG-R-G-PA).

175 *2.5. System modelling*

176 The polygeneration plants were modelled using the software Dynamic Networks Analysis (DNA) [28],  
177 which is an in-house tool developed at the Technical University of Denmark for design of energy plants,  
178 and the flowsheeting software Aspen Plus, version 7.2, for simulation of the CO<sub>2</sub>-removal processes and  
179 the methanol synthesis step. The important assumptions and design parameters used for each model are  
180 presented in the following sections. The biomass considered in the modelling process is maple wood [29],  
181 with the following ultimate analysis: 6.3 % hydrogen, 43.3 % oxygen, 0.11 % nitrogen, 49.2 % carbon and  
182 1.1 % ash. This composition is chosen based on the experimental set-up of the IH<sup>2</sup> project, and the higher  
183 heating value, on a dry basis, is 20 MJ/kg.

184 *2.5.1. Hydropyrolysis and hydrotreatment*

185 The hydropyrolysis and hydrodeoxygenation processes are modelled as a black-box, without considering  
186 the kinetics and equilibrium of each individual reaction. The model inputs (i.e. the required information,  
187 not the actual inflows) are the biomass flowrate and composition, on an ultimate basis, and the design  
188 parameters such as the pressure and temperature. The model outputs are the hydrogen demand, yields  
189 of the gas, aqueous, liquid and solid phases, and their compositions. The model is calibrated using the  
190 experimental results of the IH<sup>2</sup> project, and the simulations are conducted based on experiment 5/25 (details  
191 given in [Appendix A](#)). The system pressure is about 22 bar and the hydropyrolysis and hydrodeoxygenation  
192 temperatures is approximately 430 °C. On a weight basis, the hydrogen input corresponds to about 4.6 % of  
193 the biomass feed, and the product yields are: 28 % bio-oil, 31 % light gases, 9 % char and 36 % water. On  
194 a lower heating value basis, the hydrogen input corresponds to about 29.5 % of the biomass feed, and the  
195 product yields are: 61 % bio-oil, 43 % light gases and 15 % char. These numbers are used to fix the yield  
196 and composition of each product. Perfect phase separation is assumed, meaning that neither bio-char nor  
197 bio-oil are entrained in the gas flow.

198 *2.5.2. Gas purification*

199 The PSA unit is represented by a black-box model and the adsorption mechanisms are not modelled in  
200 details. The model takes as inputs the feed characteristics, expected hydrogen recovery rate and purity, and  
201 the model outputs are the outflow properties and power demand associated with the compression of the  
202 purge gas. The recovery rate is assumed to be 87 % and the product purity is set to 99.99 %, by analogy  
203 with the Polybed version of the PSA process [30], which consists of 10 columns and 11 steps. The recovered  
204 hydrogen is at feed pressure, i.e. about 22 bar, while the purge gas is at a desorption process of 1.1 bar.  
205 More complex layouts, such as the ones that include recompression of the purge gas followed by a second  
206 PSA column to enhance the hydrogen recovery are not considered. Other gas upgrading processes are not  
207 modelled in details in the present work. In practice, sulphur is removed prior to steam reforming or methane

208 synthesis to avoid catalyst poisoning, whilst a minimum concentration of hydrogen sulphide is required in  
209 the hydrolysis step.

### 210 *2.5.3. Reforming and water-gas-shift*

211 The reforming step aims at converting the hydrocarbon fractions into hydrogen and carbon monoxide  
212 by using high-temperature steam, in presence of a catalyst. The use of catalysts is not modelled explicitly,  
213 but the involved reactions are assumed to reach equilibrium at the reactor conditions, which are typically  
214 under 3-25 bar and 700-1100 °C. The operating parameters are set to 5 bar and 900 °C in the model, but  
215 can be varied to optimise the process performance and equipment size. An additional water-gas-shift step  
216 follows the reforming process to convert carbon monoxide. This reaction is favoured at low temperatures, in  
217 presence of catalysts. The shift process is simulated as a single stage and near-isothermal reactor at 250 °C.  
218 The use of catalysts is not modelled explicitly, but the WGS reaction is assumed to reach thermodynamic  
219 equilibrium at the reactor outlet [31,32].

### 220 *2.5.4. CO<sub>2</sub>-separation*

221 The model of the CO<sub>2</sub>-capture units with amines (chemical absorption) was developed using the com-  
222 mercial flowsheeting software Aspen Plus<sup>®</sup> version 7.2 [33], based on the electrolyte NRTL method [34] for  
223 the liquid phase and the Redlich-Kwong EOS [35] for the vapour phase. Carbon dioxide removal processes  
224 through absorption are based on local heat and mass transfers and depend as well as on the geometry of  
225 the separation columns. All absorption models are developed for steady-state conditions, accounting for  
226 the diffusion and absorption kinetics. The absorber and scrubber were modelled as rate-based instead of  
227 steady-state equilibrium, taking into account the reaction kinetics. Each column is modelled as a number of  
228 control volumes where each phase is perfectly mixed in each volume. Vapour-liquid equilibrium is assumed  
229 only at the contact interface, the heat-transfer coefficients are assumed constant, and the mass transfer is  
230 assumed to be limited by the low-flux mass-transfers. The absorption and desorption temperatures were set  
231 to 40 °C and 120 °C.

232 The models of the CO<sub>2</sub>-capture units with DEPG (physical absorption) were developed using the PC-  
233 SAFT equation of state [36]. The absorber was modelled as rate-based, while the flash tanks were represented  
234 by simple phase separators with interstage flashing. The absorption temperature was set to 25 °C for an  
235 operating pressure of 22 bar to ensure high CO<sub>2</sub> partial pressure, while the final desorption pressure was set  
236 to 1.1 bar. Two intermediate desorption stages were considered, operating at 3 bar and 8 bar to ensure equal  
237 pressure ratios. In all cases, the solvent-to-carbon ratios were adjusted to ensure a CO<sub>2</sub>-removal efficiency  
238 of 95 %, which corresponds to state-of-the-art CO<sub>2</sub>-capture systems.

### 239 2.5.5. Char valorisation

240 Char combustion aims at providing the heat required in the system, which is at high ( $\simeq 900^\circ\text{C}$ , if  
241 reforming is implemented) or moderate temperatures ( $\simeq 120^\circ\text{C}$ , if  $\text{CO}_2$  is removed by chemical absorption).  
242 Air is processed at near-atmospheric conditions, and the excess ratio was adjusted to ensure an exhaust  
243 temperature of  $1200^\circ\text{C}$ . Air preheating is implemented to minimise the quantity of heat wasted with the  
244 exhaust gases. Higher temperatures may be achieved in practice depending on the reactor material. The  
245 reactions were assumed total, meaning that carbon is fully converted into carbon dioxides.

246 Char gasification consists of chemical reactions in parallel - the overall process is governed by heat- and  
247 mass-transfer phenomena in homogeneous and heterogeneous phases, and is limited by chemical kinetics.  
248 The gas composition at the gasifier outlet is generally determined by assuming chemical equilibrium at the  
249 given operating conditions. The approach selected in this work was to specify an equilibrium temperature  
250 of  $725^\circ\text{C}$  and a constant carbon conversion of 90% [37]. A methanation catalyst should be used to ensure  
251 a methane outlet content close to equilibrium.

### 252 2.5.6. Methane synthesis

253 Methanation reactions are equilibrium reactions that are favoured at low temperatures, typically about  
254  $250^\circ\text{C}$ , and at moderate pressures, usually until 30 bar. The gas composition at the reactor outlet can  
255 therefore be computed by calculating the equilibrium concentrations and adjusting the syngas composition  
256 to account for a possible deviation to equilibrium. However, as demonstrated in experimental studies,  
257 the assumption of chemical equilibrium is reasonable if the amount of catalytic material is sufficient [38].  
258 Neglecting the formation of ethene and other by-products, the stoichiometric number (SN), i.e. the relation  
259 between the amounts of hydrogen and carbon oxides in the system, that gives the maximum methane yield  
260 obeys the following law:

$$\text{SN} = \frac{\tilde{c}_{\text{H}_2} - \tilde{c}_{\text{CO}_2}}{\tilde{c}_{\text{CO}} + \tilde{c}_{\text{CO}_2}} = 3$$

261 The methanation reactor is assumed to be a near-isothermal reactor at  $300^\circ\text{C}$  [32,38], which results in  
262 a  $\text{CO}_2$ -conversion to  $\text{CH}_4$  higher than 98% at pressure levels higher than 10 bar. The hydrogen inflow is  
263 adjusted to match the optimal stoichiometric number of 3 (2.5.6) [31,32].

### 264 2.5.7. Methanol production

265 Methanol synthesis reactions are as well favoured at low temperatures, typically about  $250^\circ\text{C}$ , and at high  
266 pressures, up to 100 bar in industrial applications. Chemical equilibrium is not reached and a temperature  
267 approach of  $3.6^\circ\text{C}$  is considered to account for the deviation to equilibrium [32]. Copper-based catalysts  
268 are standard in industrial applications, and it is preferable to process carbon monoxide instead of carbon  
269 dioxide in this case. The synthesis reactor is assumed to be a near-isothermal reactor at  $250^\circ\text{C}$  [26,32], and

270 the hydrogen inflow is adjusted to match the optimal stoichiometric number of 2 (2.5.6). The outflow gases  
271 are condensed and cooled to 25 °C, and the recovered gases are recycled into the synthesis reactor, after a  
272 purge of 5 % and preheating to 200 °C.

### 273 2.5.8. *Electrolysis*

274 Hydrogen may be produced by low- or high-temperature electrolysis as an alternative to the reforming and  
275 water-gas-shift processes. The detailed physical and chemical phenomena are not modelled in details, and  
276 both types of electrolyzers are represented by black-box models with mass and energy balances. Complete  
277 conversion of water into molecular hydrogen and oxygen is assumed, as well as constant current density  
278 and isothermal conditions. The stack pressure is taken equal to the system pressure of 22 bar. Alkaline  
279 electrolyzers generally operate between 60 °C and 80 °C, for an efficiency ranging between 52 % and 69 %.  
280 High-temperature electrolyzers typically operate between 700 °C and 900 °C, for an efficiency above 90 %.  
281 Operating temperatures of 80 °C and 750 °C are selected for low- and high-temperature electrolysis, for a  
282 corresponding efficiency of 64 % and 95 %, depending on the preheating temperature [19,20].

### 283 2.5.9. *Energy integration*

284 The goal of energy integration is to minimise the energy demands of a given system by maximising  
285 the internal heat recovery and optimising the operating conditions of each process. The use of external  
286 utilities, such as boilers and refrigeration cycles, should be minimised to avoid additional costs and electricity  
287 consumption. The first step is to identify the hot and cold streams, i.e. the flows that require cooling or  
288 heating, of each process, as well as their corresponding temperature levels and loads. The second step is to  
289 define an individual temperature approach for each stream ( $\Delta T/2$ ), which defines the minimum heat transfer  
290 driving force to design a feasible and economical heat exchanger. Individual temperature approaches of 5 °C,  
291 10 °C and 20 °C are assumed for condensing/evaporating, liquid and gaseous streams. The third step is to  
292 calculate the minimum energy requirements of the system and to optimize the size and placement of each  
293 utility.

294 In the present case, heat is required in (i) the production of steam for gasification, reforming, water-gas-  
295 shift and electrolysis (solid oxide); (ii) the steam reforming process; (iii) the CO<sub>2</sub>-capture unit (if chemical  
296 absorption) and (iv) the preheating of the process gases. It is released from (i) the methanation, water-gas-  
297 shift and methanol synthesis; (ii) the electrolysis units (if alkaline); (iii) the cooling and partial condensation  
298 of the process gases. High-temperature heat can be produced by burning char or a fraction of the non-  
299 condensable gases from the PSA, or by electrical heating. Low- to moderate-temperature heat may be  
300 provided by internal heat recovery or by further exploiting the waste heat of the combustion exhausts.

301 *2.6. Performance indicators*

302 The performance of each layout depends on the efficiency of each process operation and on the overall  
 303 system integration. The former is related to the type of product (e.g. SNG, H<sub>2</sub>, MeOH), to the selection of  
 304 a given technology (e.g. chemical or physical absorption for CO<sub>2</sub>-removal) and of its operating conditions  
 305 (e.g. temperature and pressure). The latter is related to the design of the heat recovery system and to the  
 306 integration of the external heating and cooling utilities.

307 The system efficiency  $\eta_{\text{system}}$  (Equation 1) is defined as the ratio of the useful energy outputs (e.g.  
 308 chemical energy of bio-oil and fuels) to the necessary energy inputs (e.g. chemical energy of biomass). The  
 309 system efficiency includes the demands of hydrogen, power and heat, where the processes used to generate  
 310 hydrogen and external heating are not accounted for.

$$\eta_{\text{system}} = \frac{\Delta h_{\text{bio-oil}}^0 \cdot \dot{m}_{\text{bio-oil}} + \Delta h_{\text{SNG}}^0 \cdot \dot{m}_{\text{SNG}} + \Delta h_{\text{H}_2, \text{produced}}^0 \cdot \dot{m}_{\text{H}_2, \text{produced}} + \Delta h_{\text{MeOH}}^0 \cdot \dot{m}_{\text{MeOH}}}{\Delta h_{\text{biomass}}^0 \cdot \dot{m}_{\text{biomass}} + \Delta h_{\text{H}_2, \text{external}}^0 \cdot \dot{m}_{\text{H}_2, \text{external}} + \dot{W}_{\text{external}} + \dot{Q}_{\text{external}}} \quad (1)$$

311 where  $\dot{m}$ ,  $\Delta h^0$ ,  $\dot{W}$  and  $\dot{Q}$  are the mass flow rates, lower heating values, power and heat demands.

312 A total efficiency (Equation 2) is defined: it considers the electrical losses in the upstream processes to  
 313 generate the hydrogen and heat required on-site.

$$\eta_{\text{total}} = \frac{\Delta h_{\text{bio-oil}}^0 \cdot \dot{m}_{\text{bio-oil}} + \Delta h_{\text{SNG}}^0 \cdot \dot{m}_{\text{SNG}} + \Delta h_{\text{H}_2, \text{produced}}^0 \cdot \dot{m}_{\text{H}_2, \text{produced}} + \Delta h_{\text{MeOH}}^0 \cdot \dot{m}_{\text{MeOH}}}{\Delta h_{\text{biomass}}^0 \cdot \dot{m}_{\text{biomass}} + \dot{W}_{\text{total}}} \quad (2)$$

314 If the produced char is not converted, both efficiencies will also be given with a term  $\Delta h_{\text{char}}^0 \cdot \dot{m}_{\text{char}}$ .

315 Finally, a carbon conversion efficiency (Equation 3) is derived ( $X_C$ ), defined as the ratio of carbon present  
 316 in the valuable outputs (e.g. bio-oil, SNG and CH<sub>3</sub>OH) to the carbon introduced in the system with biomass:

$$X_C = \frac{x_{C, \text{bio-oil}} \cdot \dot{m}_{\text{bio-oil}} + x_{C, \text{SNG}} \cdot \dot{m}_{\text{SNG}} + x_{C, \text{MeOH}} \cdot \dot{m}_{\text{MeOH}}}{x_{C, \text{biomass}} \cdot \dot{m}_{\text{biomass}}} \quad (3)$$

317 **3. Results**

318 The results from the modelling of the polygeneration systems based on catalytic hydrolysis are  
 319 presented and commented in the following section. Sizing of the polygeneration systems is not within the  
 320 scope of this paper, and all systems are therefore based on a 100 MWth biomass input (LHV).

321 *3.1. Standard system*

322 The standard hydrolysis system for production of bio-oil through hydrolysis is presented in  
 323 Figure 3 with the corresponding data in Table 3.

Table 3: Process data of the polygeneration system for production of bio-oil through hydrolysis and hydrodeoxygenation with internal generation of hydrogen and a burner.

Node	m (kg/s)	T (°C)	p (bar)	Node	m (kg/s)	T (°C)	p (bar)
1	5.76	25	22.4	18	1.15	219	5
2	3.46	25	22.4	19	1.30	152	5
3	9.22	25	22.4	20	0.95	152	5
4	0.52	429	22.4	21	2.45	170	5
5	8.70	429	22.4	22	2.45	750	5
6	8.70	363	22.4	23	2.45	900	5
7	8.70	367	22.4	24	2.45	250	5
8	8.70	25	22.4	25	3.40	224	5
9 {bio-oil}	1.57	25	22.4	26	3.40	200	5
9 {water}	2.24	25	22.4	27	3.40	40	5
10	4.91	25	22.4	28	2.03	40	5
11	2.87	25	22.4	29	0.42	40	5
12	2.04	25	22.4	30	0.42	223	22.4
13	0.17	25	22.4	31	0.42	25	22.4
14	1.87	25	1.1	32	10.7	25	1.1
15	0.72	25	1.1	33	10.7	950	1.1
16	1.15	25	1.1	34	11.4	1000	1.1
17	1.15	125	5	35	0.94	40	5

324 The analysis of the chemical energy flows of the hydrolysis system (Figure 4) illustrates the chemical  
 325 transformations from biomass to bio-oil and shows that this system can be self-sufficient in terms of hydrogen  
 326 and heat. The light gases have an energy content of about 40 % of the biomass input (LHV), which is slightly  
 327 higher than the combined demand of hydrogen (29.5 %) and heat (6 %). This figure also shows that the  
 328 core hydrolysis process is very energy-efficient, only having a chemical energy loss equivalent to 8.4 %  
 329 of the biomass input. The waste heat contained in the burner exhausts amounts to 12 % of the feed energy  
 330 content and could be valorized in Rankine cycles or used in other heating systems, since the exhausts have  
 331 a temperature above 900 °C. The power demand is negligible, as all process units, except for the burner,  
 332 operate at 22.4 bar, and the system efficiency is about 61 % if char is not included, and 76 % otherwise. In  
 333 practice, some electricity would be required for pressurising the biomass and compressing the recirculated  
 334 gases because of the pressure drops. The carbon efficiency is about 49 % if char is not included, and 63 %  
 335 otherwise.

336 The temperature-enthalpy curves (grand composite) of the hydrolysis system (Figure 5) show that  
337 the heating demand corresponds to the reforming process, which is satisfied by burning a fraction of the  
338 non-condensable gases. The cooling demand takes place near ambient conditions, and is met by processing  
339 cooling water. The steam production for the reforming process can be satisfied internally: heat is recovered  
340 from the water-gas-shift process, available at 250 °C, to preheat and evaporate the water, and from the  
341 cooling of the gases at the outlet of the pyrolysis and reforming steps, for further superheating.

### 342 3.2. SNG production

343 Different alternatives for char valorisation ('SNG-C' and 'SNG-G', for combustion and gasification),  
344 reformer heating, CO<sub>2</sub>-separation ('SNG-PA' and 'SNG-CA', for physical and chemical absorption) and H<sub>2</sub>  
345 production ('SNG-R' and 'SNG-E', for reforming and electrolysis) were considered for the system layouts  
346 with SNG by-production, and their performances are reported in Table 4.

347 The selection of the CO<sub>2</sub>-capture process has a considerable impact on the opportunities for energy  
348 integration and system efficiency. The integration of a chemical absorption process increases the heating  
349 demand of the entire system (7 to 11 MW per 100 MW<sub>biomass</sub>), and this energy need cannot be fully satisfied  
350 with heat recovery from the cooling of the process gases and methanation processes. It can either be met  
351 by burning char (Figure 6), which results in a smaller SNG production ('SNG-R-C-CA'), or by additional  
352 electrical heating ('SNG-R-G-CA'). The latter is presented in details in Appendix B.

353 The integration of a physical absorption unit ('SNG-R-G-PA') eliminates the need for heating at low  
354 and moderate temperature levels - external heating is then only required to drive the reforming process.  
355 The latter is presented in details in Appendix C. The system efficiency increases by up to 4 %-points, as the  
356 power demand of the Selexol CO<sub>2</sub>-capture process is smaller than the heating demand of the MEA one. A  
357 comparison of the temperature-enthalpy curves of these two systems (Figure 7) illustrates the possibilities  
358 for energy integration. In theory, as the pinch point is located at the amine regeneration temperature, excess  
359 heat from below the pinch can be lifted above through a heat pump. This would result in a better energy  
360 integration of the MEA CO<sub>2</sub>-capture unit, but reveals infeasible in practice as high temperature lifts are  
361 required.

362 The configurations 'SNG-R' are characterised by the internal production of hydrogen. Alternatively,  
363 hydrogen can be produced through electrolysis, giving the possibility to integrate electricity from renewable  
364 energies. Such systems ('SNG-E') present very different power and heat demands. The external heating  
365 demand is negligible, but the power demand increases significantly with the electrolysis process. The use of  
366 alkaline electrolyzers ('SNG-E-G-AE') results in a large discharge of waste heat at 80-90 °C, which should  
367 either be removed by using cooling water or low-temperature district heating. The implementation of  
368 solid oxide units ('SNG-E-G-SE') is beneficial as these components display a higher efficiency than alkaline  
369 electrolyzers, and they can benefit from a close integration with the other processes. The steam required in



Table 4: Performance of polygeneration systems with SNG production

Layout	SNG-R	SNG-R-C	SNG-R-G	SNG-R-G	SNG-E	SNG-E-G	SNG-E-G
		-CA	-CA	-PA	-SE	-SE	-AE
<b>Pathway</b>							
Product	SNG	SNG	SNG	SNG	SNG	SNG	SNG
H <sub>2</sub>	R	R	R	R	E	E	E
Char	-	C	G	G	-	G	G
<b>Technologies</b>							
CO <sub>2</sub>	CA	CA	CA	PA	-	-	-
Electrolysis	-	-	-	-	SE	SE	AE
<b>Inputs (MW)</b>							
Biomass	100	100	100	100	100	100	100
Heat (reformer)	9	-	11	11	-	-	-
Heat (others)	4	-	6	-	-	-	-
Hydrogen	-	-	-	-	49	63	63
Electricity	2(15)	2(2)	3(20)	3(15)	0(51)	0(66)	0(117)
<b>Outputs (MW)</b>							
Bio-oil	61	61	61	61	61	61	61
SNG	18	18	31	31	59	83	83
Char	15	-	-	-	15	-	-
<b>Efficiency</b>							
$\eta_{\text{system}}$	68 %	77 %	77 %	81 %	79 %	89 %	89 %
$\eta_{\text{system,char}}$	81 %	-	-	-	91 %	-	-
$\eta_{\text{total}}$	68 %	77 %	77 %	81 %	79 %	88 %	67 %
$\eta_{\text{total,char}}$	81 %	-	-	-	89 %	-	-
$X_C$	59 %	59 %	70 %	70 %	86 %	98 %	98 %
$X_{C,char}$	73 %	-	-	-	100 %	-	-

370 the SOEC can be generated by recovering heat from the methanation process and the cooling of gases from  
371 the hydrodeoxygenation, which reduces the need for external cooling. It can further be superheated close to  
372 the electrolysis temperature by using the heat of the hydrogen and oxygen streams yielded by the SOEC.  
373 The flow diagram and data of the layout ‘SNG-E-G-SE’ are presented in details in [Appendix D](#).

374 The highest carbon conversion efficiencies are reached when electrolysis is implemented (86-100 % com-  
375 pared to 59-73%), as the only possible sources of carbon losses in this case are the ash/char streams.  
376 Hydrogen generation through reforming of the non-condensable light gases results in losses of up to 27 % of  
377 the biomass carbon with the carbon dioxide recovered in the absorption unit.

### 378 *3.3. H<sub>2</sub> production*

379 Molecular hydrogen can be generated as a final product instead of SNG, although the number of possible  
380 configurations is more limited, as the use of electrolysis is not relevant. Moreover, producing hydrogen  
381 without adding a char gasification unit has limited benefits, since most light gases are reformed to sustain  
382 the hydrogen demand of the hydrolysis section. Two configurations are assessed, with either chemical  
383 ('H<sub>2</sub>-R-G-CA') or physical ('H<sub>2</sub>-R-G-PA') absorption for separating carbon dioxide. The flow diagram and  
384 data of the layout 'H<sub>2</sub>-R-G-CA' are presented in details in [Appendix E](#).

385 The major heating demands correspond to the reforming and amine regeneration processes, which is  
386 expected as the layout of H<sub>2</sub>-production systems is strongly similar to SNG-production ones. Both increase  
387 in comparison to the SNG cases, since all carbon oxides are processed through the reforming section instead  
388 of being converted into methane. The Selexol process is even more attractive, since the difference in system  
389 efficiency increases from 4 to 9 %-points when substituting the MEA unit. The carbon conversion efficiency  
390 of H<sub>2</sub>-generation processes is the lowest of all polygeneration systems investigated in this work.

### 391 *3.4. MeOH production*

392 Methanol can be produced by converting the carbon monoxide present in the reformed gas after compres-  
393 sion and synthesis at high pressure, and its yield can be maximised by capturing and recycling the carbon  
394 dioxide to the reformer. As for SNG and H<sub>2</sub> production systems, either physical ('MeOH-PA') or chemical  
395 absorption ('MeOH-CA') can be integrated to remove carbon dioxide. In both cases, the syngas from the  
396 reformer are split into two processing routes: a first one where the hydrogen required in the hydrolysis  
397 is generated through water-gas-shift and CO<sub>2</sub>-capture, and a second one where the remaining syngas is  
398 compressed and converted into methanol. The flow diagram and data of the layout 'MeOH-R-G-CA' are  
399 presented in details in [Appendix F](#).

400 The advantage of implementing an electrolysis unit is studied considering solid oxide electrolyzers  
401 ('MeOH-E-SE'). No water-gas-shift reactor is required, but a reforming unit is still needed to achieve the  
402 desired stoichiometry between hydrogen and carbon monoxide. The integration of the Selexol process results  
403 in an increase of the system performance by about 4 %-points, and the implementation of electrolysis gives  
404 a further increase of 4 %-points. The heat required to generate the steam used in the reforming process  
405 can be recovered from the methanol synthesis unit, while the heat demand of the amine reboiler can be

Table 5: Performance of polygeneration systems with H<sub>2</sub> and MeOH production

Layout	H2-R-G -CA	H2-R-G -PA	MeOH-R-G -CA	MeOH-R-G -PA	MeOH-E-G -PA-SE
<b>Pathway</b>					
Product	H <sub>2</sub>	H <sub>2</sub>	MeOH	MeOH	MeOH
H <sub>2</sub>	R	R	R	R	E
Char	G	G	G	G	G
<b>Technologies</b>					
CO <sub>2</sub>	CA	PA	CA	PA	PA
Electrolysis	-	-	-	-	SE
<b>Inputs (MW)</b>					
Biomass	100	100	100	100	100
Heat (reformer)	18	18	19	19	19
Heat (others)	16	-	8	-	-
Hydrogen	-	-	-	-	42
Electricity	5(39)	5(23)	6(33)	8(27)	7(70)
<b>Outputs (MW)</b>					
Bio-oil	61	61	61	61	61
Hydrogen	37	37	-	-	-
Methanol	-	-	33	33	68
<b>Efficiency</b>					
$\eta_{\text{system}}$	71 %	81 %	71 %	74 %	78 %
$\eta_{\text{total}}$	71 %	81 %	71 %	74 %	76 %
$X_C$	49 %	49 %	71 %	71 %	95 %

406 fully satisfied only by implementing electrical heating. The flow diagram and data of the layout ‘MeOH-  
407 E-G-SE’ are presented in details in [Appendix G](#). Similar carbon conversion efficiencies are reached with  
408 MeOH production as with SNG generation. A value of 95 % is reached when combining electrolysis and char  
409 gasification. This is a few percentage points lower than for SNG, since carbon is lost with the purge after  
410 the MeOH-synthesis reactor.

#### 411 4. Discussion

412 The standard system, which is characterised by the production of bio-oil and recirculation of the light  
413 gases, displays an efficiency  $\eta_{\text{system}}$  of 61 % and is self-sufficient in terms of heat and power. The steam  
414 reformer can be heated by burning either char or a fraction of the reformed gases, and the two options are  
415 equivalent efficiency-wise.

416 The results show a higher energy efficiency of polygeneration systems that produce SNG,  $\text{H}_2$  and MeOH  
417 compared to the standard system, in all cases, whether hydrogen is produced internally or externally, and  
418 whether electrical heating or char combustion is required to satisfy the demand of the reforming process. The  
419 increase in system efficiency is of 7 to 28 %-points when producing SNG, 10 to 21 %-points when producing  
420  $\text{H}_2$ , and 10 to 17 %-points when producing MeOH. The smallest improvement (7 %-points) is observed when  
421 all the light gases are recirculated and reformed, while a fraction of char is burnt to heat the reformer.  
422 The highest improvement (28 %-points) is reached when electrolysis is used to cover the hydrogen demand  
423 and char is valorized through gasification and SNG production. The systems co-producing SNG reach the  
424 highest system efficiency because methane, ethane and propane are generated inside the core hydrolysis  
425 process. Very limited upgrading is therefore needed to convert all the light gases to SNG.

426 The configurations with  $\text{H}_2$ -production by char gasification can reach a system efficiency up to 80 %,  
427 which is sensibly similar (81 %) to layouts with SNG production, using reforming, and with the same  
428 heating and  $\text{CO}_2$ -capture systems. Systems with MeOH production cannot reach as high efficiencies -  
429 they are penalized by the added processing. The power consumption increases significantly because of  
430 the compression process to 96 bar, while the heating demand increases with the inclusion of a reformer and  
431  $\text{CO}_2$ -capture unit with greater processing capacities. Despite the lower efficiency, co-production of methanol  
432 could be attractive from an economical point of view, as methanol is generally valued higher than SNG or  
433 hydrogen.

434 The total efficiency  $\eta_{\text{total}}$ , including the losses occurring in the electrolysis and electricity heating systems,  
435 is lower than the system efficiency by 0 to 2 %-points, except when hydrogen is generated by alkaline  
436 electrolysis. The biggest drop occurs when hydrogen is produced in alkaline electrolyzers. In this case, the  
437 total efficiency is 22 %-point lower than the system efficiency (comparison of SNG-E-G-SE and SNG-E-G-AE  
438 systems). No difference between the system and total efficiencies is observed when hydrogen is generated  
439 internally and char is burnt to heat the reformer.

440 The selection of the  $\text{CO}_2$ -capture unit has a considerable impact on the system design and performance.  
441 In all cases, the  $\text{CO}_2$ -removal process by chemical absorption with MEA is a large heat sink. The heat  
442 requirements cannot be satisfied by heat recovery from other process units, and electrical heating should be  
443 implemented, which results in lower efficiencies. The highest penalty is found for the system configurations  
444 producing MeOH. The grand composite curves (see e.g. Figure 7) demonstrate graphically these limitations,

445 as the pinch point is located at the amine regeneration temperature. Firstly, there is no excess heat at high  
446 temperatures that can be valorized through, for example, Rankine cycles. Secondly, in theory, excess heat  
447 from below the pinch could be transferred to higher temperatures through heat pumps, which would decrease  
448 the heat demand of the MEA process. However, such solutions are impracticable: little heat is available in  
449 the range 105-120 °C, and large temperature lifts are not feasible.

450 The integration of alternative CO<sub>2</sub>-removal methods, such a physical absorption, eliminates the heat  
451 demand at low temperatures in all scenarios. The system efficiency is higher by 4 to 10 %-points if MEA  
452 absorption processes are replaced, and the polygeneration systems become self-sufficient, excluding the  
453 steam reforming needs. The grand composite curves show that the pinch point is located at the reforming  
454 temperature for such configurations. The system efficiency could be improved by implementing a Rankine  
455 cycle (steam or organic) to convert the high- and moderate-temperature heat into power, which may be  
456 promising in large-scale applications, or by producing district heating water. Finally, using solid oxide  
457 electrolyzers is more beneficial than implementing alkaline electrolyzers. SOECs present higher electricity-  
458 to-hydrogen efficiencies and benefit from synergies with the other processes present in the polygeneration  
459 system (steam can be generated internally).

## 460 5. Conclusion

461 In this paper, novel polygeneration concepts based on catalytic hydropyrolysis and hydrodeoxygenation  
462 were analysed and compared via process simulation and thermodynamic analysis. These systems have the  
463 potential of converting biomass into high-quality bio-oil, liquid (MeOH) and gaseous (SNG and H<sub>2</sub>) fuels -  
464 and flowsheet models of twelve promising layouts were developed based on literature and industrial data.  
465 The possibilities for improving their performance by process and energy integration were investigated in  
466 details. A standard hydropyrolysis system without additional fuel co-generation displays an efficiency in the  
467 range of approximately 61 % (LHV), based on a representative published experiment (GTI). The system  
468 performance is increased by 7 to 28 %-points when co-producing SNG, 10 to 21 %-points when producing H<sub>2</sub>,  
469 and 10 to 17 %-points when producing MeOH. Carbon conversion efficiencies are highest when generating  
470 SNG or MeOH and reach a maximum when electrolysis is implemented (98 % and 95 %), since there are no  
471 carbon losses associated with the CO<sub>2</sub>-separation process. SNG production systems present higher energy  
472 efficiency compared to H<sub>2</sub> and MeOH ones, as they require less processing. Besides the choice of the by-  
473 product, the plant performance is strongly dependent on the selection of the CO<sub>2</sub>-separation process and  
474 electrolysis unit. Systems with chemical absorption suffer from a large heating demand at low temperature  
475 level, which can be satisfied only by burning bio-char, or, in most cases, by electrical heating. Systems  
476 with solid oxide electrolyser cells benefit from synergies with the fuel synthesis processes, using waste heat  
477 for steam production. The presented results highlight the potential of polygeneration, in this case for

478 hydropyrolysis based systems, and furthermore shows the potential for input of renewable electricity in fuels  
479 and chemicals production. However, the increases in efficiency come at the expense of more complex plant  
480 designs, and detailed economic analyses are needed to evaluate the competitiveness of each option.

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#### 484 **Appendix A. Experiment 5/25**

485 The so-called experiment 5/25 used maple fed for 18.4 hours [29]. The weight recovery, relative to  
486 biomass, on a dry and ash-free basis, was 103.9 % with a carbon recovery of 98.6 %. The yields were 27.9 %  
487 for liquid hydrocarbons ( $C_4^+$ ), 15.6 % for light hydrocarbons ( $C_1-C_3$ ), 10.3 % for  $CO_2$ , 6 % for CO, 8.7 % for  
488 char and 36.1 % for water. The composition of the hydrocarbon gas is, on a weight basis, 31.3 %  $CH_4$ , 42 %  
489  $C_2H_6$  and 26.8 %  $C_3H_8$ . The composition of bio-oil is, on a weight basis, 87.4 % carbon, 10.9 % hydrogen,  
490 less than 1 % oxygen, and less than 0.01 % nitrogen and sulfur. The composition of char is, on a weight basis,  
491 78.5 % carbon, 3.5 % hydrogen, 0.4 % nitrogen, and 11.7 % ash. The recovered water has about 0.6 %-wt  
492 carbon, and has a negligible content of sulfur and ammonia.

#### 493 **Appendix B. Polygeneration of bio-oil and synthetic natural gas, with chemical absorption** 494 **(SNG-R-G-CA)**

495 The layout of the polygeneration system SNG-R-G-CA is presented in Figure B.10 with the corresponding  
496 data in Table B.6.

Table B.6: Process data of the investigated polygeneration system for production of bio-oil and synthetic natural gas, with chemical absorption.

Node	m (kg/s)	T (°C)	p (bar)	Node	m (kg/s)	T (°C)	p (bar)
1	5.76	25	22.4	24	5.03	25	5
2	3.19	25	22.4	25	3	25	5
3	8.95	429	22.4	26	0.64	25	5
4	0.52	429	22.4	27	0.64	234	22.4
5	8.43	429	22.4	28	2.53	25	22.4
6	8.43	363	22.4	29	0.15	25	22.4
7	8.43	367	22.4	30	0.13	25	22.4
8	8.43	429	22.4	31	0.13	675	22.4
9 {bio-oil}	1.57	25	22.4	32	0.24	675	22.4
9 {water}	2.22	25	22.4	33	0.79	725	22.4
10	4.64	25	22.4	34	0.1	725	22.4
11	2.11	25	22.4	35	0.79	374	22.4
12	1.82	25	22.4	36	0.79	25	22.4
13	1.67	25	1.1	37	0.7	25	22.4
14	1.67	167	5	38	0.09	25	22.4
15	1.67	219	5	39	0.99	25	22.4
16	2	152	5	40	0.99	250	22.4
17	3.67	172	5	41	0.99	300	22.4
18	3.67	750	5	42	0.99	40	22.4
19	3.67	900	5	43	0.64	40	22.4
20	3.67	250	5	44	0.34	40	22.4
21	1.36	152	5	45	0.64	25	22.4
22	5.03	223	5	46	0.51	25	22.4
23	5.03	250	5	47	1.39	25	5

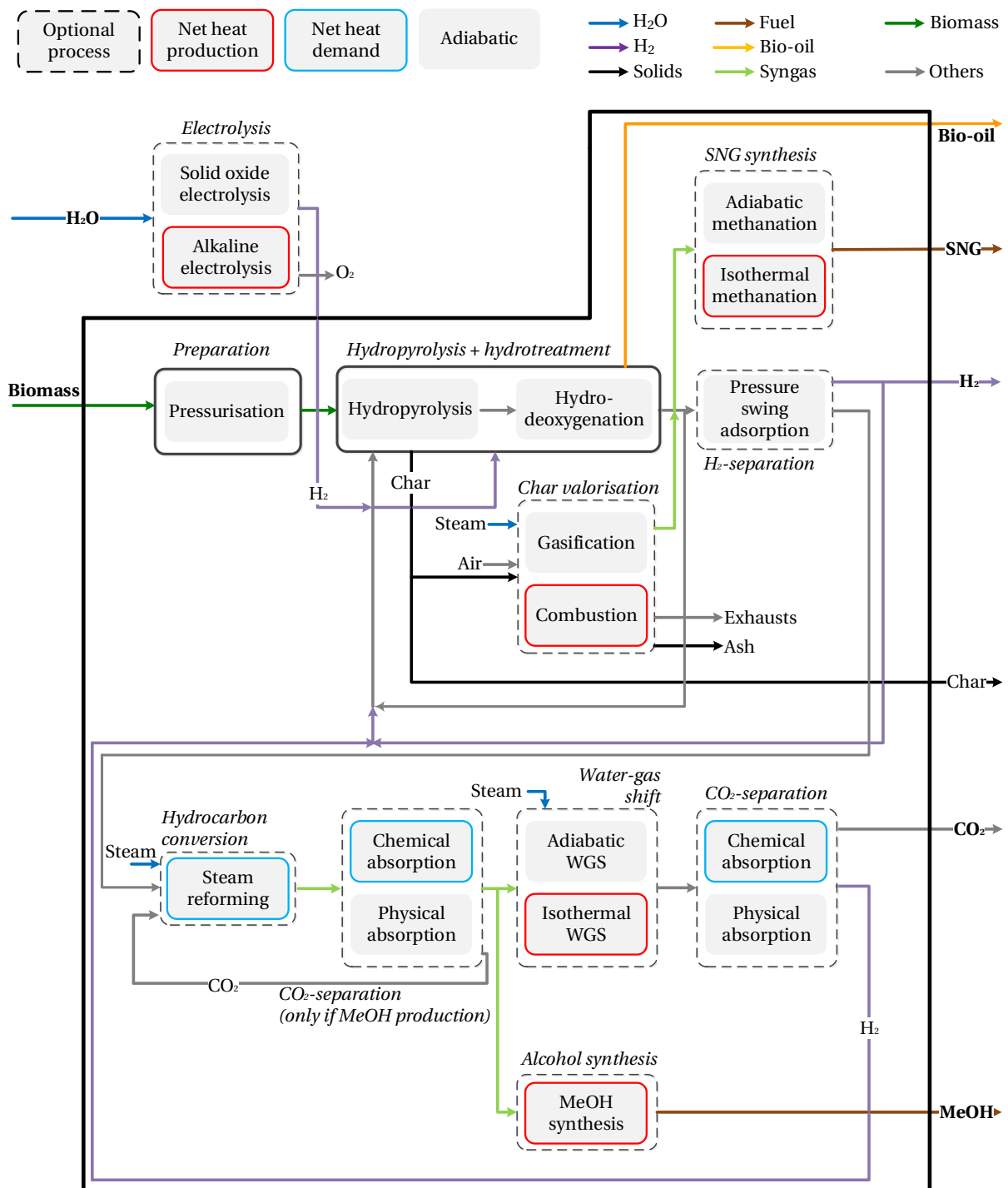


Figure 2: Superstructure of the polygeneration system for production of bio-oil, SNG, H<sub>2</sub> and MeOH through hydropyrolysis and hydrodeoxygenation.





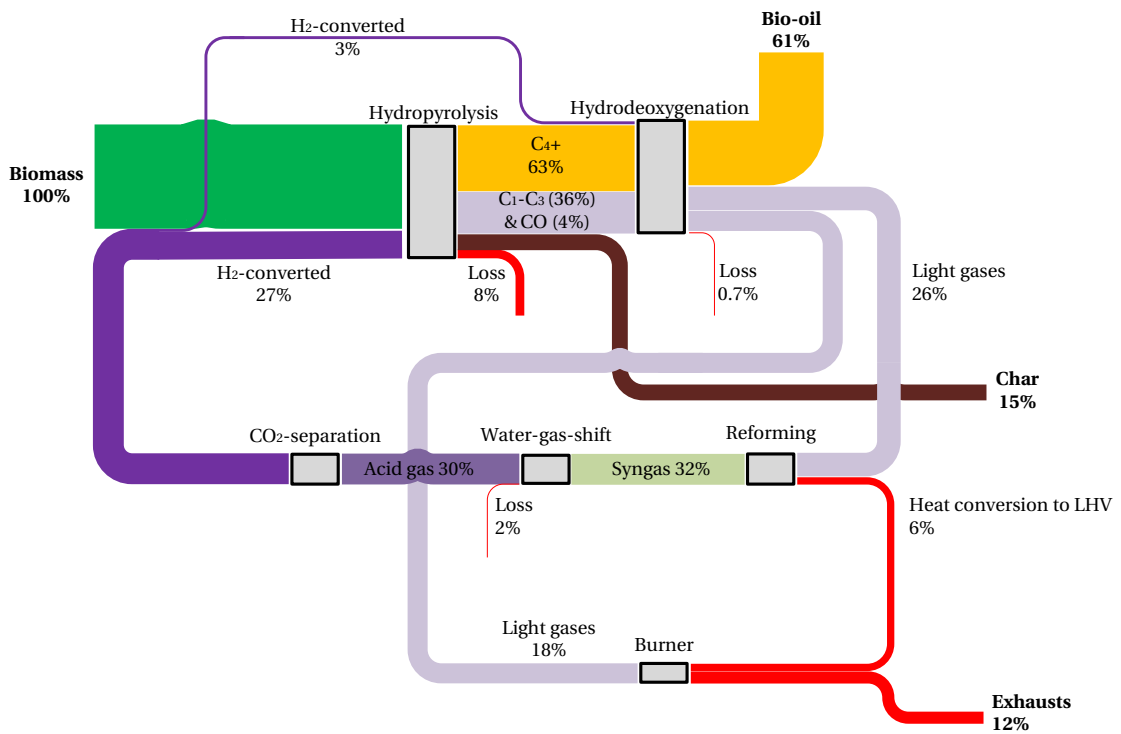


Figure 4: Sankey diagram (chemical energy flows) of the standard hydrolysis system.

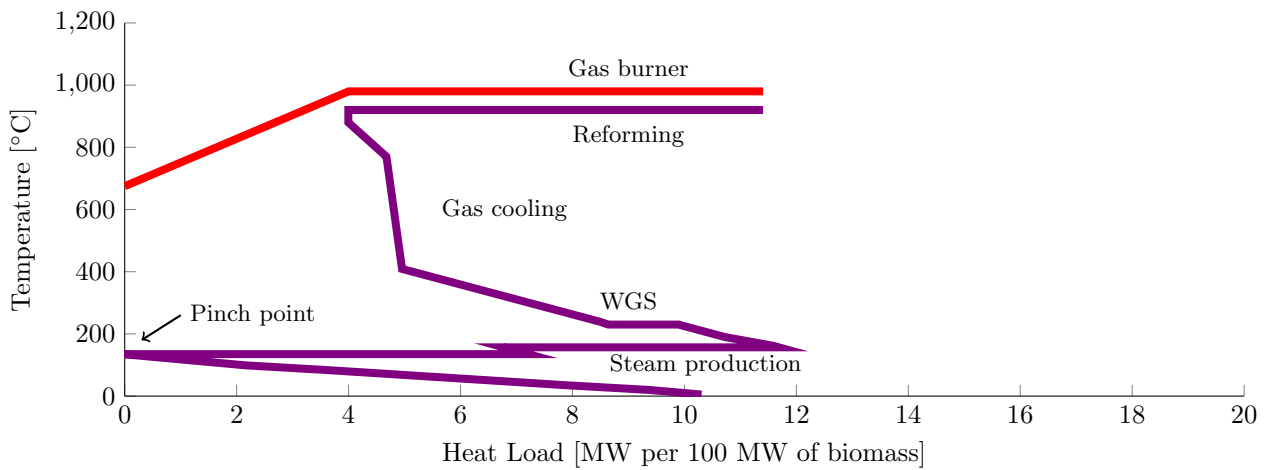


Figure 5: Composite curves for the standard hydrolysis system

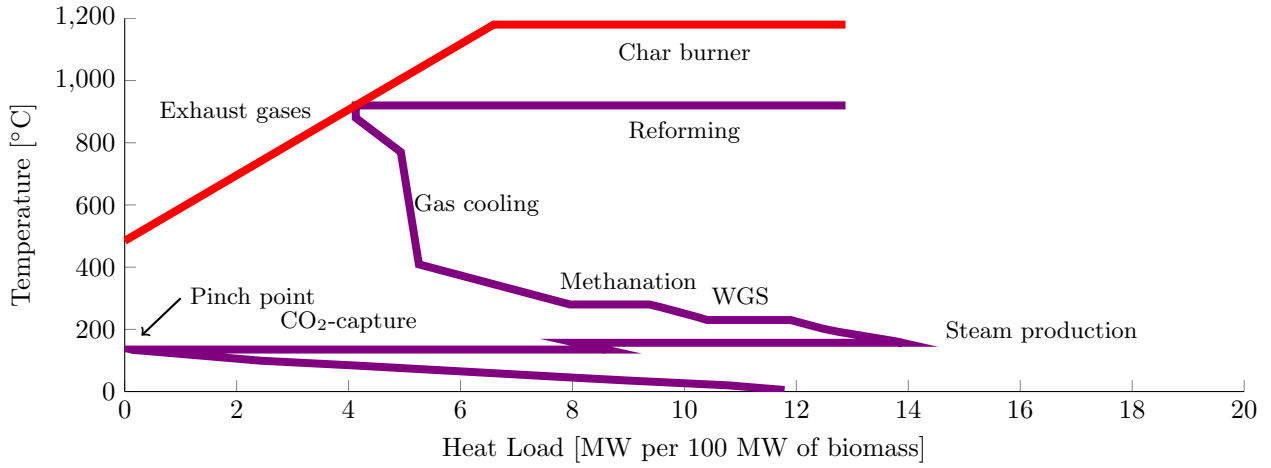
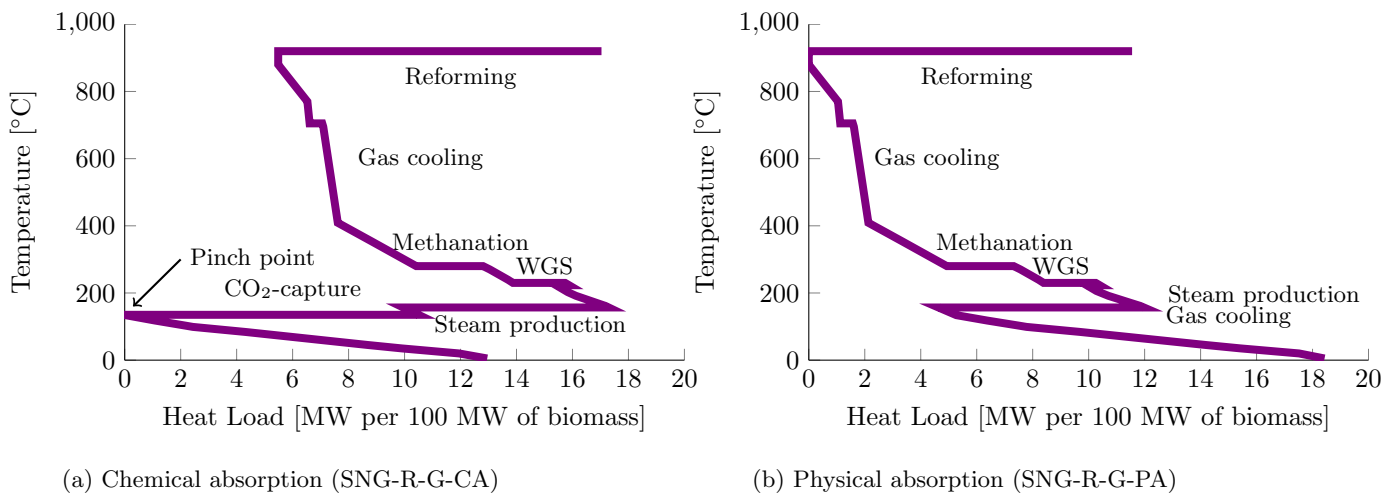


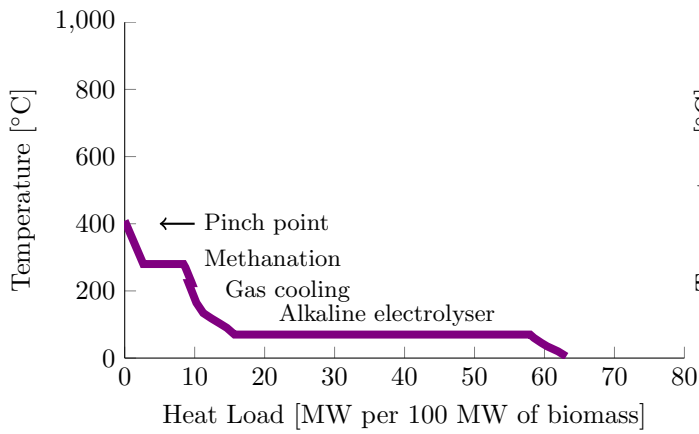
Figure 6: Composite curves for the polygeneration system with SNG production, char combustion and chemical absorption (SNG-R-C-CA)



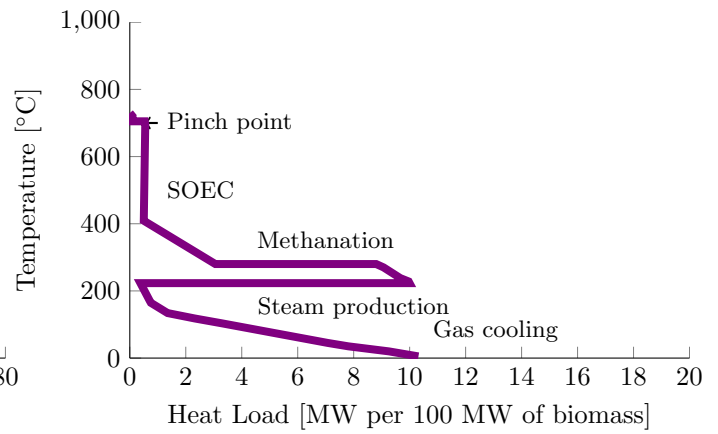
(a) Chemical absorption (SNG-R-G-CA)

(b) Physical absorption (SNG-R-G-PA)

Figure 7: Composite curves for the polygeneration systems with SNG production, gas reforming and char gasification

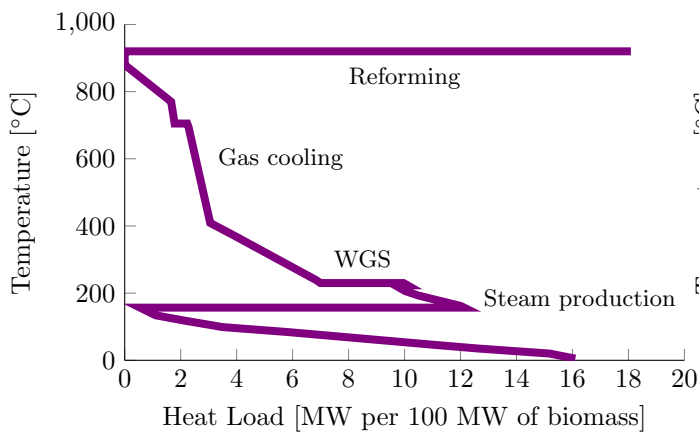


(a) Alkaline electrolysis (SNG-E-G-AE)

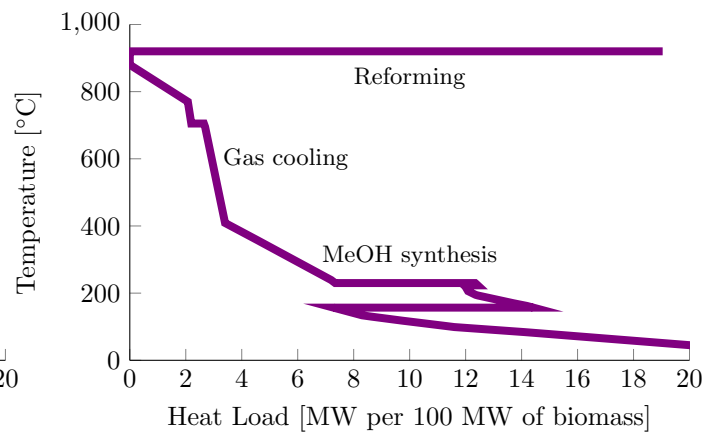


(b) Solid oxide electrolysis cell (SNG-E-G-SE)

Figure 8: Composite curves for the polygeneration systems with SNG production and electrolysis



(a) H<sub>2</sub>-production (H<sub>2</sub>-R-G-PA)



(b) MeOH production (MeOH-R-G-PA)

Figure 9: Composite curves for the polygeneration systems with H<sub>2</sub> and MeOH production

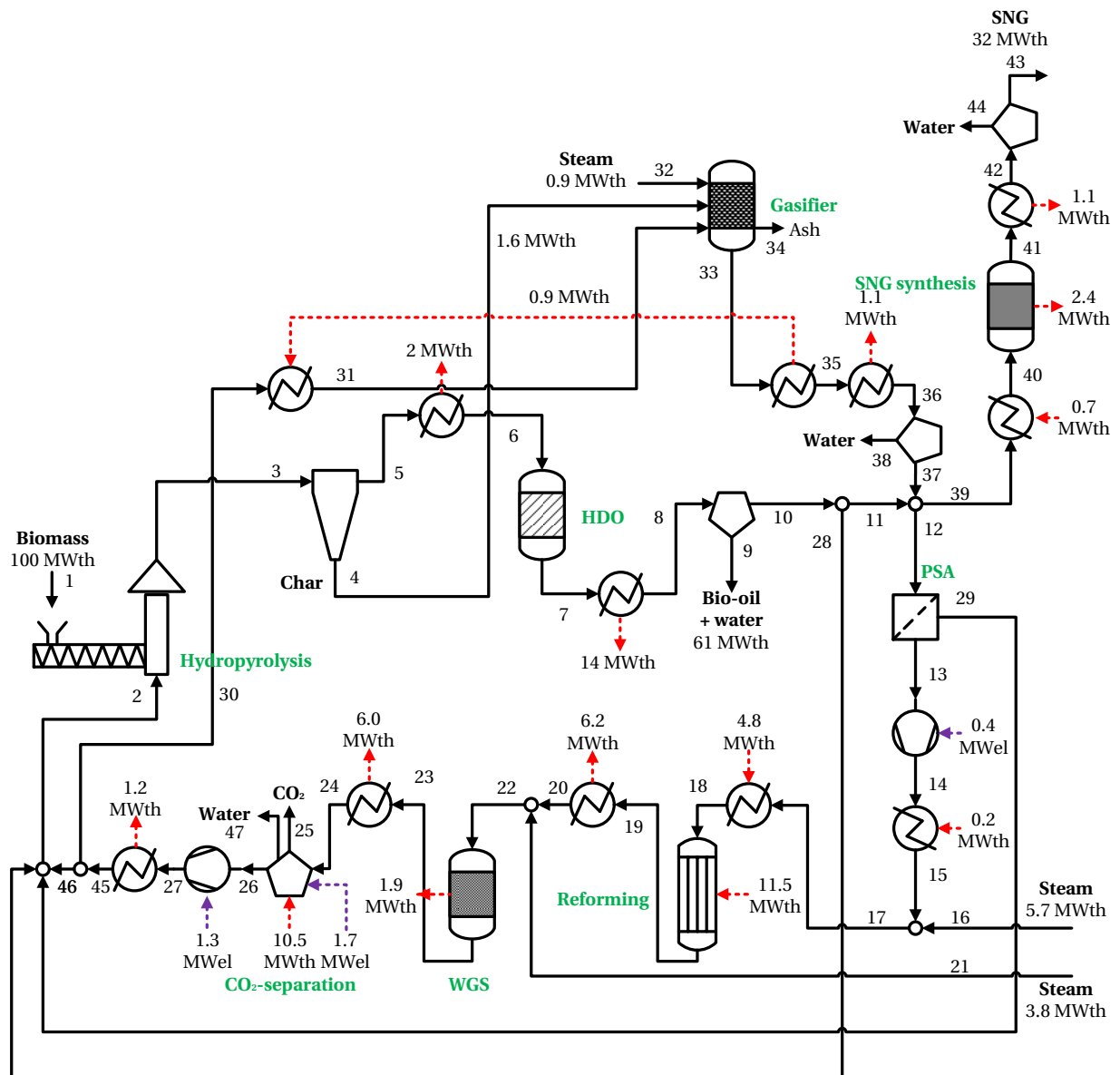


Figure B.10: Process flow diagram of the investigated polygeneration system for production of bio-oil and synthetic natural gas, with chemical absorption.



Table C.7: Process data of the investigated polygeneration system for production of bio-oil and synthetic natural gas, with physical absorption.

Node	m (kg/s)	T (°C)	p (bar)	Node	m (kg/s)	T (°C)	p (bar)
1	5.76	25	22.4	24	3.64	25	5
2	3.19	25	22.4	25	3.64	215	22.4
3 0.64 3	8.95	429	22.4	26	3.64	25	22.4
4	0.52	429	22.4	27	3	25	1.1
5	8.43	429	22.4	28	2.53	25	22.4
6	8.43	363	22.4	29	0.15	25	22.4
7	8.43	367	22.4	30	0.13	25	22.4
8	8.43	429	22.4	31	0.13	675	22.4
9 {bio-oil}	1.57	25	22.4	32	0.24	675	22.4
9 {water}	2.22	25	22.4	33	0.79	725	22.4
10	4.64	25	22.4	34	0.1	725	22.4
11	2.11	25	22.4	35	0.79	374	22.4
12	1.82	25	22.4	36	0.79	25	22.4
13	1.67	25	1.1	37	0.7	25	22.4
14	1.67	167	5	38	0.09	25	22.4
15	1.67	219	5	39	0.99	25	22.4
16	2	152	5	40	0.99	250	22.4
17	3.67	172	5	41	0.99	300	22.4
18	3.67	750	5	42	0.99	40	22.4
19	3.67	900	5	43	0.64	40	22.4
20	3.67	250	5	44	0.34	40	22.4
21	1.36	152	5	45	0.64	25	22.4
22	5.03	223	5	46	0.51	25	22.4
23	5.03	250	5	47	1.39	25	5
				48	3.64	25	5





Table D.8: Process data of the investigated polygeneration system for production of bio-oil and synthetic natural gas, with electrolysis.

Node	m (kg/s)	T (°C)	p (bar)	Node	m (kg/s)	T (°C)	p (bar)
1	5.76	25	22.4	16	0.09	25	22.4
2	3.26	25	22.4	17	0.44	25	22.4
3	9.02	429	22.4	18	0.09	675	22.4
4	0.52	429	22.4	19	0.24	675	22.4
5	8.5	429	22.4	20	0.1	725	22.4
6	8.5	363	22.4	21	0.75	725	22.4
7	8.5	367	22.4	22	0.75	384	22.4
8	8.5	25	22.4	23	0.75	25	22.4
9 {bio-oil}	1.57	25	22.4	24	0.09	25	22.4
9 {water}	2.22	25	22.4	25	0.65	25	22.4
10	4.71	25	22.4	26	2.54	25	22.4
11	1.88	25	22.4	27	2.54	250	22.4
12	2.82	25	22.4	28	2.54	300	22.4
13	4.69	25	22.4	29	2.54	40	22.4
14	4.17	25	22.4	30	0.81	40	22.4
15	0.52	25	22.4	31	1.72	40	22.4



Table E.9: Process data of the investigated polygeneration system for production of bio-oil and molecular hydrogen, with chemical absorption.

Node	m (kg/s)	T (°C)	p (bar)	Node	m (kg/s)	T (°C)	p (bar)
1	5.76	25	22.4	21	2.17	152	5
2	2.73	25	22.4	22	8.01	223	5
3	8.49	429	22.4	23	8.01	250	5
4	0.52	429	22.4	24	8.01	25	5
5	7.97	429	22.4	25	4.77	25	5
6	7.97	363	22.4	26	1.03	25	5
7	7.97	367	22.4	27	1.03	234	22.4
8	7.97	25	22.4	28	1.84	25	22.4
9 {bio-oil}	1.57	25	22.4	29	0.31	25	22.4
9 {water}	2.22	25	22.4	30	0.13	25	22.4
10	4.18	25	22.4	31	0.13	675	22.4
11	2.34	25	22.4	32	0.24	675	22.4
12	3.03	25	22.4	33	0.79	725	22.4
13	2.71	25	1.1	34	0.1	725	22.4
14	2.71	170	5	35	0.79	394	22.4
15	2.71	219	5	36	0.79	25	22.4
16	3.13	152	5	37	0.7	25	22.4
17	5.84	173	5	38	0.09	25	22.4
18	5.84	750	5	39	1.03	25	22.4
19	5.84	900	5	40	0.9	25	22.4
20	5.84	250	5	41	2.21	25	5

508 **Appendix F. Polygeneration of bio-oil and methanol, with chemical absorption (MeOH-R-G-**  
509 **CA)**

510 The layout of the polygeneration system MeOH-R-G-CA is presented in Figure [F.14](#) with the corre-  
511 sponding data in Table [F.10](#).

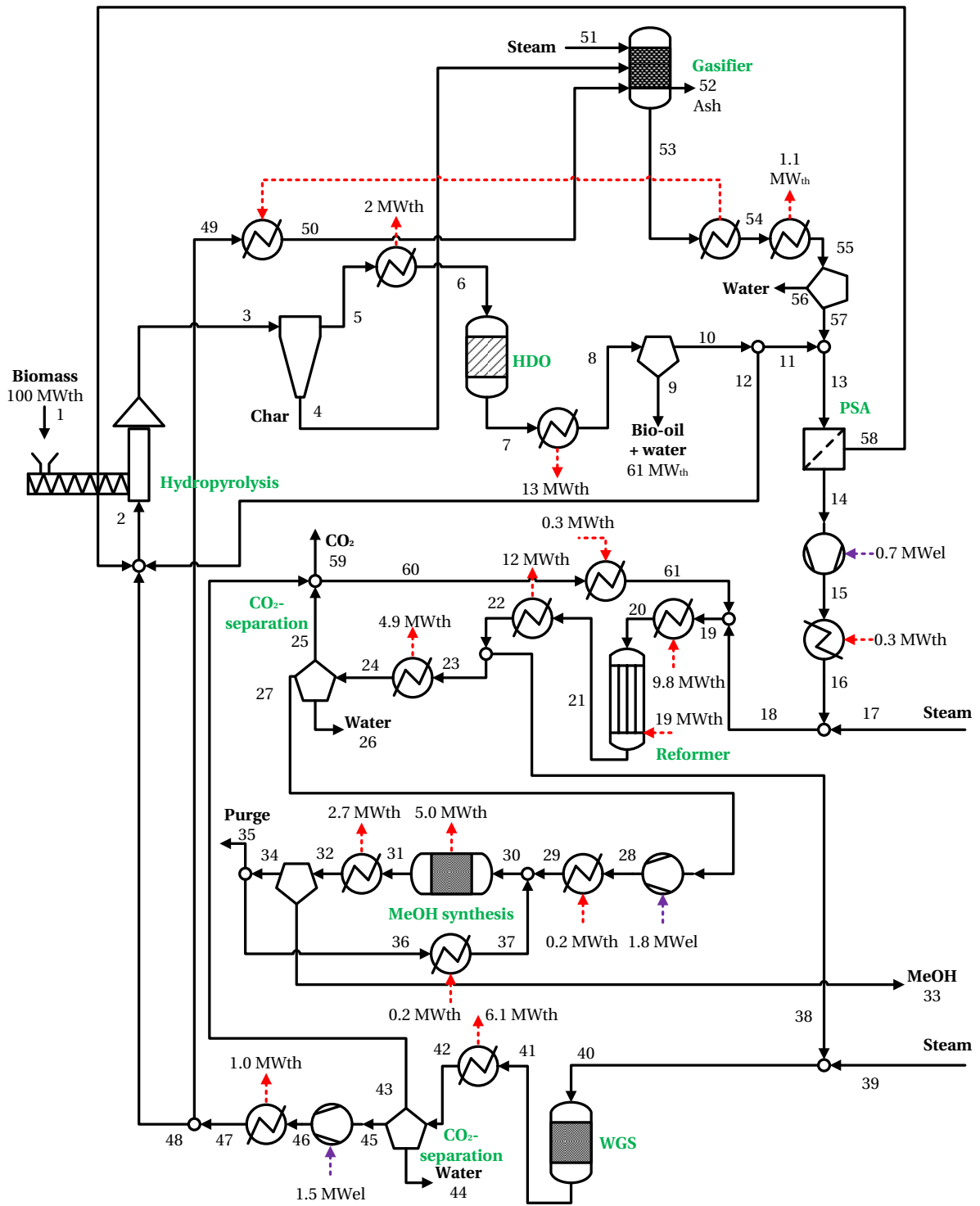


Figure F.14: Process flow diagram of the investigated polygeneration system for production of bio-oil and methanol, with chemical absorption.

Table F.10: Process data of the investigated polygeneration system for production of bio-oil and methanol, with chemical absorption.

Node	m (kg/s)	T (°C)	p (bar)	Node	m (kg/s)	T (°C)	p (bar)
1	5.76	25	22.4	31	2.10	300	96
2	2.38	25	22.4	32	2.10	25	96
3	8.14	429	22.4	33	1.65	25	96
4	0.52	429	22.4	34	0.45	25	96
5	7.62	429	22.4	35	0.02	25	96
6	7.62	363	22.4	36	0.43	25	96
7	7.62	367	22.4	37	0.43	200	96
8	7.62	25	22.4	38	4.63	250	5
9 {bio-oil}	1.57	25	22.4	39	1.55	152	5
9 {water}	2.22	25	22.4	40	6.18	222	5
10	3.83	25	22.4	41	6.18	376	5
11	2.40	25	22.4	42	6.18	25	5
12	1.43	25	22.4	43	3.37	25	5
13	3.15	25	22.4	44	2.05	25	5
14	2.78	25	1.1	45	0.76	25	5
15	2.78	173	5	46	0.76	222	22.4
16	2.78	219	5	47	0.76	25	22.4
17	3.86	152	5	48	0.58	25	22.4
18	6.64	180	5	49	0.18	25	22.4
19	8.49	185	5	50	0.18	675	22.4
20	8.49	750	5	51	0.25	675	22.4
21	8.49	900	5	52	0.1	725	22.4
22	8.49	250	5	53	0.85	725	22.4
23	3.85	250	5	54	0.85	377	22.4
24	3.85	25	5	55	0.85	25	22.4
25	0.99	25	5	56	0.1	25	22.4
26	1.19	25	5	57	0.75	25	22.4
27	1.68	25	5	58	0.37	25	22.4
28	1.68	151	96	59	2.51	25	5
29	1.68	200	96	60	1.85	25	5
30	2.10	200	96	61	1.85	219	5



Table G.11: Process data of the investigated polygeneration system for production of bio-oil and methanol, with electrolysis and with chemical absorption.

Node	m (kg/s)	T (°C)	p (bar)	Node	m (kg/s)	T (°C)	p (bar)
1	5.76	25	22.4	26	3.48	200	96
2	2.29	25	22.4	27	4.34	200	96
3	8.05	429	22.4	28	4.34	250	96
4	0.52	429	22.4	29	4.34	250	96
5	7.53	429	22.4	30	3.45	25	96
6	7.53	363	22.4	31	0.90	25	96
7	7.53	367	22.4	32	0.03	25	96
8	7.53	25	22.4	33	0.86	25	96
9 {bio-oil}	1.57	25	22.4	34	0.86	200	96
9 {water}	2.22	25	22.4	35	0.32	25	22.4
10	3.74	25	22.4	36	3.15	25	22.4
11	2.03	25	22.4	37	2.80	25	22.4
12	1.71	25	22.4	38	0.35	25	22.4
13	2.68	25	22.4	39	0.26	25	22.4
14	2.36	25	1.1	40	0.09	25	22.4
15	2.36	167	5	41	0.09	675	22.4
16	2.36	219	5	42	0.10	725	22.4
17	3.59	152	5	43	0.75	725	22.4
18	5.95	178	5	44	0.75	384	22.4
19	8.3	176	5	45	0.75	25	22.4
20	8.3	750	5	46	0.09	25	22.4
21	8.3	900	5	47	0.66	25	22.4
22	8.3	250	5	48	2.48	25	5
23	2.34	25	5	49	2.34	178	5
24	3.48	25	5	50	0.24	675	22.4
25	3.48	151	96				



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