THREE INTEGRATED PROCESS SIMULATION USING ASPEN PLUS®: PINE GASIFICATION, SYNGAS CLEANING AND METHANOL SYNTHESIS

M. Puig-Gamero, J. Argudo-Santamaria, J.L. Valverde, P. Sánchez, L. Sanchez-Silva*

Department of Chemical Engineering, University of Castilla –La Mancha, Avda. Camilo José Cela 12, 13071 Ciudad Real, Spain

*Corresponding author phone: +34 926 29 53 00 ext. 6307; fax: +34 926 29 52 56;

e-mail: marialuz.sanchez@uclm.es

Keywords: Biomass, gasification, PSA, methanol, syngas, Aspen Plus® simulation

Abstract

The methanol synthesis from syngas obtained through pine biomass gasification was studied using Aspen Plus® simulation software. The gasification process was simulated using a thermodynamic equilibrium model which is based on the minimization of the Gibbs free energy of the system. A double chamber gasifier, which allows the separation of the gasification and combustion zones to obtain a high-quality gas, was considered. Furthermore, part of the char was burnt in the combustion chamber increasing the bed temperature and generating all the energy needed in the process. On the other hand, effect of the gasification temperature and the steam to biomass (S/B) mass ratio during the gasification process on the syngas composition, tar yield and methanol production were evaluated. In this sense, the H_2/CO ratio was calculated to stablish the best operating conditions for the production of methanol, being the best calculated operational condition of the process 900ºC and a S/B mass ratio of 0.9. In order to clean the syngas for the methanol synthesis and capture the greenhouse gases, a pressure swing adsorption (PSA) process was considered. Furthermore, the influence of pressure and temperature on the methanol synthesis was researched to select the optimal conditions for methanol production. Finally, the methanol synthesis waste stream was recycled to the combustion chamber in order to analyse its effect on the process performance.

1. Introduction

The current environmental problem due to the massive use of fossil fuel for power generation, has forced the search of new and more sustainable alternatives as renewable energy and new agreements to face the continuous energy demand. For this reason, several countries agreed at the Paris Climate Change Conference (COP21) to limit the global temperature increase in less than 2ºC compared to that the beginning of the

industrial revolution by the year 2035 [1]. In this sense, the biomass is presented as one of the promising choice for the replacement of conventional fossil fuels in the near future, contributing to the reduction of greenhouse emissions. In addition, one of the main competitive advantage of biomass with respect to the rest of renewable energy is that it can obtain added value products similar to those obtained with fossil fuels and power. However, at the present, the technologies required for biomass transformation are not mature enough.

Lignocellulosic biomass can be converted to chemical products and biofuels via thermochemical or biochemical routes. However, the last one is a more expensive and complex technique than thermochemical route [2]. Pyrolysis, gasification, combustion and liquefaction are the most common thermochemical processes to convert the lignocellulosic biomass to biofuels. Among them, the gasification is considered as most cost-effective and efficient for lignocellulosic biomass conversion [2]. Moreover, the gasification is more environmentally friendly due to the low–oxidation conditions, emitting less greenhouse gases [3]. Biomass gasification can be defined as the conversion of biomass into a gaseous fuel in a partial oxidation atmosphere at high temperatures. The main gas product obtain is the syngas, which can be burnt directly, used as fuel for gas turbine, or can be used to produce added value chemicals. The gasifying agent used on gasification can be air, steam, oxygen or carbon dioxide. Air is currently the most used because of its low cost, but the syngas obtained has low heating value. Pure oxygen produce higher quality syngas but it involves high operating costs. For its part, steam gasification improves the quality of the product gas, increasing the hydrogen yield and decreasing the tar an char yield [4] .The syngas from biomass mainly consists of hydrogen and carbon monoxide but it also have methane, carbon dioxide, water vapor, nitrogen and some impurities like tars, ammonia and hydrogen sulphide.

One of the main technical barriers and problems for synthesis gas production is the presence of tars in the syngas. Among all chemical and physical techniques, catalytic conversion is the most used technique since the presence of catalyst can remove tar more effectively and, at the same time, convert tar into useful gas at lower temperature than non-catalytic gas tar conversion route [5] [6]. Dolomite, for its part, is presented as an attractive option since it is a cheap material and exhibits catalytic activity and effectiveness to reduce tars during gasification process in both laboratory and pilot scales [7, 8].

The syngas obtained from biomass gasification can be used for the synthesis of chemicals such as methanol. Methanol is an important industrial chemical, which can be used directly as a clean fuel or can be mixed with others conventional fuels. Furthermore, many chemical products such as formaldehyde, methyl tertiary butyl ether, acetic acid or gasoline can be obtained from it. The syngas obtained from biomass gasification must be cleaned before methanol synthesis. The most frequently used technology for CO_2 removal from syngas is the absorption process with MEA. However, this process is expensive and largescale is only cost-effective [9]. In this way, pressure swing adsorption (PSA) has become very prominent in the purification of gases for multiple applications. This technology reduces energy consumption without the need of using toxic and corrosive chemicals as in chemical absorption [10]. Several process to separate H_2 and CO by PSA system have been patented. Krishnamurthy et al. [11] studied a method to separate both components using two PSA systems. Recently, Batdorf et al. [12] proposed a method to remove CO_2 from effluent gas through the PSA, generating a syngas stream acceptable to produce methanol or other liquid fuels.

On the other hand, the process simulation is an increasingly important tool for the chemical industry that allows to scale up a process which requires a knowledge of the

97 influence of the operating conditions on the plant performance. In addition, the process
98 simulation also allow to reduce costs and time [13]. There are many commercial
99 simulators of chemical engineering processes, being Aspen Plus® one of the most used.

100 Although there are several studies about coal gasification simulation, nowadays,
101 more and more researches are focused on the biomass gasification. Pauls et al., simulated
102 the gasification of pine sawdust in the presence of both air and steam. They used a
103 Bubbling Fluidized Bed gasifier including a temperature-dependent pyrolysis model and
104 the inclusion of tar formation and reaction kinetics [14]. In addition, Zhai et al., proposed
105 also a two-stage biomass pyrolysis and gasification scheme for pine sawdust. In this case,
106 part of the gas product combusts in a burner outside of the gasifier to produce the flue gas
107 and the heat required for pyrolysis and steam gasification. They established a zero-
108 dimensional thermodynamic equilibrium model [15]. On the other hand, Nilsson et al.,
109 simulated also a fluidized bed dividing it into three zones: pyrolysis of biomass,
110 homogeneous and heterogeneous reactions, each one with its corresponding kinetics
111 obtained from literature and experiments[16]. Finally, Im-orb et al., separated the
112 gasification model into two sections, the first one combined pyrolysis and oxidation
113 reactions which are assumed to be at thermodynamic equilibrium, and the second one,
114 involved the char reduction reactions [17]. Fernández-López et al., simulated the
115 gasification of an animal waste biomass in a dual gasifier. They used a model based on a
116 Gibbs free energy reactor with the gasification and combustion zones separated [18].

117 Up to now, the most simulations using Aspen Plus® simulation software have focused
118 on the gasification stage with different biomasses, temperatures and steam to biomass
119 (S/B) mass ratio in order to improve the syngas composition. However, fewer studies
120 have considered the tar formation and, thus, the addition of tar reforming using natural
121 catalyst as a dolomite. Moreover, this study presents the novelty of simulating three

process integrated: the gasification process with tar reforming, the syngas cleaning using PSA and the subsequent use for the methanol synthesis, becoming a product with a high-added value. The present work includes the simulation of the biomass gasification, syngas purification and its use in the methanol synthesis becoming a product with a high-added value. In addition, the combination of different operating conditions, such as the temperature and the S/B mass ratio in the gasification process were studied to stablish the best ones for the production of methanol. In this way, the best operating conditions (temperature and pressure) in the case of methanol synthesis were also evaluated. Finally, a recycle stream was considered in order to improve the system.

2. Materials and methods

2.1 Biomass sample

The biomass selected was a pine sample from the region of Castilla-La Mancha (Spain). The Table 1 shows the ultimate and proximate analysis of the pine sample.

Table 1. Proximate and ultimate analysis of pine biomass.

Ultimate Analysis (wt.%)*					***Proximate Analysis (wt.%)****			
C	***H***	***N***	***S***	***O****	***Ash***	***VM****	***FC****	***Moisture***
52.7	5.52	0.01	0.08	41.7	2.7	61.6	31.3	4.4

daf: dry and ash free basis; O: % of oxygen calculated from difference of C, H, N and S; VM*: Volatile matter; FC*: % of fixed carbon calculated from the difference from moisture, ash and volatile matter.

2.2 Aspen plus modelling

Figure 1 shows the Aspen Plus® flowsheet for the methanol synthesis from biomass. The steps involved in the production of methanol from biomass are: gasification process,

142 syngas cleaning and methanol synthesis. In order to simplify the explanation of the
143 simulation, the three main parts will be explained step by step. Firstly, the biomass is
144 gasified using steam as gasifying agent. The product gas is fed to PSA system in which
145 the gas is cleaning and adjusting to achieve a H_2/CO ratio close to 2.4-2.5. Finally, the
146 syngas with the correct ratio is fed to methanol synthesis.

147 In the simulation, the biomass is defined as non-conventional component, specifying
148 its ULTANAL and PROXANAL analysis. The HCOALGEN and DCOALGEN models
149 were selected for the enthalpy and density of the solids calculation, respectively. The ash
150 was selected as non-conventional component and 100% of ash was fixed for the ultimate
151 and proximate analysis. The fluid-dynamic package selected was Peng-Robinson with
152 Boston Mathias function, being the appropriate for high temperature gasification
153 processes [19]. The char (it was considered to be 100 % carbon) and catalyst (Dolomite
154 and Cu/ZnO) were defined as conventional solid, whereas the rest of the components: H_2,
155 CO, CO_2, CH_4, H_2O, H_2S, N_2, NH_3, C_6H_6 and CH_3OH, were defined as fluids.

156 2.2.1 Gasification process

157 In this work, an equilibrium model based on a Gibbs free energy minimization was
158 used to model a dual fluidized bed gasifier for the conversion of pine biomass into syngas.
159 In this kind of reactors, the combustion zone is independent of the gasification zone,
160 moreover, the combustion heat is used in the rest of the process, involving energy savings.
161 On the other hand, a catalyst bed of dolomite was used to reduce the tar obtained in the
162 product gas. Figure 2 shows the Aspen Plus® flowsheet of the gasification process and
163 Table 2 lists a brief explanation of the blocks used.

164 The main assumption considered in this part of the process are the following [19, 20]:

1. Biomass feed rate is 100 kg/h.
2. Process was steady state and isothermal.
3. Char only contained carbon and ash.
4. Ash is considered to be inert
5. Pressure and temperature were uniform inside the gasifier.
6. No heat and pressure losses took place in the gasifier.
7. All gases were ideal.
8. No unconverted carbon was present in the product.
9. Drying and pyrolysis processes were instantaneous.
10. Tar composition was assumed to be C_6H_6.

Stream 1, whose composition was the biomass, was fed under ambient conditions (25ºC and 1 atm) to the block R-1 to simulate an instant drying and pyrolysis process. In this process, biomass was separated into its constituent components and ash, the yields distribution, which determined the each component mass flow that left the block R-1, was specified according to the elemental analysis of the biomass feedstock. Subsequently, the char combustion process was carried out in block R-5 to achieve the gasification temperature, decreasing the gasifier energy requirement. The gasification zone and combustion zone temperature was the same because it was considered homogenous over the whole process. The amount of char for combustion process was calculated by the design specification DS-4, (Table A4) and was split in the separator column SEP-1. Furthermore, the air flow was calculated using a design specification (DS-3, Table A3) and taking into account an air excess of 1.2 regarding the char burnt in the combustion chamber.

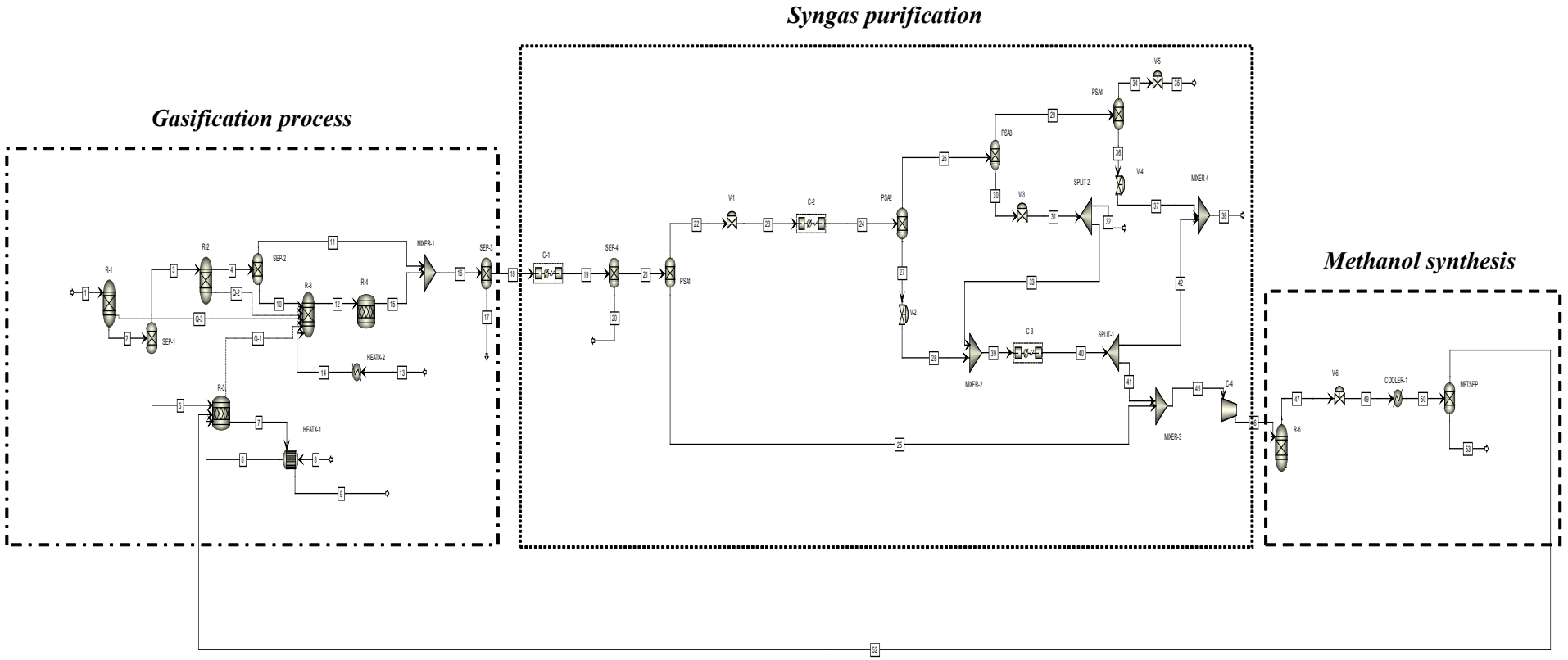


Figure 1. Aspen Plus® flowsheet process

198 Stream 3 containing O_2, H_2, H_2O, C, S and N_2 entered to the equilibrium reactor R-
199 2. In this reactor, C, H_2, CO_2, CO, CH_4, H_2S and NH_3 were fixed as the main reaction
200 products. The outlet gas was introduced into a new separator column where H_2S and NH_3
201 (stream 11) were split from the main fuel stream consisting of C, H_2, CO_2, CO and CH_4
202 (stream 10). Then, the last one was directed to the block R-3 where the gasification
203 process took place. The gasifying agent steam was added to the reactor R-3 as steam at 1
204 bar and 150 ºC (stream 14). Moreover, the energy stream Q-1 simulated the energy which
205 was transferred from the combustion chamber to the gasification one. In addition, blocks
206 R-1 and R-2 were also energy integrated with the gasification block R-3 by the energy
207 streams Q-3 and Q-2, respectively. The reactions involved in gasification process are
208 summarized below:

Water Gas: $C + H_2O \rightleftharpoons CO + H_2$	ΔH = 131 kJ/mol	(1)
Water gas shift: $CO + H_2O \leftrightharpoons CO_2 + H_2$	ΔH = -41 kJ/mol	(2)
Steam reforming: $CH_4 + H_2O \rightleftharpoons CO + 3H_2$	ΔH = 206 kJ/mol	(3)
Boudouard: $C + CO_2 \rightleftharpoons 2CO$	ΔH = 172 kJ/mol	(4)
Tar forming: $6CO + 9H_2 \rightleftharpoons 6H_2O + C_6H_6$	ΔH = -158.3 kJ/mol	(5)

209 On the other hand, the tar reforming using dolomite as a catalyst was simulated in the
210 block R-4. The aim of this block was to convert the tar to syngas due to the tar could condense
211 downstream, blocking the pipelines and causing several problems in compressor or pumps.
212 The reactions involved in the tar decomposition with dolomite are the following:

213

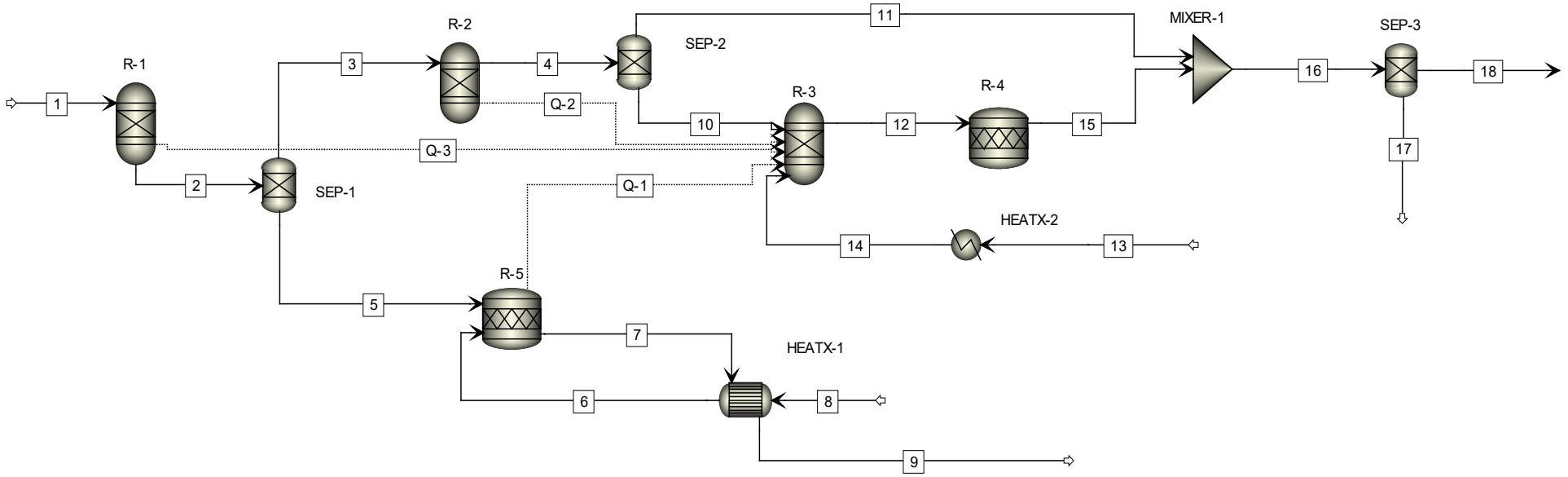


Figure 2. Aspen Plus® flowsheet simulation of the gasification process.

$$DOLOMITE \rightarrow MgO + CaO + 2CO_2 \quad (6)$$

$$C_6H_6 + 6CO_2 \rightarrow 3H_2 + 12CO \quad (7)$$

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \quad (8)$$

Finally, the gas product of gasification process (stream 16) was fed to block SEP-3 to separate the active char (stream 17) from the rest of syngas compounds.

2.2.2 Syngas cleaning: Pressure swing adsorption (PSA)

The aim of this part was to cleaning the outlet gas of gasification in order to obtain a high quality syngas which will be used for the methanol synthesis. The syngas for methanol synthesis must satisfy the following specification:

- $\frac{H_2 - CO_2}{CO + CO_2} \approx 2.1$ (9)
- $\frac{H_2}{CO} = 2.4 - 2.5$ (10)
- $\frac{CO_2}{CO} = 0.13 - 0.14$ (11)

A pressure swing adsorption was simulated to clean the syngas and obtain de optimal ratio requiered. The outlet gas of gasification was introduced into the PSA system, which consisted of four units, as shown in Figure 3. All of them were simulated in a simplified way, by ideal separators, but working at realistic temperature and pressure (35 ºC and 30 atm, respectively) [21].

The syngas obtained from gasification process (stream 18) was compressed to 30 atm and cooled down to 35ºC by the multistage compressor C-1. Then, stream 19 was fed to the column separator SEP-4 to separate the condensed water from the gas stream 21 that went to the PSA system. The PSA system was able to achieve a pure syngas stream to

239 adjust the stoichiometric ratio of methanol feed and, simultaneously, capture CO_2 and
240 CH_4 for their subsequent sequestration.

241 **Table 2.** Blocks description used in the gasification model**.**

NAME	***TYPE***	***DESCRIPTION***
R-1	RYIELD	Biomass pyrolysis reactor, it decomposed the biomass into its compounds and ash. It operated at 1 atm and 800, 900 or 1000ºC depending on the simulation.
SEP-1	SEP	Separator of the amount of char necessary to achieve the gasification temperature.
R-2	RGIBBS	It models chemical equilibrium minimizing the Gibbs free energy. It was used to produce CO_2, CO, CH_4, H_2S and NH_3. It operated at 1 atm and 800, 900 or 1000ºC depending on the simulation.
SEP-2	SEP	Separator of H_2S and NH_3 from C, H_2, CO_2, CO and CH_4.
R-3	RGIBBS	Gasifier. It operated at 1 atm and 800, 900 or 1000ºC depending on the simulation.
R-4	RSTOIC	This reactor allows to introduce a catalyst. It was used to model the tar reforming using Dolomite as a catalyst. It operated at 1 atm and 800, 900 or 1000ºC depending on the simulation.
SEP-3	SEP	It separated the active coal from the syngas.
R-5	RSTOIC	Char combustion reactor. It operated at 1 atm and 800, 900 or 1000ºC depending on the simulation.
HEATX-1	HEATX	Exchange heat between the outlet stream from R-5 and the air inlet stream which was warmed up to 150ºC
HEATX-2	HEATER	Heater to warm up the gasifying agent (water steam) to 150ºC.

242

In the first PSA unit, high purity H_2 was separated (stream 25). There was no pressure drop inside the block. The first PSA unit was depressurized to regenerate the adsorbent. Every depressurization have been simulated by a valve located at the PSA off-gas stream. Then, top stream 23 was again compressed to 30 atm in the compressor C-2 before entering into the second PSA unit (PSA2). In this step, CO was separated as the adsorbed component (stream 27), recovered in the depressurization. Top PSA-2 stream 26 was introduced in the third PSA unit (PSA3) where CH_4 and CO_2 were split in streams CH_4-rich top (29) and CO_2-rich bottom (30). On the one hand, top stream 29 entered to the last PSA unit (PSA4) for the CH_4 capture. On the other hand, a fraction of the bottom gas formed by rich CO_2 was mixed with the rich-CO stream 28 coming from the second PSA unit.

Then, stream 39, whose composition was the mixture of CO and CO_2, was compressed up to 30 atm and mixed with the rich H_2 stream (25) to adjust the specifications 9, 10 and 11. This adjustment was carried out by the design specifications DS-1 and DS-2 (Table A1 and A2). Finally, Table 3 and 4 show a brief explanation of the blocks used in the syngas cleaning and the percentage considered of component recovery in the PSA system according to F.J. Gutiérrez Ortiz et al., [9], respectively.

2.2.3 Methanol synthesis process

Once the syngas was purified and the specifications were achieved, the pure syngas stream was introduced to methanol synthesis reactor. The blocks used to simulate the methanol shyntesis are summarized in Table 5 and Figure 4 shows the methanol synthesis flowsheet. The standard operation condition of the methanol synthesis are in the ranges of 50 to 100 atm and 220 to 280 ºC [9]. In this work, the pressure and temperature of methanol synthesis were varied and evaluated.

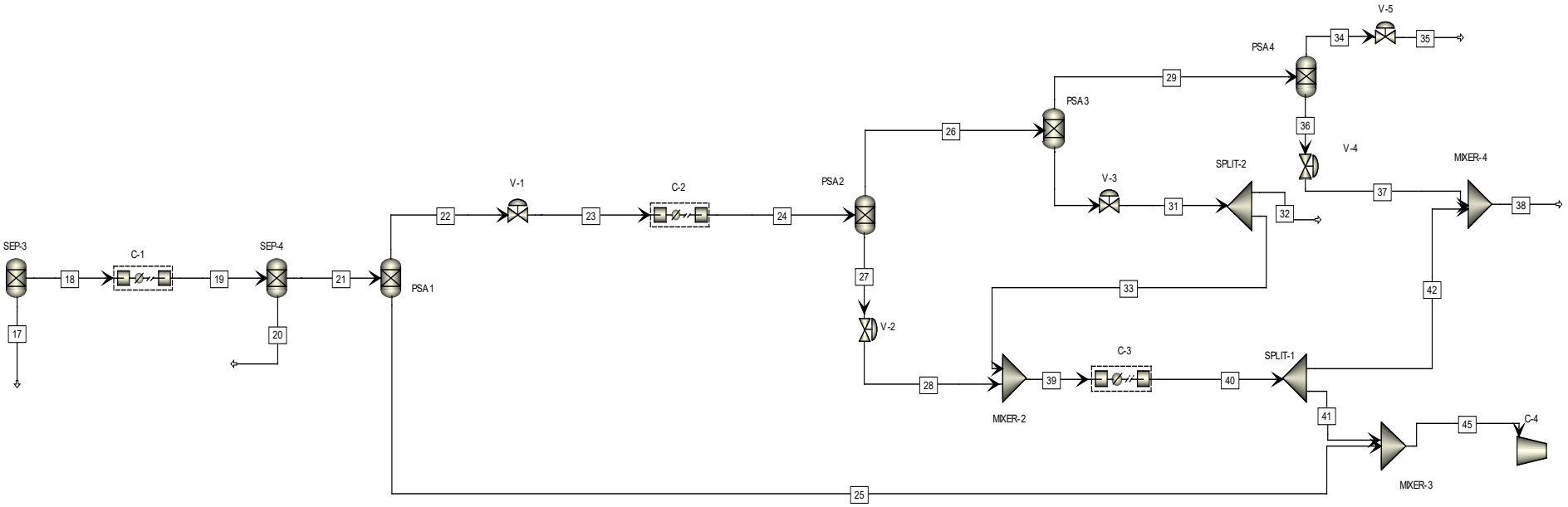


Figure 3. Aspen Plus® flowsheet simulation of the syngas cleaning.

Table 3. Blocks description used in the syngas cleaning model.

NAME	*TYPE*	*DESCRIPTION*
C-1, C-2 and C-3	MULTISTAGE COMPRESSORS	The multistage compressors were used to compress to 30 atm and cool down to 35ºC the unclean gas, the PSA2 inlet stream and the CO and CO_2 mixture, respectively.
SEP-4	SEP	Separator of the water condensed and the syngas.
PSA1, PSA2, PSA3 and PSA4	SEP	Separator to adsorb and separate at 30 and 35 atm rich H_2, rich CO, rich CO_2 and rich CH_4, respectively.

Table 4. Percentage of component recovered in the PSA system [9].

	PSA-1 (top)	***PSA-2 (bottom)***	***PSA-3 (top)***	***PSA-3 (bottom)***	***PSA-4 (top)***
H_2	95	-	4.5	0.5	-
CO	-	98	1.5	0.5	-
CO_2	-	1	9	90	-
CH_4	-	1	90	9	100
	Rich H_2 stream (25)	***Rich CO stream (27)***	***CH_4 stream (29)***	***Rich CO_2 stream (31)***	***Rich CH_4 stream (35)***

First, the pure syngas stream was compressed and heated up to the operating pressure and temperature. Then, the stream was introduced in the reactor R-6 to accomplish the methanol production. The catalyst selected to the synthesis was Cu/ZnO due to be one of the most commercially-available catalyst for methanol production. The following reactions were involved during the synthesis:

$$CO + 2H_2 \rightleftharpoons CH_3OH \quad (12)$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \quad (13)$$

The conversions were 35% and 17 % for CO and CO_2, respectively [22]. Then, reaction product was depressurized to 1 atm and cooled down to 25ºC to condense and separate the crude methanol from the gas-phase in the METSEP flash, getting by the bottom pure methanol as the final product. Finally, top stream 52, which contained unconverted H_2, was recycled to the combustion chamber to reduce the amount of char necessary to reach the gasification temperature.

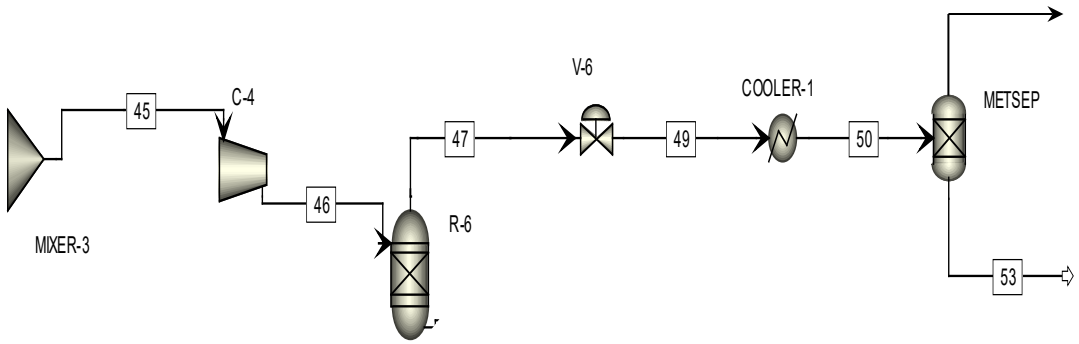


Figure 4. Aspen Plus® flowsheet simulation of methanol synthesis.

Table 5. Blocks description used in the methanol synthesis.

NAME	***TYPE***	***DESCRIPTION***
C-4	COMPRESSOR	It was used to compress and to purify the syngas.
R-6	REQUIL	Methanol synthesis reactor.
COOLER-1	COOLER	It was used to cool down to 25ºC the methanol produced to separate it.
METSEP	SEP	Separator of the crude methanol and gas-phase and impurities.

3. Results and discussion

294 3.1 Gasification simulation model

295 3.1.1 Model validation

296 The double chamber gasifier pilot-plant of the British Columbia University [20] was
297 considered to validate the present gasification model and check its accuracy. For that
298 purpose, a comparison between the predicted and experimental gas composition was
299 made. This plant was selected due the biomass used was softwood pellet, whose
300 composition (Table 6) was similar to the used in this study (Table 1). The gasifier operates
301 at 831ºC and atmospheric pressure, the gasifying agent used is steam and the steam to
302 biomass mass flow ratio is 0.2.

303 **Table 6.** Proximate and ultimate analysis of softwood biomass.

Ultimate Analysis (wt.%)*					***Proximate Analysis (wt.%)**daf*			
C	***H***	***N***	***S***	***O**diff*	***Ash***	***VM****	***FC**diff*	***Moisture***
50.8	6.26	0.22	0.10	41.6	1	81.7	17.3	5.4

304 *daf: dry and ash free basis; O*diff: % of oxygen calculated from difference of C, H, N and S;
305 VM*: Volatile matter; FC*diff: % of fixed carbon calculated from difference from moisture, ash
306 and volatile matter.

307 Table 7 compares the syngas composition between the present model and the
308 experimental data both obtained using the same operating conditions: gasification
309 temperature of 831ºC, atmospheric pressure and steam as gasifying agent.

310

311 **Table 7.** Comparison between the syngas composition (vol.% dry basis) obtained with
312 the simulation model and experimental data.

Compound	***Experimental composition (vol.% db)***	***Predicted composition (vol.% db)***

H_2	45-55	57
CO	21-25	20
CO_2	18-22	18
CH_4	2-4	2.2

Db: dry bases

The results obtained from the simulation were in good agreement with the experimental ones. Main differences could be attributed to the use of an equilibrium model in the proposed simulation while the experimental data took into account the reaction kinetics being these results more rigorous. The error obtained were only 5% and 7% for the H_2 and CO, being acceptable error. Therefore, the simulation can be considered valid to reproduce a gasification process.

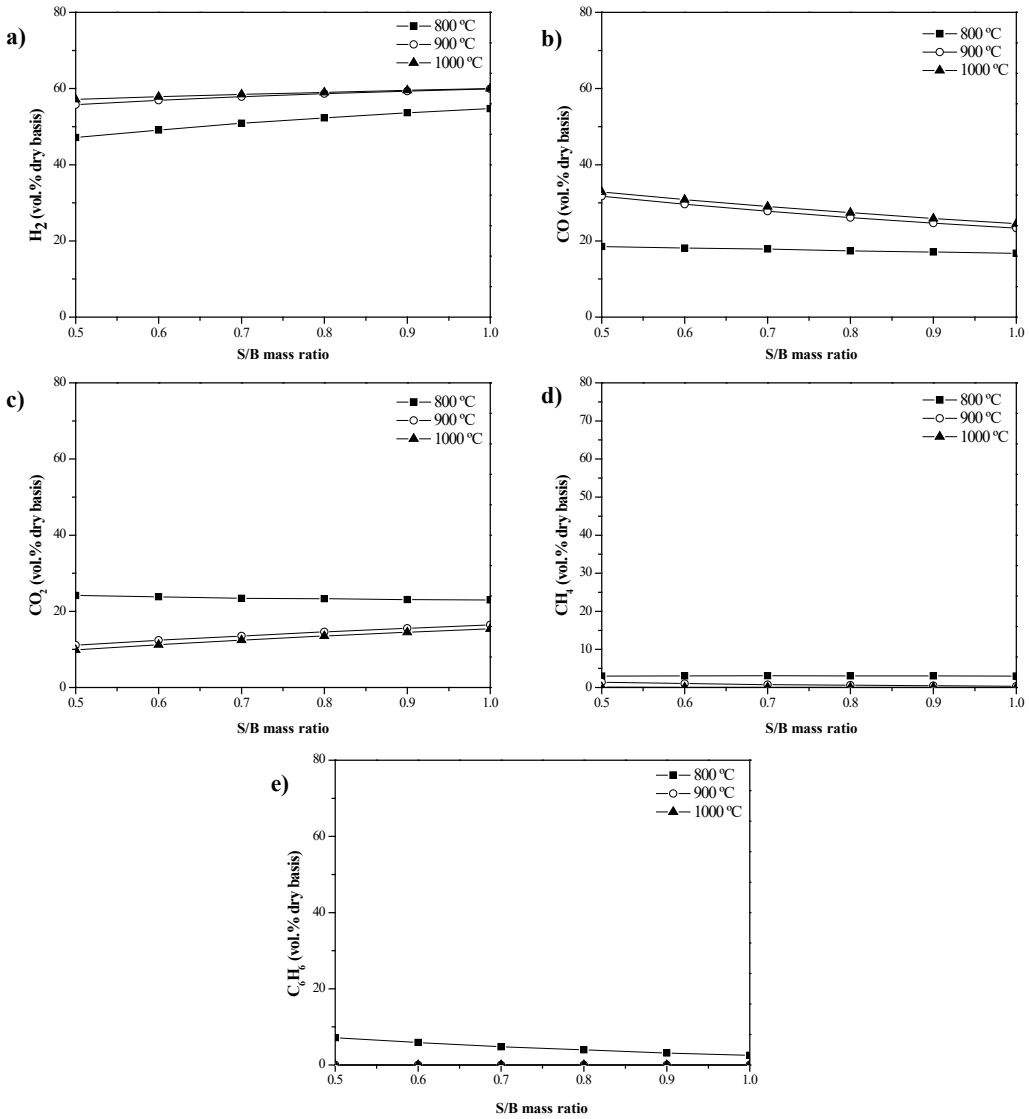
3.1.2 Sensitivity analysis

In this section, the effect of the operating conditions (temperature and steam to biomass mass ratio) on syngas composition, tar conversion and methanol production are discussed. In order to evaluate these processes, the simulation was carried out based on a simple assumption. One of these parameters was varied while the rest of them were kept constant. In this sense, the gasification temperature was varied between 800 and 1000ºC and the S/B mass ratio between 0.5 and 1 according to Shen et al. and Pala et al.[19, 23]. In addition, the feed rate was fixed at 100 kg/h for all cases.

3.1.2.1 Effect of steam to biomass (S/B) mass flow ratio

Figure 5 shows the effect of the S/B ratio on the main gases evolved (H_2, CO, CO_2, CH_4, and C_6H_6) during pine gasification at the three gasification temperatures studied (800, 900 and 1000 ºC). It can be observed that the S/B mass ratio had a weak effect on

333 the gas composition, especially when the S/B ratio achieved a value of 0.75. H_2 and CO_2
334 yield increased when the S/B mass ratio also increase whereas the CO and CH_4
335 production decreased with S/B mass ratio. These results are in good agreement with other
336 authors (Fernandez-Lopez et al., and Pala et al., [18, 19]). This fact was explained by the
337 water gas (Reaction 1), water gas-shift (Reaction 2) and steam reforming of methane
338 (Reaction 3) reactions which were favoured at high steam flow. Thus, and accordingly to
339 Le Chatelier`s principle, the higher the steam flow the higher the CO, CO_2 and H_2 yields
340 observed. However, the CO concentration decreased with increasing S/B ratio. This is
341 due to CO reacting with steam in water gas shift reaction, increasing H_2 and CO_2
342 concentrations. In the case of CH_4, its production decreased with higher steam flow due
343 to it reacting with steam in the reforming of methane. Even then, it kept practically the
344 same production in all cases.



345

346 **Figure 5.** Effect of the S/B mass ratio on the syngas composition (dry basis) a) H_2; b)
347 CO; c) CO_2; d) CH_4; e) C_6H_6 at three gasification temperatures studied.

348 Regarding tar production, the CO reacting with H_2 to obtain H_2O and C_6H_6. Thus, an
349 increase in the S/B mass ratio favoured backward the reaction decreasing tar formation.
350 Nevertheless, the quantity of tar produced was low, being practically constant especially
351 at higher temperatures.

352 Figure 6 shows the S/B mass ratio effect on the H_2/CO mole ratio in the product gas
353 composition at the three temperatures studied. It was observed that the H_2/CO ratio

increased with the S/B mass ratio. The main reason was the effect of Water gas shift reaction due to it favoured hydrogen formation accompanied with CO concentration reduction. It is really important to take into account this ratio if the syngas is going to be used in a process to produce high added-value products such as Fischer-Tropsch or methanol synthesis. To use the syngas in the methanol production, the H_2/CO ratio should be 2.4, which was achieving with 0.9 of S/B mass ratio at 900ºC.

Finally, the influence of S/B mass ratio on the methanol production was presented in Figure 7. The higher the S/B ratio, the higher the methanol production was. However, a maximum was observed at 900 ºC with S/B mass ratio of 0.9. This fact could be attributed that H_2/CO molar ratio obtained at this operating conditions was 2.4, which is needed for the methanol synthesis.

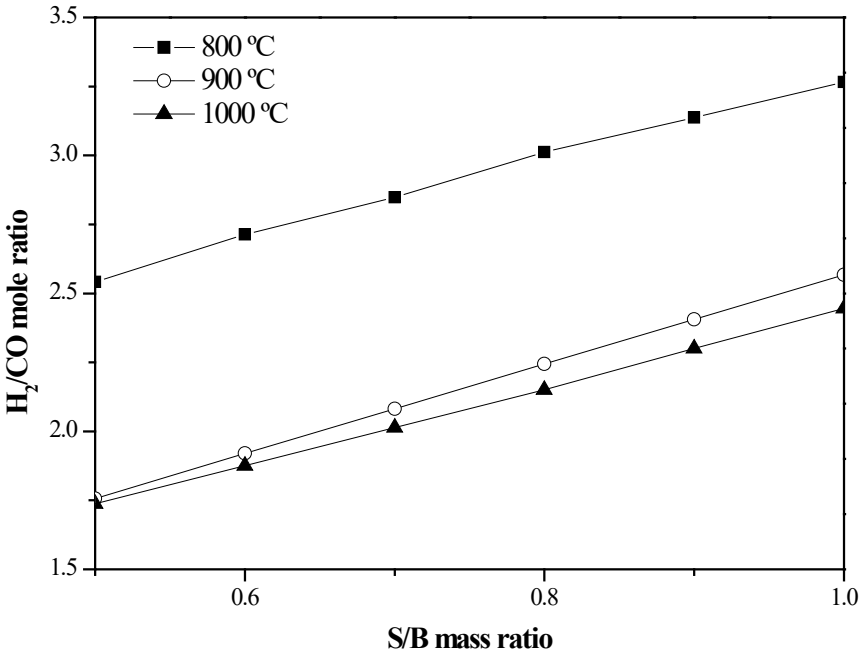


Figure 6. Effect of the S/B mass ratio on H_2/CO mole ratio at three temperatures studied.

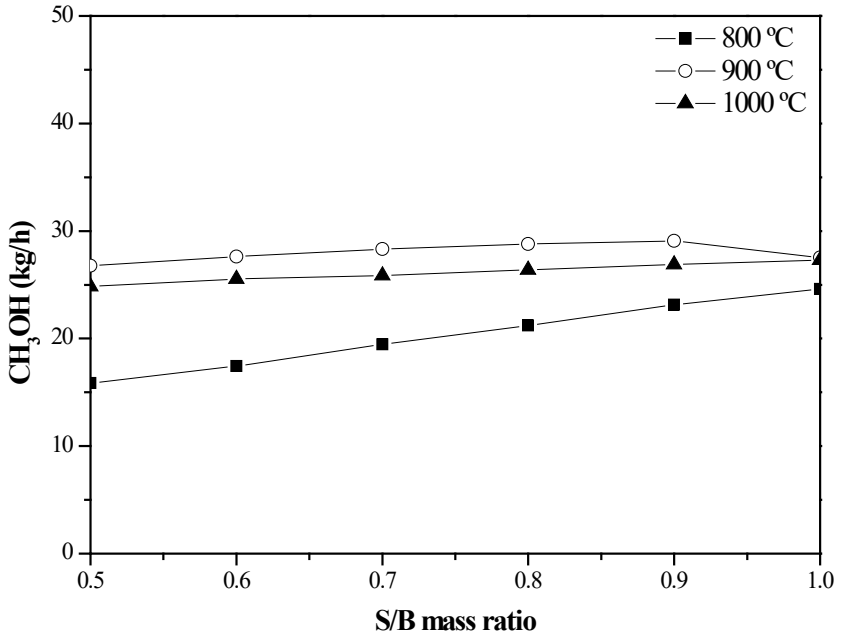


Figure 7. Effect of the S/B mass ratio on the CH_3OH composition (kg/h) at different temperatures.

3.1.2.2 Effect of gasification temperature

The gasification temperature is also a key parameter to optimize the hydrogen production. In the proposed model, three temperatures were studied to simulate the gasification: 800, 900 and 1000ºC. It was observed that H_2 and CO concentrations increased with increase in temperature whereas CO_2 and CH_4 concentrations were favoured at low temperatures (Figure 5). Similar trends were observed by Shen et al.,(2008) and Pala et al.,(2017) [19, 23]. The Boudouard reaction, water gas and steam reforming of methane are endothermic reactions. In this type of reactions (endothermic reactions) and accordingly to Le Chatelier's principle, an increase in the gasification temperature led to an increase in the products production [18]. Therefore, higher temperatures favour the CO and H_2 production, decreasing the CO_2 and CH_4 amounts in the resulted syngas. For its part, the water gas shift is an exothermic reaction, thus, it is

383 favoured at low temperatures. Therefore, it led to an increase of H_2 and CO concentration
384 with the temperature. On the other hand, water gas shift reaction is an exothermic
385 reaction, being favoured at low temperatures. Higher temperatures favoured its backward
386 reaction. For this reason, the higher the temperature, the higher the CO production and
387 the lower the CO_2 yield was. Regarding to C_6H_6 production, it can be observed the tar
388 production was higher when the gasification temperature increased. This fact is due to the
389 tar formation exothermic reaction was favoured at low temperatures [7].

390 Relating to H_2/CO molar ratio, Figure 6 shows the effect of the gasification
391 temperature on the H_2/CO molar ratio decreased when the temperature was higher. The
392 reason was that the increasing CO production was higher than the increasing H_2
393 production indicating that the Boudouard reaction was the dominant reaction over the
394 Water gas reaction for the gasification temperature range studied [4]. However, this
395 difference was more prominent at lower temperatures, being H_2/CO molar ratio similar
396 between 900-1000 ºC. On the other hand, the methanol production was favoured at high
397 gasification temperatures (Figure 7) due to the H_2 and CO production was also favoured
398 at high gasification temperatures. As aforementioned, it can be observed a maximum at
399 900 ºC with S/B mass ratio of 0.9.

400 Finally, Table 8 presents the results obtained of gas, tar and char yields at the S/B mass
401 ratio of 0.6 for the three gasification temperatures studied.

402

Table 8. Gas, tar and char yield results at three gasification temperatures studied for S/B mass ratio of 0.6.

Temperature (ºC)	*Gas yield (wt.%)*	*Tar yield (wt. %)*	*Char yield (wt. %)*
800	85.90	12.36	1.84
900	98.18	$3.0 \cdot 10^{-3}$	1.74
1000	98.16	$4.4 \cdot 10^{-10}$	1.72

The results obtained were in a good agreement with effects above explained. The higher the temperature, the higher the gas yield and the lower the tar and char yield were. Similar trends were reported by Luo et al., [24]. The increasing gas yield could be attributed to the greater production of gas in the initial pyrolysis at higher temperatures due to the enhancement of the endothermic gasification reactions. However, the difference between 900ºC and 1000ºC was negligible. Thus, a rise in gasification temperature above the 900ºC did not improve the process, but this rise could be increase the operational cost significantly.

On the other hand, tar content decreased from 12.36% to almost zero. It could be said that, at 900ºC, tar content could be considered almost non-existent but it was really important to take it into account owing to the operational problems caused.

Finally, the decreasing trend of char content with higher temperatures was caused by the higher availability of carbon to be converted in CO and CO_2 through the Water gas (Reaction 1) and Boudouard (Reaction 4) reactions, being favoured at high temperatures.

3.1.2.3 Tar cracking

One of the main technical barriers for the syngas production is the presence of tar coming from the gasification process. Tars can condensed on equipment at moderate temperatures causing some problems such as the block of filters, valves and tubes, material corrosion or catalyst deactivation. According to the simulation performed, tar production was hindered with increasing temperatures and steam flowrates. Dolomite was used as the catalyst in the decomposition of tar due to its low cost [7].

At 900ºC and 1000ºC, tar conversion was complete. Moreover, at these temperatures, tar formation was low and gas composition was not modified after the cracking. However, at 800ºC tar conversion was not complete, its conversion was enhancing when the amount of steam flow was increasing. Table 9 displays the gas composition after the tar cracking at the different S/B mass ratio studied. Figure 8 shows the comparison between the product gas composition before and after tar cracking for the S/B mass ratio of 0.6 at 800 ºC. It can be observed that, in dry basis, H_2 and CO_2 composition decreased while CO increased and CH_4 kept almost constant. This trend was explained through tar cracking reactions (6, 7 and 8). CO_2 was produced in reaction 6 and 8 but its consumption in reaction 7 was higher. However, CO was highly produced in reaction 7. For its part, H_2 was produced by means of tar cracking reaction, thus its concentration should increase. However, a decrease in H_2 was observed in Figure 8 due to it is expressed in dry basis and water content also decreased after tar cracking.

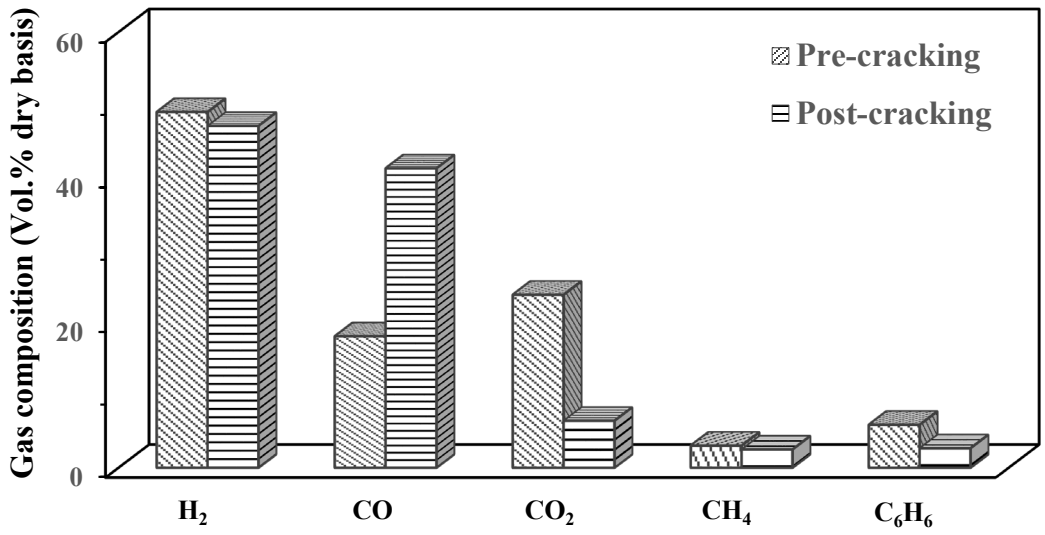
Table 9. Gas product composition (%.vol dry basis) after tar cracking at 800ºC for different S/B mass ratio.

	S/B mass ratio

	0.5	*0.6*	*0.7*	*0.8*	*0.9*	*1*
Conversion (%)	40	45	55	70	85	100
H_2^{db} (vol. %)	45.36	47.08	48.58	49.61	50.78	51.84
CO^{db} (vol. %)	43.02	41.24	40.74	41.43	40.58	39.25
CO_2^{db} (vol. %)	5.68	6.47	6.36	5.47	5.75	6.43
CH_4^{db} (vol. %)	2.46	2.52	2.56	2.51	2.50	2.47
$C_6H_6^{db}$(vol. %)	3.48	2.69	1.77	0.98	0.39	0.00

444 db: Dry basis

445



446 **Figure 8.** Gas composition (vol.% dry basis) before and after tar cracking at 800ºC and
447 S/B mass ratio of 0.6.

448 To sum up, the operational conditions selected for the gasification process were 900ºC
449 and a steam to biomass mass ratio of 0.9 because it is achieved the best results in syngas
450 composition and methanol production. Although the process at 1000ºC showed in general
451 better results, they are closed to the results obtained at 900ºC. Thus, trying to save energy

and costs, it was decided to simulate the process at 900ºC. Moreover, the H_2/CO molar ratio obtained at these conditions were 2.41, which was closed to the syngas specification needed for the methanol synthesis facilitating its syngas purification.

3.2 Methanol synthesis simulation

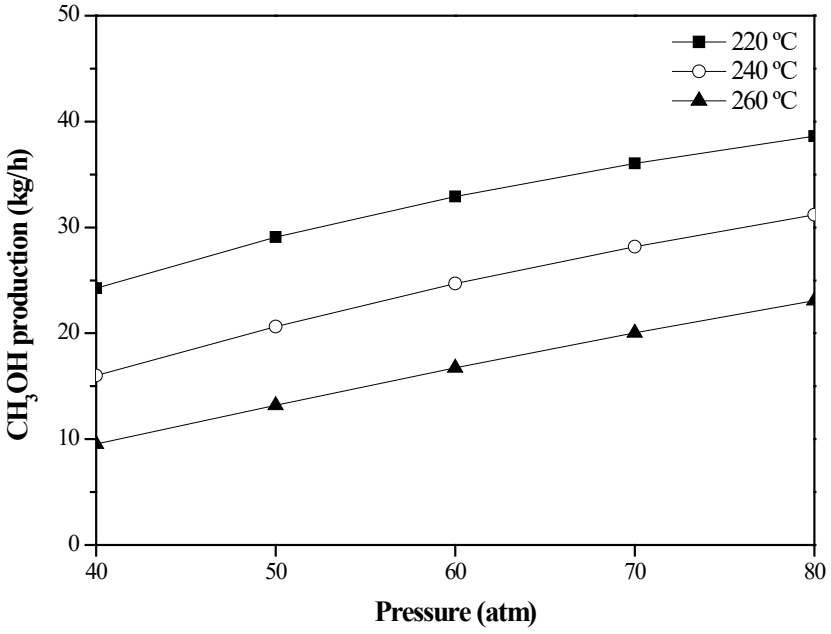
3.2.1 Model validation

Methanol synthesis model was less complex than the gasification one. The bottleneck of this process was the low conversion achieved in reactions 12 and 13. In order to validate and check the accuracy of the reactor where the methanol synthesis took place, firstly, the process was simulated with a stoichiometric reactor, fixing the fractional conversions at 0.35 for CO in reaction 12 and 0.17 for CO_2 in reaction 13 using Cu/ZnO catalyst and operating conditions (240ºC and 51 atm) both reported by Trop et al., (2014) [22] . Then, it was simulated with an equilibrium reactor fixing the pressure and temperature conditions. The results obtained were 16.5 and 15.4 kg/ h of methanol for stoichiometric reactor and equilibrium reactor, respectively. The error obtained was ±7.1%. Therefore, the model proposed could be considered as a valid model to simulate the methanol synthesis.

3.2.2 Sensitivity analysis

In order to optimize the process, the pressure and temperature influence on the methanol production was evaluated. Different studies reported that typical operation conditions of the synthesis were in the ranges from 220 to 280 ºC and 50 to 100 atm [21, 22]. At higher temperatures, the catalyst could be damaged, producing its sintering and fusion. On the other hand, lower temperatures could reduce the reaction rate [21]. For this reason, the model proposed was simulated at standard temperatures and pressures ranges. Figure 9 shows the methanol production at different temperatures and pressures studies.

476 It was observed that the methanol yield was improved at high pressures and lower
477 temperatures. Although the methanol production is favoured at high pressures, a pressure
478 of 55 atm was selected in order to avoid operational issues observed at higher pressures
479 [19, 21].

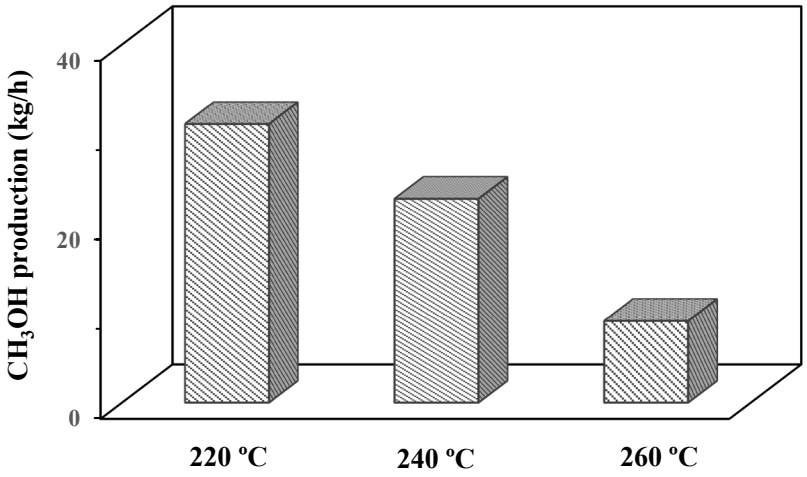


480

481 **Figure 9.** Pressure and temperature influence on CH_3OH production

482

483 Once the pressure was fixed, the temperature was varied (220-260 ºC). Figure 10
484 shows the temperature effect on methanol production at 55 atm. As aforementioned,
485 methanol production was highly favoured at low temperatures getting 32 kg/h at 220ºC,
486 whereas only 9 kg/h of methanol was obtained at the highest temperature. Therefore, the
487 optimal conditions for methanol synthesis were fixed at 220 ºC and 55 atm.



488

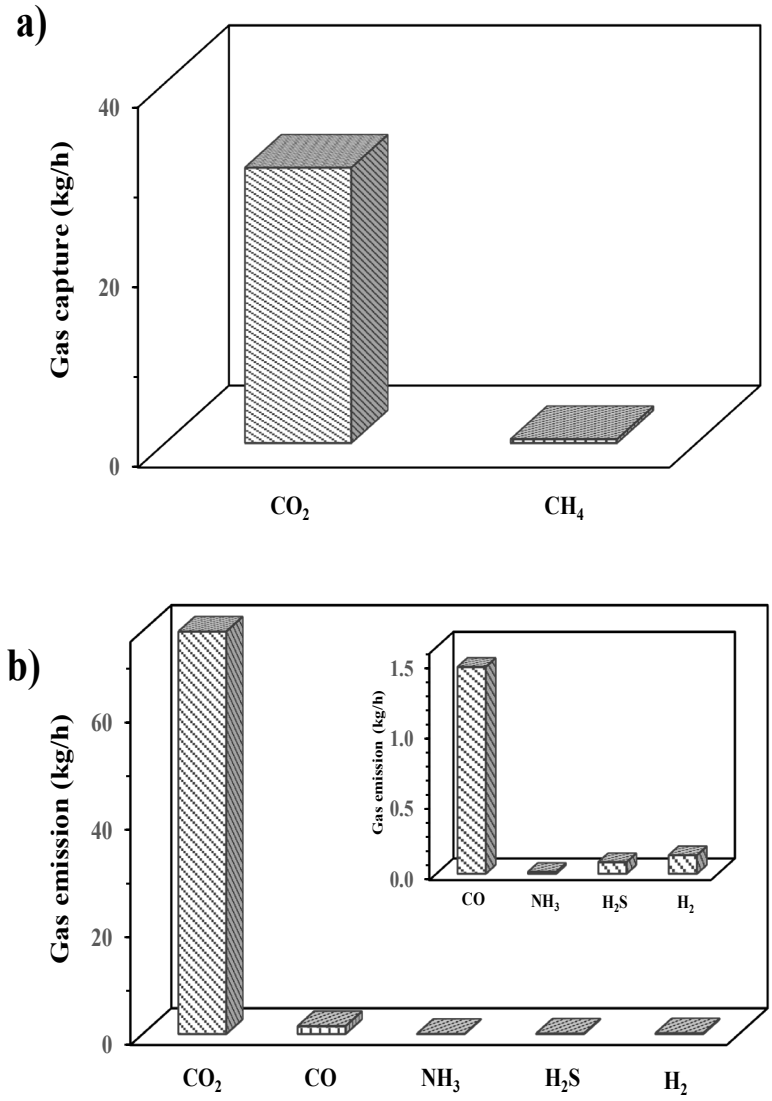
489 **Figure 10.** Temperature influence on methanol production (kg/h) at 55 atm.

490

491 3.3 Gas emission

492 The amount of greenhouse gases that the process was able to capture in the PSA
493 system, especially the amount of CO_2 and CH_4 and the other gas emissions was also
494 evaluated. Figure 11 shows the amount of CO_2 and CH_4 captured and gases released on
495 the whole process. The amount of CO2 fed in the PSA system was 42 kg/h, being the
496 amount captured 32 kg/h. Almost 80% of all is sequestered. Although most of the carbon
497 dioxide produced in the gasification was captured, there was an amount of CO_2 released
498 from the combustion chamber (75 kg/h). Taking into account the amount of CO_2 produced
499 in the process, 30% was captured. According to the international energy outlook and
500 Sikarwar et al., [2, 25], by the year 2030, it will be adsorbed the 40% of the whole CO_2
501 emissions. In the case of methane, 95% of total was captured in the fourth PSA unit.

502 Regarding the rest of the gases, NH_3 and H_2S emissions were low, being associated
503 with the biomass selected in the present simulation which had low nitrogen and sulphur
504 content.



505

506 **Figure 11.** a) Gas capture (kg/h); b) Gas emission (kg/h)

507 3.4 Optimal process improvement

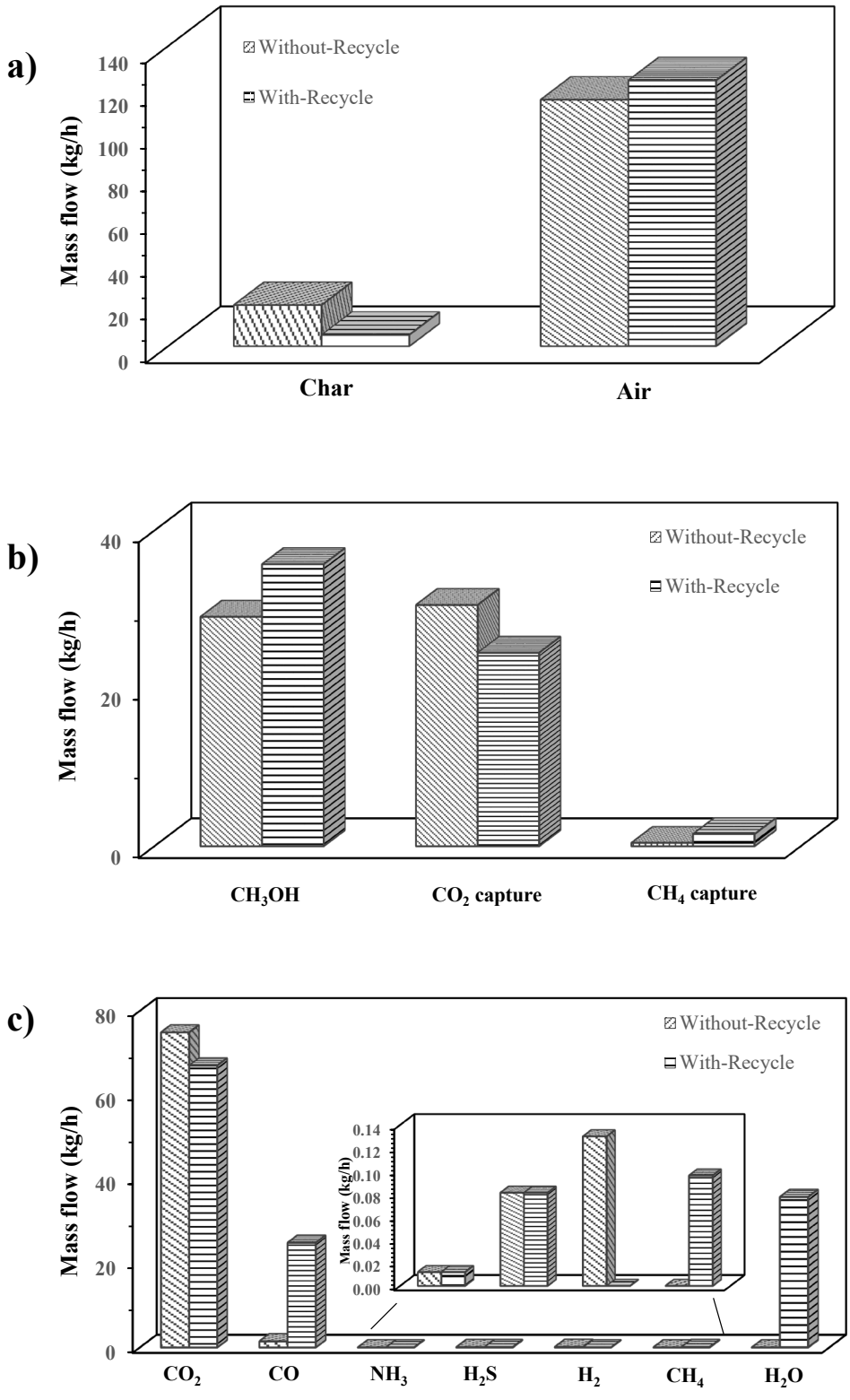
508 Once the simulation was validated, optimised and evaluated, an improvement of the
509 process was proposed. At this point, the waste stream of methanol synthesis, whose
510 composition was 70% of H_2 and 30% of the gases CO, CO_2 and CH_4, was recirculated to
511 the combustion chamber in the gasification process. Figure 12 illustrates the comparison
512 between the results obtained before and after the recycle. It can be seen that the recycle
513 improved significantly the whole process yield.

514 Regarding the combustion chamber of gasifier, before the recycle, it was necessary to
515 separate about 40% of the char to achieve the gasification temperature, but with the
516 increase of H_2 in the combustion process, it was just necessary to separate 10% of the
517 char. This separation reduction implied that there was a higher amount of char available
518 for the gasification process, favouring water gas and Boudouard reactions. In addition, it
519 also increased the energy produced in the combustion process.

520 On the other hand, the air necessary in the combustion process slightly increased
521 because the amount of gases to be burnt was higher. However, the increase of air needed
522 was low in comparison with the decrease of the char needed in the combustion chamber.

523 As the carbon available for the gasification process was higher, the amount of CO
524 produced increased, causing the improvement of methanol production. Furthermore, the
525 increasing of CO concentration involved a decrease in the CO_2 production due to the
526 gasification reactions. For this reason, it was observed that the CO_2 capture after the
527 recycle was lower. In addition, the increase in carbon content also caused the higher CH_4
528 production explaining the enhancement in CH_4 capture.

529 Finally, in relation to the gas emission, the CO_2 emission decreased, being associated
530 with the lower amount of char burnt in the combustion chamber and the higher amount
531 of hydrogen involved. H_2 reacted with the oxygen to produce water preventing that all
532 the oxygen reacted with the carbon to produce CO_2. The recycle only modified the amount
533 of carbon in the gasification process, thus, NH_3 and H_2S emissions were kept due to
534 sulphur and nitrogen content was not changed.



535

536 **Figure 12.** Comparison with and without-recycle for: a) char and air in the combustion

537 chamber; b) methanol production and GHG capture; c) gas emission.

4 Conclusions

In this work, a simulation of methanol synthesis from syngas obtained through pine biomass gasification using Aspen Plus® simulation software was developed. The next conclusions can be drawn:

- The gasification process was simulated using a thermodynamic equilibrium model which is based on the minimization of the Gibbs free energy of the system. A double chamber gasifier, which allows the separation of the gasification and combustion zones to obtain a high-quality gas, was considered. The influence of the steam to biomass (S/B) mass ratio and the temperature on the gas product composition and methanol production was studied. The best calculated operational condition of the process was 900ºC and a S/B mass ratio of 0.9.
- One of the main technical barriers for the syngas production is the presence of tar coming from the gasification process. According to the simulation performed, tar production was hindered with increasing temperatures and steam flow rates. Dolomite was used as the catalyst in the decomposition of tar due to its low cost.
- A pressure swing adsorption (PSA) process was considered to clean the syngas and simultaneously capture the greenhouse gases. Therefore, about 80% of the CO_2 and 95% of the CH_4 were sequestered.
- Once the H_2/CO molar ratio of the clean syngas was fitted, the methanol synthesis proceeded. Although the methanol production is favoured at high pressures and low temperatures, a pressure of 55 atm was selected to avoid operational issues. Thus, 220ºC and 55 atm were selected as the optimal operation conditions for the methanol synthesis.
- Finally, to improve the process yield, the methanol synthesis waste stream is recycled to the combustion chamber. With this recycle, the carbon required to burn is

562 reduced from 40 to 10%. Thus, there is a higher amount of carbon available to be used in
563 the gasification process.

564 **Acknowledgments**

565 Authors acknowledge the financial support from the Spanish government (Grant
566 No. FPU15/02653).

567 **References**

568 [1] O. Dessens, G. Anandarajah, A. Gambhir. Limiting global warming to 2 °C: What do
569 the latest mitigation studies tell us about costs, technologies and other impacts? Energy
570 Strategy Reviews. 13-14 (2016) 67-76.
571 [2] V.S. Sikarwar, M. Zhao, P.S. Fennell, N. Shah, E.J. Anthony. Progress in biofuel
572 production from gasification. Progress in Energy and Combustion Science. 61 (2017)
573 189-248.
574 [3] J.H. Pauls, N. Mahinpey, E. Mostafavi. Simulation of air-steam gasification of woody
575 biomass in a bubbling fluidized bed using Aspen Plus: A comprehensive model including
576 pyrolysis, hydrodynamics and tar production. Biomass and Bioenergy. 95 (2016) 157-66.
577 [4] L.P.R. Pala, Q. Wang, G. Kolb, V. Hessel. Steam gasification of biomass with
578 subsequent syngas adjustment using shift reaction for syngas production: An Aspen Plus
579 model. Renewable Energy. 101 (2017) 484-92.
580 [5] W.-X. Peng, S.-B. Ge, A.G. Ebadi, H. Hisoriev, M.J. Esfahani. Syngas production by
581 catalytic co-gasification of coal-biomass blends in a circulating fluidized bed gasifier.
582 Journal of Cleaner Production. 168 (2017) 1513-7.
583 [6] G. Guan, M. Kaewpanha, X. Hao, A. Abudula. Catalytic steam reforming of biomass
584 tar: Prospects and challenges. Renewable and Sustainable Energy Reviews. 58 (2016)
585 450-61.

586 [7] C. Berrueco, D. Montané, B. Matas Güell, G. del Alamo. Effect of temperature and
587 dolomite on tar formation during gasification of torrefied biomass in a pressurized
588 fluidized bed. Energy. 66 (2014) 849-59.
589 [8] J.F. González, S. Román, G. Engo, J.M. Encinar, G. Martínez. Reduction of tars by
590 dolomite cracking during two-stage gasification of olive cake. Biomass and Bioenergy.
591 35 (2011) 4324-30.
592 [9] F.J. Gutiérrez Ortiz, A. Serrera, S. Galera, P. Ollero. Methanol synthesis from syngas
593 obtained by supercritical water reforming of glycerol. Fuel. 105 (2013) 739-51.
594 [10] N. Álvarez-Gutiérrez, M.V. Gil, F. Rubiera, C. Pevida. Kinetics of CO2 adsorption
595 on cherry stone-based carbons in CO2/CH4 separations. Chemical Engineering Journal.
596 307 (2017) 249-57.
597 [11] R. Krishnamurthy. Hydrogen and carbon monoxide production by hydrocarbon
598 steam reforming and pressure swing adsorption purification. Google Patents1992.
599 [12] J.A. Batdorf. Method and apparatus for methanol and other fuel production. Google
600 Patents2010.
601 [13] N.D. Couto, V.B. Silva, E. Monteiro, A. Rouboa. Assessment of municipal solid
602 wastes gasification in a semi-industrial gasifier using syngas quality indices. Energy. 93
603 (2015) 864-73.
604 [14] J.H. Pauls, N. Mahinpey, E. Mostafavi. Simulation of air-steam gasification of
605 woody biomass in a bubbling fluidized bed using Aspen Plus: A comprehensive model
606 including pyrolysis, hydrodynamics and tar production. Biomass and Bioenergy. 95
607 (2016) 157-66.
608 [15] M. Zhai, L. Guo, Y. Wang, Y. Zhang, P. Dong, H. Jin. Process simulation of staging
609 pyrolysis and steam gasification for pine sawdust. International Journal of Hydrogen
610 Energy. 41 (2016) 21926-35.

611 [16] S. Nilsson, A. Gómez-Barea, D. Fuentes-Cano, P. Ollero. Gasification of biomass
612 and waste in a staged fluidized bed gasifier: Modeling and comparison with one-stage
613 units. Fuel. 97 (2012) 730-40.
614 [17] K. Im-orb, A. Arpornwichanop. Techno-environmental analysis of the biomass
615 gasification and Fischer-Tropsch integrated process for the co-production of bio-fuel and
616 power. Energy. 112 (2016) 121-32.
617 [18] M. Fernandez-Lopez, J. Pedroche, J.L. Valverde, L. Sanchez-Silva. Simulation of
618 the gasification of animal wastes in a dual gasifier using Aspen Plus®. Energy
619 Conversion and Management. 140 (2017) 211-7.
620 [19] L.P.R. Pala, Q. Wang, G. Kolb, V. Hessel. Steam gasification of biomass with
621 subsequent syngas adjustment using shift reaction for syngas production: An Aspen Plus
622 model. Renewable Energy. 101 (2017) 484-92.
623 [20] B. Hejazi, J.R. Grace, X. Bi, A. Mahecha-Botero. Kinetic Model of Steam
624 Gasification of Biomass in a Dual Fluidized Bed Reactor: Comparison with Pilot-Plant
625 Experimental Results. Energy & Fuels. 31 (2017) 12141-55.
626 [21] F.J. Gutiérrez Ortiz, A. Serrera, S. Galera, P. Ollero. Methanol synthesis from syngas
627 obtained by supercritical water reforming of glycerol. Fuel. 105 (2013) 739-51.
628 [22] P. Trop, B. Anicic, D. Goricanec. Production of methanol from a mixture of torrefied
629 biomass and coal. Energy. 77 (2014) 125-32.
630 [23] L. Shen, Y. Gao, J. Xiao. Simulation of hydrogen production from biomass
631 gasification in interconnected fluidized beds. Biomass and Bioenergy. 32 (2008) 120-7.
632 [24] S. Luo, Y. Zhou, C. Yi. Syngas production by catalytic steam gasification of
633 municipal solid waste in fixed-bed reactor. Energy. 44 (2012) 391-5.
634 [25] I.E. Outlook. DOE/IEA-0484. International Energy Outlook 2016, With Projections
635 to 2040. 2016. p. www.eia.gov/forecasts/ieo.

APPENDIX A

Table A1: Design specification DS-1

VARIABLE	**DEFINITION**		
H_2	Mole-flow Stream=45 Substream=MIXED Component=H_2 Units=kmol/h		
CO	Mole-flow Stream=45 Substream=MIXED Component=CO Units=kmol/h		
ESPECIFICATION		**MANIPULATED VARIABLE**	
Spec:	CO	Type:	Block-Var
Target:	H2/2.4	Block:	SPLIT-1
Tolerance:	0.01	Variable:	FLOW/FRAC
		Sentence:	FLOW/FRAC
Manipulated variable limits		ID1:	41
Lower:	0	ID2:	-
Upper:	1	ID3:	-

Table A2: Design specification DS-2

VARIABLE	**DEFINITION**		
CO_2	Mole-flow Stream=45 Substream=MIXED Component=CO_2 Units=kmol/h		
CO	Mole-flow Stream=45 Substream=MIXED Component=CO Units=kmol/h		
ESPECIFICATION		**MANIPULATED VARIABLE**	
Spec:	CO_2	Type:	Block-Var
Target:	0.13·CO	Block:	SPLIT-2
Tolerance:	0.01	Variable:	FLOW/FRAC
		Sentence:	FLOW/FRAC
Manipulated variable limits		ID1:	33
Lower:	0	ID2:	-
Upper:	1	ID3:	-

649 **Table A3:** Design specification DS-3

VARIABLE	**DEFINITION**		
FAIR	Mole-flow Stream=8 Substream=MIXED Component=O_2 Units=kmol/h		
FC	Mole-flow Stream=5 Substream=MIXED Component=C Units=kmol/h		
ESPECIFICATION		**MANIPULATED VARIABLE**	
Spec:	FAIR	Type:	Mole-flow
Target:	1.2·FC	Stream:	54
Tolerance:	0.01	Substream:	Mixed
		Component:	O_2
Manipulated variable limits		Units:	Kmol/h
Lower:	1		
Upper:	1		

650

651 **Table A4:** Design specification DS-4

VARIABLE	**DEFINITION**		
TGASIF	Stream-Var Stream=11 Substream=MIXED Variable=TEMP Units=C		
ESPECIFICATION		**MANIPULATED VARIABLE**	
Spec:	TGASIF	Type:	Block-Var
Target:	800-900-1000 ºC	Block:	SEP-1
Tolerance:	1	Variable:	FLOW/FRAC
		Sentence:	FLOW/FRAC
Manipulated variable limits		ID1:	CISOLID
Lower:	0,000001	ID2:	5
Upper:	0,999999	ID3:	C

652