The final publication is available at

http://doi.org/10.1016/j.fuel.2017.10.014

Additional Information

Liquid fuels from biomass: an energy self-sustained process integrating H_2 recovery and liquid refining

D. Catalán-Martínez; M.E. Domine; J.M. Serra*

[a] Instituto de Tecnología Química (Universidad Politécnica de Valencia – Consejo Superior de Investigaciones Científicas), av. los Naranjos s/n; 46022 Valencia, Spain.

(* corresponding author: jmserra@itq.upv.es)

Abstract

In the last years the research activities on biomass valorisation (mainly residues from urban and agricultural activities) have been intensified. Biomass is an abundant resource for energy generation and its extensive utilization may make possible to fulfil the goals determined by the national and international regulations about renewable sources and greenhouse gas emissions. In this work, simulations are carried out using ASPEN PLUS for an integrated process to produce liquid fuels from biomass in a self-sustainable energetic regime (thermal and electric) and several process factors have been considered. The process initially combines a primary pyrolysis reactor associated to a (char + gases) gasification unit in order to optimize the biomass use, followed by downstream processes to enhance the quality of final liquid fuel. The factors studied were the composition of the biomass, the primary (or pyrolytic) liquid yield, the composition of the liquid fuel, as well as the amount of the oxidant and steam used in the primary char-gasifier reactor. The use of a simplified model for liquid fuel composition let us to stablish a range of operational conditions in which both thermal and electric balance of the process are favourable. In this sense, the maximum extraction of liquid fuel was found around 20-25% by working at $10 - 25\%$ of O_2 (as pure oxygen or air) and $15 - 45\%$ of steam in the gasifier and fulfilling self-sustainable process condition, while biomass should possess C/O weight ratios ≥ 1.

Keywords:

Biomass pyrolysis; biomass gasification; bio-fuels; hydrogen membrane; hydrotreating; process optimization; process integration

1. INTRODUCTION

In the last years, the interest of viable alternative technologies for fuels and chemicals production other than petroleum refining has raised. Nowadays, the volatile price of petro-barrel together with the increase in the energy demand, the future oil resources depletion and the concern about the greenhouse gases emission due to global climate change have motivated the intensification in research efforts in clean and eco-friendly alternatives. New regulations have set the goal of utilizing transportation fuels with 10% from renewable sources by 2020 [1]. Furthermore, the actual society is increasing the waste generation that is driving to governments to promote more efficient processes to reduce the amount of residues, as well as the reuse of the generated waste and consequently reduce greenhouse gas emissions. For this reason, the interest in the thermochemical processes to valorise waste products has increased in the last years.

Different biomasses, derived from municipal or agrarian wastes could be used as renewable carbon sources which are not exploited extensively nowadays. Among others, biomass residues employed as raw materials could include: i) agricultural wastes (i.e. crops, energy crops, trees, etc.), ii) farm wastes (i.e. manure, sewage), (iii) forest and wood wastes, (iv) industrial residues from wood (and paper) industries, and v) municipal solid residues (i.e. organic without glass and metals, plastic, food processing residues, etc.). Although some of the later residues could be combined for further valorisation, they are treated separately in most of the cases, mainly due to their specific requirements (i.e. recollection and effective management, type of pre-treatment and further processing),

Technologies used for biomass and wastes conversion/transformation comprise physical, biological, and thermo-chemical methods, the latter being divided in combustion (or incineration), pyrolysis and gasification. While combustion/incineration process was largely preferred for the treatment and elimination of municipal solid wastes (MSWs) in the past, gasification (new gasifiers and fluidized bed reactors) and pyrolysis (fast pyrolysis and

catalytic fast pyrolysis) technologies have advanced in the last years appearing as an adequate solution mainly for the transformation of lignocellulosic-type biomass residues. [2] [3] [4-6]

It is widely accepted that biomass, mainly lignocellulosic-type biomass, can be processed in an integrated biorefinery, in a similar manner as petroleum in conventional refineries to produce fuels and chemicals [7] [8, 9] [10, 11]. Thermochemical conversion of biomass via gasification and pyrolysis technologies can break down the chemical bonds in biomass polymers to form intermediate gases, solids, and mainly liquids molecules that can be refined into a variety of valuable products (fuels and commodities) through different downstream processes. In principle, these conversion processes are characterized by their high flexibility, i.e. a relatively broad range of biomass compositions can be processed. However, these units are highly energy-demanding with respect to conventional petroleum-derived fuels. In addition, impurities present in some biomass fractions require special operation and/or unit design [12]. For these reasons and in order to optimize the yield of gases and liquids products, the studies of biomass transformation and valorisation through thermochemical routes are continuously growing during the last years [13-29].

Biomass is believed to be one of the future H_2 sources [30], and thermo-chemical processing of biomass is one of the most attractive and effective options to produce H_2. In this sense, the combination of slow pyrolysis with steam gasification to produce H_2 is mainly restricted by the temperatures of the process and the biomass used. The temperature of the pyrolyzer determines the nature of products formed whereas the gasification temperature determines the H_2 yield (higher H_2 production at high gasification temperatures). In addition, it is necessary to consider that the pyrolysis product composition strongly depends on the nature of the starting biomass [15], which will limit the final H_2 productivity achieved. The H_2 can also be produced in high temperatures gasification units using heterogeneous catalysts and further treatments in water gas shift reactors [30, 31].

Thermodynamic simulations of these processes allow evaluating the viability of this kind of processes and characterizing the effects of the different parameters of the plant. ASPEN PLUS

has been used to model different thermochemical processes and different biomass types. Thermodynamic simulations have addressed H_2 production from biomass using different separation units (water-gas-shift reactors with pressure swing absorbers) [16]. A kinetic study of the biomass gasification revealed that increasing the residence time in the gasification unit enables to reach high CO and H_2 yields [17]. In several ASPEN PLUS studies on pyrolysis process [19-21, 32, 33] and gasification process [22-25], the model is developed for one type of biomass or a few of biomass types. There are some studies that incorporate a solid oxide fuel cell (SOFC) system to directly produce electricity from biomass [26-29]. Biomass gasification and PEMFC system can be integrated to produce power with high efficiency. [26] Similar positive effects have been reported when ceramic membrane reactors were integrated in the process [34]. Among the different technologies for separation and purification of H_2, membrane technologies are one of the most promising for substituting conventional separation units [35-39], due to the lower energy consumption of the separation [40].

All in all, the envisaged strategy for biomass valorisation in biorefineries of the future would involve thermochemical transformation of residual biomass to render liquid fuels in combination with co-production of chemicals (e.g. H_2 and O_2 purified gases) as plant commodities. In addition, CO_2 capture could be directly implemented in these new plants.[41] This concept requires energy co-generation in the plant to attain optimal energy efficiency. Following this idea, the use of biomass to obtain liquid fuels using an integrated process in a self-sustainable plant is analysed in the present work. Different biomass compositions are supplied to a hybrid process of primary pyrolysis combined with (char + gases) gasification to produce a precursor of the liquid fuel (hereinafter primary liquid) together with optimized gaseous effluent containing H_2. This primary liquid is then refined via a hydrotreating (hydrogenation / hydro-deoxygenation) downstream process using part of the H_2 formed in the char-gasifier, which was previously separated/purified in a membrane reactor unit. The ultimate aims of the study are to maximize the liquid fuel obtained (with a goal of a 20 – 25%

of yield for the primary liquid) and the energetic viability of the integrated approach, considering separate balances of electric energy and thermal energy.

2. METHODS

2.1 General system description

Figure 1 shows an outline of the process modelled. Biomass previously dehydrated is subjected to a pyrolysis unit to produce the liquid fractions from the biomass. The volatile and char fractions are gasified in order to maximize the H_2 yield to be used in the upgrading of the primary liquid. A membrane reactor is used to reform hydrocarbon products and separate the H_2 fraction of the rest of the gases. The primary liquid is then hydrogenated to obtain the final liquid fuel (hereinafter refined liquid fuel). The tail gas is revalorized with a gas turbine.

2.1.1   Biomass composition:

Most biomass types are made of lignocellulosic materials comprising cellulose, hemicellulose and lignin [31]. Due to the complexity in defining a generic biomass composition [42], most of the previous studies of biomass processing are focused in reaching efficient process for a specific biomass (mainly woods from fruit trees) [19, 43, 44]. The present study takes into account a broad range of biomass compositions, which represents from urban wastes until agrarian biomass (trees) [45-49]. (Table 1). Biomass 1 is a generic biomass while biomasses 2 and 3 higher C contents (+5% per each biomass) and the O content decreases. Biomasses 4 and 5 represent extreme compositions: biomass 4 has a composition with high O content and low C content while biomass 5 presents a high C/O ratio, mimicking lignin compositions. The study considers 100kg/h of biomass as feed for all the cases.

2.1.2   Pyrolysis unit

The primary liquid yield studied was in the range of 10 – 30 wt. % of the initial biomass [50]. The 90 wt. % and 10 wt. % of the remainder biomass becomes in gas and char fractions, respectively. The pyrolysis bio-oil (or primary liquid) is a complex mixture of several groups

of compounds such as, aldehydes, alcohols, ketones, sugars, furans and furan derivatives, syringols, guaiacols, catechols, and other aromatic compounds, etc [51]. To simplify the problem, pyrolysis bio-oil is considered as a single component whereas the refinement consists of a full hydrogenation step of this compound. For this study, four primary liquids were studied: methylnaphthalene, 4-hydroxybenzyl alcohol (commonly named as gastrodigenin), furfural and lactic acid. The pyrolyzer operates at 500ºC and 1 bar employing 1 kg of sweep gas (CO_2) per kg of wet biomass. The stream is then cooled to 175ºC, below the boiling point of primary liquids (e.g. 240-243ºC for the methyl-naphthalene and 250ºC for the 4-hydroxybenzyl alcohol).

2.1.3 Char-gasification unit

The inlet streams in the gasifier are the char and gas fractions from pyrolysis as well as steam and oxidant gas streams. The gasification takes place at 700ºC and 1 bar. Conventional gasifiers use around 25% of the stoichiometric oxidant with respect to total oxidation. O2 and air were considered as oxidants. For the processing of the different biomasses, the following ranges of oxidation conditions were studied: 5 – 30 kg O_2 per each 100 kg of biomass and 40 – 110 kg air per each 100 kg of biomass. O_2 was studied in order to reduce the heat used to warm up the reactor. Steam was introduced in the gasifier to shift the equilibrium of the water shift reaction to produce H_2. Typically, the amount of steam injected is proportional to water content in the wet biomass. Here, the steam ratio studied is 15 – 45 kg steam per each 100 kg of biomass.

2.1.4 Membrane reactor

The H_2 necessary for further downstream processing of liquids in the plant is produced and separated in a catalytic membrane reactor unit based on selective palladium membranes. In the reactor, as the H_2 is extracted through the membrane, the equilibrium of the water gas shift (WGS) reaction can be shifted until total conversion of CO and CH_4 into CO_2 (Figure 3a). The membrane reactor operates at 525ºC and 1bar.

2.1.5 Hydrogenation reactor

Aromatic and phenolic type compounds hydrogenation (and/or hydrodeoxygenation) is typically carried out over catalyst based on Pt, Pd, Pt-Pd supported on Al_2O_3 at temperatures 200 – 450 ºC and pressures 50 – 100 bar [52-59]. The inlet streams of the reactor are the primary liquid and the extracted H_2 and are previously pressurized, i.e. at 50 and 70 bar. The reaction takes place at 400ºC and is set as the temperature for the outlet products. The reactions for the hydrogenation are r.1, r.2, r.3 and r.4, respectively:

(r. 1)

(r. 2)

(r. 3)

(r. 4)
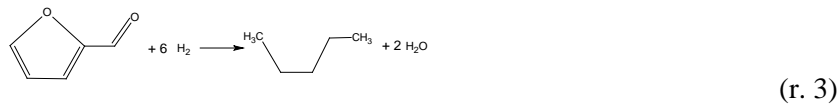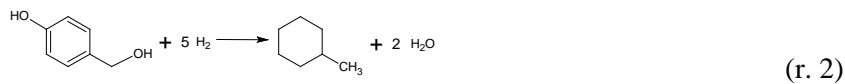
Methylnaphthalene and 4-hydroxybenzyl alcohol molecules have the same stoichiometric H_2 demand. Therefore, the molar ratio between the primary liquid obtained and H_2 generated in the gasifier must be higher than these stoichiometric values for each type of primary liquid.

2.1.6 Treatment of the final gases

The final gas obtained is a mixture of CO, CO_2, CH_4, H_2 and H_2O. A double-step gas turbine was considered to treat it. The pressure ratio of the turbine was set at 20 with a mass flow rate for the air of the turbine of 25% of the excess of the stoichiometric air.

The final gas at the outlet of the last turbine is still at high temperature. The heat of this stream can be utilized to keep the temperature in the first biomass reactors (pyrolyzer and gasifier units).

2.2 Parameter variations

7

A parametric study was made to evaluate the effect of several factors in the overall process and choose the optimal value for each parameter with the aim to maximize the yield of refined liquid fuel fulfilling the energy self-sustainability condition. A discretized description of the parametric study is displayed in Table 2.

In order to evaluate the effect of employing different composition of biomass (in their conventional values, i.e. biomass 1 – 3), different extraction of primary liquid from the pyrolyzer, and different amounts of steam and oxidant in the gasifier, an initial parametric study was done. In this initial parametric study, methyl-naphthalene was considered as primary liquid and the pressure of the refining unit was set at 50 bar.

With the results of the initial parametric study, the advanced studies evaluate the overall process when the pressure of the refining unit is increased (i), extreme biomass compositions were used (ii) and the composition of the primary liquid is changed (iii).

2.2.1   Hydrogen extraction for the refining

Hydrogen demand for the refining depends on the primary liquid yield in order to complete its upgrading, considering the reactions r.1 – r.4. For this study, the stoichiometric point for each reaction relates to the amount of hydrogen required for complete liquid hydrogenation (100% conversion). The molar ratio between the hydrogen and primary liquid of the respective inlets to the refining unit was evaluated and compared with the stoichiometric point.

2.2.2   Searching of the working operation conditions with energy-balanced process

This study aims to determine the maximum amount of refined liquid fuel that can be obtained in self-sustainable process. Considering the initial parametric study, the primary liquid yield is decreased until reaching the working operation conditions that enable the energy-balanced process (both heat and electrical) for each biomass, the complete upgrading of the liquid fuel as a function of the kind of oxidant considered.

2.3 Aspen modelling

The study was developed in stationary conditions employing software ASPEN PLUS V8.0. The diagram of the overall process in the Aspen is shown in the Figure S1 and Table S1 (Supporting Information).

The following assumptions were considered for the simulation:

- The overall process is in steady state and each reactor is operated in isothermal conditions (except the gas turbine which works in adiabatic conditions).

- Volatile compounds formation from biomass takes place instantaneously and the main volatile products consist of H_2, CH_4, CO, CO_2 and H_2O.

- All the gases are uniformly distributed within the reactor.

- The fluid dynamic equations in the reactors are not taken into account.

- The char gasification reactions reach chemical equilibrium.

- Reactions of sulphur and nitrogen type compounds are not taken into consideration.

The pyrolyzer was modelled using an equivalent serial combination comprising two stoichiometric reactors and a Gibbs reactor (Figure 2). The first stoichiometric reactor (P-1) converts dehydrated biomass in the primary liquid (e.g. methylnaphthalene or gastrodigenin). The second stoichiometric reactor (P-2) converts 90% of the remaining biomass in gas. The 10% balance represents the char fraction. Finally, a Gibbs reactor is introduced in series to balance the gases produced (P-3). The char fraction and the primary liquid are considered as inert components in the last reactor. The stream is then cooled to 175ºC, below the boiling point of primary liquids (e.g. 240-243ºC for the methyl-naphthalene and 250ºC for the 4-hydroxybenzyl alcohol).

The gasifier was modelled considering a stoichiometric reactor and a Gibbs reactor in series. The stoichiometric reactor gasifies the char fraction while the Gibbs reactor balances all the gases at 700ºC.

The membrane reactor was modelled using single units in series: (1) a first stoichiometric reactor (RMEMB1), to shift WGS equilibrium and maximize H_2 yield; (2) an ideal separator

(RMEMB2), to extract the H_2 from the reaction chamber; (3) a Gibbs reactor (RMEMB3), to balance the final gases in the reactor chamber at the temperature of the reactor; and (4) a vacuum pump (VACUUM) modelled with a multistep gas compressor with the vacuum pressure (100 mbar) in the first step and with the gas pressure in the second step (Figure 3b).

The refining unit is modelled using a stoichiometric reactor comprising reactions r.1 - r.4. The modelled hydrogenation island entails therefore a system of pumps for the liquid stream and compressors for H_2 stream (Figure 4a).

The turbine was modelled with a compressed-air inlet. The compressor of the turbine is connected with the high-pressure turbine while the low-pressure turbine produces the electrical energy. In the model, the pressurized streams (air and gas) are the inlets of an adiabatic reactor and, finally, the combustion gas obtained is introduced in the turbine units. Figure 5 presents the overall model of this sub-process. The final heat exchange of the tail gases is modelled including a last heat exchanger and the final temperature of the exhaust gases is 300ºC.

3. MODELLING RESULTS

3.1 Influence of the primary liquid yield in the pyrolyzer.

The production of the primary liquid in the pyrolysis unit is a critical factor because it determines the amount of carbon (as CO, CO_2 or CH_4) and H_2 in downstream gases. In fact, the mass flow and particular composition of the gasification products limits the H_2 yield in the membrane reactor, which is later used in the liquid hydro-treatment. As a consequence, a proper balance between the primary liquid yield in the pyrolysis unit and the H_2 yield in the membrane reactor should be reached. Considering the complete upgrading of the liquid, the primary liquid yield determines the yield of the final refined fuel following a linear relationship (Figure 4b).

Figure 6 presents the results of the molar ratio between the H_2 obtained in the membrane reactor as a function of the primary liquid from pyrolysis. These simulations results include the parametric study presented in Table 2, i.e., variation of biomass composition, primary

liquid yield, the oxidant and the steam ratios. Note that by considering the stoichiometry of hydrogenation step (reaction r.1), H_2/primary liquid molar ratios higher than 5 are needed to achieve the full conversion of primary liquids. The modelling results summarized in Figure 6 show that higher refined liquid yields are produced with decreasing H_2/liquid ratios up to the stoichiometric limit. As mentioned, the yield of primary liquid restricts the subsequent H_2 production, *i.e.* the higher the liquid yield the lower the yield of H_2/CO/CH_4 in the gasifier. The treatment of biomass with high C/O ratios (less oxidized) produces a higher H_2 yield. Finally, regardless of the energy balances and taking into account the molar balance between H_2 and primary liquid, a maximum of 25 kg of primary liquid per each 100kg of biomass can be attained for the biomasses 2 and 3 while, for biomass 1, the maximum yield is lower, i.e. 20 kg of primary liquid per each 100kg of biomass.

3.2 Energy balance

The main aim of the study is to demonstrate that the plant can work in a self-sustainable regime. For this purpose, the heat and electrical balance of the plant were analysed. The heat balances include the heat from heat exchanger (at outlet of gasifier and tail gas) and pyrolysis and gasification units whereas the electrical power comprises the demand/generation from vacuum, liquid pump, compression units and turbines. In the calculations of both balances, negative values represent cases with energy surplus (preferable for a self-sustainable process) whereas positive values represent cases where more energy consumption/demand of the overall process exceeds the generation.

Figure 7 shows the heat balance in MJ per each 100 kg of biomass treated for three different biomass compositions (biomass 1, 2 and 3, s. Table 1). The pyrolyzer is an endothermic unit due to the heat needed to warm up and to convert the biomass. The total heat balance in the gasifier unit depends on the amount of air (or oxygen) as it determines the extent of full oxidation reactions in the unit. Increasing the primary liquid yield in the pyrolyzer leads to lower yields of non-oxidized compounds in the gas streams (CH_4, CO and H_2) and, therefore, less heat is generated in the pyrolyzer though oxidation reactions. As the C/O ratio of the

biomass is higher, the overall process is less endothermic since the starting biomass is less oxidized. In addition, the difference between the use of air and oxygen can be observed in the heat balances shown in Figure 7a and Figure 7b, respectively. As expected, when the plant works with oxygen as oxidant in the gasifier unit, the thermal balance is more exothermic than when the oxidant is air.

Figure 8 shows the electrical balance of the system in terms of the electrical power in kWh per 100 kg of biomass as a function of the yield of primary liquid in the pyrolysis. The electrical balance includes the energy generated in the turbine and the power demand of compressors and pumps. In the gas turbine (see Fig. 5) cycle (Brayton cycle), energy is generated thanks to the expansion reached though increment of temperature due to the internal adiabatic combustion. Therefore, the best scenarios for the electrical balance are those in which high amounts of oxidizable compounds (H_2, CH_4, CO, etc.) are available at the inlet of the turbine. For that reason, when the primary pyrolysis liquid yield is lower or when starting biomasses present higher C/O ratios (biomasses 2 and 3, Table 1), the electrical balance is more favourable. Although the electrical balances are similar irrespective to the type of oxidant used in the gasifier, the use of oxygen leads to slightly better results.

3.3 Working operation conditions for energy-balanced process

Figure 9 describes the search space taken into account to identify the working operation conditions for energy-balanced process for the biomass 2. The 2D mappings show the outcome parameters (ratio of H_2/primary liquid, electrical and heat balance) as a function of two input variables, i.e. the amount of oxygen and steam used, both expressed in kg per 100 kg of biomass. These mappings are prepared for two different yields of primary liquid, i.e., 20 and 25%, arranged in Figure 9a-c and Figure 9d-f, respectively. In order to reach a self-sustainable regime in the plant, the following three conditions must be satisfied simultaneously (indicated as green areas in Figure 9): (1) the molar ratio of H_2/primary liquid should be higher than 5 to achieve the full hydrogenation (refining) of the primary liquid (reaction r.1); and (2-3) the energy balance (thermal and electric) should reach negative

12

values, which indicate energy surplus while positive values represent energy deficit. As can be seen in Fig. 9a, for a primary liquid yield of 25% there is an extended range of zones fulfilling the requirement of the H_2/primary liquid ratio > 5 but these preferred zones are narrower in the case of both electrical power and heat (negative) balances (Figs. 9b-c, respectively). In fact, there is not overlapping of the optimal zones (red zones) for the three factors for primary liquid yield of 25%. However, by decreasing the primary liquid yield to 20% (Fig. 9d-f), these zones with negative energy balance are enlarged, which is principally caused by the lower oxygen/biomass ratio. The lower demanded liquid yield allows a broader global optimal zone to be defined, where the three conditions are simultaneous fulfilled. Combining the three optimal zones for each condition (H_2/liquid ratio, heat and electrical balance) makes it possible to identify the global operation window for a self-sustainable regime (Figure 10).

Considering three different biomass compositions (1, 2 and 3) and two types of oxidants (oxygen and air), Table 3 presents the maximal primary liquid yields achieved for each biomass and oxidant where all the objectives are simultaneously satisfied. In a similar way as in Figure 10, Figure 11 presents the conditions where the three goals are satisfied at the specific primary liquid yield determined in the Table 3 for each biomass and oxidant. As can be seen, the primary liquid yield rises with increasing C/O ratio in the starting biomass in a self-sustainable process. Indeed, higher C/O ratios implies that the initial material is less oxidized and, consequently, more energy is available to fulfil thermal and/or electric energy balances. On the other hand, using oxygen as oxidant allows reaching higher liquid yields in self-sustainable regime due to more favourable thermal balance.

3.3.1 Overall system analysis

Table 4 shows heat and electrical power balances in detail for the overall process calculated taking into account the biomass 2 with a primary liquid yield of 20%, 80 kg air in the gasifier per each 100kg biomass and 30 kg steam in the gasifier per each 100kg biomass. Both the heat (-47.27 MJ/100kg biomass) and the electrical power (-13.52 kWh/100kg biomass) balances offer the required negative values. Thermal balance data show that the overall process needs to

use the thermal energy of the tail gases at the turbine outlet to warm up the pyrolyzer and gasifier units. The electric demand is satisfied by the gas turbine. These results are similar to the results reported in previous works [22].

The composition and molar flows of all the different streams of the process calculated for the same conditions described above are listed in Table S2 (*Supporting Information*). The outlet of the pyrolysis unit is a partially-oxidized gas where the CO and CH_4 are the principal energy-bearing gases. The outlet stream of the gasifier shows that CH_4 has been oxidized in the gasifier increasing the CO, CO_2 and H_2 amounts. The membrane reactor outlet stream shows that steam is efficiently utilized in the water shift reaction to obtain high purity H_2. The outlet stream of the hydrogenation unit shows a high excess of H_2 in this unit. Finally, the tail gases of the turbine consist of the steam, CO_2 and depleted air with traces of CO.

This study is aimed to identify the operation windows that enable to reach energy-balanced regime at the highest liquid yield. However, this operation regime may require complex heat exchange systems to close the energy balances. However, setting lower yields enables to enlarge the operation windows fulfilling energy-balanced operation and this can be favourable from the point of view of both plant operability and flexibility.

3.4 Advanced study

After analysing the effects of the different factors in the primary liquid yield and the corresponding energy balances, further analysis were made. The other extreme biomass compositions were comparatively studied to observe differences in the behaviour of the plant. Finally, the effect of changing the primary liquid composition allows obtaining a more realistic estimation about the plant operation using real primary liquid or bio-oil (mixture of different compounds whose composition depends on the pyrolysis conditions, as explained in methods). All these aspects will be treated and discussed in the following sections.

3.4.1 Study of the hydrogenation reactor

The hydrogenation step is one of the key points in the overall process allowing transforming the primary liquid obtained from pyrolyzer into the desired high-quality liquid fuel. For this step, H_2 at high pressure must be provided to the hydrogenation reactor. Figure S4 (*Supporting Information*) shows the effect of changing the pressure of the hydrogenation unit from 50 bar to 70 bar on heat and electrical balances calculated for different biomass with a primary liquid yield of 20% in the pyrolyzer, 30kg of steam per each 100kg of biomass and 80kg of air per 100kg of biomass (these conditions enable to maximize the liquid yield at energy-balanced regime). The energy balance breakdown is provided in Table S3 (*Supporting Information*) and shows the effect of the H_2 pressure on the overall process energetics. As can be seen, H_2 pressure does not affect the heat power calculated for the hydrogenation reactor but the electrical demand of liquid pump and H_2 compressor increases. Finally, the overall process is able to produce enough energy to satisfy this increase in power demand at higher hydrogenation pressures. In summary, if the primary liquid comprises a relatively high number of oxygenated compounds, which are more difficult to hydrogenate (or hydro-deoxigenate), higher hydrogenation pressures are necessary while the overall process is self-regulated and can provide enough energy to accomplish the self-sustainable regime.

3.4.2 Effect of the biomass composition

The effect of using extreme compositions of biomass on the heat and electrical balances was analysed to provide a broader vision of the potential feedstock and related plant energetics. Table 1 shows the compositions for the biomasses 4 and 5. The conditions and results of the overall process for the additional biomasses 4 and 5 are summarized in Table 5. Biomass 4 presents low C/O ratio (C/O$_{biomass\ 4}$= 0.854), i.e. the initial material has a highly oxidized fraction and, consequently, the expected outcome in terms of thermal and electrical energies is lower with respect those observed for biomass 1 to 3. On the other hand, the use of a biomass with extremely high C/O ratio (C/O$_{biomass\ 5}$= 2.398) allows attaining higher primary liquid yields keeping the energy self-sustainable regime.

For both extreme biomass compositions (4 and 5), Table S4 and S5 describe the composition of all the different streams of the process and the operation conditions of the process units. For both cases, the outlet of the pyrolysis unit is composed of partly-oxidized gas with fuel gases comprising principally CO and CH_4. The outlet stream of the gasifier evidences that CH_4 is converted into CO, CO_2 and H_2 amounts. The composition of the membrane reactor outlet-stream suggests that the *in situ* H_2 recovery enables to drive efficiently the water shift reaction to obtain H_2 for the biomass 4 (Table S4) but not for the biomass 5 (Table S5), where the membrane reactor stream shows a high amount of CO and no presence of steam. This last effect is because the steam introduced in the gasifier is not enough to drive the equilibrium of the water gas shift reaction to full conversion towards CO_2, however, there is enough H_2 to refine all the primary liquid. Therefore, it is not necessary to introduce more steam since this would worsen the energy balance. Further, the outlet stream of the hydrogenation unit shows high excess of H_2 in this unit, even if more H_2 could be potentially produced by further shifting the remaining CO to $H_2 + CO_2$ to rise H_2 yield. Finally, the tail gas is a mixture of the steam, CO_2, the depleted air and CO traces.

3.4.3   Analysis of the effect of the composition of the primary liquid

The composition of the primary liquid produced from pyrolyzer strongly influences the overall process and the final amount of upgraded liquid fuel produced. In first place, considering the stoichiometry of the reactions (r1 – r4), the weight relation between the primary liquid compounds and the refined liquid compounds are 103.55%, 78.65%, 75.11% and 48.96% for the methyl naphthalene, gastrodigenin, furfural and lactic acid as primary liquid compounds. For the partially oxidized compounds (gastrodigenin, furfural and lactic acid), there is a decrease in the liquid yield (since primary liquid until refined liquid) because the release of water during the reaction while for the methylnaphthalene there is an increase in the liquid yield because all the hydrogen is incorporated in the refined compound. Figure 12 and Table S6 present simulation results (energy balances) considering (1) different model compounds (i.e. methyl-naphthalene, 4-hydroxybenzyl alcohol, furfural and lactic acid) as primary

16

pyrolysis products of for the biomass 2; and (2) selected operation conditions: primary liquid yield of 20%, 80 kg air / 100kg biomass and 30 kg steam / 100kg biomass.

The analysis of both heat and electrical energy terms reveals that (i) the lactic acid presents the best balance results; (ii) 4-hydroxybenzyl alcohol or gastrodigenin and furfural present similar intermediate values; and (iii) the methylnaphthalene is the less favourable case. The nature of the molecule (molecular weight[1], unsaturation and oxygen content) determines the H_2 demand in the hydrogenation step and the final liquid yield.

The heat simulation results[2] from Figure 12a show that increasing the molecular weight (MW) of the primary liquid leads to lesser yields of non-oxidized gas compounds (fuel gas) and this leads to worse energetic results. Regarding the final heat exchanger, lower yields of fuel gas decreases the temperature of the outlet of the turbine and, therefore, decreases the heat flow useful for transfer to pyrolysis and char gasification units. Figure 12b shows the electric power results[3] and the trend of the results evidences that a slight decrease in the energy demands for vacuum and gas compression is observed as the molecular weight of the primary liquid increases. Increasing the molecular weight of the primary liquid induces a drop in the energy supplied by the turbine since a lower flow rate of non-oxidized gas compounds is available for the combustion.

Table S7 shows the values for the high heating value (HHV) for the couples: primary liquid compound and refined compound. The results show that, as the molecular weight of the liquid decreases, the HHV of the primary liquid decreases while HHV of the refined fuel increases. The final yield of the refined fuel declines with decreasing molecular weights (Figure 4b) although the energy content increases.

---

[1] 90.09g/mol for the lactic acid, 96.09g/mol for the furfural, 124.15g/mol for the gastrodigenin, 142.21g/mol for the methyl-naphthalene

[2] Note that the pyrolysis and char gasifier are energy demanding processes while the exchanger after the gasifier and the final heat exchanger are recovering heat

[3] Vacuum, compression of H_2 and compression of gases are energy-demanding processes while the turbine produces net electric power

In general, the composition of the primary liquid (or pyrolytic bio-oil) is a consequence of the conditions in the pyrolysis and this step significantly affects the overall process design. An increase in the pyrolysis temperature above 550 – 600ºC decreases the primary liquid yield that can be obtained. On one hand, processes with less endothermic pyrolysis step (lower pyrolysis temperatures) produce heavier liquids and lower gaseous streams with lower CO, CO_2 and H_2 yields. Thus, lower H_2 yield gives rise to a reduction in the refined liquid fuel yield. Therefore, due to the lower fuel gas yield, the turbine power is lower and both electrical and thermal energy balances become less favourable. On the other hand, the process with a highly-endothermic pyrolysis step (higher pyrolysis temperature) produces lighter primary liquids and higher CO, CO_2 and H_2 yields. As a consequence, higher amounts of primary liquid can be refined because there is more available H_2 and also fuel gas at the inlet of the turbine and, therefore the electrical and thermal energy balances are more favourable. In summary, a trade-off between the amounts of primary liquids and gas streams produced during pyrolysis step will define the overall process design and the corresponding heat and electrical energy balances. The performance of pyrolysis unit has a large impact in the overall process energetics and mass balances and ultimately determines the primary liquid yield and composition. As a consequence, the pyrolyzer is the most critical unit to accomplish the energy-balanced regime while maximizing the biomass transformation into liquid fuels.

4. CONCLUSIONS

This study analysis the integrated biomass transformation into both energy and chemicals and uses the overall process energy (thermal and power) to supply the energy demands of the different units in the plant. Specifically, the production of liquid fuels from biomass in a self-sustainable process was analysed in this work. The system was designed to process different types of biomass. Biomass with high C/O ratios (≥ 1.2) allows reaching higher primary liquid (or pyrolytic bio-oil) yields via an energetically self-sustainable process, with liquid yields after pyrolysis around 20 – 25% working at 10 – 25% of O_2 (as pure oxygen or air) and 15 – 45% of steam in the gasifier.

The yield of the primary liquid produced in the pyrolysis step determines the heat and electrical energy balances of the process. Thus, when higher liquid yields ($\geq 20\%$) are obtained, the process must also provide adequate amount of fuel gas (H_2, CO, CH_4, and other hydrocarbons) to produce heat and electrical energy in downstream processes. The tail gases (N_2, H_2O, CO, CO_2, etc.) at the turbine outlet has to bear enough heat to balance the pyrolysis and gasifier units, consequently, high oxidizable fractions (fuel gas) are needed at the turbine inlet to reach self-sustainable regime, i.e., favourable thermal and electric balances. Therefore, it is necessary to reach an optimal balance between the primary liquid yield and the energy balances.

The study of different biomass compositions reveals that biomass 2 and 3 with C/O ratios of 1.2 and 1.5, respectively, give the most favourable liquid fuel yields and both thermal and electrical energy balance are favourable. After pyrolysis, those biomass types (2 and 3) generate liquid and gases in adequate proportions that match the H_2 consumption during hydrogenation step. Nevertheless, biomasses 1 and 4 with relatively lower amount of C in their compositions are suitable for treatment in this integrated approach offering acceptable liquid fuel yields (c.a. 20%) at favourable energy balances.

In addition, the operational conditions (mainly temperature) of the pyrolysis unit determine the primary liquid and gas compositions. Higher pyrolysis temperatures produce lighter bio-oils and higher gas yields, and, as a consequence of these lighter primary liquids (bio-oils) more favourable thermal and electrical energy balances are reached. In fact, it would be not necessary to work at very high pyrolytic liquid yields to attain good energy balances, on the contrary, a trade-off between the yields of liquids and gases fractions is crucial to reach a self-sustainable overall process. This study has identified windows of operation conditions in the transformation of different biomass types into refined liquids that enable to reach an energetic self-sustainable plant regime, that implies reaching a balance among (i) the yield of refined liquid, (ii) the energy produced in the process (both heat and electrical) and (iii) the hydrogen yield to be used in the refining of the primary liquid.

In the perspective of bio-economy concept, this self-sufficient operation is crucial to enable the design and development of decentralized waste treatment factories for the transformation of a large variety of biomass residues in both urban and rural areas. This approach encompasses several advantages, such as i) facilitating plant logistics, ii) enlargement of biomass feedstocks utilization, iii) developing alternative fuels from non-conventional raw materials, and remarkably, iv) minimizing GHG emissions due to avoidances of transport and additional heat and power generation from fossil sources.

5. ACKNOWLEDGMENTS

6. REFERENCES

1. UNION, P., *DIRECTIVE 2009/28/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23âApril 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC andâ2003/30/EC*. 2009, EC.
2. Cleveland, C.J. and R.U. Ayres, *Encyclopedia of Energy: Ec-Ge*. 2004: Elsevier Academic Press.
3. Klass, D.L., *Chapter 7 - Thermal Conversion: Combustion*, in *Biomass for Renewable Energy, Fuels, and Chemicals*. 1998, Academic Press: San Diego. p. 191-224.
4. Butler, E., et al., *A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading.* Renewable & Sustainable Energy Reviews, 2011. **15**(8): p. 4171-4186.
5. Gayubo, A.G., et al., *Pyrolytic lignin removal for the valorization of biomass pyrolysis crude bio-oil by catalytic transformation.* Journal of Chemical Technology and Biotechnology, 2010. **85**(1): p. 132-144.
6. Iliopoulou, E.F., et al., *Pilot-scale validation of Co-ZSM-5 catalyst performance in the catalytic upgrading of biomass pyrolysis vapours.* Green Chemistry, 2014. **16**(2): p. 662-674.
7. Alonso, D.M., J.Q. Bond, and J.A. Dumesic, *Catalytic conversion of biomass to biofuels.* Green Chemistry, 2010. **12**(9): p. 1493-1513.
8. Huber, G.W., S. Iborra, and A. Corma, *Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering.* Chemical Reviews, 2006. **106**(9): p. 4044-4098.
9. Corma, A., S. Iborra, and A. Velty, *Chemical routes for the transformation of biomass into chemicals.* Chemical Reviews, 2007. **107**(6): p. 2411-2502.

10. Deneyer, A., et al., *Compositional and structural feedstock requirements of a liquid phase cellulose-to-naphtha process in a carbon- and hydrogen-neutral biorefinery context.* Green Chemistry, 2016. **18**(20): p. 5594-5606.

11. Tuck, C.O., et al., *Valorization of Biomass: Deriving More Value from Waste.* Science, 2012. **337**(6095): p. 695-699.

12. Asadullah, M., *Biomass gasification gas cleaning for downstream applications: A comparative critical review.* Renewable and Sustainable Energy Reviews, 2014. **40**(0): p. 118-132.

13. Bensaid, S., R. Conti, and D. Fino, *Direct liquefaction of ligno-cellulosic residues for liquid fuel production.* Fuel, 2012. **94**(0): p. 324-332.

14. Abnisa, F. and W.M.A. Wan Daud, *A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil.* Energy Conversion and Management, 2014. **87**(0): p. 71-85.

15. Parthasarathy, P. and K.N. Sheeba, *Combined slow pyrolysis and steam gasification of biomass for hydrogen generation—a review.* International Journal of Energy Research, 2015. **39**(2): p. 147-164.

16. Salemme, L., et al., *Analysis of the energy efficiency of solar aided biomass gasification for pure hydrogen production.* International Journal of Hydrogen Energy, 2014. **39**(27): p. 14622-14632.

17. Adeyemi, I. and I. Janajreh, *Modeling of the entrained flow gasification: Kinetics-based ASPEN Plus model.* Renewable Energy, 2015. **82**: p. 77-84.

18. Henriksen, U., et al., *The design, construction and operation of a 75 kW two-stage gasifier.* Energy, 2006. **31**(10–11): p. 1542-1553.

19. Ward, J., M.G. Rasul, and M.M.K. Bhuiya, *Energy Recovery from Biomass by Fast Pyrolysis.* Procedia Engineering, 2014. **90**(0): p. 669-674.

20. Shemfe, M.B., S. Gu, and P. Ranganathan, *Techno-economic performance analysis of biofuel production and miniature electric power generation from biomass fast pyrolysis and bio-oil upgrading.* Fuel, 2015. **143**: p. 361-372.

21. Görling, M., M. Larsson, and P. Alvfors, *Bio-methane via fast pyrolysis of biomass.* Applied Energy, 2013. **112**: p. 440-447.

22. Jana, K. and S. De, *Biomass Integrated Combined Power Plant with Post Combustion Co2 Capture – Performance Study by ASPEN Plus®.* Energy Procedia, 2014. **54**: p. 166-176.

23. Zheng, H., N. Kaliyan, and R.V. Morey, *Aspen Plus simulation of biomass integrated gasification combined cycle systems at corn ethanol plants.* Biomass and Bioenergy, 2013. **56**: p. 197-210.

24. Louw, J., et al., *Thermodynamic modelling of supercritical water gasification: Investigating the effect of biomass composition to aid in the selection of appropriate feedstock material.* Bioresource Technology, 2014. **174**: p. 11-23.

25. Ramzan, N., et al., *Simulation of hybrid biomass gasification using Aspen plus: A comparative performance analysis for food, municipal solid and poultry waste.* Biomass and Bioenergy, 2011. **35**(9): p. 3962-3969.

26. Beheshti, S.M., H. Ghassemi, and R. Shahsavan-Markadeh, *An advanced biomass gasification–proton exchange membrane fuel cell system for power generation.* Journal of Cleaner Production.

27. Doherty, W., A. Reynolds, and D. Kennedy, *Computer simulation of a biomass gasification-solid oxide fuel cell power system using Aspen Plus.* Energy, 2010. **35**(12): p. 4545-4555.

28. Doherty, W., A. Reynolds, and D. Kennedy, *Process simulation of biomass gasification integrated with a solid oxide fuel cell stack.* Journal of Power Sources, 2015. **277**: p. 292-303.

29. Damartzis, T., S. Michailos, and A. Zabaniotou, *Energetic assessment of a combined heat and power integrated biomass gasification–internal combustion engine system by using Aspen Plus®.* Fuel Processing Technology, 2012. **95**: p. 37-44.

30.   Taufiq-Yap, Y.H., et al., *Hydrogen production from wood gasification promoted by waste eggshell catalyst.* International Journal of Energy Research, 2013. **37**(14): p. 1866-1871.

31.   Su, S., et al., *Production of hydrogen by steam gasification from lignin with Al2O3·Na2O·xH2O/NaOH/Al(OH)3 catalyst.* Journal of Fuel Chemistry and Technology, 2010. **38**(3): p. 270-274.

32.   Yan, H.M. and D.K. Zhang, *Modeling of a Low Temperature Pyrolysis Process Using ASPEN PLUS.* Developments in Chemical Engineering and Mineral Processing, 1999. **7**(5-6): p. 577-591.

33.   Luo, Z., S. Wang, and K. Cen, *A model of wood flash pyrolysis in fluidized bed reactor.* Renewable Energy, 2005. **30**(3): p. 377-392.

34.   Rezvani, S., et al., *Comparative assessment of coal fired IGCC systems with CO2 capture using physical absorption, membrane reactors and chemical looping.* Fuel, 2009. **88**(12): p. 2463-2472.

35.   Al-Mufachi, N.A., N.V. Rees, and R. Steinberger-Wilkens, *Hydrogen selective membranes: A review of palladium-based dense metal membranes.* Renewable and Sustainable Energy Reviews, 2015. **47**: p. 540-551.

36.   Hatlevik, Ø., et al., *Palladium and palladium alloy membranes for hydrogen separation and production: History, fabrication strategies, and current performance.* Separation and Purification Technology, 2010. **73**(1): p. 59-64.

37.   Gallucci, F., et al., *Recent advances on membranes and membrane reactors for hydrogen production.* Chemical Engineering Science, 2013. **92**: p. 40-66.

38.   Tao, Z., et al., *A review of advanced proton-conducting materials for hydrogen separation.* Progress in Materials Science, 2015. **74**: p. 1-50.

39.   Lewis, A.E., et al., *PdAu and PdAuAg composite membranes for hydrogen separation from synthetic water-gas shift streams containing hydrogen sulfide.* Journal of Membrane Science, 2014. **465**: p. 167-176.

40.   Penner, S.S., *Steps toward the hydrogen economy.* Energy, 2006. **31**(1): p. 33-43.

41.   Garcia-Fayos, J., et al., *Oxygen transport membranes in a biomass/coal combined strategy for reducing CO2 emissions: Permeation study of selected membranes under different CO2-rich atmospheres.* Catalysis Today, 2015. **257**: p. 221-228.

42.   Vassilev, S.V., et al., *An overview of the chemical composition of biomass.* Fuel, 2010. **89**(5): p. 913-933.

43.   Kohl, T., T.P. Laukkanen, and M.P. Järvinen, *Integration of biomass fast pyrolysis and precedent feedstock steam drying with a municipal combined heat and power plant.* Biomass and Bioenergy, 2014. **71**(0): p. 413-430.

44.   Meng, A., et al., *Pyrolysis and simulation of typical components in wastes with macro-TGA.* Fuel, 2015. **157**: p. 1-8.

45.   Li, Y., L.W. Zhou, and R.Z. Wang, *Urban biomass and methods of estimating municipal biomass resources.* Renewable and Sustainable Energy Reviews, 2017. **80**: p. 1017-1030.

46.   Cho, H.S., H.S. Moon, and J.Y. Kim, *Effect of quantity and composition of waste on the prediction of annual methane potential from landfills.* Bioresource Technology, 2012. **109**: p. 86-92.

47.   McKendry, P., *Energy production from biomass (part 1): overview of biomass.* Bioresource Technology, 2002. **83**(1): p. 37-46.

48.   Baxter, L.L., *Ash deposition during biomass and coal combustion: A mechanistic approach.* Biomass and Bioenergy, 1993. **4**(2): p. 85-102.

49.   Jenkins, B.M., et al., *Combustion properties of biomass.* Fuel Processing Technology, 1998. **54**(1–3): p. 17-46.

50.   Raclavská, H., et al., *Effect of temperature on the enrichment and volatility of 18 elements during pyrolysis of biomass, coal, and tires.* Fuel Processing Technology, 2015. **131**: p. 330-337.

51. Mushtaq, F., R. Mat, and F.N. Ani, *A review on microwave assisted pyrolysis of coal and biomass for fuel production.* Renewable and Sustainable Energy Reviews, 2014. **39**: p. 555-574.

52. Elizalde, I., M.A. Rodríguez, and J. Ancheyta, *Modeling the effect of pressure and temperature on the hydrocracking of heavy crude oil by the continuous kinetic lumping approach.* Applied Catalysis A: General, 2010. **382**(2): p. 205-212.

53. Bi, P., et al., *From lignin to cycloparaffins and aromatics: Directional synthesis of jet and diesel fuel range biofuels using biomass.* Bioresource Technology, 2015. **183**: p. 10-17.

54. Galiasso Tailleur, R. and J.R. Nascar, *The effect of aromatics on paraffin mild hydrocracking reactions (WNiPd/CeY–Al2O3).* Fuel Processing Technology, 2008. **89**(8): p. 808-818.

55. Fujikawa, T., et al., *Kinetic behavior of hydrogenation of aromatics in diesel fuel over silica–alumina-supported bimetallic Pt–Pd catalyst.* Applied Catalysis A: General, 2001. **205**(1–2): p. 71-77.

56. Calemma, V., R. Giardino, and M. Ferrari, *Upgrading of LCO by partial hydrogenation of aromatics and ring opening of naphthenes over bi-functional catalysts.* Fuel Processing Technology, 2010. **91**(7): p. 770-776.

57. Venezia, A.M., et al., *Hydrogenation of aromatics over Au-Pd/SiO2-Al2O3 catalysts; support acidity effect.* Applied Catalysis A: General, 2004. **264**(1): p. 43-51.

58. Murcia-Mascarós, S., B. Pawelec, and J.L.G. Fierro, *Hydrogenation of aromatics over PtPd Metals supported on a mixed γ-ZrP–silica carrier promoted with lithium.* Catalysis Communications, 2002. **3**(7): p. 305-311.

59. Rezaei, P.S., H. Shafaghat, and W.M.A.W. Daud, *Production of green aromatics and olefins by catalytic cracking of oxygenate compounds derived from biomass pyrolysis: A review.* Applied Catalysis A: General, 2014. **469**: p. 490-511.
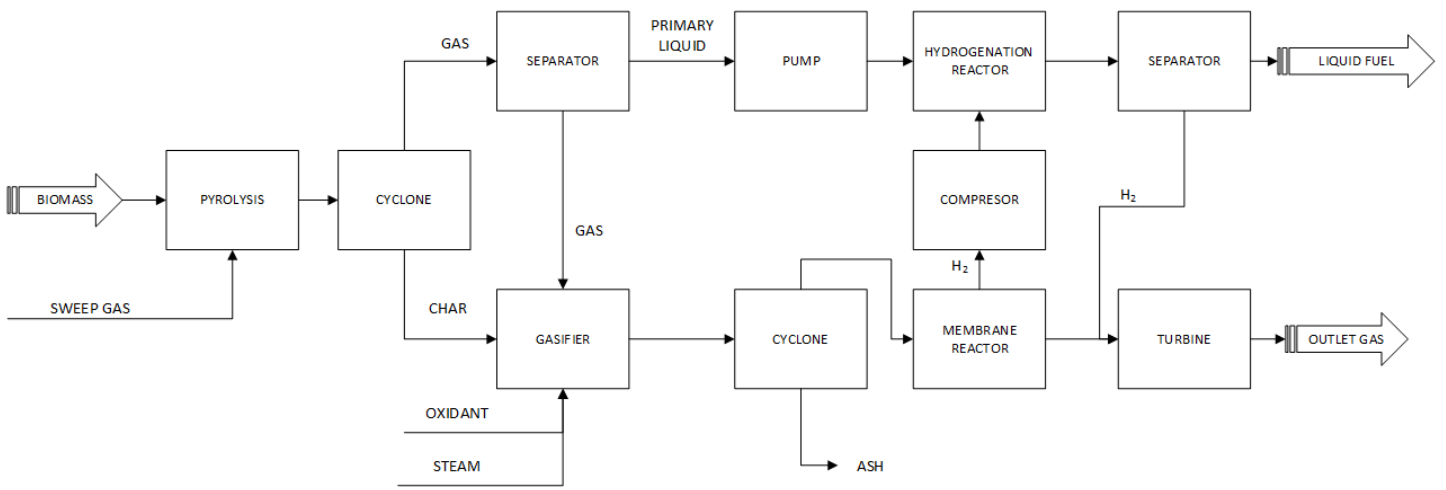
Figure Captions

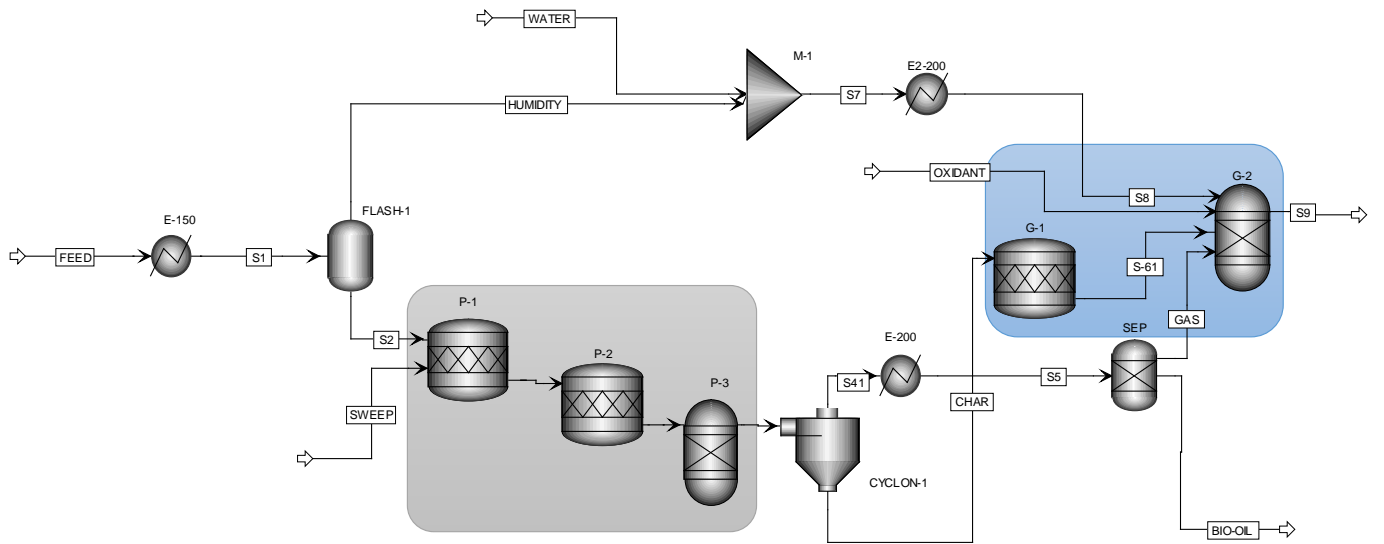Figure 1: View of the diagram of the process.

Figure 2: Description of the model of the pyrolysis and gasifier units. (grey zones: units to simulate the pyrolysis process; blue zones: units to simulate the gasification process)
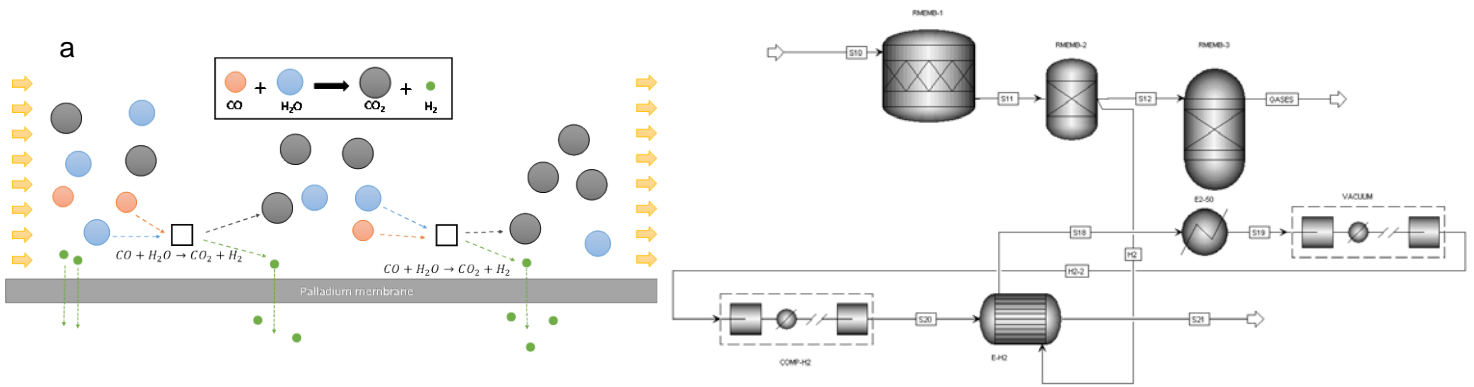
Figure 3: Membrane reactor. (a) Displacement of the water shift reaction to favour H2 formation; (b) Model of the membrane reactor in ASPEN PLUS.
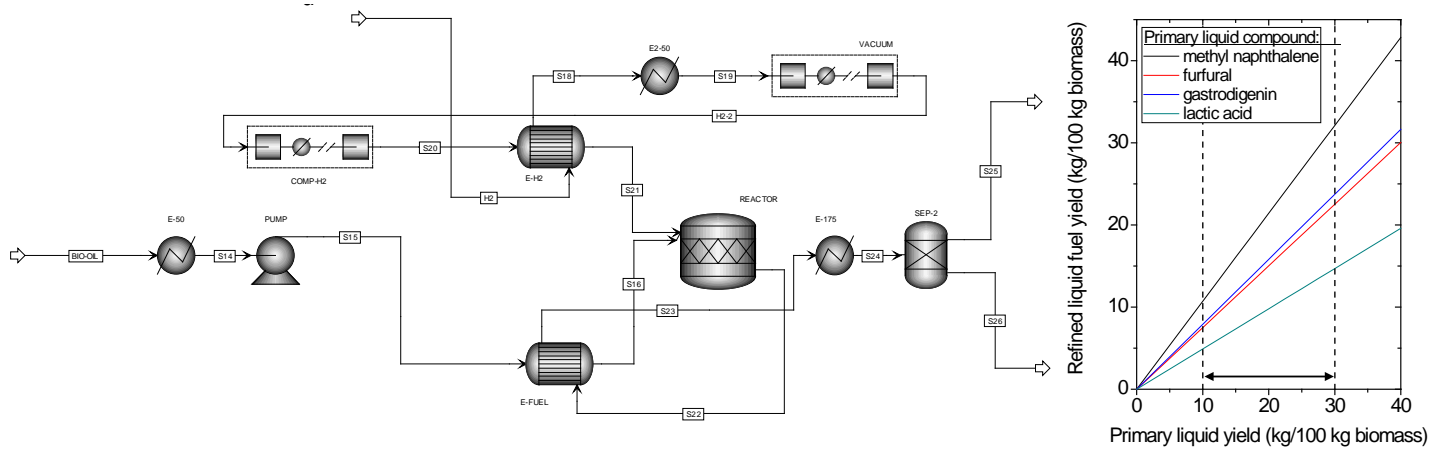
Figure 4: (a) Compressor and pump units and hydrogenation reactor; (b) Refined liquid fuel obtained according the primary liquid yield of the pyrolyzer.
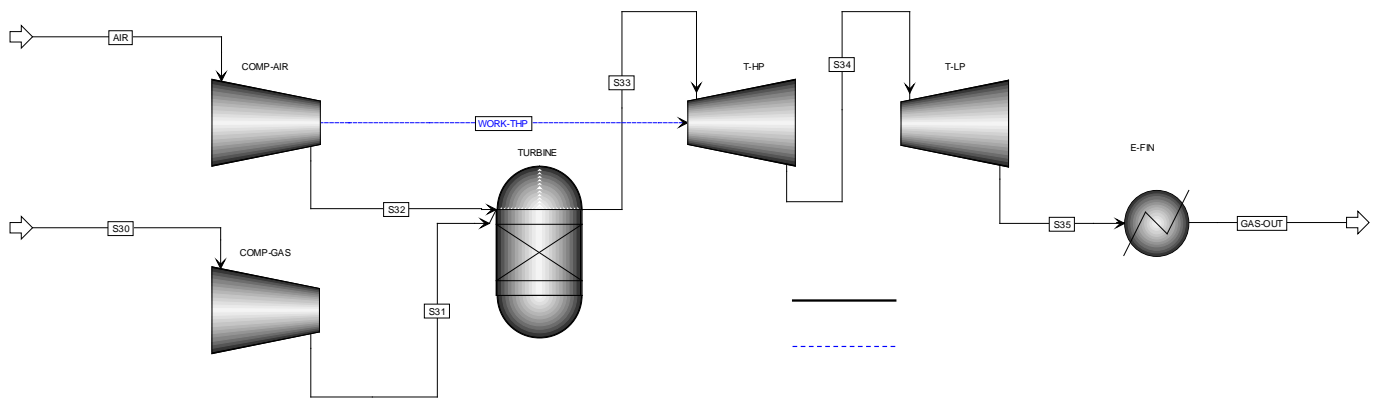
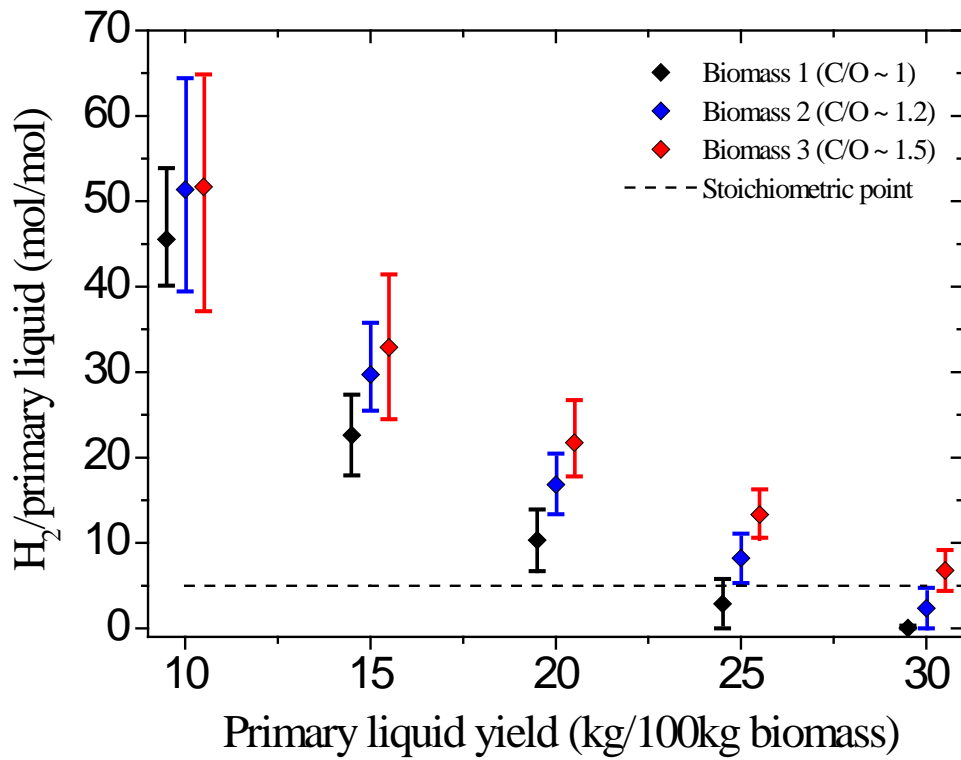Figure 5: Treatment of the final gases. Compressors and gas turbine.

Figure 6: Effect of the primary liquid yield in the molar ratio H_2 – primary liquid. The range for each data point represents the different results at different steam and oxidant type introduced in the gasifier process. Upper: maximum value; symbol: average; lower: minimum value.
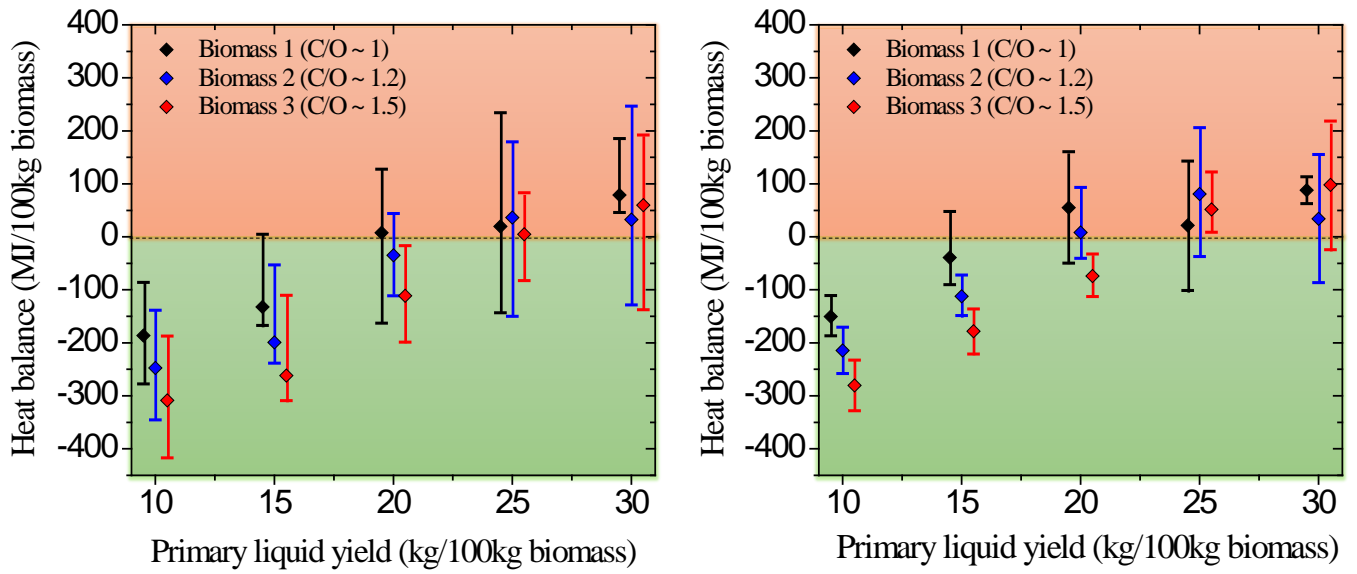
Figure 7: Effect of the primary liquid yield in the heat balance of the process. Right: system with oxygen as oxidant; left: system with air as oxidant. Upper: maximum value; diamond symbol: average; lower: minimum value

Figure 8: Effect of the primary liquid yield in the electrical balance of the process. Right: system with oxygen as oxidant; left: system with air as oxidant

Figure 9: Description of the search space for the biomass 2 with oxygen as oxidant: Simulation results of H_2/primary liquid ratio, electrical power and heat balance for a primary liquid yield of (a-c) 25% and (e-f) 20%. $yield_{PL}$: primary liquid yield

Figure 10: Global optimal zone for biomass 2 with oxygen as oxidant with a primary liquid yield of 20%.

Figure 11: Global optimal zones: (a – c) using oxygen as oxidant; (d – f) using air as oxidant. (a and d) biomass 1; (b and e) biomass 2; (c and f) biomass 3.

Figure 12: Energy results for different compositions of the primary liquid. (a) heat results; (b) electrical results.

Table 1: Description of the different types of biomass studied.

Table 2: Description of the parameters studied.

Table 3: Optimal primary liquid yield in the pyrolyzer for each biomass.

Table 4: Energy analysis for the biomass 2 with a primary liquid yield of 20%, 80 kg air in the gasifier per each 100kg biomass and 30 kg steam in the gasifier per each 100kg biomass.

Table 5: Effect of use extreme composition of biomass.

Figure 1: View of the diagram of the process

Figure 2: Description of the model of the pyrolysis and gasifier units. (grey zones: units to simulate the pyrolysis process; blue zones: units to simulate the gasification process).

Figure 3: Membrane reactor. (a) Displacement of the water shift reaction to favor H_2 formation; (b) Model of the membrane reactor in ASPEN PLUS.

Figure 4: (a) Compressor and pump units and hydrogenation reactor; (b) Refined liquid fuel obtained according the primary liquid yield of the pyrolyzer.

Figure 5: Treatment of the final gases. Compressors and gas turbine.

Figure 6: Effect of the primary liquid yield in the molar ratio H$_2$ – primary liquid. The range for each data point represents the different results at different steam (15 – 45 kg steam/kg biomass) and oxidant type (pure O$_2$: 2.5 – 30 kg/kg biomass; air: 40 – 110 kg/kg biomass) introduced in the gasifier process. Upper: maximum value; symbol: average; lower: minimum value.

Figure 7: Effect of the primary liquid yield in the heat balance of the process. Right: system with oxygen as oxidant; left: system with air as oxidant. The range for each data point represents the different results at different steam (15 – 45 kg steam/kg biomass) and oxidant type (pure O_2: 2.5 – 30 kg/kg biomass; air: 40 – 110 kg/kg biomass) introduced in the gasifier process. Upper: maximum value; diamond symbol: average; lower: minimum value
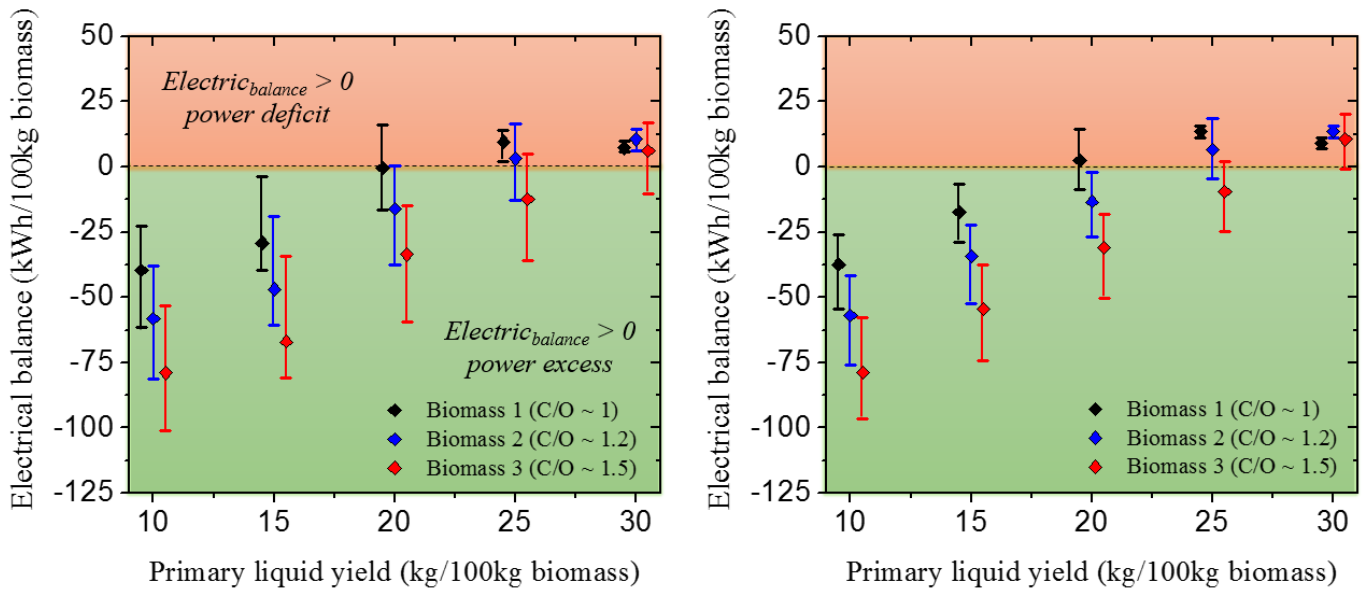
Figure 8: Effect of the primary liquid yield in the electrical balance of the process. The range for each data point represents the different results at different steam (15 – 45 kg steam/kg biomass) and oxidant type (pure O_2: 2.5 – 30 kg/kg biomass; air: 40 – 110 kg/kg biomass) introduced in the gasifier process. Right: system with oxygen as oxidant; left: system with air as oxidant
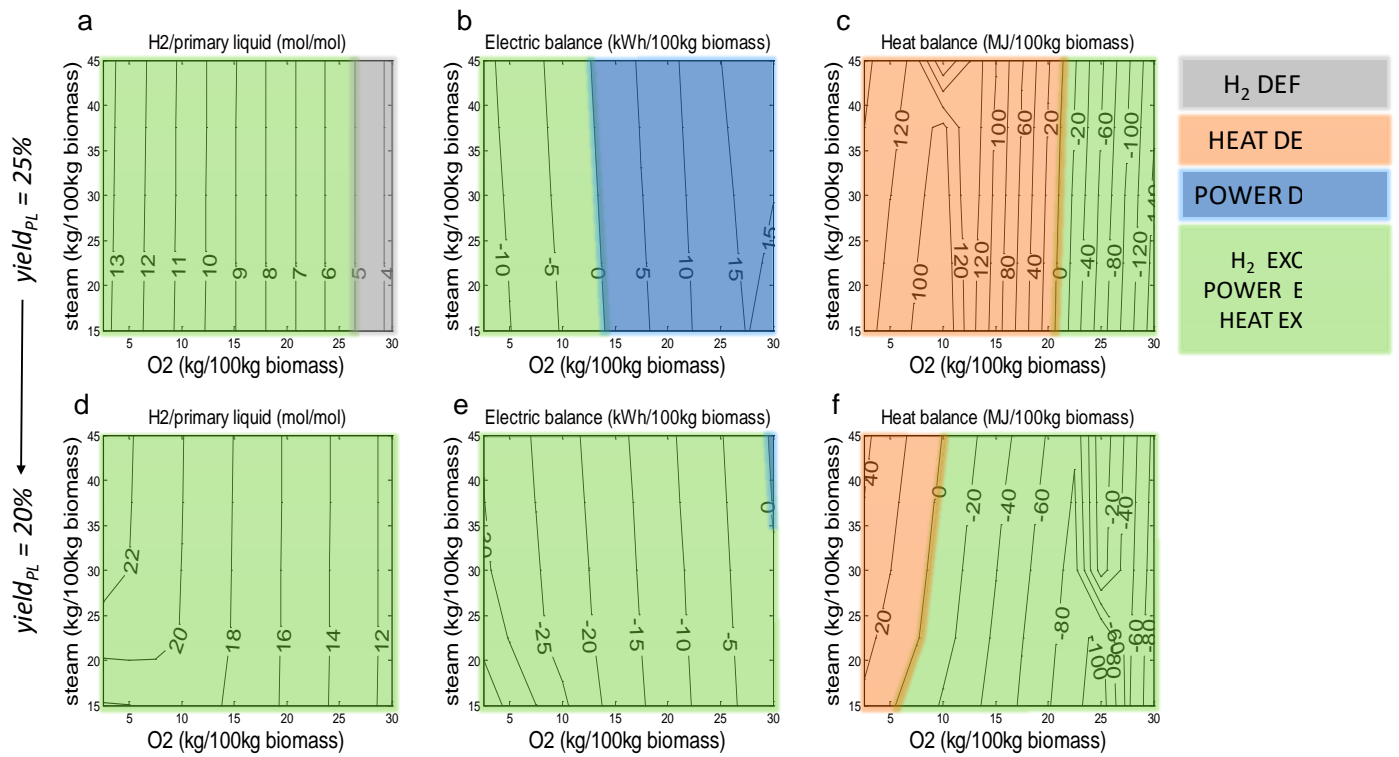
Figure 9: Description of the search space for the biomass 2 with oxygen as oxidant: Simulation results of H_2/primary liquid ratio, electrical power and heat balance for a primary liquid yield of (a-c) 25% and (e-f) 20%. $yield_{PL}$: primary liquid yield
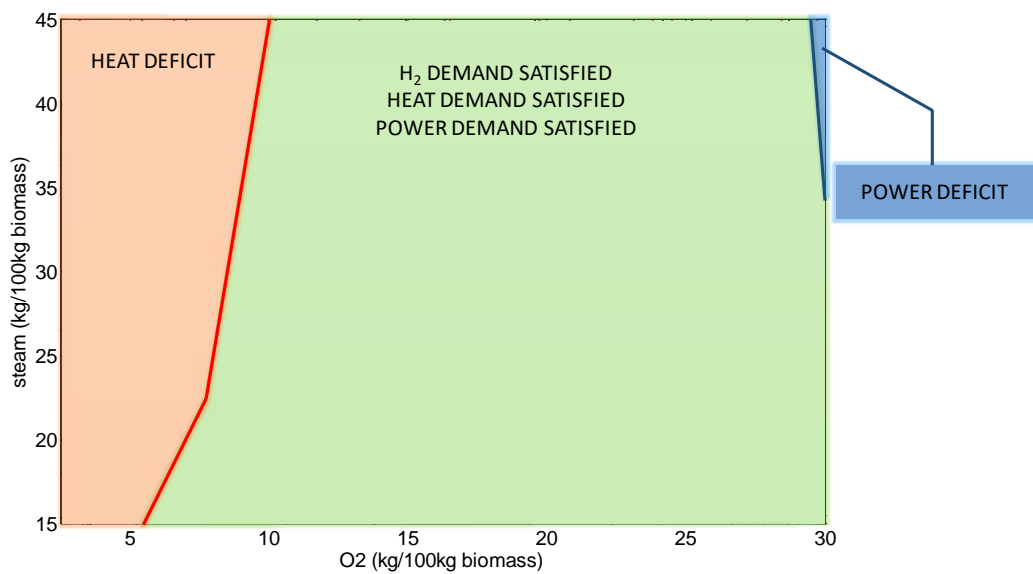
Figure 10: Global optimal zone for biomass 2 with oxygen as oxidant with a primary liquid yield of 20%.

Figure 11: Global optimal zones: (a − c) using oxygen as oxidant; (d − f) using air as oxidant. (a and d) biomass 1; (b and e) biomass 2; (c and f) biomass 3.

Figure 12: Energy results for different compositions of the primary liquid. (a) heat results; (b) electrical results.

Tables

Table 1: Description of the different types of biomass studied.

	% in weight				
	Biomass 1	Biomass 2	Biomass 3	Biomass 4	Biomass 5
Proximate analysis					
Fixed Carbon	29.89	29.89	29.89	50.00	50.00
Volatile matters	52.11	52.11	52.11	39.00	39.90
Moisture carbon	15.00	15.00	15.00	8.00	1.10
Ash	3.00	3.00	3.00	3.00	9.00
Ultimate analysis	(C/O=0.937)	(C/O=1.205)	(C/O=1.499)	(C/O=0.854)	(C/O=2.398)
H	6.07	6.07	6.07	6.56	5.88
N	0.15	0.15	0.15	0.00	0.10
C	46.25	51.25	56.25	43.05	66.35
O	47.53	42.53	37.53	50.39	27.67

Table 2: Description of the parameters studied.

Parameter	Units	Values
Type of primary liquid modelled	-	Methyl-naphthalene
		4-hydroxybenzyl alcohol
		Furfural
		Lactic acid
Primary liquid yield in the pyrolyzer	kg primary liquid/100kg biomass (%)	10 – 30
Oxidant used	-	Oxygen – Air
Ratio of oxygen	kg O_2 /kg biomass	0 – 30
Ratio of air	kg air/kg biomass	40 – 110
Ratio of steam	kg steam/100kg biomass	15 – 45

Table 3: Optimal primary liquid yield in the pyrolyzer for each biomass.

Primary liquid yield (%)	Biomass 1	Biomass 2	Biomass 3
Oxygen	15	20	25
Air	15	20	20

Table 4: Energy analysis for the biomass 2 with a primary liquid yield of 20%, 80 kg air in the gasifier per each 100kg biomass and 30 kg steam in the gasifier per each 100kg biomass.

	Value
HEAT ANALYSIS	
PYROLYSIS (MJ/100kg biomass)	158.17
GASIFIER (MJ/100kg biomass)	30.12
Heat exchanger outlet gasifier (MJ/100kg biomass)	-67.03
Heat exchanger final gas (MJ/100kg biomass)	-168.53
HEAT BALANCE (MJ/100kg biomass)	**-47.27**
ELECTRICAL ENERGY BALANCE	
VACUUM (kWh/100kg biomass)	2.25
COMPRESSION H_2 (kWh/100kg biomass)	11.79
COMPRESSION GASES (kWh/100kg biomass)	34.42
TURBINE (kWh/100kg biomass)	-61.99
PUMP (kWh/100kg biomass)	0.03
LIQUID TURBINE (kWh/100kg biomass)	-0.02
ELECTRICAL ENERGY BALANCE (kWh/100kg biomass)	**-13.53**

Table 5: Effect of use extreme composition of biomass.

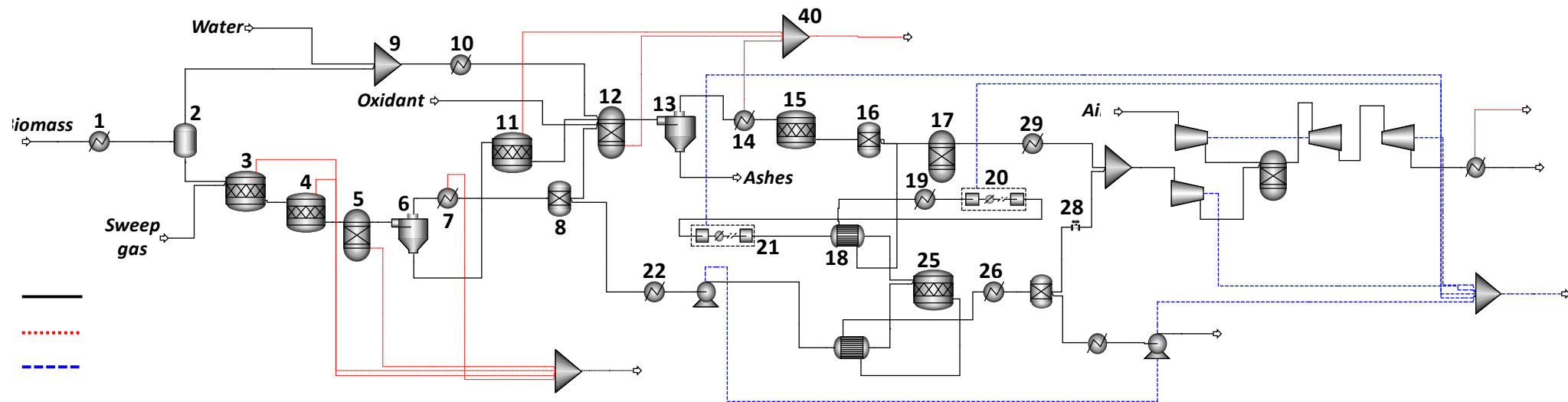|	Biomass 4	Biomass 5
Primary liquid yield	15%	25%
Air used in the gasifier (kg air/100kg biomass)	60	85
Steam used in the gasifier (kg steam/100kg biomass)	30	30
HEAT ANALYSIS		
PYROLYSIS (MJ/100kg biomass)	141.48	327.19
GASIFIER (MJ/100kg biomass)	114.00	60.76
Heat exchanger outlet gasifier (MJ/100kg biomass)	-68.08	-70.43
Heat exchanger final gas (MJ/100kg biomass)	-234.10	-452.76
HEAT BALANCE (MJ/100kg biomass)	**-46.70**	**-135.23**
ELECTRICAL POWER ANNALYSIS		
VACUUM (KWh/100kg biomass)	2.65	3.20
COMPRESSION H_2 (KWh/100kg biomass)	13.91	16.77
COMPRESSION GASES (KWh/100kg biomass)	35.84	39.45
TURBINE (KWh/100kg biomass)	-75.71	-125.41
PUMP (KWh/100kg biomass)	0.02	0.04
LIQUID TURBINE (KWh/100kg biomass)	-0.02	0.04
ELECTRICAL ENERGY BALANCE (KWh/100kg biomass)	**-23.31**	**-65.92**

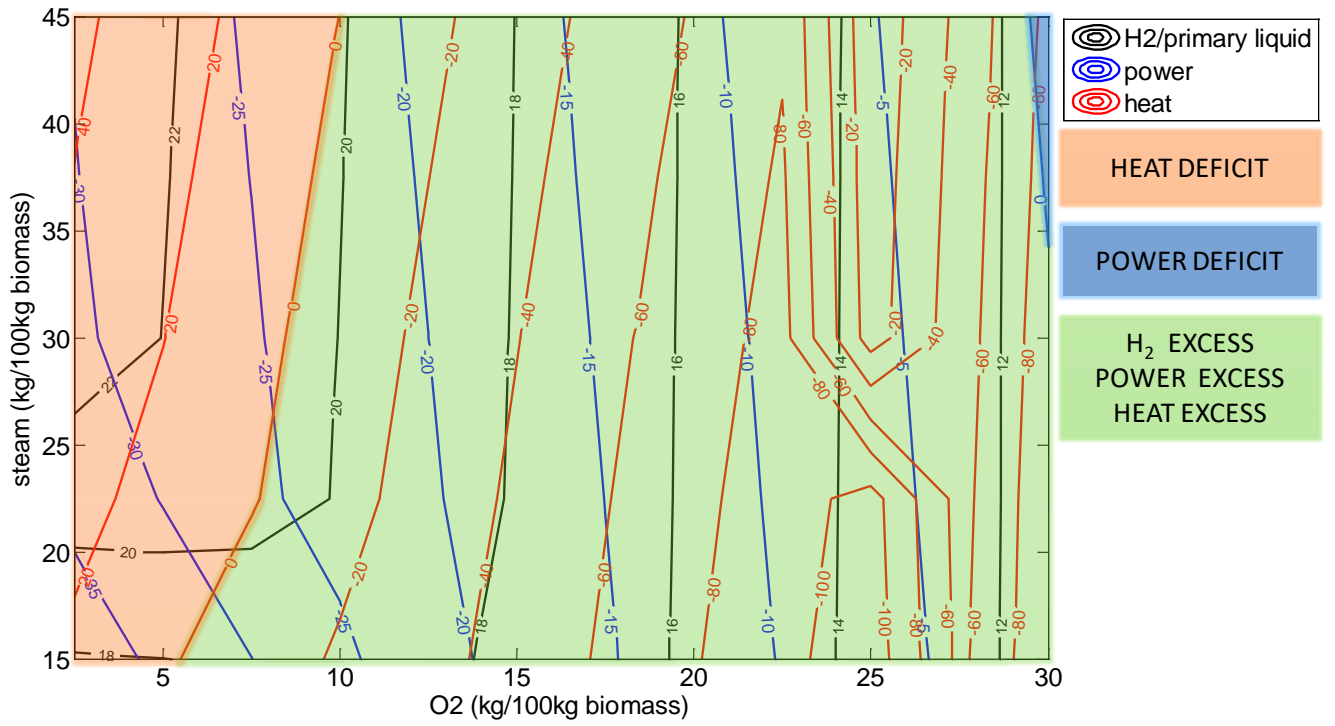Figure S1: View of the ASPEN diagram of the process (See unit description in Table S1)

Figure S2: Global optimal zone for biomass 2 with oxygen as oxidant with a primary liquid yield of 20%.
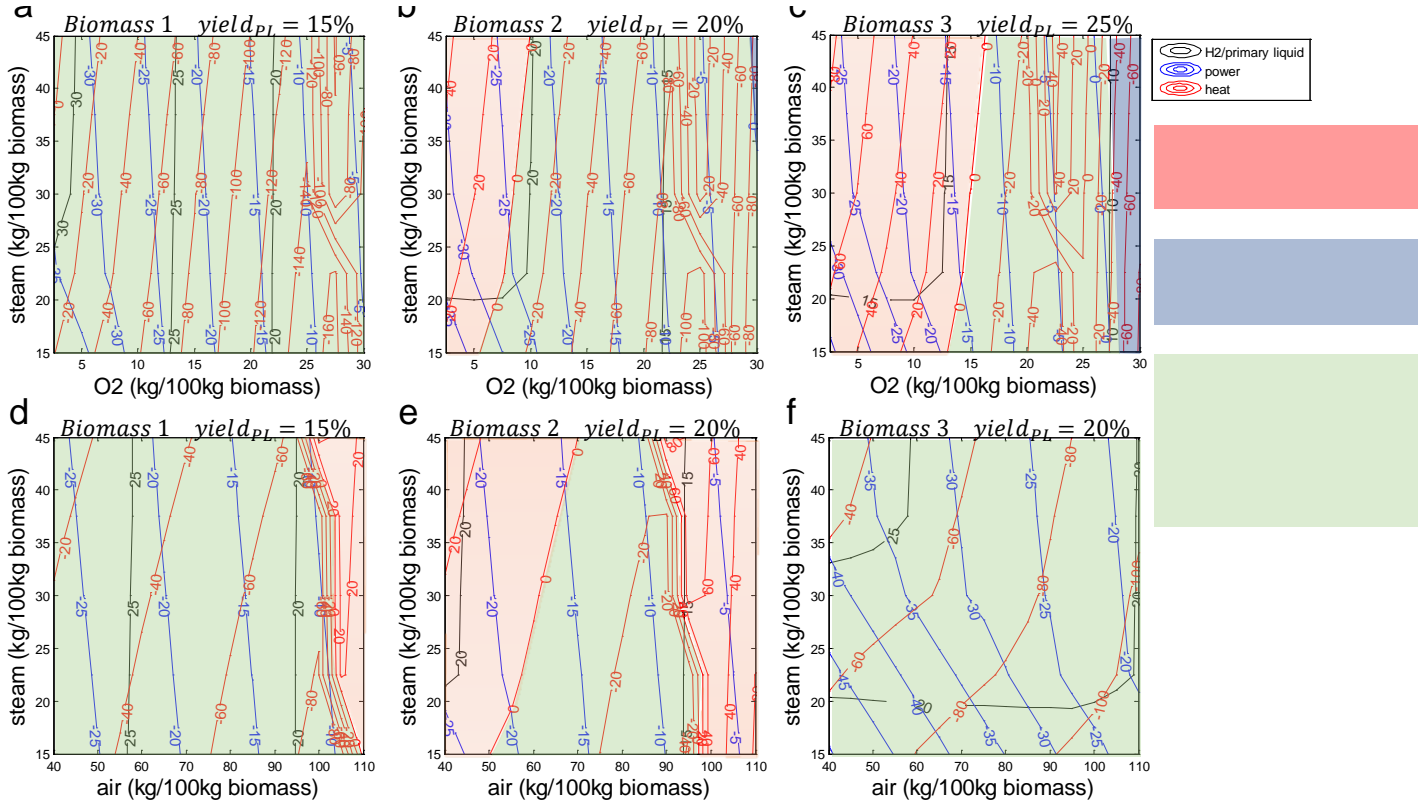
Figure S3: Global optimal zones . (a – c) using oxygen as oxidant; (d – f) using air as oxidant. (a and d) biomass 1; (b and e) biomass 2; (c and f) biomass 3.
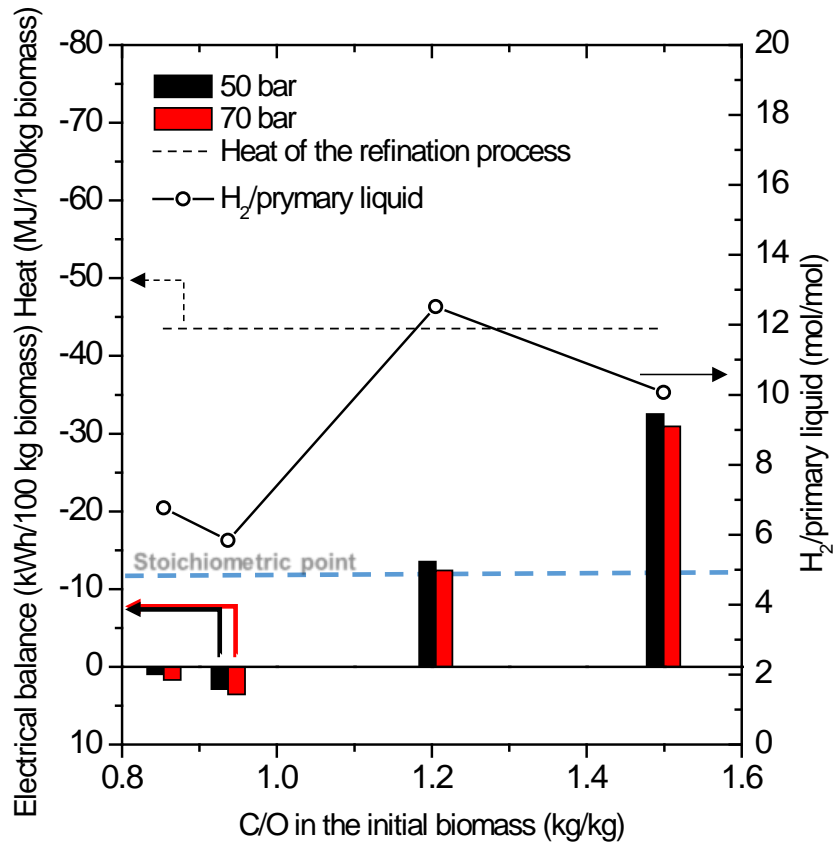
Figure S4: Effect of the pressure in the refining process for different biomass compositions.

Table S1: Description of the ASPEN units of the process

Id	Aspen id	Unit	Id	Aspen id	Unit	Id	Aspen id	Unit	Id	Aspen id	Unit
1	E-150	Heat exchanger	11	G-1	Stoichiometric reactor	21	COMP-H2	Compressor multistage	31	COMP-GAS	Compressor
2	FLASH-1	Evaporator	12	G-2	Gibbs reactor	22	E-50	Heat exchanger	32	COMP-AIR	Compressor
3	P-1	Stoichiometric reactor	13	CYCLON-2	Cyclone	23	PUMP	Pump	33	TURBINE	Gibbs reactor
4	P-2	Stoichiometric reactor	14	E-550	Heat exchanger	24	E-FUEL	Heat exchanger	34	T-HP	Turbine
5	P-3	Gibbs reactor	15	MEMB-1	Stoichiometric reactor	25	REACTOR	Stoichiometric reactor	35	T-LP	Turbine
6	CYCLON-1	Cyclone	16	MEMB-2	Separator	26	E-175	Heat exchanger	36	E-FIN	Heat exchanger
7	E-200	Heat exchanger	17	MEMB-3	Gibbs reactor	27	SEP-2	Separator	37	E-FUEL	Heat exchanger
8	SEP	Separator	18	E-H2	Heat exchanger	28	VALVE	Valve	38	PUMP-FUEL	Pump
9	M-1	Mixer	19	E2-50	Heat exchanger	29	E3-50	Heat exchanger	39	M-3	Mixer
10	E2-200	Heat exchanger	20	VACUUM	Compressor multistage	30	M-2	Mixer	40	M-4	Mixer
									41	M-5	Mixer

Table S2: Composition of each stream of the process for the biomass 2 with a primary liquid yield of 20%, 80 kg air in the gasifier per each 100kg biomass and 30 kg steam in the gasifier per each 100kg biomass. PYRO: outlet stream of the pyrolysis unit; GASIFIER: outlet stream of the gasifier unit; MEMB: outlet stream of the membrane reactor, retenate; HYDRO: outlet stream of the hydrogenation unit; IN-TUR: inlet stream of the turbine; TAIL GAS: outlet stream of the system

	PYRO	GASIFIER	MEMB	HYDRO	IN-TUR	TAIL GAS
Temperature ºC	500	700	500	400	526	300
Pressure bar	1	1.5	1.5	50	20	1
Vapor Frac	1	1	1	1	1	1
Total Flow kmol/hr	3.24	8.70	8.70	1.74	8.00	11.53
Total Flow kg/hr	119.50	221.86	221.86	24.66	220.44	345.44
Total Flow l/min	3471.49	7819.47	6212.43	32.54	442.84	9153.71
Enthalpy kcal/mol	-51.18	-33.88	-36.65	0.47	-39.88	-36.57
Mass Flow kg/hr						
H_2O	2.7652	36.5685	20.0493	0.0000	20.0184	49.0378
C	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2	0.5019	2.8023	4.6508	3.2323	3.2473	0.0001
O_2	0.0000	0.0000	0.0000	0.0000	0.0000	3.2807
CO_2	73.4237	95.3902	135.7452	0.0000	135.6947	135.8646
CO	14.7268	25.6843	0.0000	0.0000	0.1123	0.0042
N_2	0.0000	61.3666	61.3666	0.0000	61.3666	157.2520
CH_4	8.0686	0.0459	0.0459	0.0000	0.0000	0.0000
1-MET-01	20.0113	0.0000	0.0000	0.0000	0.0000	0.0000
C11H2-01	0.0000	0.0000	0.0000	21.4297	0.0000	0.0000
Non-conventional						
CHAR	12.3753					

1-MET-01: 1-methylnaphthalene
C11H2-01: 1-Methyldecalin

Table S3: Effect of the hydrogenation pressure. Biomass 2 with a primary liquid yield of 20%, 80 kg air in the gasifier per each 100kg biomass and 30 kg steam in the gasifier per each 100kg biomass

		BIOMASS 1		BIOMASS 2		BIOMASS 3		BIOMASS 4	
		50 bar	70 bar	50 bar	70 bar	50 bar	70 bar	50 bar	70 bar
Electrical power									
Pump	kWh/100kg biomass	0.03	0.05	0.03	0.05	0.03	0.05	0.03	0.05
Compressor	kWh/100kg biomass	7.05	7.73	11.79	12.93	16.41	18.00	7.69	8.43
Total	kWh/100kg biomass	2.85	3.53	-13.53	-12.38	-32.52	-30.92	0.95	1.68
Heat power									
Heat reaction	MJ/100kg biomass	-43.54	-43.54	-43.54	-43.54	-43.54	-43.54	-43.54	-43.54
Process									
Hydrogen excess	kg/100kg biomass	1.36	1.36	3.24	3.24	2.55	2.55	1.62	1.62

Table S4: Composition of the streams for the biomass 4 with a primary liquid yield of 15%, 60 kg air in the gasifier per each 100kg biomass and 30 kg steam in the gasifier per each 100kg biomass. PYRO: outlet stream of the pyrolysis unit; GASIFIER: outlet stream of the gasifier unit; MEMB: outlet stream of the membrane reactor, retenate; HYDRO: outlet stream of the hydrogenation unit; IN-TUR: inlet stream of the turbine; FINAL GAS: outlet stream of the system

	PYRO	GASIFIER	MEMB	HYDRO	IN-TUR	FINAL GAS
Temperature C	500	700	500	400	528.4	300
Pressure bar	1	1.5	1.5	50	20	1
Vapor Frac	1	1	1	1	1	1
Mole Flow kmol/hr	3.71	8.83	8.83	2.30	8.31	14.13
Mass Flow kg/hr	124.18	213.95	213.95	20.50	212.89	412.89
Volume Flow l/min	3974.69	7933.32	6302.88	42.97	461.34	11223.6
Enthalpy kcal/mol	-52.68	-35.21	-38.06	1.40	-40.35	-33.16
Mass Flow kg/hr						
H2O	7.4810	41.3440	23.3160	0.0000	23.2510	63.0380
C	0.0000	trace	0.0000	0.0000		trace
H2	0.8670	3.4720	5.4890	4.4240	4.4520	< 0,001
O2	trace	trace	0.0000	0.0000	trace	11.1490
CO2	81.9370	94.9980	139.0390	0.0000	138.9740	139.2490
CO	10.5000	28.0300	0.0000	0.0000	0.1840	0.0090
N2	0.0000	46.0250	46.0250	0.0000	46.0250	199.4420
CH4	8.3750	0.0820	0.0820	0.0000	trace	trace
1-MET-01	15.0210	0.0000	0.0000	0.0000	0.0000	0.0000
C11H2-01	0.0000	0.0000	0.0000	16.0860	0.0000	0.0000
No conventional						
CHAR	14.7920					

1-MET-01: methylnaphtalene
C11H2-01: 1-Methyldecalin

Table S5: Composition of the streams for the biomass 5 with a primary liquid yield of 25%, 85 kg air in the gasifier per each 100kg biomass and 30 kg steam in the gasifier per each 100kg biomass. PYRO: outlet stream of the pyrolysis unit; GASIFIER: outlet stream of the gasifier unit; MEMB: outlet stream of the membrane reactor, retenate; HYDRO: outlet stream of the hydrogenation unit; IN-TUR: inlet stream of the turbine; FINAL GAS: outlet stream of the system.

	PYRO	GASIFIER	MEMB	HYDRO	IN-TUR	FINAL GAS
Temperature C	500	700	500	400	561	300
Pressure bar	1	1.5	1.5	50	20	1
Vapor Frac	1	1	1	1	1	1
Total Flow kmol/hr	3.79	9.78	9.78	2.58	8.95	24.28
Total Flow kg/hr	126.84	229.81	229.81	31.62	228.03	728.03
Total Flow l/min	4058.52	8793.49	6986.27	48.16	517.35	19288.78
Enthalpy kcal/mol	-27.85	-22.86	-25.45	0.81	-27.42	-20.01
Mass Flow kg/hr						
H_2O	0.0455	17.3923	0.0000	0.0000	0.2163	45.4691
C	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2	0.0957	4.6757	6.6219	4.8499	4.9247	0.0005
O_2	0.0000	0.0000	0.0000	0.0000	0.0000	50.3752
CO_2	27.3416	72.8100	115.2979	0.0000	113.6891	183.3935
CO	63.6099	68.7760	41.7342	0.0000	43.4459	0.0513
N_2	0.0000	65.2021	65.2021	0.0000	65.2021	448.7436
CH_4	10.7514	0.9491	0.9491	0.0000	0.5552	0.0000
1-MET-01	24.9983	0.0000	0.0000	0.0000	0.0000	0.0000
C11H2-01	0.0000	0.0000	0.0000	26.7702	0.0000	0.0000
No conventional						
CHAR	12.9620					

1-MET-01: 1-methylnaphthalene
C11H2-01: 1-Methyldecalin

Table S6: Effect of the primary liquid composition. Biomass 2 with a primary liquid yield of 20%, 80 kg air in the gasifier per each 100kg biomass and 30 kg steam in the gasifier per each 100kg biomass. PL1: methylnaphthalene as primary liquid; PL2: hydroxybenzyl alcohol as primary liquid; PL3: furfural as primary liquid; PL4: lactic acid as primary liquid

	Units	PL1	PL2	PL3	PL4
HEAT ANALYSIS					
PYROLISIS	MJ/100kg biomass	158.17	243.64	224.61	253.69
GASIFIER	MJ/100kg biomass	30.12	72.09	100.28	79.69
Heat exchanger outlet gasifier	MJ/100kg biomass	-67.03	-68.16	-69.47	-68.72
Heat exchanger final gas	MJ/100kg biomass	-168.53	-305.00	-311.28	-422.45
HEAT BALANCE	**MJ/100kg biomass**	**-47.27**	**-57.42**	**-55.86**	**-157.79**
ELECTRICAL ENERGY BALANCE					
VACUUM	kWh/100kg biomass	2.25	3.36	3.56	3.27
COMPRESSION H$_2$	kWh/100kg biomass	11.79	17.63	18.69	17.14
COMPRESSION GASES	kWh/100kg biomass	34.42	37.84	37.75	39.80
TURBINE	kWh/100kg biomass	-61.99	-89.34	-91.27	-119.92
PUMP	kWh/100kg biomass	0.03	0.03	0.03	0.03
LIQUID TURBINE	kWh/100kg biomass	-0.02	-0.02	-0.03	-0.02
ELECTRICAL ENERGY BALANCE	**kWh/100kg biomass**	**-13.53**	**-30.51**	**-31.27**	**-59.70**

Table S7: High heating values (HHV) for the primary liquid and for the refined liquid compounds.

Primary liquid compound	*HHV (MJ/kg)*	Refined liquid compound	*HHV (MJ/kg)*
Methyl-naphthalene	*40.733*	**Methyl-decalin**	*42.521*
Gastrodigenin	*28.218*	**Methyl-cyclohexane**	*46.253*
Furfural	*24.050*	**Pentane**	*48.302*
Lactic acid	*14.640*	**Propane***	*51.016*

* this refined compound are not liquid, however, the study considered this compound to characterize the effect to decrease the MW of the primary liquid in the overall process

Primary liquid compound	*HHV (MJ/kg)*	Refined liquid compound	*HHV (MJ/kg)*