Full Length Article

# Syngas production by bio-oil steam gasification in a fountain confined conical spouted bed reactor

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A R T I C L E   I N F O

A B S T R A C T

The combination of delocalized units for the fast pyrolysis of biomass to produce bio-oil followed by centralized units for the gasification of bio-oil appears as an economically attractive option for the full-scale production of syngas because transportation of bio-oil is less costly than that of biomass. First goal of this study lies in the validation of a bio-oil feeding device made up of a line-thermostated at 60–80 °C and a non-atomizing injector cooled by water. This injector allows feeding the crude bio-oil in continuous mode into the conical spouted bed reactor without being clogged by the pyrolytic lignin in the bio-oil. The effect of gasification temperature on gas properties, tar composition, and carbon conversion efficiency were assessed in the 800–900 °C range. The results show that temperature promotes tar reduction (from 40.7 to 12.5 g/Nm$^3$), carbon conversion efficiency (from 91.2 to 96.3 %) and gas yield (from 1.37 to 1.85 Nm$^3$/kg on a dry basis) as temperature is increased from 800 to 900 °C. A novel aspect of this study is the detailed characterization of the tar evolution with temperature, which, to our knowledge, is an aspect that has not been approached in the literature related to raw bio-oil gasification.

## 1. Introduction

Biomass gasification is considered a simple and efficient technology for producing low or medium calorific value gas for the synthesis of fuels and chemical platforms or for generating electricity [1–4]. However, one of the main barriers for the large-scale implementation of either energy or bio-fuel production from solid biomass is the high cost associated with the logistics of feedstock [5]. In fact, biomass is first collected and then transported to a centralized larger gasification facility due to the advantages of economy of scale, which allows producing biofuels more economically [6,7]. Thus, the high water content and the low energy density of the raw biomass, as well as the large amount of biomass that has to be supplied to the facility, increases the costs of transportation and storage of biomass [8]. In order to improve the economic feasibility and competiveness of the advanced bio-fuel production pathway, the bio-oil can be first produced in distributed or mobile plants near the harvest sites, and then be shipped to a central gasification facility for conversion to syngas [9–13].

It should be highlighted that bio-oil is a more suitable raw material than biomass in terms of storage and transportation, as it has between 3 and 5 times higher energy density and is more easily handled than solid biomass [8,9]. An additional advantage of bio-oil gasification is that ashes from biomass, which may disturb the gasification stage, are retained in the fast pyrolysis char, and this simplifies the syngas purification requirements [5]. Furthermore, amongst other applications, this char could be used as fuel to provide heat to the pyrolysis process, recycled as soil amender (most of the minerals are retained in this solid residue) or used for producing adsorbents or catalysts [14–16]. Moreover, the bio-oil produced by fast pyrolysis has better prospects for use in gasification processes, as high yields are obtained by this process (in the 70–75 wt% range) in a single phase solution in which water is the prevailing component, with viscosity being lower than that derived from slow pyrolysis, which facilitates its atomization for gasification [6,17,18].

Li et al. [18] also confirmed that the two-stage bio-oil gasification was more economical than biomass gasification. These authors evaluated the economic feasibility of an integrated production pathway combining fast pyrolysis and bio-oil gasification and compared with the

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study by Swanson et al. [19], who assessed biomass gasification alone. They concluded that a total capital investment (TCI) of $510 million and a minimum fuel selling price of $5.6 per gallon of gasoline equivalent (gge) were needed for a bio-oil gasification plant processing 2000 metric per day, whereas the TCI was of $560 million and the minimum selling price of $5.4/gge for biomass gasification plant of the same capacity.

The increasing interest in gas to liquid (GTL) processes by means of the methanol, dimethyl ether and Fischer-Tropsch synthesis is making syngas production essential [6,20]. Air is the cheapest gasifying agent for gas production, but it contains about 78 vol% of nitrogen, thus reducing the $H_2/CO$ ratio of the gas to lower values than those required in GTL processes [21]. Conversely, the use of steam as gasifying agent has interesting advantages: the product gas is free of nitrogen, its $H_2$ concentration is higher (and therefore the $H_2/CO$ ratio) and its heating value is also higher (greater than10 $MJ/m^3$) [22]. Different reactor configurations have been used for the gasification or steam reforming of bio-oil, which can be classified as follows: fixed bed, fluidized bed and entrained flow gasifiers [6]. Fluidized beds are the most commonly used in steam reforming processes for both raw bio-oil [23–28] and bio-oil model compounds [29,30], as this technology provides good contact of bio-oil droplets with hot solid particles leading to high heat and mass transfer rates. Entrained flow gasifiers also allow attaining high conversion efficiencies with low tar concentrations in the bio-oil gasification [21,31]. These reactors are common in large-scale oil gasification plants and they rarely have been considered for conventional biomass gasification because the feedstock needs to be previously pulverized.

The conical spouted bed reactor (CSBR) is an alternative to the fluidized bed, as it is suitable for handling materials of irregular texture, allows attaining high heat and mass transfer rates and is of flexible design [32,33]. Thus, the CSBR is highly versatile, as it can operate in a wide range of gas velocities from the conventional spouting regime to the dilute spouting regime (jet spouting regime), with the residence time of the gas phase being from a few seconds to well below the second [34]. This range of residence times is very suitable for fast pyrolysis, i.e., undesired secondary reactions may be minimized and bio-oil production maximized [35,36]. Another interesting regime that may be attained by inserting a fountain confiner is the so-called fountain enhanced regime, which is characterized by a narrower residence time distribution and severe expansion of the bed [37]. This regime improves the contact between the reacting gases and the bed material, and therefore promotes tar cracking and reforming reactions [38,39]. One of the challenges of this technology is related to its application for treating liquids that are especially difficult to handle, such as bio-oil.

This study deals with the use of the CSBR as a hybrid technology. Thus, bio-oil is first produced by fast pyrolysis under the conventional spouting regime and this liquid is then converted into syngas using steam as gasifying agent under the fountain enhanced spouting regime. This strategy is an interesting alternative to direct biomass gasification, as the cost-effective transport of bio-oil could make the implementation of this biomass valorization route profitable. Furthermore, this paper assesses the suitability of a bio-oil feeding device developed by our research group made up of a non-atomizing bio-oil injector. The bio-oil was produced at 500 °C in the CSBR operating under conventional spouting, and collected in the condensation system. It was then gasified in the CSBR operating under fountain enhanced regime. The effect of temperature (800, 850 and 900 °C) on the gasification performance (gas yield and composition, $H_2$ production, tar concentration and carbon conversion efficiency) was assessed. In addition, a study was conducted of the tar characteristics and its evolution with temperature, which, to our knowledge, is an aspect that has not been approached in the literature related to bio-oil gasification.

## 2. Experimental section

### 2.1. Biomass characterization

The biomass used in this study for bio-oil production was forest pinewood waste (*pinus insignus*). Before performing the fast pyrolysis experiments, the biomass was crushed and ground to a particle size from 1 mm to 2 mm and dried to a moisture content below 10 wt%. The ultimate analysis was carried out in a LECO CHNS-932 elemental analyzer, which showed that the pinewood biomass was made up of 49.33 wt% C, 6.06 wt% H, 0.04 wt% N and 44.54 wt% O on a dry basis. Regarding the proximate analysis, it was performed in a TGA Q500IR thermogravimetric analyzer and revealed that the biomass had 73.4 wt% of volatile matter, 16.7 wt% of fixed carbon, 0.5 wt% of ashes and 9.4 wt% of moisture. The higher heating value (HHV) was measured in a Parr 1356 isoperibolic bomb calorimeter and was of 19.8 MJ/kg.

### 2.2. Pyrolysis and gasification unit

The pyrolysis and gasification runs were conducted in the same bench-scale conical spouted bed reactor plant, although certain modifications were made for performing either pyrolysis or gasification experiments. This plant was set up and fine-tuned for fast pyrolysis and gasification based on previous studies [32,33,35,36,38,40,41]. As observed in Fig. 1, the plant consists of the following elements: i) devices for feeding either the biomass or the bio-oil, water (if needed), and the spouting gas (nitrogen), ii) a CSBR reactor, equipped with a non-porous draft tube, and also the fountain confiner in the case of the gasification experiments, iii) a fine particle retention system made up of a high efficiency cyclone followed by sintered steel filter, and; iv) a volatile condensation system.

The main modification carried out in this bench scale plant to allow operation under pyrolysis and gasification conditions is associated with the configuration of reaction system. In both cases, the reaction unit is a CSBR, which is made of stainless steel and equipped with a non-porous draft tube. The use of the non-porous draft tube increases operation versatility (widens the range of gas flowrates) and improves the spouting regime performance and bed stability [42,43]. Moreover, a fountain confiner, which is a tube welded to the lid of the reactor, was incorporated into the CSBR when bio-oil gasification experiments were conducted. The fountain confiner permits operating with very fine particles under stable conditions, improves the gas–solid contact in the fountain region, increases the gas residence time and narrows its distribution [44]. The combination of both draft tube and fountain confiner permits operating from conventional spouting to fountain enhanced spouting, depending on the requirements of the process. Either conventional or fountain enhanced regime can be attained by acting on the bed properties (amount and particle size) and the spouting gas flow rate. More information about the conventional and the fountain enhanced regimes, the reactor dimensions and the description of the devices such as the fountain confiner and draft tubes used in this work, were reported elsewhere [44]. The reactor is placed inside a radiant oven (with two independent sections) to provide the required heat for operating up to 900 °C. Two thermocouples located at reactors lower section (in the gaseous stream inlet) and in the upper section (in the bed zone), respectively, control the reaction temperature.

Different gases were fed into CSBR depending on the process. Nitrogen was used as spouting agent in pyrolysis runs and its flow rate was controlled by means of a mass flow controller that allows feeding up to 40 L/ min. However, steam was required for the gasification process, and therefore an ASI 521 pump for water dosing. Then, the water is vaporized prior to feeding into the reactor by means of an evaporator located within the hot box. Both $N_2$ and steam were heated to the reaction temperature with a preheater located just below the reactor. It is to note that air was used instead of $N_2$ during the preheating period.

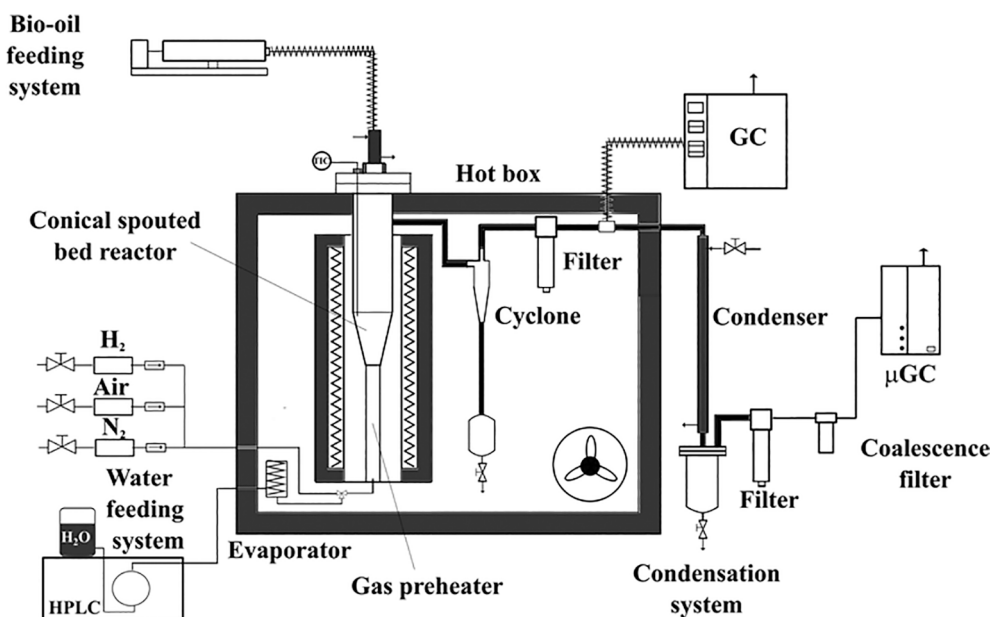The same fine particle retention and volatile condensation systems

**Fig. 1.** Scheme of the CSBR bench scale plant.

were used in both biomass pyrolysis and bio-oil gasification experiments. Thus, the volatiles formed in the biomass pyrolysis with the inert gas or the compounds derived from bio-oil gasification process (aerosols, incondensable and condensable gases as well as the non-reacted steam) leave the reactor together and circulates through a fine-particle retention system composed of a high-efficiency cyclone followed by a 25 μm sintered steel filter. This fine-particle retention system is placed inside the hot box, which is maintained at 290 °C to prevent the condensation of heavy compounds. Subsequently, the outlet stream circulates through a condensation system cooled by tap water consisting of a double shell tube condenser and a 60 μm stainless steel filter, with the latter being located within a 1 L vessel. The whole condensation system ensures the total condensation and retention of the bio-oil when biomass pyrolysis is performed and that of tar and unreacted steam after bio-oil gasification.

Another modification made to conduct either pyrolysis or gasification experiments is related to the feeding device. In the case of biomass pyrolysis experiments, the system for continuous biomass feeding consists of a cylindrical vessel equipped with a vertical shaft connected to a piston placed below the pinewood sawdust. More details about the piston feeder could be found elsewhere [38]. Regarding gasification experiments, Fig. 1 shows the scheme of the bio-oil feeding device. The bio-oil was fed by means of a syringe pump (*PHD 4400*), which controls its volume flow rate. The syringe outlet was connected to the injector by a thermostated line, which heats the bio-oil to moderate temperatures between 60 and 80 °C in order to improve its fluidity and avoid pipe clogging due to the formation of lumps or soot. In fact, the surface tension and viscosity of the bio-oil are low in this temperature range [6], and, furthermore, cracking reactions involving the lighter compounds of the bio-oil are hindered. Subsequently, the bio-oil was introduced into the reactor by means of the injector (Fig. 2). It should be noted that this element has to be cooled to prevent any coking or secondary reactions of bio-oil components at the reactor entrance due to the high gasification temperatures. Accordingly, the injector is provided with a cooling jacket, in which tap water was used as refrigerant, whose flow rate can be modified to maintain the temperature in the 60–80 °C range. It is noteworthy that the injector design is crucial to ensure a suitable performance and avoid operational problems. Thus, a fine pipe ensures high injection pressure and bio-oil linear velocity, which are relevant facts for the suitable performance of this device. Preliminary tests showed that a pipe of 0.5 mm in internal diameter was the optimum for bio-oil feeding.
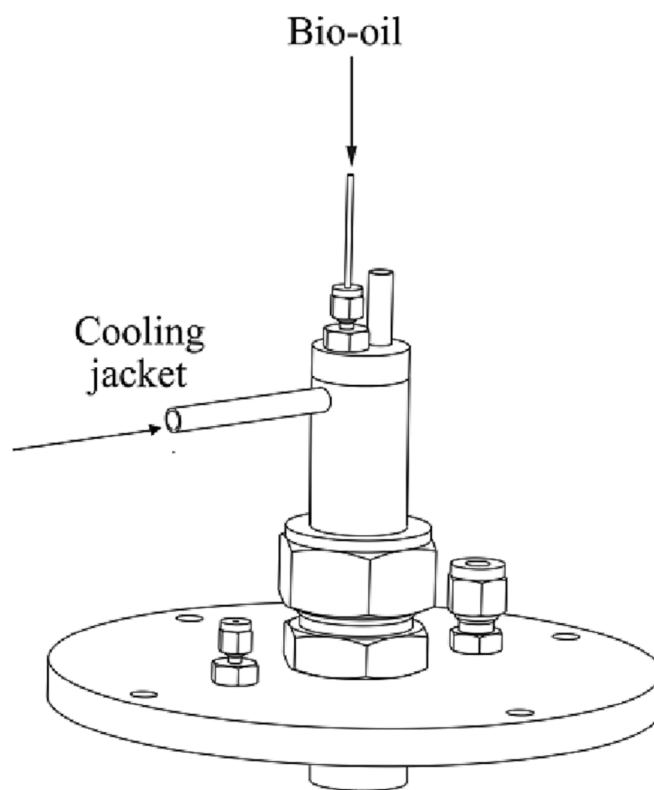


**Fig. 2.** Schematic diagram of the injector provided with a cooling jacket.

### 2.3. Experimental procedure for pyrolysis

Pyrolysis runs were carried in a continuous mode by feeding 0.75 g/min of biomass at 500 °C, which is the temperature that maximizes the bio-oil yield from pinewood sawdust in a conventional spouted bed reactor (above 72 wt%), as proven in previous studies [32,45]. The reactors bed is composed of 100 g of sand with a particle size from 0.3 to 0.63 mm, whereas the fluidizing gas ($N_2$) flow rate was 9 NL/min. These conditions were established to operate under conventional spouting

regime (without fountain confiner); that is, with a gas velocity of around 1.2 times higher than the minimum spouting one in order to guarantee a high heat transfer rate and bed isothermicity.

## 2.4. Gasification procedure

As previously stated, in order to pursue a more efficient gasification process, the experimental runs were carried out under fountain enhanced spouting regime (with fountain confiner) using gas velocities of around four times that corresponding to the minimum spouting one. In order to achieve this regime, the reactor was loaded with 100 g of olivine, with particles in the 90–150 μm size, and the water flow rate was of 1.5 mL/min. Previous studies of biomass gasification proved that a steam/biomass ratio of 2 is required for operating with a high gas flow rate to ensure vigorous spouting conditions [46]. Therefore, all the gasification experiments were performed by feeding 0.75 g/min of bio-oil, which corresponds to a steam/bio-oil (S/B) ratio of 2. Considering the density of the bio-oil, the pumping flow rate for a S/B of 2 corresponds to 0.664 mL/min.

In order to assess the effect of temperature on the bio-oil gasification performance and on the product distribution, the runs were conducted at 800, 850 and 900 °C by continuous feeding of bio-oil for 20 min, which ensured steady state operation. Besides, the runs were repeated at least three times under the same operating conditions in order to ensure reproducible results.

## 2.5. Product analysis

The bio-oil was analysed in order to determine the ultimate composition, water content, density as well as calorific values. The water content was determined by Karl-Fischer Titration (*Metrohm 870 KF Titrino plus*, ASTM D1744), whereas the density was measured according to ASTM D4052. The ultimate analysis of the bio-oil was carried out in a LECO CHNS TruSpec elemental analyser. Note that sulphur was not measured since the detection limit of this analyser is of 0.1 wt%, and the sulphur content in the samples is well below this value. Additionally, the higher and lower heating values (HHV and LHV) of the bio-oil samples were determined according to Eq. (1) [47] and Eq. (2) [48], respectively:

$$HHV\left(\frac{kJ}{kg}\right) = 0.335C + 1.423H - 0.154O \tag{1}$$

$$LHV\left(\frac{kJ}{kg}\right) = HHV\left(\frac{kJ}{kg}\right) - 218.3H \tag{2}$$

where C, H and O are the contents of carbon, hydrogen and oxygen, respectively, in the bio-oil given in mass percentage.

In the gasification experiments, the volatile stream leaving the reactor, which included non-condensable gases and tar, was analysed on-line using a GC/FID (Agilent 7890). The sample was injected into the GC by means of a thermostated line kept at 280 °C to prevent the condensation of heavy tar components. The analysis of the non-condensable gases (once the tar is separated from the gaseous stream in the condensation system) was performed with a micro GC (Varian 4900), which has three independent modules with different columns (molecular sieve, porapak and plot alumina) that allows both identification and quantification of the gaseous products (previously calibrated). Moreover, the identification of the tar collected in the condensation system was carried out by gas chromatography/mass spectrometry (GC/MS, Shimadzu UP-2010S) once it had been diluted in analytical grade acetone. The yields of both gas and tar fractions were determined based on the information obtained from the micro-GC and GC, respectively.

## 2.6. Reaction indices

In order to assess the bio-oil gasification process performance, the following reaction indices were monitored:

- *Carbon conversion efficiency (%)*. This parameter is defined as the moles of carbon in the gaseous product stream divided by those fed in the bio-oil (calculated from its ultimate analysis).
- *Gas yield ($Nm^3$/kg)*. It is the volume flow rate of the gas produced divided by the mass flow rate of the bio-oil fed into the gasifier.
- *$H_2$ production (wt%)*. It is the $H_2$ mass flow rate produced per mass flow rate of bio-oil in the feed.
- *Tar concentration ($g/Nm^3$)*. This parameter provides the amount of tar produced (in mass) per $m^3$ of dry syngas produced.

## 3. Results and discussion

### 3.1. Bio-oil characterization

Bio-oil is considered a microemulsion composed of a continuous phase constituted by an aqueous solution containing holocellulose decomposition products and small products from lignin decomposition (aqueous phase), and a discontinuous or dispersed phase composed of macromolecules derived from lignin pyrolysis (organic phase), with this being stabilized by the continuous aqueous phase [49–52]. Hence, the bio-oils produced from fast pyrolysis make usually a single phase and, furthermore, they are not prone to phase separation and have lower viscosities than those derived from slow pyrolysis, thereby this type of bio-oil being especially suitable for steam gasification. In fact, the bio-oil collected in the condensation system makes up a stable single phase and does not undergo any phase separation. Moreover, no pretreatment was carried out to the bio-oil. After producing the bio-oil, it was stored in a fridge to slow down the aging until it was gasified. It is to note that raw bio-oil was fed in these experiments rather than its aqueous fraction, as is the case in most of the studies reported in the literature [53–57].

The features of the bio-oil obtained from biomass fast pyrolysis, i.e., water content, density and calorific value, were determined by elemental analysis, Table 1. It is noteworthy that the carbon content and calorific value were slightly lower than those measured in the bio-oils obtained from certain woody biomasses or in those obtained in previous runs in conventional CSBRs [32], whereas the content of oxygen was slightly higher (usually between 40 and 55 %) due to the higher content of water, as shown in Table 1. This difference might be associated with the aging process that undergoes the bio-oil during storage (in this case during 6 months). It is well known that bio-oil is an unstable liquid because some of the species are highly reactive, and undergo aging during storage, leading to an increase in water content [58,59], as observed in this study. Nevertheless, the high water content of the bio-oil is an interesting advantage for its gasification because, on the one

**Table 1**
Fuel properties of the bio-oil obtained in this study and the typical values published in the literature for those produced from lignocellulosic biomass.

| Properties | This work | Typical composition [49,51,60,61] |
|---|---|---|
| Ultimate analysis (wt%) | | |
| *Carbon* | 31.4 | 32–48 |
| *Hydrogen* | 9.3 | 7–9 |
| *Nitrogen* | 0.1 | 0–0.9 |
| *Sulfur* | <0.1 | <0.1 |
| *Oxygen\** | 59.2 | 40–55 |
| Water (wt%) | 46.1 | 20–40 |
| Density | 1.13 | 1–1.3 |
| HHV (MJ/kg) | 14.7 | n.a. |
| LHV (MJ/kg) | 12.6 | 14–19 |

n.a.: not available

\* Calculated by subtraction.

hand, steam requirements are lower, and, on the other hand, water improves atomization by reducing the oil viscosity, which facilitates its feeding into the reactor and reduces the formation of thermal $NO_x$ when air is used as gasification agent [48,58]. The remaining properties of this bio-oil were within the range of the typical lignocellulosic ones described in the literature.

The analysis of the bio-oil composition was conducted by means of GC/MS (Shimadzu UP-2010S) provided with a DB-1MS column. More than 110 compounds were identified with high quality, revealing that bio-oil was made up of a very complex mixture of oxygenated compounds. These compounds were lumped into 7 main functional groups, with their composition being as follows: acids (2.9 wt%), aldehydes (2.1 wt%), alcohols (2.2 wt%), ketones (6.9 wt%), phenols (17.8 wt%), furans (3.6 wt%), and saccharides (4.8 wt%). The unidentified fraction was 13.6 wt% of the whole bio-oil.

### 3.2. Bio-oil gasification at different temperatures

During the steam gasification stage, the bio-oil undergoes different steps, which are mainly as follows: (i) evaporation of water and light volatiles; (ii) pyrolysis to yield gases, tar and soot (Eq. (3)); (iii) reforming and cracking of bio-oil oxygenated compounds, light hydrocarbons and tar to form smaller molecules (Eqs. (4)–(8)); and (iv) water–gas shift (WGS) reaction (Eq. (9)).

Bio-oil pyrolysis: Bio-oil → Gases (CO, $CO_2$, $CH_4$, $H_2$, $C_nH_m$) + oxygenates + soot　　(3)

Bio-oil steam reforming: $C_nH_mO_k + (n\text{-}k)H_2O \rightarrow nCO + (n + m/2\text{-}k)H_2$　(4)

Hydrocarbon steam reforming: $C_nH_m + nH_2O \rightarrow nCO + (n + m/2)H_2$　　(5)

Methane steam reforming:

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \qquad (6)$$

Bio-oil cracking: $C_nH_mO_k \rightarrow C_xH_yO_z + CO + H_2 + CO_2 + CH_4$　　(7)

Hydrocarbon cracking: $C_nH_m \rightarrow C_xH_y + CO + H_2 + CO_2 + CH_4$　　(8)

Water gas shift (WGS):

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad (9)$$

One of the advantages of bio-oil gasification lies in avoiding operation with solid biomass, as the latter needs to be ground to adequate particle size due to heat and mass transfer limitations, which reduces gasification efficiency. Apart from this fact, it is well established in the literature that char gasification is the kinetic controlling step in biomass gasification, i.e., its reaction rate is orders of magnitude slower than that of pyrolysis and homogenous oxidations steps [62–64]. Therefore, the design of the gasifier is usually conditioned by char gasification in order to increase its residence time, and therefore attain its full conversion. Nevertheless, very fine droplets are introduced into the reactor (much smaller than biomass particles) when bio-oil is the feed, which avoids mass transfer restrictions and enhances the aforementioned reactions [6]. It should be noted that certain studies of bio-oil gasification report the formation of soot (impure carbon particles) in the pyrolysis and reforming stages [65]. However, an analysis of the bed subsequent to the gasification runs in our equipment showed that the carbon fraction detected was negligible, probably due to the severity of the gasification process (high temperatures and a S/B ratio of 2), which promoted carbon heterogeneous reactions of steam gasification (Eq. (10)) and $CO_2$ gasification (Eq. (11)).

Carbon steam gasification:

$$C(s) + H_2O \rightarrow CO + H_2 \qquad (10)$$

Carbon $CO_2$ gasification : $C(s) + CO_2 \rightarrow 2CO$　　(11)

Since the overall steam gasification is an endothermic process, high temperatures and excess steam (equilibrium reaction conditions) promote steam reforming reactions (Eqs. (4)–(6)) towards hydrogen production. However, although temperature has a great impact on the extent of aforementioned reactions, it also conditions the global economy of the process (due to its endothermic nature). In addition, temperature has also a negative impact on the equilibrium of the WGS reaction (Eq. (9)), which is of marked exothermic nature. Therefore, the selection of the adequate temperature is essential to improve the overall gasification performance and obtain a syngas with the desired $H_2/CO$ ratio.

#### 3.2.1. Influence of gasification temperature on reaction indices

The influence of temperature on the reaction indices (gas yield, $H_2$ production, tar content in the syngas and carbon conversion efficiency) is shown in Fig. 3. The results for the gas and $H_2$ productions are given on dry and wet basis.

As observed in Fig. 3, an increase in temperature improves the efficiency of the gasification process given that the tar content is reduced whereas the gas yield is increased. The gas yield and $H_2$ production on a wet basis increased from 0.75 Nm³/kg and 2.43 wt% at 800 °C to 1.00 Nm³/kg and 4.30 wt% at 900 °C, respectively, due to the promotion of steam reforming and cracking reactions (Eqs. (3)–(8)). As the water amount in the crude bio-oil was high (46.1 wt%), these indices were recalculated on a dry basis in order to compare the results with those obtained in biomass gasification, which are usually given on a dry basis. In fact, the water content of the bio-oil depends on the composition of the raw biomass and the technology used for pyrolysis. In this case, a CSBR technology was used, which is known to produce a bio-oil with a high water content. Thus, gas yield and $H_2$ production on a dry basis increased from 1.37 Nm³/kg and 4.51 wt% at 800 °C to 1.85 Nm³/kg and 7.96 wt% at 900 °C, respectively. Likewise, the enhancement of steam reforming and cracking reactions (Eqs. (3)–(8) greatly reduced the tar concentration from 40.7 g/Nm³ at 800 °C to 12.5 g/Nm³ at 900 °C. Furthermore, the carbon conversion efficiency increased considerably from 91.2 % at 800 °C to 95.5 % at 850 °C, but moderately from 850 to 900 °C. In the case of the HHV of the gas (calculated based on Eq. (1)), it showed a slightly decreasing trend from 16.2 to 15.5 KJ/kg, as the carbon and hydrogen amounts in the gas decreased with temperature whereas that of oxygen increased.

Few studies in the literature deal with the gasification of crude bio-oil and a comparison of reaction indices is rather complicate because they were obtained using different technologies and operating conditions (temperature ranges, gasification agents, with or without catalyst, and so on). Nevertheless, all the authors agree that high temperatures improve the bio-oil gasification performance [8,21,25,65,66]. Zheng et al. [21] used air–steam mixture in the rice husk bio-oil gasification carried out in an entrained flow gasifier and reported that the gas yield (on dry a basis) increased from 1.1 to 1.9 Nm³/kg and the carbon conversion efficiency from 69 to 93 % in the 700–1000 °C range. Hwang et al. [8] also performed the experiments in an entrained flow reactor using Ni-Al catalyst and steam, and they reported that the tar content decreased from 5.5 g/Nm³ at 600 °C to 0.1 g/Nm³ at 1000 °C. In the same line, Sakaguchi [67] conducted runs in a fluidized bed reactor and without catalyst, and observed that the carbon conversion increased from approximately 53 to 67 % when the gasification temperature was raised from 747 to 832 °C. Furthermore, these results were confirmed by a bio-oil steam gasification model in a fluidized bed reactor developed by Ghezelchi and Wu [66].

Based on the results obtained in this study, it can be stated that gasification in a fountain enhanced conical spouted bed is a fast, simple and effective conversion process of bio-oil into product gas. In fact, the spouted bed provides an excellent contact of bio-oil droplets with the hot solid particles in the bed, which leads to high heat and mass transfer rates. Furthermore, the confinement of the fountain allows attaining longer gas residence times of the gaseous stream, which improves tar
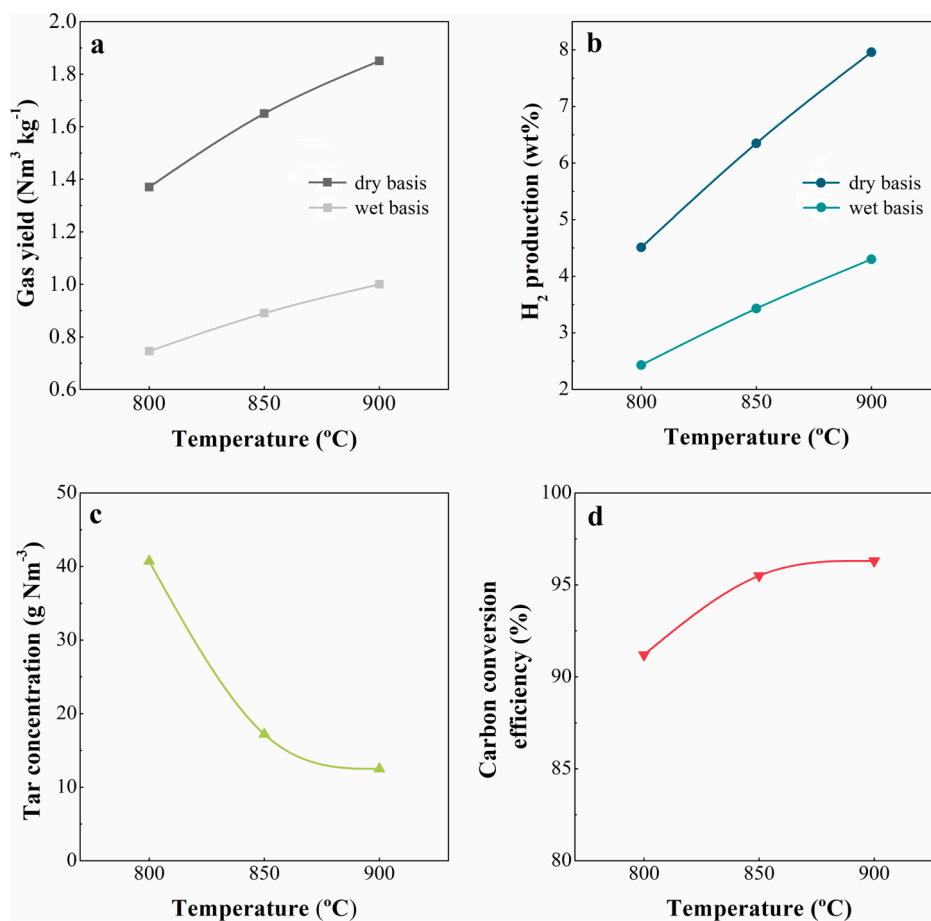
**Fig. 3.** Effect of temperature on bio-oil gasification reaction indices.

cracking efficiency. Compared to the biomass (pine wood sawdust) gasification carried out using olivine as primary catalyst under similar conditions, higher gas yields and $H_2$ productions were obtained in the bio-oil gasification. Moreover, the tar concentration in the gaseous stream obtained at 800 and 850 °C was also lower [38]. Despite the good performance of this technology, the tar concentration is still high for use of this stream in most applications [68]. Olivine has proven to be an interesting catalyst for gasification because it leads to stable fluidization behaviour, has suitable mechanical properties and is cheaper than other primary catalysts, but incorporation of certain metals is required to improve its reforming and cracking activity [46]. In fact, future studies dealing with the incorporation of metals are foreseen to improve the tar cracking ability, which was already proven elsewhere when iron was incorporated into olivine [46]. Likewise, Quan et al. [69] also demonstrated that Fe/olivine has good activity for steam reforming of bio-oil.

### 3.2.2. Influence of gasification temperature on gas composition

Fig. 4 displays the composition of the gases formed at different temperatures (800, 850 and 900 °C) for a S/B ratio of 2. Due to the high concentration of methane, this compound was considered separately from the other gaseous hydrocarbons, which are lumped together ($C_2$-$C_4$ fraction).

As observed in Fig. 4, an increase in temperature enhances the $H_2$ concentration in the gaseous stream (from 37.1 vol% at 800 °C to 48.3 vol% at 900 °C), whereas the opposite trend was observed for the concentrations of CO, $CH_4$ and $C_2$-$C_4$ hydrocarbons. Note that CO concentration decreased from 29.7 vol% at 800 °C to 24.7 vol% at 850 °C, with this value remaining steady at 900 °C. The effect of temperature on $CO_2$ was not very pronounced, since it first increased from 17.8 to 19.4 vol% when temperature was increased from 800 to 850 °C, and then
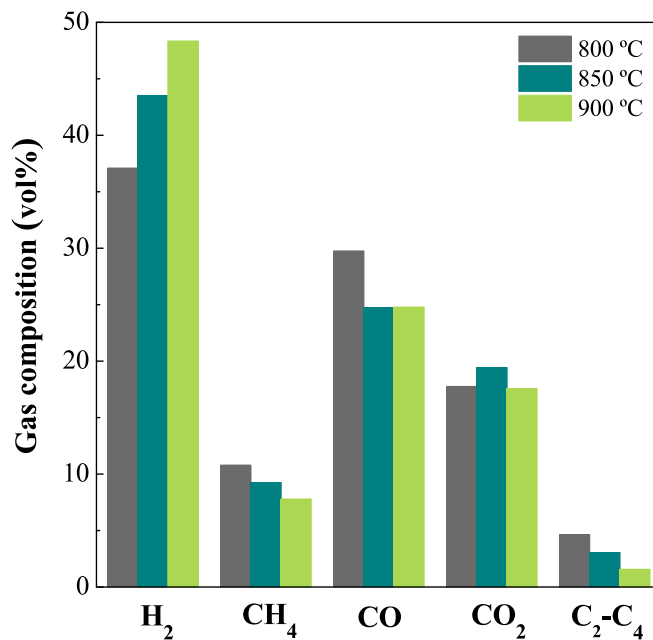


**Fig. 4.** Effect of gasification temperature on the gas composition in the 800–900 °C range.

decreased to 17.5 vol% at 900 °C.

As previously stated, the higher concentration of $H_2$ at higher temperatures is related to the higher rates of cracking and reforming

reactions (Eqs. (3)–(8)) and the shift of the equilibrium towards the products in the steam reforming reactions (Eqs. (4)–(6)) due to their endothermic nature, thus promoting a higher formation of $H_2$ at higher temperatures. Conversely, the enhancement of these reactions with temperature resulted in a decrease in the concentration of methane and $C_2$-$C_4$ fraction. These trends are consistent with the results reported by other authors for the steam gasification of bio-oil or solid biomass [21,38,70,71]. Nevertheless, the trends of CO and $CO_2$ with increasing temperature have not a straightforward explanation, since the WGS reaction is involved (Eq. (9)) apart from endothermic reactions. Since WGS is an equilibrium-limited exothermic reaction, it is thermodynamically favored at low temperatures and kinetically promoted at high temperatures, thus making the productions of CO and $CO_2$ mutually competitive [72,73]. Different authors stated that WGS Gibbs free energy increases with temperature and becomes positive at temperatures of around 825 °C, indicating that the reaction becomes thermodynamically unfavorable at elevated temperatures [74,75]. We observed in this study that increasing temperature from 800 to 850 °C promoted the formation of $CO_2$ at the expense of lowering that of CO (promotion of WGS), whereas the reverse WGS prevailed at 900 °C, which reduced the concentration of $CO_2$ in the syngas.

Fig. 5 shows the $H_2$/CO and CO/$CO_2$ ratios at different temperatures. It is interesting to analyze both parameters, since the $H_2$/CO ratio is essential for the applicability of the syngas as a raw material for many chemical plants, whereas the CO/$CO_2$ ratio is an index of the carbon amount converted to CO.

Fig. 5 shows that the $H_2$/CO ratio increased when temperature was increased, with the peak value being 1.95 at 900 °C. Several studies in the literature prove that temperature has a positive effect on the $H_2$/CO ratio in both air and steam bio-oil/biomass gasification, with this ratio being higher as the S/B ratio is increased [21,28,66,76,77]. Overall, the $H_2$/CO ratios of the syngas in this study (1.25–1.95) fell within the requirements in the oxo-synthesis process for aldehyde and alcohol production ($H_2$/CO ~ 1) and in the Fischer–Tropsch process for the production of synthetic fuels and methanol ($H_2$/CO ~ 2) [21,78,79].

The CO/$CO_2$ ratio showed a different trend, as it first decreased from 1.67 to 1.27 when temperature was increased from 800 to 850 °C and then increased again to 1.41 at 900 °C. The comparison of this parameter with the literature is not straightforward due to the complex effect of temperature on CO and $CO_2$ production. Furthermore, this trend greatly
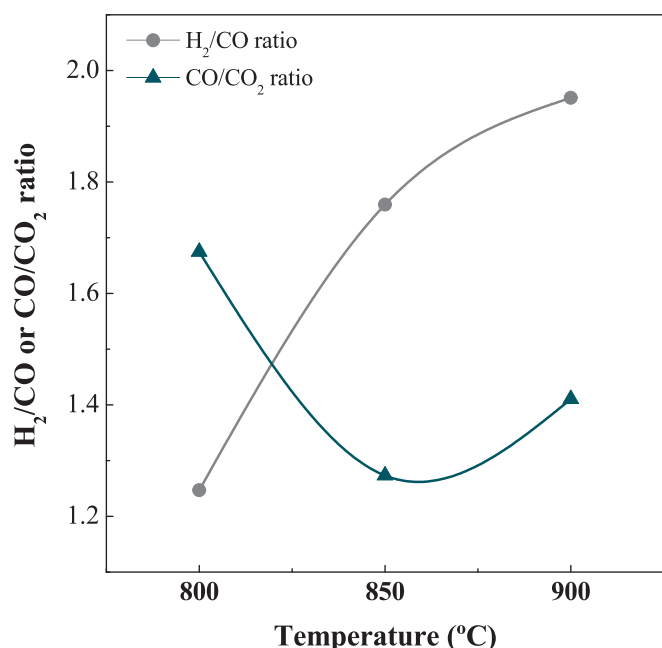
depends on the operating conditions, as not only temperature, but the S/B ratio and the catalyst affect reaction kinetics and equilibria, especially that of the WGS. Thus, certain papers report a downward trend as the gasification temperature is increased in the gasification of both bio-oil and biomass [21,76,80,81], whereas others report an upward trend [82,83]. It should be noted that, according to Zheng et al. [6], rather high $H_2$/CO ratios and low CO/$CO_2$ ones are preferred when syngas production is the aim. Thus, given that carbon conversion efficiency is similar at 850 and 900 °C, and $H_2$/CO and CO/$CO_2$ ratios at 850 °C fulfill the criteria mentioned by Zheng et al. [6], temperatures of around 850 °C are the optimum for bio-oil gasification.

### 3.2.3. Influence of gasification temperature on tar concentration

Tar is a complex mixture of aromatic hydrocarbons with a molecular weight larger than that of benzene. The characterization of tar was conducted according to the criteria proposed by Anis and Zainal [81], which include the following groups: (i) single ring light aromatics; (ii) heterocycles, which include aromatic rings that contains heteroatoms; (iii) light polyaromatic hydrocarbons (PAHs, composed of 2 or 3 aromatic rings), and; (iv) heavy PAHs (with more than 3 rings). Note that not only the total tar concentration is the key factor for the final application of the gaseous product, but tar conforming compounds also play a crucial role, as all of them contribute to the overall tar dew point. The influence of temperature on each tar fraction concentration is shown in Fig. 6. A detailed composition of the tar fraction obtained at different temperatures is shown in Table 2.

Fig. 6 reveals that light PAHs is the major fraction in the tar in the whole range of temperature studied. Furthermore, the concentration of all tar fractions decreases as temperature is increased, except that of heavy PAHs, which decreases to 2.2 g/$Nm^3$ at 850 °C and then increases again slightly to 3.1 g/$Nm^3$ at 900 °C. It is well stablished in the literature that as temperature increases, decomposition reactions such as cracking and reforming are promoted, thus favoring the formation of $H_2$, CO and light hydrocarbons at the expense tar content reduction [21,84]. However, the increase in the concentration of the heavy PAHs above 800 °C is due to the promotion of certain mechanisms with temperature, such as H-abstraction, $C_2H_2$-addition followed by cyclization or direct
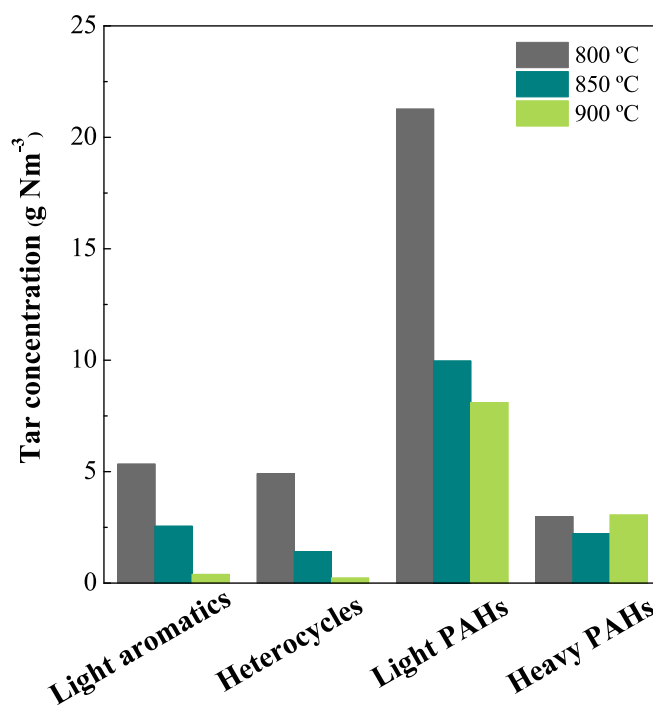


**Fig. 5.** $H_2$/CO and CO/$CO_2$ ratios for the syngas at different temperatures.



**Fig. 6.** Evolution of the concentration of each tar fraction in the gaseous stream with temperature.

**Table 2**

Detailed composition (wt%) of the tar fraction obtained at different temperatures.

| Compound (wt%) | 800 °C | 850 °C | 900 °C |
|---|---|---|---|
| **Light aromatics** | **13.11** | **14.82** | **3.13** |
| Toluene | 11.82 | 14.14 | 3.13 |
| Xylene | 0.39 | – | – |
| Styrene | 0.99 | 0.68 | – |
| **Heterocyclic** | **12.04** | **8.21** | **1.82** |
| Phenol | 5.54 | 4.62 | 1.17 |
| Methyl phenol | 6.01 | 3.16 | 0.64 |
| 1-Ethenyl 2-Methyl benzene | 0.49 | 0.37 | – |
| **Light PAHs** | **52.21** | **57.93** | **64.81** |
| Indene | 12.35 | 5.01 | – |
| Naphthalene | 16.70 | 31.66 | 31.80 |
| 1-Methyl naphthalene | 1.98 | 1.52 | 0.78 |
| 2-Methyl naphthalene | 1.43 | 0.97 | 2.76 |
| Biphenyl | 0.90 | 1.14 | 1.63 |
| Acenaphthene | 0.95 | 0.33 | 1.28 |
| Biphenylene | 4.92 | 4.36 | 1.31 |
| Dibenzofuran | 1.62 | 1.38 | 0.35 |
| Fluorene | 0.79 | – | – |
| 1-H-Phenalene | 1.43 | 0.97 | 1.31 |
| Anthracene | 5.64 | 6.94 | 15.04 |
| Phenanthrene | 2.07 | 2.22 | 4.83 |
| 9-Methyl anthracene | 0.56 | 0.83 | 1.12 |
| 1-Methyl phenanthrene | 0.38 | 0.34 | 1.10 |
| 2-Phenyl naphthalene | 0.51 | 0.25 | 1.49 |
| **Heavy PAHs** | **7.31** | **12.94** | **24.47** |
| Pyrene | 3.62 | 6.71 | 13.06 |
| Fluoranthene | 3.45 | 5.98 | 11.07 |
| 4H-Cyclopenta[*def*]phenanthrene | 0.23 | 0.25 | 0.35 |
| **Unidentified** | **15.33** | **6.11** | **5.77** |

combination of single-ring species [85,86].

To our knowledge, there are no studies in the literature dealing with tar characteristics and their evolution with temperature in the gasification of bio-oil. In view of the results obtained in this study, the chemical composition of the tar obtained in the gasification of bio-oil is very similar to that observed in several studies of biomass gasification [87,88 83–85]. Furthermore, the trend of the tar fractions with temperature (Fig. 6) and the concentration of the individual compounds (Table 2) in this study is similar to that observed in the gasification of biomass in a conical spouted bed reactor operating under enhanced fountain regime [38]. According to the latter study, an increase in temperature shifts tar composition from phenolic and alkyl-substituted PAH compounds to non-substituted PAHs which are more stable species and include compounds such as naphthalene, anthracene or fluoranthene, which also holds true in this work. Likewise, the overall yield of these compounds decreased with temperature (Fig. 6), although their concentration increased, as shown in Table 2. Naphthalene was the major light PAH found in the whole range of temperatures studied. More information about tar formation and evolution pathways in the gasification of biomass (also applicable to bio-oil gasification) can be found elsewhere [38,46].

### 3.3. Comparison between bio-oil gasification and biomass gasification

Bio-oil gasification is an alternative and novel strategy to biomass gasification for $H_2$ rich-gas production [6]. Overall, bio-oil is more suitable than biomass in terms of storage and transportation. As the energy density of bio-oil is from 3 to 5 times higher than that of biomass, it allows reducing the expensive transportation costs associated with biomass logistics [13]. Thus, this novel strategy aims to take advantage of the economy of scale, which indeed improves the viability of bio-oil gasification. Bio-oil gasification strategy involves the production of bio-oil in distributed or mobile plants near the harvest sites and its transportation to a central biorefinery unit for gasification [8,89]. Moreover, unlike biomass gasification, no char is produced in the gasification of bio-oil. Thus, there is no char accumulation, and therefore no

need of maintenance stop to solve the problems associated with the char. Another advantage of this process is related to the valorization of the char produced in the pyrolysis step, which may also enhance $H_2$ production. Thus, this char may be mixed with the bio-oil to form a bio-slurry, which may be fed into the gasification unit [90]. Taking all the above into account, the gasification performance of both thermochemical routes has been compared in Table 3. It is to note that biomass gasification results were obtained in a previous study by the authors [38].

As observed in Table 3, the carbon conversion efficiency considerably improved at any temperature when bio-oil was gasified. The lower efficiencies obtained in the gasification of biomass are related to the generation of char, which is not produced in the gasification of bio-oil. Char gasification reactions are very slow, even at standard gasification temperatures, i.e., they are the rate-controlling step in biomass gasification [22,91,92]. Thus, char yield was reduced by increasing temperature from 9.0 wt% at 800 °C to 3.2 wt% at 900 °C, and therefore carbon conversion efficiency increased from 78 % at 800 °C to 93 % at 900 °C. It is worth noteworthy that the difference in carbon conversion efficiency between the two strategies is smaller as the temperature is higher due to the enhancement of char gasification reactions with temperature.

Likewise, the gas and hydrogen yields obtained in the gasification of bio-oil were also higher than those in the gasification of biomass. Thus, at 900 °C, they were 1.85 $Nm^3$/kg and 7.96 wt%, respectively, whereas those for the gasification of biomass were 1.65 $Nm^3$/kg and 6.35 wt%, respectively. Regarding tar concentration, higher values should be obtained in the gasification of bio-oil due to its higher content of volatile matter. Nevertheless, Table 3 shows that bio-oil gasification leads to lower values of tar except at the highest temperature studied of 900 °C.

## 4. Conclusions

The conical spouted bed reactor is a highly efficient hybrid technology for the production of syngas by combining biomass fast pyrolysis and subsequent gasification of the bio-oil produced. Moreover, a device for feeding the whole raw bio-oil was developed and tuned for bio-oil gasification at high temperatures. This device is made up of a thermostated line and a non-atomizing injector, which allow a smooth feeding of the bio-oil without any pipe or reactor clogging.

The bio-oil was successfully gasified at 800, 850 and 900 °C with a S/B ratio of 2 under fountain enhanced regime, which promoted tar cracking and reforming reactions. An increase in gasification temperature improved process efficiency in terms of syngas production and tar reduction, with the maximum carbon conversion efficiency being 96.3 % at 900 °C. Besides, the hydrogen content also increased with temperature from 4.51 wt% at 800 °C to 7.96 wt% at 900 °C on a dry basis, which resulted in an increase in $H_2$/CO ratio from 1.2 to 2, respectively. Concerning the $H_2$/CO ratio, the values obtained are within the range required for GTL processes (synthesis of methanol, dimethyl ether, and Fischer-Tropsch, amongst others), i.e., between 1 and 2. Moreover, tar content decreased by around 70 % in the 800–900 °C range, recording the lowest value (12.7 g/$Nm^3$) at 900 °C.

Regarding the tar composition, the main fraction in the whole range of temperatures was that of light PAHs, with those of aromatics and heterocycles being more significant than that of heavy PAHs at 800 °C, but less significant at 850 and 900 °C. Tar monitoring also revealed that an increase in temperature led to more stable species in the range of secondary and tertiary tars (heavy PAHs) due to rearrangement reactions.

### CRediT authorship contribution statement

**Maria Cortazar:** Investigation, Methodology, Visualization, Writing – review & editing. **Jon Alvarez:** Writing – original draft, Investigation, Resources, Validation, Visualization, Writing – review & editing. **Gartzen Lopez:** Methodology, Conceptualization, Validation, Writing –

**Table 3**
Comparison of reaction indices involving the gasification of bio-oil and biomass (biomass gasification results are on a wet basis, whereas those of bio-oil are on a dry-ash free basis).

| Temperature (°C) | Gas Yield (Nm$^3$/kg) | | H$_2$ production (wt%) | | Tar concentration (g/Nm$^3$) | | Carbon conversion efficieny (%) | |
|---|---|---|---|---|---|---|---|---|
| | Bio-oil | Biomass | Bio-oil | Biomass | Bio-oil | Biomass | Bio-oil | Biomass |
| 800 | 1.37 | 0.98 | 4.51 | 2.91 | 40.7 | 49.2 | 91.2 | 78.0 |
| 850 | 1.65 | 1.30 | 6.35 | 4.99 | 17.2 | 20.6 | 95.5 | 86.1 |
| 900 | 1.85 | 1.65 | 7.96 | 6.35 | 12.5 | 6.7 | 96.3 | 93.0 |

review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Maider Amutio:** Conceptualization, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Maite Artetxe:** Conceptualization, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Javier Bilbao:** Writing – review & editing, Visualization, Supervision. **Martin Olazar:** Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

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