



Full Length Article

In line upgrading of biomass fast pyrolysis products using low-cost catalysts

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ABSTRACT

Biomass pyrolysis and the in-line catalytic cracking of the pyrolysis volatile stream has been approached in this study. The pyrolysis step was carried out in a conical spouted bed reactor at 500 °C, whereas the inert sand or the cracking catalysts (γ -Al₂O₃, spent FCC and olivine) were placed in a fixed bed reactor at 600 °C. Product analysis was carried out on-line by means of chromatographic methods, and the distribution and composition of the main products obtained have been related to the features characterizing each catalyst (physical properties, chemical composition and acidity).

Decarbonylation reactions were favoured over decarboxylation ones when acid catalysts (spent FCC and γ -Al₂O₃) were used, whereas olivine promoted ketonization and aldol condensation reactions. The Fe species in the olivine structure enhanced reforming and WGS reactions. Bio-oil cracking was more severe as catalyst acidity was increased, leading to an increase in the hydrocarbon fraction. The Al₂O₃ derived bio-oil was substantially deoxygenated, with a considerable reduction in the phenolic fraction, which accounted mainly for alkyl-phenols. The three materials tested led to a significant decrease in acid and phenolic compounds in the volatile stream, making it suitable for further catalytic valorization for the production of H₂, fuels and chemicals.

1. Introduction

The harsh reduction in fossil fuel reserves and the increasing concern about the environmental pollution have boosted the development of new strategies for the valorization of alternative sustainable sources in order to mitigate the problems associated with CO₂ emissions and global warming [1–3]. In this regard, biomass has been considered one of the most suitable renewable alternatives for future energy and fuels due to its availability and carbon neutral emissions. Thus, in recent years, there is an increasing interest in the development of new strategies for the production of value-added and sustainable biofuels, chemicals, and bioproducts [4–7], in which biomass is used as a raw material. Amongst them, thermochemical processes have deserved a remarkable attention in the literature [1,5,6], particularly biomass steam gasification [8–11], biomass fast pyrolysis [12–15], and the steam reforming of the bio-oil produced in the pyrolysis process [16,17].

Biomass steam gasification is one of the most studied and developed technologies for the production of H₂ rich syngas. However, the excessive tar content in the syngas is currently a challenge to be overcome [8,18].

Alternatively, the bio-oil produced in the pyrolysis reaction has attracted increasing attention for the production of other high value-added products, such as H₂, automotive fuels and chemicals, by means of several catalytic and thermochemical routes [19–21]. The bio-oil is a complex mixture of oxygenated compounds and water, and is mainly composed of small carboxyl and carbonyl molecules (acids, ketones, aldehydes), sugar-derived compounds (furans, anhydrosugars), and lignin-derived compounds (phenols, aromatic oligomers) [22,23]. Nevertheless, its direct application involves several drawbacks associated with its properties (low heating value, low volatility, thermal instability and strong corrosiveness [24,25]), along with the difficulties involving its feeding (due to incomplete vaporization and re-polymerization of unstable compounds). Accordingly, bio-oil stabilization (for its further utilization as fuel or raw material in other catalytic processes) has deserved a remarkable attention in the literature. Thus, a wide range of strategies (physical, thermal or catalytic treatments) have been extensively analyzed for bio-oil conditioning, as are: esterification, aldol condensation, ketonization, in situ cracking, and mild hydro-deoxygenation [19,26–29].

In spite of the aforementioned drawbacks, the bio-oil can be used as

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fuel by mixing with diesel (with the bio-oil content being of up to 75 wt %), or for the production of several feedstocks based on bio-oil compounds, i.e., synthesis of wood adhesives or resins from phenolic compounds [30]. Besides, the bio-oil can be catalytically transformed downstream by the following routes: i) deep hydrodeoxygenation (HDO) in order to produce fuels, ii) ex-situ catalytic cracking for the production of olefins and BTX aromatics or for vapour upgrading by carrying out a second step, and iii) steam reforming aimed at the production of H₂ [6,19,20,31].

In all these processes, the selection of suitable catalytic materials plays a key role for their industrial scale viability. Thus, a wide range of catalysts have been used in order to attain the desired purity of the products obtained, decrease the severity of reaction conditions, attenuate catalyst deactivation and/or reduce catalyst costs [32]. In the hydrodeoxygenation (HDO) process, bifunctional catalysts are considered the most promising ones, since they strike a suitable balance between catalysts activity (provided by the acid sites) and catalyst deactivation by coke deposition [33]. In the catalytic cracking process, catalysts with acidity and shape selectivity, such as zeolite based ones (HZSM-5, Y-type zeolite, H-mordenite and so on), are preferred in order to produce olefins and BTX aromatics [34]. Concerning the steam reforming process, metal supported catalysts (particularly Ni and noble metals based catalysts supported on Al₂O₃) are commonly used, and extensive research has been made in order to improve their activity and stability [6,16,35].

Nevertheless, the fast catalyst deactivation by coke deposition in the aforementioned routes is still the main challenge to overcome [16,34,36]. It is well-established that the mechanisms of catalyst deactivation and coke formation are greatly influenced by the feed composition [37]. Thus, certain bio-oil compounds, namely, aldehydes, saccharides (mainly levoglucosan) and phenolic compounds, such as the guaiacols produced from the thermal degradation of lignin, are considered the main responsible for coke formation in the catalytic pyrolysis process [38–40]. Within this scenario, the upgrading of the bio-oil by catalytic cracking prior to its valorization in a second step may help to overcome the fast catalyst deactivation. Accordingly, different catalytic materials have been widely investigated, as are acid metal oxides (mainly Al₂O₃), basic materials (such as MgO and CaO), or other transition metal oxides (such as ZrO₂, ZnO, TiO₂, Fe₂O₃) [27,41]. Besides, the use of inexpensive catalysts, waste products or natural minerals is gaining increasing attention due to its low cost and availability [24,38,42]. Accordingly, Ro et al. [38] analyzed the product selectivity of lignin pyrolysis in a fixed bed reactor by using low-cost additives (bentonite, olivine, and spent FCC catalyst) as in-situ catalysts, and HZSM-5 catalysts placed downstream in a fixed bed reactor. They reported higher catalytic activity and lower coke deposition when bentonite was tested. Valle et al. [32] approached the modification of the raw bio-oil by its continuous catalytic upgrading over dolomite in a low-cost reaction system. They concluded that the composition of the upgraded bio-oil is suitable for downstream valorization processes, such as the production of H₂ by steam reforming or aromatic hydrocarbons by a two-step hydrogenation-cracking process. However, no studies have been reported in the literature on the joint process of continuous biomass pyrolysis and in-line catalytic modification of the volatile stream; that is, there are no detailed studies aimed at ascertaining the main bio-oil compounds responsible for the catalyst activity decay in the steam reforming reactions. The aim of this paper is therefore to analyze the feasibility of continuous bio-oil upgrading for its further transformation into high value-added products. Accordingly, continuous pinewood sawdust pyrolysis and in-line catalytic conditioning by means of different low cost materials (inert sand, olivine, spent FCC catalyst and γ -Al₂O₃) has been analyzed by paying special attention to product yields and compositions. Thus, a detailed knowledge of the modified stream will allow ascertaining its suitability for further valorization in other catalytic routes (this study focuses on steam reforming). Furthermore, it will also allow understanding catalyst deactivation in order to

improve the catalyst performance. The main mechanisms of bio-oil transformation on these catalysts will also be analyzed in this study.

2. Experimental

2.1. Feedstock

The biomass used is forest pine wood (*pinus insignis*), which has been crushed, ground and sieved to a particle size in the 1–2 mm range. This particle size eases continuous feeding operation. Table 1 summarizes the most important properties (ultimate analysis, proximate analysis and the higher heating value) of the biomass used in this study, whose empirical formula is CH_{1.47}O_{0.67}. The ultimate analysis has been determined in LECO CHN-932 and VTF-900 elemental analyzers. An ultra-microbalance SARTORIUS M2P is on-line with a computer for the processing of the data provided by the analyzers. The proximate analysis (volatile matter, fixed carbon and ashes) has been determined in a thermogravimetric analyzer (TA Instrument TGA Q5000IR). The higher heating value (HHV) has been measured in a Parr 1356 isoperibolic bomb calorimeter.

2.2. Catalyst conditioning and characterization

Inert silica sand, olivine, γ -Al₂O₃ and spent FCC catalysts have been tested in order to ascertain their capacity for improving the composition of the biomass pyrolysis volatile stream for its subsequent reforming for H₂ production. Silica sand and olivine have been supplied by Minerals Sibelco, γ -Al₂O₃ by Alfa Aesar and the FCC spent catalyst is the one used in the FCC unit at Petronor Refinery in Muskiz, Spain. Thus, materials with different features have been selected: i) inert silica sand, ii) olivine with basic character and activity for reforming oxygenate compounds [43,44], iii) γ -Al₂O₃ and spent FCC catalyst of moderate acidity and adequate for promoting oxygenate cracking [45–47]. Apart from their suitable catalytic activity, the selection of the materials was based on their low cost, and bearing in mind their possible application as guard beds prior to the stream valorization in a second catalytic step of steam reforming. Furthermore, the use of a spent FCC catalyst involves reusing and therefore valuing a refinery waste material.

Prior to use, the spent FCC catalyst was agglomerated with bentonite (50%) in order to increase mechanical strength as well as provide meso and macropores to the catalyst to avoid the blockage of the zeolite external pores by coke deposition [48,49]. Firstly, the spent FCC catalyst was regenerated by calcination with air at 575 °C for 1 h for burning all the coke deposited in the refinery unit. It was then agglomerated by wet extrusion with bentonite, and dried overnight. Finally, the catalyst was calcined at 575 °C for 2 h. All the catalysts were ground and sieved to a particle size in the 0.8–1.6 mm range.

The physical properties of the catalysts were determined by N₂

Table 1
Pine wood sawdust characterization.

Ultimate analysis (wt%) ^a	
Carbon	49.33
Hydrogen	6.06
Nitrogen	0.04
Oxygen ^b	44.57
Proximate analysis (wt%) ^c	
Volatile matter	73.4
Fixed carbon	16.7
Ash	0.5
Moisture	9.4
HHV (MJ kg ⁻¹)	19.8

^a on a dry and ash free basis, daf.

^b by difference.

^c on an air-dried basis.

adsorption–desorption (Micromeritics ASAP 2010). The chemical composition was measured by X-ray Fluorescence (XRF) spectrometry. This analysis was carried out under vacuum using a sequential wavelength dispersion X-ray fluorescence spectrometer (WDXRF), PANalytical AXIOS, equipped with Rh tube and three detectors. The samples were prepared mixing flux Spectromelt A12 from Merck (ref. No. 11802) with powder catalyst in a ratio of approximately 20:1. Before the chemical analysis, the samples were melted in an induction micro-furnace.

The total surface acidity of all materials was analyzed by NH_3 -TPD in an AutoChem II 2920 Micromeritics equipment. Thus, the procedure was as follows: i) Removal of the possible impurities adsorbed on the sample with a He stream following a ramp of $15\text{ }^\circ\text{C min}^{-1}$ to $550\text{ }^\circ\text{C}$, ii) NH_3 adsorption ($150\text{ }\mu\text{L min}^{-1}$) until reaching sample saturation; (iii) desorption of the physisorbed NH_3 with a He stream at $150\text{ }^\circ\text{C}$, and (iv) continuous signal recording by TCD of the chemisorbed NH_3 following temperature programmed desorption from 150 to $550\text{ }^\circ\text{C}$.

2.3. Experimental equipment and procedure

The experimental equipment used in this study is shown in Fig. 1, which is composed of a conical spouted bed reactor (CSBR) and an in-line fixed bed reactor. Continuous biomass pyrolysis ($500\text{ }^\circ\text{C}$) was carried out in a conical spouted bed reactor, whose suitable performance for biomass pyrolysis and gasification has already been proven [22,50–53]. The main dimensions of the CSBR are as follow: height of the conical section, 73 mm ; diameter of the cylindrical section, 60.3 mm ; angle of the conical section, 30° ; diameter of the bed bottom, 12.5 mm , and diameter of the gas inlet, 7.6 mm . These dimensions were selected based on previous hydrodynamic studies, and ensure a stable operation in a wide range of gas flow rates [54–57]. 50 g of silica sand ($0.3\text{--}0.35\text{ mm}$) were used as bed material in the CSBR. In addition, the unit was provided with a lateral outlet pipe located above the bed surface to continuously remove the char particles from the CSBR.

The biomass was continuously fed (0.75 g min^{-1}) into the CSBR by means of a solid feeding system that allowed continuous feeding in the

range from 0.5 g min^{-1} to 5 g min^{-1} . The feeding system consisted of a vessel equipped with a vertical shaft connected to a piston placed below the bed material. As the piston rised, the biomass was fed into the reactor helped by a vibration system.

The gas feeding system is provided with three mass flow meters, which allow feeding N_2 (used as fluidizing agent during the heating process), H_2 (for the reduction of metal-based catalysts in further reforming studies), and air (used for coke combustion). Besides, the water to generate the steam used as fluidizing agent in the pyrolysis step was fed by a high precision Gilson 307 pump. A water flow rate of 3 mL min^{-1} was used in all runs, with the steam/biomass weight ratio being 4. Before entering the reactor, the water was vaporized and the steam preheated to $500\text{ }^\circ\text{C}$. The CSBR and the preheater were placed inside a radiant oven of 1250 W .

The biomass pyrolysis volatiles formed in the CSBR circulate through a fixed bed reactor ($600\text{ }^\circ\text{C}$) connected in-line, where the inert or catalyst (silica sand, olivine, $\gamma\text{-Al}_2\text{O}_3$ or spent FCC) were placed. It is to note that, given the low activity of these low-cost materials, the masses of the catalysts used correspond to the same bed length in all the runs. Thus, the significant differences in the densities of the materials were considered (sand, 2600 kg m^{-3} ; olivine, 3300 kg m^{-3} ; FCC, 1246 kg m^{-3} , and $\gamma\text{-Al}_2\text{O}_3$, 1666 kg m^{-3}), and so the bed masses were 44.2 g of silica sand, 46.2 g of olivine, 17.3 g of spent FCC catalyst and 19.9 g of $\gamma\text{-Al}_2\text{O}_3$. Accordingly, all runs were carried out with a gas hourly space velocity (GHSV) of 3100 h^{-1} . The fixed bed reactor was placed inside a radiant oven of 550 W .

Both reactors were placed inside a convection oven kept at $270\text{ }^\circ\text{C}$ in order to avoid the condensation of the volatiles formed in the pyrolysis step, which were fed into the catalytic step. The outlet stream was fed into the product condensation device prior to its analysis.

The product stream leaving the fixed bed reactor was analyzed in-line by a GC Agilent 6890 provided with a HP-Pona column and a flame ionization detector (FID). The sample was injected to the GC by means of a thermostated line kept at $280\text{ }^\circ\text{C}$ to avoid the condensation of heavy oxygenated compounds. Cyclohexane (not formed in the process) was used as an internal standard to validate the mass balance closure,

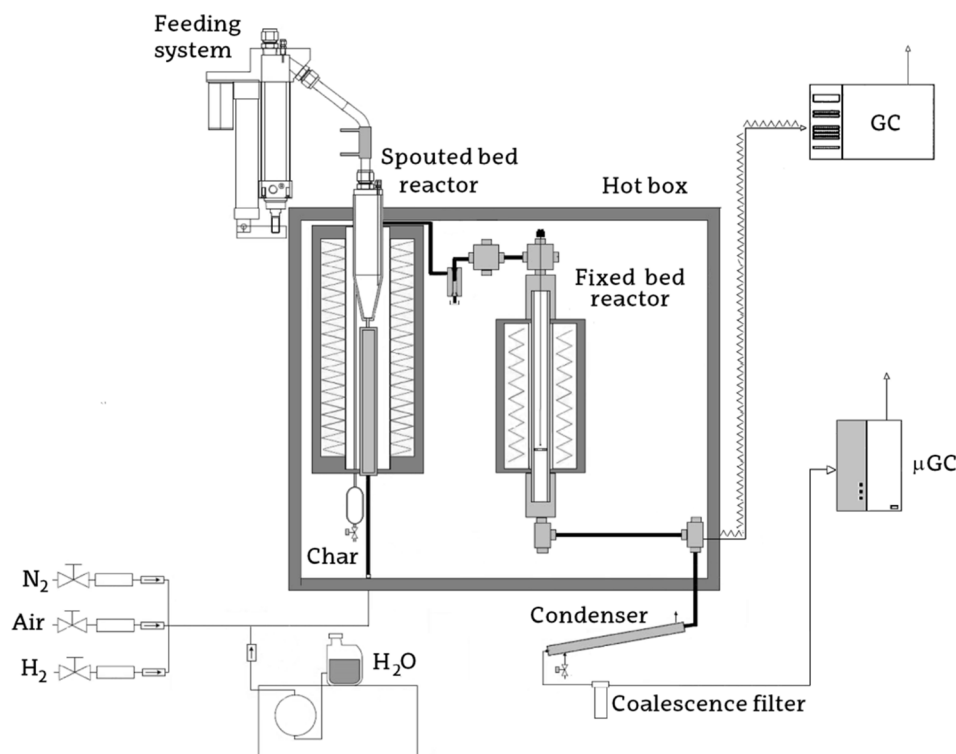


Fig. 1. Scheme of the laboratory scale equipment.

which was fed into the product stream at the outlet of the catalytic reactor. Furthermore, the non-condensable gases were analyzed by means of a micro GC Varian 4900, which allowed detailed quantification of the product stream. The liquid compounds (dissolved in acetone to avoid the clogging of the GC-MS injector) were identified by means of a GC-MS spectrometer (Shimadzu 2010-QP2010S) provided with a BPX-5 (50 m × 0.22 mm × 0.25 μm). The temperature sequence of the oven was as follows: steady heating from 45 °C to 290 °C following a ramp of 3 °C min⁻¹ for separating the volatile products, with this temperature being kept for 5 min in order to ensure total removal of all products from the column. The column was connected to a mass spectrometer, which operated under the following conditions: ion source and interface temperatures 200 °C and 300 °C, respectively, operating in the 40–400 m/z range.

3. Results

3.1. Catalyst characterization

The physical and chemical properties as well as the acidity of the materials used are shown in Table 2. It can be seen that the materials selected for biomass pyrolysis volatile stream modification have several differences in their main properties. Regarding physical properties, it can be observed that silica sand and olivine have a very low surface area, whereas FCC and γ-Al₂O₃ have BET surface areas of 81 and 100 m² g⁻¹, respectively. Accordingly, sand and olivine are not porous materials, and spent FCC and γ-Al₂O₃ catalysts are mesoporous materials with an average pore diameter of 168–169 Å. It should be noted that the spent FCC catalyst is based on HY zeolite; however, it has been agglomerated with bentonite to increase its mesoporous structure for facilitating the diffusion of bulky molecules and so avoid the blockage of zeolite external pores by coke deposition [58]. Thus, mesoporous materials with a uniform pore size promote the interaction of large organic molecules with the active sites [27]. The spent FCC catalyst has a microporous surface area of 57 m² g⁻¹, which is evidence of the presence of a zeolite on its structure.

Table 2
Physical and chemical properties, and acidity of the materials used.

	Sand	γ-Al ₂ O ₃	FCC	Olivine
<i>Physical properties</i>				
S _{BET} (m ² g ⁻¹)	0.6	100	81	2.4
S _{micropore} (m ² g ⁻¹)	1.1	12	57	0.7
V _{pore} (cm ³ g ⁻¹)	–	0.42	0.09	0.003
d _{pore} (Å) BJH	–	169	168	–
d _p (mm)	0.8–1.6	0.8–1.6	0.8–1.6	0.8–1.6
ρ _{parent} (kg m ⁻³)	2600	1666	1246	3300
<i>Chemical properties</i>				
NiO (wt%)	–	–	0.05	–
MgO (wt%)	–	–	1.09	48.79
SiO ₂ (wt%)	98.0	0.02	53.93	43.18
Fe ₂ O ₃ (wt%)	–	–	2.10 ^a	7.68
CaO (wt%)	–	–	0.24	0.12
Al ₂ O ₃ (wt%)	–	99.98	31.90	0.04
Na ₂ O (wt%)	–	–	0.38	0.06
TiO ₂ (wt%)	–	–	0.85	0.02
MnO (wt%)	–	–	0.01	0.11
P ₂ O ₅ (wt%)	–	–	0.22	–
V ₂ O ₅ (wt%)	–	–	0.20	–
K ₂ O (wt%)	–	–	0.24	–
La ₂ O ₃ (wt%)	–	–	1.25 ^b	–
SO ₃ (wt%)	–	–	0.13	–
Cl (wt%)	–	–	0.15 ^b	–
<i>Acidity</i>				
Total acidity (μmol _{NH3} g _{cat} ⁻¹)	–	106.3	46.7	6.2

^a Expressed as total Fe₂O₃.

^b Determined by semi-quantitative software.

Concerning the chemical composition of each material, sand and γ-Al₂O₃ contain small amounts of impurities. The spent FCC catalyst is mainly composed of SiO₂ and Al₂O₃, as well as various metal oxides, which are accumulated in the catalyst in the consecutive reaction-regeneration cycles in the refinery unit. The high amount of Fe₂O₃ (7.68 wt%) in the olivine is noteworthy, as it plays an important role in its catalytic activity by promoting the reforming of oxygen compounds [59]. Olivine has been widely used in biomass gasification for tar reduction due to its activity for cracking and reforming reactions and its low cost compared to metal catalysts [43,60]. Several researches stated that the catalytic activity of olivine depends on the amount of Fe present on its composition, as well as on its oxidation state, with Fe being more active as its reduction state is increased [43,61].

Moreover, the total acidity of γ-Al₂O₃ is higher than the one of the spent FCC catalyst, 106 and 47 μmol_{NH3} g_{cat}⁻¹, respectively. The low acidity of the spent FCC catalyst is attributed to the fact that it has been agglomerated with bentonite, which decreased the amount of HY zeolite to 8 wt%. Acid catalysts enhance dehydration and decarbonylation of oxygen components to form carbon monoxide and water as primary products in the deoxygenation reaction [62], as well as cracking, oligomerization, alkylation, isomerization, cyclization and aromatization via a carbonium ion mechanism [27]. It is to note that the moderate acidity of the catalysts used in this case lead to lower deoxygenation activity, but also to lower coke formation by secondary cyclization and condensation reactions [63,64]. Conversely, basic catalysts, such as olivine, enhance ketonization and aldol condensation reactions, leading mainly to the formation of carbon dioxide and water [62].

3.2. First step: biomass pyrolysis

Continuous biomass fast pyrolysis has been carried out in a CSBR at 500 °C with the aim of maximizing the bio-oil yield. Previous studies have shown the good performance of this reactor for biomass pyrolysis [22,51,65]. Thus, this reactor provides several advantages compared with other reactor configurations, namely: i) short residence time of the volatiles in the reactor (of around 20 ms due to the high velocity of the gas, thus minimizing volatile transformation by secondary reactions, and so maximizing the bio-oil yield in the biomass pyrolysis), ii) high heat and mass transfer rates, i.e., the high velocity of both gas and solid phases and their countercurrent contact improve heat and mass transfer rates, and iii) rapid removal of the char from the reactor by the segregation of char from sand in the fountain, which allows continuous operation. Besides, its simple design eases the scalability of the pyrolysis process.

According to the previous biomass pyrolysis studies, a moderate temperature of 500 °C minimizes secondary reactions, which is a promising fact to decrease the gas yield from bio oil cracking [22,65]. In fact, the most important parameters for maximizing bio oil production in the biomass pyrolysis are [66]: i) very high heating rates, ii) high heat and mass transfer rates; iii) moderate temperatures (of around 500 °C), iv) very short residence times, and, v) rapid char removal from the reactor.

Table 3 shows the yields of the main products obtained in the biomass steam pyrolysis at 500 °C in a CSBR. The inert nature of steam in the biomass pyrolysis has been previously verified, i.e., product distribution is the same as when N₂ is used as fluidizing agent [67]. Under the conditions studied, the char yield is 17.3 wt%, and is continuously removed from the pyrolysis reactor by means of a lateral outlet. This char is suitable for the production of diverse products, such as adsorbents, fertilizers, catalyst supports and soil amenders [68–70].

As observed, the gas fraction is mainly composed of carbon monoxide (2.3 wt%) and carbon dioxide (4.7 wt%). The low yield of methane (0.2 wt%) and light hydrocarbons (almost negligible) is indicative of the low extent of secondary cracking reactions in the volatile stream [71]. Thus, a high yield of bio-oil is obtained (75.4 wt%), and so the overall yield of volatile compounds fed into the next step is 82.7 wt%.

Table 3

Yields of the main products obtained in the biomass pyrolysis in the CSBR at 500 °C.

Compound	Yield (wt%)
Gas	7.3
CO	2.3
CO ₂	4.7
CH ₄	0.2
Light HCs (C ₂ -C ₄)	0.1
H ₂	0.1
Bio-oil	75.4
Acids	3.1
Aldehydes	2.5
Ketones	7.3
Alcohols	1.8
Polycyclic Aromatic Alcohols	0.2
Phenols	16.6
Alkyl-phenols	1.6
Catechols	8.3
Guaiacols	6.7
Furans	2.3
Saccharides	4.5
Hydrocarbons	0.0
Non-aromatics	0.0
Light aromatics (BTX)	0.0
PAHs	0.0
Others	0.1
Unidentified	12.6
Water	24.5
Char	17.3

Regarding the bio-oil, more than 100 compounds have been identified in this fraction, and therefore the yields of only the functional groups and main compounds have been included in Table 3. It can be observed that bio-oil is composed of acids (3.1 wt%), aldehydes (2.5 wt%), alcohols (1.8 wt%), ketones (7.3 wt%), phenols (16.6 wt%), furans (2.3 wt%) and saccharides (4.5 wt%). Among the different functional groups, phenols are the most abundant ones, which are formed from the degradation of lignin [72]. The high yield of saccharides is noteworthy, mainly levoglucosan (4.5 wt%), which is the major individual compound in the bio oil, and is obtained as a primary product by cellulose depolymerization.

The bio-oil contains a significant amount of water coming from the raw biomass moisture (10 wt%) and also from dehydration reactions involving cellulose and hemicellulose [73,74]. The high water and oxygen content in the bio-oil, as well as the low pH and low heating value, make bio-oil upgrading to be essential for subsequent use [75,76].

3.3. Catalytic cracking of biomass pyrolysis volatiles

The catalysts used for the steam cracking of the biomass pyrolysis volatile stream are γ -Al₂O₃, spent FCC and olivine. The pyrolysis step has been carried out at 500 °C and the cracking step at 600 °C. Inert silica sand has also been used in order to assess the effect of thermal cracking on the volatile stream. The overall product distribution obtained in the two-step pyrolysis-cracking process is a complex mixture of many compounds, and so the products have been grouped into three fractions: i) the gas fraction composed mainly of CO and CO₂, as well as low amounts of H₂ and C₁-C₄ hydrocarbons; ii) the bio-oil, which is a complex mixture of oxygenated compounds and water; iii) the char fraction, which is the non-volatilized biomass fraction. Fig. 2 shows the effect of each catalyst on the product fraction yields. The yields of each fraction obtained in the pyrolysis step at 500 °C have also been included. The char fraction is continuously removed from the pyrolysis reactor, and is not therefore fed into the second catalytic step. Accordingly, the yield of char remains constant (17.3 wt%) in all the runs, independently of the catalyst used.

As observed, all the catalysts are active for cracking, as they increase the yield of the gas fraction in detriment of that of the bio-oil.

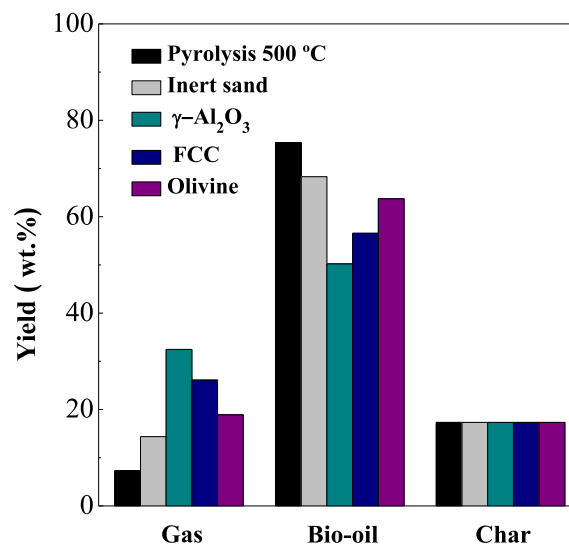


Fig. 2. Effect of the catalysts on the product fraction yields.

Furthermore, bio-oil cracking is more severe as the acidity of the catalyst is higher. Thus, when the spent FCC catalyst is used, the gas yield increases from 7.3 wt% to 26.1 wt%, and when γ -Al₂O₃ is used to 32.5 wt%. However, a basic catalyst, such as olivine, has lower cracking activity, as it only increases the gas yield to 18.9 wt%. Apart from their different character, the catalysts have significant differences in their physical properties, with γ -Al₂O₃ and spent FCC catalyst being mesoporous materials and olivine a non-porous material. Thus, the limited porous structure hinders the diffusion of bulky oxygenated compounds into the bed material, leading to a lower extension of cracking and deoxygenation reactions [77].

As observed in Fig. 2, thermal cracking is significant when inert silica sand is used. Thus, the bio-oil yield decreases from 75.4 wt% to 68.3 wt% and the gas yield increases from 7.3 wt% to 14.4 wt%. Therefore, apart from the effect of the catalyst acidity/basicity, the fact that the cracking step is performed 100 °C above that of pyrolysis leads to bio-oil thermal cracking reactions in parallel to catalytic ones.

Fig. 3a and 3b show the effect of the catalyst on the gas fraction composition and on the yields of the individual components, respectively. As observed in Fig. 3a, CO₂ is the main compound in the gas fraction at the inlet of the cracking reactor (obtained by pyrolysis at 500 °C). However, when inert sand is used, a sharp increase in CO and CH₄ concentrations (45 and 12 vol%, respectively) is observed, at the expense of decreasing that of CO₂ (28 vol%), which is due to the thermal cracking reactions.

Moreover, the particular features of FCC and γ -Al₂O₃ catalysts, especially the total acidity, modified significantly the gaseous product composition, leading to the highest concentrations of CO and HCs, which is evidence of the higher extension of the cracking reactions as when compared with the use of olivine or inert sand. Accordingly, when γ -Al₂O₃ and FCC catalysts are used, the CO concentration accounts for almost 50 vol% of the gas fraction when any one of these catalysts is used, with that of CO₂ being 20.0% and 29.1 vol% respectively. Moreover, the use of γ -Al₂O₃ and FCC catalysts also leads to an increase in CH₄ and light hydrocarbon concentrations, particularly that of the olefin fraction, which stem from the decarbonylation of oxygenated intermediates or alkyl aromatics [78]. The higher concentration of CO than CO₂, as well as the increase in the yields of aromatics and olefins, was also observed by Ro et al. [38], who analyzed the upgrading of the lignin-derived bio-oil using different catalysts (bentonite, olivine, spent FCC catalyst and HZSM-5). The promotion of decarbonylation over decarboxylation reactions was also reported by Wang et al. [79] in the catalytic pyrolysis of hybrid poplar wood.

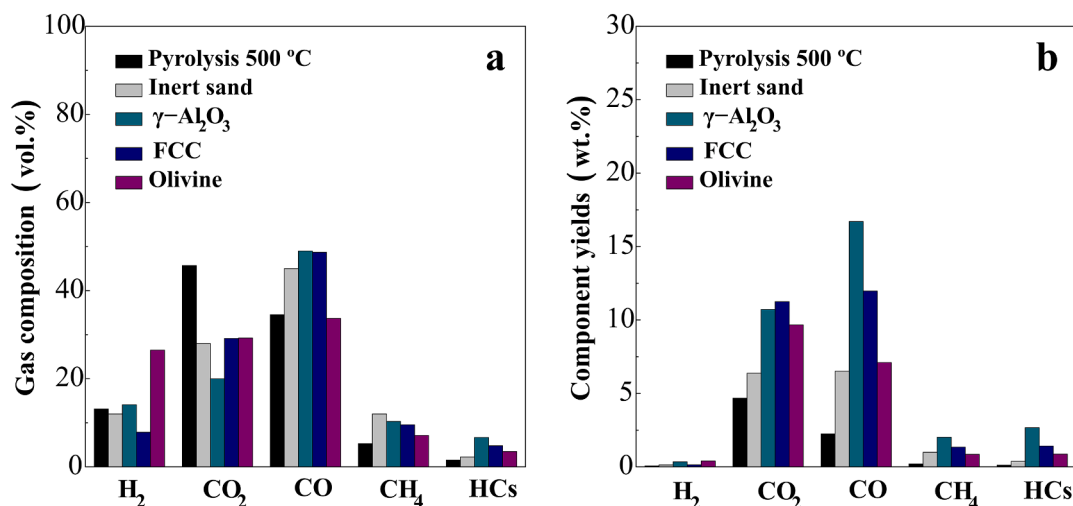


Fig. 3. Effect of the inert and cracking catalysts on the gas fraction distribution: a) gas composition; b) yields of gaseous components.

Significant features are also observed in the composition of the gas fraction obtained using olivine: 33.7 vol% CO, 29.2 vol% CO₂, 26.4 vol% H₂, 7.1 vol% CH₄ and 3.5 vol% C₂-C₄ hydrocarbons. Thus, apart from the deoxygenation reactions of dehydration, decarbonylation and decarboxylation, olivine also enhances oxygenate compound reforming and the water gas shift reaction, which lead to the formation of CO, CO₂ and H₂. This is mainly due to the chemical composition of olivine, with contains Fe⁰ on its surface, promoting reforming and WGS reactions [80,81].

Given the differences observed in the overall gas yield obtained depending on the catalytic material (Fig. 2), the yields of individual gaseous products have been displayed in Fig. 3b. As observed, γ -Al₂O₃ and spent FCC catalyst, who account for a gas yield of 32.5 and 26.1 wt %, respectively, showed the highest yields of CO, CH₄ and light hydrocarbons. Thus, the yields of these compounds increase with catalyst acidity, which is clear evidence that acidity promotes cracking reactions. Besides, these acid catalysts enhance decarbonylation reactions rather than decarboxylation ones, with CO being the main compound in the gaseous stream.

Moreover, it is noteworthy that CO₂ yield was higher than that of CO and remaining gaseous compounds only when olivine was used. The basic nature of olivine enhances ketonization and aldol condensation reactions, which involve the formation of CO₂ and water [62].

Table 4 shows the bio-oil composition once the pyrolysis volatiles

Table 4
Effect of inert sand and cracking catalysts on the bio-oil composition (wt%).

	Pyrolysis 500 °C	Inert sand	γ -Al ₂ O ₃	FCC	Olivine
Acids	4.0	4.1	0.0	0.0	2.3
Aldehydes	3.3	5.4	1.1	0.5	3.8
Ketones	9.6	9.2	4.2	4.8	9.7
Alcohols	2.4	0.7	0.0	0.0	0.5
Polycyclic Aromatic Alcohols	0.3	2.5	6.5	8.5	6.7
Phenols	22.0	17.5	15.9	17.9	13.1
Alkyl-phenols	2.2	2.3	15.9	5.2	2.7
Catechols	11.0	5.6	0.0	11.6	6.6
Guaiacols	8.8	9.5	0.0	1.1	3.8
Furans	3.1	3.3	0.6	3.1	1.4
Saccharides	6.0	4.1	0.0	0.0	4.2
Hydrocarbons	0.0	0.1	8.5	6.1	1.1
Non-aromatics	0.0	0.1	0.7	0.0	0.0
Light aromatics (BTX)	0.0	0.0	0.7	0.3	0.0
PAHs	0.0	0.0	7.1	5.8	1.0
Others	0.1	0.0	0.0	0.2	3.2
Unidentified	16.7	15.7	13.0	13.4	15.6
Water	32.4	37.5	50.1	45.7	38.6

have passed through each catalyst bed. As aforementioned, the products identified have been grouped based on their functional groups, and the composition of the main compound families is shown in Table 4.

As observed in Table 4, all the catalysts significantly modify the composition of the bio-oil. It is to note that similar trends were observed for both the yields and the concentrations of individual bio-oil compounds. Furthermore, temperature has also a significant influence when these catalysts are used. As aforementioned, the first step of biomass pyrolysis is conducted at 500 °C, whereas the second catalytic step is carried out at 600 °C. Accordingly, the amount of phenols, which are formed from the depolymerisation of lignin macromolecules [82], was substantially reduced with all the catalysts used, with this decrease being especially noteworthy in the fraction of catechols and guaiacols.

When the inert sand was used, a decrease in the phenolic concentration was observed due to the sharp reduction in the catechol fraction (from 11.0 to 5.6 wt%), with alkyl-phenols and guaiacols being hardly affected by thermal cracking. Moreover, the saccharide fraction, which is formed from the depolymerisation of cellulose and hemicellulose and is mainly composed of levoglucosan [74,83], decreased from 6.0 to 4.1 wt% due to the poor thermal stability of the other saccharide compounds [22]. The fraction of acids, ketones and furans, which are formed from the decomposition of cellulose and hemicellulose in the biomass [82,83], did not undergo a substantially modification, whereas the aldehyde concentration increased from 3.3 to 5.4 wt%, mainly by enhancing the formation of benzaldehyde instead of lighter species, such as formaldehyde and acetaldehyde [82]. A considerable reduction in the alcohol fraction was observed as opposed to that of polycyclic aromatic alcohols, which increased from 0.3 to 2.5 wt%. In fact, olefinic alcohols may undergo aromatization reactions leading to heavier polycyclic aromatic alcohols.

As mentioned before, the use of spent FCC and γ -Al₂O₃ catalysts led to low bio-oil yields (56.6 and 50.2 wt% respectively) due to the features of these materials, especially the total acidity (see Table 2), which promoted cracking reactions [27]. The bio-oil composition obtained with these materials is also a consequence of secondary reactions leading to a substantial increase in the hydrocarbon concentration (6.1 and 8.5 wt%, over FCC and Al₂O₃, respectively). Accordingly, the higher acidity of these catalysts compared to olivine promotes hydrocarbon formation [38].

Concerning the phenol functional group, although similar concentrations were obtained (17.9 and 15.9 wt% for FCC and γ -Al₂O₃ catalysts, respectively), significant differences were observed in the distribution of catechols, guaiacols and alkyl-phenols. Thus, while catechols are the main phenolic compounds in the bio-oil obtained with the FCC catalyst (11.6 wt%), followed by alkyl-phenols (5.2 wt%), the

phenolic fraction obtained with Al_2O_3 catalyst was only composed of alkyl-phenols, which is due to the secondary recombination and cyclization reactions via Aldol condensation [22,74]. The higher selectivity of Al_2O_3 catalyst to alkyl-phenols revealed the effective dealkoxylation of guaiacols and catechols [84]. Thus, the guaiacol fraction in the volatiles derived from biomass pyrolysis at 500 °C may undergo oxygen-aromatic carbon bond cleavage to form phenol/aromatic hydrocarbons or undergo oxygen-alkyl carbon bond cleavage to form benzenediols or benzenetriols (catechols). This catechol fraction may then be converted into alkyl-phenols by deoxygenation reactions. Guaiacol cracking can be initiated by homolytic cleavages of $\text{CH}_3\text{-O}$ or O-H bonds leading to the formation of methane, dihydroxybenzene (catechols), o-cresol (alkyl-phenol), and 2-hydroxybenzaldehyde, among others [27,85].

It is noteworthy that FCC and $\gamma\text{-Al}_2\text{O}_3$ catalysts led to full disappearance of acids, light alcohols, and saccharides, and to a significant reduction in the concentration of aldehydes and ketones. Thus, the small oxygenate and olefin molecules in the volatile stream formed in the biomass fast pyrolysis may be converted into aromatics via aromatization, with oxygen being released as CO , CO_2 , and H_2O [27,86]. As aforementioned, the FCC catalyst has a microporous structure due to the presence of HY zeolite. The shape-selectivity of this zeolite promotes the diffusion of the mentioned compounds (acids, aldehydes, alcohols, ketones, and furans) into the zeolite channels and the reactions of deoxygenation ending up in the formation of aromatic hydrocarbons [87]. Moreover, the basic properties of the bentonite, which is the binder to agglomerate the spent FCC catalyst, promote ketonization reactions involving carboxylic acids and carbonyl compounds [27]. In the case of Al_2O_3 , its better textural properties, as well as its higher acidity, enhance further decomposition on the acid sites of the catalyst, and therefore increase the hydrocarbon fraction. Furthermore, there is a higher concentration of water in the bio-oil stream treated with FCC and $\gamma\text{-Al}_2\text{O}_3$ catalysts (45.7 and 50.1 wt%, respectively) due to secondary cracking-dehydration reactions.

Regarding olivine, a decrease in the amount of acids, aldehydes, and furans was observed compared to inert sand. The ketone fraction remained almost constant (at around 9 wt%), although longer chain ketones were formed when olivine was used. Therefore, basic catalysts promote, on the one hand, ketonization of acids and, on the other hand, aldol condensation of small ketone and aldehyde molecules to larger chain ketones by carbon-carbon coupling reactions [27,62]. A more detailed analysis is hindered by the complexity of the reactions occurring when the pyrolysis volatiles cross the catalyst bed and the fact that several reactions may occur simultaneously and lead to opposite effects. The concentration of phenols also decreased from 17.5 to 13.1 wt% (mainly guaiacol compounds), and the yield of hydrocarbons (mainly naphthalene compounds) increased to 1.1 wt% as a result of secondary cracking reactions. Besides, the presence of Fe^0 metal in the olivine chemical composition promotes deoxygenation reactions, leading to an increase in the production of these aromatic hydrocarbons [38].

The results shown in Table 4 are evidence of a less oxygenated nature of the bio-oil obtained when acid catalysts were used. Accordingly, the yields of the oxygenated compounds, i.e., all the functional groups shown in Table 4, except the one of hydrocarbons, decreased as follows: pyrolysis 500 °C (67.5 wt%) > inert sand (54.5 wt%) > olivine (46.9 wt%) > spent FCC catalyst (37.4 wt%) > $\gamma\text{-Al}_2\text{O}_3$ (28.8 wt%).

3.4. Discussion and future prospects

The treatment described in this study pursues the production of an upgraded volatile stream for its further in-line catalytic valorization in a third step for the production of H_2 in a steam reforming process or the production of fuels, chemicals and aromatic hydrocarbons by other catalytic routes.

As aforementioned, the main challenge to overcome in these processes is the fast catalyst deactivation by coke deposition. Several

researches have reported that certain bio-oil compounds, such as phenolic ones, are the main precursors of coke formation [38,39]. However, amongst the different compound lumps contained in the phenolic fraction (alkyl-phenols, catechols and guaiacols), it is not clear which is the main responsible for catalyst deactivation. Moreover, other authors have emphasized the relevance of removing the acids from the pyrolysis volatile stream in order to avoid operational problems in further catalytic valorization processes [32]. Thus, Gayubo et al. [40] attributed the formation of deactivating coke to mainly phenols and aldehydes, whereas Remón et al. [88] reported that, apart from guaiacol phenolic compounds, furfural (aldehyde) and levoglucosan (saccharide) have high tendency to produce coke in steam reforming reactions.

In this study, several low-cost materials have been used downstream the pyrolysis process in order to condition the volatile stream by removing and/or reducing undesirable compounds. The significant differences in the catalysts used led to volatile streams of considerable compositional diversity, which allowed delving into the understanding of the relationship between the composition of the feed into the reforming step and catalyst deactivation.

Accordingly, the use of olivine led to a significant removal of acids and phenols, with the latter due mainly to the reduction in the guaiacol fraction. Besides, the chemical composition of olivine, with Fe^0 on its surface, plays a positive role in the bio-oil oxygenate decomposition and reforming reactions.

The use of acid catalysts (FCC and $\gamma\text{-Al}_2\text{O}_3$) results in a bio-oil composition with a considerable reduction in the aldehyde fraction, and free of acids, alcohols and saccharides at the expense of hydrocarbon formation. The phenolic fraction was considerably reduced compared to the pyrolysis conducted at 500 °C (from 22.0 wt% to 17.9 and 15.9 wt% for FCC and Al_2O_3 catalysts, respectively) as a consequence of thermal and catalytic cracking. Moreover, the higher acidity of $\gamma\text{-Al}_2\text{O}_3$ catalyst promoted the conversion of heavy oxygenated compounds into alkyl-phenols, whereas catechols were the major fraction when the FCC catalyst was used.

Future studies will be conducted using these low-cost materials (inert sand, Al_2O_3 , spent FCC catalysts and olivine) as guard beds in order to attenuate the fast catalyst deactivation in the in-line biomass pyrolysis-steam reforming process. Thus, the stability of reforming catalysts and their deactivation will be analyzed with the aim of understanding the role played by the volatile composition, and knowledge will be acquired about the main species responsible for the deactivation of the reforming catalyst.

4. Conclusions

The conical spouted bed reactor allows attaining a reproducible volatile stream for its in-line catalytic pyrolysis. The modification of the pyrolysis volatile stream composition by catalytic cracking was analyzed by using different low cost catalysts and inert sand placed downstream in a fixed bed reactor. The features characterizing each material (physical properties, chemical composition and acidity) play a key role in the transformation of the volatile stream, leading to remarkable differences in the distribution and composition of the gaseous stream.

The biomass pyrolysis conducted at 500 °C in a CSBR led to a gas yield of 7.3 wt% (with CO and CO_2 being the main products), and a bio-oil yield of 75.4 wt%, which was composed of mainly phenols, ketones, and saccharides. At 600 °C, thermal cracking was evidenced when inert sand was used, increasing the yield of the gas to 14.4 wt%, and so reducing that of the bio-oil to 68.3 wt%. Thus, thermal cracking reactions occurred in parallel to the catalytic ones with all the catalysts tested.

Bio-oil cracking was more severe as catalyst acidity was increased, i.e., olivine < spent FCC catalyst < Al_2O_3 . Besides, acid catalysts enhanced decarbonylation over decarboxylation reactions, with CO being the main compound in the catalytic cracking. The chemical composition of olivine, with Fe phase on its structure, also promoted

reforming and water gas shift reactions, leading to the formation of CO, CO₂ and H₂.

The bio-oil composition was affected when either inert sand or any catalyst was used. Alcohols, saccharides, and especially the phenolic fraction were substantially reduced due to thermal cracking when the inert sand was used. This significance of this drop depended on the catalyst used. The basic character of olivine promoted ketonization of acids, and aldol condensation of ketones and aldehydes, leading to the formation of CO₂ and water. Concerning FCC and γ -Al₂O₃ catalysts, both led to a substantial increase in the hydrocarbon fraction (6.1 and 8.5 wt %, respectively). Accordingly, the acidity of these catalysts played a key role in the cracking of pyrolysis volatile oxygenates, since the acid sites promoted deoxygenation reactions, as well as cracking, oligomerization, alkylation, isomerization, cyclization and aromatization, which greatly increased the hydrocarbons fraction. The phenolic fraction was influenced by the type of catalyst employed by promoting the formation of catechols and alkyl-phenols when FCC and Al₂O₃ catalyst, respectively, were used.

The results provided in this study are of special relevance for further studies wherein the production of H₂ will be approached by feeding the bio-oil stream leaving the catalytic process into the two step biomass pyrolysis-steam reforming strategy.

CRedit authorship contribution statement

Enara Fernandez: Investigation, Visualization, Writing - review & editing. **Laura Santamaria:** Writing - original draft, Visualization, Writing - review & editing. **Maite Artetxe:** Writing - original draft, Conceptualization, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Maidor Amutio:** Conceptualization, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Aitor Arregi:** Validation, Visualization, Writing - review & editing. **Gartzten Lopez:** Conceptualization, Validation, Writing - review & editing, Visualization, Supervision, Project administration. **Javier Bilbao:** Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **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.

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