# Tar conversion of biomass syngas in a downstream char bed

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**Abstract**

The catalytic conversion of biomass-derived tars over char during long tests (over 6 hours) is studied. The syngas is generated in a steam-blown fluidized-bed gasifier employing wood pellets and conducted to a second tubular reactor where non-activated char particles are fluidized. The gasifier operated at 750 °C whereas the temperature of the secondary reactor was varied between 750 °C and 875 °C. The evolution of the tar conversion, gas composition and internal structure of the used catalysts were studied. At 750 °C, the initial catalytic activity of the char was low and deactivation occurs rapidly. However, as the reactor temperature increased, the catalytic activity of the char improved significantly. At 875 °C, the initial conversion of tar was above 70 % and over 64 % after 5 h of operation. Moreover, the conversion of the heaviest tars was above 80 % during the entire test. At this temperature, the decrease in tar conversion is attributed to the consumption of the char by steam gasification since its catalytic activity increased during of the test. In these conditions the char bed with an initial weight of 32 g converted approximately 12 g of tars (benzene not included) after 5 h of operation.

## 1- Introduction

Gasification is a thermo-chemical route for conversion of solid fuels, such as biomass and wastes, into a syngas that can be used in a variety of applications [1,2]. Fluidized bed (FB) gasification has several advantages over that in fixed/moving bed or entrained-flow for distributed energy production [3]. However, in all types of FB gasifiers the process temperature must be kept relatively low to prevent agglomeration and sintering of bed material. The low temperature results in incomplete carbon conversion and a high concentration of heavy tars in the gas. The condensation of heavy tars in downstream equipment is the main bottleneck for the use of the syngas in any application where the gas needs to be cooled down.

During the last decades, different methods have been developed to reduce the tar concentration in the gas based on physical separation (wet/physical methods) or reforming/cracking of the tar in the hot gas. Wet methods have been tested using water [4,5] or organic solvents [6], and have been reported to be technically efficient. However, this way to clean the gas seems to be too complex and expensive for small or medium-size plants [1]. The reforming/cracking of tar using metallic catalysts (mainly Ni-based) in a downstream vessel is also efficient [7,8] but the presence of certain contaminants in the syngas causes their rapid deactivation. The fast

deactivation by poisoning or coking and the relatively high price of metallic-based catalysts have driven the search for alternative catalysts such as olivine, dolomite, alkali-catalysts and char [7,9].

Char presents several advantages over traditional catalysts [10]. Char is a byproduct from the process (pyrolysis or gasification), therefore it is available and cheap unless special treatment is required for its activation; it is relatively resistant to poisoning by sulfur and chlorine and it can be burnt once used. Additionally, according with the results of different works, char converts preferentially the heavier compounds of the tar mixture [10-12]. This is a significant advantage when the aim is to reduce the tar dew point of the gas (so that it can be burned in an engine) as it is mainly determined by the concentration of polyaromatic compounds. However, char may deactivate rapidly due to coking under some operating conditions [10,13-15].

The Viking staged gasifier, developed at the Technical University of Denmark, produces the pyrolysis of wood chips in a screw conveyor to, subsequently, partially oxidize the gas either with air [11,16] or with $O_2/CO_2$ [17] mixtures. After oxidation, the gas, at temperatures as high as 1200 $^oC$, is transferred to a fixed bed of the char produced during pyrolysis. This configuration, has demonstrated to convert most of the heavy tars present in the syngas, although it is difficult to scale up. A different system, the FLETGAS process [3], would convert most of the heavy tar in the syngas using a secondary char bed while improving the scalability of the system due to the use of fluidized beds.

The catalytic activity of char and activated carbons depends on the amount and chemical composition of the surface available for tar reaction [18-19]. Both parameters depend, in turn, on the original parent material and the severity (temperature and gas residence time) of the activation process. Non-activated chars typically present total surface areas below 300 $m^2/g$ while this value can increase above 1000 $m^2/g$ after activation [20]. However, a significant portion of this area could be non-accessible for the conversion of large molecules, such as naphthalene (kinetic diameter 0.74 nm [21]), due to diffusional limitations in narrow micropores (internal diameter below 2 nm) and pore mouth blocking [18].

The presence of different functional groups, such as oxo-groups (-CO, -COH or -COOH) or alkali and alkaline earth metals (AAEM), distributed over the char surface has been reported to be responsible for its high activity towards tar conversion [18-20,22-24]. According to the results presented by Feng et al. [25], the activation process either with $H_2O$ or with $CO_2$ not only increases the concentration of surface oxo-groups but also promotes the migration of AAEM species from the char matrix to the char surface, creating carbon-metal complexes, which increase the catalytic activity of the char surface. A recent publication suggests the presence of two different types of surface in the original char [26]. The first type would be responsible for the initial high activity of the catalyst towards tar conversion but, in absence of gasification agents, its deactivation occurs rapidly. The second type of surface would present a lower activity but its deactivation, if occurs, is much slower.

Fig. 1 presents a simplified scheme of the tar conversion mechanism over char. The tar compound in the syngas reacts with the functional groups, or active sites, dispersed on the char surface. At sufficiently high temperature [27-29] the adsorbed tar compound undergoes polymerization, creating a soot/coke deposit over the original char surface [13,15]. The reactivity of the soot deposit is much lower towards steam gasification [30,31] and towards catalytic tar conversion [13,15] than the original char surface. Therefore, if the soot gasification rate is lower than the soot deposition rate, the original char surface gets covered by soot, the

total surface area decreases and, consequently, the activity of the char diminishes with time. On the contrary, when gasification is faster than deposition, the char can maintain or even increase its initial activity. Therefore, the selection of experimental conditions ensuring a positive net rate of carbon conversion (gasification − deposition) is necessary to maintain the activity of the char [10,13-15,30].

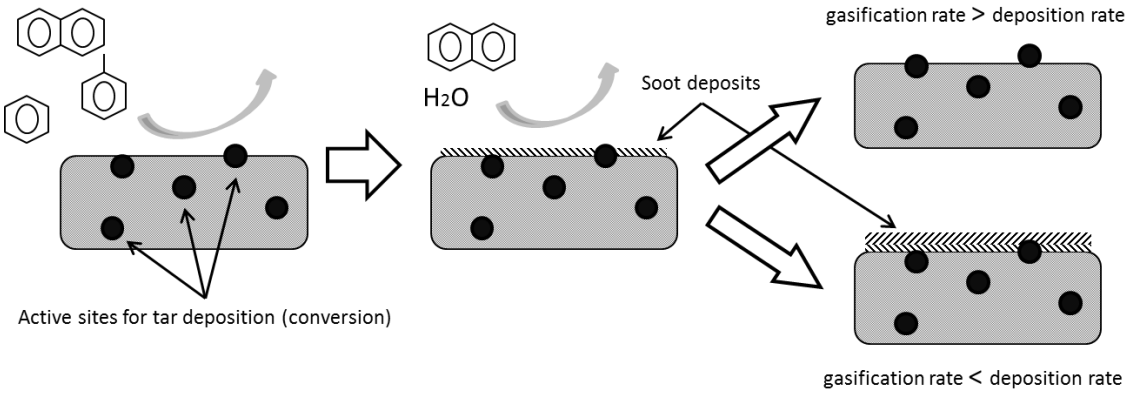



Figure 1: Tar conversion mechanism over char. Reprinted from [13]

Most of the studies analyzing tar conversion over char have been conducted using a simulated syngas doped with model tars instead of using a real gasification gas. The use of simulated (and simplified) syngas as surrogate syngas is convenient when a careful control of experimental conditions is necessary to isolate processes and investigate detailed aspects of mechanisms of conversion. However, the use of real pyrolysis/gasification gas containing dozens/hundreds of different compounds is more useful to verify the activity of char in a real gasification process since the competition between different tar compounds for the active sites can influence their conversion [32]. Matsuhara et al. [15] studied the conversion of a coal pyrolysis gas over a fixed bed of char produced by pyrolysing the same coal. A significant improvement on the tar conversion was measured when the char bed temperature was increased from 750 $^{o}$C to 900 $^{o}$C. In spite of the relatively low gas spatial velocity (gas flowrate, divided by the mass of char in the bed) a significant char deactivation was observed during the first 20 minutes of test. However, at the highest temperature tested (900 $^{o}$C), a net carbon consumption was reported and no significant deactivation of the char bed was detected after 40 min of test.

The present paper aims at investigating the technical viability of using non-activated biomass char for tar conversion. For this purpose, a real gasification gas has been produced in a steam blown bubbling fluidized bed reactor operated at 750 $^{o}$C using wood pellets as fuel. The syngas produced was then treated at temperatures between 750 $^{o}$C and 875 $^{o}$C in a secondary fluidized bed reactor filled with non-activated char particles produced by beech wood pyrolysis. The process is maintained for times over 6 hours to track the evolution of the char activity towards tar catalytic conversion. Both the evolution of the syngas composition (including light gases and tar compounds) and the characteristics of the spent chars (after used) are reported.

## 2- Experimental

### 2.1- Materials

### 2.1.1- Biomass

Spruce wood pellets with a diameter of 6 mm and a length of about three times the diameter were used as feedstock in the FB gasifier. The elemental composition and ash content in dry basis of the pellets are shown in Table 1. The moisture content was of 7% w.b. CHNS content was determined in an elemental analyzer (Elementar Vario EL-III). The ash content was determined by DIN norm 51719. The content of inorganic species was measured by ICP-OES (Varian 720-ES) after digestion in a microwave with $H_2O_2$ and $HNO_3$.

Table 1: Ultimate analysis and elemental analysis of ashes of the different materials used.

| | C | H | N | S | O | Ash | Fe | Mg | Na | P | Ca | K |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (wt.%, dry basis) | | | | | | mg/kg (dry basis) | | | | | |
| Wood pellets – FB gasifier | 49.5 ±0.1 | 6.6 ±0.1 | 0.1 ±0.0 | 0.1 ±0.1 | 43.5 ±0.1 | 0.3 | 30.1 ±1.0 | 150.4 ±4.1 | 13.2 ±0.4 | 49.8 ±1.3 | 1025 ±30 | 341.0 ±21.3 |
| Char from beech wood chips | 88.3 ±0.3 | 1.8 ±0.0 | 0.3 ±0.0 | 0.1 ±0.0 | 6.4 ±0.3 | 3.1 | 131.7 ±6.8 | 1854 ±89 | 245.3 ±13.5 | 500.8 ±16.2 | 8330 ±383 | 6065 ±180 |

### 2.1.2- Char

The char used in the secondary reactor was produced via slow pyrolysis of beech wood chips in a $N_2$ atmosphere in a two-step process. First, the beech wood was pyrolyzed at approximately 450 °C in a $N_2$ blown continuous screw reactor. The retention time of the biomass/char in the reactor was 30 min. In a second step, the char was subjected to pyrolysis at 700 °C (measured in the center of the bed) in a semi-batch fixed-bed reactor (batch bed of char with continuous flow of $N_2$). The time required to heat the char from ambient temperature to 700 °C was 1 h and the char was then kept for one more hour at 700 °C. The elemental composition and ash content in dry basis of the fresh char employed in the experiments are shown in Table 1.

## 2.2- Test rig

The tests were performed using the syngas produced in a lab-scale FB biomass gasifier. This syngas was fed to a secondary FB reactor filled with char in order to investigate the tar conversion and the deactivation behavior of the char. Fig. 2 presents the flowchart of the experimental set-up.

### 2.2.1- Fluidized bed gasifier

The fluidized bed reactor was heated by an electrical oven in order to keep the bed temperature constant at 750 °C. The reactor was made of stainless steel and had an inner diameter of 80 mm and a height of 150 mm at the bottom-part, while the freeboard region consisted of a conical part of 80 mm height where the inner diameter opens up to 250 mm followed by a cylindrical part of 110 mm of height. 900 g of olivine with an average particle size of 260 µm was used as bed material, having an experimental minimum fluidization velocity of 0.044 m/s. A constant flowrate of 0.3 kg/h of pellets was fed to the gasifier during the experiments. Steam preheated to 400 °C was used as fluidization media. The flowrate of steam fed to the gasifier was measured by an orifice plate and regulated with a needle valve to obtain a constant flowrate of 0.28 kg/h. This corresponds to a steam equivalence ratio of 4, defined as the ratio of the steam fed (0.93 $kg_{H2O}/kg_{biomass}$) to that for stoichiometric conversion of the fuel into $H_2$ and CO (0.233 $kg_{H2O}/kg_{biomass}$ for a representative fuel composition of $CH_{1.44}O_{0.66}$) and it is comparable to the oxygen equivalence ratio used for combustion [33]. The fluidization velocity was 0.05 m/s

(slightly above that of minimum fluidization). The amount of feedstock supplied was controlled by a screw discharging on the bubbling bed. The feedstock tank was rinsed with 0.15 kg/h of nitrogen. The whole system including bed and feedstock tank was pressurized to an absolute pressure of 1.5 bar. Table 2 presents the average syngas composition produced in the gasifier. Due to small fluctuations in the conditions of the FB gasifier slight differences (below ±2 $\%_v$) in the composition of the different syngas compounds were measured.

| Compound | Concentration |
|---|---|
| $H_2$ ($\%_{v\ dry\ syngas}$) | 35.1 ± 0.4 |
| CO ($\%_{v\ dry\ syngas}$) | 17.7 ± 0.2 |
| $CO_2$ ($\%_{v\ dry\ syngas}$) | 16.9 ± 0.1 |
| $CH_4$ ($\%_{v\ dry\ syngas}$) | 6.3 ± 0.1 |
| $N_2$ ($\%_{v\ dry\ syngas}$)* | 24.1 ± 0.2 |
| $H_2O$ ($\%_{v\ wet\ syngas}$) | 49.7 |
| GC-tar ($g/Nm^3_{dry\ syngas}$) | 14 |

*by difference.

Table 2: Average syngas composition produced in the FB gasifier

The syngas was filtered in a sinter metal candle where particulate matter was removed. The filter and all gas lines were electrically heated to a temperature of 350 °C to prevent condensation of the tars. The gas flow after the filter can either be adjusted to go directly to a flare or through the secondary reactor, as shown in Fig. 2.

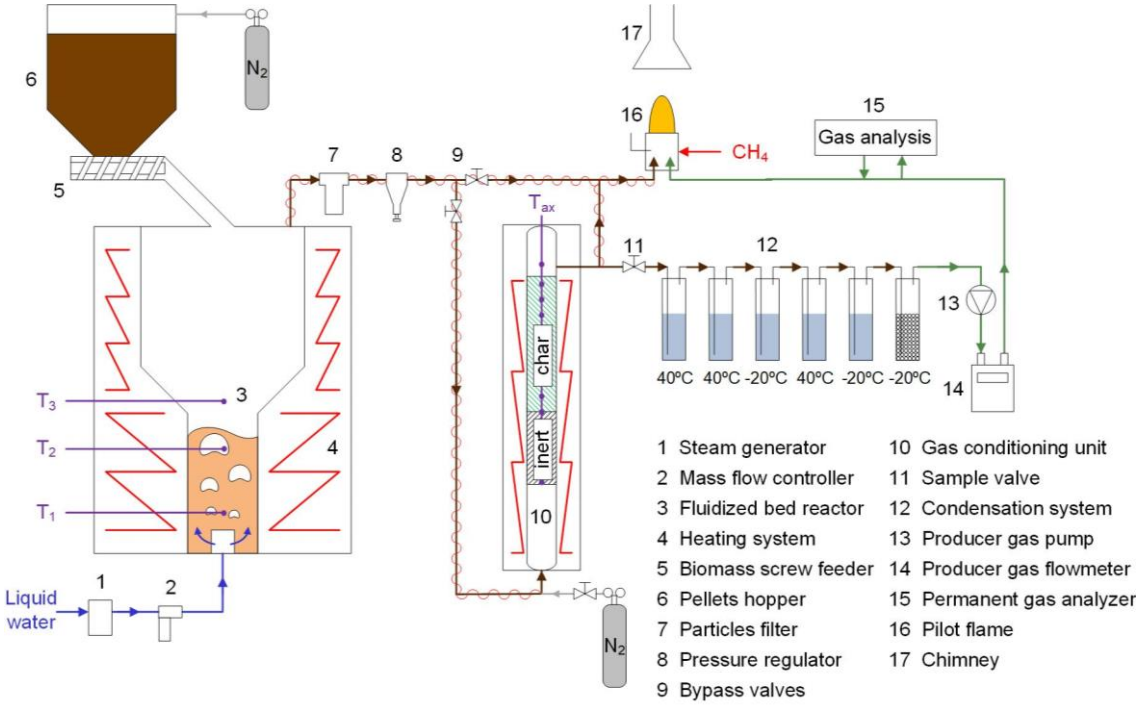



Figure 2: Flowchart of the experimental set-up

2.2.2- Secondary char bed reactor

A FB configuration was selected for the secondary reactor. This configuration brings benefits over fixed/moving beds. On the one hand, fluidized beds prevent the appearance of high temperature gradients typically occurring in fixed beds, that may provoke rapid deactivation (due to low temperatures) or sintering phenomena (due to high temperatures) of the char. In

addition, fixed beds might clog during operation with dusty gas, such as the syngas produced in fluidized bed gasifiers, due to the blocking of the bed pores by the fine particles carried by the gas. However fluidized beds also present disadvantages compared to fixed/moving beds as the poor contact between gas–char contact due to the bypass of gas through the bubbles.

The FB tar conversion unit used in this work consists of an electrically heated cylindrical tube with an inner diameter of 37.2 mm. The syngas enters the reactor at the bottom at a temperature of 350 °C and flows through a fixed bed of inert ceramic beads of 15 cm height to preheat the gas to the target temperature in the reactor. An initial char bed of 32 g (discounting the initial elutriation of fines), corresponding to a fixed bed height of 16 cm, was located on top of the ceramic beads. The char used had an approximately disk like shape with a mean diameter of 3.6 mm and a mean height of about 1 mm. The minimum fluidization velocity of the char was measured to be approximately 0.48 m/s. The temperature inside the char bed was measured at 4 heights (5, 10, 15 and 20 cm above the bed of inert ceramic beads) in the center of the reactor and, during operation, the temperature in the bed was uniform and remained constant, indicating a proper mixing of the char particles.

During the experiments the spatial velocity was 24 $Nm^3_{wet\ syngas}/kg_{char}h$ while the superficial gas velocity (volumetric gas flowrate divided by the open cross section of the reactor) in the secondary reactor was between 0.75 m/s and 0.84 m/s, about 1.56 - 1.75 times the minimum fluidization velocity of the char. The residence time of the syngas (τ) in the char bed was calculated dividing the volume occupied by the char bed (considering it as a fixed bed with a total weight of char of 32 g) by the flowrate of syngas produced in the FB gasifier; τ between 0.18 s and 0.2 s were obtained.

### 2.3- Operation procedure

Before each test the gasifier was operated for 3 h, bypassing the syngas directly to the flare, in order to ensure constant regime of operation. Within the 3 h of stabilization, the secondary reactor was filled with fresh char and heated to the desired temperature. During the heat-up of the secondary reactor, a constant $N_2$ flow of 10 Nl/min was set to ensure an inert atmosphere preventing combustion of the char. As the target temperature in the reactor was reached, the $N_2$ flow was stopped and the syngas produced in the FB gasifier was led through the secondary reactor. It took about 30-45 minutes until the heating of the reactor adapted to the new flow conditions and the char temperature reached a constant value. Once the desired temperature was reached in the char bed, several tar samples were taken following the procedure described in the tar protocol [34] using isopropanol as solvent. The tar-free syngas exiting the tar sampling train was analyzed in a gas analyzer in order to quantify the concentration of the main permanent gases.

Table 3 presents the target temperature in the secondary reactor and the time of tar samplings taken in the seven tests performed. After the test, the char in the reactor was cooled down with $N_2$ until its temperature was below 100 °C. The used char was collected and stored for further analysis. It should be noted that during some of the tar samplings the temperature in the secondary reactor did not reach the target temperature. These tar samples are noted in Table 3 as not valid and therefore not considered for presenting results of tar conversion.

Table 3: Target temperature in the secondary reactor and tar samplings taken during the experiments with char bed

| Test | Target temperature | Tar sampling 1 | Tar sampling 2 | Tar sampling 3 | Tar sampling 4 | End test |
|---|---|---|---|---|---|---|
| (-) | (°C) | (hh:mm) | (hh:mm) | (hh:mm) | (hh:mm) | (hh:mm) |
| 1 | 850 | 00:39 (not valid, low T) | 01:49 | - | - | 2:39 |
| 2 | 850 | 00:55 | 02:35 | 04:15 | - | 4:35 |
| 3 | 850 | 00:45 (not valid, low T) | - | - | - | 1:00 |
| 4 | 850 | 00:20 (not valid, low T) | 01:50 | 3:20 | - | 3:35 |
| 5 | 750 | 00:35 | 01:44 | 03:04 (not valid, low T) | - | 3:49 |
| 6 | 850 | 00:45 | 01:45 | 04:15 | 06:15 | 6:30 |
| 7 | 875 | 01:16 | 02:06 | 03:26 | 04:56 | 5:11 |

220

221 2.4- Experimental conditions

222 2.4.1- Experimental conditions in the FB gasifier

223 The FB gasifier producing the syngas necessary for the tests operated at 750 ± 5 °C and 1.5 ±
224 0.01 bar. Due to the low operation temperature, the char produced during the fuel
225 devolatilization stage was not completely converted. Consequently, char accumulated in the
226 dense bed of the gasifier during the tests. The FB gasifier was opened to remove the char
227 accumulated only two times during the whole campaign being the amount recovered 58 g
228 (removed after Test 4, see Table 3) and 31 g (removed after Test 7) respectively. Olivine and
229 char particles were separated by sieving since the latter were significantly larger. Considering
230 the total amount of olivine in the reactor, 900 g, char accumulation in the bed is not considered
231 to significantly influence the fluidization quality, which was assumed to be governed by the
232 olivine particles.

233

234 2.4.2- Experimental conditions in the secondary reactor

235 As explained before the secondary reactor was loaded before each test with 32 g of char. The
236 amount of char remaining in the secondary reactor at the end of each test was below 32 g for
237 all the conditions tested (see Fig. 3). Blue dots represent the char remaining in the char bed after
238 the five experiments at 850 °C while the orange and green dots represent the char remaining
239 after the experiments at 750 °C and 875 °C, respectively. The black dot represents the initial
240 amount of char in the bed. The reduction in the amount of char in the bed could indicate a net
241 C consumption during the experiments. However, some attrition/elutriation phenomena may
242 have occurred resulting in some losses of char. Although elutriation loss is expected to be a
243 minor amount compared to the initial char load, it was not systematically investigated.
244 Therefore, this uncertainty prevents establishing a clear boundary temperature dividing positive
245 and negative C balance conditions.

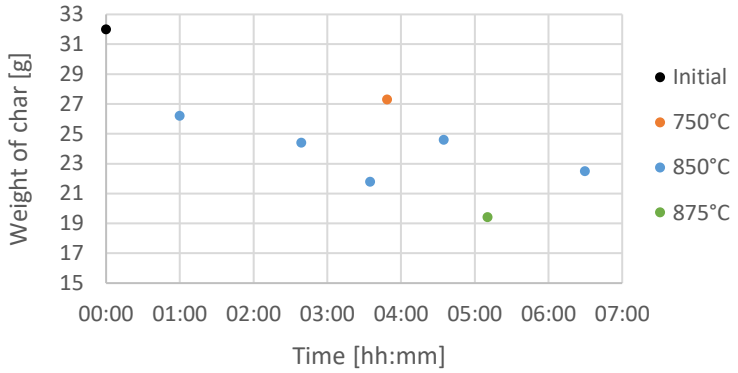



Figure 3: Char bed weight after the tests. Orange dot: test at 750 °C; Blue dots: tests at 850 °C; Green dot: test at 875 °C.

Fig. 4 displays the temperature profile during one test at 850 °C. When the syngas is driven into the preheated secondary reactor the temperature of the char bed decreases rapidly (till about 830 °C in Figure 4) due to the lower temperature (350 °C) of the piping connecting the FB gasifier and the secondary reactor. It is necessary between 30 and 45 min to reach the target temperature again. This lower temperature at the beginning is the reason why the first sampling of tests number 1, 3 and 4 conducted at 850°C were considered as not valid. Once the temperature was reached, very slight fluctuations, ±5 °C were observed. During operation, the temperature at the four different heights in the char bed remains almost equal and constant with time, indicating a proper mixing of the char particles in the bed.

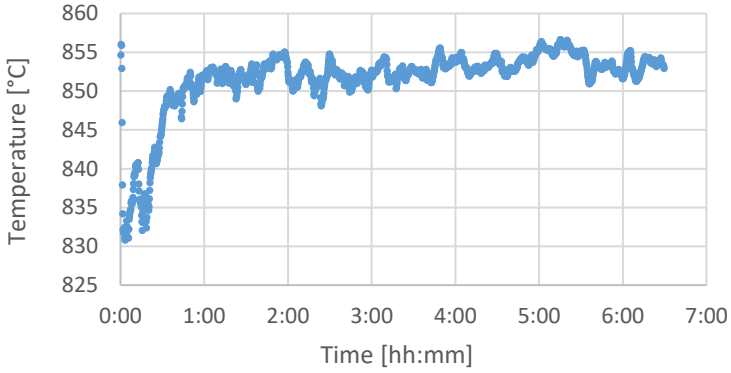



Figure 4: Evolution of the mean temperature of the char bed during the test number 6 at 850 °C

2.5- Analysis

2.5.1- Gas and tar analysis

During tar samplings a tar-free syngas stream was led to an ABB AO2020 gas analyzer, where concentration of the permanent gases CO, $CO_2$, $CH_4$, $O_2$ and $H_2$ were measured. The amount of $N_2$ was calculated by difference. Tar samples were analyzed by GC-FID using a Shimadzu GC 2010 equipped with an Agilent 19091S-433 capillary column. The concentration of 25 compounds from benzene to perylene were given. Analytical standards of each quantified compound were used for calibration during the analytical protocol. However, due to some analytical problems, the concentration of phenol and cresols were not properly determined. Therefore, the information concerning tar class 2 (TC2) compounds (heteroatomic aromatic tars) are not given. The different tar compounds were lumped according with the classification described in [35]

being TC3 monoaromatic tars (without O or N on its composition), TC4 aromatic compounds with 2-3 aromatic rings and TC5 aromatic compounds with 4-7 aromatic rings.

2.5.2- Char analysis

The CHNS content of the spent char samples was determined in an elemental analyzer (Elementar Vario EL-III) and the content of inorganic species was measured with an ICP-OES (Varian 720-ES) after digestion in a microwave with $H_2O_2$ and $HNO_3$.

To characterize the surface physical structure of the chars, i.e. specific surface area, pore volume, and pore size distribution, $N_2$ adsorption measurements were performed. The adsorption/desorption isotherms were measured in an Autosorb MP-1 (Quantachrome Instruments) in the relative pressure range of $\sim 2 \times 10^{-5} - 0.99$. The BET (Brunauer-Emmett-Teller) model was applied to determine the total specific surface area. The total volume was determined at a relative pressure close to 1, assuming that in these conditions all $N_2$ in the pores is in liquid state. Micropore and mesopore specific surface area and volume were determined with the QSDFT model (Quenched Solid Density Functional Theory) applied to the adsorption branch, considering slit/cylindrical pores. The conditioning of the char samples previous to the adsorption measurements included drying at 106 °C for 90 minutes, followed by milling and degassing in vacuum at 150 °C for 8 hours to remove species adsorbed on the char surface.

SEM-EDX analysis was performed to examine morphology, structure variation and surface composition of the spent char samples. The SEM-EDX analyses of the different chars were carried out by means of FEGSEM (Field Emission Gun Scanning Electron Microscopy) FEI Teneo™.

## 3- Results and discussion

3.1- Tar evolution

Preliminary experiments were conducted to measure the composition in the raw gas and to estimate the possible extent of thermal tar cracking in the secondary reactor without char. This was done in order to obtain a reference concentration of tar to which the extent of heterogeneous catalytic conversion over char can be referred. Fig. 5 presents the composition of the tar mixture of the raw gas and after thermal cracking in the secondary reactor preheated at 850 °C without char but with the pre-bed of ceramic beads loaded. The results presented for the raw gas are the average of three tests taken at the beginning, in the middle and at the end of the seven tests presented in Table 3. The tar results for the thermal cracking at 850 °C are the average of two samples taken in one day of operation. The obtained standard deviations are very low for each case (see Fig. 5), which shows the stability of the producer gas composition (during the campaign). The thermal tar cracking tests at 850 °C led to a slight increase in the concentration of benzene compared to the raw gas, from 5600 mg/Nm$^3$ to 6300 mg/Nm$^3$, while the reduction over the concentration of tar classes 3, 4 and 5 in the syngas was almost negligible. Therefore, the influence of thermal tar cracking at this temperature is minor. The composition of the tar mixture in these tests were used to calculate the tar conversion in the experiences with char at 750 °C (raw gas) and at 850/875 °C (thermal tar cracking at 850 °C).

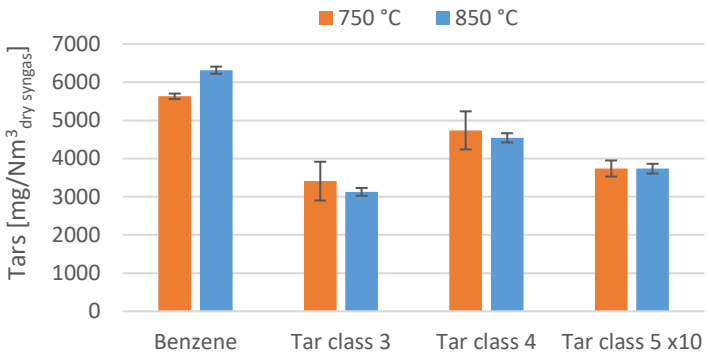
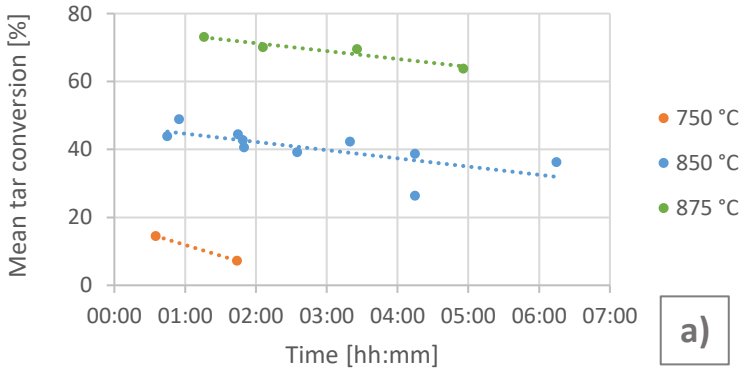
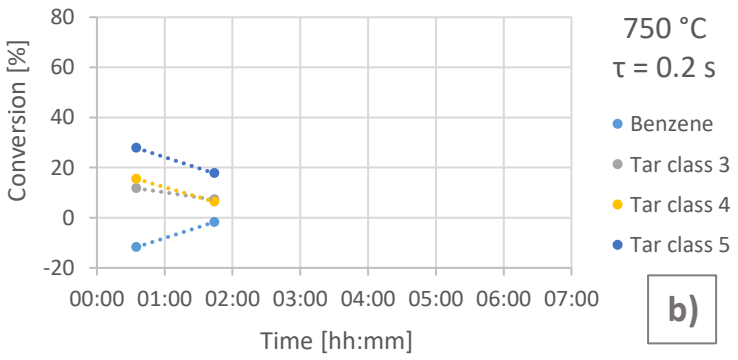



Figure 5: Yields of the different tar classes of the raw gas (750 °C) and with the secondary reactor at 850 °C in absence of char bed

Fig. 6 shows the evolution of tar conversion obtained for the different tar classes over the char bed at the three temperatures tested in the secondary reactor. In Fig. 6a the evolution of the average tar conversion (excluding benzene) at the three temperatures tested is presented. According to the results, the char bed temperature has an important impact on the average tar conversion. After 1-2 hours of operation the mean tar conversion at 750 °C was around 10 % while at 850 °C and 875 °C the tar conversion increased up to 45 % and 70 % respectively. This is probably due to the enhancement in the steam gasification rate of char/soot, promoting the presence of active sites onto the char surface with increasing temperature. The increase in the tar conversion as temperature was raised from 850 °C to 875 °C is especially remarkable.



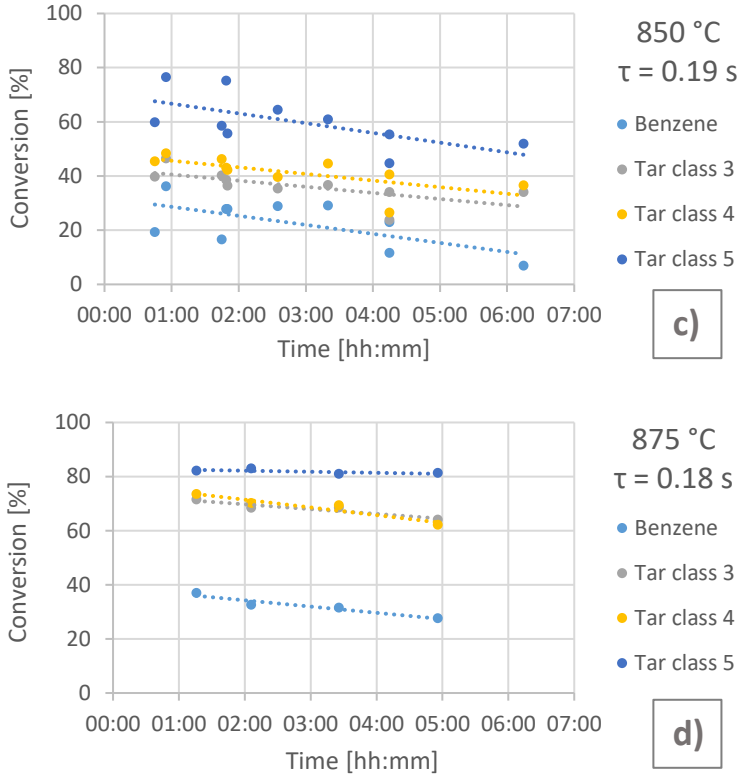



Figure 6: Evolution of the tar conversion during the experiments. 6a: Evolution of the mean tar conversion (excluding benzene) at different temperatures. 6b, 6c, 6d: Evolution of the conversion of the different tar classes at 750, 850 and 875 °C, respectively.

At 750 °C (Fig. 6b) the conversion of the different tar classes was rather low, even at the beginning of the test. Only 28 % of the heaviest tars (TC5) were converted using a char bed after 35 min of operation. The conversion of these heavy tars further decreased to below 18 % one hour later. The trend measured for lighter tars was similar but the conversions are slightly lower since, as expected, heavier tar molecules are converted faster over char than lighter tars. In the two tar samples taken at 750 °C the conversion of benzene was negative indicating a slight increase in the benzene concentration with respect to the reference test without char. This result, in agreement with previous work [32], could be explained by the enhancement of cleavage of alkyl and polyaromatic tars into smaller compounds, such as benzene, over the surface of the char.

Fig. 6c presents the conversion of the different tar classes obtained in the five tests, of different duration, performed at 850 °C. The dispersion of the experimental results is, most likely, the consequence of small differences in the gasifier conditions during the different days of operation. When the secondary reactor temperature was increased from 750 °C to 850 °C the conversion of the different tar classes over char was significantly enhanced. After 45 min of exposure of the char bed to the syngas-tar mixture the conversion of TC5 was around 70 %, while for TC4 and TC3 the conversions were between 40 and 50 %. Benzene was, as expected, the compound with the lowest conversion over the char bed. With increasing time of exposure of the char bed to the syngas-tar mixture, a reduction in tar conversion was observed for every tar class. This reduction was, after 6 h of test, around 30 % for TC3, TC4 and TC5 as compared with the initial conversion (i.e., the conversion of TC3 was reduced from around 70% to 50%). For benzene the conversion decrease was even larger. This reduction in the conversion of the

different tar classes could be explained by the 30 % of reduction in the weight of char in the bed after 6 h of experiment since the activity of the char, defined as the ratio between the tar conversion rate at time t and the initial tar conversion rate at each temperature, was stable during the operation at 850 °C (see Fig. 7).

Increasing the char temperature to 875 °C (Fig. 6d) led to a further enhancement of the initial tar conversion for the different tar classes. After 75 min of test the conversion of TC5 was above 80 % with a syngas residence time in the char bed of 0.18 s. The conversions of TC3 and TC4 were above 70 % while the reduction in the concentration of benzene was between 30 and 40 %. The most important difference with the results obtained at 850 °C was the evolution conversion along the time for the different tar classes. While the conversion of TC5 kept practically constant at 875 °C after 5 h of test, it was significantly reduced with time at 850 °C. For the other tar classes, the decay in the conversions measured was much lower at 875 °C than at 850 °C. These observations suggest that an adequate selection of the experimental conditions in the secondary char reactor could provide high conversion of heavy tars for long operation times. This is especially relevant since heavy polyaromatic tars are the compounds of the syngas responsible for the high tar dew point and its end-use related problems.

In order to analyze the catalytic activity of the char during the experiments, the tar conversion rate (excluding benzene) was calculated based on experimental results. Fig. 7 presents the evolution with time of the tar conversion rate, in milligrams of tar converted per second and gram of char remaining in the bed, for the three temperatures studied. Since the experimental data of the amount of char remaining in the bed at the different temperatures tested is insufficient to model the char conversion process, a linear char consumption was assumed for the calculations. This simplification does not provide a detailed evolution of char consumption, but it allows to track the evolution of tar conversion rate trend (increase/decrease). At 750 °C the tar conversion rate was rather low, even at the beginning of the experiment. At 850 °C the char activity was clearly higher and the measured catalytic conversion rate of tars seemed to reach a plateau at values around 0.015 $mg_{tar}/(s \cdot g_{char})$. However, at 875 °C the tar conversion rate per gram of char seemed to rise slightly from 0.024 to 0.031 $mg_{tar}/(s \cdot g_{char})$ during the experiment. After 5 h of test at 875 °C the char bed with an initial weight of 32 g had converted approximately 12 g of tars (benzene not included) and the catalytic activity of the material was slightly higher than the initial one (at the beginning of the test). This result highlights the capability of non-preactivated biomass chars to be used as catalysts for tar abatement in reactor systems where the experimental conditions can be controlled to avoid rapid deactivation. A tar conversion device aiming at operating in continuous would provide, in the conditions analyzed, a high tar conversion rate and a low catalyst (char) consumption.

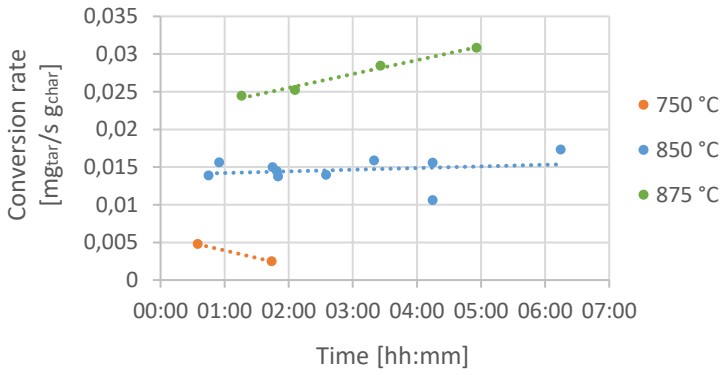
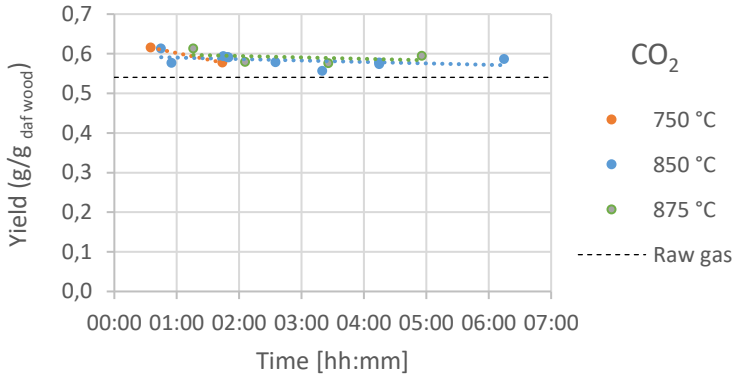
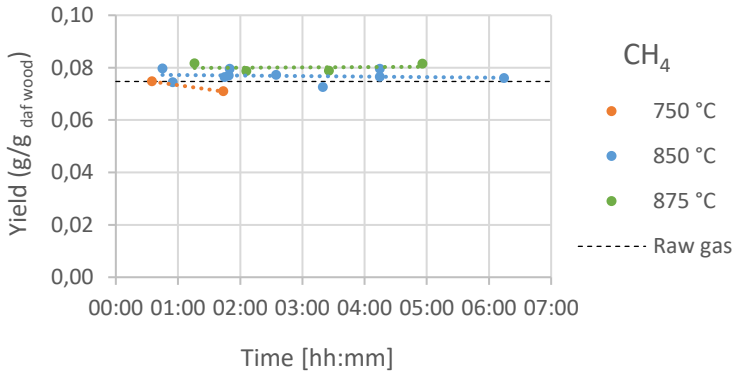


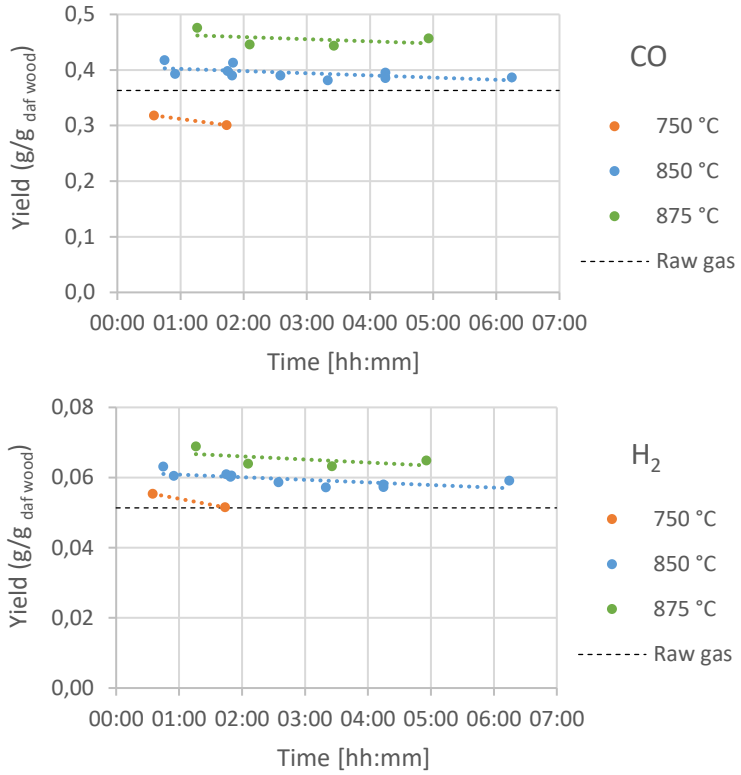

Figure 7: Evolution of the tar conversion rate at different temperatures.

### 3.2- Permanent gases evolution

Fig. 8 shows the yields of the main gaseous species in the syngas after the secondary char bed at the three temperatures studied, as well as those in the raw gas for reference. CO and $H_2$ are clearly influenced by the char bed temperature and by the duration of the test. The gasification rate of char increases at higher temperatures, which explains the higher CO and $H_2$ yields obtained at higher temperatures. The reduction in CO and $H_2$ yields with time can be explained by the progressive consumption of the char bed during the tests. In contrast, the yield of $CO_2$ in the syngas increase slightly after the char bed, but it is hardly affected by the temperature in the secondary reactor, nor by the duration of the test, likely due to the consequence of the enhancement of the water gas shift reaction provoked by the presence of catalytic elements in the char. The yield of $CH_4$ shown in Fig. 8b is slightly influenced by the char bed temperature indicating a net production of this compound in the secondary reactor, probably as a result of the enhancement with temperature of conversion of alkyl-aromatic species over char, such as toluene [12]. The thermal conversion of volatiles in the secondary reactor could be also partially responsible of the increase in $CH_4$ yield [36].






406

407

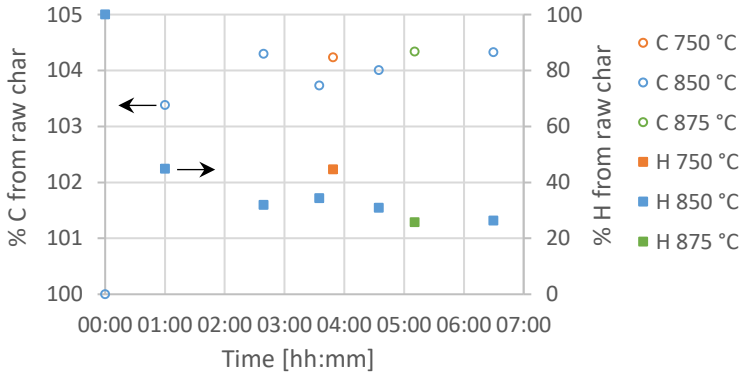
408 Figure 8: Evolution of the yield of the main permanent gases at different temperatures.
409 Horizontal black dotted lines represent the corresponding yield of the species in the raw
410 syngas

411

412 3.3- Char characterization

413 3.3.1 – Elemental composition

414 Fig. 9 shows the evolution of the carbon and hydrogen content of the spent char after each
415 experiment in relation to the contents in the original raw char. It can be seen that there is a
416 tendency of increase in the carbon content and decrease in the hydrogen content along time for
417 the experiments at 850 °C, especially during the first hour of the experiment. In the case of
418 hydrogen, this tendency is enhanced at 875 °C and reduced at 750 °C. These tendencies may be
419 due to cleavages of functional groups with hydrogen and oxygen in the char structure, which are
420 enhanced at the beginning of the test because the char was produced at a lower temperature
421 (700 °C) than those in the experiments.




422

Figure 9: Carbon and hydrogen content of spent char (as a percentage of C and H content in raw char) along the time of the test at the three temperatures.

Figure 10 presents the analysis by ICP of the main inorganic elements in the char samples. A slight tendency of increase in the concentration of inorganic elements during conversion can be observed. This is probably due to char gasification, which decreases the content of organic elements while increasing the content of inorganics. According to the results, no major release of the main alkali and alkali earth metals (K, Ma and Ca) was measured and, in spite of the higher volatility of alkali metals compared to that of alkaline-earth metals [37], the Ca/K ratio decreased when the temperature is raised to 875 °C.

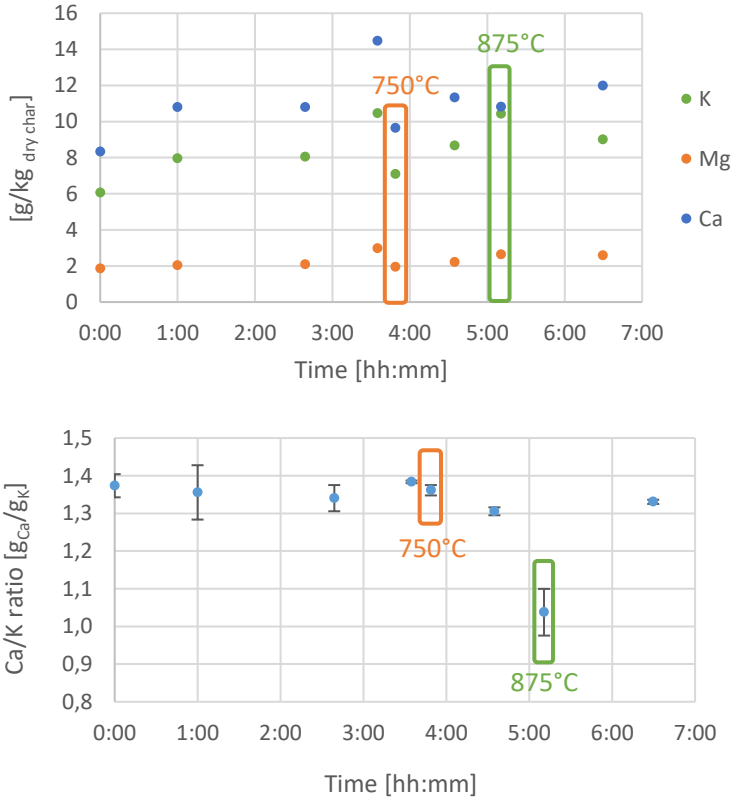


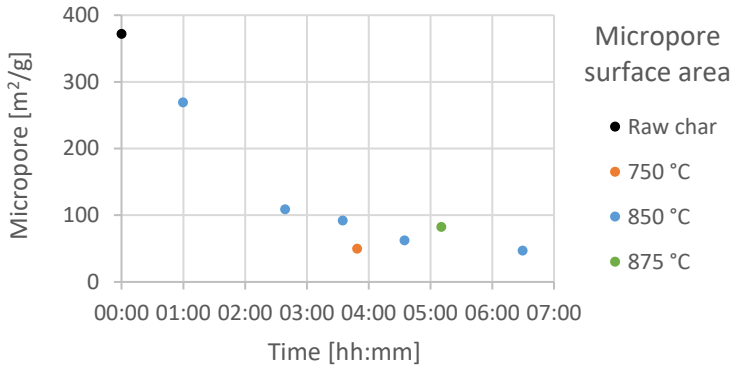

Figure 10: Content of main inorganic elements (top) and Ca/K mass ratio (bottom) in spent char. The values of the experiment at 750 °C are inside an orange box and at 875 °C inside a green box; other experiments were conducted at 850 °C.

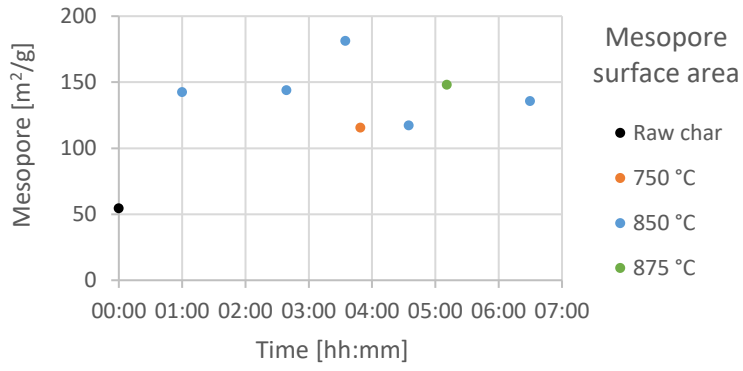
### 3.3.2 – Surface area and pore volume

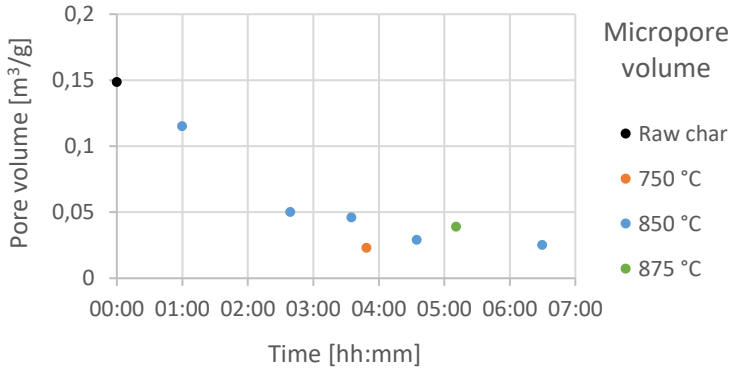
During the exposure to the tar loaded syngas, the char bed undergoes structural changes modifying its characteristics as a catalyst. Fig. 11 presents the evolution of the internal structure (surface area and pore volume) of the char during the tests. The original char (raw char) is characterized by a rather large total specific surface area (SSA), originated mainly by micropores. This behavior is typical of char produced from woody biomass at temperatures above 600 °C in a $N_2$ atmosphere [38]. Analyzing the evolution of the char structure at 850 °C within the first two hours, a significant reduction in both micropore surface area and micropore volume can be observed, accompanied by an increase in mesoporosity. Consequently, after two hours of test, most of the total pore volume and above 50 % of the total surface area correspond to mesopores. This initial evolution of the char internal structure may be the consequence of the

collapse, due to the rapid initial char gasification, of the walls separating the original micropores. At longer residence times the amount of micropores in the char continued decaying to below 0.025 $m^3/g$ and 50 $m^2/g$ while the amount of mesopores stabilized around 0.2-0.25 $m^3/g$ and 140 $m^2/g$. Since the volume of mesopores did not increase after the first two hours, the reduction in the amount of micropores must be the consequence of the pore mouth blocking mechanism [18] produced by the deposition and coking of tars on the pore entrance.

During the test at 850 °C the activity of the char decayed around 15-20 % (see Fig. 7). However, after the initial rapid modification of the char structure, the reduction in the micropore area was above 80 % while the mesopore area remained almost constant. These observations let us to conclude that, during the tests, the tar conversion process is taking place mainly in the mesopores of the char. In a recent work a linear correlation between the total mesopore area available in the char bed and the tar conversion rate constant were found [19], highlighting the significance of mesopores for tar conversion. As mentioned in the Introduction, diffusional limitation could inhibit the conversion of tar compounds inside narrow micropores.



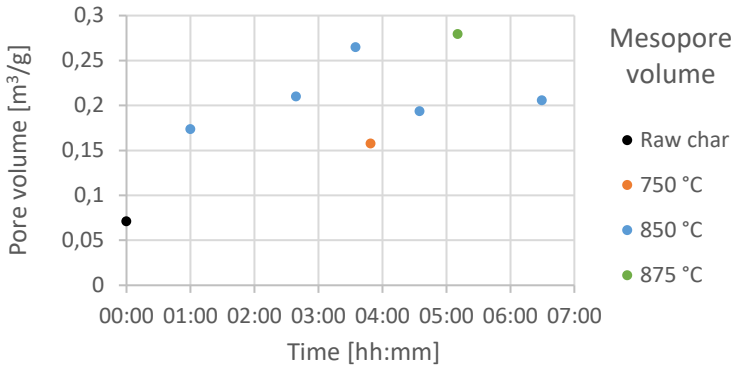
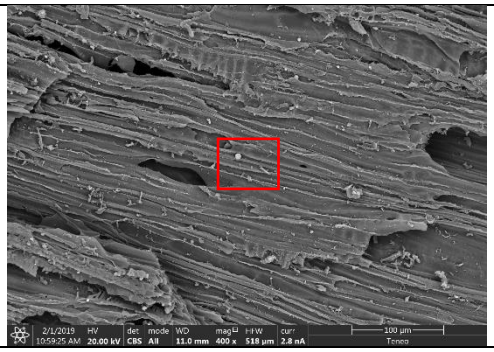
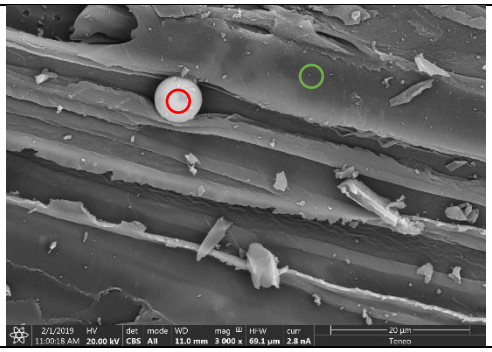



Figure 11: Evolution with time of the micropore and mesopore surface areas and volumes at the different temperature.

### 3.3.3 – SEM-EDX analysis

Fig 12 presents the results of the SEM-EDX analysis made on four different char samples; the original "raw" char, the char after 3 h and 49 min of exposure to the syngas at 750 °C (Test 5 in Table 3), the char after 6 h and 30 min of exposure to the syngas at 850 °C (Test 6) and the char after 5 h and 11 min of exposure to the syngas at 875 °C (Test 7). Two pictures at different magnifications are presented to show a general perspective of the char surface (400x magnification) and a closer image where the presence of inorganic clusters can be visualized and analyzed by EDX (3000x magnification). The red squares presented over the 400x magnification pictures represent the area magnified at 3000x on the picture of the right. The red and the green circles on the image at 3000x of magnification indicate the area where the EDX analysis were made. The atomic ratios of the white clusters dispersed on the char surface (red circles) and the atomic ratios of the dark carbonaceous surface (green circles) obtained by EDX are presented on the right tables.

<table>
<tr><th>Sample (time of exposure)</th><th>Magnification 400x</th><th>Magnification 3000x</th><th>EDX analysis<br>R: red circle<br>G: green circle</th></tr>
<tr><td>Raw char</td><td>  </td><td>  </td><td>
<table>
<tr><th>Element</th><th>Atomic ratio R</th><th>Atomic ratio G</th></tr>
<tr><td>C</td><td>29.0</td><td>85.0</td></tr>
<tr><td>O</td><td>33.0</td><td>13.7</td></tr>
<tr><td>Na</td><td>1.3</td><td>0.1</td></tr>
<tr><td>K</td><td>0.1</td><td>0.5</td></tr>
<tr><td>Mg</td><td>9.3</td><td>0.4</td></tr>
<tr><td>Ca</td><td>13.1</td><td>0.2</td></tr>
<tr><td>Si</td><td>6.4</td><td>0.1</td></tr>
<tr><td>Al</td><td>3.9</td><td>0.1</td></tr>
<tr><td>Fe</td><td>3.9</td><td>-</td></tr>
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</td></tr>
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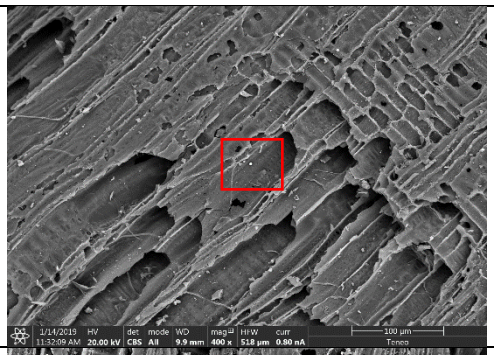
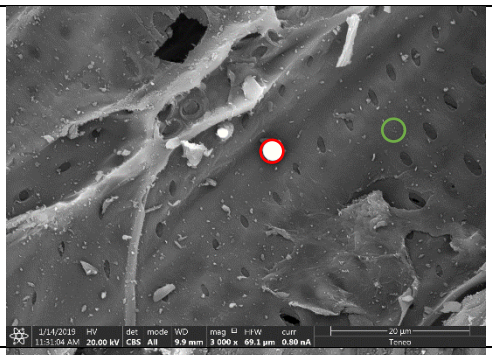
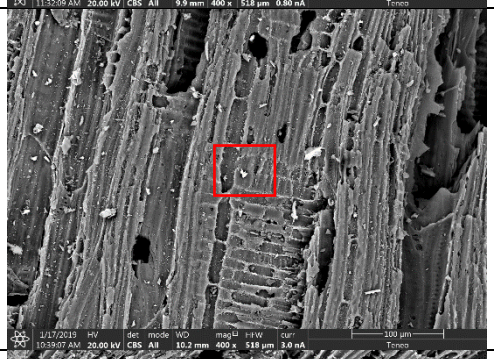
750 °C (3:49) Test 5

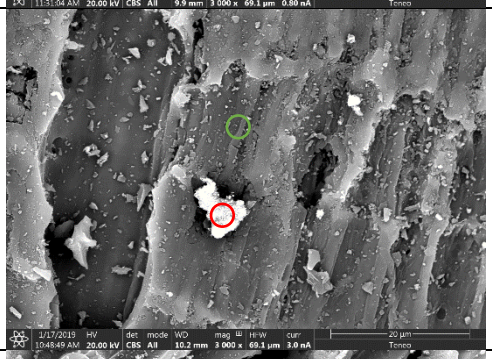




| Element | Atomic ratio R | Atomic ratio G |
|---|---|---|
| C | 50.8 | 84.9 |
| O | 27.9 | 14.3 |
| Na | 0.8 | - |
| K | - | 0.5 |
| Mg | 6.6 | - |
| Ca | 7.8 | 0.3 |
| Si | 0.4 | - |
| Al | 1.7 | - |
| Fe | 4.0 | - |

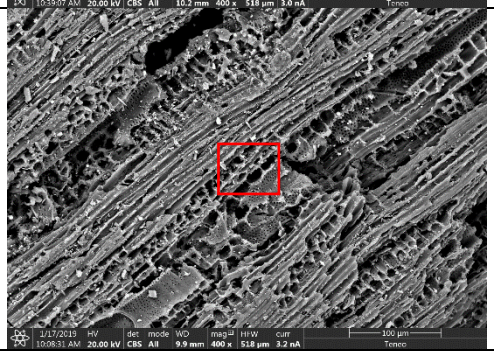
850 °C (6:30) Test 6

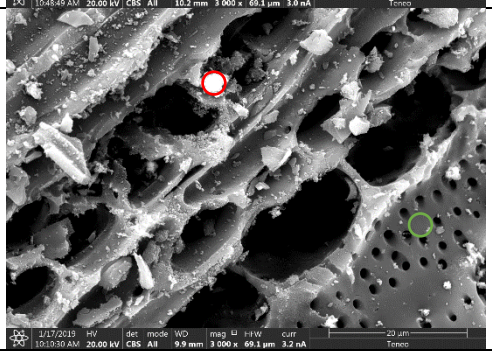




| Element | Atomic ratio R | Atomic ratio G |
|---|---|---|
| C | 51.0 | 78.6 |
| O | 31.6 | 19.9 |
| Na | 0.6 | 0.4 |
| K | 0.1 | 0.2 |
| Mg | 8.6 | 0.4 |
| Ca | 3.4 | 0.2 |
| Si | 3.7 | 0.1 |
| Al | 0.4 | 0.2 |
| Fe | 0.6 | - |

875 °C (5:11) Test 7





| Element | Atomic ratio R | Atomic ratio G |
|---|---|---|
| C | 58.5 | 74.2 |
| O | 28.0 | 24.4 |
| Na | 0.9 | 0.5 |
| K | 0.3 | 0.3 |
| Mg | 5.1 | 0.2 |
| Ca | 5.0 | 0.2 |
| Si | 0.2 | 0.1 |
| Al | 0.8 | 0.1 |
| Fe | 1.4 | - |

Figure 12: SEM images and EDX analysis of char samples produced at different temperatures. SEM images at 3000x are the area confined in red squares in the SEM images at 400x. EDX analysis R and G represent the elemental analysis in the area confined by red and green circles in the SEM images at 3000x.

All the samples analyzed, regardless the severity of the conversion process, present the characteristic fibrous structure of wood-derived chars. However, at the highest temperature tested (875 °C), several pores not present at lower temperatures can be observed. In Fig. 13, an image at 24000x of magnification over the surface of the char after exposure to the syngas at 875 °C reveals the ongoing consumption of the char matrix and the formation of new pores (the smallest pores in the picture fall within the size range of mesopores).

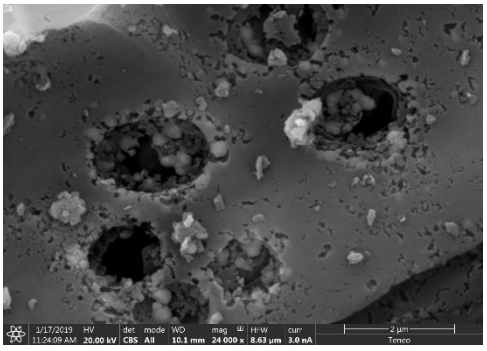


Figure 13: SEM image at 24000x of the spent char after 5 h and 11 min of exposure to the syngas at 875 °C.

In agreement with previous study [19], two different phases can be visually distinguished: a dark continuous phase and clusters of a white phase onto the dark surface. According to the images presented in Fig. 12 the proportion of white clusters is much lower in the raw char and the spent char at 750 °C than for spent chars at 850 °C and 875 °C. Additionally, a significant difference can be observed in the shape of these clusters. In the two first images (raw char and the spent char at 750 °C) the clusters are apparently round-shaped while in the chars of the two last images the clusters adopt an irregular structure. According to the EDX analysis presented, these white clusters are characterized by a low atomic proportion of C and a high proportion of alkaline-earth metals (Mg and Ca). On the other hand, the dark phase is mostly composed of C and O with traces of other elements. It is important to highlight that, in spite of the different proportion found for alkaline-earth metals, alkali metals present similar atomic proportions in both phases. Therefore, while magnesium and calcium tend to segregate during the conversion process into a different phase (white clusters), potassium, a well-known catalytic element, seems to present larger atomic proportions in the dark phase (char matrix).

The absence of white clusters in the char sample obtained at 750 °C is, most likely, the consequence of the higher tar deposition rate compared to the char/soot gasification rate. In these conditions the tar adsorbed onto the active sites of the char surface undergoes polymerization creating soot deposits, reducing the char porosity and hindering the interaction of active sites with gaseous tar. At 875 °C the temperature is high enough to gasify soot at a higher rate than the deposition rate. During gasification of the char matrix, the volatile alkali metals are released to the gas stream while the less volatile alkaline-earth metals tend to accumulate in the observed white clusters. However, white clusters are most likely released to the gas phase during the char conversion since, according to ICP analysis, the Ca/K ratio does not significantly vary during the tests at 850 °C, whereas it decreases as reactor temperature is raised to 875 °C.

According to this, the presence of a high concentration of white clusters can indicate high activity of the char. However, even if the presence of AAEM elements is straightforwardly related with the char activity [19], the influence of white clusters on tar conversion process is not clear yet. White clusters may be directly involved in tar catalytic conversion or maybe it is the dark phase (char matrix) that, in high gasification rate conditions, provides the active sites necessary for a high tar conversion rate. Future experiments will be targeted to analyze these options.

## 4- Conclusions

The present work analyzes the catalytic conversion of the tars present in a real syngas, produced in a steam-blown FB gasifier, over a FB of non-activated wood-derived char. Temperatures between 750 °C and 875 °C with spatial velocities of 24 $Nm^3/kg_{char}h$ corresponding to gas residence time on the char bed between 0.18 s and 0.2 s were tested. The evolution of the tar conversion in the bed, the gas species in the syngas and the internal structure of the used catalysts were determined in order to analyze the viability of using this material for syngas cleaning downstream char reactors.

The main conclusions are:

- A long-term test conducted at 875 °C during 5 hours resulted in tar conversions in the range of 64 – 73 % along the test. The reduction in conversion with time was probably due to char consumption (gasification) rather than deactivation.
- Long-term tests conducted at 850 °C showed initial tar conversions close to 50 %, with a tendency of char deactivation along the test till around 35 % after 6 hours of service. The test conducted at 750 °C showed much lower conversion (≈ 15 %) and a significant deactivation after 2 hours.
- High tar conversion rates and increasing activities of the char can be achieved using non-activated biomass chars given that the reactor conditions promote high enough carbon consumption (from deposited soot) by gasification.
- The heaviest tars present in a real syngas mixture are converted faster than lighter tars over a char catalyst, confirming literature results using syngas doped with tar compounds.
- The results suggest that the tar conversion takes place mainly in the mesopores of the char particles.
- The presence of a high concentration of white clusters over the char surface, containing a significant proportion of alkaline-earth elements, are indicative of a high activity of the char towards tar conversion.

**Acknowledgments**

The authors want to express their appreciation to and Mr. Israel Pardo Arias and Mr. Hernán Almuiña Villar for their support and advice during SEM-EDX analysis and setting up the tar cracking reactor, respectively. The authors gratefully acknowledge the financial support given by European Union's Horizon 2020 Research and Innovation Programme under grant agreement number 731101 (BRISK II) and by the Spanish Ministry of Economy and Competitiveness and the European Union-FEDER in the project NETuWAS (CTM2016-78089-R).

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