

## OXYGEN/STEAM CHARCOAL GASIFICATION IN A FLUIDIZED ALUMINA BED

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Mixtures of oxygen and steam were used as gasifying agents to produce a gas stream with high hydrogen content. The effects of the equivalence ratio (ER) and steam to carbon ratio (S/C) on gasification performance were studied at 900 °C. The highest hydrogen yield (0.412 Nm<sup>3</sup>/kg charcoal) and apparent energy efficiency (33.43%) were achieved using a mixture that had a S/C ratio of 0.625 and an ER equal to 0.3 (pure oxygen). The results showed that the carbon conversion improved when the ER and the S/C ratio were augmented, and that the production of tars increased when the S/C ratio was increased. The use of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as bed material was effective in the cracking of the tars, as well as on the cracking of hydrocarbons heavier than methane.

### 1. Introduction

Due to the much lower chemical complexity of char (also referred to as bio-char or charcoal) when compared to lignocellulosic biomass, hydrogen gas with low cleaning requirements (less contaminant content) could theoretically be produced from charcoal steam gasification followed by a water gas shift (WGS) step [1, 2]. Despite of being less efficient as a consequence of N<sub>2</sub> dilution, air is the most common and generally preferred gasifying agent in biomass gasification technologies, because it is a cheap and readily available oxidizer. In order to avoid the N<sub>2</sub> dilution, pure oxygen can be used as well. Mixtures of oxygen and steam may enhance the performance of gasification processes by increasing the hydrogen content of the produced gas stream, having in consideration the end use of the syngas [1-4].

In spite of the extensive application of gasification technologies to virtually all organic materials, scientific literature regarding the gasification of bio-char has been mainly focused on TGA/DTG analysis [5-6] and TGA-like experimental setups [7-8], and a few number studies can be found regarding charcoal gasification in fixed-bed reactors [9-10]. Charcoal gasification has been carried out in entrained-flow reactors [11]. However, the experimental conditions used in those setups are substantially different from the ones present in real fluidized-bed reactors (FBR). So far, only one publication was found regarding the steam gasification of lignocellulosic pyrolysis char in FBR in continuous regime [12].

A common problem of concern in gasification systems is the tar contents of the producer gas, as well as undesired reactions that lead to the production of gases other than hydrogen and carbon monoxide, *i.e.*, syngas. In a previous work [13] the use of silica sand was compared with alumina as bed material. The results showed that the use of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> improved the gasification of biomass charcoal by reducing the amount of gases other than syngas and carbon dioxide as well as the tar content of the outlet stream. This effects were attributed to improvements in heat transfer (because alumina has a higher heat transfer coefficient than silica sand), and to a catalytic effect in the cracking of bigger gas molecules as previously demonstrated by García and cols. [14]. In this work several mixtures of steam and oxygen were used as gasifying agents to produce a gas stream with high hydrogen content. The effects of the equivalence ratio (ER) and steam to carbon ratio (S/C) on gasification performance were studied in a fluidized-bed lab scale atmospheric rig at 900 °C, using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as bed material.

### 2. Experimental

Commercial vegetable charcoal was purchased and prepared to be used in the gasification experiments. It was ground and sieved, and the fraction having a particle size distribution of 250-500  $\mu$ m was selected. High purity  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Puralox, Sasol Germany GmbH) having a mean particle diameter of 237  $\mu$ m, was selected as reaction bed in the gasification experiments. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was activated by ex-situ calcination at 600 °C during 3 hours in a muffle furnace and kept in a desiccator before its use as fluidization bed material. Further details on the alumina characterization can be found elsewhere [14]. Commercial gases (at purity >99.999 %) were supplied by Air Liquide Spain. Other chemicals used in the gasification runs included: nitrogen, helium and argon, as well

as standard gas mixtures (N<sub>2</sub>, H<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub>S) for the calibration of the gas chromatograph (MicroGC, Agilent G2801A).

The charcoal used as raw material was characterized in terms of elemental analysis (C, H, N and S contents, O content determined by difference), using an elemental analyzer (Leco, TruSpec Micro). Proximate analysis (moisture, ash and volatile matter contents expressed as mass percentages with respect to the “as received” raw material) were determined according to the European standards: UNE-EN 14775:2013 (ash content), UNE-EN 32002:1995 (moisture) and UNE-EN 1774-1:2011 (volatile matter). The mass balance closure, calculated by difference to 100 %, was attributed to the fixed carbon content. The energy content of the raw material was determined by calculating the lower heating value (LHV). The surface area of the charcoal was also determined by Brunauer-Emmett-Teller (BET) method using N<sub>2</sub> adsorption-desorption measurements at 77 K (TRISTAR II 3000 V6.08A analyzer from MICROMERITICS). Results are shown in Table 1 (expressed as mean± standard deviation of three replicates).

Table 1 – Elemental and proximate analyses, surface area and heating value of the charcoal.

Proximate analysis (wt. %, as received)	
Moisture	3.6 ± 0.1
Ash	4.2 ± 0.5
Volatiles	19.0 ± 0.3
Fixed carbon <sup>(*)</sup>	73.2
Ultimate analysis (wt. %, dry and ash free)	
C	80.0 ± 0.4
H	3.11 ± 0.06
N	1.8 ± 0.1
S	0.02 ± 0.01
O <sup>(*)</sup>	15.07
Surface area (m <sup>2</sup> /g)	49.5
LHV (MJ/kg)	30.38 ± 0.02

\* by difference

The gasification experiments were conducted at a lab-scale (<1 kg/h) bubbling fluidized-bed gasifier operating at atmospheric pressure. The experimental set up was composed by a solid feeding system (screw feeder and solid hopper), a fluidized-bed reactor heated by an electrical furnace, a particle cleaning system composed by a gas cyclone and a hot glass fibre filter, a condensation system composed by two ice-cooled condensers followed by a cotton filter, and a gas volumetric meter and online chromatographic analysis system. The layout of the experimental rig is presented elsewhere [1] as well as its detailed description and operation [4]. Mixtures of oxygen and steam were used as fluidizing/gasifying agents.

The producer gas was analysed online for H<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub>S. The carbon content of the liquids collected in the condensation system was determined using a total organic carbon analyser (Shimadzu TOC-L). These results were interpreted as indicators of the amount of tars present in the liquid samples, meaning that the higher the carbon content in the condensate, the higher the tar content [1, 13]. The ER definition assumed was presented by Basu [15]. Apparent energy efficiency (AAE, %) was calculated according to equation 1:

$$AAE = \frac{Vol_{gas} \times LHV_{gas}}{m_{charcoal} \times LHV_{charcoal}} \times 100 \quad (\text{Equation 1})$$

### 3. Results and discussion

Aiming to study the effect of the steam to carbon (S/C) ratio on charcoal gasification performance, Runs 1, 2 and 3 were carried out maintaining the ER constant (at 0.3), while increasing the S/C ratio by 0.125 in each run (Table 2). The charcoal carbon fraction converted into gas improved when the S/C ratio was increased, being higher from Run 1 to Run 2 than from Run 2 to Run 3. The increase in the amount of carbon in the liquid seems to indicate that more tars were produced when the S/C ratio was increased. The gas yield increased from Run 1 to Run 2 (around 25 vol.%) as well as the apparent energy efficiency, but the LHV<sub>gas</sub> decreased slightly. From Run 2 to Run 3 the gas yield was maintained in mass basis and decreased in volume basis, indicating changes in the composition of the produced gas. The apparent energy efficiency also decreased from Run 2 to Run 3, but was higher than in Run 1, also evidencing differences in the composition of the produced gas caused by the increase in the S/C ratio. Moreover, in spite that higher carbon conversions were verified when the water partial pressure was increased in the gasifying mixture, the use of a S/C ratio higher than 0.625 caused negative

effects on the properties of the produced gas as well as on the process energy efficiency. As previously stated, this effect has been reported by other authors [16, 17] during the gasification of charcoal. Owing to the fact that the gas yield, the energy efficiency and the gas calorific power obtained in Run 2 were higher than in Runs 1 and 3, a S/C ratio of 0.625 was used in the experiments undertaken for studying the ER effect on the gasification performance.

*Table 2 – Operating conditions and product distribution in the gasification experiments.*

	Run 1	Run 2	Run 3	Run 4	Run 5
Equivalence ratio (ER)	0.3	0.3	0.3	0.25	0.35
Steam to carbon ratio (S/C)	0.500	0.625	0.750	0.625	0.625
Carbon in the solid (wt. %)	48.65	35.38	33.58	42.41	26.06
Carbon in the liquid (wt. %)	0.04	0.11	0.13	0.07	0.07
Carbon in the gas (wt. %)	51.32	64.51	66.29	57.52	73.87
Gas yield (Nm <sup>3</sup> /kg char)	0.99	1.25	1.20	1.14	1.31
Gas yield (kg/kg char)	1.10	1.37	1.37	1.22	1.54
LHV <sub>gas</sub> (MJ/Nm <sup>3</sup> )	8.32	8.15	7.56	8.19	7.55
LHV <sub>gas</sub> (MJ/kg)	7.49	7.44	6.64	7.68	6.45
Apparent energy efficiency (%)	27.03	33.43	29.91	30.85	32.69

In order to study the effect of the ER on gasification of the charcoal, Run 4 was completed using an ER of 0.25 and Run 5 using an ER of 0.35, while maintaining the S/C ratio constant at 0.625 (the same used in Run 2 as above mentioned). The comparison between Runs 2, 4 and 5 shows that both the carbon conversion into gas, and gas yield increased with the increase in the ER. However, the LHV<sub>gas</sub> dropped, indicating changes in the composition of the produced gas, possibly caused by the consumption of the fuel gases. Contrary effects were reported by He and cols. [16] caused by increasing the ER from 0.25 up to 0.41 while maintaining a S/C ratio of 0.35, meaning that in their experiments the carbon conversion as well as the LHV<sub>gas</sub> improved with the increase in the ER. The only consideration that can be done on this regard is that the difference between their results and the ones presented in this work could be caused by the difference in the S/C ratio. This difference may have changed the individual gas partial pressures in reaction atmosphere within the gasifier, which in turn changed the equilibrium between the reactions occurring in the reactor.

Table 3 shows the average gas composition of the permanent gases produced during the gasification experiments. Those results may be explained by the occurrence of homogeneous reactions between steam and other gases present in the reaction medium as well as by the heterogeneous gas-solid reactions between those gases and charcoal [3, 4, 18]. Moreover, oxidation reactions may also play an indirect role by increasing the CO<sub>2</sub> partial pressure within the gasifier, as well as by increasing the steam partial pressure within the reactor [3, 4, 14]. As shown in Table 3, hydrocarbons higher than methane were not detected in the producer gas.

*Table 3 - Average gas composition (vol.%) of the producer gas in the gasification experiments.*

	Run 1	Run 2	Run 3	Run 4	Run 5
	30.45	33.02	32.24	34.97	29.44
	35.26	31.29	27.51	29.49	30.09
	32.04	33.34	38.01	32.63	37.97
	1.61	1.75	1.68	1.93	1.60
	n.d.	n.d.	n.d.	n.d.	n.d.
	n.d.	n.d.	n.d.	n.d.	n.d.
	0.01	0.01	0.01	0.01	0.01
	0.02	0.02	0.02	0.01	0.01
	0.62	0.57	0.53	0.96	0.88

\* n.d.: not detected

As previously mentioned, Runs 1, 2 and 3 were developed keeping the ER constant at 0.3 and varying the S/C ratio between 0.5 and 0.75 by increments of 0.125, aiming to study the effect of that variable on the charcoal gasification performance. As expected, the CO partial pressure dropped and the CO<sub>2</sub> content increased with the rise in the S/C ratio, due to the water gas shift reaction. However, the CO<sub>2</sub> variation was not proportional between these runs, evidencing the occurrence of other reaction pathways taking place during Run 3, such as Boudouard, oxidation and/or reforming reactions.

The hydrogen and methane percentages increased from Run 1 to Run 2 and dropped slightly from Run 2 to Run

3, indicating that oxidation reactions took place as evidenced by the hydrogen and methane decreases from Run 2 to Run 3, justifying this way the significant increase in the CO<sub>2</sub> partial pressure in the produced gas. These changes in the partial pressure of these four gases also seem to explain the decrease on the LHV<sub>gas</sub> along Runs 1 to 3, which was more abrupt from Run 2 to Run 3. Other authors [12, 16, 17] reported similar effects during the gasification of charcoal, implying that the excessive increase of the steam partial pressure in the gasifying agent can lead to deterioration of the produced gas quality. The gas composition results also hint a certain catalytic activity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for cracking C<sub>2</sub> hydrocarbons, consistent with the work of García and cols. [14].

Runs 2, 4 and 5 were undertaken using the same S/C ratio of 0.625 and varying the ER between 0.25 and 0.35, aiming to study the effect of this variable on the gasification of charcoal, as earlier stated. As expected, the hydrogen content in the producer gas decreased with the increase in the oxygen partial pressure in the reacting mixture as a result of oxidation. The CO content rose from Run 2 to Run 4 possibly due to the impact of reforming and steam reactions. The CO partial pressure dropped in Run 5, while CO<sub>2</sub> increased constantly the ER was augmented. Given that the hydrogen partial pressure decreased simultaneously with methane and carbon monoxide, the explanation would be that combustion reactions were intensified by the increase of the oxygen partial pressure in the fluidizing gas fed to the reactor. Additionally, the LHV of the producer gas and consequently the apparent energetic efficiency also dropped, which is consistent with the pointed reasoning. The results presented in Table 4 show that the higher the ER (Runs 2, 4, 5), the higher the CO<sub>2</sub> yield, evidencing the occurrence of oxidation reactions with the increase in the oxygen partial pressure in the fluidizing gas. Likewise, the higher the S/C ratio (Runs 1, 2 and 3), the higher the CO<sub>2</sub> production, supporting the occurrence of steam reactions with the increase of the water content in the gasifying gas. The exception of this tendency was verified in the experiments with air, where the amount of CO<sub>2</sub> produced was lower in Run 1.

*Table 4 – Volumetric gas yields (Nm<sup>3</sup>/kg of charcoal).*

	Run 1	Run 2	Run 3	Run 4	Run 5
H <sub>2</sub>	0.301	0.412	0.388	0.400	0.387
CO	0.348	0.390	0.330	0.337	0.396
CO <sub>2</sub>	0.316	0.416	0.457	0.373	0.499
CH <sub>4</sub>	0.016	0.022	0.020	0.022	0.021
H <sub>2</sub> /CO	0.86	1.06	1.17	1.19	0.98
CO/CO <sub>2</sub>	1.10	0.94	0.72	0.90	0.79

As expected, the H<sub>2</sub>/CO ratio increased with the increase in S/C ratio in the fluidizing gas, evidencing the occurrence of the water gas shift reaction. Moreover, the higher the S/C ratio, the lower the CO/CO<sub>2</sub> ratio, meaning that the distribution of the carbon present in the initial charcoal was converted into CO<sub>2</sub> as a consequence of the water gas-shift reaction.

#### 4. Conclusions

In this gasification study, the carbon fraction conversions verified in all experiments were low. The highest carbon conversion (73.87 wt.%) was achieved using a steam to carbon (S/C) ratio of 0.625 and an equivalence ratio (ER) of 0.35. The results show that the carbon conversion into gas was improved when both the ER and the S/C ratios were increased. The highest hydrogen yield (0.412 Nm<sup>3</sup>/kg charcoal) and apparent energy efficiency (33.43%) were achieved using a gasifying mixture that corresponded to a S/C ratio of 0.625 and an ER equal to 0.3 (pure oxygen). The production of tars increased with the S/C ratio. The use of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as bed material was effective in the cracking of the tars, as well as on the cracking of hydrocarbons heavier than methane.

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