



# Air-steam gasification of char derived from sewage sludge pyrolysis. Comparison with the gasification of sewage sludge



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## HIGHLIGHTS

- Increased content of fixed carbon in the solid after sewage sludge pyrolysis.
- Higher gas yield from dried and ash-free (*daf*) char than from sewage sludge (*daf*).
- Average tar yield decreased by 45% when gasifying char instead of sewage sludge.
- Average CO yield was 70% higher when gasifying char (*daf* basis for solids).
- Temperature was the most influential factor for most of the studied variables.

## ARTICLE INFO

### Article history:

Received 16 January 2014

Received in revised form 24 March 2014

Accepted 25 March 2014

Available online 13 April 2014

### Keywords:

Air-steam gasification

Sewage sludge

Char

Fast pyrolysis

Fluidized bed

## ABSTRACT

Air-steam gasification of char derived from fast pyrolysis of sewage sludge has been experimentally evaluated in a fluidized bed as a route towards a full recovery of energy from sewage sludge. The results have been compared with those obtained from the direct gasification of sewage sludge in order to evaluate how the previous pyrolysis stage affects the subsequent gasification process. The fixed carbon content in the solid increased after the pyrolysis stage so that heterogeneous reactions of carbon with steam or CO<sub>2</sub> assumed greater importance during char gasification than during sewage sludge gasification. Furthermore, char gasification led to an improvement in the gas yield –calculated on a dry and ash-free basis (*daf*)– due to the increased concentration of carbon in the organic fraction of the solid after the pyrolysis step, with an increase in the average CO yield of about 70% –in terms of g/kg solid *daf*–. The reduction in the fraction of carbon which forms tar is another advantage of char gasification over the direct gasification of sewage sludge, with an average decrease of about 45%. Regarding the influence of the operating conditions, the response variables were mainly controlled by the same factors in both processes.

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## 1. Introduction

Sewage sludge is the waste generated during successive treatment stages of urban wastewaters. In recent years the production of sewage sludge in the EU has considerably increased due to the expansion in the amount and capacity of wastewater treatment plants [1,2]. For instance, the production of sewage sludge in Spain increased by 41% in the period 2000–2009 [3]. For this reason, the economical and environmentally-friendly treatment of sewage sludge has become an important issue. The traditional methods of treatment or disposal of sewage sludge include its use as fertilizer on croplands, incineration and landfilling [1,2,4]. However, as a result of the environmental and health problems caused by the

application of these techniques, energy recovery from sewage sludge by thermo-chemical treatments such as pyrolysis or gasification technologies could be an interesting alternative [2].

A large number of lab-scale studies on sewage sludge pyrolysis for liquid production (fast pyrolysis) can be found in the literature [5–11]. The liquid yield and its physicochemical properties depend on the operational conditions (mainly on the temperature) and on the composition of the sewage sludge [6]. Char is the main by-product of sewage sludge fast pyrolysis. Common solid yields of around 35–55 wt.% are found in the literature [8–11], but it should be noted that the ash content in these solids is much higher than those of lignocellulosic origin. The use of this solid by-product as adsorbent material has been investigated by some authors. The results show that char obtained from sewage sludge pyrolysis is not a very porous material (its surface area ranges 50–150 m<sup>2</sup>/g) because of its high inorganic content [12]. Despite this, some

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authors have reported a certain capacity of this kind of material to remove contaminants such as  $H_2S$ ,  $NO_x$ , metals, dyes and phenols [12–16]. Physical activation of this kind of char was proposed as part of a three-stage thermo-chemical treatment of sewage sludge in a previous work in our group [17].

On the other hand, the remaining organic fraction in char gives it a moderate calorific value which could be further exploited through thermo-chemical processes. In fact, the gasification of char resulting from fast pyrolysis of different types of biomass is being investigated by some authors as a route towards an integral valorization of biomass [18–22]. Furthermore, as part of volatile matter is removed from biomass during pyrolysis, the gasification of char obtained from pyrolysis instead of the direct gasification of biomass should lead to a reduction in the formation of tar during the process, which is one of the main hurdles for the development of gasification technology.

The present work is focused on the gasification of char obtained from sewage sludge fast pyrolysis. An experimental study has been carried out in a lab-scale fluidized bed reactor in order to evaluate the feasibility of gasifying this kind of char. The influence of several operating conditions (temperature, composition of the gasification medium and gasifying agent to biomass ratio) on the gasification performance has been analyzed statistically in order to determine the relative influence of each factor. Moreover, results from char gasification have been compared with those obtained from the direct gasification of sewage sludge under the same operating conditions [23] in order to evaluate how the previous pyrolysis stage affects the subsequent gasification process.

## 2. Materials and methods

### 2.1. Char obtained from sewage sludge pyrolysis

Char obtained from the fast pyrolysis of anaerobically digested and thermally dried sewage sludge is the feedstock for the gasification experiments performed in this work. Table 1 presents the results of the proximate and ultimate analyses and heating value of the char, as well as the results obtained for the original sewage sludge. The fixed carbon content in this kind of char is considerably lower than in other types of biomass chars [18–22] as the composition of sewage sludge and lignocellulosic materials are quite different.

### 2.2. Experimental setup

Char was produced during sewage sludge fast pyrolysis in a lab-scale fluidized bed reactor operating at a temperature of 530 °C. The pyrolysis plant and the operating conditions are described in detail elsewhere [24].

**Table 1**  
Proximate and ultimate analyses and lower heating value of both the char derived from sewage sludge pyrolysis and the sewage sludge itself (SS).

		Char	SS
<i>Proximate analysis (wt.%, wet basis)</i>			
Moisture	ISO-589-1981	1.70	6.48
Ash	ISO-1171-1976	74.20	39.04
Volatiles	ISO-5623-1974	15.02	50.09
Fixed carbon	By difference	9.08	4.39
<i>Ultimate analysis (wt.%, wet basis. Carlo Erba 1108 elemental analyzer)</i>			
C		15.49	29.50
H		0.97	4.67
N		1.85	5.27
S		0.35	1.31
LHV (MJ/kg)	IKA C-2000 calorimeter	5.0	11.8

Char gasification experiments have also been carried out in a lab-scale fluidized bed reactor operating at atmospheric pressure, with continuous feed of solid (around 2.1 g/min of char) and continuous removal of ash. Ash from previous gasification tests constituted the solid bed by itself from the beginning of the runs. The gasifying/fluidizing agent used in the process consisted of different mixtures of steam and enriched air (air + oxygen). Air flow was kept constant in all the experiments and different flows of pure oxygen were fed together with the air, thus enriching the air at different percentages.

The vapors and gases produced during the gasification process remained inside the reactor around 17–18 s and then passed through a cyclone and a hot filter (both at 450 °C) in which the solid particles swept by the gas were collected. Water and condensable organic compounds (tar) were collected in two ice-cooled condensers. The volume of particle- and tar-free gas was measured by a volumetric meter and its composition was analyzed on-line using a micro gas chromatograph (Agilent 3000-A). The experiments were carried out during 60 min. Fig. 1 shows a diagram of the laboratory installation. A more detailed description of the plant can be found elsewhere [23].

Ash content in the solid by-product was determined according to ISO-1171-1976 and its carbon content was analyzed using a Leco TruSpec Micro Elemental Analyzer. Water content in the condensed fraction was analyzed off-line by Karl Fischer titration in order to determine the amount of tar by difference. However, tar production was almost negligible and all the results from the Karl Fischer titration were about 100 wt.% of water, so non-significant differences in tar production were found by this way. Therefore, in order to evaluate the effect of the factors, tar production from char gasification was approximated to the amount of organic carbon present in the condensate ( $g C_{\text{condensate}}$ ), measured by means of a total organic carbon analyzer (TOC-L CSH/CSN Shimadzu analyzer).

### 2.3. Experimental design and data analysis

A  $2^k$  factorial experimental design was planned in order to determine the influence of some operating factors on the char gasification performance. This kind of experimental design allows the existence of interactions between the factors to be identified. In other words, it can be seen whether a factor influences a response variable in a different way depending on the value of another factor.

Three factors have been studied in this work: (i) gasification temperature, measured inside the bed (ranging between 770 and 850 °C); (ii) gasifying ratio (GR) between the mass flow of gasifying agent (oxygen plus steam) and the mass flow of dry and ash-free (daf) basis char (ranging between 0.8 and 1.1 g/g char daf) and (iii) composition of the gasification medium, represented by the  $H_2O/O_2$  molar ratio (ranging between 1 and 3). The three studied factors, together with their respective ranges of study, were chosen based on our previous work on sewage sludge gasification [23] in order to compare the performance of both processes and evaluate how a previous pyrolysis stage affects the subsequent gasification process. The temperature and the ratio between the flow of oxygen or steam and the feed of biomass are among the most studied factors in the air-steam gasification of biomass [22,25].

As seen in Table 2, the experimental design consisted of 8 runs ( $2^k$  runs, where  $k$  is the number of factors, in this case 3). Furthermore, three replicates at the center point (CP) were added to the experimental design in order to evaluate the experimental variability as well as to determine if the response of each variable was linear or not within the studied range. Coded values of the factors were used to identify the term with the greatest influence on each response variable, that is,  $-1$  for the lower limits ( $T = 770$  °C,  $GR = 0.8$

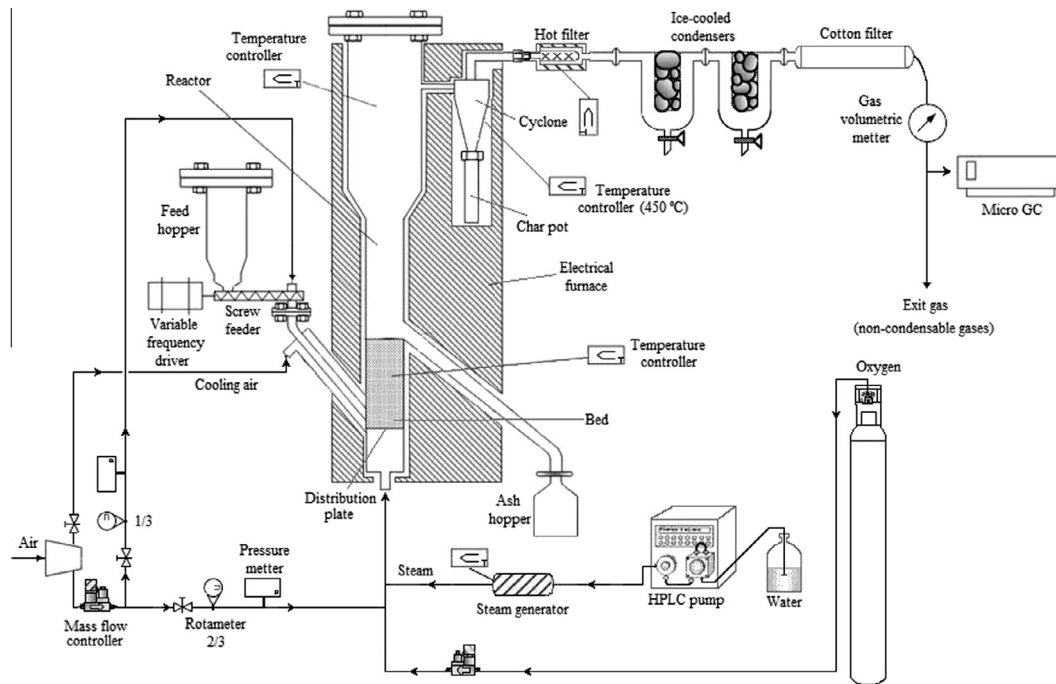


Fig. 1. Laboratory-scale gasification setup.

**Table 2**  
Operating conditions in the char gasification experiments.

Experiment number	1	2	3	4	5	6	7	8	CP (9, 10, 11)
Coded values ( $T$ , $GR$ , $H_2O/O_2$ )	1,1,1	-1,1,1	1,-1,1	-1,-1,1	1,1,-1	-1,1,-1	1,-1,-1	-1,-1,-1	0,0,0
Temperature ( $^{\circ}C$ )	850	770	850	770	850	770	850	770	810
g gasifying agent/g char <i>daf</i> ( $GR$ )	1.1	1.1	0.8	0.8	1.1	1.1	0.8	0.8	0.95
$H_2O/O_2$ molar ratio in the gasifying agent	3	3	3	3	1	1	1	1	2
Equivalence ratio ( $ER$ )	0.17	0.17	0.12	0.12	0.32	0.32	0.23	0.23	0.19
Steam to char <i>daf</i> mass ratio ( $S/B$ )	0.71	0.71	0.52	0.52	0.39	0.39	0.27	0.27	0.52

and  $H_2O/O_2 = 1$  and +1 for the upper ones ( $T = 850^{\circ}C$ ,  $GR = 1.1$  and  $H_2O/O_2 = 3$ ).

The response variables analyzed were the following: (i) distribution of products (solid, gas and tar); (ii) gas composition, determined on-line using a micro-gas chromatograph; (iii) production of each gaseous component, based on the amount of char *daf* fed; (iv) lower heating value of the product gas ( $LHV_{gas}$ ); (v) cold gasification efficiency and (vi) carbon yield to gas phase.

The experimental results have been analyzed statistically by means of analysis of variance (ANOVA), using a confidence level of 95% for the F-distribution to identify the terms that significantly affect each response variable. Design-Expert<sup>®</sup> 7 software (from Stat-Ease, Inc.) was used for the analyses.

### 3. Results and discussion

Experimental results obtained from the char gasification tests are shown in Table 3. Furthermore, as a result of the ANOVA analyses, Table 4 presents the relative influence of each factor on the response variables. Average data represent the average of the whole set of results obtained, whereas the coefficients associated to the different factors ( $T$ ,  $GR$  and  $H_2O/O_2$ ) show the effect that the change of each factor has on the studied responses (in terms of coded values for the factors); the existence of significant interactions between the factors is also denoted by means of coefficients. In order to compare these results with those corresponding to the direct gasification of sewage sludge, Table 5 presents a summary of

the ANOVA results obtained when sewage sludge was the feedstock for the gasification process [23]. This comparative study is based on a single type of sewage sludge and char. Therefore, although the expected trends for other kind of materials will be similar, extrapolation of the results should be done carefully.

#### 3.1. Product distribution

##### 3.1.1. Solid yield and carbon fraction remaining as solid

The solid fraction was the most abundant by-product during char gasification because of the high ash content in the char. The solid yield varied between 73 and 82 wt.% (based on the amount of char fed), though this solid was mainly composed of ash (93–96 wt.%). Its carbon content ranged between 3.8 and 6.2 wt.% (Table 3). The fraction of carbon remaining as solid after char gasification can be calculated from the above data as follows:

Carbon fraction as solid (wt.%)

$$= gC_{\text{solid by-product}} / gC_{\text{char fed}} \cdot 100 \quad (1)$$

It should be noted that the amount of solid introduced in the reactor as initial bed (ash from previous gasification tests) was also part of the solid collected after the experiments and contained a small amount of carbon (between 3 and 5 wt.%). This amount of carbon is not included in  $gC_{\text{solid by-product}}$ .

The fraction of carbon remaining as solid after char gasification ranged between 15 and 43 wt.% (Table 3), whereas the maximum

**Table 3**  
Experimental results from char gasification.

	1,1,1	−1,1,1	1,−1,1	−1,−1,1	1,1,−1	−1,1,−1	1,−1,−1	−1,−1,−1	0,0,0 <sup>a</sup>
Solid yield (g solid/100 g char)	75.7	78.5	75.0	78.5	73.1	77.1	75.2	81.3	77.5 ± 1.7
Carbon content in the solid product (wt.%)	3.9	6.2	4.5	6.1	3.9	4.5	3.9	5.8	5.6 ± 0.6
Carbon fraction remaining as solid (wt.%)	19.5	41.3	25.4	43.1	14.7	26.2	18.8	40.9	33.8 ± 2.6
Gas yield ( $m_{STP}^3/kg$ char)	0.36	0.27	0.31	0.24	0.35	0.28	0.32	0.24	0.29 ± 0.01
Gas yield ( $m_{STP}^3/kg$ char <i>daf</i> )	1.47	1.12	1.30	0.99	1.46	1.15	1.31	1.00	1.21 ± 0.01
Carbon fraction forming tar (wt.%)	1.3	0.7	2.9	3.3	1.0	5.7	3.2	5.8	2.8 ± 0.7
<i>Gas composition (dry basis)</i>									
H <sub>2</sub> (vol.%)	29.3	26.3	27.8	24.8	21.5	19.0	22.0	20.2	25.2 ± 0.6
CO (vol.%)	19.5	12.0	20.2	12.8	22.7	14.0	23.7	15.2	15.9 ± 0.2
CO <sub>2</sub> (vol.%)	18.9	24.2	16.2	20.8	22.6	29.5	18.5	24.1	21.9 ± 0.1
CH <sub>4</sub> (vol.%)	0.76	0.91	0.77	0.92	0.59	0.70	0.64	0.84	0.88 ± 0.01
C <sub>2</sub> H <sub>x</sub> (ppmv)	150	190	160	220	180	220	150	200	180 ± 10
H <sub>2</sub> S (vol.%)	0.25	0.12	0.14	0.07	0.17	0.08	0.12	0.06	0.10 ± 0.01
N <sub>2</sub> (vol.%)	31.3	36.5	34.9	40.7	32.5	36.7	35.0	39.6	36.1 ± 0.6
H <sub>2</sub> /CO molar ratio	1.50	2.20	1.38	1.93	0.95	1.36	0.93	1.33	1.58 ± 0.04
CO/CO <sub>2</sub> molar ratio	1.03	0.49	1.25	0.62	1.00	0.47	1.28	0.63	0.73 ± 0.01
LHV <sub>gas</sub> (MJ/ $m_{STP}^3$ )	5.96	4.71	5.87	4.65	5.44	4.09	5.63	4.43	5.07 ± 0.07
Cold gasification efficiency (%)	62.9	41.1	57.2	37.6	57.4	36.2	55.3	35.7	47.0 ± 0.6
Carbon yield to gas phase (wt.%)	71.0	55.5	62.1	47.9	82.9	67.1	72.2	55.7	61.5 ± 1.5

<sup>a</sup> Mean value ± standard deviation.

**Table 4**  
Relative influence of the studied factors on the response variables for char gasification.

	Average	<i>T</i>	<i>GR</i>	H <sub>2</sub> O/O <sub>2</sub>	<i>T-GR</i>	<i>T-H<sub>2</sub>O/O<sub>2</sub></i>	<i>GR-H<sub>2</sub>O/O<sub>2</sub></i>	<i>T-H<sub>2</sub>O/O<sub>2</sub>-GR</i>	Curvature
Carbon fraction remaining as solid (wt.%)	30.13	−9.16	−3.30	3.59	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
Gas yield ( $m_{STP}^3/kg$ char <i>daf</i> )	1.23	0.16	0.08	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>b</sup>
Carbon fraction forming tar (wt. %)	2.94	−0.90	−0.81	−0.93		0.95		<sup>a</sup>	<sup>a</sup>
H <sub>2</sub> /CO molar ratio in the product gas	1.48	−0.26	<sup>a</sup>	0.31	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
CO/CO <sub>2</sub> molar ratio in the product gas	0.85	0.29	−0.10	<sup>a</sup>	−0.03	<sup>a</sup>	0.01	<sup>a</sup>	<sup>b</sup>
<i>Yield of gaseous compounds (g/kg char <i>daf</i>)</i>									
H <sub>2</sub>	40.93	6.03	1.86	5.43	0.33	0.90	1.18	<sup>a</sup>	<sup>b</sup>
CO	427.16	135.09	<sup>a</sup>	−34.61	<sup>a</sup>	−9.78	<sup>a</sup>	<sup>a</sup>	<sup>b</sup>
CO <sub>2</sub>	815.96	−29.09	104.91	−69.95	<sup>a</sup>	<sup>a</sup>	−18.75	<sup>a</sup>	<sup>a</sup>
CH <sub>4</sub>	10.33	<sup>a</sup>	<sup>a</sup>	1.01	<sup>a</sup>	<sup>a</sup>	0.32	<sup>a</sup>	<sup>b</sup>
C <sub>2</sub> H <sub>4</sub>	0.28	−0.023	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
H <sub>2</sub> S	3.54	1.62	1.03	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
LHV <sub>gas</sub> (MJ/ $m_{STP}^3$ )	5.09	0.63	<sup>a</sup>	0.20	<sup>a</sup>	<sup>a</sup>	0.08	<sup>a</sup>	<sup>a</sup>
Cold gasification efficiency (%)	47.90	10.27	1.45	1.77	0.48	<sup>a</sup>	0.83	<sup>a</sup>	<sup>b</sup>
Carbon yield to gas phase (wt.%)	64.29	7.76	4.82	−5.16	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>b</sup>

<sup>a</sup> Non-significant term.

<sup>b</sup> Significant curvature.

**Table 5**  
Relative influence of the studied factors on the response variables for sewage sludge gasification.

	Average	<i>T</i>	<i>GR</i>	H <sub>2</sub> O/O <sub>2</sub>	<i>T-GR</i>	<i>T-H<sub>2</sub>O/O<sub>2</sub></i>	<i>GR-H<sub>2</sub>O/O<sub>2</sub></i>	<i>T-H<sub>2</sub>O/O<sub>2</sub>-GR</i>	Curvature
Carbon fraction remaining as solid (wt.%)	9.01	−5.76	−1.74	3.29	<sup>a</sup>	−1.50	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
Gas yield ( $m_{STP}^3/kg$ SS <i>daf</i> )	1.12	0.17	0.02	<sup>a</sup>	0.02	−0.02	<sup>a</sup>	0.03	<sup>b</sup>
Carbon fraction forming tar (wt.%)	5.28	−1.11	<sup>a</sup>	<sup>a</sup>	−0.56	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
H <sub>2</sub> /CO molar ratio in the product gas	2.21	−0.14	0.08	0.62	0.02	−0.06	0.11	−0.05	<sup>b</sup>
CO/CO <sub>2</sub> molar ratio in the product gas	0.52	0.16	−0.11	<sup>a</sup>	−0.04	−0.03	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
<i>Yield of gaseous compounds (g/kg SS <i>daf</i>)</i>									
H <sub>2</sub>	37.03	9.06	−1.37	5.68	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
CO	250.10	78.79	−17.51	−32.67	−5.03	−21.95	<sup>a</sup>	9.65	<sup>a</sup>
CO <sub>2</sub>	763.42	<sup>a</sup>	101.57	−92.53	21.59	<sup>a</sup>	−14.93	15.91	<sup>a</sup>
CH <sub>4</sub>	50.23	1.49	−3.13	4.80	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
C <sub>2</sub> H <sub>x</sub>	46.13	−3.28	<sup>a</sup>	3.35	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
H <sub>2</sub> S	12.66	1.73	1.56	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	0.62	<sup>a</sup>
LHV <sub>gas</sub> (MJ/ $m_{STP}^3$ )	5.49	0.37	−0.31	0.40	<sup>a</sup>	−0.17	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
Cold gasification efficiency (%)	55.12	8.51	<sup>a</sup>	3.47	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
Carbon yield to gas phase (wt.%)	72.48	6.33	3.33	−6.07	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>

<sup>a</sup> Non-significant term.

<sup>b</sup> Significant curvature.

value for sewage sludge gasification was about 24 wt.%. This difference may be explained by the different structure of the carbonaceous matter in the solids. Most of the carbon in sewage sludge

is in the form of volatile matter (85 wt.% of the carbon content) which can be easily released during the gasification stage. However, the volatile matter in sewage sludge was considerably

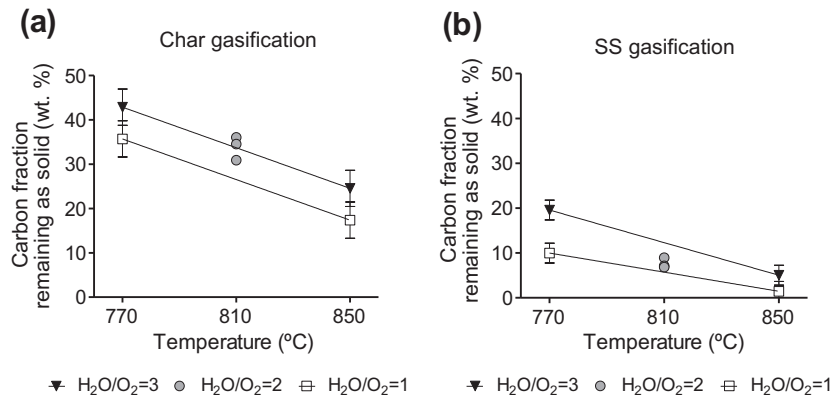


Fig. 2. Carbon fraction remaining as solid after (a) char gasification and (b) sewage sludge gasification (gasifying ratio = 0.95 g/g solid daf).

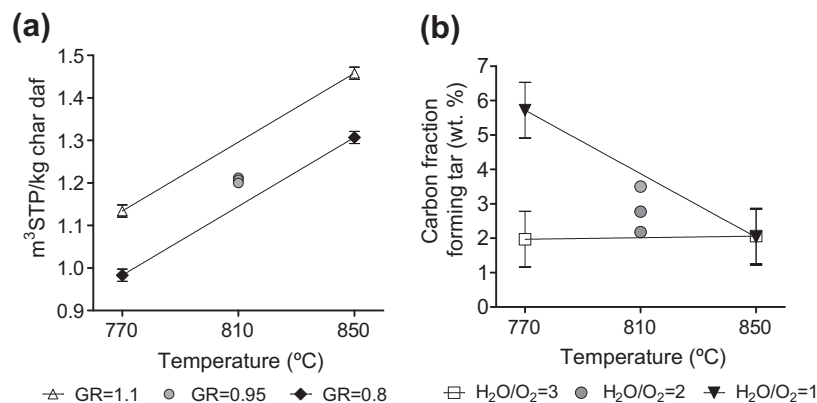


Fig. 3. (a) Gas yield during char gasification ( $H_2O/O_2 = 2$ ). (b) Carbon fraction forming tar during char gasification (gasifying ratio = 0.95 g/g char daf).

reduced during the pyrolysis stage and about 59 wt.% of the carbon in char is in the form of fixed carbon, which is more difficult to gasify than the volatile matter.

According to the ANOVA results (Table 4), temperature is the most influential factor on the carbon fraction remaining as solid. Higher reaction temperatures favor carbon gasification [26], so that the carbon fraction remaining as solid was reduced by as much as half when the temperature increased from 770 to 850 °C (Fig. 2a). Carbon conversion is also enhanced by increasing the gasifying ratio (GR) and/or decreasing the  $H_2O/O_2$  ratio, thus indicating that carbon reactivity with oxygen is greater than its reactivity with steam. The same trends were observed in the direct gasification of sewage sludge (Table 5), although the carbon fraction remaining as solid was even more sensitive to the variation of the factors in that case. Furthermore, the interaction between the temperature and the  $H_2O/O_2$  ratio was denoted as a significant term, with negligible influence of the gasification medium composition at the higher temperature (Fig. 2b). The error bars shown in the figures of results (Figs. 2, 3 and 5) correspond to the least significant difference (LSD).

As mentioned above, carbon conversion was higher for sewage sludge gasification than for char gasification. However, results for char gasification can be recalculated considering both stages (pyrolysis + gasification) as a whole and taking the initial amount of carbon in sewage sludge as a reference for calculating the carbon conversion. In this way, the fraction of carbon remaining as solid after char gasification is reduced to 4–11 wt.%, thus improving the carbon conversion obtained in the direct gasification of sewage sludge.

### 3.1.2. Gas production

The gas yield from char gasification varied between 0.24 and 0.36  $m^3_{STP}/kg$  char ( $N_2$ -free basis), or between 0.40 and 0.52  $m^3_{STP}/kg$  char if  $N_2$  is included (where STP means standard conditions of temperature and pressure at 0 °C and 1 atm). Comparing these data with those corresponding to sewage sludge gasification (0.49–0.72  $m^3_{STP}$   $N_2$ -free/kg SS) [23], it can be observed that the production of gas has been reduced by half, mainly due to the higher ash content in char. The production of gas during the pyrolysis stage (around 0.06–0.07  $m^3_{STP}$   $N_2$ -free/kg SS) is not high enough to offset the difference in the production of gas from the gasification of both materials.

On the other hand, if the gas yield ( $N_2$ -free basis) is calculated taking into account only the organic content in the raw material, it ranged between 0.99 and 1.47  $m^3_{STP}/kg$  char daf for char gasification and 0.89–1.32  $m^3_{STP}/kg$  SS daf for sewage sludge gasification [23], thus indicating that the previous pyrolysis stage leads to structural changes in the organic fraction of the solid that improve the production of gas. Gas yield results obtained from the gasification of sewage sludge-derived char (expressed on a  $N_2$ -free and daf basis) are in the same range as those obtained from char derived from lignocellulosic materials, such as bagasse char [18] or char derived from ramie residues [22].

As with the gasification of sewage sludge, temperature is the most influential factor on the production of gas during char gasification (Table 4). An average gas yield improvement of about 30% was obtained when the temperature varied from 770 to 850 °C in the gasification of char (Fig. 3a). Although to a lesser extent, the increase in the gasifying ratio (GR) is also favorable for the production of gas, whereas the nature of the gasification medium does not exert a significant influence on the gas yield obtained from the



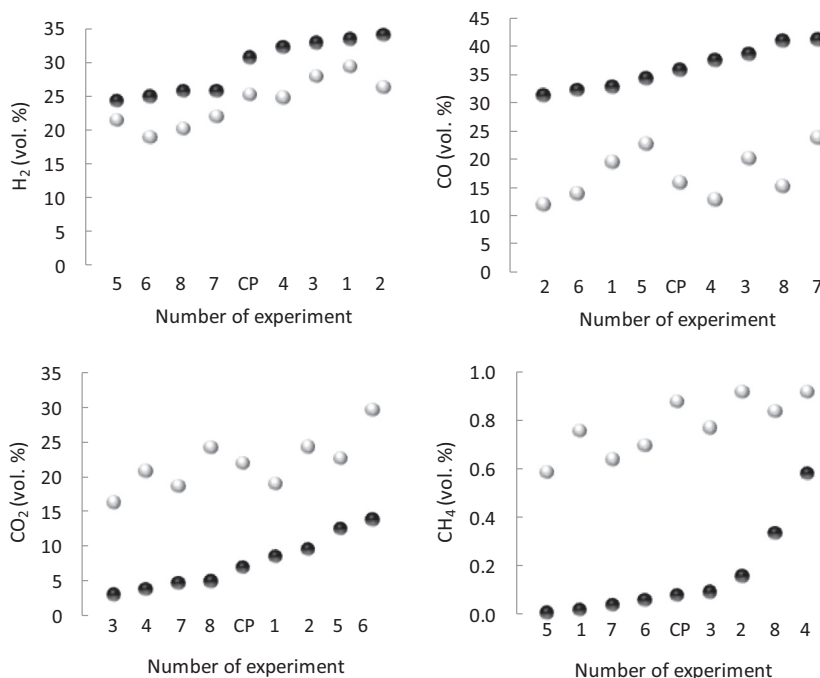


Fig. 4. Equilibrium (●) and experimental (○) fractions of H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> in the product gas from char gasification.

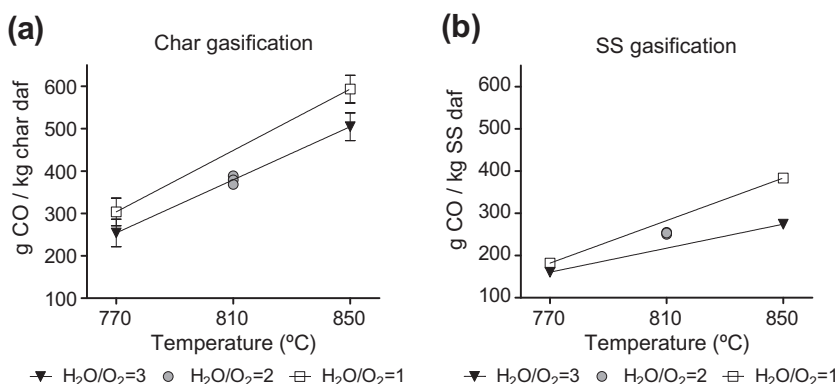


Fig. 5. CO production during (a) char gasification and (b) sewage sludge gasification (gasifying ratio = 0.95 g/g solid daf).

gasification of either char or sewage sludge. Therefore, as can be noted, the negative effect of H<sub>2</sub>O/O<sub>2</sub> on the gasified carbon fraction (discussed in the previous section) does not result in a significant gas yield decrease. The production of H<sub>2</sub> may be the major reason for this disagreement because, as discussed below, H<sub>2</sub> formation is promoted by increasing the H<sub>2</sub>O/O<sub>2</sub> ratio (mainly through the water–gas shift reaction), thus counteracting the decrease in the production of gaseous carbon-compounds.

Gas yield does not follow a linear trend with all factors, as curvature appears as a significant term in the ANOVA analysis. This means that at least one of the three factors has a quadratic effect on the evolution of gas production. Some studies reported in the literature show that excess steam is not favorable for the production of gas during steam gasification and suggest optimal values for steam to carbon ratios in order to maximize it [20,22,25,27]. The observed curvature may therefore be associated with the presence of steam in the gasification medium.

### 3.1.3. Tar production

The fraction of carbon which forms tar can be calculated as follows:

Carbon fraction as tar (wt.%)

$$= \frac{gC_{\text{condensate}}}{gC_{\text{char fed}}} \cdot 100 \quad (2)$$

The fraction of carbon which formed tar during char gasification ranged between 0.7 and 5.8 wt.% (Table 3) and according to the ANOVA results (Table 4), it can be reduced by increasing any of the studied factors, though the effect of temperature disappears at the higher H<sub>2</sub>O/O<sub>2</sub> ratio and the effect of H<sub>2</sub>O/O<sub>2</sub> is negligible at the higher temperature (Fig. 3b). On the other hand, the average carbon fraction forming tar during sewage sludge gasification was about 1.8 times higher than during char gasification and only the temperature and its interaction with the gasifying ratio were found to be significant terms (Table 5).

The production rates of tar and gas allow the tar content in the product gas to be calculated (g tar/m<sup>3</sup><sub>STP</sub>). The tar content in the gas from char gasification (by approximation of the amount of tar to the amount of organic carbon present in the condensate) ranged between 2 and 13 g tar/m<sup>3</sup><sub>STP</sub> under most operating conditions, while the results for sewage sludge gasification ranged between 11 and 45 g tar/m<sup>3</sup><sub>STP</sub> [23].

### 3.2. Gas composition

The composition of the product gas from a gasification process is the result of many complex and competing reactions. The most representative reactions include the water–gas shift reaction (WGS), oxidation reactions, water–gas reactions (reactions of carbon with steam), steam and dry reforming of hydrocarbons, the methanation reaction and the Boudouard reaction [25–27].

As can be seen in Table 3,  $H_2$  (19.0–29.3 vol.%), CO (12.0–23.7 vol.%),  $CO_2$  (16.2–29.5 vol.%),  $CH_4$  (0.59–0.92 vol.%) and  $N_2$  (31.3–40.7 vol.%) were the main gases detected by the micro GC during char gasification. Other minor compounds were also detected in the gas, such as  $C_2H_x$  hydrocarbons (mainly  $C_2H_4$ ) or  $H_2S$ , which is released during the process due to the presence of sulfur-compounds in the char (Table 1). Statistical results from the analysis of gas composition have not been included in this work because it was preferred to analyze the yield of each gaseous compound in terms of g/kg char *daf* (Section 3.3). However, the variation of the product gas composition has been evaluated through two molar ratios:  $H_2/CO$  and  $CO/CO_2$ . On the one hand, the  $H_2/CO$  ratio in the product gas is increased by reducing the temperature and/or increasing  $H_2O/O_2$  in the gasification medium, this last factor being the most influential (Table 4). These trends are consistent with those obtained for sewage sludge gasification (Table 5), although in that case the gasifying ratio also played a significant role in the evolution of the  $H_2/CO$  ratio (positive effect), as well as the interactions between the factors and the curvature term. Higher values of  $H_2/CO$  were obtained from sewage sludge gasification (1.46–3.25) than from char gasification (0.93–2.20). On the other hand, temperature is the most influential factor on the  $CO/CO_2$  ratio in the exit gas in both processes. The  $CO/CO_2$  ratio can be improved by increasing the temperature and/or reducing the amount of gasifying agent fed to the reactor (Table 4). The curvature has been denoted as a significant term in the evolution of  $CO/CO_2$ , as well as some interactions between the factors. The same trends were observed for sewage sludge gasification, although in that case the  $CO/CO_2$  ratio followed a linear response. Higher values of  $CO/CO_2$  have been obtained from char gasification (0.49–1.28) than from sewage sludge gasification (0.30–0.88).

The theoretical composition of the gas at equilibrium conditions was also calculated in order to determine if the gasification process was kinetically or thermodynamically controlled. The HSC Chemistry® 6.1 software was used to obtain the theoretical composition of the gas under the same operating conditions tested in the laboratory. The results from the theoretical simulations varied within the following ranges:  $H_2$  (24.3–33.9 vol.%), CO (31.3–41.1 vol.%),  $CO_2$  (3.0–13.8 vol.%),  $N_2$  (24.8–28.7 vol.%),  $CH_4$  (87–5801 ppmv),  $H_2S$  (0.35–0.40 vol.%) and  $NH_3$  (17–42 ppmv). The  $H_2/CO$  and  $CO/CO_2$  ratios at equilibrium conditions ranged 0.62–1.09 and 2.33–12.90, respectively. Experimental fractions of  $H_2$  and CO were lower than their corresponding theoretical values, whereas experimental fractions of  $CO_2$  and  $CH_4$  were above their corresponding theoretical values (Fig. 4). The significant differences observed in the concentration ranges reveal that chemical equilibrium was not reached during the experimental tests.

### 3.3. Production of each gaseous compound

The production or yield of each gas ( $H_2$ , CO,  $CO_2$ ,  $CH_4$ ,  $C_2H_4$  and  $H_2S$ ) is expressed in terms of mass of gas (g) produced per kilogram of char *daf* fed.

According to the ANOVA results (Table 4), gasification temperature is the most influential factor on the production of both  $H_2$  and CO during char gasification. These gases are involved in many reactions both as reactants and as products, but the temperature rise seems to enhance their formation rather than their consuming

reactions. Although to a lesser extent, the production of  $H_2$  is also improved by increasing the  $H_2O/O_2$  ratio, unlike the CO yield which decreases with  $H_2O/O_2$ . Both trends are consistent with the WGS reaction ( $CO + H_2O \leftrightarrow H_2 + CO_2$ ), which is one of the most representative reactions for a steam gasification process. Besides increasing the steam presence, the oxygen presence is reduced with the increase in  $H_2O/O_2$ , so combustion reactions should be mitigated. The negative effect of  $H_2O/O_2$  on the production of CO suggests that the WGS reaction outweighs the combustion reactions in the evolution of the CO yield. The same trend was found when directly gasifying the sewage sludge (Table 5). Similarly, Franco et al. [27] found that the WGS reaction appeared to be the most dominant reaction in the steam gasification of biomass for the temperature range of 730–830 °C. For higher temperatures (830–900 °C), steam reforming of carbon (water–gas reactions) prevailed, although these reactions also appeared to contribute significantly at temperatures lower than 830 °C for some types of biomass. In the present study, an upward trend in CO production with increasing temperature was found. As the process is controlled by kinetics, this behavior cannot be explained through the WGS reaction alone, but through the steam reforming of carbon ( $C + H_2O \leftrightarrow CO + H_2$ ), the Boudouard reaction ( $C + CO_2 \leftrightarrow 2 CO$ ) and the steam and dry reforming of hydrocarbons in which CO is formed, which seem to gain importance at higher temperatures. As shown in Fig. 5, the positive effect of temperature on the CO yield slightly diminishes with increased steam presence due to the enhancement of the WGS reaction.

The gasifying ratio (GR) does not significantly affect the CO yield and only slightly influences the  $H_2$  yield in a positive way during char gasification (Table 4). However, the amount of gasifying agent is the most influential factor on the production of  $CO_2$ : the higher the gasifying ratio, the greater the amount of  $CO_2$  produced. Increasing the gasifying ratio means more oxygen and more steam fed to the gasifier, so combustion reactions, as well as  $CO_2$  formation through other reactions promoted by the presence of steam (such as the WGS reaction), take place to a greater extent. The gasification temperature and the composition of the gasification medium also exert a significant influence on the production of  $CO_2$ . The temperature rise reduces the formation of  $CO_2$  and, as discussed above, favors the production of CO, thus suggesting once again the importance of the Boudouard reaction at high temperatures. The negative effect of  $H_2O/O_2$  on the  $CO_2$  yield reveals that combustion is the main source of  $CO_2$  in the process.

Regarding the production of light hydrocarbons ( $CH_4$  and  $C_2H_4$ ) during char gasification, the experimental variability was considerable (15% for  $C_2H_4$ ), so only those factors with a very clear effect were denoted as significant terms in the ANOVA analysis. The composition of the gasification medium was found to be the only factor affecting the production of  $CH_4$ : increasing  $H_2O/O_2$  involves greater  $CH_4$  production, thus suggesting that its consumption through combustion reactions outweighs its steam reforming process. Methane formation via the methanation reaction ( $C + 2H_2 \leftrightarrow CH_4$ ) may also be promoted by increasing the  $H_2O/O_2$  ratio due to an increased presence of  $H_2$  in the gasification medium. On the other hand, temperature is the only factor affecting the  $C_2H_4$  yield (Table 4) and, as expected, a downward trend with increasing temperature was found, since higher temperatures provide more favorable conditions for thermal cracking and reforming reactions [25].

Lastly, according to the ANOVA results (Table 4), the production of  $H_2S$  during the gasification of char is significantly affected by the gasification temperature and the gasifying ratio, although the effect of the latter factor is less significant. The production of  $H_2S$  is promoted by the temperature rise (process controlled by kinetics). Moreover, the production of  $H_2S$  is favored by the steam presence ( $COS + H_2O \leftrightarrow H_2S + CO_2$ ) [28].

Some other conclusions can be drawn by comparing the results derived from char gasification and sewage sludge gasification:

- Average yield to  $H_2$  was very similar for both feedstocks (41 g/kg char *daf* and 37 g/kg SS *daf*), whereas average yields to CO and  $CO_2$  (g/kg *daf*) were 70% and 6% higher in the gasification of char, respectively. The production of light hydrocarbons and  $H_2S$  was much lower when char was gasified due to the previous release of these compounds in the pyrolysis stage (about 4–5 mg  $H_2S$ /g sewage sludge released during the pyrolysis step). However, it should be noted that if gas yields are calculated with respect to the whole feedstock and not only considering the dry and ash-free material, the production of all the gas components is clearly greater during the gasification of sewage sludge.
- The production of each gas is mainly controlled by the same factor in both processes. The gasification temperature is the most influential factor on the production of  $H_2$ , CO and  $H_2S$ ; the gasifying ratio is the most significant factor on the  $CO_2$  yield, and the composition of the gasification medium exerts the greatest influence on the  $CH_4$  yield. However, some differences related to minor influences of the factors have also been found. For example, temperature did not affect the production of  $CO_2$  in the gasification of sewage sludge while it had a negative effect during char gasification. An increased reactivity of char with  $CO_2$  (Boudouard reaction) may explain this difference. Furthermore, the gasifying ratio did not affect the production of CO in the gasification of char, but it had a negative effect during the gasification of sewage sludge. This implies that the consumption of CO through combustion or through the WGS reaction during char gasification is offset by an increased production of CO from heterogeneous reactions between carbon and steam (water–gas reactions) or carbon and  $CO_2$  (Boudouard reaction), since the fixed carbon content is higher in char (9.08 wt.%) than in sewage sludge (4.39 wt.%).
- The production of each gas during the gasification of sewage sludge follows a linear response with the factors, whereas curvature appears as a significant term in the production of some gases during char gasification.

### 3.4. Lower heating value of the product gas

The lower heating value of the gas is calculated as follows:

$$LHV_{gas} = \sum(x_i \cdot LHV_i) \quad (3)$$

where  $x_i$  and  $LHV_i$  are the volumetric fraction and the lower heating value (MJ/m $^3_{STP}$ ) of each gaseous component, respectively. Therefore, the variation in the gas heating value only depends on the gas composition evolution.

The lower heating value of the product gas from char gasification ranged between 4.09 and 5.96 MJ/m $^3_{STP}$  (Table 3), thus defining this gas as a low heating value gas [26]. According to the ANOVA results (Table 4), the gas heating value follows a linear trend with the gasification temperature and the  $H_2O/O_2$  ratio, the temperature being the most influential factor. As remarked above, the temperature rise leads to a decrease in the production of  $CO_2$  and a simultaneous increase in the yields of  $H_2$  and CO. These variations outweigh the decrease in the content of light hydrocarbons, thus resulting in a positive effect of the temperature on the gas heating value. The composition of the gasification medium also exerts a significant influence on the gas heating value: when  $H_2O/O_2$  is increased, the content of  $CH_4$  increases and the content of  $CO_2$  decreases, so both effects contribute to improve the  $LHV_{gas}$ . The effect of the gasification medium is intensified when more gasifying agent is fed to the reactor (significant interaction between the gasifying ratio and  $H_2O/O_2$ ).

Despite feeding different flows of nitrogen to the reactor, gas lower heating values from char gasification (4.09–5.96 MJ/m $^3_{STP}$ ) are in the same range as those obtained from sewage sludge gasification (4.12–6.20 MJ/m $^3_{STP}$ ) [23]. Temperature plays the most important role in the evolution of the gas heating value when char is gasified (Table 4), while the three studied factors exerted similar relative influences on the gas heating value from sewage sludge gasification (Table 5).

### 3.5. Cold gasification efficiency

The cold gasification efficiency, without taking into account the sensible heat of the gases, is defined as follows:

$$\text{Gasification efficiency (\%)} = (\text{Gas}_{\text{volume}} \cdot LHV_{\text{gas}}) / (\text{Char}_{\text{mass}} \cdot LHV_{\text{char}}) \cdot 100 \quad (4)$$

where  $\text{Gas}_{\text{volume}}$  is the total production of gas (m $^3_{STP}$ , including the amount of  $N_2$ ),  $\text{Char}_{\text{mass}}$  is the amount of char fed during each experiment (kg), and  $LHV_{\text{gas}}$  and  $LHV_{\text{char}}$  are the lower heating values of the product gas and of the char expressed on MJ/m $^3_{STP}$  and MJ/kg, respectively.

The cold efficiency for char gasification ranged between 36% and 63% (Table 3). These values are quite similar to those obtained for the gasification of sewage sludge (39–66%) [23]. According to the ANOVA results (Table 4), the response of char gasification efficiency does not follow a linear trend with all the factors since the curvature was denoted as a significant term. Temperature is clearly the most influential factor on the gasification efficiency, and its variation from 770 to 850 °C improved the char gasification efficiency by about 20%. As remarked above, both the gas heating value and the gas yield were enhanced at high temperatures. The other factors ( $H_2O/O_2$  and gasifying ratio) also have a positive effect on the char gasification efficiency, but play a less important role in its variation. Moreover, some interactions between the factors appear as significant terms in the evolution of the char gasification efficiency: the positive effects of temperature and  $H_2O/O_2$  are intensified by increasing the gasifying ratio.

Temperature and  $H_2O/O_2$  also have a positive effect on the sewage sludge gasification efficiency (Table 5), the temperature being the most influential factor. However, the gasifying ratio did not exert a significant influence in this case because its positive effect on the production of gas was counteracted by its negative effect on the gas heating value. The response of the sewage sludge gasification efficiency was linear with its two significant factors.

### 3.6. Carbon yield to gas phase

The carbon yield to gas phase is defined as follows:

$$\text{Carbon yield to gas phase (\%)} = gC_{\text{product gas}} / gC_{\text{char fed}} \cdot 100 \quad (5)$$

Although the conversion of solid carbon during char gasification reached 57–85 wt.%, the carbon yield to gas phase was slightly lower (between 48 and 83 wt.%), since not all the converted carbon produced gaseous compounds. However, both variables are linked since a decreased carbon fraction remaining as solid led to an increased production of carbon-containing gases. This link is shown by the ANOVA results, as the same factors that affected the carbon fraction remaining as solid also affect the carbon fraction which forms gas, but in opposite directions. The same trends were observed when gasifying sewage sludge (Table 5), though the difference between carbon conversion (76–98 wt.%) and carbon yield to gas phase (62–90 wt.%) was more significant because of the greater formation of tar.

Although carbon yield to gas phase achieved in sewage sludge gasification was higher than that for char gasification, gas



production calculated on a *daf* basis was better for char gasification. This may be explained by the increased concentration of carbon in the dried and ash-free fraction of the solid after the pyrolysis step (0.64 g C/g char *daf* vs. 0.54 g C/g SS *daf*).

#### 4. Conclusions

Gasification of char obtained from fast pyrolysis of sewage sludge has been experimentally studied in this work. The results have been compared with those obtained from the direct gasification of sewage sludge in order to evaluate how the previous pyrolysis stage affects the subsequent gasification process. Most of the carbon in the sewage sludge was in the form of volatile matter (85 wt.%), while almost 60 wt.% of the carbon in char was in the form of fixed carbon, thus causing differences in the gasification performances of both materials. The carbon fraction remaining as solid after char gasification was higher than that for sewage sludge gasification. Despite this, gas production (expressed on a dry and ash-free basis, *daf*) was improved when gasifying char due to the increased concentration of carbon in the dried and ash-free fraction of the solid after the pyrolysis step (0.64 g C/g char *daf* vs. 0.54 g C/g SS *daf*).

The comparison of theoretical and experimental results showed that equilibrium conditions were not reached during the gasification experiments of either char or sewage sludge, so both processes were controlled by kinetics. The average yield to  $H_2$  (expressed as g/kg solid *daf*) was very similar for both feedstocks, whereas average yields to CO and  $CO_2$  (g/kg solid *daf*) were 70% and 6% higher in the gasification of char, respectively. On the other hand, the production of light hydrocarbons and tar was significantly reduced during char gasification due to the reduction in the volatile matter of the solid after the pyrolysis step. The gasification efficiency and the gas heating value varied in similar ranges in both processes.

All the studied variables were mainly controlled by the same operating factor (temperature, composition of the gasification medium or gasifying agent to biomass ratio) in both char gasification and sewage sludge gasification. Temperature was the most influential factor on the carbon conversion, gasification efficiency, gas yield, production of  $H_2$ , CO and  $H_2S$  and CO/ $CO_2$  ratio in the product gas from both processes, affecting all of them positively. The gasifying ratio was the most significant factor on the production of  $CO_2$  (positive effect), whereas the composition of the gasification medium exerted the greatest influence on the  $CH_4$  yield and  $H_2/CO$  ratio in the product gas (enhanced by the presence of steam). Temperature also played the most important role in the evolution of the gas heating value when char was gasified, while the three studied factors exerted similar relative influences on the gas heating value from sewage sludge gasification.

In summary, results show how the increased content of fixed carbon in the solid after the pyrolysis step leads to a greater importance of heterogeneous reactions at high temperatures, such as the steam reforming of carbon or the Boudouard reaction.

#### Acknowledgements

The authors gratefully acknowledge the financial support provided by the Spanish Ministry of Science and Technology (research project CTQ2010-20137) and the Spanish Ministry of Education (pre-doctoral grant awarded to N. Gil-Lalaguna, AP2009-3446).

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