

Air-steam gasification of sewage sludge in a fluidized bed. Influence of some operating conditions.

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Abstract

An experimental work was carried out to investigate the viability of energy recovery from the air-steam gasification of sewage sludge. The relative influence of different factors, as well as the effect of their possible interactions, has been determined by means of analysis of variance. Temperature was found to be the most influential factor for most of the variables analyzed. Solid yield (35-41 wt. %) and tar content (11-45 g/m³_{STP}) were largely reduced with temperature, whereas gas production (0.89-1.32 m³_{STP}/kg sewage sludge dry and ash free), carbon yield to gas phase (62-90 wt. %), gasification efficiency (39-66 %), and H₂ and CO yields (20-52 and 137-414 g/kg sewage sludge dry and ash free, respectively) were improved at high temperature. Other important parameters for the end-use of the gas such as its heating value (4.12-6.20 MJ/m³_{STP}) and its H₂/CO molar ratio (1.46-3.25) were greatly influenced by the composition of the gasification medium, since the increase in the steam to oxygen ratio was favourable for both. The comparison of experimental and theoretical results highlights that equilibrium was not reached during the experimental runs.

Keywords: air-steam gasification; sewage sludge; fluidized bed.

1. Introduction

Biomass is one of the most important primary renewable energy sources. The conversion of biomass to energy encompasses a wide range of materials, conversion technologies and end-use applications of the products, such as power/heat generation, transportation fuels and chemical feedstocks. Sewage sludge, which is the waste produced by wastewater treatment processes, can be considered an important renewable biomass energy source [1].

As a result of the application of the Urban Wastewater Treatment Directive (UWWTD) 91/271/EEC [2], new municipal wastewater treatment strategies have been developed during the last two decades in order to improve the quality of effluents. Existing treatment plants have been upgraded and new and more effective treatment plants have been designed and implemented. In parallel to the improvement of the effluent quality, environmental awareness about sewage sludge management has gained strength. The main commercial means of sewage sludge disposal include its use as fertilizer, land filling or incineration [3, 4]. However, because of increasing legal limitations on sewage sludge land filling and agricultural reuse, energy recovery from sewage sludge remains an attractive and sustainable way of management. Thermal processes such as pyrolysis, gasification or combustion of sewage sludge have thus attracted considerable scientific interest. This paper presents an experimental work on sewage sludge gasification.

Gasification is the conversion of a carbonaceous material into a gas fuel by heating it in a gasification medium such as air, oxygen or steam. Gas from gasification consists of a mixture of carbon monoxide, carbon dioxide, hydrogen, methane and other light hydrocarbons, nitrogen (if air is used as gasifying agent) and steam. This gas can be used to power gas engines and gas turbines or used as a chemical feedstock to produce

liquid fuels [5]. During gasification, a mixture of heavy and condensable hydrocarbons (tars) is also produced. The presence of tar in the gas causes problems associated with condensation, formation of aerosols and polymerization leading to more complex structures which limit the subsequent utilization of the gas.

Operating conditions during gasification (such as the nature of the biomass, pressure, temperature, residence time or gasification medium) play an important role in both tar formation and gas quality. The higher the temperature, the lower the tar content in the product gas [6], but other factors such as the risk of ash sintering limit the operating temperature. The use of different gasifying agents such as air, steam, steam-oxygen mixtures or carbon dioxide has been reported in the literature. Both gas composition and gas heating value are noticeably affected by the gasification medium because of the variation of selectivity in the gasification reactions [7]. Generally, steam gasification enhances H₂ production compared to air gasification, and also leads to a higher gas heating value because the dilution of the gas with nitrogen is avoided [8]. However, the steam gasification reactions are endothermic and require a continuous supply of energy. Given this background, biomass gasification with mixtures of air and steam appears to be a potential solution from the economic point of view, since the partial combustion of biomass inside the gasifier can supply the required energy for the process, turning it into an autothermal process. The improvement in gas quality by feeding a flow of steam together with the air stream during biomass gasification has been reported in several experimental studies [9-12].

In the particular case of sewage sludge, experimental studies based on air gasification [13-17] and steam gasification [18] have been reported in the literature. In general, the gas composition and the gas heating value from sewage sludge gasification are close to typical values obtained from other kinds of biomass, which demonstrates

the potential of sewage sludge as a raw material for the gasification process. However, tar formation and other additional problems such as the formation of other pollutants (H_2S , HCl or NH_3) hinder the development of sewage sludge gasification, so new efforts are required in order to optimize the process.

In this work, an experimental study (based on a 2^k factorial design) on sewage sludge gasification in a fluidized bed with mixtures of air and steam has been developed in order to find out the influence of several operating conditions (temperature, composition of the gasification medium and gasifying agent to biomass ratio) on the gasification performance. Furthermore, experimental results have been compared with theoretical data which were determined considering equilibrium conditions.

2. Materials and methods

2.1. Sewage sludge

Anaerobically digested and thermally dried sewage sludge (SS) was supplied by a Spanish urban wastewater treatment plant. Feedstock analyses were performed at the Instituto de Carboquímica (ICB-CSIC) in Zaragoza (Spain) according to standard methods: moisture according to ISO-589-1981, ash according to ISO-1171-1976, volatiles according to ISO-5623-1974, ultimate analysis (CHNS) using a Carlo Erba 1108 and heating value according to ISO-1928-89 (Table 1). More details about the sewage sludge characterization, such as FTIR and X-ray diffraction analyses, can be found elsewhere [19]. Sewage sludge was smashed and sieved to obtain a feed sample in the size range of 250-500 μm .

2.2. Experimental setup

Sewage sludge gasification runs have been carried out in a laboratory-scale fluidized bed reactor operating at atmospheric pressure, with continuous feed of solid and

continuous removal of ash. The gasifier was a tubular reactor made of refractory steel (AISI 310) divided into two parts: a bed zone, with an inner diameter of 40 mm, and a freeboard zone, with an inner diameter of 63 mm. Sewage sludge was continuously fed to the reactor by a feeding system composed of a screw-feeder and a variable speed motor. The solid feed rate in each experiment was around 2.1 g/min. Ash from previous sewage sludge gasification tests constituted the solid bed by itself from the beginning of the runs. When the amount of bed material inside the reactor exceeded the height of the bed zone, it left the reactor by overflow through a lateral pipe and was collected in a separate vessel. The reactor was heated by an electrical furnace with three different heating zones (bed, free-board and cyclone), which could be controlled independently. The bed temperature was one of the factors under study, ranging between 770 and 850 °C (the same as in the free-board), while the cyclone temperature was set at 450 °C. A schematic diagram of the experimental setup can be found elsewhere [20].

The gasifying/fluidizing agent used in the process consisted of different mixtures of steam and enriched air (air + oxygen). Furthermore, an additional flow of nitrogen was necessary in two of the experiments (those with the lowest air requirement) in order to avoid differences in the dilution effect of the gas with nitrogen and in the fluidization rate (which was around 5-7 times greater than the minimum fluidization rate). The feed rate of these gases (air, oxygen and nitrogen) was adjusted by using mass flow controllers. The water was fed through a HPLC pump and vaporized before mixing into the gas stream. The composition and the amount of gasifying agent were the other factors under study in this work. The mixture of oxygen, steam and approximately 2/3 of the total air required was fed into the fluidized bed reactor through its distribution plate, while the remaining air was fed with the solid to facilitate its movement through

the feeding pipe, which was externally refrigerated to prevent reactions taking place outside the bed.

The vapors and gases produced during gasification remained inside the reactor between 7 and 8 seconds 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. Next, the gases and vapors passed through two ice-cooled condensers, where water and condensable organic compounds (tar) were collected. A cotton filter was situated after the condensers in order to remove small particulates and aerosols swept by the gas. 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), which determined the volume percentages of H₂, O₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₂H₂ and H₂S. Water content in the condensed fraction was analyzed off line by Karl Fischer titration (so the amount of tar was determined by difference) and the tar composition was analyzed by gas chromatography with mass spectroscopy and flame ionisation detectors (MS/FID GC). The experiments were carried out during 90 min to ensure that the stationary state was reached [21].

2.3. Experimental design and data analysis

The influence of three operating factors (temperature, gasifying agent to biomass ratio and composition of the gasification medium) on sewage sludge gasification performance has been studied experimentally by means of a 2^k factorial design, where k indicates the number of factors studied (in this case 3) and 2^k represents the number of runs (in this case 8). Furthermore, three replicates at the center point (CP) were carried out in order to evaluate both the experimental error and the curvature shown by the evolution of each response variable, that is to say, whether this evolution is linear or not within the experimental range studied. This experimental design is suitable not only for

studying the influence of operating conditions, but also the influence of their possible interactions. An interaction occurs when a factor influences a response variable in a different way depending on the value of another factor.

The three analyzed factors were: (i) bed reactor temperature (which ranges 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 basis (*daf*) sewage sludge (which ranges between 0.8 and 1.1 g/g SS *daf*); (iii) nature of the gasification medium, represented by the H₂O/O₂ molar ratio (which ranges between 1 and 3). The overall flow rate of gasifying agent was kept constant when the H₂O/O₂ molar ratio was modified. These three factors together with their respective ranges of study were chosen on the basis of works of other authors concerning gasification of different kinds of biomass in fluidized bed reactors [9-12].

As can be seen in Table 2, the experimental design consists of 8 runs plus 3 replicates at the center point (810°C, 0.95 g/g SS *daf*, 2 mol H₂O/mol O₂). As usually occurs when an experimental design is planned, the lower and upper limits of the factors are coded as -1 (in this case T=770 °C, GR=0.8 and H₂O/O₂=1) and 1 (in this case T=850 °C, GR=1.1 and H₂O/O₂=3), respectively. The use of coded levels enables an easy identification of the term with the greatest influence on the response variable: the higher the coefficient, the more influential the factor.

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

Statistical analyses of the results have been carried out by analysis of variance (ANOVA), using the Design-Expert® 7 software (from Stat-Ease, Inc). ANOVA analysis evaluates whether the effect of the factors, the interactions between them and the curvature have a significant influence or not on the response variables. A confidence level of 95% for the F-distribution was selected to determine the significant effects.

3. Results and discussion

3.1. Distribution of products

Experimental results for the distribution of products are presented in Table 3.

Furthermore, as a result of the ANOVA analysis, Table 4 shows the relative influence of each factor on the product distribution. In this table, the average data represent the average of the whole set of results obtained for each response variable, the coefficients associated to the different factors (T, GR and H₂O/O₂) show how the response variables evolve when varying each factor (considering the coded values for the factors within the studied range), and the coefficients associated to the interactions show whether a factor influences a response variable in a different way depending on the value of another factor.

3.1.1. Solid yield and carbon content in the solid

The solid yield is defined as the mass (g) of solid product collected per 100 g of sewage sludge fed. Because of the high ash content in the sewage sludge (39 wt. %), the solid residue is an important by-product in its gasification process and its yield varied between 35 and 41 wt. %, whilst typical values for other kinds of biomass such as wood or straw are below 8 wt. % [22].

Carbon content in the solid product was analyzed using a Leco TruSpec Micro Elemental Analyzer (Table 3). According to the ANOVA results (Table 4), carbon

content in the solid product is reduced by increasing both the gasification temperature (higher reaction rate) and the gasifying ratio, and by decreasing the H₂O/O₂ ratio (Fig. 1), which seems to indicate that carbon oxidation is faster than its steam gasification. Although temperature is the most influential factor for the carbon reaction, its effect depends on other operating conditions, since its interaction with the H₂O/O₂ ratio is a significant term (Fig. 1a). This fact shows that carbon reactions with oxygen are more sensitive to temperature changes than the reactions with steam.

The results of the solid yield together with those of the carbon content in the solid (Table 3) suggest that inorganic ash compounds could have been released to the gas phase during the gasification process, since some data of solid yield are even below the original ash content of the sewage sludge (39 wt. %). Both the transformation and the release to gas phase of ash compounds during thermo-chemical processes have been shown in other studies [23, 24], although this was usually found to take place at higher temperatures.

3.1.2. Gas yield

The gas yield is defined as the volume of gas produced (m³_{STP} N₂-free basis, where STP means standard conditions of temperature and pressure at 0°C and 1 atm) per kilogram of SS *daf* fed. The gas yield data from the sewage sludge gasification varied between 0.89 and 1.32 m³_{STP}/kg SS *daf*, so these values are close to the typical ones found in the literature for similar operating conditions and different kinds of biomass [7, 9, 12].

The ANOVA analysis (Table 4) shows that the gas yield does not follow a linear response within the studied range of the factors, since the curvature is a significant term. Temperature is clearly the most influential factor for the production of gas. The significant increase of the gas yield with temperature may be due to different processes

that are favored by higher temperatures: greater production of gas in the initial stage of pyrolysis, cracking and steam reforming of tars and endothermic reactions of char gasification [12]. The increase of GR also favors the production of gas, although its effect is less significant than that corresponding to temperature. Significant interactions of temperature with both the GR and the H₂O/O₂ ratio have been found: the effect of temperature on the gas yield is intensified at the highest value of the GR (Fig. 2a) and at the lowest H₂O/O₂ ratio (Fig. 2b).

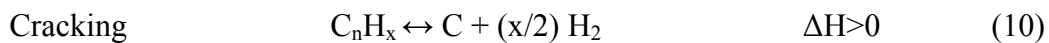
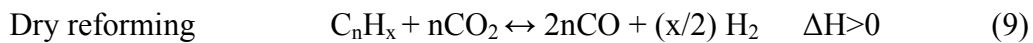
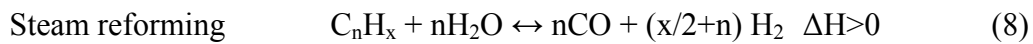
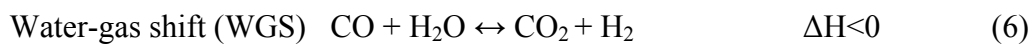
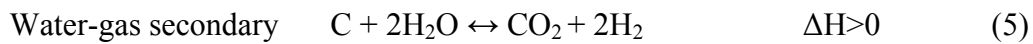
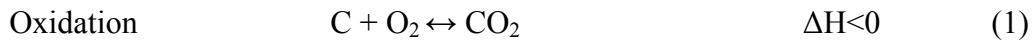
3.1.3. Tar content in the product gas

The tar content is defined as the mass (g) of condensable organic compounds collected in each experiment per m³_{STP} of dried gas measured after condensing the vapors. The lowest values of tar content obtained in this work are close to the typical values found for fluidized bed biomass gasifiers which, according to Corella et al. [25], usually range between 8 and 15 g/m³_{STP}.

As occurred with the gas yield, the tar content in the gas does not follow a linear response within the studied range of the factors, as the curvature is a significant term. Temperature is also the most influential factor for tar content (Table 4). The rise in the gasification temperature from 770 to 850 °C causes a clear reduction in tar formation (Fig. 3a) because of the enhancement of tar cracking and reforming reactions [6]. The tar content is also reduced by decreasing the H₂O/O₂ ratio in the gasification medium, suggesting that tar combustion reactions are faster than tar steam reforming, and by increasing the GR, although the effect of the latter factor is less significant. The influence of the GR on the tar content disappears when working at the highest temperature (Fig. 3a) or at the highest H₂O/O₂ ratio (Fig. 3b).

3.2. Gas composition

The gas composition from a gasification process is the result of many complex and competing reactions. The most representative of these reactions are given below:



As usual in a biomass gasification process, the main gases produced during sewage sludge gasification are H_2 , CO , CO_2 and light hydrocarbons, CH_4 being the most abundant of them. In addition, H_2S is also released during the process due to the presence of sulfur-compounds in the sewage sludge (Table 1). Statistical analyses of gas composition have not been included in this work because it was considered preferable to analyze the production or the specific yield of each gaseous compound (g/kg SS *daf*), as detailed in the next section.

The average gas composition (dry basis) obtained in each experiment is reported in Table 3. Considerable differences in the fractions of the gaseous compounds have been found. For example, H_2 (11.0-25.1 vol. %), CO (5.7-14.1 vol. %), CO_2 (12.6-23.8 vol. %) or CH_4 (2.6-4.1 vol. %) can double or halve their percentages depending on the operating conditions. These volume percentages lead to H_2/CO and CO/CO_2 molar ratios in the exit gas ranging from 1.46-3.25 and 0.29-0.88, respectively. The H_2/CO

molar ratio is an important parameter in view of possible end uses of the gas, and values close to 2 are usually required in processes such as methanol or Fischer Tropsch synthesis [26]. According to the ANOVA results (Table 4), the composition of the gasification medium is clearly the most influential factor for this ratio. The higher the H_2O/O_2 ratio used as gasifying agent, the higher the H_2/CO molar ratio obtained in the gas product. Working at lower temperatures also leads to an increase in the H_2/CO molar ratio.

The CO/CO_2 ratio shows how the carbon initially contained in the sewage sludge is distributed among both compounds. The higher the gasification temperature, the higher the CO/CO_2 ratio obtained in the product gas. Furthermore, the GR exerts a negative influence on the CO/CO_2 ratio, although its effect is less significant than that of the temperature.

3.3. Production of each gaseous compound

The production or yield of each analyzed gas (H_2 , CO , CO_2 , CH_4 , C_2H_x and H_2S) is defined as the mass (g) of each gas produced per kilogram of SS *daf* fed.

Both experimental and theoretical yields of gases are analyzed in this section. The theoretical production of each gas during sewage sludge gasification at equilibrium conditions has been determined using HSC Chemistry® 6.1 software, simulating the same operating conditions that had been previously tested in the laboratory, that is, following the same 2^k factorial design. According to the theoretical results obtained, the gas product from sewage sludge gasification at equilibrium conditions should only contain H_2 , CO , CO_2 , CH_4 , H_2S and NH_3 .

The experimental and the theoretical yields of gases are compared in Fig. 4. The points in the same vertical line represent the results obtained under the same operating conditions. As can be seen, experimental and theoretical data appreciably differ one

from the other, which means that equilibrium was not reached during the experimental runs, maybe due to insufficient residence time of the gases in the reactor. Experimental yields of H₂ and CO are clearly below their corresponding theoretical data (up to four and five times lower in the most unfavorable conditions, respectively). The lower the gasification temperature, the greater is the difference between the experimental and the theoretical data. In contrast, experimental yields of CO₂ and CH₄ are above their corresponding theoretical values. CH₄ is mainly produced during the pyrolysis step and is hardly reformed during the subsequent process.

The experimental and theoretical yields of gases have been analyzed statistically by means of ANOVA. In the case of the theoretical results, most of the yields revealed a curvature, so the design was augmented with central composite points in order to determine the evolution of the response variables in the studied ranges and to find out which factor(s) is (are) causing the curvature. Table 5 presents the ANOVA results for both the experimental and the theoretical results.

As can be seen in Table 5, temperature is the most influential factor for the experimental yield of H₂. Although this gas is involved in many reactions both as reactant and as product, the temperature rise leads to a global increase in its experimental yield. The same trend for H₂ production has usually been reported in the literature [11, 12, 27]. Although to a lesser extent, the H₂ experimental yield is also enhanced by increasing the H₂O/O₂ ratio. On the one hand, the increase in the steam presence favors H₂ formation (4, 5, 6, 8) and, on the other hand, H₂ combustion is mitigated by reducing the proportion of oxygen in the gasification medium. The GR affects the experimental production of H₂ in a negative way: H₂ consumption outweighs H₂ formation when both the ER and the S/B ratio are increased. In contrast to the experimental results, the H₂O/O₂ ratio is the most influential factor for the theoretical

yield of H₂ (Table 5) and it is also the factor responsible for the curvature observed. The influence of the temperature is much less significant in this case and, unlike the experimental results, this factor adversely affects the theoretical production of H₂. The WGS reaction (6) may explain this observed trend at equilibrium conditions due to its exothermic nature.

As occurred with the H₂ experimental yield, temperature is the most influential factor for the experimental production of CO (Table 5). Higher temperatures favor the production of CO through reactions such as steam and dry reforming (8, 9), the Boudouard reaction (3) or the water-gas primary reaction (4). However, negligible variations or even the opposite trend in CO production are found in the literature [10, 11], which reveals the importance of the nature of the biomass and the operating conditions in the evolution of CO production. Both the GR and the H₂O/O₂ ratio affect the experimental yield of CO in a negative way. When the GR is increased, the higher amount of oxygen fed to the gasifier promotes the oxidation of CO to CO₂ and, in addition, the higher presence of steam favors CO consumption through the WGS reaction. Moreover, the negative effect of the H₂O/O₂ ratio might indicate that the consumption of CO in the WGS reaction outweighs its combustion process. Both negative effects are significantly intensified at higher temperatures. In contrast to the experimental results, the GR is the most influential factor for the theoretical production of CO (Table 5) and the H₂O/O₂ ratio shows a positive effect. The three interactions between the factors are significant terms in the theoretical production of CO: (i) the negative effect of the GR is slightly reduced when working at high temperatures, maybe due to the endothermic nature of the Boudouard reaction (in which CO is produced); (ii) the positive effect of the temperature is slightly reduced when working at high H₂O/O₂ ratios, since increasing the steam presence shifts the WGS equilibrium towards CO

consumption; (iii) the negative effect of the GR is intensified when the highest H_2O/O_2 ratio is used as gasification medium.

Regarding the production of CO_2 , the GR is the most influential factor for both the experimental and the theoretical yields (Table 5). When the GR is increased more oxygen and steam are fed to the gasifier, thus the increased production of CO_2 can be attributed to a higher extent of combustion reactions, as well as to other reactions promoted by the presence of steam, such as the WGS reaction (6) or the secondary water-gas reaction (5), in which CO_2 is produced. The positive effect of the GR on the experimental yield of CO_2 is intensified at higher temperatures and lower H_2O/O_2 ratios. Although to a lesser extent, the increase in the H_2O/O_2 ratio negatively affects the production of CO_2 . This trend suggests that combustion reactions are the main source of CO_2 . In contrast to the theoretical results, the experimental yield of CO_2 is not significantly influenced by the temperature. Theoretical results show that CO_2 and CO yields are influenced by the same significant factors and interactions, but all of them show opposite effects since CO production is normally linked with CO_2 consumption, and vice versa (3, 6, 9).

Regarding the experimental production of light hydrocarbons (CH_4 and C_2H_x), the H_2O/O_2 ratio is the most influential factor for it (Table 5). Increasing the H_2O/O_2 ratio in the gasification medium enhances the production of both CH_4 and C_2H_x , thus suggesting that the steam reforming of light hydrocarbons occurs more slowly than its combustion process. The formation of CH_4 via the methanation reaction (7) may also be promoted by increasing the H_2O/O_2 ratio due to an increased presence of H_2 in the gasification medium. Although to a lesser extent, CH_4 production is negatively affected by the increase in the GR, as its combustion and steam reforming reactions are promoted by increasing the ER and the S/B ratio, respectively. This expected effect is

not observed for the C_2H_x experimental yield probably because of its large experimental variability. Unlike the results shown by other authors [12, 27], the experimental yield of CH_4 is found to increase slightly with the temperature, maybe as a result of the thermal cracking of heavier hydrocarbons, while the experimental yield of C_2H_x follows the opposite trend with temperature. In relation to the theoretical results, the presence of C_2H_x in the equilibrium gas is practically negligible. CH_4 is produced at equilibrium conditions, but its theoretical yield is much lower than its experimental yield. Temperature is the most influential factor for the theoretical yield of CH_4 (Table 5). It has a negative effect due to the enhancement of the endothermic reactions in which CH_4 is consumed, such as steam and dry reforming (8, 9), and the restriction of the methanation reaction (7) due to its exothermic nature. The negative effect of the temperature on the theoretical yield of CH_4 is intensified by increasing the H_2O/O_2 ratio and/or decreasing the GR. The temperature also seems to be the factor responsible for the curvature shown by the theoretical yield of CH_4 .

Lastly, according to the ANOVA results, the experimental production of H_2S is favored by increasing both the temperature and the GR, although the effect of the latter is slightly smaller than that of the temperature (Table 5). In contrast to the experimental results, non-significant influences of the studied factors on the theoretical production of H_2S have been found within the studied intervals. H_2S is the only sulfured-compound considered in the equilibrium gas, thus a constant yield of H_2S has been obtained for all the simulated conditions (25.54 g/kg SS *daf*).

3.4. Lower heating value of the product gas

The lower heating value of the gas (LHV_{gas}) is calculated as $\sum (x_i \cdot LHV_i)$, where x_i and LHV_i are the volumetric fraction and the lower heating value (MJ/m^3_{STP}) of each gaseous component, respectively. The LHV of the product gas obtained from the

sewage sludge gasification ranged between 4.12 and 6.20 MJ/m³_{STP}, thus this gas can be considered as a low heating value gas. Similar values of LHV_{gas} are usually reported in the literature for air gasification or air-steam gasification of other kinds of biomass [5].

As a result of the ANOVA analysis, Table 5 presents the coded coefficients that explain the influence of the factors on the theoretical and experimental gas heating values. As can be seen, the theoretical gas heating values are higher than those obtained experimentally under the same operating conditions. The lower production of CO₂ obtained at equilibrium conditions compared to its experimental production leads to a lower dilution effect of the gas from the energy point of view, which outweighs the lower production of light hydrocarbons (gas components with the highest heating value) at equilibrium conditions.

The composition of the gasification medium is the most influential factor for the experimental LHV_{gas}. When the H₂O/O₂ ratio is increased, the hydrocarbon content increases and the CO₂ content decreases, so both effects contribute to improve the LHV_{gas}. The influence of temperature on the experimental LHV_{gas} is almost as important as that of the composition of the gasification medium. Although the experimental production of CO₂ (in terms of g/kg SS *daf*) is not affected by the temperature, this result is not the same when considering the concentration data, since a clear reduction in the CO₂ fraction with temperature is observed (Table 3). The effect of this reduced fraction of CO₂ on the gas calorific value is more significant than that of the reduced fraction of light hydrocarbons, so a global positive effect of temperature on the LHV_{gas} has been found in this study. In contrast to this, results in the literature usually show a negative effect of the temperature on the LHV_{gas} [12], thus showing that the evolution of the gas composition depends on the raw material and the operating conditions. Although its effect is slightly smaller, the GR negatively affects the

experimental LHV_{gas} , since both the production of CO_2 and the consumption of light hydrocarbons are favored at higher GR.

The theoretical results show that the GR and the $\text{H}_2\text{O}/\text{O}_2$ ratio have almost the same relative influence on the LHV_{gas} , whereas the gasification temperature does not affect it significantly (Table 5).

3.5. Cold gasification efficiency

The cold gasification efficiency is defined as the ratio between the energy contained in the gas product ($\text{m}^3_{\text{STPgas}} \cdot LHV_{\text{gas}}$) and the energy contained in the mass of sewage sludge fed ($\text{kg}_{\text{SS}} \cdot LHV_{\text{SS}}$). Cold gasification efficiency assumes a temperature of 25 °C of the product gases, so the sensible heat of the gas is not taken into account.

The experimental values of cold gasification efficiency varied between 39 and 66% and, according to the ANOVA results (Table 5), the temperature and the $\text{H}_2\text{O}/\text{O}_2$ ratio are the only factors that affect it significantly. Temperature is the most influential factor and its variation from 770 to 850 °C improves the cold gasification efficiency by 17%. This enhancement is based on the increase of both LHV_{gas} and gas production with temperature. Although to a lesser extent, the $\text{H}_2\text{O}/\text{O}_2$ ratio also affects the experimental gasification efficiency in a positive way, since the LHV_{gas} increases with the $\text{H}_2\text{O}/\text{O}_2$ ratio and the production of gas is not affected by it.

The theoretical cold gasification efficiencies are much higher than the experimental data. Unlike the experimental results, the $\text{H}_2\text{O}/\text{O}_2$ ratio is the most influential factor for the theoretical cold gasification efficiency, as well as being the factor responsible for the curvature exhibited by the results. As occurred with the theoretical LHV_{gas} , increasing the GR negatively affects the theoretical cold gasification efficiency, whereas the gasification temperature does not affect it significantly.

3.6. Carbon yield to gas phase

The carbon yield to gas phase is defined as the ratio between the mass of carbon contained in the product gas and the mass of carbon contained in the sewage sludge fed. The conversion of solid carbon during the sewage sludge gasification reached 76-98 wt. %. However, not all the solid carbon leads to the formation of gaseous compounds, as tar is also produced. Therefore, the experimental results of carbon yield to gas phase are slightly lower than the aforementioned range (62-90 wt. %), whereas a carbon yield to gas phase of 100% is expected at equilibrium conditions.

According to the ANOVA results (Table 5), carbon yield to gas phase shows a linear response with the factors within the studied intervals. Temperature is the most influential factor, and its variation from 770 to 850 °C improves the carbon yield to gas phase by 13 wt. %. The rise in temperature not only favors the heterogeneous reactions between the carbon contained in the sewage sludge and the gas compounds (3, 4, 5), but also enhances the tar cracking and reforming reactions, so a greater amount of carbon leaves the gasifier as part of the product gas. The effect of the gasification medium is slightly lower than that of the temperature. Carbon yield to gas phase is increased at higher fractions of oxygen and lower fractions of steam, which suggests that carbon oxidation reactions (1, 2) take place faster than the heterogeneous water-gas reactions (4, 5). To a lesser extent, carbon yield to gas phase is also favored by the GR, since a greater amount of gasifying agent is available to react with the carbon contained in the sewage sludge.

3.7. Tar composition

The tar composition was analyzed by gas chromatography (MS/FID GC). Fig. 5 shows a representative chromatogram of the components detected in most of the tar

samples. Some researchers have divided tar components into several groups based on their molecular weight [28]. A similar classification of tar compounds has been considered in this work in order to analyze the effect of the operating conditions on the fractions of the following families of compounds: heterocyclic aromatics containing N (including n-methyl-pyridine, benzonitrile, n-methyl-benzonitrile, quinoline, n-methyl-quinoline, indole, n-phenyl-pyridine, n-naphthalenecarbonitrile, benzoquinoline and 5H-indeno[1,2-b]pyridine); heterocyclic aromatics containing O (phenol and benzofuran); compounds containing S (2-benzothiophene and propanenitrile, 3,3'-thiobis-); light aromatics with 1 ring (styrene) and light PAH compounds with 2 or 3 rings (indene, naphthalene, n-methyl-naphthalene, biphenyl, biphenylene, fluorene, anthracene and phenantrene).

The areas of the main peaks shown by the GC-FID have been used to compare the composition of the different samples. Therefore, the results presented in this work do not represent actual compositions of the tar samples, but they are useful for analyzing how the factors influence the fraction of each family of compounds. The percentages of the GC-FID-areas obtained for each sample are shown in Table 6. According to the ANOVA results, the temperature and the H_2O/O_2 ratio are the only factors affecting tar composition. Light aromatics and O-aromatics are the most sensitive families to temperature. Their fractions are found to decrease with temperature. Similar results have been reported by other researchers [29], showing that phenolic compounds, paraffines, olefins and alkylated aromatics are easily cracked at high temperatures. The S-compounds fraction has been found to increase with temperature, probably as a result of the aforementioned decrease in the fractions of other compounds.

On the other hand, N-aromatics and light PAH fractions are the most sensitive families to the H_2O/O_2 ratio. The increase in this ratio leads to a decrease in the fraction

of light PAHs, thus the presence of steam seems to prevent the polymerization reactions. According to Corella et al. [30], tars generated in gasification with steam are easier to eliminate than tars generated in gasification with air. Tar molecular weight depends on the presence of H free radicals, which is related to the steam added during gasification [31]. A simultaneous increase in the fraction of N-aromatics was found, but this may only be a consequence of the aforementioned decrease in the light PAH fraction.

4. Conclusions

Temperature was found to be the most influential factor for most of the response variables analyzed during sewage sludge gasification. Higher temperatures are favorable for reducing the tar content and improving the gas yield, the gasification efficiency and the carbon yield to gas phase. On the other hand, the gas heating value and the H₂/CO molar ratio in the product gas are clearly favored by increasing the steam presence and reducing the oxygen presence in the gasification medium. The significant differences between the theoretical and the experimental yields of gases, as well as the differences in the effects of the factors, show how important it is to distinguish between kinetic and thermodynamic control in a gasification process.

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Table 1. Proximate and ultimate analyses and heating value of sewage sludge.

Proximate analysis (wt. %, wet basis)	
Moisture	6.48
Ash	39.04
Volatiles	50.09
Fixed carbon	4.39
Ultimate analysis (wt. %, wet basis)	
C	29.5
H	4.67
N	5.27
S	1.31
HHV (MJ·kg ⁻¹)	12.8
LHV (MJ·kg ⁻¹)	11.8

Table 2. Operating conditions of gasification tests.

Experiment number	1	2	3	4	5	6	7	8	9, 10, 11
Coded values	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 (°C)	850	770	850	770	850	770	850	770	810
g gasifying agent/g sewage sludge <i>daf</i>	1.1	1.1	0.8	0.8	1.1	1.1	0.8	0.8	0.95
H ₂ O/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 biomass <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

Table 3. Experimental results: product distribution and gas composition.

	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*
Product distribution									
Solid yield (g solid/100 g SS)	36.8	40.1	40.1	40.7	35.6	39.2	38.4	40.0	38.2 ± 0.1
Carbon content in the solid product (wt. %)	4.56	7.61	5.66	10.20	0.51	6.20	1.00	7.09	5.89 ± 0.33
Gas yield (m ³ _{STP} /kg SS)	0.72	0.51	0.65	0.53	0.72	0.52	0.71	0.49	0.61 ± 0.01
Gas yield (m ³ _{STP} /kg SS <i>daf</i>)	1.32	0.94	1.20	0.97	1.32	0.96	1.30	0.89	1.13 ± 0.01
Tar content (g/m ³ _{STP})	18.8	43.6	18.6	44.5	12.1	22.4	10.9	45.3	14.8 ± 1.4
Gas composition (vol. %, dry basis)									
H ₂	24.2	18.4	25.1	20.4	18.0	11.0	20.6	13.6	19.3 ± 0.1
CO	8.7	5.7	10.2	7.3	11.6	7.0	14.1	7.7	9.4 ± 0.1
CO ₂	17.1	18.6	12.6	15.5	20.7	23.8	16.0	19.8	18.1 ± 0.2
CH ₄	3.1	3.5	3.6	4.1	2.6	2.8	2.9	3.4	3.3 ± 0.1
C ₂ H _x	1.7	2.1	1.4	2.2	1.3	1.6	1.4	2.0	1.7 ± 0.2
H ₂ S	0.44	0.38	0.33	0.33	0.44	0.42	0.38	0.31	0.40 ± 0.02
N ₂	44.9	51.4	46.8	50.2	45.3	53.4	44.5	53.2	47.8 ± 0.2
H ₂ /CO molar ratio	2.79	3.25	2.46	2.81	1.54	1.57	1.46	1.77	2.06 ± 0.01
CO/CO ₂ molar ratio	0.51	0.30	0.81	0.47	0.56	0.29	0.88	0.39	0.52 ± 0.01

*mean value ± standard deviation

Table 4. Relative influence of the significant factors on the carbon content in the solid product, gas yield, tar content in the gas, and H₂/CO and CO/CO₂ molar ratios in the product gas.

	Carbon content in the solid (wt. %)	Gas yield (m ³ _{STP} /kg SS <i>daf</i>)	Tar content in the gas (g/m ³ _{STP})	H ₂ /CO molar ratio in the gas	CO/CO ₂ molar ratio in the gas
Average	5.50	1.12	27.03	2.21	0.52
T	-2.42	0.17	-11.91	-0.14	0.16
GR	-0.63	0.019	-2.78	0.081	-0.11
H ₂ O/O ₂	1.65	*	4.35	0.62	*
T-GR	*	0.017	3.15	0.021	-0.044
T-(H ₂ O/O ₂)	0.53	-0.024	*	-0.059	-0.026
GR-(H ₂ O/O ₂)	*	*	2.62	0.11	*
T-(H ₂ O/O ₂)-GR	*	0.028	-2.89	-0.049	*
Curvature	*	**	**	**	*

*non-significant term; **curvature is significant

Table 5. Relative influence of the significant factors on the yield of each gaseous compound, the lower heating value of the gas, the cold gasification efficiency and the carbon yield to gas phase (experimental and theoretical results).

	Yield of gaseous compounds (g/kg SS <i>daf</i>)						LHV _{gas} (MJ/m ³ _{STP})	Cold gasification efficiency (%)	Carbon yield to gas phase (%)
	H ₂	CO	CO ₂	CH ₄	C ₂ H _x	H ₂ S			
<i>Coefficients obtained for the experimental results</i>									
Average	37.03	250.10	763.42	50.23	46.13	12.66	5.49	55.12	72.48
T	9.06	78.79	*	1.49	-3.28	1.73	0.37	8.51	6.33
GR	-1.37	-17.51	101.57	-3.13	*	1.56	-0.31	*	3.33
H ₂ O/O ₂	5.68	-32.67	-92.53	4.80	3.35	*	0.40	3.47	-6.07
T-GR	*	-5.03	21.59	*	*	*	*	*	*
T-(H ₂ O/O ₂)	*	-21.95	*	*	*	*	-0.17	*	*
GR-(H ₂ O/O ₂)	*	*	-14.93	*	*	*	*	*	*
T-(H ₂ O/O ₂)-GR	*	9.65	15.91	*	*	0.62	*	*	*
Curvature	*	*	*	*	*	*	*	*	*
<i>Coefficients obtained for the theoretical results</i>									
Average	99.53	883.23	595.21	0.60	--	25.54	6.56	98.47	100
T	-1.19	24.54	-36.44	-0.76	--	*	*	*	*
GR	-3.09	-86.09	136.58	-0.46	--	*	-0.35	-5.64	*
H ₂ O/O ₂	14.85	36.77	-58.69	0.32	--	*	0.34	9.94	*
T-GR	*	4.96	-8.85	0.38	--	*	*	*	*
T-(H ₂ O/O ₂)	*	-4.34	7.57	-0.27	--	*	*	*	*
GR-(H ₂ O/O ₂)	2.34	15.66	-24.30	*	--	*	0.12	2.00	*
T-(H ₂ O/O ₂)-GR	*	*	*	*	--	*	*	*	*
(H ₂ O/O ₂) ²	-4.44	-11.12	16.84	*	--	*	*	-2.39	*
T ²	*	*	*	0.42	--	*	*	*	*
GR ²	*	*	*	*	--	*	*	*	*

*non- significant term

Table 6. Tar composition (percentage of area in the GC-FID signal of each family of tar compounds).

Experiment	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*
N-aromatics	74.6	68.2	57.1	68.7	46.5	44.0	44.7	60.5	50.0 ± 14.4
O-aromatics	3.0	7.7	0.34	7.7	0.6	2.1	1.0	6.0	2.6 ± 0.8
S-compounds	3.6	2.9	4.4	5.1	7.9	2.5	5.7	1.0	4.9 ± 0.1
Light aromatics (1 ring)	9.7	12.2	4.4	13.4	5.1	9.9	3.6	9.8	6.5 ± 1.8
Light PAH compounds (2-3 rings)	9.1	9.1	33.8	5.14	39.9	41.5	45.0	22.7	36.0 ± 8.8

*mean value ± standard deviation

Carbon content in the solid (wt. %)

Carbon content in the solid (wt. %)

Fig. 1. Carbon content in the solid product (wt. %). (a) Interaction between temperature and $\text{H}_2\text{O}/\text{O}_2$ molar ratio (GR=0.95). (b) Effect of the gasifying ratio ($T=810\text{ }^\circ\text{C}$; $\text{H}_2\text{O}/\text{O}_2=2$).

Gas yield ($\text{m}^3_{\text{STP}} / \text{kg SS daf}$)

Gas yield ($\text{m}^3_{\text{STP}} / \text{kg SS daf}$)

Fig. 2. Gas yield. (a) Interaction between temperature and gasifying ratio ($\text{H}_2\text{O}/\text{O}_2=2$);
(b) Interaction between temperature and $\text{H}_2\text{O}/\text{O}_2$ molar ratio ($\text{GR}=0.95$).

Tar content (g / m³_{STP})

Tar content (g / m³_{STP})

Fig. 3. Tar content in the gas. (a) Interaction between temperature and gasifying ratio ($H_2O/O_2=2$); (b) Interaction between H_2O/O_2 and gasifying ratio ($T=810\text{ }^\circ\text{C}$).

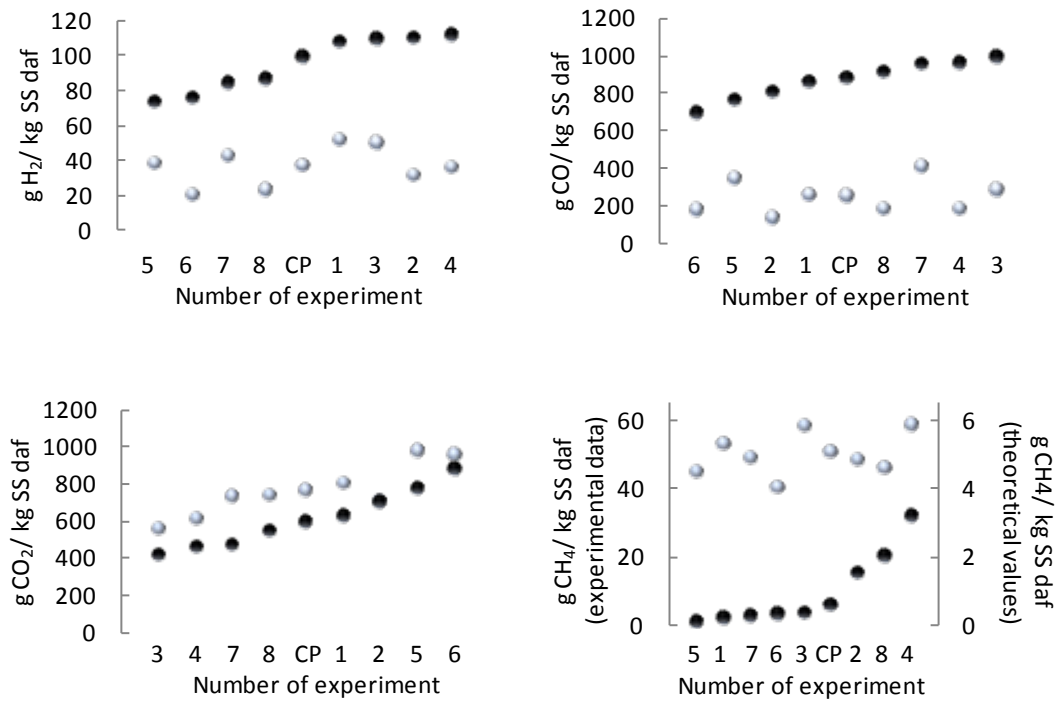
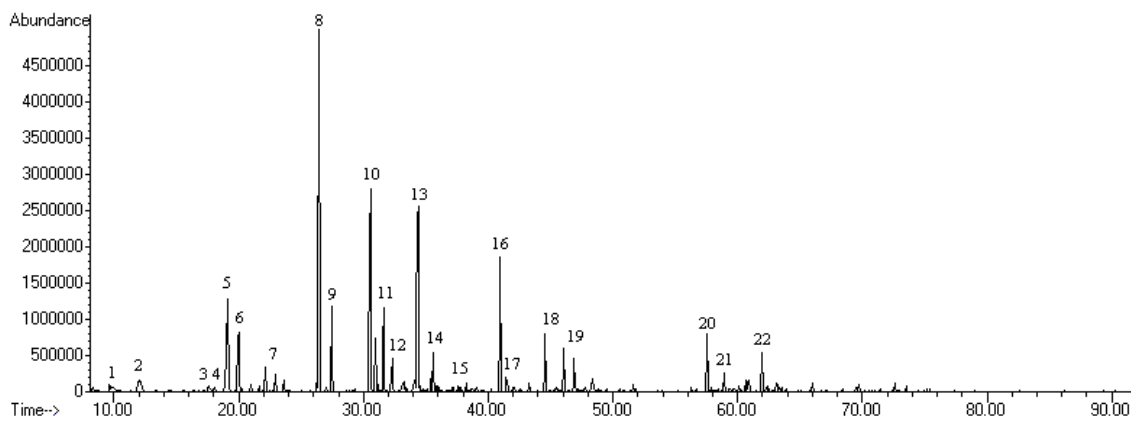


Fig. 4. Theoretical (●) and experimental (●) production of H_2 , CO , CO_2 and CH_4 .



1. Pyridine, n-methyl- (9.6)	9. 2-Benzothiophene (27.5)	17. n-Naphthalene carbonitrile (44.5)
2. Styrene (11.9)	10. Quinoline (30.6)	18. Fluorene (46.9)
3. Phenol (17.5)	11. Naphthalene, n-methyl- (31.0)	19. Propanenitrile, 3,3'-thiobis- (48.4)
4. Benzofuran (17.6)	12. Quinoline, n-methyl- (33.1)	20. Anthracene / Phenanthrene (57.6)
5. Benzotrile (19.2)	13. Indole (34.3)	21. Benzoquinoline (58.9)
6. Indene (20.0)	14. Biphenyl (35.6)	22. 5H-Indeno[1,2-b]pyridine (61.9)
7. Benzotrile, n-methyl- (22.1)	15. Biphenylene (40.9)	
8. Naphthalene (26.4)	16. Pyridine, n-phenyl- (41.4)	

Fig. 5. Total ion chromatogram (TIC) of a tar sample obtained at 850 °C, GR=0.8 and H₂O/O₂ molar ratio=3.