

# SEWAGE SLUDGE VALORISATION BY MEANS OF PYROLYSIS AND GASIFICATION

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## ABSTRACT

In this work, the main results about the investigations into the pyrolysis and the gasification of sewage sludge of the Thermo-chemical Processes Group are being presented. Pyrolysis has been carried out in three different experimental systems: two kinds of fixed bed reactors and a fluidized bed reactor. In these experiments, the influence of the operational conditions on product distribution and on some characteristics of these products has been studied. Pyrolysis of sewage sludge in fluidized bed has been studied in order to maximize liquid fuel product yield and optimize its composition. In fixed bed pyrolysis experiments, the influence of pyrolysis conditions on the production of a solid product (char) and its adsorbent properties have been studied. Gasification of sewage sludge has been studied in fluidized bed with the aim of finding the operational conditions that maximize the production of gas and minimize the presence of tar in this gas.

## KEYWORDS

Sewage sludge; Pyrolysis; Gasification; Waste valorisation, Laboratory scale plant.

## 1 INTRODUCTION

Sewage sludge is the solid waste left over when the wastewater treatment plants have done their work. This waste consists of a complex heterogeneous mixture of organic and inorganic materials [1]. Depending on its origin, it can contain heavy metals, pathogens and other substances that can be dangerous for the environment and for the human health. Due to the rising legal limitations concerning water disposal, the production of this waste is increasing [2]. The most usual ways to manage this waste are agricultural land application, composting and landfilling. Due to the hazardous composition of some sewage sludge, not all of them can be used in agricultural applications. Landfilling is not a good solution as the sewage sludge is not valued, heavy metals can leach and, moreover, a lot of space is needed. Therefore, it is necessary to raise new alternatives, such as energetic applications, to manage it in a safe way for the environment.

Pyrolysis and gasification are two of the technologies that are being studied in this sense, presenting different product applications [3, 4]. By means of gasification, a gas with a certain heating value to generate heat or electricity when burnt is produced. In pyrolysis processes, diesel-like oil is obtained, and also a solid byproduct called char, that could be used for the

preparation of adsorbents under certain conditions [5]. At the same time, in these processes, pathogenic bacteria destruction and volume reduction are accomplished.

The application of these technologies to sewage sludge has not been entirely optimized yet. In the case of gasification, the main drawback is the high tar and dust content of the synthesis gas produced [6]. In the case of pyrolysis, some difficulties are found when fitting the properties of pyrolysis liquid in order to use it in the same way as conventional oil [7]. In the Thermo-chemical Processes Group (GPT) of the University of Zaragoza, the energetic and environmental optimization of pyrolysis and gasification has been investigated in laboratory scale plants. In this sense, the group has worked in finding out the operational conditions that optimize the energy obtained in these processes. In this work, data about product distribution and energetic profitability will be presented, for each one of these processes.

## 2 MATERIALS

The sewage sludge used in this study comes from a wastewater treatment plant in Madrid. It has been anaerobically digested and thermally dried. Prior to its usage in the laboratory plants, it has been crushed and sieved to a size range that depends on the reaction system used.

Because of its origin, sewage sludge composition presents a very high ash percentage compared with other residues or biomasses. Proximate and ultimate analyses were made to the received sewage sludge (see *Table 1*).

*Table 1: Proximate analysis (moisture basis) and ultimate analysis (moisture basis).*

Parameter	Analytical standard	% by weight	Parameter	Equipment used	% by weight
Moisture	ISO-589-1981	6.74	Carbon	Carlo Erba 1108	28.54
Ash	ISO-1171-1976	39.87	Hydrogen*	Carlo Erba 1108	4.32
Volatiles	ISO-5623-1974	46.96	Nitrogen	Carlo Erba 1108	4.14
Fixed Carbon	By difference	6.43	Sulfur	Carlo Erba 1108	0.76

\*The % of hydrogen includes the hydrogen of the moisture.

## 3 EXPERIMENTAL SYSTEM

### 3.1 Fluidized bed reactor plant

The experiments of sewage sludge pyrolysis and gasification were carried out in the same experimental plant, with some modifications for each one. The laboratory scale plant operates at atmospheric pressure, with continuous feed of solids and fluidizing gas (nitrogen in case of pyrolysis, and air for gasification), and also with a continuous ash removal system. The experimental plant is shown in *Figure 1*.

Sewage sludge is smashed and sieved to provide a feed sample in the size range of 250-500  $\mu\text{m}$ , sand is also sieved in the size range 150–250  $\mu\text{m}$  in pyrolysis experiments, and 150–250  $\mu\text{m}$  in gasification experiments. Sewage sludge and sand, in weight proportion 100:20, are fed to the reactor by a variable speed screw feeder through a sloping pipe, entering the reactor 10 mm above the distributor plate. The slopping pipe is refrigerated with air in order to avoid that the reaction takes place in the pipe.

Two thirds of the fluidizing gas flow rate is introduced through the distributor plate in order to get the bed fluidizing, and the rest of the flow goes into the reactor together with the solid feed in order to facilitate its entry. The gas flow rate is controlled by a mass flow controller.

The fluidized bed reactor is made of refractory steel (AISI 310), with an inner diameter of 38 mm and a height of 800 mm. Depending on the aim of experiment, the bed reactor is filled with sand, a mixture of char and sand, or a mixture of sewage sludge ash and sand. Char and ash are obtained from previous experiments. The bed is filled with these mixtures in order to minimize the non-stationary period [8]. The bed height is kept constant at two different height (150 mm and 300 mm), by means of a concentric pipe, with a diameter of 12 mm, which goes through the distributor plate, enabling the bed material to overflow and be collected in a char vessel. This system to remove the ash is very useful for materials with so many quantity of ash, such as sewage sludge.

The reactor is heated by two electrical furnaces, one for the bed and another for the free-board. The temperature of the bed zone is controlled by a temperature controller, by means of this controller the bed temperature is kept constant at the experiment temperature. Then there is a cyclone, which is heated by an electrical furnace and its temperature is controlled and kept at 450°C (for pyrolysis experiments) in order not to crack the pyrolysis vapours because the temperature was too high and in order not to condense the vapours because the temperature was too low. In case of gasification this temperature is kept at 400°C in order to avoid heavy tar condensation.

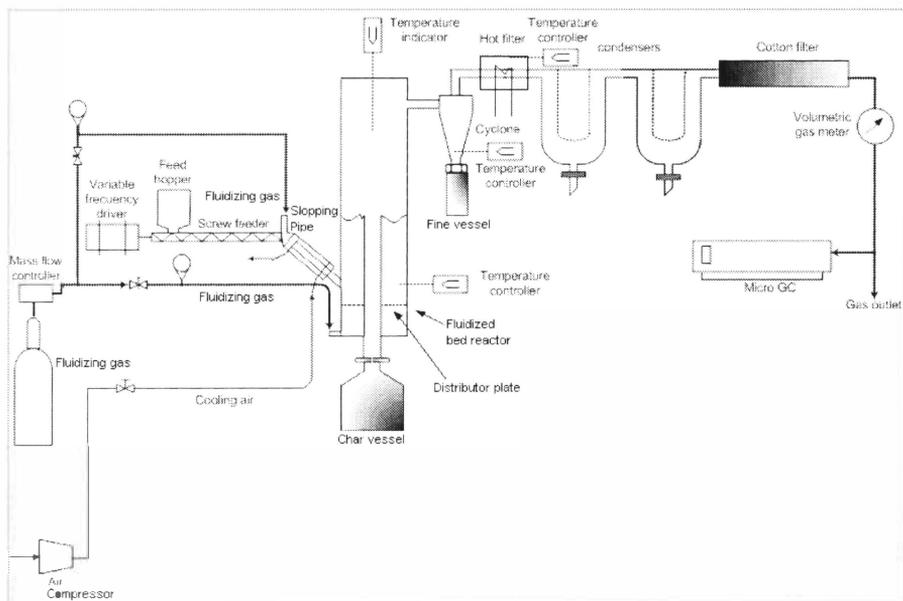
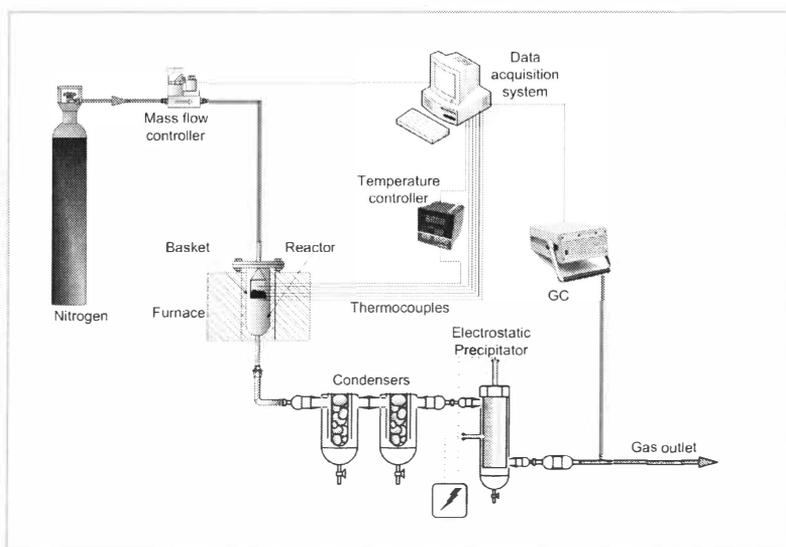


Figure 1. Schematic diagram of the fluidized bed laboratory plant.

After the cyclone, there is a hot filter, where more solids are removed from vapours. In pyrolysis experiments, it is important to separate the solid particles because they make the liquid stability decrease, possibly due to the catalytic effect. In case of gasification process, it is desirable to obtain a gas free of particles. The temperature of this filter is also kept at 450°C in pyrolysis, and 400°C in gasification. After the heated filter, the liquid recover system is located. The liquid recover system is composed by two cooled condensers and a cotton filter. The condensers are cooled with ice, water and salt in order to get 0°C. When the gas flow arrives at the liquid recover system, the organic vapours and the water condensate. The high heating value of the liquid product is determined in a calorimetric bomb. Once the gas flow has left the liquid recover system, it is just formed by non-condensable gases (NCG). The production of non-condensable gases is measured by a volumetric gas meter. The gas composition is determined by means of a micro gas chromatograph (Agilent 3000A) connected online to the process.

### 3.2 Fixed bed slow pyrolysis reactor

As pyrolysis heating rate could play an important role in pyrolysis products characteristics, two different fixed bed pyrolysis plants were developed in order to achieve low or high heating rates of the samples. Pyrolysis of sewage sludge at low heating rates (up to 15°C/min) can be performed in the fixed bed reaction system shown in *Figure 2*. The reactor consists of a vertical cylindrical refractory steel tube placed into an electrical furnace. Sewage sludge samples are placed into a steel basket that hangs from a steel wire. The wire end is fixed to the top of the reactor. The basket is centred inside the reactor and suspended at a certain height (determined in preliminary experiments) that minimises temperature profiles along the sample. Up to 6 thermocouples can be used to measure the sample temperature during pyrolysis. A temperature controller enables adequate sample heating rate and final temperature for each experiment.



*Figure 2. Schematic diagram of fixed bed slow pyrolysis reactor.*

Nitrogen is chosen as inert gas passing through the reactor, to ensure pyrolysis atmosphere during the experiments. A mass flow controller is used to provide constant and precise inert gas flow through the entire system.

Gaseous and condensable fractions generated during pyrolysis are carried out of the reactor by the nitrogen flow. This mixture flows then through the gas cleaning system. In the first stage of gas cleaning, two ice condensers cool down the gas, so most of the condensable fraction (consisting of bio-oil and water) is collected. Then, an electrostatic precipitator achieves collection of the rest of the volatiles, due to the high voltage applied between its electrodes. The composition of permanent gases that flow outside the cleaning system is determined by means of an Agilent 3000A GC-TCD chromatograph in a semi-continuous manner.

Product distribution for a pyrolysis experiment can be determined combining gravimetric measurements of condensable and solid (char) fractions with chromatographic analyses of the gases. The steel basket dimensions allow a maximum sewage sludge capacity of 30 g. Sewage sludge is smashed and sieved to provide a feed sample in the size range of 250-500  $\mu\text{m}$ .

For all slow pyrolysis experiments, the samples were left into the reactor for 1 hour (isothermal time) after the target temperature was reached at the selected heating rate.

### 3.3 Fixed bed fast pyrolysis reactor

Because of the limited heating rates that can be achieved in the system mentioned above (up to 15 $^{\circ}\text{C}/\text{min}$ ), another fixed bed reaction system was designed. This newer system was intended to be used in order to perform fast pyrolysis experiments (sudden heating of the sample from room temperature). A scheme of the experimental system can be seen in *Figure 3*.

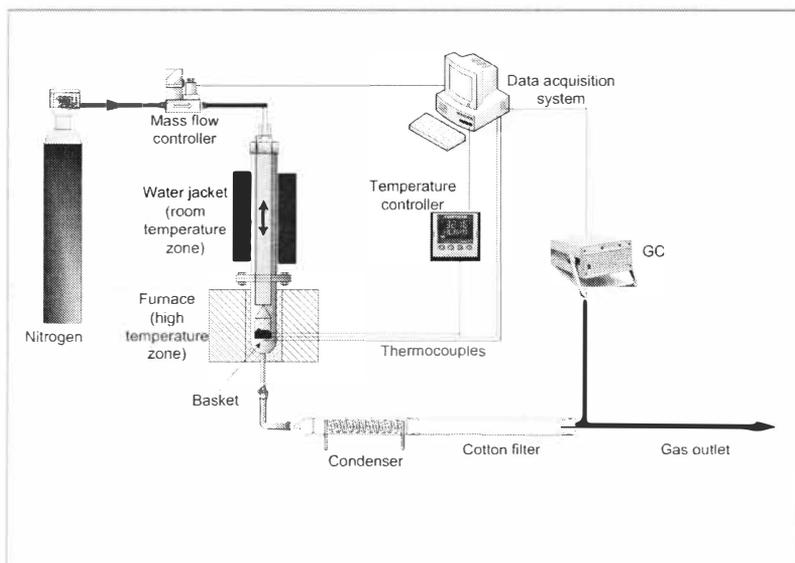


Figure 3. Schematic diagram of fixed bed fast pyrolysis reactor.

The reactor is composed of two separate zones. In the upper part of the reactor, a water jacket ensures low temperatures, whereas the lower part is placed inside an electrical furnace. An inner steel cylinder (with the sample basket hanging from it) can be moved vertically from the low temperature zone to the high one, so flash pyrolysis of sewage sludge is achieved. In this system, heating rate can be as high as 200°C/min and is not a controllable parameter, unlike in the slow pyrolysis plant. A temperature controller is used to reach the desired final pyrolysis temperature, and nitrogen is also used as inert gas, flowing downwards the reactor with a flow rate set by a mass flow controller. Sample temperature can be measured by means of four type K thermocouples placed inside the basket.

Outside the reactor, pyrolysis gases and condensable compounds flow together with nitrogen through a gas cleaning system consisting of a condenser (externally cooled to -2°C) and a cotton filter. Finally, gas composition is analyzed by the same chromatograph as mentioned for slow pyrolysis system.

Product distribution can be determined in the same way as in the slow pyrolysis plant. The maximum sewage sludge capacity of the steel basket in this system is 3 g. Sewage sludge is smashed and sieved to provide a feed sample in the size range of 250-500 µm.

## 4 EXPERIMENTAL

In this section, a brief glance is taken at the results of both thermochemical pathways considered for sewage sludge valorization, according to several sets of experiments carried out by the research group.

### 4.1 Fluidized bed gasification of sewage sludge

Gasification experiments were performed in order to obtain a gas with the highest heating value, and with the lowest quantity of tar. Tar reduction can be improved with primary measures, changing the operation parameters, such as temperature, gas residence time, etc. This benefits the application of a catalyst in a secondary treatment, obtaining thus very low tar values. In previous works, bed temperature ( $T_b$ ), the stoichiometric ratio ( $\lambda$ , defined as the ratio between the actual flow rate of the air and the stoichiometric flow rate required for fuel combustion) and residence gas time was studied [6]. In these works was found that a  $T_b=850^\circ\text{C}$ ,  $\lambda = 30\%$  and a bed height of 300 mm gave the best yield as a compromise between tar reduction and heating value of gas produced. In the present work, other parameters have been analyzed with the same purpose: the freeboard temperature ( $T_f$ ), and the particle size ( $d_p$ ).

In this set of experiments the freeboard temperature has been studied between 600 and 850°C. Two particle size distributions have been considered: one size ranged from 250 to 500 µm, and another from 500 to 800 µm. Tar obtained (referred as percentage of total sewage sludge fed) and high heating values of gases of these experiments are shown in *Table 1*.

*Table 2. Tar production and gas high heating value obtained for gasification in fluidized bed experiments.*

Reaction	Gasification in fluidized bed	
Freeboard temperature (°C)	600	850
Tar produced (% of DSS fed)	10.16	8.62
Higher heating value of gas (kcal/kg)	1032	1192
Particle size range (µm)	250 - 500	500 - 800
Tar produced (% of DSS fed)	8.98	11.5
Higher heating value of gas (kcal/kg)	946	950

As can be seen in *Table 2*, tar reduction and gas higher heating value are better at a freeboard temperature of 850°C. This trend has also been observed in gasification for other biomasses [9]. Regarding particle size, operation with the lower diameter studied is recommended. In the range of 250–500 µm, tar values present an important decrease compared with the yield obtained operating with a major particle distribution size. The gas heating value did not seem to be affected by differences in the particle diameter. Nevertheless, this trend is opposite to some results from literature. A small particle suffers reactions in the upper part of the reactor, where a more reducing atmosphere is found [10]. The diffusion of the volatiles formed from these particles is faster and the cracking is less severe, resulting in a high quantity of tar. [10]. It would be desirable to apply an experimental design to probe statistically the observed influence of the particle size.

#### **4.2 Fluidized bed pyrolysis of sewage sludge**

In this experimental set, attention was focused on liquid yield and in its higher heating value (HHV). Pyrolysis liquids obtained from other biomasses have already been used for energetic applications [11]. For this reason, the energetic valorization of sewage sludge via pyrolysis can be considered as an interesting alternative. Taking into account HHV as the main characteristic that can define a valuable fuel, the main goal of this set of experiments was to find out the operational conditions that maximize this parameter together with the liquid yield. Pyrolysis of sewage sludge and other raw materials has been studied in fluidized bed systems to obtain bio-oil, due to the suitability of this kind of reactor to get a high liquid yield [3]. In this set of experiments, bed temperatures range was selected between 450 and 650°C, because this interval was known to give the highest liquid yield, according to previous studies [12, 13]. Liquid yield and HHV results of these experiments are shown in *Table 2*.

As can be seen in *Table 3*, both highest liquid yield and HHV values are obtained for 550°C. It was expected that the liquid yield was maximized at temperatures ca. 550°C according to the literature [12, 13]. Liquid yield of pyrolysis is found to be composed of two different phases - aqueous and organic. Regarding this, HHV values of the organic phase were very close (around 7,500 kcal/kg for all temperatures), but when overall HHV has been calculated (moisture basis) the differences between them have increased considerably. For this reason, it can be said that temperature affects the moisture content of the pyrolysis liquid, but does not have significant influence on the HHV of the organic phases.

Table 3. Product distribution for fixed bed pyrolysis experiments.

Reaction	Fast Pyrolysis in fluidized bed		
	Temperature (°C)	450	550
Liquid yield (%)	23.4	33.48	28.1
Higher heating value based on moisture (kcal/kg)	4796	5661	3997

Summing up, at 550°C a high liquid yield is achieved - considering the big amount of ash that the sewage sludge has. At this temperature, HHV value complies with the minimum requirements given in literature for energetic usage of these kinds of liquids [7].

### 4.3 Fixed bed pyrolysis of sewage sludge

In this set of experiments, attention was focused on char product resulting from pyrolysis. Some authors have reported sewage sludge pyrolysis char may be suitable for the production of an adsorbent product [5]. Thus, this can be an attractive way for solid volume reduction from char, combined with char reutilization. Considering BET surface area as the main characteristic that defines adsorptive properties, the objective of this set of experiments was to try to determine the conditions that maximize this parameter.

As has been said before, two types of pyrolysis have been studied. In slow pyrolysis experiments two factors were varied (final temperature and heating rate). In the case of fast pyrolysis, only final temperature was varied. Adequate temperature range for both sets of experiments varied between 600 and 900°C, according to previous studies found in bibliography [14]. Regarding heating rate in slow pyrolysis experiments, values of this parameter ranged from 2 to 14°C/min. Char yield and BET surface area results are shown in Table 3.

As can be deduced from the results table, char yield is higher when higher heating rates are applied in slow pyrolysis, but this value is the lowest for fast pyrolysis experiments. This clearly indicates the different reaction pathways involved for each pyrolysis type. Also, char yield is lower when pyrolyzing at higher temperatures.

Table 4. Product distribution for fixed bed pyrolysis experiments.

Reaction	Slow pyrolysis				Fast pyrolysis	
	Heating Rate, (°C/min)				(ca. 200°C/min)	
Temperature (°C)	600	900	600	900	600	900
Char yield (%)	56.7	50.1	64.6	60.8	52.6	47.0
BET surface area (m <sup>2</sup> /g)	16.6	56.9	18.4	59.9	38.9	76.1

Regarding adsorptive properties of the chars, BET surface areas increase significantly at high temperatures in the case of slow pyrolysis, whereas the same trend is found for fast pyrolysis. In the latter, higher BET surface areas are found. Nevertheless, the values of this parameter are very far from the ones reported for pyrolytic chars of other types of biomass [15], mainly because of the high ash content of sewage sludge. This fact evidences the need for

supplementary activation stages (physical or chemical) in order to increase surface area, if one thinks of obtaining a valuable solid by-product as a result of pyrolysis.

## 5 CONCLUSIONS

Sewage sludge valorization by means of thermochemical processes leads to three product fractions, each one of them with potential reutilization possibilities. Research done in the Thermo-chemical Processes Group has been focused on optimization of selected product fractions or their specific characteristics from the point of view of energetic valorization and waste minimization. This work has provided a better understanding of the thermo-chemical processes tested in laboratory scale and given new guidelines to optimize these processes. Some remarkable features, such as volume reduction of the residue and heating value of the products, have been encouraging for the research group to continue investigating sewage sludge thermochemical valorization.

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