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Characterization of the bio-oil obtained by fast pyrolysis of sewage sludge in a conical spouted bed reactor

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ABSTRACT

Sewage sludge fast pyrolysis bio-oil, produced in a conical spouted bed reactor (CSBR) in the 450–600 °C range, has been characterized. On the one hand, the effect of temperature on bio-oil composition has been analyzed by means of online chromatography and, furthermore, the ultimate analysis and the higher heating value of each liquid have been determined. On the other hand, the bio-oil collected at 500 °C, at which the liquid yield is maximized (77 wt.% on dry ash free), has been characterized in detail by determining its density, viscosity, water content and pH. The major organic compounds in the bio-oil were oxygenated and nitrogenated ones (phenols, ketones, alcohols, amides and nitriles among others). It is noteworthy that the bio-oil obtained in this work contains a lower amount of O than those derived from lignocellulosic materials; therefore, the concentrations of C and H in this bio-oil, as well as the lower heating value (LHV), are higher. In addition, the simulated distillation reveals that >70% of the sewage sludge pyrolysis oil corresponds to the gasoil range. The fuel properties of sewage sludge bio-oil evidence that it has the potential to substitute conventional fuels; however, some properties need to be improved, i.e., the heating value should be increased and the nitrogen content reduced by subjecting this bio-oil to further treatments.

1. Introduction

Sewage sludge refers to the residual solid material remaining in wastewater treatment processes, and generally stems from primary (mechanical) and secondary (biological) treatments. This waste is a complex heterogeneous mixture of microorganisms, undigested organic compounds (paper, oils, fecal material and so on), as well as certain inorganic compounds. The final composition of the sewage sludge varies depending on the pollutant loading of the wastewater reaching the plant and the additional treatments (anaerobic or aerobic digestion) carried out in order to stabilize the organic matter and reduce the water content and pathogens in the final product [1].

The recent banning of ocean disposal and new stringent European landfilling regulations aimed to the protection of the public health and environment have given way to a steady increase in the production of sewage sludge in the last years [2]. Thus, apart from the conventional disposal methods, such as agricultural reuse or incineration, which are the most used treatments in Europe [3], new efficient and environmentally friendly technologies for sludge valorisation must be developed. In this scenario, pyrolysis, and particularly fast pyrolysis [4], is a feasible technology for an adequate stabilization and disposal of this waste due to the following aspects: i) its mass is reduced at least by 50%; ii) organic compounds are destroyed; iii) NO_x and dioxin emissions are reduced and; iv) the heavy metals contained in the material are concentrated in the solid residue (char). Furthermore, a liquid product is obtained, namely, bio-oil, which has a high heating value, is free of inorganic compounds and can be easily stored [5].

Sewage sludge management by fast pyrolysis requires the knowledge of bio-oil characteristics in order to suggest the appropriate applications and upgrading treatments. Moreover, the viability of bio-oil valorisation requires the diversification of its applications according to the socio-economic characteristics of each environment. Therefore, bio-oil can be a valuable raw material involving the following applications: i) extraction of components, such as phenolic compounds for the synthesis of phenolic resins [6]; ii) direct use (without upgrading) as fuel in furnaces and boilers, especially for district heating, to replace heavy fuel oil [7]; iii) reforming by physical/thermal processes (molecular distillation, esterification) or catalytic transformation [4,8,9]; iv) production of fuels and raw materials, such as olefins, aromatics [10] or hydrogen [11] and; v) co-feeding into an FCC unit [12]. Therefore, it is essential to analyze in depth the bio-oil by determining its composition and physicochemical properties, which are the bases for assessing the liquid quality and suitability for the aforementioned applications.

The bio-oil from sewage sludge is a dark brown organic fluid that consists of a mixture of water and several organic compounds, such as acids, phenols, esters, ketones and lignin derived oligomers [13]. This bio-oil is very similar in appearance and in certain properties to those obtained from lignocellulosic biomass. Nevertheless, the bio-oil from sewage sludge has a basic nature with pH values between 8 and 10

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[14], whereas the liquids obtained from lignocellulosic materials are acid with pH in the 2–4 range. This basicity is due to the presence of ammonia and nitrogen containing compounds, such as nitriles, amines and amides, all of them derived from the dead bacteria in the sludge.

The fuel properties of the sewage sludge bio-oil will depend not only on the initial composition of the feedstock, but also in the pyrolysis conditions and the technology used [5]. Accordingly, some properties, such as chemical composition, viscosity, water content and pH, can vary widely affecting to a large extent the bio-oil quality [15]. Thus, water content has a great significance in the bio-oil homogeneity or liquid phase stability, as well as in the density and heating value [5]. High yields of water will break the microemulsion formed between water and water soluble organic compounds with water insoluble ones, mainly lignin-derived oligomers, leading to the formation of two or more phases [15]. As a consequence of the different technologies, conditions and raw materials used, the chemical and physical properties of the sewage sludge pyrolysis oils detailed in the literature differ substantially [16–19].

In this work, the bio-oil obtained in a CSBR was characterized, given that this reactor has proven to perform satisfactorily in the pyrolysis of this material in continuous mode [20]. The cyclic and vigorous movement of the solid that gives way to high heat and transfer rates, low residence times and rapid char removal makes this reactor suitable for maximizing bio-oil yield. Accordingly, the aim of this work is to study the effect of temperature on the physicochemical properties of the oils obtained by the fast pyrolysis of sewage sludge in a CSBR in order to assess the best possible routes for their valorisation. Additionally, the determination of the simulated distillation curve of the product obtained at 500 °C was also carried out in order to evaluate the feasibility of its application as fuel.

2. Experimental

2.1. Characterization of the raw material

The sewage sludge used was previously subjected to anaerobic digestion and thermally dried in the wastewater plant itself, which is located in Barcelona (Spain). The sludge sample has a particle size in the 0.5–3 mm range, and therefore does not require being ground and sieved for feeding it into the CSBR reactor.

The main characteristics of the raw material are summarized in Table 1. The ultimate and proximate analyses have been carried out in a LECO CHNS-932 elemental analyzer and in a TGA Q500IR thermogravimetric analyzer, respectively. The calorific value has been measured in a Parr 1356 isoperibolic bomb calorimeter. As observed, the contents of nitrogen, sulfur and ash are higher than in lignocellulosic biomass materials, thus leading to a different composition of the pyrolysis products.

Table 1
Sewage sludge properties.

Properties	
Ultimate analysis (wt.%)[a]	
Carbon	40.6
Hydrogen	7.1
Nitrogen	7.7
Sulfur	3.3
Oxygen[b]	41.2
Proximate analysis (wt.%)[c]	
Volatile matter	54.2
Fixed carbon	8.6
Ash	37.2
Moisture (wt.%)	5.6
HHV (MJ kg^{-1})	11.1

[a] On a dry and ash free basis.
[b] O content is calculated by difference: O (%) = 100 − C(%) − H(%) − N(%) − S(%).
[c] On a dry basis.

The information about chemical composition of the ashes was previously reported elsewhere [20].

2.2. Bench scale pyrolysis plant and experimental procedure

Sewage sludge fast pyrolysis has been carried out in a CSBR, which is an innovative technology that has been successfully used for the pyrolysis of lignocellulosic biomass [21–24], as well as for other waste materials, such as tires [25] or plastics [26]. This technology has been proven suitable for the handling of particles of irregular texture, fine particles, sticky solids and those with a wide size distribution. One of the main features of this reactor lies in the low residence time of the volatiles, i.e., <100 ms in the spout zone and an order of magnitude higher in the annulus zone [26].

A schematic diagram of the bench-scale unit has been described in previous papers where it was performed the fast pyrolysis of several types of lignocellulosic biomasses [22,23] and sewage sludge [20]. It is noteworthy that the solid fraction (char) is continuously removed from the bed through a lateral outlet pipe located at the reactor wall, thus avoiding its accumulation throughout the pyrolysis process. The volatile products leave the reactor and pass through a fine-particle retention system composed of a high-efficiency cyclone followed by a sintered steel filter. Both devices are placed in a hot box at 290 °C to prevent the condensation of heavy compounds. The gases leaving the filter circulate through a volatile condensation system consisting of a double-shell tube condenser cooled by tap water and two coalescence filters.

2.3. Bio-oil analysis

Bio-oil yield and composition have been determined using a gas chromatograph (Varian 3900) equipped with a flame ionization detector (FID), which is connected online to the outlet of the pyrolysis reactor by means of a thermostated line. The identification of the compounds that make up the bio-oil has been performed by GC/MS (Shimadzu UP-2010S). The chromatographic method used to analyze the bio-oil was explained in detail in a previous work published by the authors [27]. The mass balance has been validated by introducing an internal standard (cyclohexane) through an inlet located in the heated line running from the reactor to the chromatograph. The bio-oil contains a high amount of oxygen and nitrogen compounds and, unlike hydrocarbons, the FID response to these compounds is not proportional to their mass. The calibration performed to calculate the FID device's response factors to chemical compounds with oxygen and nitrogen was reported in a previous work [20]. Fourier transform infrared spectroscopy (FTIR) measurements were performed in a Thermo Nicolet 6700 instrument in order to determine the organic functional groups of the bio-oil sample obtained at 500 °C.

The water content of the bio-oils was determined by Karl-Fischer Titration (ASTM D1744). Other fuel properties, such as density, viscosity and pH of the bio-oil collected in the experiments at 500 °C were also measured. The pH value and the viscosity were determined by the ASTM D974-2010 and ASTM D445-2010 standards, respectively, whereas the density was measured according to ASTM D4052. Additionally, the pyrolysis oil was fractionated by simulated distillation by means of an Agilent 6890 chromatogram provided with a FID detector and according to the ASTM-D2887-84 standard (boiling range distribution of petroleum fraction by gas chromatography). The higher heating values (HHV) of the bio-oil samples were determined by a bomb calorimeter and the lower heating values (LHV) were calculated according to Eq. (1) [28]:

$$\text{LHV (kJ/kg)} = \text{HHV (kJ/kg)} - 218.3 \times \text{H (\%)} \quad (1)$$

where H is the hydrogen content in mass percentage.