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Sewage sludge valorization by flash pyrolysis in a conical spouted bed reactor

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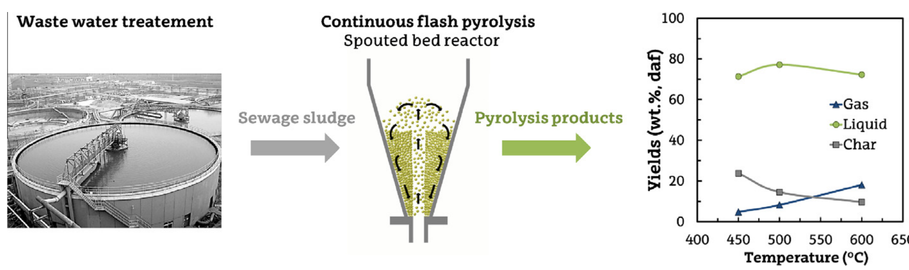
HIGHLIGHTS

- The conical spouted bed reactor is suitable for sewage sludge flash pyrolysis.
- A maximum liquid yield of 77 wt.% daf is obtained at 500 °C.
- An efficient char removal system is crucial for avoiding secondary reactions.
- The liquid is a mixture of water, oxygenated and nitrogenated organic compounds.
- The char retains most of the heavy metals of the sewage sludge.

GRAPHICAL ABSTRACT



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ABSTRACT

Sewage sludge valorization by flash pyrolysis has been carried out in a conical spouted bed reactor with continuous biomass feed and char removal. The effect of temperature on product yields and composition has been studied in the 450–600 °C range and a maximum liquid yield of 77 wt.% daf (dry and ash free basis) has been obtained at 500 °C. The liquid collected has a water content of 23–27 wt.% and is mainly composed of oxygen-containing compounds (phenols, ketones and acids amongst others), whose yield decreases with temperature, and nitrogen-containing compounds, such as amides and pyrroles. In addition, the importance of an efficient char removal system has been assessed by operating with and without char accumulation in the bed. The char fraction retains most of the heavy metals contained in the sludge and they may have applications in agriculture or as adsorbent.

1. Introduction

Sewage sludge resulting from urban wastewater treatment processes is an unavoidable residue, whose production is steadily growing all over the world. Thus, in Europe the annual production of sewage sludge accounted for more than 10 million tons in 2010 and is expected to increase up to 13 million tons for 2020 [1] due to the implementation of the Urban Waste Water Treatment Directive (91/271/EEC), which forced the improvement of wastewater treatment processes, increasing the number of existing plants [2].

Urban sewage sludge is a heterogeneous mixture of organic and inorganic materials, which generally come from primary (mechanical) and secondary (biological) treatments, consisting of proteins, lipids, carbohydrates and a high ash concentration, including heavy metals that are hazardous to the environment [3]. Nowadays, sewage sludge disposal methods include agricultural reuse (42%), incineration (27%) or landfill (14%) [4], but all of them involve several drawbacks related to air or soil pollution, mainly attributed to heavy metals and other toxic compounds contained in the sludge [5]. Furthermore, the quality standards for the agricultural application of sludge are expected to increase, restricting the percentage of waste material to be incorporated into the soil [6].

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In this scenario, new efficient and environmentally friendly technologies for sludge valorization must to be developed [7]. Thermal processes for energy recovery, such as pyrolysis or gasification are gaining attention, as the process products may be used as bio-fuels or source of chemicals, attaining an additional minimization of environmental impacts [3]. Sewage sludge pyrolysis, and more specifically anaerobically digested sludge pyrolysis [8,9], is regarded as one of the most feasible methods for large scale sludge valorization [4]. Flash pyrolysis at moderate temperatures (400–600 °C) produces a liquid fraction that is easily stored, with a yield between 51 and 80 wt.% (on a dry ash free basis), which may be used as fuel or source of chemicals [10]. Furthermore, a solid fraction that concentrates the heavy metals in the sludge is also formed, which may have several applications as adsorbent for water treatment processes [11].

Sewage sludge flash pyrolysis has been accomplished mainly at fluidized bed systems, given that this kind of reactor performs well for bio-oil production from biomass pyrolysis [10]. In this study, sewage sludge pyrolysis is carried out in a conical spouted bed reactor (CSBR), which is an innovative technology that has been successfully used for lignocellulosic biomass pyrolysis, including pinewood [12], rice husk [13] and forest shrub wastes [14], as well as other waste materials, such as tires [15,16] or plastics [17,18]. Indeed, the excellent performance of this reactor has been confirmed in the scaling-up of the biomass pyrolysis process, with the development of a 25 kg h^{-1} pilot plant [19]. Furthermore, spouted bed reactors have been also successfully applied in several physical and thermochemical processes, such as drying [20,21], coating [22,23], gasification [24,25] or reforming [26,27]. The conical spouted bed has several advantages over the fluidized beds, in particular for handling solids with irregular texture. The vigorous cyclic movement leads to high heat and mass transfer rates [28] and great versatility in the gas flow rate, which allows operating with short gas residence times [29]. These characteristics make this reactor suitable for liquid production from sewage sludge because secondary reactions that reduce the liquid yield are minimized, which is crucial for the handling of materials with high ash content that may act as a cracking catalyst [13].

The aim of this paper is to study the feasibility of the valorization of urban wastewater derived sewage sludge by flash pyrolysis in a CSBR, in terms of liquid product yield and composition, paying special attention to the pyrolysis temperature and reactor configuration in order to attain an efficient char extraction.

2. Materials and methods

2.1. Sewage sludge characterization

An anaerobically digested and thermally dried sewage sludge supplied by an urban wastewater plant located in Barcelona (Spain) has been used in this study. The sludge sample has a particle size in the 0.5–3 mm range, and therefore does not require to be ground and sieved for feeding it into the pyrolysis reactor.

Table 1 shows the ultimate and proximate analysis, which have been carried out in a LECO CHNS-932 elemental analyzer and in a TGA Q500IR thermogravimetric analyzer, respectively, and the calorific value that has been measured in a Parr 1356 isoperibolic bomb calorimeter. The sewage sludge differs from other biomass materials in its high nitrogen, sulfur and ash contents, which have an impact on the pyrolysis performance and products formed. Due to the significant ash content in the sludge, its chemical composition including silica and major metal compounds has been quantified by X-ray Fluorescence (AXIOS, PANalytical) (Table 2).

FTIR (Thermo Nicolet 6700) analysis of the sewage sludge has also been carried out and the spectrum obtained is shown in Fig. 1. The interpretation of the spectrum has been based on the literature [30–34]. The broad and intense band between 3800 and 3200 cm^{-1} corresponds to O–H and N–H stretching vibrations, the former related to water, alcohols, phenols and carboxylic acids, and the latter to amines and amides. The small peaks in the 3000–2850 cm^{-1} range indicate the presence of aromatic and aliphatic structures. The weak shoulders at 2500 and 2300 cm^{-1} may be associated with the S–H and C–N stretching vibrations. Furthermore, the two peaks around 1650 cm^{-1} correspond to C=O vibration caused by the presence of acids and aldehydes, representative of the lipid content in the sludge. The next peak at 1550 cm^{-1} is related to amides, which come from proteins in the sewage sludge. The band at 1400–1450 cm^{-1} should be attributed to the deformation vibrations of CH_3 and CH_2 groups found in cellulose, as well as C=C aromatic groups, which suggest the presence of lignin structures. The wide band in the 1300–800 cm^{-1} region should be attributed to the contribution of, on the one hand, polysaccharides and, on the other hand, to the presence of Si–O, which is one of the main constituents of sludge ash (Table 2). Finally, the last stretch below 850 cm^{-1} should be associated with aromatic hydrogen and cycloaliphatic structures. Therefore, the

Table 1
Sewage sludge properties.

Properties	
Ultimate analysis (wt.%)	
Carbon	25.5
Hydrogen	4.5
Nitrogen	4.9
Sulfur	2.1
Oxygen*	25.8
*Proximate analysis (wt.%)***	
Volatile matter	54.2
Fixed carbon	8.6
Ash	37.2
Moisture (wt.%)	5.6
H/C**	1.80
O/C**	0.62
N/C	0.20
HHV (MJ kg^{-1})	11.1

* By difference
** On a dry basis

Table 2
Sewage sludge ash composition.

Major compounds	Concentration (wt.%)
SiO_2	25.0
P_2O_5	18.5
CaO	17.7
Al_2O_3	16.5
Fe_2O_3	9.4
SO_3	3.1
MgO	2.7
K_2O	1.7
Na_2O	1.2
TiO_2	0.8
MnO	0.1
Others	3.3
Trace elements	**Concentration (ppm)**
Zn	4660
Sr	2002
Cu	1384
Ba	1144
Cr	637
Ni	410
Pb	323
Sn	232
Hg	2