Fuel 159 (2015) 810–818

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Fast co-pyrolysis of sewage sludge and lignocellulosic biomass in a conical spouted bed reactor

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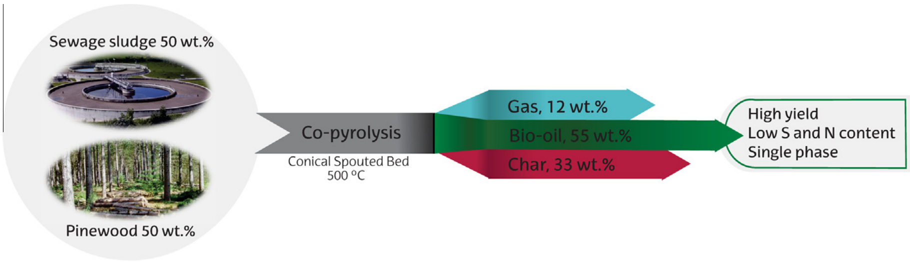
HIGHLIGHTS

- The CSBR is suitable for the fast pyrolysis of sewage sludge and biomass mixtures.
- Synergetic effects enhancing gas production have been observed.
- This bio-oil is a mixture of water, oxygenated and nitrogenated compounds.
- The reaction pathway of pyrolysis changes due to the interactions between components.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 May 2015
Received in revised form 9 July 2015
Accepted 13 July 2015
Available online 21 July 2015

Keywords:
Pyrolysis
Sewage sludge
Biomass
Spouted bed reactor
Bio-oil

ABSTRACT

Co-pyrolysis of sewage sludge and lignocellulosic biomass has been studied in order to improve the composition of the bio-oil derived from sewage sludge fast pyrolysis as well as progress on the viability of this waste valorization. Fast pyrolysis of a mixture of 50 wt.% sewage sludge and 50 wt.% pinewood sawdust has been carried out in continuous mode at 500 °C in a conical spouted bed reactor (CSBR) and the results obtained have been compared with those obtained in the fast pyrolysis of each raw material separately. Significant synergetic effects have been observed in both the previous thermogravimetric study and the pyrolysis in the bench scale plant, in which gas production is promoted. The bio-oil (55 wt.% yield) is mainly composed of oxygenated compounds (49 wt.%, with phenols and ketones being the main products) and water (32 wt.%), with a lower concentration of nitrogen-containing products (9 wt.%) and without any sulphur compound, thus being a suitable raw material for its subsequent valorization. The results obtained prove the capacity of the conical spouted bed reactor for minimizing the reactions of bio-oil transformation into gases (mainly promoted by the catalytic activity of the ash in the sludge), which is due to the low residence time of the volatiles in the reactor.

1. Introduction

The increasing production of urban wastewater resulting sewage sludge [1] requires the development of new and alternative valorization technologies due to the risks for environment and health associated with the current disposal methods, such as agricultural reuse (42%), incineration (27%) or landfill (14%) [2]. In this scenario, thermal processes for energy recovery, such as pyrolysis or gasification, are gaining attention [3]. Hence, pyrolysis is regarded as one of the most feasible methods for large scale sludge valorization of anaerobically digested sewage sludge [4], as the products can be used as bio-fuels or source of chemicals [1]. Furthermore, this strategy would help to meet the current requirements for replacing fossil derived fuels by alternative and renewable raw materials [5].

The liquid product derived from sewage sludge fast pyrolysis, whose yield ranges between 51 and 80 wt.% on a dry ash free basis, is a complex mixture of mainly water and oxygen- and nitrogen-containing compounds, as well as hydrocarbons and sulphur-derived products [1]. This heterogeneous nature may lead to instability, as well as NO_x and SO_2 emission problems if the

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http://dx.doi.org/10.1016/j.fuel.2015.07.039
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liquid is used as fuel, thereby requiring further treatments prior to its utilization. These problems would be reduced if sewage sludge is co-pyrolyzed with lignocellulosic biomass [6], whose valorization by fast pyrolysis has been widely studied and has attained a considerable development stage [7,8].

The industrial implementation of biomass pyrolysis requires suitable reactors that may treat jointly different types of heterogeneous and irregular materials that are geographically delocalized [9] and whose composition is also influenced by seasonal variations [10]. Thus, the conical spouted bed reactor (CSBR) has been proven to be suitable for the valorization by fast pyrolysis of different wastes, as are: sewage sludge [11], lignocellulosic biomass (pinewood sawdust [12], forest shrub wastes [13] and rice husk [14]) and other materials, such as tires [15,16] or plastics [17,18]. In addition, this reactor has also been successfully applied in other thermochemical processes, such as drying [19,20], coating [21,22], gasification [23,24] or reforming [25,26]. The vigorous cyclic movement of the bed particles and the high velocity of the gas lead to high heat and mass transfer rates, which allows attaining bed isothermicity [27]. Moreover, the conical shape of the reactor allows operating with biomasses of different textures and granulometries without segregation problems [28,29] in a wide range of gas residence times, down to a few milliseconds [30]. These characteristics make the CSBR suitable for large scale bio-oil production by fast pyrolysis, given that secondary reactions that reduce the liquid yield are minimized, which has been confirmed by scaling up the biomass pyrolysis unit to a 25 kg h^{-1} pilot plant [31].

This work deals with the co-pyrolysis of pinewood sawdust (a model lignocellulosic biomass) and sewage sludge with the aim of assessing the feasibility of their combined valorization. Furthermore, synergies between these two raw materials have been explored in the mechanism of pyrolysis, concerning both the yields of product fractions and the composition of the bio-oil. In fact, significant interactions are expected due to the high ash content of sewage sludge, which catalyzes secondary reactions involving bio-oil components, such as dehydration, cracking and dehydrogenation [6,32,33], and therefore the bio-oil yield would be considerably reduced [34,35].

The studies reported in the literature about sewage sludge and biomass co-pyrolysis have been carried out mainly in fixed bed reactors [6,34–37], attaining in all cases low bio-oil yields (between 21 and 33 wt.%) due to the high amount of ashes derived from sludge and the synergetic effects occurring during the pyrolysis process. In addition, some authors have also studied the co-pyrolysis behaviour of mixtures of sewage sludge and different biomass types, and the kinetics of the process by thermogravimetry [6,32,38]. It is noteworthy that the CSBR technology allows operating in continuous mode and limits to some extent the secondary reactions and synergies between the raw materials due to the low residence time of the volatiles and continuous removal of char from the reaction environment, thereby enhancing bio-oil formation.

The mixture studied consisted of 50 wt.% pinewood sawdust and 50 wt.% sewage sludge in order to clearly ascertain synergies in the process and assess the capability of the CSBR to handle mixtures of these two different materials with a low transformation of bio-oil into gases. Nevertheless, given the high capacity of industrial pyrolysis units, the content of sewage sludge to be fed with biomass will presumably be lower than 50%.

2. Materials and methods

2.1. Raw materials

An anaerobically digested and thermally dried sewage sludge has been used, which has been supplied by an urban wastewater treatment plant located in Barcelona (Spain). Particle size of this dry sludge is between 0.5 and 3 mm. The biomass is pinewood (*pinus insignis*) sawdust, which has been crushed and ground to a particle size in the 1–2 mm range and dried to a moisture content below 10%. Table 1 shows the main characteristics of the raw materials, as are: proximate and ultimate analyses, determined in a LECO CHNS-932 elemental analyzer and in a TGA Q500IR thermogravimetric analyzer, respectively, and the calorific value measured in a Parr 1356 isoperibolic bomb calorimeter.

As observed, the main differences between both raw materials lie in the nitrogen, sulphur and, especially, ash content. Given the impact this ash in the sewage sludge has on the process, the chemical composition (silica and major metal compounds) has been determined by X-ray Fluorescence (AXIOS, PANalytical) (Table 2). The high ash content results in a lower fraction of pyrolyzable material in the sewage sludge, and therefore a higher yield of solid fraction.

Fig. 1 shows the FTIR (Thermo Nicolet 6700) spectra of the sewage sludge and biomass, which have been interpreted based on the literature [39–42]. As observed, the main difference between the two raw materials lies in the 1200–1700 cm^{-1} wave number range. Analyzing the FTIR spectra, it should be noted that the broad band between 3700 and 3000 cm^{-1} corresponds to the stretching vibration of hydrogen bonded O—H in the water, alcohols, phenols and carboxylic acids, as well as N—H stretching vibrations due to amines and amides in the sewage sludge. The peak at 3000–2800 cm^{-1} indicates the presence of aromatic and aliphatic structures, with the latter being more abundant in the case of pinewood. In addition, three peaks are observed in this material in the 1800–1600 cm^{-1} range. The first peak at 1750 cm^{-1} corresponds to C═O stretching, attributed to carbonyl and carboxyl groups (esters, ketones, aldehydes and acids) and the peak at 1650 cm^{-1} is related to O—H absorbed in conjugated C—O bonds, which appears followed by the peak at 1600 cm^{-1} due to aromatic C═C vibrations in the lignin. These peaks are also present in the sewage sludge, which evidences that lipids and lignin are contained in this waste. Lignin in the biomass is detected by the bands at 1600 cm^{-1} and 1500 cm^{-1}, attributed to the vibration of aromatic C═C bonds, and at 1270 cm^{-1} to guaiacyl ring breathing with C═O stretching. The peak at 1550 cm^{-1} in the sewage sludge, but not in the biomass, is related to amides, which are contained in the proteins of the sewage sludge. Furthermore, the cellulose and hemicellulose content of the biomass are represented by the C—H deformation vibration at 1370 cm^{-1}, C—O—C vibrations at 1170 cm^{-1}, C—O

Table 1
Characterization of the sewage sludge and the biomass (pinewood sawdust).

Properties	Sewage sludge	Biomass
Ultimate analysis (wt.%)		
Carbon	25.5	49.0
Hydrogen	4.5	6.0
Nitrogen	4.9	–
Sulphur	2.1	–
Oxygen[a]	25.9	44.4
Proximate analysis (wt.%)[b]		
Volatile matter	54.2	81.0
Fixed carbon	8.6	18.4
Ash	37.2	0.6
Moisture (wt.%)	5.6	9.4
H/C	2.1	1.5
O/C	0.8	0.7
N/C	0.2	–
HHV (MJ kg^{-1})	11.1	19.8

[a] By difference.
[b] On a dry basis.