

SUSTAINABLE FUELS OBTAINED FROM THE PYROLYSIS PROCESS OF SEWAGE SLUDGE

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Abstract

Combustion of fossil fuels, greenhouse gas emissions, large amounts of sewage sludge, lead to environmental pollution and global warming. For this reason we must think of feasible solutions to disposal the sewage sludge by capitalization it and energy recovery. One of the most interesting technologies for disposal the sewage sludge is the pyrolysis process. After the pyrolysis process of sewage sludge are obtained three types of products: bio-oil, syngas and biochar. Bio-oil can be used as an alternative fuel for fossil fuels after refining. Bio-char can be used as an adsorbent after an activation process for the capture and storage CO₂. Pyrolysis is considered an environmentally friendly process because it reduces the emission of greenhouse gases, while heavy metals are concentrated in the final residue. In this paper are presented the advantages of sewage sludge pyrolysis.

Keywords: Bio-char, bio-oil, pyrolysis, sewage sludge, syngas

1. INTRODUCTION

Greenhouse gas emissions are considered the main factor of climate changes, generating a negative impact on the environment. Carbon dioxide is the gas with the largest contribution to global warming, due to its extensive production through burning fossil fuels, activities of the industrial sector and electricity generation (Hong et al., 2016; Chiang and Juang, 2017). Due to anthropogenic activities, the CO₂ concentration increased considerably from 280 ppm to 400 ppm during the last 10 years (Lee and Park, 2015; Rashidi and Yusup, 2016; Jang et al., 2018). It has been estimated that the atmospheric concentration of CO₂ will reach 570 ppm in 2100, which will generate extreme climate changes, such as: melting glaciers and ice caps which causes rising planetary ocean levels, heavy rainfall, extreme droughts (Lee and Park, 2015). All these issues are of great concern, and research is focused on developing CO₂ capture and storage technologies to prevent climate change (Deng et al., 2014; Hong et al., 2016).

Sewage sludge is a solid waste resulting from the treatment of wastewater from treatment plants and is in increasing quantities. The production of sewage sludge in Europe is of 10.13 million tons, compared to China, where there are more than 25 million tons produced annually (Milieu, 2010; Lu et al., 2013). At present, the disposal methods of sewage sludge are as following: incineration, use

in agriculture and landfill. Due to potential contaminants of sewage sludge, such as heavy metals, organic compounds, pathogens, it can no longer be used in agriculture, according to the European Directive 86/277/EEC (Fonts et al., 2012; Cantinho et al., 2016). Another disposal method of sewage sludge is soil storage, but it becomes of risk for plants, animals and human health due to the high content of heavy metals, viruses and pathogenic bacteria (Singh and Agrawal, 2008). Disposal of sewage sludge by incineration has the advantage of reducing the amount of sludge by up to 70%, but it may release pathogens, toxic organic compounds, dioxins and furans, nitrogen oxides, sulfur oxides, heavy metals, all of which are harmful to the environment and human health (Khiari et al., 2004; Hwang et al., 2007; Fytili and Zabaniotou, 2008).

The use of renewable energy and the development of carbon capture and storage technologies are important because they reduce CO₂ in the atmosphere produced by power and industrial plants. CO₂ captured from industrial sources can be used in various ways, such as transportation and injection into geological formations such as saline aquifers, gas fields, coal mines (Jacobson, 2009; Liu and Wilcox, 2011).

The production of biofuels from biomass or wastes is performed through the processes of pyrolysis, gasification, incineration and roasting. Among them, the most appropriate and used is the pyrolysis process due to the high calorific value and the heat it generates (Capareda, 2013; Gao et al., 2014). The use of sewage sludge in the pyrolysis process produces biofuels such as: bio-oil, syngas and biochar (Pokoma, 2009). The pyrolytic products obtained can be used in the composition of aromatic agents, fertilizers or resins (Iguanzo et al., 2002; Tian et al., 2011). The pyrolysis process of sewage sludge considerably reduces environmental pollution (Manara and Zabaniotou, 2012). The pyrolysis parameters can be adjusted to improve the production of some of the products: biochar, bio-oil or syngas (Maguyon and Capareda, 2013). To improve the yield of bio-oil, fast pyrolysis is used, at moderate temperatures of 500 °C, high heating rate and rapid vapor condensation (Fonts et al., 2012; Yin et al., 2012).

The pyrolysis process of the sewage sludge consists of the decomposition of organic substances, under nitrogen atmosphere and in the absence of oxygen, at a certain temperature, with the production of syngas, bio-oil and biochar (Liu et al., 2011; Liu et al., 2017; Zhang et al., 2017). Pyrolysis of sewage sludge has a lightning trajectory and rapid development because of its benefits: reducing the amount of sewage sludge, application of the final products as a sustainable energy source (Leng et al., 2016; Peng et al., 2016; Yu et al., 2016). Prior to the pyrolysis process, the sewage sludge must be dried in order to remove the high content of water, such as to conduct an efficient thermal process (Kan et al., 2016).

2. SEWAGE SLUDGE CHARACTERISTICS

Wastewater that reaches treatment plants is treated by several methods: preliminary, primary and secondary treatments. The first stage, the preliminary treatment, consists in sifting the raw sludge to remove coarse residues such as rock, gravel, textiles, sand, while the suspended organic matter remains in the water. The primary treatment remove the solids, oils, greases and other floating materials and a proportion of the organic load. Properly performed, the primary treatment processes should remove from 50% to 70% of the solid suspensions and from 25% to 40% of the organic load. The sludge resulting from the primary treatment has a water content of 93-99% and a high content of suspended organic matter. Secondary treatment is actually a biological process, purification, a biotreatment with biological agents performed in order to stabilize organic matter

(Pathak et al., 2009; Tinto et al., 2016). The concentration of solids in the secondary sludge is in proportion of 0.8-1.2% (Tezel et al., 2011).

The sewage sludge is a complex waste, being composed of microorganisms, fats, proteins, peptides, dioxins, furans, polycyclic aromatic hydrocarbons and other compounds (Dress, 2002). Table 1 shows the main characteristics of activated sewage sludge, as well as the physical-chemical characteristics: moisture, ash, volatile matter and fixed carbon.

Table 1. Physical-chemical and chemical characteristics of sewage sludge, as described (Tchobanoglous et al., 2003; Fonts et al., 2009; Pokoma et al., 2009a; Samanya et al., 2012; Yuan et al., 2015; Castello et al., 2019; Zaharioiu et al., 2020)

Parameter	Activated sludge
Total dry solids (%)	0.8-1.2
Volatile solids (%)	59.0-68.0
Protein (%)	32.0-41.0
Phosphorus (%)	0.5-0.7
Grease and fats (%)	5.0-12.0
Cellulose (%)	7.0-9.7
C (%)	34.5
H (%)	5.0
N (%)	6.26
S (%)	0.86
O (%)	17.11
C ^{fixed} (%)	8.04
Calorific Value (kcal/kg)	3456

Table 2. Levels of heavy metals generally found in sewage sludge and their maximum permissible limits (Ningbo et al., 2020)

Heavy metals	Concentration (mg/kg)	Limits* (mg/kg)
As	5.6-56.1	No limit
Ba	41.5-1300	No limit
Cd	0.83	20-40
Cr	18.6	No limit
Pb	4.0-429.8	750-1200
Hg	0.1-1.1	16-25
Mo	1.7-75	No limit
Ni	8.6-420	300-400
Se	2	No limit
Zn	0.0-7500	2500-4000
Cu	75.8	1000-1750

*Note: * maximum permissible limits in accordance with the EU regulations*

The ash resulting from the sewage sludge contains minerals, such as quartz, calcite and microline, which are formed from Fe, Ca, K and Mg. The energy value of the sewage sludge depends on the type of sludge, increasing with the decrease of moisture and ash content. The energy value of the

sewage sludge obtained from wastewater industries treatment plants is higher than the energy value of the sewage sludge obtained from the wastewater urban treatment plants (Parnaudeau and Dignac, 2007; Fonts et al., 2009b).

Sewage sludge may be contaminated with different levels of heavy metals, such as: Cr, Ni, Cu, Zn, Pb, Cd and Hg, as shown in Table 2, comparatively with the maximum permissible limits accepted by the European Union (Fonts et al., 2009a; Alvarez et al., 2015).

3. PYROLYSIS PROCESS

Before being subjected to the pyrolysis process, the sewage sludge must be dried, usually at temperatures of 100-105 °C for 24 hours (Chen et al., 2018; Yongjie et al., 2018).

Pyrolysis is a process of decomposition of materials, producing vapors that can be condensed, bio-oil, and non-condensable vapors (syngas), as shown in Figure 1.

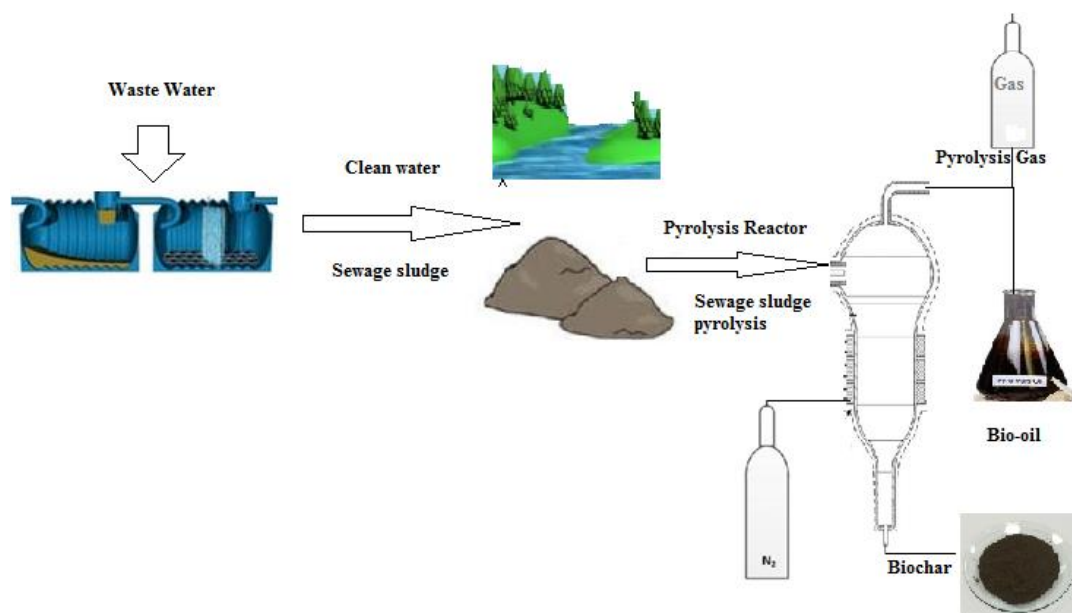


Figure 1. Scheme of the process of pyrolysis, from raw material to final products (Alvarez et al., 2015)

After the formation of pyrolysis products, a solid residue remains, called bio-char. The pyrolysis process is differentiated from the gasification process by the following aspects: gasification is performed under oxygen atmosphere in a proportion of 20% - 40% obtaining combustible gas; pyrolysis takes place under inert nitrogen atmosphere, at higher temperatures of 500 °C -1000 °C, being a thermochemical reaction (Kim and Parker, 2008).

Pyrolysis is considered an environmentally friendly process because it reduces the emission of greenhouse gases, while heavy metals are concentrated in the final residue. The pyrolysis process applied to the sewage sludge can be of two types (Gopinath et al., 2021).

1. slow pyrolysis - performed at 300 °C -800 °C, with a temperature increase rate of 1 °C/s;
2. rapid pyrolysis - performed at 500 °C -1000 °C with a temperature increase rate of 10 °C - 200 °C /s

The type and composition of the final products obtained from the pyrolysis process of the sewage sludge may differ depending on the temperature of the pyrolysis process. The average temperature

is used to optimize the production of bio-oil (Yaman, 2004; Stuard et al., 2006; Briens et al., 2008; Fonts et al., 2009b; Ferreiro-Domingues et al., 2012; Karaca et al., 2018). In addition to the temperature parameter, others can be varied, such as: sludge particle size, residence time, heating rate (Basu, 2010). During the pyrolysis process, two temperature ranges can be identified. The first interval is between 180 °C-550 °C, where the pyrolysis of the reactive compounds takes place, for the most part, and less the pyrolysis of the less active compounds (Uban and Antal, 1982; Conesa et al., 1997; Conesa et al., 1998; Fonts et al., 2001; Magdziarz and Werle, 2014). During this temperature range, the loss of volatile matter, the rupture and the appearance of free radicals that lead to the formation of gases such as CO and CO₂ and the bio-char residue, are achieved (Balat, 2008). The second temperature range, 385 °C-550 °C, is conducted for the pyrolysis of less reactive compounds. The organic compounds remaining in the bio-char can then be transformed into tar and secondary bio-char (Kouloumbis et al., 2000; Shao et al., 2008; Kargbo, 2010; Siddiquee and Rohani, 2011; Yin, 2012; Gao et al., 2014; Nowicki and Ledakowicz, 2014).

3.1. SYNGAS

The pyrolysis process of the sewage sludge generates the syngas, which consists of hydrocarbons such as CH₄, along with CO₂, CO, H₂, O₂, N₂ and water (Shen and Zhang, 2003).

At lower pyrolysis temperatures (250-350 °C), the predominant gas is CO₂, but also N₂. Increasing the temperature of the pyrolysis process leads to an increase in CO and H₂, and a decrease in CO₂. Hydrocarbons (CH₄, C₂H₄, C₂H₆) form in a high yield, in particular CH₄ at the pyrolysis process temperature of 600 °C, and C₂H₄ and C₂H₆ at 450 °C (Inguanzo et al., 2002).

3.2. BIO-OIL

The bio-oil obtained following the pyrolysis process of the sewage sludge has a dark brown color (Ju et al., 2010). It consists of an aqueous phase, an inorganic phase and a mixture of organic compounds. The water must be removed from the bio-oil by filtration, the obtained liquid being reddish-brown (Onay, 2007; Briens et al., 2008; Meier et al., 2013). It contains hydrocarbons, such as alkanes, alkenes, alkynes, aromatic hydrocarbons. The amount of hydrocarbons increases with the reaction temperature, but also the water content increases with the reaction temperature, from 27% to 54% (Park et al., 2010).

Bio-oil can be used as an alternative fuel for fossil fuels. For this, bio-oil must undergo a process of fragmentation, recovery and refining (Park et al., 2010). The physical-chemical properties of bio-oils can vary depending on the applied technology, but also on the raw material being used. The main problem in the use of bio-oils in diesel engines is the amount of water in their component, but also the lower calorific value and high acidity. The physical-chemical properties of bio-oils are directly related to the behavior of the fuel used in the engine, the performance of the system and the engine (Pokoma et al., 2009). Sometimes there can be ignition complications if the fuel quality is low. For these reasons, bio-oil must be improved according to the standard of motor fuels (Yang et al., 2013).

3.3. BIO-CHAR

The process of pyrolysis of sewage sludge results in a final residue called bio-char. It is rich in carbon, but also in inorganic components (Bridgwater, 2012). Bio-char has high ash content (65.9%) due to the high content of inorganic substances from the raw material, sewage sludge, remaining in the biochar following the pyrolysis process. The energy value of biochar is, as

presented in the literature, 7.4 MJ/kg (Fonts et al., 2012; Lu et al., 2013). Due to the high ash content of biochar, its energy value is low.

Bio-char can be used as an adsorbent after undergoing a process of thermal and chemical activation (Gu et al., 2013). Adsorbent developed from bio-char can be used for the capture and storage CO₂ and other gaseous pollutants, such as H₂S and CO₂, after undergoing a process of thermal and chemical activation (Monsalvo et al., 2012; Gu et al., 2013). The preparation of biochar as an adsorbent has several stages: drying of the sewage sludge to remove the high water content, carbonization of the dehydrated sewage sludge and chemical and physical activation to obtain the biochar (Bonfiglioli et al., 2014).

4. ECONOMICAL AND ENVIRONMENTAL ADVANTAGES

The pyrolysis process and its products have several economic and environmental advantages. The main advantage is the disposal of wastes, such as sewage sludge, in order to develop alternative and renewable fuels that contain high levels of environmentally friendly carbon. The raw material is available in large quantities and for free. This process develops autonomous energy with high economic potential, given the environmental potential.

The pyrolysis has the potential for different chemicals production, thus developing alternative, economic and environmental resources (Agrafioti et al., 2013). Even if the sewage sludge has in its composition heavy metals (chromium, lead, copper, nickel), some of them evaporate at high specific temperatures during the pyrolysis process (arsenic, cadmium, mercury), while others accumulate in bio-char, usually their levels being within the allowed limits (Lester et al., 1983; Ormrod and Webster, 2000; Angerbauer et al., 2008; Barbosa et al., 2009; Azuara et al., 2010; Jahirul et al., 2012).

5. CONCLUSIONS

Growing global population, chaotic energy consumption, declining fossil fuels, and increasing waste production have caused major concerns due to their long-term effects on the environment, causing greenhouse gas emissions, which are responsible of global warming.

Wastes such as sewage sludge represent an alternative for the production of sustainable and renewable fuel, as such wastes are generated in large volumes, for free, being less polluting as biofuel. The resulted biofuels from the pyrolysis of sewage sludge are efficient compared to fossil fuels. Among the different types of processes for energy production, pyrolysis, gasification, incineration, the pyrolysis process is the most appropriate because it takes place under nitrogen atmosphere and in the absence of oxygen, generating valuable final products, bio-oil, syngas and bio-char.

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