BIO-OIL AND BIOGAS FROM THE PYROLYSIS OF SEWAGE SLUDGE, AND NON-ISOTHERMAL DEGRADATION ON USY ZEOLITE

^a Pedroza, M. M.¹; ^b Souza, J. F.; ^c Vieira, G. E. G.; ^b Bezerra, M. B. D.

^a Federal Institute of Education, Science, and Technology of Tocantins (IFTO) – Palmas/TO – Brazil

^b Federal University of Rio Grande do Norte (UFRN) – Natal/RN – Brazil

^c Federal University of Tocantins (UFT) – Palmas/TO – Brazil

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ABSTRACT

This paper examines the pyrolyzation of sewage sludge using a bench scale reactor and the characterization of its products. Non-isothermal degradation via thermogravimetry was used to estimate activation energy of regular and catalytic degradation under inert atmosphere. The pyrolysis reactor, a rotating cylinder coupled to a gas-washing column with a centrifuge at the top, was used to condensate pyrolysis vapors. The experimental procedure was divided into two parts: (I) pyrolysis of a sewage sludge guided by a 2^3 experimental design with center point, at temperatures of 520, 560, and 600 °C; inert flow rates of 3, 4.5, and 6 L h⁻¹; centrifugation rotation frequencies of 20, 23, and 26 Hz; under a constant biomass flow rate of 408 g h⁻¹; (II) determination of the activation energy of thermal degradation, with and without the USY zeolite catalyst, using an isoconversional analysis of integration. For the later, three heating rates were tested: 5, 10, and 20 °C min⁻¹. The bio-oil obtained in the bench-scale pyrolysis reactor had the following characteristics: pH from 6.0 to 8.1, density from 1.0 to 1.1 g mL⁻¹, solid contents from 0.7 to 0.8%, and higher heating values from 17.4 to 18.4 MJ kg⁻¹. The bio-oil consisted mostly of aliphatic and monoaromatic hydrocarbons, substituted aromatics, polyaromatic hydrocarbons, long amides, and amines. The components found in the gas phase were: H₂, CO, CO₂, CH₄, C₂, C₃, C₄, C₅, and C₆. The syngas maximum content was 59.2%. Results from the thermal analysis showed that the USY was effective in decreasing the thermal degradation activation energy. Near the temperature when the pyrolysis occurred, the activation energy dropped from 78.5 to 62.6 kJ mol⁻¹, and the conversion was 80%. The average values observed for the activation energy with and without catalyst, at conversions from 40 to 80%, were 103.9 and 155.0 kJ mol⁻¹, respectively, which indicates that the USY zeolite successfully enabled a new pathway for the sewage sludge's thermal degradation.

KEYWORDS

sewage sludge; pyrolysis; thermal degradation; isoconversional analysis; USY zeolite

¹ To whom all correspondence should be addressed.

Address: Avenida Joaquim Teotônio Segurado, Quadra 202 sul, ACSU-SE 20, Conjunto 1, Lote 8, Plano Diretor Sul, Palmas - TO, Brazil.

ZIP Code: 77020-450 | e-mail: mendes@ifto.edu.br

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1. INTRODUCTION

The production of sewage sludge has been increasing in developing countries due to population growth. The disposal of waste presents a major environmental problem for public and private sanitation companies. One can estimate that Brazil produces between 150 and 220 000 tons of dry matter per year. Whereas only 30% of the urban population have their sewage collected and treated properly, it is expected that the generation of sludge would exceed 400 000 tons per year if the sewers were fully treated in the country (Oliveira Silva et al., 2012).

The three most common treatment methods for waste sludge are: (i) elimination in landfills, (ii) use in agriculture, and (iii) incineration. None of these methods is free of disadvantages. The presence of heavy metals in the sludge makes this material improper for use in agriculture. The incineration process is considered expensive, and it also generates air, ground, and water pollution. The disposal in landfills is the most commonly used method for the disposal of sewage sludge from wastewater treatment plants in Brazil. The major drawbacks of this practice are the decrease in useful life of landfills for the disposal of urban solid wastes (Pedroza, 2011), and the risks associated with this process for human health. To address these problems, researchers worldwide are working on the development of sewage sludge processing technologies. Among the most interesting newly developed technologies are pyrolysis, gasification, and wet oxidation due to their low energy requirements (Breulmann et al., 2017; Dai et al., 2015). Pyrolysis, in particular, has the advantage of producing three different phases which have many applications. The main product is the pyrolysis liquid, also called bio-oil, that has great potential to be used as bio-fuel after undergoing chemical and physical treatments such as catalytic hydrogenation, esterification, distillation (Boateng et al., 2015; Kim et al., 2014), among several others. The second most important products are the pyrolysis gases, which usually have high heating values, also with potential to be used as a fuel, as well as a source of hydrogen. The third most important pyrolysis product is the charcoal, also known as char, which, in the case of sewage sludge, contains high amounts of active metals that are able to catalyze the production of hydrocarbons, (Nascimento et al., 2017), mostly

from methane to butane. For this reason, pyrolysis is considered a viable route to transform sewage sludge into valuable fuels and, at the same time, reduce the amount of the product that is released into the environment. Currently, there are only a reduced number of published works addressing this issue, and a limited number of variables investigated. The configuration of the experiments usually involves a fixed bed, without the use of catalysts. Gao et al. (2014) studied the effect of temperature and residence time on product quality, the kinetics was determined via TG-FTIR. Agraoti et al. (2013) used a muffle furnace to pyrolyze sewage sludge impregnated with K_2CO_3 , their research focused on the yield and quality of the char. Fonts et al. (2012) did a thorough review on the conversion of sewage sludge into liquids. In their research, the authors mention the various kinds of processes and how those are affected by parameters such as residence time, temperature, and carrier gas.

An interesting and effective way of enhancing the properties of pyrolysis products is to use catalysts (Leng et al., 2015; Azuara et al., 2015). However, due to difficulties in producing catalysts for actual bench-scale pyrolysis reactors, catalysts usually are screened in a much smaller scale (mg) where coking (Jae et al., 2014) and deactivation (Boateng et al., 2010; Aguilar et al., 2015), as much as the amount needed for pyrolysis, are minimal. The results are similar between scales, reason why the use of micropyrolyzers has become quite common as they emulate bench-scale reactors with the main advantage of keeping the temperature rigorously steady. Thermobalances, unlike micropyrolyzers, do not offer such advantage. Instead, they offer a wide range of options for kinetic studies because of their capability of measuring mass changes as a function of temperature (Jain et al., 2016; Yuan et al., 2015), which proves to be simple and effective for catalyst screening based on activation energy changes.

Given this context, this study aims to determine the chemical characteristics of sewage sludge pyrolysis products (bio-oil and gas) using a bench-scale reactor, and investigate the effect of the USY zeolite on the activation energy of sewage sludge non-isothermal degradation via thermogravimetry.

Figure 1. Schematic diagram of the pyrolysis unit. 1 - Biomass hopper; 2 - Feed system; 3 - Rotameter; 4 - Pyrolysis reactor; 5 - Furnace; 6 - Char collectors; 7 - Reactor inclination system; 8 - Temperature control system; 9 - Vapor washing column; 10 - Centrifuge; 11 - Bio-oil collectors; 12 - Vent; 13 - Gas collector.

2. MATERIALS AND METHODS

2.1 Sewage sludge characterization, preparation, and mass balance

Samples of sewage sludge were collected from a UASB reactor located in the city of Palmas/TO, Brazil. They were dried for 24 h in oven at 103 °C, crushed, and then sieved to fine pieces of about 0.5-1 mm to ensure homogeneity and facilitate analytical procedures.

Proximate and elemental analyses were carried out following standard procedures. The elemental analysis was performed using a Perkin Elmer CHNS analyzer. Moisture was determined via ASTM D 3173-85, ash and volatile matter were determined following the methodology described by [Sanchez et al. \(2009\)](#). Fixed carbon was obtained by difference. A Parr 1341 bomb calorimeter was used to determine Higher Heating Values (HHV). Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) was used to analyze the composition of inorganic material. The cellulose, hemicellulose, and lignin contents were determined via the Klason method, reported by [Pedroza \(2011\)](#). Mass balance was determined gravimetrically. The gas phase was determined by

difference, that is, 100% - liquids - solids.

Before pyrolyzation, the sewage sludge was dried at 70 °C for 3 hours to keep moisture below 10%.

2.2 Customized bench-scale rotating cylinder reactor

The pyrolysis unit, shown in Figure 1, was designed to process up to 1 kg of biomass per hour. The continuous feeding system consists of a biomass mixer (hopper) and a helical spring. The spring is intended to facilitate the flow of biomass into the reactor. Nitrogen was used to facilitate the flow of gases and enhance heat transfer. The reactor, that is 100 cm by 10 cm, is heated by a furnace and rotates at 33.7 rpm. Biomass feeding rate was 480 g h⁻¹. The carbon-rich char produced during pyrolysis was retrieved in gas-solid separators. The separation system consisted of five cylindrical metal tubes arranged in series. The centrifuge is used to condense vapors, which are instantly transformed into bio-oil at the top of the vapor's washing column, and collected in stainless steel reservoirs. The gases were sampled with the help of a customized air mattress and analyzed for their composition.

In this unit, one is allowed to vary the temperature, nitrogen's flow rate, and the frequency at which the centrifuge rotates. To identify the optimal combination of variables, able of maximizing or minimizing the yields, a set of experiments were designed to explore the influence of each of these variables. The temperature, controlled by the furnace, was permitted to vary from 520 to 600 °C; nitrogen's flow rate was controlled by a calibrated rotameter, varied from 3 to 6 L h⁻¹; and the centrifuge rotation frequency was controlled by a frequency inverter, varied from 20 to 26 Hz. Eleven experiments were conducted in the pyrolysis unit. The results were used to develop an equation able to predict hydrogen formation.

2.3 Pyrolysis products characterization

Prior to conducting the analysis, the bio-oil was dissolved in dichloromethane before injection in a Varian CP3800 Gas Chromatograph coupled to a Mass Spectrometer. Details on the GC/MS procedures are reported in previous work published by Sousa et al. (2016). The density was measured by a pycnometer at 20 °C. The viscosity was determined using a Thermo Scientific rheometer, model Haake, at 20 °C. The pH was determined with a TECNAL pH-meter, also at 20 °C. The gas phase was sampled with portable gas cylinders and analyzed for its composition using an HP 5890 Gas Chromatograph equipped with a Thermal Conductivity Detector. The caloric value of the gas was calculated using the ISO 6976 (1995) (2016 revision).

2.4 Catalyst

The USY zeolite used in the kinetic study was provided by PETROBRAS and had the following composition: SiO₂ (71.18%), Al₂O₃ (27.02%), SO₃ (1.78%), and Cr₂O₃ (0.02%).

2.5 Thermogravimetric analysis

The equipment used for the thermal analysis was a Shimadzu 51H thermobalance. The temperature ranged from 25 to 900 °C using three heating rates: 5.0, 10.0 and 20.0 °C min⁻¹, all under 6 L h⁻¹ of nitrogen. The mass of sample was ~20 mg. The concentration of catalyst, when used, was 2%. All experiments were conducted in duplicate.

2.6 Kinetics

The isoconversional kinetic analysis of thermal decomposition of solids was based on the Arrhenius law for non-isothermal conditions (Rueda-Ordóñez & Tannous, 2016). This kind of analysis has been successfully applied to the pyrolysis kinetics of many biomass materials (Slopiecka et al., 2012; White et al., 2011; Mishra & Bhaskar, 2014) due to the simplicity and ability to represent this complex pyrolysis reaction (Amutio et al., 2013).

Likewise, the non-isothermal degradation of the sewage sludge can be assumed to take place as a 1-step reaction:

Which can be expressed by Equation 2, where the effective activation energy E is as a function of conversion, $E = f(\alpha)$ (Santos et al., 2010):

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad (2)$$

Where $f(\alpha) = (1 - \alpha)^2$; $(1 - \alpha)$ is the remaining fraction of volatiles in the sample; k is the velocity constant, commonly expressed by the Arrhenius Equation (3):

$$k = k_0 \cdot \exp\left(-\frac{E}{RT}\right) \quad (3)$$

Where k_0 (s⁻¹) is the pre-exponential factor; E (kJ mol⁻¹) is the apparent activation energy; R (8.314 kJ mol⁻¹ K⁻¹) is the universal gas constant; and T (K) is the temperature of degradation.

The conversion α can be determined for different temperatures using Equation 4:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (4)$$

Where m_0 (mg) is the initial mass of sample; m_t (mg) is the mass of sample at time t (min); and m_f (mg) is the remaining mass of sample after reaction. Combining Equation 2 with the heating rate $\beta = dT/dt$, the following is obtained:

$$\frac{d\alpha}{dT} = \frac{k}{\beta} \cdot f(\alpha) \quad (5)$$

Where da/dT (s^{-1}) is the rate of reaction. Substituting the Arrhenius Equation (3) into Equation 5:

$$\frac{1}{f(\alpha)} d\alpha = \frac{k_0}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (6)$$

Which can be integrated as follows:

$$\int_0^\alpha \frac{1}{f(\alpha)} d\alpha = g(\alpha) = \frac{k_0}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (7)$$

When it comes to large E values, such as that $E/2RT \gg 1$, the right-hand side of Equation 7 can be approximated by the following expression:

$$\int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \approx \frac{R}{E} T^2 \exp\left(-\frac{E}{RT}\right) \quad (8)$$

Equation 8 is used to determine the activation energy for any conversion value. Once the equation is integrated and rearranged:

$$\log \frac{\beta}{T_\alpha^2} = \log \left(\frac{R}{E_\alpha} \frac{k_0}{g(\alpha)} \right) - \frac{E_\alpha}{R} \frac{1}{T_\alpha} \quad (9)$$

The calculation of activation energy using this methodology requires at least three heating rates for each conversion as a function of temperature. The conversions are chosen systematically based on the TGA/DTG curve behavior near the temperature range at which pyrolysis takes place. All this translates to plots of $\log(\beta/T_\alpha^2)$

versus $1/T_\alpha$ which should be straight lines with slopes equivalent to E_α/R .

3. RESULTS AND DISCUSSION

3.1 Mass balance

The mass balance for the sewage sludge, using this reactor, was not influenced by the operating conditions under investigation. Table 1 shows the average values of each phase. Zhang et al. (2011) reported similar values using a wide range of temperatures (from 600 to 1000 °C) in a tubular reactor.

The production of char traditionally happens in large quantities mostly due to the low content of volatile matter, which is converted into gas and liquid. The bio-oil usually is below 10% due to the high temperature under which the reactor operates, and also because of the inefficiency of the condensation system. The water content is considered to be part of the vapors that were supposed to be condensed due to its little affinity for the organic phase. This characteristic is also related to the nature of the sewage sludge.

3.2 Sewage sludge characteristics

The general characteristics of the sewage sludge are presented in Table 2. Iron was found in large

Table 1. Mass balance (%).

Bio-oil	Char	Water	Gas
8.8 ± 1.1	52.7 ± 3.9	14.3 ± 2.2	19.6 ± 2.6

Table 2. Characteristics of the sewage sludge as received (db = dry basis; daf = dry ash-free basis).

Moisture (%)	6.0	Fe ($mg\ kg^{-1}$)	28911	Cellulose (%)	4.2
Volatile matter (%db)	53.9	Zn ($mg\ kg^{-1}$)	891	Hemicellulose (%)	12.8
Ash (%db)	38.1	Mn ($mg\ kg^{-1}$)	82	Lignin (%)	17.9
Fixed carbon (%db)	2.0	Cu ($mg\ kg^{-1}$)	219		
Carbon (%daf)	28.0	Ni ($mg\ kg^{-1}$)	24		
Hydrogen (%daf)	4.6	Cr ($mg\ kg^{-1}$)	39		
Oxygen (%db)	23.2	Pb ($mg\ kg^{-1}$)	47		
Nitrogen (%daf)	4.9				
Sulphur (%daf)	1.2				
HHV ($MJ\ kg^{-1}$)	21.1				

Table 3. Characteristics of bio-oil from sewage sludge pyrolysis at different temperatures.

Temperature (°C)	520	560	600
pH	6.0	6.2	8.1
Density (g mL ⁻¹)	1.0	1.1	1.1
HHV (MJ kg ⁻¹)	18.4	17.4	17.9
Solids content (%)	0.8	0.7	0.8
C (%)	42.4	44.0	43.5
H (%)	9.9	9.4	9.0
O (%)	39.8	40.0	39.9
N (%)	7.4	6.2	7.3
S (%)	0.5	0.4	0.3

quantities (28911 mg kg⁻¹). The high nitrogen content is typical for this kind of biomass, mostly because it contains residues of proteins and peptides from microorganisms used in the treatment process. The second most abundant metal was zinc (891 mg kg⁻¹). The content of lignocellulosic material in the sewage sludge is related to its source. For a population whose diet is rich in fiber, the levels of cellulose and lignin of the sewage sludge are expected to be high. In this study, such contents were much lower than those of lignocellulosic biomass, such as elephant grass, that is 70% (Braga et al., 2014). This usually means that the resulting bio-oil is expected to be less unstable and prone to polymerization catalyzed by components derived from lignin and cellulose.

3.3 Pyrolysis bio-oil characteristics

The properties of bio-oil obtained at different temperatures are presented in Table 3. The pH values are higher than those reported for bio-oils from the pyrolysis of sugarcane trash (Treedet & Suntivarakorn, 2012), which was 3 for regular bio-oil and 2 for dehydrated bio-oil. That is mostly due to the presence of phenols and nitrogenated compounds. Nitrogenated compounds identified in bio-oils from sewage sludge are classified into five different groups based on their structural names, including nitriles, pyridines, amides, amines, and polyaromatics.

The solid contents (~0.8%) were much higher than those observed by Fonts et al. (2009), that was 0.03%. Sousa et al. (2016) pyrolyzed elephant grass in a 40 kg h⁻¹ fluidized bed reactor and found the solid contents to be ~3.18%. Actually, the solid contents were more affected by other factors such as gas flow rate and efficiency of the char

recuperation apparatus, than temperature or configuration of the reactor where pyrolysis was conducted. Electrostatic precipitation has been reported to be the most efficient condensation system (Oasmaa et al., 2008). This study used a vapor washing column and a centrifuge. Still, 0.8% of solids in the bio-oil were not expected to cause instability or catalyze unwanted reactions during storage. The density and viscosity are also major characteristics of bio-oils. The density varied from 1.0 to 1.1 g mL⁻¹ and was only slightly higher than that of biodiesel (Yang et al., 2013), which was ~0.88 g mL⁻¹; and lower than those (~1.3 g mL⁻¹) reported in the literature for bio-oil from different sources (Fonts et al., 2009; Oasmaa et al., 2008).

The oxygen content varied from 39.8 to 40.0%. The high oxygen content is associated with the presence of many highly polar groups, which leads to high viscosity and phase separation, as well as poor chemical stability. A significant fraction of the oxygenated compounds in pyrolysis oils is derived from water by hydrolysis. Pyrolysis liquids are not as stable as conventional petroleum oil due to their high content of highly reactive oxygenated compounds (Oasmaa et al., 2008). There are several ways of reducing the oxygen content of bio-oils. The most common and recommended one is the in situ catalytic upgrading (Bridgwater, 2012), where a solid catalyst, usually zeolites, helps minimize secondary reactions such as polymerization, giving more stability to the bio-oil and, therefore, favouring a noble application of this product. Despite the aforementioned disadvantages caused by oxygenated compounds (aromatics included), bio-oil has been successfully used in boilers and has shown potential for use in diesel engines and turbines (Alcala & Bridgwater, 2013; Fontoura et al., 2015; Boateng et al., 2016),

Figure 2. Areas of the functional groups of sewage sludge bio-oil. AHs = Aliphatic hydrocarbons; MAHs = Monoaromatic hydrocarbons; SAs = Substituted aromatics; PAHs = Polyaromatic hydrocarbons.

small scale power generators (Shemfe et al., 2015; Martin & Boateng, 2014), and even a 150 kg h⁻¹ FCC unit (Pinho et al., 2015). The HHV of bio-oil varied from 17.4 to 18.4 MJ kg⁻¹. Oasmaa et al. (2008) reported values ranging from 13 to 18 MJ kg⁻¹. The heating values of the pyrolysis liquid are usually half of that of gasoline, and those values correlate with the water content (Garcia-Perez et al., 2007), that usually is high.

The results from the chromatographic analysis show that the bio-oil from sewage sludge consists of aliphatic hydrocarbons, monoaromatic and polyaromatic, long chain carboxylic acids; aldehydes, ketones, nitriles, esters, alcohols, amides, and amines. The absence of sulfur compounds is also typical. Figure 2 shows the areas of the peaks of functional groups of the main constituents. Aliphatic hydrocarbons were found in greater quantities (60% at 600 °C) than all the others, regardless of the temperature. The aromatic substituted compounds ranged from 10 to 14% at the three temperatures investigated.

The concentrations of MAHs, SAs, and PAHs increased with temperature. The highest PAH concentration was 16% at 600 °C (Figure 2). Hu et

al. (2014) also reported that the final temperature and residence time of pyrolysis influence PAH formation. The authors pyrolyzed sewage sludge at various temperatures (450, 550, 650, 750, and 850 °C) and also observed that PAH concentration increases sharply with temperature. The highest PAH contents were found at 750 °C, and were 7.1 mg kg⁻¹ of low molar mass, 18.1 mg kg⁻¹ of middle molar mass, and 4.3 mg kg⁻¹ of high molar mass. The authors also presented a formation mechanism. They proposed that the pyrolysis of alkanes at high temperature generates alkenes and dienes via dehydrogenation, also called Diels-Alder reaction mechanism, which, by cyclization and subsequent aromatization, produces aromatic compounds.

3.4 Biogas characteristics

The components found in the sewage sludge pyrolysis gases were H₂, CO, CO₂, and light hydrocarbons such as CH₄, C₂, C₃, C₄, C₅, and C₆. Zhang et al. (2011) also pyrolyzed sewage sludge at 600 °C and obtained exactly the same components. Domínguez et al. (2006) pyrolyzed wet sewage sludge in a quartz reactor at temperatures from 500 to 900 °C and found the following gases: H₂,

Table 4. Operating conditions and properties of sewage sludge pyrolysis gases (N₂ free basis).

Exp.	Operating conditions			Gas composition (%)				$\hat{C}$ (kJ m ⁻³)
	T (°C)	Q _{N2} (L h ⁻¹)	F _{rot} (Hz)	CO ₂	H ₂	CO	C _n H _m	
1	600	3	20	30.2	43.0	10.8	16.0	10.23
2	520	6	20	25.5	31.9	12.5	30.1	13.76
3	520	6	26	30.1	36.0	15.3	18.6	10.94
4	560	4.5	23	27.0	40.4	14.3	18.3	10.47
5	520	3	26	29.1	30.2	10.9	29.8	14.14
6	600	6	20	32.0	45.2	8.2	14.6	9.74
7	560	6	23	28.1	40.9	13.6	17.4	10.92
8	600	3	26	30.0	45.5	13.7	10.8	7.89
9	520	3	20	24.4	31.9	10.4	33.3	14.38
10	600	6	26	29.0	46.2	13.0	11.8	9.48
11	560	4.5	23	27.3	40.2	13.9	18.6	10.28

O₂, N₂, CO, CO₂, CH₄, C₂H₄, and C₂H₆. **Hossain et al. (2009)** studied the evolution of volatiles and found that CO₂ is formed at much lower temperatures, while CO formation occurs at temperatures up to 500 °C. Hydrocarbons were identified from 300 to 600 °C, while hydrogen began to evolve at 300 °C showing a constant formation rate at the pyrolysis final temperature. However, according to **Inguanzo et al. (2002)**, the content of H₂ increases continuously with temperature. **Casajus et al. (2009)** used a fixed-bed reactor at several different temperatures and found that hydrogen was the main constituent of the gas and that it started production at 400 °C, with the maximum being reached between 600 to 700 °C.

Experimental design results are presented in Table 4. T is the pyrolysis temperature in °C; Q_{N2} is the flow rate of nitrogen in L h⁻¹; and F_{rot} is the frequency rotation (Hz) under which the centrifuge operated. $\hat{C}$ is the gas calorific value, in kJ m⁻³. All hydrocarbons, from C1 to C6, were grouped into C_nH_m.

The highest hydrogen content was 46.2%, which was obtained under the following operation conditions: temperature of 600 °C, inert flow rate of 6 L h⁻¹ and centrifuge rotation frequency of 26 Hz. The lowest concentration (30.2%) was observed under the conditions: temperature of 520 °C, inert flow rate of 3 L h⁻¹, and centrifuge rotation frequency of 26 Hz.

The caloric value ranged from 7.89 to 14.38 kJ m⁻³. The highest caloric value was observed under the following experimental conditions: reactor

temperature of 500 °C, inert gas flow rate of 6 L h⁻¹, and rotation frequency of 20 Hz. The highest concentrations of hydrocarbons were also observed under these experimental conditions, indicating that the caloric value of the gas phase is influenced by the evolution of hydrocarbons during pyrolysis. **Inguanzo et al. (2002)** reported that there is a direct relationship between the composition of hydrocarbons and the caloric value of the gas phase. The authors reported a value of 17 MJ m⁻³ for the gases obtained at 455 °C.

One can observe that high temperatures promoted dehydrogenation of heavy hydrocarbons. Furthermore, the H₂ can be formed from secondary cracking of the vapors during pyrolysis. The initial moisture content of the sewage sludge may have generated an atmosphere rich in water vapor. The carbon monoxide in the gas phase may have reacted with it favouring the formation of more H₂ in the well-known water-gas shift reaction. The high iron content may also have influenced the reaction since iron can act as catalyst in dehydrogenation reactions, thus, furthering the production of hydrogen (**Hu et al., 2014**). Carbon monoxide and methane are also formed in the process. Aromatization reactions are also responsible for the formation of hydrogen. Such reactions occur between the components of pyrolysis vapors and are maximized when the gas residence time in the reactor is high, when it should not exceed 3 seconds (**Bridgwater, 2012**).

The thermal degradation of carboxylic groups occurs between 160 and 600 °C with an intensification at temperatures above 550 °C

Figure 3. Observed versus predicted values: H_2 from sewage sludge pyrolysis.

(Mishra et al., 2015; Leng et al., 2015; Azuara et al., 2015), and this may justify the high CO_2 concentration in the pyrolysis gases at 600 °C. Table 4 also shows an increase in CO concentration when the temperature increased from 520 to 560 °C and, then, a decrease in concentration at 600 °C. Literature reports that the concentrations of CO and CH_4 are reduced by the formation of water vapor from the gas-shift reaction, which increases the production of CO_2 (Zhang et al., 2011; Karayildirim et al., 2006).

Figure 3 shows the comparison between the values observed experimentally and those predicted by the model. The regression coefficient R^2 is 0.96. To confirm the significance of the model parameters and that experimental data are well represented, the F-test (ANOVA) was performed.

The experimental data revealed the existence of an optimal region for the generation of H_2 with the following operating conditions: temperature (550-600 °C), inert gas flow rate (4.5-6 $L h^{-1}$), and rotation frequency (23-26 Hz). The maximum content of CO_2 was 32.0%. This experiment was performed at 600 °C, centrifuge rotation frequency of 20 Hz, nitrogen flow rate of 6 $L h^{-1}$. The concentration of CO ranged from 8.2 to 15.3%. The maximum content of CO was determined under the

following experimental conditions: temperature of 520 °C, nitrogen flow rate of 6 $L h^{-1}$, and centrifuge rotation frequency of 26 Hz.

The main mechanism of CO and CO_2 formation involves cracking, decarboxylation, and decarbonylation of sewage sludge pyrolysis vapors. CO_2 and alkanes are formed during decarbonylation. Alkenes, water, and CO are formed during decarboxylation. CO and CO_2 are also formed from the thermal decomposition of oxygenated organic compounds (lipids, carbohydrates, cellulose, and lignin) and to a lesser extent from the decomposition of inorganic salts such as carbonates (Jaramillo-Arango et al., 2016). Synthesis gas with a concentration of 59.2% was obtained at 600 °C, 3 $L h^{-1}$, and 26 Hz. Other researchers also have reported that the syngas production from sewage sludge is affected negatively by temperature (Zhang et al., 2011; Inguanzo et al., 2002).

The hydrocarbons found in the gas phase in this study were CH_4 , C_2H_2 , C_2H_4 , and C_3H_8 . In some experiments, C4, C5, and C6 were also detected. Methane was found in larger quantities, the average values of 16.6 and 7.7% were detected at 520 and 600 °C, respectively. C2 and C3 contents proved to be inversely proportional to the

Figure 4. TG and DTG curves of sewage sludge with and without the USY catalyst.

temperature during the pyrolysis, such phenomenon has also been reported (Zhang et al., 2011). Xiong et al. (2013) showed that light hydrocarbon concentrations are capable of affecting reactions in the gas phase, especially if the residence time is high. Casajus et al. (2009) reported that the maximum hydrocarbon concentration occurred at 500 °C, where methane was the most abundant gas in the mixture. Domínguez et al. (2006) reported that the breakdown of tar, and especially partial gasification of char, may affect reactions in a process referred to as pyrolysis secondary reactions.

3.5 Activation energy calculation

Figure 4 shows TG and DTG curves for both catalytic and non-catalytic thermal degradation of sewage sludge at three heating rates (5, 10, and 20 °C min⁻¹). It is observed that up to a temperature of 400 °C, all TG curves show a similar behavior with respect to mass loss with and without the USY

catalyst. The most aggressive mass loss was observed at 5 °C min⁻¹, without the catalyst. Sewage sludge is a very heterogeneous material that contains high amounts of inorganic ash, which undergoes degradation or decomposition only at high temperatures. If the organic matter is well mixed with the ash, this may cause delays in the heat transfer and subsequent separation (or diffusion of the organic matter from within the ash particles) that can only be evidenced at high heating rates such as 10 or 20 °C min⁻¹. The catalyst may also have contributed, as noted, at temperatures above 400 °C (near pyrolysis) and at 10 °C min⁻¹.

Sewage sludge mass loss in TGA is a slow process that occurs in extended temperature ranges, usually from 140 to 450 °C. The mass loss percentage at 140.2 °C, without USY, and at 5 °C min⁻¹ was 12.5%, which is very close to the value obtained for the moisture content of the sample in the classical gravimetric analysis, that is 12.0%. At

20 °C min⁻¹, the final temperatures for water loss, with and without USY, were 135.6 and 145.6 °C, respectively. Decomposition of organic matter was observed in two events from 203.3 to 547.0 °C (with USY, at 5 °C min⁻¹). The mass losses for these temperatures were 18.1 and 18.0%, respectively. There was a decrease in the thermal degradation rate at temperatures above 600 °C. The ash contents, at 5 °C min⁻¹, without USY, detected at the temperatures of 600, 815, and 900 °C were 33.58, 31.02, and 29.92%, respectively. This decrease in ash content may be due to the breaking of inorganic carbon present as carbonate compounds (CO_3^{2-} , HCO_3^-), decomposition of inorganic oxides, and also lignin. The decomposition of lignin starts at low temperatures, but it continues up to 900 °C. Below 600 °C, mass losses usually are associated with the thermal degradation of organic matter (Biagini et al., 2002). Above 600 °C, mass losses may be related to the degradation of inorganic material, such as calcium

carbonate.

To determine the kinetic parameters, the conversion was evaluated from 200 to 600 °C, that is, when pyrolysis of organic matter takes place. The conversions were calculated from the TG curves, considering the non-isothermal temperature range. The mass of catalyst was neglected during calculations. Details of events, conversions, and temperatures are summarized in Table 5. Four events of mass loss were observed at 5 and 10 °C min⁻¹ and only two events at the rate of 20 °C min⁻¹, in both noncatalytic and catalytic treatments. The DTG curves demonstrate mass loss due to elimination of moisture, which is graphically represented by two events, the first one at 62.0 °C and the second at ~140.2 °C. T_i is the temperature of the initial event; T_f is the temperature of the final event; $\Delta T = T_i - T_f$; and Δm is the loss of mass that occurs in ΔT . Table 6 presents intermediate results, while activation energy values

Table 5. Mass loss events identified from TG/DTG curves of sewage sludge.

β (°C min ⁻¹)	Event	Without USY				With USY			
		T_i (°C)	T_f (°C)	ΔT (°C)	Δm (%)	T_i (°C)	T_f (°C)	ΔT (°C)	Δm (%)
5	1	23.2	62.0	38.8	10.2	28.2	81.0	52.8	8.0
5	2	90.7	140.2	49.5	2.3	100.6	142.6	42.0	2.6
5	3	169.0	324.3	155.3	21.1	203.3	350.3	147.0	18.1
5	4	367.8	486.7	118.9	17.2	409.8	547.0	137.2	18.0
10	1	20.2	75.0	54.8	10.1	25.2	94.2	69.0	9.0
10	2	100.6	142.6	42.0	2.2	99.6	166.9	67.3	3.8
10	3	149.9	360.6	210.7	24.2	171.7	359.0	187.3	20.5
10	4	365.8	478.7	112.0	9.0	379.6	540.0	160.4	20.8
20	1	24.1	135.6	115.5	10.2	26.0	145.6	119.6	13.1
20	2	156.9	531.3	374.4	35.6	185.4	576.3	390.9	30.0

Table 6. Values of α for different heating rates, with and without catalyst, used in the calculation of the activation energy.

α		Without USY			With USY		
		5 °C min ⁻¹	10 °C min ⁻¹	20 °C min ⁻¹	5 °C min ⁻¹	10 °C min ⁻¹	20 °C min ⁻¹
0.4	$\ln(\beta/T_{\alpha 1}^2)$	-10.98	-10.28	-9.68	-11.07	-10.35	-9.70
0.4	$1000 T_{\alpha 1}^2$	1.84	1.85	1.77	1.76	1.79	1.75
0.5	$\ln(\beta/T_{\alpha 2}^2)$	-11.12	-10.42	-9.80	-11.22	-10.50	-9.90
0.5	$1000 T_{\alpha 2}^2$	1.72	1.73	1.66	1.63	1.66	1.58
0.6	$\ln(\beta/T_{\alpha 3}^2)$	-11.29	-10.57	-9.93	-11.39	-10.66	-10.04
0.6	$1000 T_{\alpha 3}^2$	1.59	1.60	1.56	1.51	1.53	1.47
0.7	$\ln(\beta/T_{\alpha 4}^2)$	-11.44	-10.77	-10.11	-11.52	-10.80	-10.16
0.7	$1000 T_{\alpha 4}^2$	1.47	1.45	1.42	1.40	1.42	1.39
0.8	$\ln(\beta/T_{\alpha 5}^2)$	-11.52	-10.91	-10.34	-11.64	-10.91	-10.39
0.8	$1000 T_{\alpha 5}^2$	1.38	1.34	1.26	1.33	1.35	1.24

Table 7. Effect of the USY catalyst on activation energy of sewage sludge thermal degradation.

α	Without USY				With USY			
	$T_{\alpha 1}$ (°C)	$T_{\alpha 2}$ (°C)	$T_{\alpha 3}$ (°C)	E_a (kJ mol ⁻¹)	$T_{\alpha 1}$ (°C)	$T_{\alpha 2}$ (°C)	$T_{\alpha 3}$ (°C)	E_a (kJ mol ⁻¹)
0.8	450.69	468.00	516.34	78.5	479.34	468.09	534.58	62.6
0.7	450.69	468.00	516.34	78.5	479.34	468.09	534.58	62.6
0.6	357.25	350.69	368.01	189.3	389.98	379.62	407.30	134.4
0.5	308.11	306.26	327.98	111.8	340.03	330.55	359.9	78.3
0.4	268.62	266.75	292.87	96.3	294.84	286.02	298.42	57.9

are presented in Table 7.

All the values of activation energy observed during pyrolysis with the USY catalyst were lower than those without it. One can see that, during the non-catalytic and catalytic treatments, the activation energy reaches a maximum and, then, it immediately decreases when the conversion is above 60%. One can also observe that for each conversion α , temperatures in the catalytic treatment were slightly higher than those in the non-catalytic treatment. This is probably due to heat exchange between the catalyst and the sewage sludge. It also implies that the reaction required lower activation energy to take place.

The results found in this work are consistent with those found by [Barneto et al. \(2009\)](#), who also reported that the degradation of the sewage sludge is slow from 160 to 450 °C. In addition, it is plausible to state that from 450 °C and at a heating rate of 5 °C min⁻¹, the degradation becomes more pronounced, favouring intramolecular reactions and leading to lower activation energies.

4. CONCLUSIONS

The chemical properties of sewage sludge such as high heating value (21.07 MJ kg⁻¹) and carbon content (26.97%) indicated it has potential for use as a precursor for the production of biofuels.

Samples of bio-oil presented pH values near neutrality and showed low viscosity, which can be attractive for large-scale applications. The HHV was 17.85 MJ kg⁻¹. The chromatographic analyses revealed a significant content of aliphatic hydrocarbons (which explains the low viscosity of the bio-oil), aliphatic oxygen, and the absence of sulfur compounds, raising the possibility of applying this product as source of fine chemicals.

The chemical characteristics of bio-oil are related to the physicochemical characteristics of the sewage sludge. Some of the functional groups present in the biomass are present in the form of other compounds in the pyrolysis liquid. Lignin and humic acids present in the sludge contributed to the formation of aromatics in the bio-oil.

The gas phase consisted of hydrogen, carbon monoxide, carbon dioxide, methane, and other hydrocarbons (C₂, C₃, C₄, C₅, and C₆). Hydrogen was the most abundant gas at high temperatures. Synthesis gas with a concentration of 53.4% was obtained at the following conditions: temperature of 600 °C, inert gas flow rate of 6 L h⁻¹, and centrifuge rotation frequency of 20 Hz. Following the characteristics reported in this work, the synthesis gas may be of interest for synthesis reactions, such as Fischer-Tropsch.

Although pyrolysis is classified as endothermic, the calorimetric profile also showed events of energy release. This energy release may be associated with intramolecular reactions and rearrangement of the molecular structure of organic compounds composing the organic matter. The USY catalyst proved effective in thermal degradation reactions by reducing the activation energy and enhancing heat exchange with the sewage sludge.

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