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Pyrolysis: an alternative technology for sustainable energy from sewage sludge

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Abstract

Sewage sludge production tends to grow due to the increased amount of treated sewage. Additionally, the limitations of the disposal lead to the need for alternative processes for technological use of this residue and pyrolysis is a promising way to obtain products with potential energy, such as bio-oil. In this work, the characterization of wastewater and the application of catalytic pyrolysis sludge had the addition of Fe_2O_3 as a catalyst, in order to optimize the bio-oil production. The sewage sludge characterization presented five values: moisture content 6.85% (m/m), ash 33.33% (m/m), volatile solids 54.99% (m/m), fixed carbon 4.83% (m/m) and calorific value 21.80 MJ.kg^{-1}. The thermal behavior of the sewage sludge was analyzed by thermogravimetric analysis (TGA), to check the catalytic activity of iron oxide with increasing volatilization and cracking of the organic substances present in sewage sludge, and thus reducing the formation of solid fraction. In the pyrolysis process an experimental planning of 2^3 with a central point has been used, and the effect of variables was analyzed at different process temperatures (450°C, 500°C and 550°C), time (120 min, 150 min and 180 min), heating rates (10°C.min^{-1}, 20°C.min^{-1}, and 30°C.min^{-1}) in the yield of obtained products. Statistical analysis showed that the temperature influenced the yields of bio-oil in a positive and significant way, the maximum yield was in the order of 15.60% (m/m) under the following conditions: temperature 550°C, time 180 min and 10°C.min^{-1} heating rate. Moreover, the bio-oil obtained from sewage sludge by pyrolysis can be used in the chemical industry and in power generation.
Keywords: sewage, sludge, pyrolysis, analysis, thermogravimetric, biomass.

1 Introduction

Biomass is one of the main and most important renewable energy sources, including through their conversion a wide range of materials, technologies and end-use applications products such as power generation, heat, biofuels for transport and supplies for chemical industries. Its generation and the efficient use appear as one of the biggest challenges of contemporary society (Bridgwater [1]).

Among the biomasses, the residual sewage sludge generated by the sewage treatment plants, is a major environmental problem for sanitation companies. Its management is a complex activity and it has a high cost when poorly executed. As a result, it can compromise the health benefits expected from such systems (Vieira *et al.* [2]).

Sewage sludge is composed of a heterogeneous mixture of undigested organic compounds and inorganic materials. In its constitution, it has a variety of functional groups, such as acids, alcohols, amines, amides, nitriles, ketones and hydrocarbons (Pedroza *et al.* [3]).

Different destinations are used for sewage sludge generated in treatment plants, among these processes are included the disposal in landfills, agricultural use, incineration and composting. Pyrolysis is an alternative that has been considered one of the promising ways. Additionally, its application to sewage sludge to obtain products with potential energy shows up as a way to leverage and add value to this waste turning it into raw material; consequently, reducing the environmental impacts caused by sewage sludge, as well as improper disposal. Moreover, the fact the sewage sludge to be abundant worldwide, makes the application of the pyrolysis process to that waste well successful and of great scientific and technological interest (Fonts *et al.* [4]; Gao *et al.* [5]).

In this context, this study aimed at the implementation of the pyrolytic process to sewage sludge with the addition of Fe_2O_3 in a proportion of 5% (m/m) to evaluate the performance of the fractions obtained and thus to determine the best process conditions in the pyrolysis, aiming a higher yield of bio-oil. Sewage sludge was characterized in order to discuss its influence in the pyrolysis and performed thermogravimetric analysis (TGA) to observe its thermal behavior and check the catalytic activity of the iron oxide.

2 Materials and methods

2.1 Collection and drying of sewage sludge

The sewage sludge used in this project was produced in a UASB (Upflow Anaerobic Sludge Blanket), during the dry season, in a sewage treatment plant, located in Palmas, Tocantins, Brazil.

The drying of the sewage sludge was performed in handmade solar oven until the constant weight. After that, it was milled using a mill and homogenized in a Tyler sieve with apertures of 0.355 mm.

2.2 Characterization of sewage sludge

The moisture of the sewage sludge was determined according to ASTM 3173 standard [6]. In addition, the content of volatile solids and ash were obtained according to ASTM 2415 [7] and the fixed carbon was determined by the difference. The gross calorific value was determined using the Parr bomb calorimeter 1341, Model 1241, performed in excess of O_2 and pressure of 20 to 30 atm.

2.3 Thermogravimetric analysis (TGA) and differential thermal analysis (DTA)

The evaluation of the thermal behavior of the sewage sludge was performed by thermogravimetric analysis (TGA), using a simultaneous equipment TGA/DTA of the TA Instruments, model 2960. The analyses were performed in an environment with air flow and nitrogen, both with a flow of 100 $ml.min^{-1}$, a heating rate of $10°C.min^{-1}$ from the temperature 30°C to 1000°C in alumina crucibles. The air flow allowed us to analyze what happens during the combustion of sewage sludge and the nitrogen flow to what occurs during the pyrolysis of sewage sludge. The TGA curves (thermogravimetric), DTG (derivative thermogravimetric) and DTA (differential thermal analysis) were obtained using the software TA Instruments (Universal Analysis Software).

2.4 Pyrolysis process

In the pyrolysis process, an amount of 40 grams of sewage sludge was used with the addition of 5% (m/m) Fe_2O_3. The fixed-bed reactor operates in an inert environment promoted by nitrogen flow, which occurs from the right to the left in the quartz tube, promoting the exit of gases to a condensing system, which leads to a system of collection and removal of condensational products as shown by the schematic drawing of Figure 1.

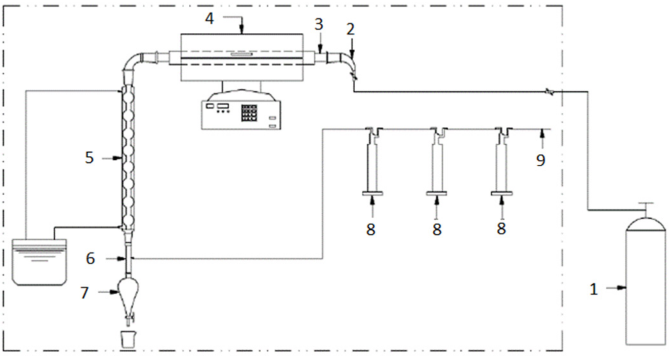

Figure 1: Scheme of the pyrolysis system. Legend: (1) nitrogen cylinder; (2) inert gas inlet; (3) quartz reactor tube; (4) oven; (5) condenser; (6) gas outlet; (7) separating funnel; (8) gas scrubbers; and (9) gases outlet.

2.5 Statistical design of the pyrolysis process

To carry out the pyrolysis experiments, 2^3 factorial design with a central point was adopted to assess the yields of products for process parameters, aiming the production of bio-oil. The factors used in the process were: temperature (°C), time (min) and heating rate (ºC.min^{-1}) (as shown in table 1). Furthermore, 9 experiments were performed, one being in the central point in triplicate random.

Table 1: Levels of factors used in the experimental design with 2^3 central point in the thermocatalytic pyrolysis process of sewage sludge.

Factors	Inferior level (-)	Central point (0)	Superior level (+)
Temperature (ºC)	450	500	550
Time (min)	120	150	180
Rate (ºC/min)	10	20	30

3 Results and discussion

3.1 Characterization of sewage sludge

Immediate analysis is fundamental to the study of the technological route of reuse of biomass waste and its application in the pyrolysis processes. Table 2 presents the average results of the humidity, volatile solids, ash, fixed carbon and a gross calorific value.

Table 2: Characteristics of sewage sludge.

Immediate analysis			
Humidity (% m/m)	Volatile solids (% m/m)	Ash (% m/m)	Fixed carbon (% m/m)
6.85	54.99	33.33	4.83
Gross calorific value (MJ.kg^{-1})			
21.80			

Sewage sludge had a moisture content similar to what (Sanchez *et al.* [8]) obtained, 6.8% (m/m), to analyze anaerobic sludge. The presence of moisture in the sludge is directly associated with factors such as weather conditions, seasonality, origin and treatment which the sewage was submitted. Its determination is relevant because of its influence on the energy consumption of the pyrolysis, where (when) the loss of moisture in the form of water vapor has a strong endothermic reaction.

The volatile solids content was 54.99% (m / m). Among the organic compounds that make up the fraction of the volatile solids are lignocellulosic materials, such as cellulose, hemicellulose and lignin, which have the characteristic of volatilization between 200 and 400°C, humic acids and carboxylic acids (Pedroza *et al.* [3]). Its importance is due to the fact that the organic material undergoes desorption followed by volatilization in the first stages of the pyrolysis, and subsequently, it passes through the cracking and the chemical rearrangement, forming new compounds which will constitute bio-oil when it is condensed.

The percentage of sewage sludge ash was close to what Sanchez *et al.* [8] and Gascó *et al.* [9] found, respectively 32.4% (m/m) and 32.5% (m/m). The high ash content in the sewage sludge promotes the contact between the metals and the organic matter, making that the volatile detachment reactions occur at lower temperatures (Mohan *et al.* [10]). Along with the fixed carbon and organic matter not degraded thermally, the ash, composes the resultant solid fraction of the pyrolysis process.

The gross calorific value of sewage sludge was 21.80 $MJ.kg^{-1}$. Fonts *et al.* [11] used in his study three types of sludge and presented the following calorific values, 12.3, 8.9 and 11.9 $MJ.kg^{-1}$, values below the present study is possibly related to higher volatile content compared to that observed by Fonts *et al.* [11] 47%, 38.3% and 46.6%. The gross calorific value can be influenced by the type of biomass, chemical composition as well as the humidity and the ash content if the organic matter was digested or not (Vieira *et al.* [2]).

3.2 Thermogravimetric analysis and differential thermal analysis

The thermal behavior of the sewage sludge in this study was made by thermogravimetric analysis (TGA), derivative thermogravimetric (DTG), and differential thermal analysis (DTA). The figure 2 presents the TGA's, DTG's, and DTA's curves of the sewage sludge in an oxidizing atmosphere.

In the TGA/DTG curve of the sewage sludge in air, three events are observed. First, between 35.39°C and 100.1°C, showed 4.62% of mass loss percentage at the temperature of 100.6°C, corresponding the free water loss. The second event, observed between 100.6°C and 141.2°C, is related to the dehydration regarding to the water adsorption on sewage sludge pores, corresponding to a mass loss of 6.44%, amount close to the one obtained in determining the moisture content by classical thermal gravimetric analysis (6.85% m/m). Dweck *et al.* [12], after the analysis of sewage sludge, observed that the free water is released until 150°C, before the combustion stage. In the DTA curve, it can be seen the two endotherms peaks, that are related to these two events.

The third event presents two overlapping pikes between 141.26°C, and 566.50°C, regarding the release of volatile material. The loss in this interval was equal to 62.97%, therefore, generating 37.03% of ashes. In this phase, the biggest mass loss occurs, having heat release during combustion, as can be observed through the exothermic event in DTA's curve, in figure 2.

From the TGA/DTG's curves, placed in figure 3, the nitrogen atmosphere analysis in the pyrolysis of sewage sludge, three events happen. Two events can be identified, the first one between 31.39°C and 105.50°C, and the second one between 105.50°C and 138.59°C, corresponding to the loss of moisture and light volatiles materials, with a mass loss percentage of 4.61% and 5.89%, respectively

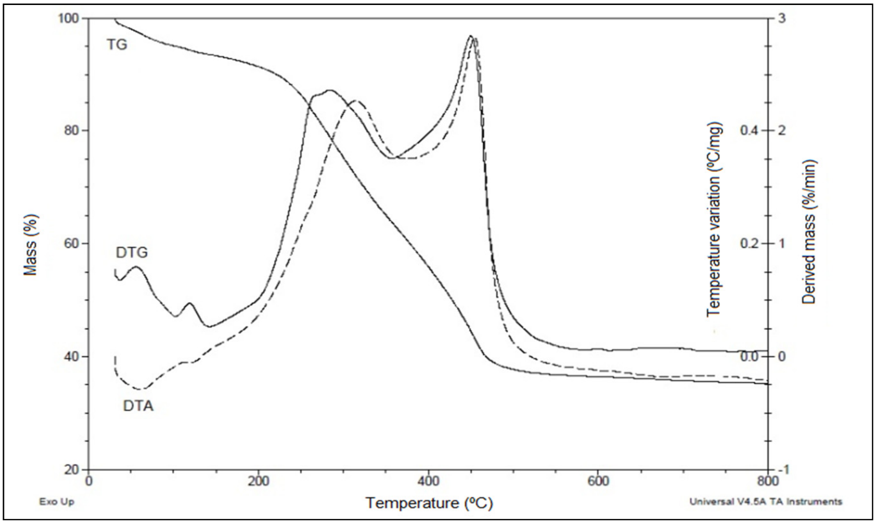

Figure 2: TGA's, DTG's, and DTA's curves of the sewage sludge in air.

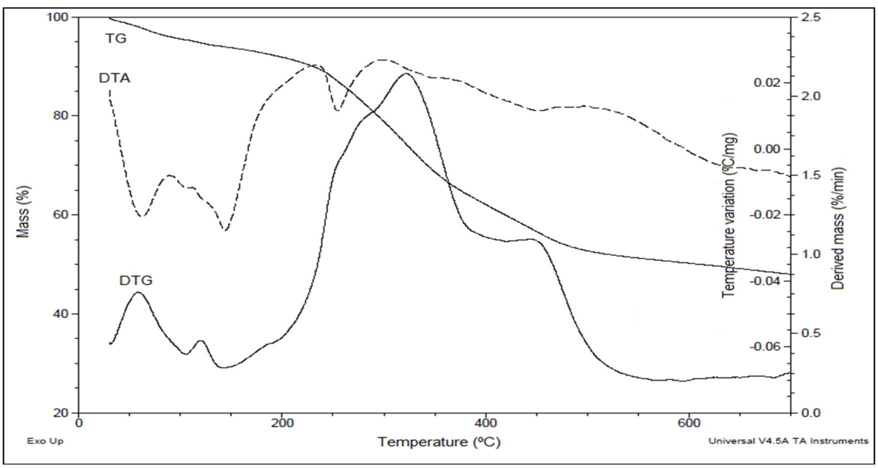

Figure 3: TGA's, DTG's, and DTA's curves of the sewage sludge in nitrogen.

in the first and the second events, both corresponding DTA peaks are endothermic, likewise happened in the in air analysis at this temperature interval.

In the third event, between 138.59°C and 566.50°C, the overlapped peaks indicate the liberation by cracking of organic materials contained in the sewage. This stage corresponds to the 49.07% of mass loss from the sewage sludge. The sewage sludge's range of decomposition of organic matter is very close to the result obtained by Karayildirim *et al.* [13], that corresponded to a thermal decomposition range from 200 to 500°C, indicating the volatile material release.

Figure 4 represents a subtraction of the TGA's curve in inert atmosphere with the TGA's curve in oxidizing atmosphere of the sewage sludge with either added catalyzer (Fe_2O_3), resulting in the carbonaceous residue's curve. In this procedure, is observed that the water losses do not affect the outcome for both events are not influenced by the analysis atmosphere, being, therefore, detected in the same form and same temperature ranges in pyrolysis, or combustion of sewage sludge.

When the 239°C temperature is reached, it can be observed that the mass loss of the sewage with iron oxide becomes greater than the mass loss in the corresponding curve to the sewage sample without a catalyzer. The maximum mass loss point occurs at 479°C, where the sewage without a catalyzer presents 20.48% of organic material, whereas the sample with iron oxide presents 14.59%, indicating a greater conversion. Alexandre [14], when evaluating the pyrolysis sewage's behavior with the addition of calcium oxide observed that the maximum mass loss point happened at 478.5°C, showing 18.7% of mass percentage.

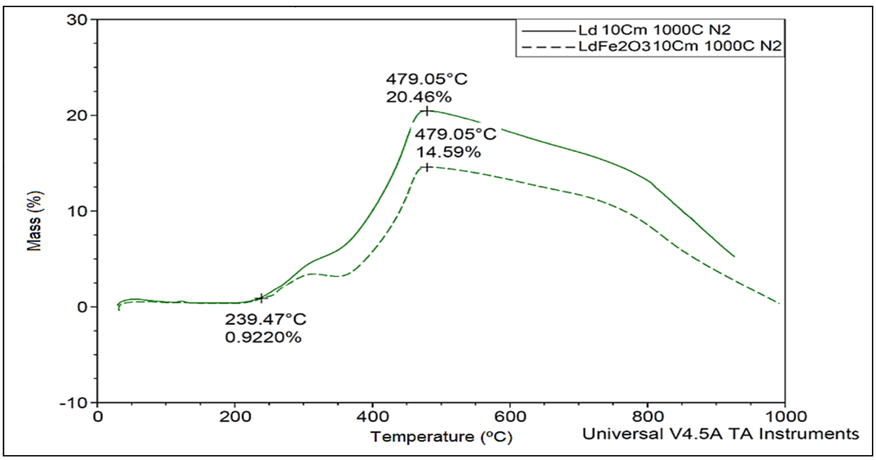

Figure 4: Beginning of the catalytic activity of the Fe_2O_3 in nitrogen.

3.3 Performance of the products obtained from the pyrolysis of sewage sludge

The results obtained from the statistic planning were treated to estimate the coefficients of the main effects and its interactions, investigating the parameter that influence the product's performances obtained through the pyrolysis process of sewage sludge. The performance of the bio-oil, aqueous, solid, and gas fractions are presented in table 3.

According to the Pareto chart, generated from the factorial planning shown in figure 5, indicates that the temperature growth from 450°C to 550°C propitiated positive effect to the bio-oil production in the pyrolysis process of sewage sludge. Inguanzo *et al.* [15], observed that the liquid fraction's performance was greater when the temperature increases from 450°C to 650°C. Above this temperature, it was not observed a fraction's growth. According to Fonts *et al*. [11], the decrease of bio-oil temperatures above 650°C occurs because of the secondary reactions, such as cracking, elevating the production of gas fraction. The heating variation rate from 10°C.min^{-1} until 30°C.min^{-1} and the process span from 120 minutes to 180 minutes did not present relevant effects in the performance, as well as its interactions, shown in figure 5. In this way, the obtained data indicate that the bio-oil making can be performed base on parameters that cause less energy expenditure, like less time and greater heating rate.

Table 3: Planning 2^3 results obtained for the product obtained in the pyrolysis process of the sewage sludge with addition of Fe2O3. Label: OF: bio-oil fraction; AF: aqueous fraction; SF: solid fraction; GF: gas fraction.

Experiment	Factor			Performance (%)			
	Temp. (°C)	Time (min)	Rate (°C.min^{-1})	OF	AF	SF	GF*
1	450	120	10	13.82	12.59	60.92	12.67
2	550	120	10	15.53	14.40	58.90	11.16
3	450	180	10	13.83	12.06	60.97	13.14
4	**550**	**180**	**10**	**15.60**	**13.28**	**56.52**	**14.60**
5	450	120	30	13.53	12.40	62.87	11.20
6	550	120	30	15.37	13.84	57.77	13.02
7	450	180	30	14.39	13.16	61.39	11.06
8	550	180	30	15.53	13.51	59.81	11.16
9	500	150	20	15.23	13.21	59.63	11.93

*Performance calculation of the gas fraction made by difference.

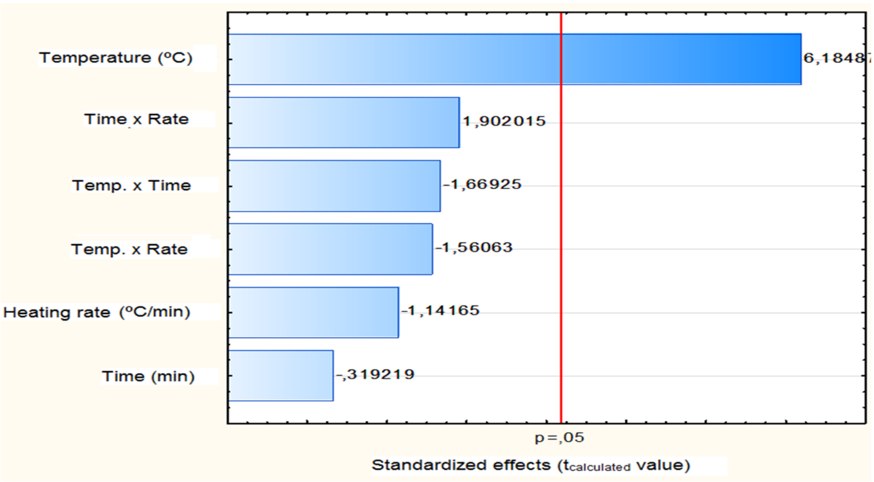

Figure 5: Pareto chart obtained from the 2^3 factorial planning with central point to the bio-oil making from the pyrolysis of sewage sludge with Fe_2O_3.

The R^2 values found from the regression coefficients indicate a good mathematical model adjustment, meaning that 93.94% of the variations are explained or adjusted by presented model by eqn (1), at a 95% confidence interval.

$$\mathbf{14.98 + 0.99X1} - 0.05X2 - 0.18X3 - 0.27X4 - 0.25X5 - 0.31X6 \qquad (1)$$

The variance analysis for the bio-oil production is presented in table 4. For confirmation of the utilized parameters, the F test was performed, where, to be statistically significant, the F value obtained from the regression, described as $F_{calculated}$, has to be greater than the value of $F_{tabulated}$ (Rodrigues and Lemma [16]). Comparing the value of $F_{calculated}$ from the fractions with the value of $F_{tabulated}$, a relevant regression to the bio-oil is identified. Therefore, the experimental data are well represented by the model obtained for significant variables, and can be used for predictive purposes among the factors studied.

Table 4: ANOVA for bio-oil production from pyrolysis of sewage sludge. Label: S.Q.: Sum of Squares; F.D.: Freedom Degree; M.S.: Mean Square.

Variation factors	**S. Q.**	**F. D.**	**M. S.**	**$F_{calculated}$**	**P-valor**
Regression	5.64	6	0.94	10.74	0.0005
Error	0.35	4	0.0875		
SS Total	5.76	10			
$R^2 = 0.93941$; $F_{tabulated}(6;4;0.05) = 6.16$					

The bio-oil maximum performances were found in higher temperature conditions, according to the observed in the response surface graph generated from the model presented in Figure 6. The maximum bio-oil performance was 15.60%, which corresponds to the experiment performed with the following parameters: temperature of 550ºC, heating rate of 10ºC.min^{-1}, and residence time of 180 minutes. Whereas the minimum bio-oil performance was 13.53%, obtained in the experimental conditions at a temperature of 450ºC, heating rate of 30ºC.min^{-1}, and residence time of 120 minutes, as it is presented in Figure 6.

4 Conclusion

The sewage sludge's characteristics in this study showed a high percentage of volatile solids (54.99% m/m) and ashes (33.33% m/m), and low percentages of moisture in the sample (6.85% m/m). The low moisture is desirable in the biomass to be applied in the pyrolysis process. The high percentage of ashes is a consequence of inorganic compounds from sewage production.

This study gave means to watch the catalytic activity of the iron oxide by the TGA/DTG/DTA, simultaneously with the increase volatilization and cracking of organic substances present in the sewage sludge. Therefore, the ability of this

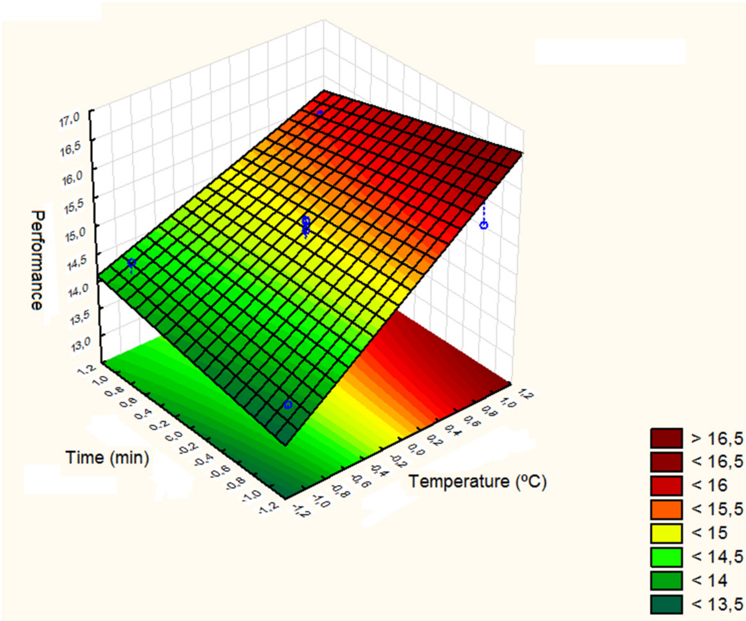

Figure 6: Response surface for the making of bio-oil from the pyrolysis of sewage sludge.

process in reducing the solid fraction was recognized when compared to the pyrolysis of sewage sludge without the addition of iron oxide.

In the pyrolysis of sewage sludge, using a proportion of 5% (m/m) of iron dioxide, the best conditions for obtaining bio-oil through 2^3 factorial statistical design with central point, were in the experiment that used the highest temperature (550ºC), greatest time (180 min), and the smallest heating rate (10ºC.min^{-1}), with a performance of 15.6% (m/m), where the temperature was the unique parameter to be influenced significantly. Thus, it could be observed that the sewage sludge in this study can be used as an energetic alternative in big cities, implying, therefore, in a sustainable and economic gain.

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