

Mixture of biomass to energy reuse

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Abstract Focusing on the reuse of the energy and aiming at the thermal and kinetic characterization of sewage sludge and its mixture, with pruning residues (50 mass%), the thermogravimetry was used. The kinetic study was elaborated from the local isoconversional integral method in heating rates 10.0, 20.0 and 30.0 °C min⁻¹ at a temperature ranging from 219 to 386 °C at nitrogen atmosphere, in a flow of 100 mL min⁻¹. The average activation energy of sewage sludge sample revealed the value of 219 kJ mol⁻¹ and that of the mixture 161 kJ mol⁻¹, supporting the incorporation of pruning residues in the sewage sludge. During the degradation process, a remarkable increase in activation energy was noticed that ranged from 20 to 70% conversion in the sewage sludge sample, and regarding the mixture, an almost linear behavior was observed during the decomposition reaction. There was no evidence of kinetic compensation effect in the performed studies. The evaluation of the thermal characteristics, as well as the kinetic study of the degradation of sewage sludge and its mixture with pruning residues, can lead to important insights and contribute to a better use of energy regarding the environmental issues.

Keywords Sanitary waste · Pruning residues · Mixture · Kinetic

Introduction

The various types of waste generated daily in large centers are solid urban, agricultural, industrial, among others. They are constant objects of studies, as it was discussed a few years ago regarding their proper disposal and/or reuse. In this issue, urban and industrial solid stand out for offering suitable conditions options for generating employment and income [1], as well as being excellent in energy recovering, avoiding environmental impacts due to pollution that they can cause to the environment.

Some solid wastes have been already used widely in power generation, such as agricultural waste, different types of wood and plant waste such as sugarcane [2]. These residues are also commonly called biomass, which can replace fossil fuels in three forms, solid (briquettes, pellets, and char), liquid (ethanol and biodiesel) and gas (production of gas and biogas) [3]. The application of industrial and sanitary wastes as an alternative fuel in power cogeneration has been studied by several authors [4, 5].

The process of combining biomass with other wastes aimed at power generation has been studied for a long time as an alternative to prevent that the residues be disposed of in landfills. The combination of biomasses as pine, chestnut and eucalyptus sawdust, pulp waste, coffee husks and grape waste was studied by Gil et al. [6], indicating good results in obtaining energy.

The reactivity of the mixture between the pine sawdust and olive residue, via pyrolysis and combustion, became better due to the higher volatile content present in the olive residue, and this thermal behavior was studied by

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Lajiji et al. [7]. A study on the thermal behavior of residues from sugarcane industry, such as bagasse, filter cake and vinasse, in individual form and combinations of mixtures among themselves using thermogravimetry under the N₂, CO₂, N₂/O₂ and CO₂/O₂ atmosphere aiming energy reuse was also developed by Silva et al. [8]. They found higher levels of ash in the filter cake and vinasse (47 and 40%, respectively) compared to bagasse (5%). The vinasse, in turn, started to decompose at a lower temperature (160 vs. 250 °C bagasse and filter cake) in atmospheres of synthetic air and CO₂/O₂ due to the absence of fibers in their structure. The mass loss events observed in steps at the following temperatures up to 150, 310 and 500 °C are attributed to moisture, decomposition of hemicellulose and cellulose and lignin degradation, respectively. In the CO₂ atmosphere, the events occurred at higher temperatures for all samples.

Knowing of the physicochemical and biological characteristics, beyond the origin of different types of waste, guides us as the classification of the same and guides us as to its use. In this sense, the study behavior during the process of degradation, combustion and pyrolysis [9] is necessary for a better reuse. Thermogravimetry (TG) is crucial for providing information in a simple, fast and reliable thermal and kinetic behavior of biomass for the energy recovery and the utilization of sewage sludge, reducing the possible environmental impact.

Objective

The aim of this study was to determine the activation energy of the sewage sludge and their mixing samples with pruning residue regarding energy reuse using the local linear integral isoconversional method based on interactive theorem for integral average value, analogous to the method of Wanjun–Donghua [10, 11].

Materials and methods

The samples used in this study were selected from sewage sludge (SS) from the sewage treatment station after thermal drying process at 300 °C, and urban waste prunings (UWP), both from the city of Araraquara/SP. The SS samples were collected at different points of a reservatory at the end of the process, and so, a representative sample of them was obtained after the mixture and dividing into quarters, according to the Techniques Law Brazilian Association (NBR 10007, 2004) [12]. The UWP sample was ground in a knife mill and dried in an oven at 60 °C for one week. The SS and UWP samples were ground in a cryogenic mill SPEX 6800 to decrease the particle size

in accordance with the operation program described in Table 1.

The SS sample was analyzed individually, and a mixture (1:1) of SS and UWP was prepared, resulting in the M sample.

For the kinetic study was used approximately 7 mg of the SS, UWP and M samples, using heating rates of 10.0, 20.0 and 30.0 °C min⁻¹, α-alumina crucible and temperature of 30–700 °C in a nitrogen atmosphere at a flow rate of 100 mL min⁻¹.

The kinetic parameters, activation energy (E_a) and pre-exponential factor ($\ln A$), were obtained through the local linear integral isoconversional method. This method is based on interactive theorem for integral average value, analogous to the method of Wanjun–Donghua, where the kinetics of the reactions of decomposition can be initially described by the differential Eq. (1), given by:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} f(\alpha) \quad (1)$$

Assuming that the parameters E_α , A_α , and the local heating rate β_α are constants in $[\alpha - \Delta\alpha, \alpha + \Delta\alpha]$, from Eq. (1), we can obtain that:

$$\Delta g(\alpha) = \int_{\alpha-\Delta\alpha}^{\alpha+\Delta\alpha} \frac{1}{f(\alpha)} d\alpha = \frac{A}{\beta} \int_{T_{\alpha-\Delta\alpha}}^{T_{\alpha+\Delta\alpha}} e^{-\frac{E}{RT}} dT \quad (2)$$

where $\Delta g(\alpha) = g(\alpha + \Delta\alpha) - g(\alpha - \Delta\alpha)$ e $g'(\alpha) = 1/f(\alpha)$. The function g is known as an integral form of the kinetic model.

By applying the mean value theorem to the integral in Eq. (2),

$$\Delta g(\alpha) = \frac{A_\alpha}{\beta_\alpha} (T_{\alpha+\Delta\alpha} - T_{\alpha-\Delta\alpha}) e^{-\frac{E_\alpha}{RT_\alpha}} \quad (3)$$

For some τ_α in $[T_{\alpha-\Delta\alpha}, T_{\alpha+\Delta\alpha}]$, rearranging Eq. (3) and applying logarithm lead to

$$\ln \left[\frac{\beta_\alpha}{\Delta T_\alpha (1 + \gamma)} \right] = B_\alpha e^{-\frac{E_\alpha}{RT_\alpha}} \quad (4)$$

where $B_\alpha = \left[\frac{A_\alpha}{\Delta g(\alpha)} \right]$; since $\Delta g(\alpha)g'(\alpha)$ and $g'(\alpha) = 1/f(\alpha)$ we can obtain that:

$$A_\alpha \approx \frac{2\Delta\alpha e^{B_\alpha}}{f(\alpha)} \quad (5)$$

Table 1 Operating program used for cryogenic grinding of the samples

Milling cycles	2
Pre-freeze	2.0 min
Milling	1.0 min
Freezing between cycles	1.0 min

For a given conversion and a series of $n \geq 3$ non-isothermal experiments carried out at different heating rates $\beta_{\alpha,i}$, $i = 1, 2, \dots, n$, Eq. (4) can be used to develop a local linear integral isoconversional method.

For the proximate analysis (moisture, organics, fixed carbon and ash contents), approximately 10 mg of the SS, UWP and M samples was used at a heating rate of $50 \text{ }^\circ\text{C min}^{-1}$ to $110 \text{ }^\circ\text{C}$, the CO_2 atmosphere at a flow rate of 130 mL min^{-1} . It was followed by an isotherm of 15 min and new heating at $50 \text{ }^\circ\text{C min}^{-1}$ to $600 \text{ }^\circ\text{C}$. Then, another 30-min isotherm was applied, and there was an exchange of atmosphere to synthetic air during this isotherm, ending with heating [13].

The equipment used for both analyses, the kinetic study and proximate analysis, was the TG-DTA simultaneously, SDT-2960 from TA Instruments.

The determination of the high heat value (HHV) of the SS, UWP and M samples was performed in a calorimetric bomb from Parr Instrument Company, Model 1341 Plain Jacket, using approximately 400 mg of each sample mixed with 400 mg of benzoic acid.

Results and discussion

Figure 1 shows DTG curves for the SS sample in the heating rates 10.0 , 20.0 and $30.0 \text{ }^\circ\text{C min}^{-1}$ in a nitrogen atmosphere. The interval of the temperature for the kinetic study of the SS sample was selected between 210 and $390 \text{ }^\circ\text{C}$.

Figure 2 presents the DTG curves for sample M in the heating rates 10.0 , 20.0 and $30.0 \text{ }^\circ\text{C min}^{-1}$ in a nitrogen atmosphere. The temperature interval for the kinetic study of the M sample was selected between 240 and $390 \text{ }^\circ\text{C}$.

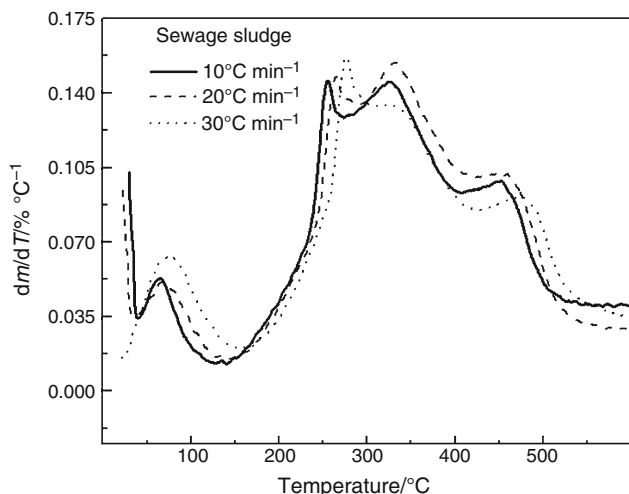


Fig. 1 DTG curves of sample SS in nitrogen atmosphere, heating rates 10.0 , 20.0 and $30.0 \text{ }^\circ\text{C min}^{-1}$

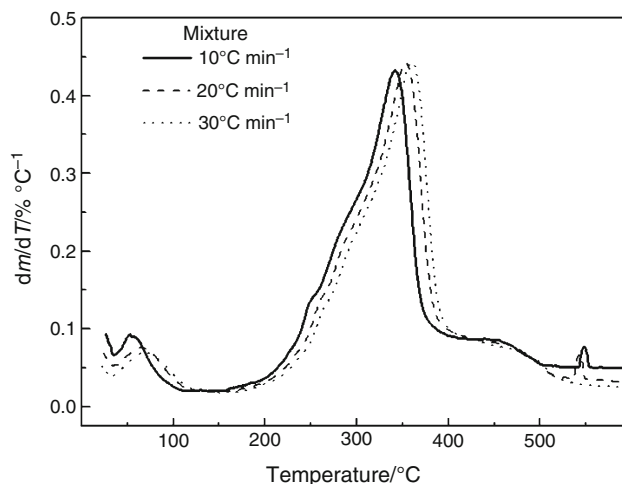


Fig. 2 DTG curves of sample M in nitrogen atmosphere, heating rates 10.0 , 20.0 and $30.0 \text{ }^\circ\text{C min}^{-1}$

Figure 3 presents the DTG curves for the UWP sample in the heating rates 10.0 , 20.0 and $30.0 \text{ }^\circ\text{C min}^{-1}$ in a nitrogen atmosphere. The temperature interval for the kinetic study of the UWP sample was selected between 250 and $360 \text{ }^\circ\text{C}$.

These intervals were correlated with the (α) degree conversion, whose values were comprised between 5% and 95% of the reaction occurrence. Then, they were determined for the kinetic parameters E_a and $\ln A$ according to the local linear integral isoconversional method.

The average values referent to the E_a of the SS, UWP and M samples are, respectively, 219 , 184 and 161 kJ mol^{-1} . The smaller E_a value of M can be attributed to the presence of pruning residues in the sample, favoring the thermal reactivity, as this material has a high content of volatile organic [14] and that the released heat

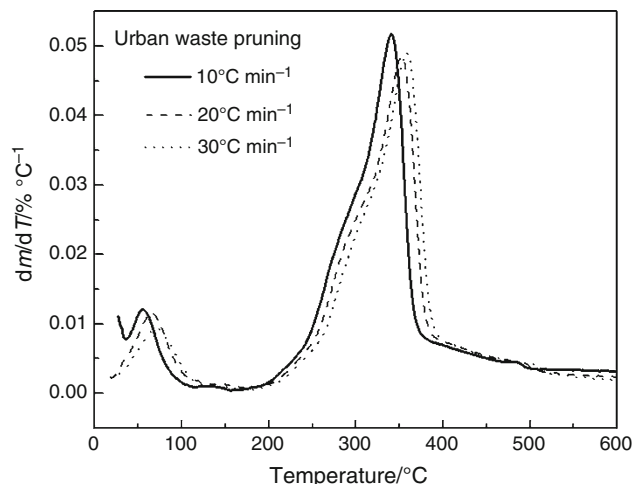


Fig. 3 DTG curves of sample UWP in nitrogen atmosphere, heating rates 10.0 , 20.0 and $30.0 \text{ }^\circ\text{C min}^{-1}$

during the reaction contributes for the decreasing of the activation energy.

The obtained variation for the E_a for the SS sample was 138–261 kJ mol⁻¹, whereas that for the M sample was 107–175 kJ mol⁻¹. A kinetic study in the non-steady state for the calculation of E_a by TG evaluating the thermochemical and thermocatalytic processes of sewage sludge, using the mathematical model “model-free kinetics” applying isoconversional techniques, found the values from 58 to 109 kJ mol⁻¹ in the conversion interval of 40–80% [15]. Values between 30 and 161 kJ mol⁻¹ were determined by a conversion interval from 10 to 80% applying the Kissinger–Akahira–Sunose method [16].

A mixture of 50% of the mass of sewage sludge and sugar cane bagasse showed the E_a average of 155 kJ mol⁻¹. However, only the sludge presented 137 kJ mol⁻¹, probably due to the digestion process undergone by this residue during sewage treatment, once that this process is anaerobic [13] and the treatment of sewage sample of this study originates from the aerobic system formed by aeration ponds then settling pond.

Table 2 shows the data for immediate analysis for SS, UWP and M samples. A content of 54.96% of volatile carbon in M sample and 40.1% in the SS sample was determined. The sewage sludge from the city of Lodz in Poland and São Bento do Sul, Santa Catarina/Brazil showed volatile carbon contents slightly higher, 44.6%, [17] and 43.3% [18]. For similar sample, it was found to UWP volatile carbon content of 74.9% [19] and 78.7% [20] straw of corn, suggesting compatibility between them.

Figure 4 shows the correlation between E_a and degree of conversion for the SS, UWP and M samples. A significant increase in E_a value which is observed from 20 to 70% degree of conversion, in the SS sample, showing that there is a complexity in the reaction constituents because of the sample type, multiple reactions may occur. The UWP and M sample showed no major changes to E_a , remaining constant around 184 and 161 kJ mol⁻¹, respectively. This behavior is probably due to the simplest reactions because of the higher amount of volatile material present in the waste pruning, and so there is no evidence of kinetic compensation effect throughout this sample decomposition reaction because for the simple reactions that occurred in the process.

Table 2 Properties of the samples of sewage sludge, urban waste pruning and mixture

	SS/%	UWP/%	M/%
Moisture	5.74	6.86	5.93
Volatile carbon	40.1	67.69	54.96
Fixed carbon	11.01	21.55	16.75
Ash	43.15	3.90	22.36

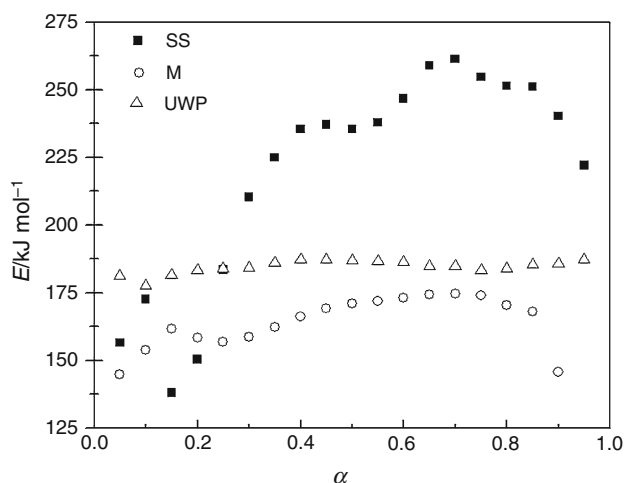


Fig. 4 Relationship between E_a and for the samples SS, M and UWP

Figure 5 shows the correlation between $\ln A$ and E_a for the SS sample. A kinetic compensation effect can be partially evidenced in the interval of E_a between 135 and 237 kJ mol⁻¹, equivalent from 20 to 70% of conversion grade of the SS sample by the linearity between E_a and $\ln A$. Similar behavior with manure samples from landfill in São Carlos/SP—Brazil was also observed by Almeida et al. [21]. In this decomposition, it was observed simple and posterior reactions to this interval, by the complexity of the sample is observed the existence of parallel reactions with different mechanisms [22].

The HHV of the SS, UWP and M samples is shown in Table 3. The high calorific power of the mixture,

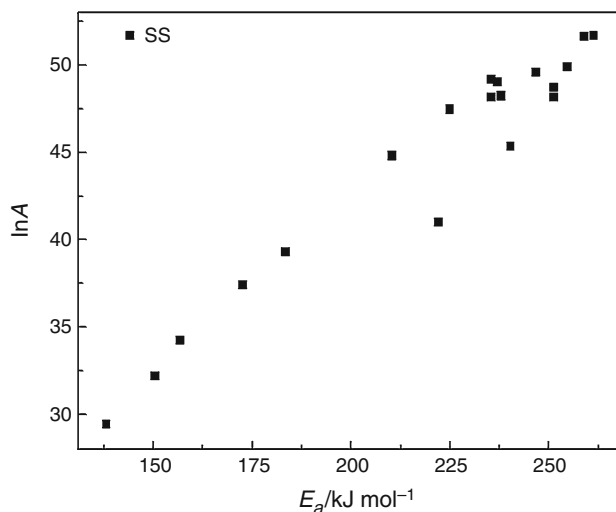


Fig. 5 Relationship between $\ln A$ and E_a for the sample SS

Table 3 HHV determined for samples SS, UWP and M

	SS	UMP	M
HHV/kJ g ⁻¹	15.63	13.72	20.36

20.36 kJ g⁻¹, in comparison with pure samples, can be explained by the synergism occurred between the SS and UWP samples. It may confirm the data referent to activation energy, the incorporation of pruning waste in sewage sludge favored thermal behavior of the mixture, with a low activation energy and high calorific power, which makes this an interesting mix in the reuse process.

Conclusions

The kinetic parameters applied from the TG showed that the sludge samples sewage and urban pruning residue have a high activation energy, showing to be more interesting the incorporation of pruning residues for the energetic point of view. The calorific value of this mixture also showed this fact due to the heat released during the decomposition process, showing a synergism between the samples of sewage sludge and urban waste pruning.

The organic carbon contents found in the mixture contributed to confirm the kinetic energy data and calorific power.

The adopted isoconversional method proved to be an effective strategy for providing concrete benefits of sample degradation kinetics and contributed to the implementation of these wastes in the energy recovery, minimizing the environmental impacts of improper disposal of them.

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