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Research Article

Thermal Decomposition of Pure Waste and Binary Mixtures

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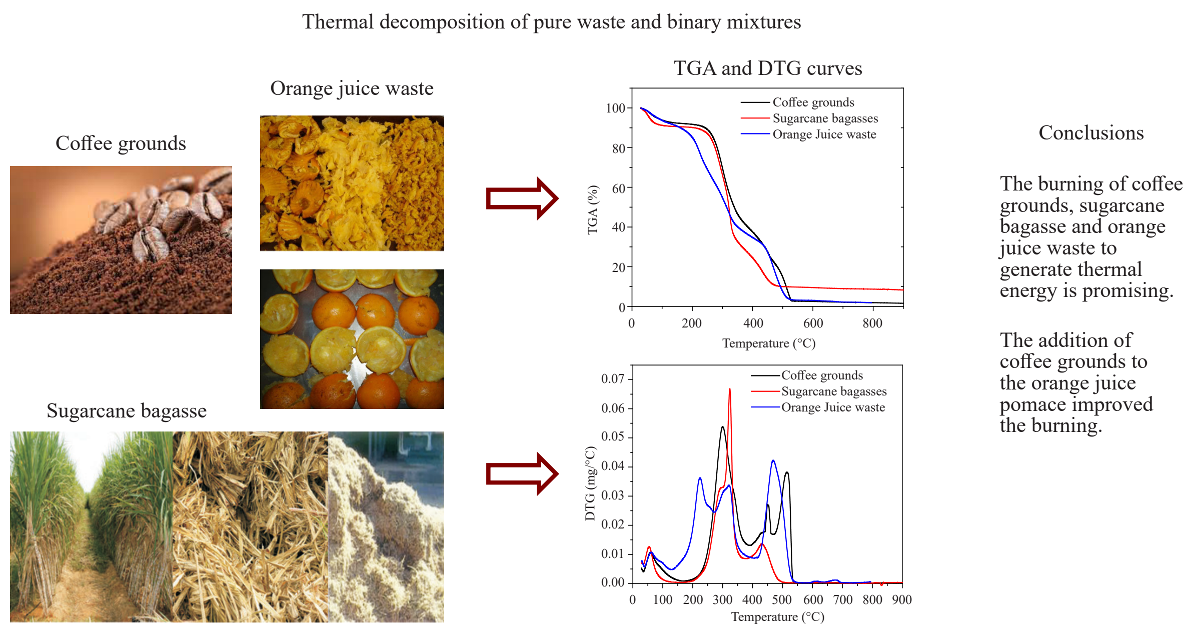
Abstract: In this study, the thermal decomposition of pure organic residues - coffee grounds, sugarcane bagasse and orange juice residues - and their binary mixtures with coffee grounds were analyzed. The results of thermogravimetric analyses at 10 °C/min under an oxidizing atmosphere showed that sugarcane bagasse and coffee grounds had individually higher reaction rates in the devolatilization zone, while orange juice residues burned more quickly in the combustion zone. There were significant mass interactions between the coffee grounds and orange juice residues in the binary mixtures, which led to higher reaction rates in the combustion of the mixture than in the pure residues. In the mixture of coffee grounds and sugarcane bagasse, there were no significant mass interactions. These encouraging findings can optimize the generation of bioenergy from these wastes and their mixtures, therefore, one must understand the different interactions during thermal decomposition to then develop sustainable strategies for utilizing biomass.

Graphical abstract:



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***Keywords*:** thermal decomposition, biomass mixtures, energy use, combustion

Nomenclature

CG	Coffee grounds
SB	Sugarcane bagasse
OW	Orange juice waste
TGA	Thermogravimetric analysis
DTG	Differential thermogravimetry
X	Mass fraction (kg/kg)
t	Time (s)

1. Introduction

Brazil is among the countries that grow the largest quantities of sugar cane, coffee and oranges. Each of these commodities undergoes different processing steps and is commercially valued in multi-industry applications.

Sugar and alcohol are produced from sugar cane with solid residue, which is a by-product rich in lignocellulose. The burning of sugarcane waste generates enough thermal energy not only to meet the demand of the sugar and ethanol plant but also to produce excess electrical energy sold to the government.

Orange juice waste, in turn, is quite heterogeneous and non-uniform, a mixture of peel, pulp, and crushed seeds, which consists of approximately 50% of the oranges in the citrus industries.[1] Traditional alternatives to dispose of orange juice waste involve landfilling, composting, pectin extraction, and livestock feeding. Although energy recovery from this solid waste is feasible, it must be pointed out that some alternatives could be cost-expensive and non-environmentally friendly.[2-3]

The coffee bean, after going through processing stages, can be consumed directly or can even become raw material in the soluble coffee industry. The coffee grounds resulting from the consumption of the drink are a toxic solid residue that must be disposed of with care due to the high content of organic compounds.[4] Despite the high calorific value and lignocellulosic content, the generation of thermal energy from coffee grounds is not as common as that from sugar cane. The main ways of valuing coffee grounds as biomass are through the production of pellets for combustion and fermentation.[5-7]

In view of the great demand for thermal energy, combustion is an interesting alternative for energy reuse as it has a good cost-benefit ratio and requires little pre-treatment.[8] Recent studies also show that combustion efficiency can be improved by mixing different wastes. According to Limousy et al.,[9] the mixture of coffee grounds with wood sawdust had greater energy release and lower fine particulate emissions than would be expected during the burning of the two pure biomasses. This is probably due not only to the more heterogeneous solid structure of the mixture of coffee grounds and wood sawdust but also to the mutual interactions between components.[10] Furthermore, Allesina et al.[11] showed that there was an increase from 37.7% to 41.2% in combustion efficiency when adding dry coffee grounds to wood sawdust.

Although biomass combustion techniques are rapidly developing, there is a lack of available information on the interaction of coffee grounds with other residues during burning. Therefore, there must be a better understanding of the thermal degradation of solid waste, as well as mixtures between different wastes, to improve energy use.[12] Given the encouraging results for solid fuels from mixtures of coffee grounds with wood sawdust, and the large availability of biomass in Brazil, this work analyzed thermal decomposition seeking better knowledge about the interaction of coffee grounds residue with sugarcane bagasse and orange residues in an oxidative environment.

2. Materials and methods

2.1 *Materials*

The coffee grounds were supplied from an automatic coffee machine and subsequently dried in a conventional heating chamber at 105 °C for 24 h. After drying, the coffee grounds were sieved into different particle size fractions and the fraction corresponding to the average particle diameter of 400 µm was chosen for the thermal experiments. The same was done for the sugarcane bagasse, opting for the fraction of particles with average diameters less than 1,000 µm.

The waste of Pear-type orange juice, *Citrus sinensis*, had only peel, seeds, and lint. After being crushed in an industrial blender, model Metalurgica 7000 Light, it was dried in a heating chamber with air circulation and renewal at 105 °C for 24 hours. The dried biomass was crushed in a knife mill to once again reduce its size.

2.2 *Thermogravimetric analysis*

The analysis of the thermal decomposition of the waste was carried out on a TA Instruments thermobalance model SDT Q600 V20.9. Samples with an initial mass of approximately 9.0 mg were heated at a rate of 10 °C/min from room temperature to 900 °C. The tests were conducted under an oxidizing atmosphere, with a synthetic air inlet flow of 30 mL/min. Sample mass was measured throughout the experiments to determine thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) analysis profiles. The experiments were carried out with five different samples of biomass, coffee grounds, sugarcane bagasse, orange juice waste and two binary mixtures of solid residues, one with 50% by mass of coffee grounds and 50% of sugarcane bagasse and another with 50% coffee grounds and 50% orange juice waste.

2.3 *Theoretical parameters*

The moisture content was given as the mass lost between the initial temperature of the sample and the final temperature of the drying stage.[13] The ash content was the percentage of the remaining mass of the sample in relation to the initial mass at a temperature of 800 °C.[13]

2.4 *Analysis of binary mixtures*

A comparison was made between the experimental DTG curve and the theoretical DTG curve based on results assuming an ideal mixture of residues. The theoretical DTG curve was constructed from the curves of each one of the three solid wastes. In other words, the theoretical DTG curve of the mixture was the sum of the behavior of individual components as given by Equations 1 and 2.[10]

$$\left(\frac{dX}{dt}\right)_{\mathrm{CG/SB}} = 0.5\left(\frac{dX}{dt}\right)_{\mathrm{CG}} + 0.5\left(\frac{dX}{dt}\right)_{\mathrm{SB}} \tag{1}$$

$$\left(\frac{dX}{dt}\right)_{\mathrm{CG/OW}} = 0.5\left(\frac{dX}{dt}\right)_{\mathrm{CG}} + 0.5\left(\frac{dX}{dt}\right)_{\mathrm{OW}} \tag{2}$$

The theoretical DTG curve for the mixture of coffee grounds (CG) with sugarcane bagasse (SB) was given by Equation 1, while the theoretical DTG curve for the mixture of coffee grounds with orange juice waste (OW) was given by Equation 2. Where X is the loss of residue mass and t is the time.

3. Results and discussions

3.1 *Solid residues*

The mass loss and mass loss rate curves as a function of temperature, at a heating rate of 10 °C/min for samples of coffee grounds (CG), orange juice waste (OW), and sugarcane bagasse (SB) are shown in Figure 1 and 2. Both the TGA and DTG curves showed that there were four stages of mass loss: evaporation of excess moisture, two stages of oxidative devolatilization of the components, and coal combustion. The coffee grounds and orange juice waste were completely consumed in the thermal degradation kinetics, while the sugar cane bagasse left residual matter after reaching 600 °C.

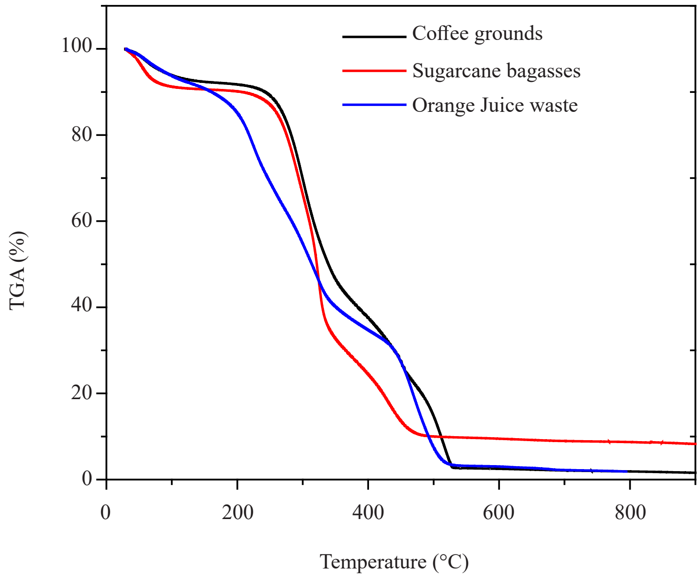

Figure 1. TGA curves of coffee grounds, orange juice waste, and sugarcane bagasse in an oxidative atmosphere at a heating rate of 10 °C/min

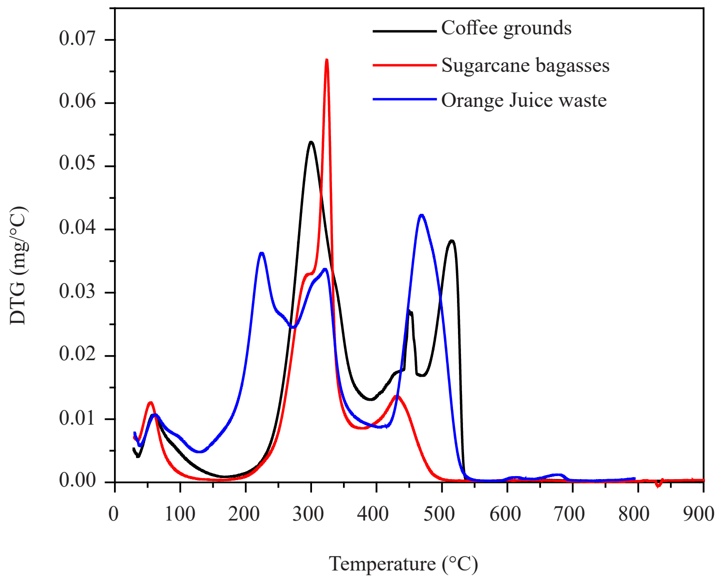

Figure 2. DTG curves of coffee grounds, orange juice waste and sugar cane bagasse in an oxidative atmosphere at a heating rate of 10 °C/min

The temperature ranges for each of the stages of the three solid wastes are in Table 1. In stage I there is volatilization of the lighter molecules and mainly water evaporation, which corresponds to the first peak of the DTG curve for the three residues. In this interval, there was a mass loss of approximately 7.84% for coffee grounds, 7.96% for orange juice waste, and 9.40% for sugar cane bagasse, which can be assumed as the moisture content of the solid. It is worth mentioning that sugar cane bagasse had the highest moisture content among other biomasses mostly because it was the only solid residue that had not been previously dried in a heating chamber.

Stage II corresponds to the range from 128 °C-167 °C to 271 °C-390 °C taking into account the three residues simultaneously. At this stage, thermal degradation of the main components of these biomasses begins: hemicellulose, cellulose, and lignin. The highest peak of this stage depends on the type of residue. The analysis of each one of the biomasses shows that the first peak of hemicellulose degradation is at 251 °C and that of cellulose is at 296 °C.[14] Therefore, there was a decomposition of biomass within the expected temperature ranges. From approximately 186 °C, lignin devolatilization also began at this stage.[15] Then, in stage III, there is total thermal degradation of lignin and hemicellulose.[14] It is worth mentioning that the different devolatization rates are due to the variation in the chemical composition of each residue and the interactions of components with each other.

Table 1. Temperature ranges of combustion stages and percentage of moisture and ash content

	Stage I	Stage II	Stage III	Stage IV	Moisture	Ash
	Drying (°C)	Devolatilization (°C)	Devolatilization (°C)	Combustion (°C)	% (b.u)	%
Coffee grounds	38-167	167-390	390-471	471-541	7.84	1.88
Orange juice waste	38-128	128-271	271-408	408-552	7.96	1.85
Sugarcane bagasse	38-150	150-380		380-543	9.40	8.70

In stage IV, there is combustion at 380 °C-552 °C of the coal resulting from the previous stages. After the peak of this stage, the remaining mass gradually burned up to 800 °C. The ash content was approximately 1.8% for both SG and OW, that is, in the end, there was almost complete burning of these biomasses. The residual mass remaining after burning the SB was 8.70%.

In stages II and III of devolatilization, the breakdown reactions of molecules were faster for sugarcane bagasse, coffee grounds and orange juice waste, in that order. In stage IV of combustion, reaction rates were higher for orange juice waste, coffee grounds and sugarcane bagasse. Due to the high devolatilization rate of sugarcane bagasse, there was less solid mass available for burning and, consequently, combustion rates were lower. The opposite happened with orange juice waste, which had low devolatilization rates and high combustion rates. In the context of reaction rates, coffee grounds were the intermediate biomass. The stages of thermal decomposition shown in Table 1 are in accordance with the literature for coffee grounds, sugarcane bagasse and orange bagasse respectively.[1,12,16] While dry biomasses of coffee grounds, sugarcane bagasse and solid orange juice residue have thermal properties that differ from each other, mixtures have intermediate properties, therefore, there must be an interaction between the different solid matters in such a way that leads to a change in thermal decomposition. This is the topic of the following section.

3.2 *Mixtures: Coffee grounds-orange juice waste*

Figure 3 shows the results of experimental and estimated differential thermogravimetry for the binary mixture of 50% coffee grounds and 50% orange juice waste, together with the DTG curves for each of the two residues. It could be seen that there is an influence of each component on the thermal decomposition of the mixture, resulting from the mass interactions between the residues.

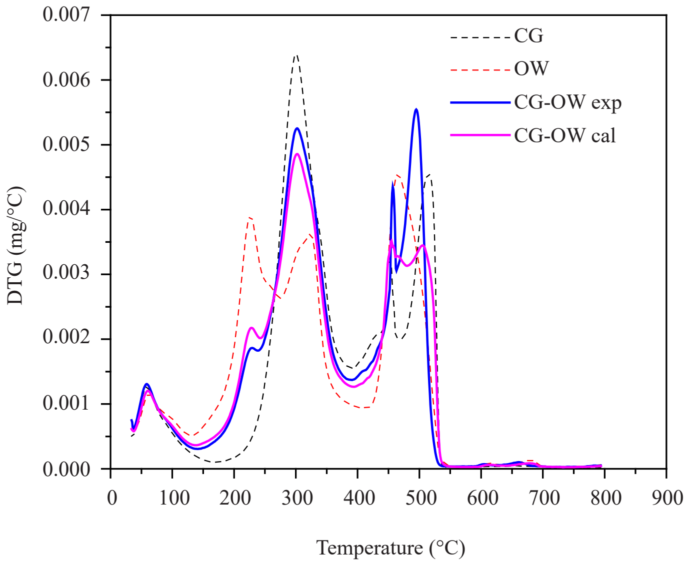

Figure 3. DTG curves of coffee grounds (CG), orange juice waste (OW) and mixtures in an oxidative atmosphere at a heating rate of 10 °C/min

As previously stated, the first stage of thermal decomposition is drying, which was quite similar for the two solid wastes, the same being true for the experimental and estimated values of the mixture. In stages II, III and IV, the thermal decomposition of the binary mixture was a function of the type of waste. There was a sharp peak starting at approximately 150 °C and ending at approximately 400 °C within stage II of the thermal decomposition of the mixture. The beginning of devolatilization of the mixture occurs at a temperature higher than that of orange juice waste (128 °C) and lower than that of coffee grounds (167 °C), partly due to the first peak in the decomposition of hemicellulose and partly due to the presence of lignin in orange juice waste. These components led to small peaks at approximately 225 °C under the effect of a sharp peak at the same temperature for the decomposition of orange juice waste. At the point of maximum devolatilization, there was a greater influence of coffee grounds, whose decomposition had a sharp peak at 300 °C. This shows that the first stage of devolatilization of coffee grounds had more influence on the mixture than the second stage of devolatilization of orange juice waste, probably due to the large amount of cellulose available.

In the first stage of devolatilization of the mixture, the experimental and theoretical DTG curves were very similar, with small differences between them. The point of maximum experimental devolatilization is greater than the estimated one, while the disturbance due to stage II of orange juice waste decomposition is greater for the estimated curve. These results showed that there was not an intense mass interaction between the residues.

Stage III of thermal decomposition of the mixture of orange juice waste and coffee grounds was between 390 °C and 460 °C. The combustion of orange juice waste played a key role in stage III, which had a sharp increase within this temperature range with a maximum of 460 °C. However, the end of the devolatilization of lignin and hemicellulose from coffee grounds after reaching the maximum led to a sharp decrease in the thermal decomposition rate of the mixture. The peak of the experimental DTG curve at this stage was more pronounced and in a smaller range of temperatures than the peak of the theoretical DTG curve, showing that there was a mass interaction between both solid residues.

Stage IV of the thermal decomposition of the mixture, in which there was combustion, was in the range of 460 °C to 525 °C. At 460 °C there was the highest rate of thermal decomposition of the mixture, leading to complete combustion of the coffee grounds and the remainder of the orange juice waste. Specifically in combustion, there was a considerable influence from the mass interactions of the coffee grounds with the orange juice waste, as the peak of thermal decomposition of the mixture was much more pronounced than that of both solid residues. Therefore, adding coffee grounds to the orange juice waste improves combustion because the process ends at a lower temperature. It is worth mentioning that this does not produce more ash throughout the process.

3.3 *Mixtures coffee grounds-sugarcane bagasse*

Figure 4 shows the experimental and theoretical differential thermogravimetry results for the binary mixture of 50% coffee grounds and 50% sugarcane bagasse, along with the DTG curves for the two residues.

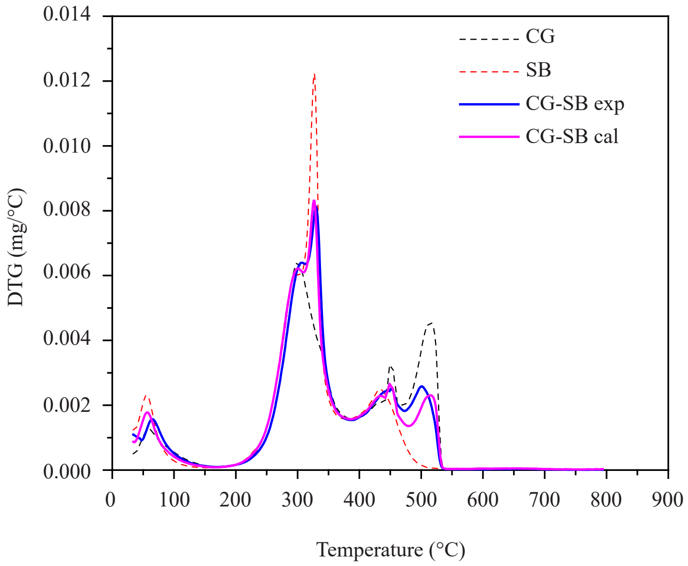

Figure 4. DTG curves of coffee grounds (CG), sugarcane bagasse (SB) and mixture in an oxidative atmosphere at a heating rate of 10 °C/min

In stage I of thermal decomposition, in which the biomass dries, there was no significant difference between the experimental and theoretical results due to the higher initial moisture content of the sugarcane bagasse. Stage II of devolatilization of the main components of the mixture was between 160 °C and 375 °C. The thermal decomposition of both the mixture and the sugarcane bagasse and coffee grounds was similar up to 300 °C. From this temperature on there was a difference between the two biomasses that make up the mixture, while the rate of thermal decomposition of the coffee grounds decreased, that of the sugarcane bagasse increased. This led to a lower thermal decomposition peak at 325 °C for the binary mixture. Stage III of the binary mixture, which corresponds to the second stage of devolatilization, was from 375 °C to 475 °C. In this temperature range, the peak of the DTG curve of the mixture was small because the devolatilization of coffee grounds occured at lower temperatures. Furthermore, in this temperature range, there was combustion of sugarcane bagasse, whose thermal decomposition peak was also small. Likewise, the thermal decomposition peak of the mixture in stage IV, in which the residue is burned between 475 °C and 540 °C, was also small. This is mainly due to the fact that sugarcane bagasse was thermally decomposed in this temperature range, leaving only the charcoal from the coffee grounds at the end. The ash content of the mixture after combustion was 6.75%. The experimental and theoretical DTG curves of a binary mixture of coffee grounds with sugarcane bagasse had good agreement, with the exception of stage IV, in which the decomposition rates of the experimental profile were higher than those estimated from the two residues. This means that the mass interactions between the coffee grounds and sugarcane bagasse were more important for combustion than for drying and devolatilization.

4. Conclusions

The results of this work showed, through thermogravimetric analyses, that the burning of coffee grounds, sugarcane bagasse and orange juice waste to generate thermal energy is promising. While sugarcane bagasse and coffee grounds had higher rates of thermal decomposition during devolatilization, orange juice waste had higher rates during combustion. The addition of coffee grounds to the orange juice pomace improved the burning to the point of even exceeding the theoretically estimated value, showing that there were significant mass interactions between both biomasses. There was good agreement between the experimental and theoretical results for the binary mixture of sugarcane bagasse and coffee grounds, therefore, there was no significant synergistic interaction between the two biomasses. In this case, it can be said that the burning of the mixture resulted from the individual and simultaneous burning of each of the two residues. Finally, the results on the thermal degradation of mixtures show that it may be interesting to have cooperation between companies that generate different waste. In addition, they also show that adding coffee grounds with other waste can make energy production economically viable.

Authors' contributions

Thalyne de Almeida Ferreira Rocha: Investigation, data curation. Guilherme Henrique Alves Pinto: Software, investigation, data curation, writing - original draft preparation. José Teixeira Freire: Conceptualization, data curation, writing - original draft preparation, writing - reviewing and editing. Fábio Bentes Freire: Conceptualization, methodology, data curation, supervision, writing - original draft preparation, writing - reviewing and editing.

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Data availability statement

The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Conflict of interest

The authors declare they have no competing interests.

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