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Characterization and Potential Evaluation of Residues from the Sugarcane Industry of Rio Grande do Sul in Biorefinery Processes

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Abstract

Brazil is the world largest producer of sugarcane (*Saccharum officinarum*) leading to a great generation of residues such as bagasse and straw, which represent two thirds of sugarcane energetic potential. Regarding these residues energetic potential, it is interesting to study their application in biorefinery processes. Thus, this work aimed at performing a chemical characterization of sugarcane straw and bagasse from RB867515 cultivar grown in Rio Grande do Sul-Brazil aiming at their use as feedstock in biorefinery processes. The obtained results were compared to data from other states and it was possible to conclude that edaphoclimatic conditions of Rio Grande do Sul have little influence in sugarcane residues chemical composition. Sugarcane bagasse presents larger potential for energetic use because of its volatiles content (74.82%) slightly higher than straw (68.90%), besides its high lignin content (21.85%) and higher calorific value (18.70 MJ/kg). Both sugarcane residues produced in Rio Grande do Sul have potential use as substrate in the obtainment of high value-added products from their cellulosic fractions (41.30% and 37.25%, respectively). The evaluation of energetic and chemical potential of sugarcane bagasse and straw produced in Rio Grande do Sul leads to the conclusion that these materials have high potential for use as feedstock in biorefineries.

Keywords

Saccharum officinarum, Straw, Bagasse, Biomass

1. Introduction

The demand of materials from renewable resources which can replace oil based chemicals and fuels is increasing lately because of the progressive depletion of natural resources, instability of oil prices and environmental impact caused by pollution [1] [2]. Several developing and developed countries are investing in the development of products renewable and sustainable, which do not cause harm to the environment, based mainly on lignocellulosic biomass [3] [4].

Among the bioproducts that can be obtained from biomass, bioethanol can be highlighted. During sugarcane processing, 12 tons of bagasse and 12 tons of straw are generated per hectare of sugarcane. It is possible to increase bioethanol production, as well as produce other high value added products, without increasing the cultivated sugarcane area, by using sugarcane residues in biorefinery processes. Bagasse and straw comprise two thirds of sugarcane energetic potential, so that the use of these residues as feedstock in biorefineries is a promising alternative to attend the growing world demand for sustainable products from a renewable resource [5].

Brazil is the world largest sugarcane producer with an estimated production of 658.7 million tons of sugarcane in the harvest 2015/16 [6]. Sugarcane production in Rio Grande do Sul represents a small fraction of the country production. One of the limitations of producing sugarcane in this state is the humid subtropical climate, once sugarcane develops better in tropical climates with lower chance of frost [7]. In order to overcome the cold weather and drought usual in the state, more resistant varieties of sugarcane have been studied, such as RB cultivars. These cultivars are suitable for ethanol production and when tested in Rio Grande do Sul achieved average to high agricultural productivity, regular conditions when exposed to cold stress, good plant health and fast growth [8].

Once lignocellulosic chemical composition varies significantly according to type of plant, type of tissue, growing conditions and plant age, in order to have an integral use of biomass, efficiently in a biorefinery, it is necessary to perform a characterization regarding chemical and energetic potential of the lignocellulosic biomass. Through characterization, it is possible to determine the potential of each type of biomass for production of different products, as well as the choice of the best type of pretreatment and conversion technique to obtain a feasible and lucrative process [9].

In this context, this work aimed to characterize and study the potential of sugarcane cultivar RB867515 residues, straw and bagasse, produced in Rio Grande do Sul, Brazil, to obtain high value added products through biorefinery processes.

2. Material and Methods

2.1. Feedstock

The raw materials used in the experiments were sugarcane cultivar RB867515 residues, straw and bagasse, grown in Pelotas, a city in Rio Grande do Sul, Brazil, provided by Embrapa Clima Temperado.

2.2. Sample Processing

Samples were dried at room temperature for four days. After drying, samples were milled in a knife mill. Then, the samples were classified using a set of sieves, such that the fractions which passed through 40 mesh sieve but were retained in the 60 mesh sieve were used in the experiments.

2.3. Immediate Chemical Analysis

Immediate chemical analysis is used to determine moisture, ash, volatiles and fix carbon contents. Moisture content was obtained following TAPPI T264 om-88. Ash content was obtained following TAPPI T211om-88 [10]. Volatiles and fix carbon were determined following ABNT NBR 8112 standard [11]. Samples used in the moisture content determination were used in the volatiles determination. These samples were left in a muffle at 950˚C for 7 minutes, 2 minutes in the front part and five minutes in the back part. After this process, samples were placed in a desiccator for cooling and finally weighing. Volatiles content was calculated using Equation (1). Fixed carbon is calculated using Equation (2), in which MC corresponds to moisture content, V to volatiles content and A to ashes content.

$$\text{Volatiles }\% = \frac{\text{initial sample mass-finalsample mass}}{\text{initial sample mass}} \times 100\% \tag{1}$$

$$\text{Fix carbon} = 100 - \left(MC + V + A\right) \tag{2}$$

2.4. Elemental Analysis

Elemental analysis was performed following Pregl-Dumas method, an automated calorimetric method, used to determine carbon, hydrogen, oxygen, nitrogen and sulfur in the samples. The elemental analysis equipment manual was followed. The samples were burned in an elemental analyzer TRUSPEC non-dispersive, Leco brand, equipped with an infrared detector. In this equipment, the samples were burned in oxygen atmosphere at the temperature of 950˚C. Sulfur analysis was performed in elemental analyzer Leco SC-632, equipped with an infrared detector. In this equipment, samples were burned in oxygen atmosphere at the temperature of 1350˚C. Oxygen determination was obtained by difference, as shown in the equation below [12]:

$$\%\text{O} = 100 - \left(\%\text{C} + \%\text{H} + \%\text{N} + \%\text{S} + \%\text{Ashes}\right) \tag{3}$$

2.5. Calorific Value

In order to estimate the energetic potential of the samples, their high calorific value was determined using a bomb calorimeter, Parr brand, type 6300, following the equipment manual.

2.6. Chemical Analysis

Chemical analysis was performed in the samples to determine the contents of cellulose, hemicelluloses, lignin, extractives and ashes, this last one previously determined in the immediate chemical analysis.

Carbohydrates, cellulose and hemicelluloses, were determined by Saeman method, in which polysaccharides are hydrolyzed, and the sugar monomers formed are quantified using ionic exchange chromatography. Carbohydrates analyzed were glucans, xylans, galactans, mannans, arabinans, as well as acetyl and uronic groups were determined. The ionic exchange chromatographer used was IC-3000 Dionex with pulsed amperometric detector HPAE-PAD. Sugars were separated using a protection column Carbo-Pac PA1 and an analytic column connected in series. Sample peaks observed on the chromatogram were compared to standard peaks of the sugars analyzed and quantification was obtained by the analyte area on a calibration curve of each compound, following TAPPI 222om-88 standard.

Total extractives determination in the samples was based on TAPPI T204om-88 and TAPPI T264om-88, through extraction of volatiles compounds in biomass using ethanol: toluene (1:2), followed by ethanol 95% and hot water in this order of polarity.

Lignin content determination was adapted from TAPPI 222om-88 standard, in which Klason lignin, insoluble lignin content, is obtained [11]. Klason lignin filtrate was diluted and analyzed by ultraviolet absorption in the wavelength of 280 nm and 215 nm. Soluble lignin amount in the filtrate was determined by the following equation [13]:

$$\text{Soluble lignin content} = \frac{(4538 \times A_{215}) - A_{280}}{300 \times DW} \times 10 \tag{4}$$

in which:

A_{215} = Absorbance in the wavelength of 215 nm;

A_{280} = Absorbance in the wavelength of 280 nm;

DW = Dry weight of the sample used in Klason lignin determination.

2.7. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed using equipment model SDT Q600 TA Instrument in 90 μL alumina crucibles. Samples were heated from 25˚C to 800˚C, in N_2 atmosphere, at a heating rate of 10˚C/min, in which samples of nearly 5.0 to 6.0 mg were used. Thermogravimetric curves were registered between 25˚C and 800˚C.

3. Results and Discussion

3.1. Immediate Chemical Analysis

The average of the results obtained in the immediate chemical analysis of sugarcane straw and bagasse grown in Rio Grande do Sul are shown in **Table 1** along

Table 1. Immediate chemical composition of sugarcane straw and bagasse.

Biomass	State	Moisture (%)	Ashes (%)	Volatiles (%)	Fix Carbon (%)	References
Bagasse	RS	8.58	3.56	74.82	13.05	Authors 2016*
	GO	18.38	3.38	84.54	12.08	**[14]
	SP	10.51	4.00	69.39	16.10	*[15]
Straw	RS	12.19	3.86	68.90	15.05	Authors 2016*
	SP	10.25	7.00	66.40	16.35	*[15]
	MG	3.12	9.17	87.6	3.22	**[16]

a. *Results in wet basis. **Results in dry basis. RS: Rio Grande do Sul; GO: Goiás; SP: São Paulo; MG: Minas Gerais.

with results obtained in other studies using the same types of biomass grown in other regions of Brazil.

The observed differences can be explained by transportation and storage conditions of the samples, which can cause differences in their moisture content. Concerning the observed differences when comparing the results of the current study with [14] and [16] studies, differences can be explained by the fact that in these studies results were expressed in dry basis, while in the current study results were expressed in wet basis.

Regarding ash content in sugarcane straw, the value obtained in the current study (3.86%) is lower than the value obtained by [15] (7.00%) and [16] (9.17%). These differences in the ash content can be explained by the part of the sugarcane from which straw was collected, once straw collected near the soil presents ash content around 7% - 8%, while straw collected in the middle or green leaves of sugarcane present ash content around 2% - 3% [2].

Immediate chemical analysis is one of the most important parameters to evaluate biomass energetic potential. It is desired moisture content to be the lowest possible in biomass, once higher the moisture, more energy is necessary to start the burning process, in other words, more energy is required to vaporize water and less energy is supplied to the endothermic reaction [17]. Ashes have a negative influence in the calorific value, so lower contents of ashes are desirable for energetic uses. Higher volatiles content is desired, because these compounds increase biomass energetic potential. Yet, fix carbon content is directly related to coal content formed at the end of combustion process. Higher fix carbon content has a positive influence in increasing biomass high calorific value [14] [18].

3.2. Elemental Analysis

The average of the results obtained in the elemental analysis of sugarcane straw and bagasse grown in Rio Grande do Sul are shown in **Table 2** along with results obtained in other studies using the same types of biomass grown in other

Table 2. Elemental composition of sugarcane straw and bagasse.

Biomass	State	C (%)	H (%)	N (%)	S (%)	O (%)	References
Bagasse	RS	43.35	6.25	0	0.05	45.79	Authors 2016
	MG	46.4	5.9	0.7	0	43.4	[19]
	GO	45.57	5.57	0.305	0.04	45.135	[14]
Straw	RS	40.90	6.30	0.60	0	48.34	Authors 2016
	SP	41.6	5.8	0.45	0.08	40.04	[20]
	MG	45.0	5.8	0.7	0	42.9	[19]

RS: Rio Grande do Sul; MG: Minas Gerais; GO: Goiás; SP: São Paulo.

regions of Brazil. It is important to highlight that the ash content used to calculate oxygen content was the one obtained through immediate chemical analysis.

The results obtained for elemental composition of both sugarcane straw and bagasse do not differ significantly from the elemental composition of the same residues produced in different states of Brazil, proving that edaphoclimatic conditions of Rio Grande do Sul have no significant influence in elemental composition of sugarcane straw and bagasse.

Determination of elemental composition is important since from biomass main components amount, it is possible to do stoichiometric calculations for several uses in thermochemical processes. In combustion and gasification, these values allow to calculate amount of CO_2 and H_2O produced in complete combustion; amount of air required for fuel gasification; amount of adsorbent required to remove sulfur from combustion gas; besides to estimate high and low calorific value [21].

3.3. Calorific Value

The average of the results obtained in the determination of high calorific value of sugarcane straw and bagasse grown in Rio Grande do Sul are shown in **Table 3** along with results obtained in other studies using the same types of biomass grown in other regions of Brazil.

The results obtained allow concluding that the edaphoclimatic conditions of Rio Grande do Sul do not have significant influence in the high calorific value of sugarcane bagasse and straw, once the results obtained were similar to results found in other studies.

Calorific value is a parameter highly influenced by biomass chemical composition. Moisture and ash contents are the factors that mostly influence biomass calorific value, the higher these contents are, the lowest will be biomass high calorific value, while lignin and extractives when present in larger amounts reflect in higher biomass calorific value. Thus, it is observed that biomass energetic potential is directly influenced by its composition, showing the importance of evaluating biomass composition previously to its industrial use [25].

3.4. Chemical Characterization

Chemical characterization was performed to evaluate the use of sugarcane bagasse

Table 3. High calorific value of sugarcane straw and bagasse.

Biomass	State	High calorific value (MJ/kg)	References
Straw	RS	18.30	Authors 2016
	MG	18.80	[22]
	SP	19.20	[22]
	PR	19.00	[22]
	MT	18.80	[22]
	AL	19.30	[22]
	MG	18.17	[19]
Bagasse	RS	18.70	Authors 2016
	PR	15.55	[17]
	MG	18.25	[23]
	MS	15.37 - 17.15	[24]

RS: Rio Grande do Sul; MG: Minas Gerais; SP: São Paulo; PR: Paraná; MT: Mato Grosso; AL: Alagoas; MS: Mato Grosso do Sul.

and straw as feedstock in biorefinery processes. The averages of the results obtained in the chemical characterization, including contents of cellulose (C), hemicelluloses (H), lignin (L), total extractives (TE) and ashes (A), of sugarcane straw and bagasse grown in Rio Grande do Sul are shown in **Table 4** along with results obtained in other studies using the same types of biomass grown in other regions of Brazil.

Cellulose content found for sugarcane straw cultivated in Rio Grande do Sul is below the amounts of cellulose found by [22] for sugarcane cultivated in other states. Yet, cellulose content found for sugarcane bagasse produced in Rio Grande do Sul is similar to cellulose contents found in bagasse produced in other states. Larger amounts of cellulose in lignocellulosic biomass favor biofuels production such as ethanol and 2,3-butanediol produced from fermentable sugars derived from polysaccharides present in biomass. Glucose obtained from cellulose can also be used as substrate for producing biopolymers, such as polyhydroxyalkanoates (PHA). Some enzymes as α-amylases, cellulases, among other enzymes and some organic acids as itaconic, succinic and lactic acids can be produced using glucose from cellulose as substrate through fermentation. Larger amounts of cellulose favor the obtainment of bioproducts by fermentation, as long as pretreatment and hydrolysis processes are efficient, releasing glucose, which is used in the fermentation processes [29].

Hemicelluloses content found for sugarcane straw cultivated in Rio Grande do Sul is below the amounts of cellulose found by [22] for sugarcane cultivated in other states. Yet, hemicelluloses content found for sugarcane bagasse produced in Rio Grande do Sul is similar to cellulose contents found in bagasse produced in other states. In the biorefinery context, among products that can be obtained from pentoses present in hemicelluloses, there is furfural, which is a promising alternative, since it is a versatile compound that can be used in the synthesis of

Table 4. Chemical characterization of sugarcane straw and bagasse.

Biomass	State	C* (%)	H* (%)	L* (%)	A* (%)	TE* (%)	Total (%)	References
Straw	RS	37.25	19.90	21.65	3.86	13.85	96.51	Authors 2016
	MG	45.30	31.51	16.70	5.90	16.10	99.41	[22]
	SP	44.44	30.70	19.80	3.90	16.70	98.84	[22]
	PR	44.98	30.92	18.90	4.80	16.80	99.60	[22]
	MT	43.57	30.53	19.40	5.30	16.70	98.80	[22]
	AL	43.02	31.85	20.20	4.40	14.10	99.47	[22]
Bagasse	RS	41.30	28.05	21.85	3.56	6.35	101.11	Authors 2016
	PE	41.12	27.76	21.03	4.08	5.16	99.16	[26]
	SP	40.5	24.5	26.4	1.6	0.6	93.6	[27]
	PR	41.8	22.9	30.4	3.1	6.7	104.9	[28]

*C: cellulose, H: hemicelluloses, L: lignin, A: ashes, TE: total extractives. RS: Rio Grande do Sul; MG: Minas Gerais; SP: São Paulo; PR: Paraná; MT: Mato Grosso; AL: Alagoas; PE: Pernambuco.

several important chemicals, as furan and furfuryl alcohol. Also, it is largely employed in several industrial applications in oil refineries, plastics and pharmaceuticals production, and agrochemical industry [30]. Xylose, present in hemicelluloses, can also be used in the production of xylitol, a sweetening agent used in several applications, which can be prepared through xylose hydrogenation [31]. Some fungi, as the basidiomycete *Trametes hirsuta*, have lignolytic enzymes (laccases), so that they are capable of producing ethanol from lignocellulosic residues. This basidiomycete is capable of converting not only glucose, but also xylose in ethanol, as well as it is capable of degrading lignocellulosic residues, dispensing the need to perform enzymatic hydrolysis [32]. Comparing the results obtained for sugarcane straw and bagasse produced in Rio Grande do Sul, since sugarcane bagasse presents higher amount of hemicelluloses, it is suitable for production of high value added products derived from hemicelluloses, such as xylitol, furfural and their derivatives.

Lignin contents found for sugarcane bagasse and straw cultivated in Rio Grande do Sul are within the range of lignin contents found for these residues cultivated in other states. When the objective is to explore biomass energetic potential, high amounts of lignin are desired, since lignin contains a larger amount of oxygen when compared to cellulose and hemicelluloses, which reflects in higher calorific value [25]. Yet, when the objective is to produce high value added through fermentation of monosaccharides, obtained from cellulose and hemicelluloses hydrolysis, smaller amounts of lignin are desirable, since lignin is one of the main fermentation inhibitors [33].

Ashes and extractives are minor compounds in lignocellulosic biomass. The values found for both sugarcane straw and bagasse are within the range of values found for ash content in sucroenergetic residues produced in other regions of Brazil. Regarding extractives content, although the result obtained for sugarcane straw produced in Rio Grande do Sul (13.85%) is a little lower than the values found for straw produced in other states, it is still close value. Yet, the extractives content found for sugarcane bagasse produced in Rio Grande do Sul (6.35%) is close to the result found by [26] (5.16%) [28] (6.7%), but differs from the result obtained by [27] (0.6%). These differences may be explained by different methodologies employed to determine extractives content. It is important to highlight that higher content of extractives and lower content of ashes are interesting for biomass energetic uses.

3.5. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis allows to follow mass losses in the sample being analyzes as a function of temperature. Through thermogravimetric curves, it is possible to relate different regions of mass losses as a function of temperature with different biomass components. Thermogravimetric curves obtained for sugarcane bagasse and straw samples are shown in **Figure 1** and **Figure 2**, respectively.

[15] studied thermal decomposition of different types of lignocellulosic biomass including sugarcane bagasse and evidenced the presence of three zones of mass loss in the thermogravimetric analysis, one around 100˚C attributed to water loss, and other two regions, one around 200˚C - 350˚C and the other around 350˚C - 500˚C due to organic matter degradation. This behavior was also observed in the sugarcane straw and bagasse samples in the current study.

[34] evidenced that hemicelluloses decomposition occurs predominantly under 230˚C due to instability of acetyl groups. Cellulose degradation occurs

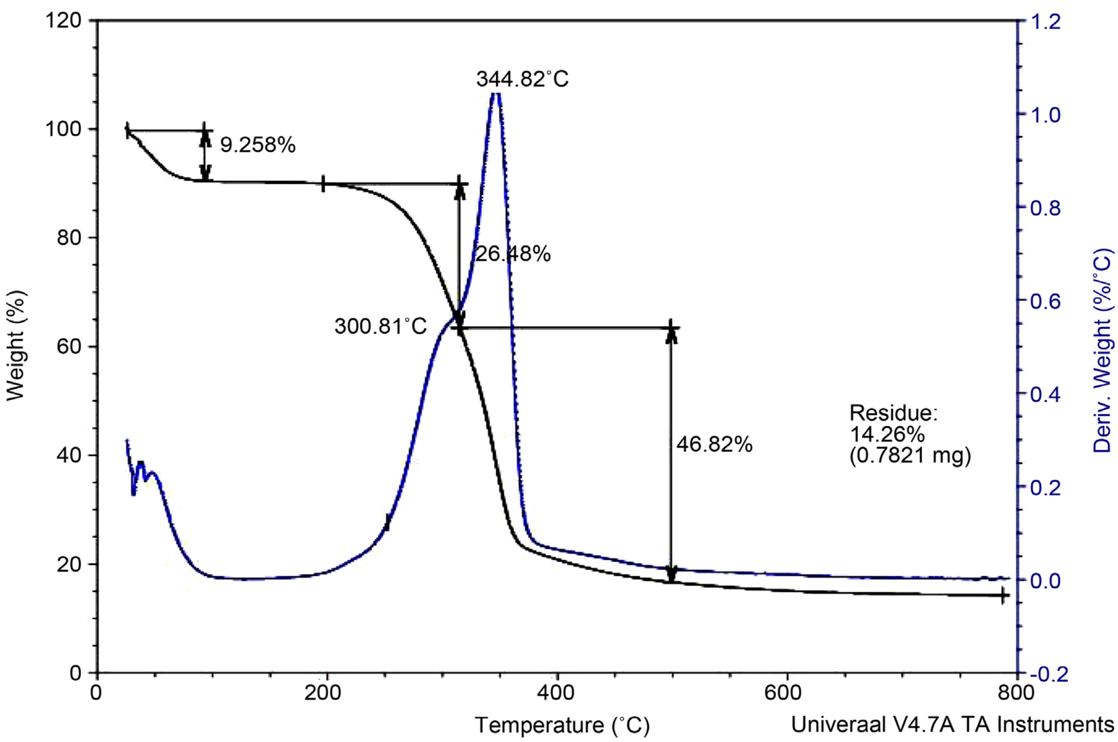

Figure 1. Thermogravimetric curve of sugarcane bagasse produced in Rio Grande do Sul.

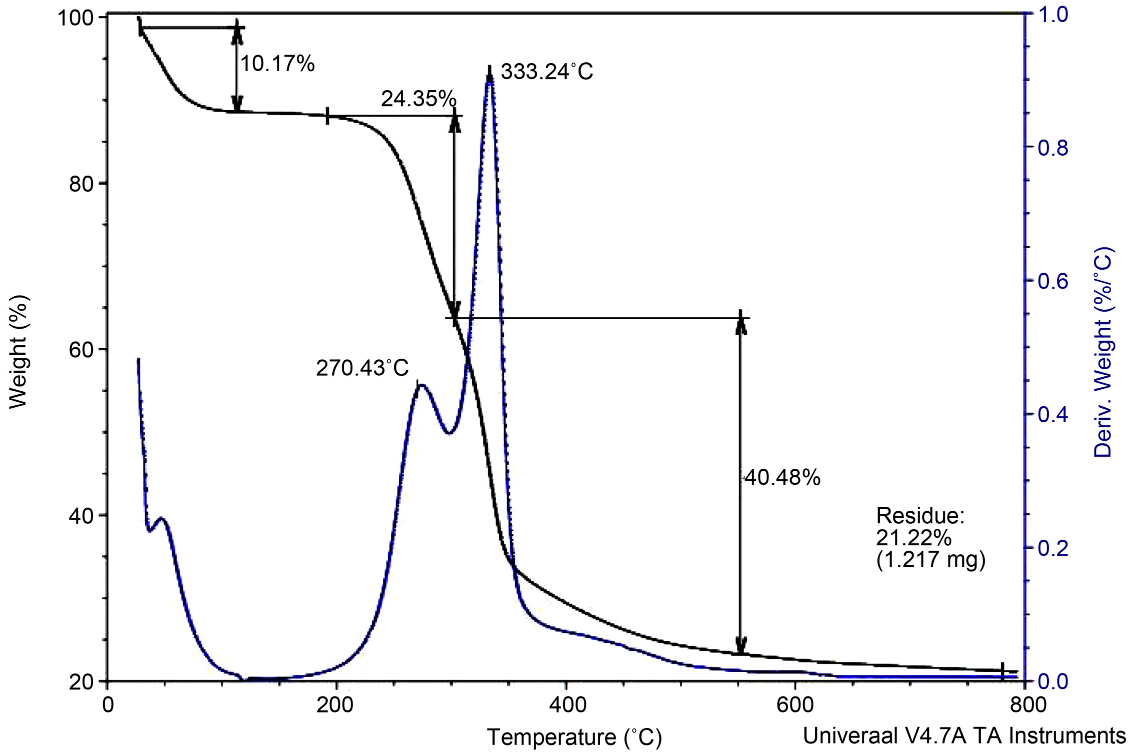

Figure 2. Thermogravimetric curve of sugarcane straw produced in Rio Grande do Sul.

normally in the range of 275˚C - 500˚C. Yet, lignin decomposition happens through an extensive temperature range, wherein under 500˚C about 40% of lignin is decomposed, while the rest is degraded in higher temperatures [35] [36]. Thus, the second zone of mass loss in each thermogravimetric curve is mainly related to thermal degradation of hemicelluloses along with smaller amounts of cellulose and lignin, while the third zone in each curve is predominantly related to thermal degradation of cellulose along with smaller amounts of hemicelluloses and lignin. The solid residue remaining at the end of the process consists of fix carbon and ashes [15].

4. Conclusions

Overall, from the results obtained in the current study, it is possible to conclude that edaphoclimatic conditions of Rio Grande do Sul have no significant influence and chemical composition and energetic potential of sugarcane straw and bagasse when compared to other regions in Brazil. Bagasse presents higher potential for energetic uses compared to straw due to slightly higher volatiles content, along with high lignin content and high calorific value. Both bagasse and straw have potential to be used as substrates to obtain high value added products from their cellulosic fractions, such as organic acids, biofuels and biopolymers. Bagasse presents higher potential of use as substrate for production of high value added products derived from hemicellulose, such as xylitol and furfural, because of its higher hemicelluloses content.

Finally, sugarcane straw and bagasse produced in Rio Grande do Sul present huge potential of use in biorefinery processes. However, more studies and improvement of technologies employed are needed for a better use of chemical and energetic fractions present in sugarcane to achieve higher efficiencies and yields in biorefinery processes.

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