ISSN 2359-6562 (ONLINE) 2359-6562 (CD-ROM)

ENERGY POTENTIAL OF SPENT GRAINS FROM BROWN PORTER STYLE BEER PRODUCTION

CARLOS GUILHERME LOPES GROTTO[1], CARLA JOVANIA GOMES COLARES[1], AILTON TEIXEIRA DO VALE[2], DOUGLAS HENRIQUE PEREIRA[1]

[1] Colegiado de Ciencias exatas e Biotecnológicas, Universidade Federal do Tocantins, campus de Gurupi, rua Badejós,77402-970, Gurupi -TO, Brasil. cguilhermelopes@gmail.com, carla.colares@mail.uft.edu.br, doug@uft.edu.br.
[2] Departamento de Floresta, Universidade de Brasília, Campus Darcy Ribeiro, 70910-900, Brasília-DF, Brasil. ailton.vale@gmail.com.

ABSTRACT: This study aimed to evaluate the energy potential of residual biomass (brewer spent grains - BSG) of *Brown Porter* type beer malt. Analyses of calorific value, moisture, lignin content, ash content, volatile materials and fixed carbon were carried out to investigate the energy potential of BSG. For a better understanding of the thermal degradation behavior of BSG, a thermogravimetric analysis was performed and the TGA curves evidenced the degradation of lignocellulosic matter as hemicellulose and cellulose (120°C and 350°C) and lignin (350°C and 600°C). The observed moisture content measured was 12.69%. The BSG analyzed showed good potential for direct energy generation, 16.57 MJ kg^{-1}, of useful calorific value when the moisture of the material is disregarded. This result is supported by the values measured for the lignin content (31.79% in dry mass) and with carbon, hydrogen, nitrogen and oxygen contents values of 44.85%, 7.06%, 3.53% and 40.70%, respectively. Another positive point is that the ash content of BSG produces less ash, 3.86%, than other biomasses as rice husks and sugarcane bagasse, which facilitates its application in the combustion process. The characterization of the grains used for the production of different types of beer is important for the best use of the residues for power generation, providing alternatives for the beer market.

Keywords: waste, brown porter malt bagasse, energy source.

POTENCIAL ENERGÉTICO DE GRÃOS GASTOS DA PRODUÇÃO DE CERVEJA DO ESTILO BROWN PORTER

RESUMO: O trabalho teve como objetivo avaliar o potencial energético da biomassa residual (grãos gastos da cervejaria - BSG) do malte da cerveja tipo *Brown Porter*. Análises de poder calorífico, umidade, teor de lignina, teor de cinzas, materiais voláteis e carbono fixo foram realizadas a fim de investigar o potencial energético da biomassa BSG. Para um melhor entendimento do comportamento de degradação térmica, foi realizada uma análise termogravimétrica e as curvas TGA evidenciaram a degradação da matéria lignocelulósica como hemicelulose e celulose (120°C e 350°C) e lignina (350°C e 600°C). O teor de umidade observado medido foi de 12,69%. A BSG analisada apresentou bom potencial de geração de energia direta, 16,57 MJ kg^{-1}, de poder calorífico útil quando desconsiderada a umidade do material. Este resultado é apoiado pelos valores medidos para o conteúdo de lignina (31,79% em massa seca) e pelos valores de carbono, hidrogênio, nitrogênio e oxigênio de 44,85%, 7,06%, 3,53% e 40,70%, respectivamente. Outro ponto positivo é que o teor de cinzas da BSG produz menos cinzas, 3,86%, do que outras biomassas como casca de arroz e bagaço de cana-de-açúcar o que facilita sua aplicação no processo de combustão. A caracterização dos grãos utilizados na produção dos diferentes tipos de cerveja é importante para o melhor aproveitamento dos resíduos para geração de energia, proporcionando alternativas para o mercado cervejeiro.

Palavras-chaves: resíduos, bagaço de malte brown porter, fonte de energia.

Recebido em 24/10/2020 e aprovado para publicação em 25/07/2021
DOI: http://dx.doi.org/10.17224/EnergAgric.2021v36n2p204-217

1 INTRODUCTION

Beer is the most consumed alcoholic beverage in the world. This fact is directly related to the increase in consumption in recent decades in emerging countries such as China (COLEN; SWINNEN, 2016). The essential ingredients present in a beer are: malted cereals - malt (usually produced from barley that undergoes a malting process), yeast, hops, water, and in some styles, other starchy adjuncts such as rice and syrup (LI; WANG; LIU 2017).

Different amounts and characteristics of the ingredients generate different types of beer. Porter is a style of dark beer produced with large amounts of hops and brown malt. Therefore, it has very specific characteristics that differentiate it from other types of beer (SIEBERT, 2017).

Along with beer production, also it is the growing the generation of brewery waste such as malt bagasse (brewer spent grains – BSG), which represents 85% of the total product generated by the brewing industry and it is; therefore, considered the most important by-product of this process (MELLO; MALI, 2014). According Olszewski et al. (2020), for 100 L of brewed beer, approximately 20 kg of wet BSG are generated and according to Sganzerla et al. (2021), the amount of Brazilian annual BSG production can be estimated at 2.8×10^6 ton year^{-1} (in wet weight).

Biomasses as the BSG are composed of carbon, oxygen, and hydrogen that form molecules of cellulose, hemicellulose, and lignin which are called as lignocellulosic biomass (LIÑÁN-MONTES et al., 2014). Due to the chemical characteristics of this type of waste, it can be used for energy generation (ANWAR; GULFRAZ; IRSHAD, 2014). During the combustion, this biomass source produces lower greenhouse gas emissions (AKHTAR; AMIN, 2011), what is considered ecologically sound, economically viable (WANG et al., 2018), and a sustainable way of energy production (KHAN et al., 2019).

In the production of beer and malt drinks, the energy demand is huge (FADARE *et al*., 2010), so the application of the waste resulted from this process for energy generation, it is a great opportunity for the beer production sector. The heat generated by the BSG during burning can be satisfactory and presents interesting amounts of heat per unit of volume to generate energy for the brewery itself (CORDEIRO; EL-AOUAR; ARAÚJO, 2013).

Recently, researchers have been addressing characterizations of BSG (DIEGO-DÍAZ et al., 2018; JUCHEN et al., 2018) that pointed out to the potential uses of this waste as an important source of value-added elements. The possibility of use as energy has also been described and compared with the possibility of use as food, which can help to make beer production a self-sustaining energy process. However, the variety of styles of craft/industrial beers influences the diversity of malts used and little is known about the specificity of the residue of each style of beer. Thus, it is necessary to understand the characteristics of the specific residual biomass of certain styles of beer for its better use and reuse. In this context, this work aims to characterize and evaluate the energy potential of BSG of the production of a specific beer style: Brown Porter, a dark beer in which a mixture of malts is used.

2 MATERIALS AND METHODS

The Brown Porter beer biomass samples were obtained after the production of beer at the Food Biotechnology Laboratory of the Federal University of Tocantins (UFT) in Gurupi Brazil, during the month of February 2020. The material used for production was *1*) malt: Pale Ale; Chocolate and Special X, *2*) Hops: Admiral and Fuggle and *3*) Yeast: Ale Yeast; *4*) Mineral Water.

The BSG was stored in a glass container at room temperature for three days. Experiments were prepared and carried out according to pre-defined standards for the following parameters:

2.1 Proximate chemical analysis

The proximate chemical analysis was based on Standard 8112 of Brazilian Association of Technical Standards - ABNT (ABNT, 1986) in which the initial step was to carry out moisture analysis, after drying the material in an oven for 24 h. It is important to emphasize that this is a fundamental step for better use of the waste and for greater sustainability of the beer production process, because the high moisture of this waste, when used immediately after beer production, can result in factors such as difficulty in transportation over long distances, difficulty in storage and decrease in the useful calorific value (CORDEIRO; EL-AOUAR; ARAÚJO, 2013). After this step the moisture contente, volatile materials, fixed carbon and ash content were analyzed.

2.2 Extract contents and soluble, insoluble and total lignin

The extrac contents, soluble, insoluble and total lignina were determined by following the Manual Technical Association of Pulp and Paper Industry, number T 204 cm-97 and T 222 om-11 (TAPPI, 2007). The lignin levels were performed from the stage of removal of the extractives in solvent (TEMPLETON; EHRMAN, 1995). Afterwards, the extraction and quantification of soluble and insoluble lignin was performed. The total lignin was obtained by adding the soluble and insoluble lignina.

The extractives content (E_x), soluble (SLig), insoluble (InsLig) and total (Tlig) lignin were determinated by Equations 1- 4:

$$E_x = \frac{m_2 - m_1}{m}\ 100 \qquad (1)$$

Where, m is sample mass minus moisture, in g; m_1 is the mass of the extraction flask, in g; and m_2 is the mass of the extraction flask + extracts after drying at 105°C in an oven for 2 hours, in g.

$$Slig = \frac{m_2 - m_1}{m} . 100 \qquad (2)$$

Where, m is the mass of the sample discounted to moisture, in g; m_1 is the mass of the filter crucible, in g; and m_2 is the mass of the filter crucible + insoluble lignin free from extracts, in g.

$$InsLig = \frac{\frac{A}{110} . F . \frac{87}{1000}}{m} . 100 \qquad (3)$$

Where, m is the mass of the sample discounted to moisture, in g; A is the absorbance read by the spectrophotometer; and F is the dilution fator.

Finally the total lignin is:

$$Tlig = SLig + InsLig \qquad (4)$$

2.3 Thermogravimetric analysis

Performed using thermogravimetric analysis Instruments 2960 Simultaneous DSC-TGA (differential scanning calorimetry - thermogravimetric analysis, DSC-TGA) equipment, in which the mass loss was verified in a temperature range of 20°C to 600°C, heating rate of 30°C min^{-1} in the presence of synthetic air atmosphere with a flow rate of 30 mL min^{-1}.

2.4 Infrared spectroscopy

The acquisition of spectra in the medium infrared in dry mass was performed in a spectrophotometer of the brand Perkin Elmer IR Spectrum Two. 1 mg of sample was used together with 100 mg (ratio 1:100 m m^{-1}) of potassium bromide (KBr), to which they were mixed and macerated with the aid of a grade and pistil. The material was pressed to form a pellet, which was inserted in the spectrophotometer for reading in the spectral range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and a scan of 32, being acquired a spectrum per sample.

2.5 Calorific value

The analysis of the higher heating value was carried out in a calorimetric pump, basic model C 2000 of the IKA brand after previous drying, following the Brazilian Regulatory Norm (NBR) 8633/84 of the Brazilian Association of Technical Standards – ABNT (ABNT, 1984). The results obtained in the experimental form (higher calorific value – HCV) were also compared with the results obtained through calculations using values of the elementary analysis (CHANNIWALA;

PARIKH, 2002) and proximate chemical analysis (DEMIRBAS et al., 1997).

The HCV determinated by elementary analysis (HCV_E) (CHANNIWALA; PARIKH, 2002), proximate chemical analysis (HHV_{PC}) (DEMIRBAS et al., 1997) and useful calorific value (UCV) (PARIKH; CHANNIWALA; GHOSAL, 2005). These parameters were calculated through the application of Equations 5-8. :

$$HCV_E = 0.3491\ C + 1.1783\ H - 0.1034\ O - 0.0151\ N - 0.0211A + 0.1005\ S \quad (5)$$

$$HHV_{PC} = 0.312(MC) + 0.1534(VMC) \quad (6)$$

$$UCV = (LCV \times (1 - (0.01 \times MC))) - (600 \times 0.01 \times MC) \quad (7)$$

$$LCV = HCV - (600 \times 0.09 \times H) \quad (8)$$

Where: C, H, O, N, S are the percentages determined by the elementary analysis, A is the percentage of ash, MC is the moisture content, VMC is the volatile material content, LCV is the lower calorific value, and HCV is the higher calorific value (experimentally measured).

2.6 Elementary Analysis

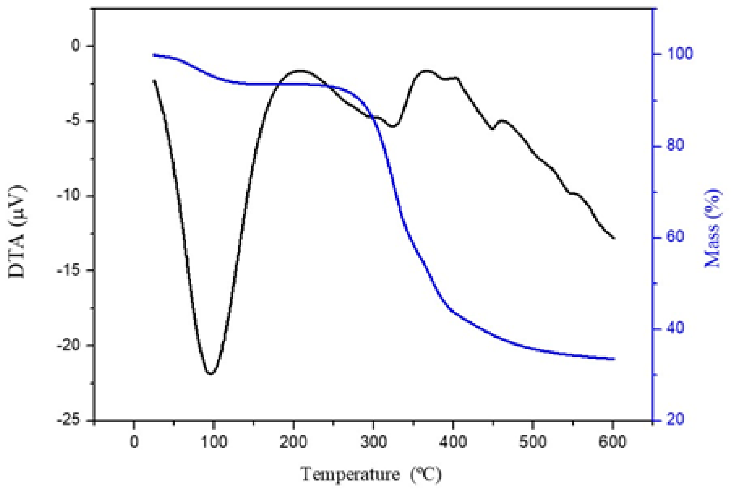
For elementary analysis the samples previously dried (0% moisture) and sieved in a 200-mesh sieve were used to obtain the percentages of carbon (C), nitrogen (N) and hydrogen (H). An elementary analysis (CHN) was performed on a Flash 2000 elementary analyzer. The oxygen (O) content (%) was determined by the difference, considering that elements make up 100% of the sample.

3 RESULTS AND DISCUSSION

3.1 Thermogravimetric Analysis

Figure 1 shows the thermogravimetric (DSC-TGA) analysis of BSG. The DSC-TGA curves indicate that the material is stable up to 25 °C. Above this temperature, thermal decomposition occurs in two steps relative to TG curve. The first step occurs between 50-180 °C, and it is associated with the endothermic peak in the DSC curve at 98 °C, value attributed to the dehydration relative to moisture present in the residue (BERNAL et al., 2002; SANCHEZ-SILVA et al., 2012). The second step occurs between 120-335 °C, and it is relative to the exothermic and endothermic peak at 207ºC and 320°C, values associated to the degradation of cellulose and hemicellulose (BERNAL et al., 2002; SANCHEZ-SILVA et al., 2012).

Figure 1. The thermogravimetry analize (TGA) and differential thermal analyze (DTA) curves for the BSG.



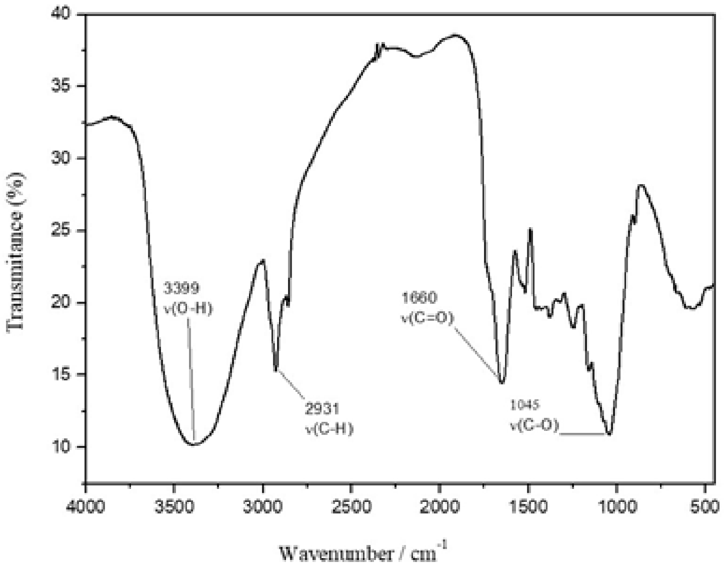
Source: The author.

In the last zone (335°C and 600°C), it is observed the degradation of the polymer that requires more energy to break the bonds that is the lignin (CARRIER et al., 2011; SANCHEZ-SILVA et al., 2012). In the end, at a temperature of 600° some material had not been degraded. A part of this material represents a biomass that can still burn, and a smaller part represents the ashes of the material that is composed mostly by inorganic compounds (ACQUAH et al., 2017).

3.2 Infrared (IR) absorption spectroscopy

Figure 2 shows the main infrared (IR) bands of BSG. Through the spectrum of Figure 2, it is possible to identify the main functional groups, and as expected, the bands present in the BSG have characteristics similar to the characteristic functional groups of cellulose, hemicellulose and lignin (LOPES GROTTO et al., 2020; RAMBO et al., 2015).

Figure 2. Mean infrared spectrum of BSG.



Source: The author.

Analyzing the results of the IR, it is possible to identify an intense band in the region of 3399 cm^{-1}, showing the presence of symmetrical stretching vibrations of groups -

OH of alcohols and phenols present in lignin, cellulose and hemicellulose (HOLLER; et al. 2009; XU et al., 2008). The presence of silano groups (Si-OH) (TARLEY; ARRUDA, 2004) ocurrs due to the presence of silica, also the water present on the BSG is responsible for the stretching in the region mentioned (3399 cm^{-1}).

The band in the region of 2931 cm^{-1} showed the presence of aliphatic stretch C-H, that is found in cellulose, hemicellulose and lignin molecules. The band identified in 1658 cm^{-1} is related to the stretching vibration of C=O present in ketones, esters, aldehydes and carboxylic acids (HOLLER et al., 2009; XU et al., 2008).

The presence of C-O is related to strain vibrations identified in the 1043 cm^{-1} band, showing the presence of groups of carboxylic acids. It should be noted that the BSG presented functional groups characteristic similar to works already reported in the literature (FONTANA; PETERSON; CECHINEL, 2018; FONTANA et al., 2016; MANATURA, 2020). The molecular structures of cellulose, hemicellulose and lignin with their respective functional groups have already been reported in a previous work by our group (LOPES GROTTO et al., 2020).

3.3 Proximate Chemical Analysis

The data measured for proximate chemical analysis, moisture content (MC), volatile material content (VMC), ash content (AC) and fixed carbon content (FCC) of BSG for Brown Porter-style beer are shown in Table 1.

Table 1. Proximate chemical analysis of BSG.

Analysis	**Brown Porter**	**CORDEIRO; EL-AOUAR; ARAÚJO 2013**	**ARAÚJO et al. 2020**	**BOREL et al. 2018**
MC (%)	12.69 ± 0.14	15	6.68 ± 0.58	3.97 ± 0.00
VMC (%)	88.13 ± 2.50	95.95	74.11 ± 0.42	83.30 ± 0.29
AC (%)	3.86 ± 0.11	0.74	2.78 ± 0.12	3.22 ± 0.03
FCC (%)	8.00 ± 2.44	3.31	16.44 ± 0.28	9.51 ± 0.31

MC: moisture content; VMC: volatile material content; AC: ash content; FCC: fixed carbon content.

With regard to proximate chemical analyses, there is a great relationship between these and the calorific value of fuels. High levels of ash and moisture tend to negatively influence the energy efficiency of biomass (FERREIRA et al., 2014; LOPES GROTTO et al., 2020). The MC measured for the BSG was 12.69%.

Malt bagasse generates 4.21% of ash content. In residual biomass, this value can vary between 0.2% and 6.6% (VAMVUKA; KAKARAS, 2011). Another important factor is the value of the fixed carbon content (FCC) that was 8.0%. The FCC is directly related to the energy efficiency of the biomass because the higher the FCC, the higher is the combustion of the material (DINIZ et al., 2004). In this context, the FCC measured for the malt residues are adequate for energy generation.

For volatile materials content (VMC), Brown Porter BSG showed a value of 88.13%. It is noted that this biomass represents a high VMC. This causes it to burn quickly, which favors ignition, with intense release of volatile particles, but it has low resistance, reducing the time of burning. On the other hand, the burning of volatile materials can represent between 50% and 70% of the components on a dry base of a biomass; thus, contributing to the release of energy during combustion (MANYÀ; ARAUZO, 2008).

The results for MC, VMC, AC and FCC (Table 1) are similar to those reported for others BSG, confirming the measured for the Brown Porter-style beer (BOREL et al., 2018; CORDEIRO; EL-AOUAR; ARAÚJO, 2013; ARAÚJO et al., 2020). Orellana et al. (2020) worked with agro-forest residues by determing the volatile material content and fixed carbon content for wood 81.51% and 17.80%; for beans 83.26% and 7.70%; corn 76.23% and 18.02%; coffee 71.66% and 20.64%, respectively, which demonstrates the good results of BSG when compared to other agro-forest residues.

3.4 Calorific value

The calorific value of biomass is an indication of the energy connected to the combustion process that can be converted into thermal energy. It is considered the most important parameter to measure the efficiency of a fuel (PROTÁSIO et al., 2011).

The results for the higher calorific value (HCV) of the analyzed sample are shown in Table 2. The HCV were also determined by elementary analysis (HCV_E) (CHANNIWALA; PARIKH, 2002), proximate chemical analysis (HHV_{PC}) (DEMIRBAS et al., 1997) and useful calorific value (UCV) (PARIKH; CHANNIWALA, GHOSAL, 2005).

Table 2. Higher calorific value of BSG. Results in MJ.kg^{-1}.

Analysis	*Brown Porter*	CORDEIRO; EL-AOUAR; DE ARAÚJO 2013	ARAÚJO et al. 2020	BOREL et al. 2018
HCV	20.16	21.04	20.24	21.6 ± 2.8
HCV_E	19.65	----	----	----
HCV_{PC}	16.03	----	----	----
UCV*	16.57	----	----	----

*Data obtained through the results measured by the experimental HCV.

The results show that the biomass analysed in this work presented a calorific value (HCV) of 20.16 MJ kg^{-1}. There is a difference between the results of HCV_E and HCV_{PC}, where the HCV_E measured is the most approximate to HCV. Thus, it is understood that when gauging HCV from biomass such as BSG the equation that takes into account the values of elementary analysis is more accurate.

The reduction in the UCV, when compared to HCV, is justified by the moisture present in the residues because it is a necessary energy to volatilize water molecules which makes the heating power. The reduction of UCV in relation to HCV shows the need to work with dry biomass to maximize the caloric value. Farinhaque (1981) states that moisture content above 25% not only reduces the caloric value, but also the temperature of the combustion chamber and the exhaust gases, forming unburned gases that under different conditions would generate energy. Thus, it is understood that a drying phase should be ideal for increasing the energy content of biomass such as BSG, reducing moisture, which can contribute to the reduction of losses of calorific value, making the biomass more viable for energy generation.

Comparing the HCV of BSG for Brown Porter-style beer with values reported in the literature, Table 2, it is possible to observe that the values of this work are very close to those reported by De De Araújo et al. (2020), HCV = 20.24 MJ kg^{-1}, and lower than the values reported by Cordeiro, El-Aouar and Araújo (2013) and Borel et al. (2018), HCV = 21.04 MJ kg^{-1} and HCV = 21.6 MJ kg^{-1}, respectively.

3.5 Lignin content

The results for soluble, insoluble, total and extractive lignin in dry mass are presented in Table 3. The total lignin measured were 31.79% and the high lignin content is one of the explanations of good energy results regarding the parameters analyzed in Tables 1 and 2. It is important to highlight that the amount of lignin is of great interest by areas of energy demand due to its chemical structure, percentage of carbon, and calorific value, that positively influences the energy efficiency of a fuel (GOUVEA et al., 2017; LOPES GROTTO et al., 2020). Other works reported in the literature, Table 3, prove the good results determined for the BSG from Brown Porter-style beer (BOREL et al., 2018; VANREPPELEN et al., 2014).

Table 3. Lignin and extractive contents in dry mass (% d.m.) of BSG.

Analysis/Biomass	***Brown Porter***	**BOREL et al., 2018**	**VANREPPELEN et al., 2014**
Extractive	8.11 ± 0.43	5.26 ± 0.06	4.7 ± 0.3
Soluble Lignin	8.08 ± 0.50	-----	-----
Insoluble Lignin	23.71 ± 0.23	----	----
Total Lignin	31.79	29.37± 4.03	11.3 ± 0.4

3.6 Elementary Chemical Analysis

Elemental chemical analysis was performed and the percentages of carbon (C), hydrogen (H), nitrogen (N) and (O) are represented in Table 4. The main component observed in the composition of BSG evaluated is carbon (44.85%) due to the presence of organic molecules in the main biomass components (lignin, cellulose and hemicellulose) (FERREIRA et al., 2014; LOPES GROTTO et al., 2020). For hydrogen, nitrogen and oxygen contents, the values registered were 7.06%, 3.53%, and 40.70%, respectively.

Table 4. Elementary Chemical Analysis (%) of BSG.

BSG	**C**	**H**	**N**	**O**
Brown Porter	44.85	7.06	3.53	40.70
DE ARAÚJO et al., 2020	46.64	6.92	3.84	39.62
BOREL et al., 2018	47.2 ± 1.3	7.2 ± 0.1	3.6 ± 0.4	37.6 ± 1.7

Table 4 shows other values of elemental chemical analysis of BSG retrived from other works reported in the literature and the results from BSG for Brown Porter-style beer corroborate with those reported in previous works (BOREL et al., 2018, DE ARAÚJO et al., 2020).

3.7 Comparison with biomass usually used as energy

Comparing the results obtained in the work for Brown Porter-style beer with others biomass sources frequently used for energy production as rice husk and sugarcane bagasse, it is possible to infer that:

I- The VMC, HCV, lignin and the percentage of carbon measured are higher than those reported for rice husk and sugarcane bagasse (GALINA et al., 2019; LIM et al., 2012; VARMA; MONDAL, 2016; PAULA et al., 2015; VIEIRA, 2013).

II - The AC and FCC determined for BSG are smaller than those found for biomass of rice and sugarcane husks (LIM et al., 2012; MANYÀ; ARAUZO, 2008).

4 CONCLUSION

According to the analyses carried out in this work, it is possible to observe the good energy potential of the BSG from Brown Porter beer production. The material has good levels of volatile materials, characteristics that favor a fast and simple burning process. The observed ash content is favorable when compared to other biomasses that are widely used for energy generation such as rice husks. The lignin and carbon contents measured, help in the understanding of energy efficiency during the burning process because the biomass presented high values of superior and useful calorific power. The results presented in this work show the relevance of characterizing biomass in a specific way. The brewing industry produces several types of beer, which may have different characteristics. With this type of characterization, it is possible to optimize the reuse of this material, making its use increasingly advantageous and economically sustainable. The results obtained in this work show that the use of BSG is an excellent alternative for energy production.

5 ACKNOWLEDGMENT

The authors acknowledge funding from CAPES (Coordination of Improvement of Higher Education Personnel - Brazil), Funding Code 001 CAPES and the PROPESQ/Federal University of Tocantins (Edital para tradução e publicação de artigos científicios da Universidade Federal do Tocantins - PROPESQ/UFT, nº29/2020).

6 REFERENCES

ABNT. **NBR 8112**: Carvão vegetal - Análise imediata - Método de ensaio. Rio de Janeiro: ABNT, 1986.

ABNT. **NBR 8633**: Carvão vegetal – determinação do poder calorífico. Rio de Janeiro: ABNT, 1984.

ACQUAH, G. E.; VIA, B. K.; FASINA, O. O.; ADHIKARI, S.; BILLOR, N.; ECKHARDT, L. G. Chemometric modeling of thermogravimetric data for the compositional analysis of forest biomass. **PLOS ONE**, San Francisco, v. 12, n. 3, p. e0172999, 2017. DOI: https://doi.org/10.1371/journal.pone.0172999. Disponível em: https://journals.plos.org/plosone/article?id=10.1371/journal.pone.0172999. Acesso em: 10 mar. 2020.

AKHTAR, J.; AMIN, N. A. S. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. **Renewable and Sustainable Energy Reviews**, Oxford, v. 15, n. 3, p. 1615-1624, abr. 2011. DOI: https://doi.org/10.1016/j.rser.2010.11.054. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S1364032110004235. Acesso em: 10 abr. 2020.

ANWAR, Z.; GULFRAZ, M.; IRSHAD, M. Agro-industrial lignocellulosic biomass a key to unlock the future bio-energy: A brief review. **Journal of Radiation Research and Applied Sciences**, Amsterdam, v. 7, n. 2, p. 163-173, abr. 2014. DOI: https://doi.org/10.1016/j.jrras.2014.02.003. Disponível em: https://www.tandfonline.com/doi/full/10.1016/j.jrras.2014.02.003. Acesso em: 25 jun. 2020.

ARAÚJO, T. P.; QUESADA, H. B.; BERGAMASCO, R.; VARESCHINI, D. T.; DE BARROS, M. A. S.D. Activated hydrochar produced from brewer’s spent grain and its application in the removal of acetaminophen. **Bioresource Technology**, Amsterdam, v. 310, p. 123399, ago. 2020. DOI: https://doi.org/10.1016/j.biortech.2020.123399. Disponível em: https://www.sciencedirect.com/science/article/abs/pii/S0960852420306714. Acesso em: 07 jul. 2020.

BERNAL, C.; COUTO, A. B.; BREVIGLIERI, S. T.; CAVALHEIRO, E. T. G. Influência de alguns parâmetros experimentais nos resultados de análises calorimétricas diferenciais - DSC. **Química Nova**, [*S. l.*], v. 25, n. 5, p. 849-855, 2002. DOI: https://doi.org/10.1590/S0100-40422002000500023. Disponível em: http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0100-40422002000500023&lng=pt&nrm=iso&tlng=pt. Acesso em: 10 jul. 2020.

BOREL, L. D. M. S.; LIRA, T. S.; RIBEIRO, J. A.; ATAÍDE, C. H.; BARROZO, M. A. S. Pyrolysis of brewer’s spent grain: Kinetic study and products identification. **Industrial Crops and Products**, Amsterdam, v. 121, p. 388-395, 2018. DOI: https://doi.org/10.1016/j.indcrop.2018.05.051. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0926669018304692. Acesso em: 20 jun. 2020.

CARRIER, M.; LOPPINET-SERANI, A.; DENUX, D.; LASNIER, J. M.; HAM-PICHAVANT, F.; CANSELL, F.; AYMONIER, C. Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass. **Biomass and Bioenergy**, Oxford, v. 35, n. 1, p. 298-307, jan. 2011. DOI: https://doi.org/10.1016/j.biombioe.2010.08.067. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0961953410003314. Acesso em: 20 jun. 2020.

CHANNIWALA, S. A.; PARIKH, P. P. A unified correlation for estimating HHV of solid, liquid and gaseous fuelsq. **Fuel,** v. 81, n. 8, p. 1051-1063, may 2002. DOI: https://doi.org/10.1016/S0016-2361(01)00131-4. Disponível em: https://www.sciencedirect.com/science/article/pii/S0016236101001314. Acesso em: 18 abr. 2020.

COLEN, L.; SWINNEN, J. Economic Growth, Globalisation and Beer Consumption. **Journal of Agricultural Economics**, Chichester, v. 67, n. 1, p. 186-207, 2016. DOI: https://doi.org/10.1111/1477-9552.12128. Disponível em: http://doi.wiley.com/10.1111/1477-9552.12128. Acesso em: 10 jul. 2020.

CORDEIRO, L. G.; EL-AOUAR, Â. A.; ARAÚJO, C. V. B. Energetic characterization of malt bagasse by calorimetry and thermal analysis. **Journal of Thermal Analysis and Calorimetry**, Budapest, v. 112, n. 2, p. 713-717, maio 2013. DOI: https://doi.org/10.1007/s10973-012-2630-x. Disponível em: http://link.springer.com/10.1007/s10973-012-2630-x. Acesso em: 16 mar. 2020.

DEMIRBAS, A.; GULLU, D.; ÇAGLAR, A.; AKDENIZ, F. Estimation of Calorific Values of Fuels from Lignocellulosics. **Energy Sources**, Denver, v. 19, n. 8, p. 765-770, out. 1997. DOI: https://doi.org/10.1080/00908319708908888. Disponível em: http://www.tandfonline.com/doi/abs/10.1080/00908319708908888. Acesso em: 16 mar. 2020.

DIEGO-DÍAZ, B.; FERNÁNDEZ-RODRÍGUEZ, J.; VITAS, A. I.; PEÑAS, F. J. Biomethanization of solid wastes from the alcoholic beverage industry: Malt and sloe. Kinetic and microbiological analysis. **Chemical Engineering Journal**, Amsterdam, v. 334, p. 650-656, fev. 2018. DOI: https://doi.org/10.1016/j.cej.2017.10.075. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S1385894717317898. Acesso em: 10 fev. 2020.

DINIZ, J.; CARDOSO, A. L.; STAHL, J. A.; MARTINS, A. F. Poder calorífico da casca de arroz, caroço de pêssego, serra- gem de eucalipto e de seus produtos de pirólise. **Ciência e Natura**, Santa Maria, v. 26, n. 2, p. 1-8, 2004. DOI: https://doi.org/10.5902/2179460X9674. Disponível em: https://periodicos.ufsm.br/cienciaenatura/article/view/9674/5792. Acesso em: 05 jun. 2020.

FADARE, D. A.; NKPUBRE, D. O.; ONI, A. O.; FALANA, A.; WAHEED, M. A.; BAMIRO, O. A. Energy and exergy analyses of malt drink production in Nigeria. **Energy**, [*S. l.*], v. 35, n. 12, p. 5336-5346, dez. 2010.
DOI: https://doi.org/10.1016/j.energy.2010.07.026. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0360544210004019. Acesso em: 03 jun. 2020.

FARINHAQUE, R. **Influência da umidade no poder calorífico da madeira de bracatinga (*Mimosa scabrella*, Benth), e aspectos gerais de combustão**. Curitiba: Fundação de Pesquisas

Florestais do Paraná, 1981. (Série Técnica n. 6). Disponível em: https://www.scienceopen.com/document?vid=1fcd2688-8f95-4e24-8d86-76d76713f3b8. Acesso em: 18 jun. 2020.

FERREIRA, I. T. et al. Estimativa do potencial energético de resíduos celulósicos de fabricação de papel através de análise imediata. **Revista Brasileira de Energias Renováveis**, [*S. l.*], v. 3, n. 4, p. 284- 297, nov. 2014.
DOI: https://doi.org/10.5380/RBER.V3I4.38618. Disponível em: file:///C:/Users/dougl/Downloads/38618-143401-1-PB.pdf. Acesso em: 04 maio 2020.

FONTANA, I. B.; PETERSON, M.; CECHINEL, M. A. P. Application of brewing waste as biosorbent for the removal of metallic ions present in groundwater and surface waters from coal regions. **Journal of Environmental Chemical Engineering**, Curitiba, v. 6, n. 1, p. 660-670, fev. 2018. DOI: https://doi.org/10.1016/j.jece.2018.01.005. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S2213343718300058. Acesso em: 06 maio 2020.

FONTANA, K. B.; CHAVES, E. S.; SANCHEZ, J. D. S.; WATANABE, E. R. L. R.; PIETROBELLI, J. M. T. A.; LENZI, G. G.Textile dye removal from aqueous solutions by malt bagasse: Isotherm, kinetic and thermodynamic studies. **Ecotoxicology and Environmental Safety**, Philadelphia, v. 124, p. 329-336, fev. 2016. DOI: https://doi.org/ 10.1016/j.ecoenv.2015.11.012. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0147651315301561. Acesso em: 13 jun. 2020.

GALINA, N. R.; ROMERO LUNA, C. M.; ARCE, G. L. A. F.; ÁVILA, I. Comparative study on combustion and oxy-fuel combustion environments using mixtures of coal with sugarcane bagasse and biomass sorghum bagasse by the thermogravimetric analysis. **Journal of the Energy Institute**, Kidlington, v. 92, n. 3, p. 741-754, jun. 2019. DOI: https://doi.org/10.1016/j.joei.2018.02.008. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S1743967117309236. Acesso em: 18 maio 2020.

GOUVEA, A. F. G.; CARVALHO, A. M. M. L.; SILVIA, C. M.; CARNEIRO, A. C. O.; TRUGILHO, P. F.; FREITAS, F. P.; VALADARES, L. B.; GOMES, C. M.; COSTA, E. B. Estudo da adição da lignina kraft nas propriedades mecânicas dos briquetes de resíduos da indústria moveleira. **Ciência Florestal**, Santa Maria, v. 27, n. 3, p. 1029, ago. 2017. DOI: https://doi.org/10.5902/1980509828678. Disponível em: https://periodicos.ufsm.br/cienciaflorestal/article/view/28678. Acesso em: 08 maio 2020.

LOPES GROTTO, C. G.; COLARES, C. J. G.; LIMA, D. R.; PEREIRA, D. H., DO VALE A. T. Energy potential of biomass from two types of genetically improved rice husks in Brazil: A theoretical-experimental study. **Biomass and Bioenergy**, Oxford, v. 142, p. 105816, nov. 2020. DOI: https://doi.org/10.1016/j.biombioe.2020.105816. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0961953420303512. Acesso em: 18 maio 2020.

HOLLER, F. J.; SKOOG, D.; CROUCH, A.; STANLEY, R. **Princípios de Análise Instrumental**. 6. ed. Porto Alegre: Bookman, 2009.

JUCHEN, P. T.; PIFFER, H. H.; VEIT, M. T.; GONÇALVES, G. C.; PALÁCIO, S. M.; ZANETTE, J. C. Biosorption of reactive blue BF-5G dye by malt bagasse: kinetic and equilibrium studies. **Journal of Environmental Chemical Engineering**, Amsterdam, v. 6, n. 6, p. 7111-7118, dez. 2018. https://doi.org/10.1016/j.jece.2018.11.009. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S2213343718306882. Acesso em: 03 jun. 2020.

KHAN, T. A.; SAUD, A. S.; JAMARI, S. S.; RAHIM, M. H. A.; PARK, J. W.; KIM, H. J. Hydrothermal carbonization of lignocellulosic biomass for carbon rich material preparation: A review. **Biomass and Bioenergy**, Oxford, v. 130, p. 105384, nov. 2019. DOI: https://doi.org/10.1016/j.biombioe.2019.105384. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0961953419303332. Acesso em: 07 maio 2020.

LI, Q.; WANG, J.; LIU, C. Beers. *In*: FOOD AND BEVERAGES INDUSTRY. **Current Developments in Biotechnology and Bioengineering**. [*S. l.*]: Elsevier, 2017. chap. 12, p. 305-351. Disponível em: https://www.sciencedirect.com/science/article/pii/B9780444636669000121. Acesso em: 03 maio 2020.

LIM, J.S.; ABDUL MANAN, Z.; WAN ALWI, S. R.; HASHIM, H. A review on utilisation of biomass from rice industry as a source of renewable energy. **Renewable and Sustainable Energy Reviews**, Oxford, v. 16, n. 5, p. 3084-3094, jun. 2012. DOI: https://doi.org/10.1016/j.rser.2012.02.051. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S1364032112001451. Acesso em: 12 maio 2020.

LIÑÁN-MONTES, A.; DE LA PARRA-ARCINIEGA, S. M.; GARZA-GONZÁLEZ, M. T.; GARCÍA-REYES, R. B.; SOTO-REGALADO, E.; CERINO-CÓRDOVA, F. J. Characterization and thermal analysis of agave bagasse and malt spent grain. **Journal of Thermal Analysis and Calorimetry**, Budapest, v. 115, n. 1, p. 751-758, jan. 2014. DOI: https://doi.org/10.1007/s10973-013-3321-y. Disponível em: http://link.springer.com/10.1007/s10973-013-3321-y. Acesso em: 10 jun. 2020.

MANATURA, K. Inert torrefaction of sugarcane bagasse to improve its fuel properties. **Case Studies in Thermal Engineering**, Amsterdam, v. 19, p. 100623, jun. 2020. DOI: https://doi.org/10.1016/j.csite.2020.100623. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S2214157X19305118. Acesso em: 08 jun. 2020.

MANYÀ, J. J.; ARAUZO, J. An alternative kinetic approach to describe the isothermal pyrolysis of micro-particles of sugar cane bagasse. **Chemical Engineering Journal**, Amsterdam, v. 139, n. 3, p. 549-561, jun. 2008. DOI: https://doi.org/10.1016/j.cej.2007.09.005. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S1385894707006109. Acesso em: 13 maio 2020.

MELLO, L. R. P. F.; MALI, S. Use of malt bagasse to produce biodegradable baked foams made from cassava starch. **Industrial Crops and Products**, Amsterdam, v. 55, p. 187-193, abr. 2014. DOI: https://doi.org/10.1016/j.indcrop.2014.02.015. . Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0926669014000934. Acesso em: 14 maio 2020.

OLSZEWSKI, M. P.; NICOLAE, S. A.; ARAUZO, P. J.; TITIRICI, M. M.; KRUSE, A. Wet and dry? Influence of hydrothermal carbonization on the pyrolysis of spent grains. **Journal of Cleaner Production**, Amsterdam, v. 260, n. 1, p. 121101, 2020. DOI: https://doi.org/10.1016/j.jclepro.2020.121101. Disponível em: https://www.sciencedirect.com/science/article/pii/S0959652620311483. Acesso em: 07 jun. 2020.

ORELLANA, B. B. M. A.; VALE, A. T.; ORELLANA, J. B. P.; CHAVES, B. S.; MOREIRA, A. C. O. Caracterização de resíduos agroindustriais da região do distrito federal para fins energéticos. **Energia na agricultura**, Botucatu, v. 35, n. 1, p. 46-61, mar. 2020. DOI: https://doi.org/10.17224/EnergAgric.2020v35n1p46-61. Disponível em: http://revistas.fca.unesp.br/index.php/energia/article/view/3622. Acesso em: 15 maio 2020.

PAULA, L.; TRUGILHO, P. F.; NAPOLI, A.; BIANCHI, M. L. Characterization of residues from plant biomass for use in energy generation. **Cerne**, Lavras, v. 17, p. 237-246, 2015. DOI: https://doi.org/10.1590/S0104-77602011000200012. Disponível em: https://www.scielo.br/j/cerne/a/CY478JQ7bpBT36MwW7CGCgj/?lang=en. Acesso em: 18 maio 2020.

PARIKH, J.; CHANNIWALA, S. A.; GHOSAL, G. K. A correlation for calculating HHV from proximate analysis of solid fuels. **Fuel**, Oxford, v. 84, p. 487-494, 2005. DOI: https://doi.org/10.1016/j.fuel.2004.10.010. Disponível em: https://www.sciencedirect.com/science/article/pii/S0016236104003072. Acesso em: 09 maio 2020.

PROTÁSIO, T. P.; BUFALINO, L.; TONOLI, G. H. D.; COUTO, A. M.; TRUGILHO, P. F.; GUIMARÃES JÚNIOR, M. Relação entre o poder calorífico superior e os componentes elementares e minerais da biomassa vegetal. **Pesquisa Florestal Brasileira**, Colombo, v. 31, n. 66, p. 113-122, jun. 2011. DOI: https://doi.org/10.4336/2011.pfb.31.66.113. Disponível em: http://www.cnpf.embrapa.br/pfb/index.php/pfb/article/view/200/211. Acesso em: 12 jun. 2020.

RAMBO, M.K.D.; RAMBO, M.C.D.; ALMEIDA, K.J.C.R.; ALEXANDRE, G.P Estudo de análise termogravimétrica de diferentes biomassas lignocelulósicas utilizando a análise por componentes principais. **Ciência e Natura**, Santa Maria, v. 37, n. 3, p. 862-868, out. 2015. DOI: https://doi.org/10.5902/2179460X18332. Disponível em: http://cascavel.ufsm.br/revistas/ojs-2.2.2/index.php/cienciaenatura/article/view/18332. Acesso em: 10 maio 2020.

SANCHEZ-SILVA, L.; LÓPEZ-GONZÁLEZ, D.; VILLASEÑOR, J.; SÁNCHEZ, P.; VALVERDE, J. L.Thermogravimetric–mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis. **Bioresource Technology**, Amsterdam, v. 109, p. 163-172, abr. 2012. DOI: https://doi.org/10.1016/j.biortech.2012.01.001. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0960852412000053. Acesso em: 12 maio 2020.

SGANZERLA, W. G.; BULLER, L. S.; MUSSSATTO, S. I; FORSTER-CARNEIRO, T. Techno-economic assessment of bioenergy and fertilizer production by anaerobic digestion of brewer's spent grains in a biorefinery concept. **Journal of Cleaner Production**, Amsterdam, v. 297, p. 126600, 2021. DOI: https://doi.org/10.1016/j.jclepro.2021.126600. Disponível em: https://www.sciencedirect.com/science/article/pii/S0959652621008209. Acesso em: 11 maio 2020.

SIEBERT, T. Agro-processing of fermented beverages: beer. **FarmBiz**, Lyttelton, v. 3, n. 6, p. 36-37, 2017. https://doi.org/10.1016/j.jrras.2014.02.003. Disponível em: https://www.tandfonline.com/doi/full/10.1016/j.jrras.2014.02.003. Acesso em: 10 jun. 2020.

TARLEY, C. R.; ARRUDA, M. A. Z. Biosorption of heavy metals using rice milling by-products. Characterisation and application for removal of metals from aqueous effluents. **Chemosphere**, Oxford, v. 54, n. 7, p. 987-995, fev. 2004. https://doi.org/10.1016/j.chemosphere.2003.09.001. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0045653503008543. Acesso em: 07 maio 2020.

TAPPI. **Solvent extractives of wood and pulp**. TAPPI test methods. Atlanta: TAPPI Press, 2007.

TEMPLETON, D.; EHRMAN, T. Determination of Acid-Insoluble Lignin in Biomass. LAP-003. *In*: MIDWEST RESEARCH INSTITUTE. **Chemical Analysis and Testing Task**. Laboratory Analytical Procedures. [*S. l.*]: National Renewable Energy Laboratory, 1995. p. 1-13.

VAMVUKA, D.; KAKARAS, E. Ash properties and environmental impact of various biomass and coal fuels and their blends. **Fuel Processing Technology**, Amsterdam, v. 92, n. 3, p. 570-581, mar. 2011. DOI: https://doi.org/10.1016/j.fuproc.2010.11.013. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0378382010003760. Acesso em: 25 maio 2020.

VARMA, A. K.; MONDAL, P. Physicochemical Characterization and Pyrolysis Kinetic Study of Sugarcane Bagasse Using Thermogravimetric Analysis. **Journal of Energy Resources Technology**, New York, v. 138, n. 5, p. 052205, set. 2016. DOI: https://doi.org/10.1115/1.4032729. Disponível em: https://asmedigitalcollection.asme.org/energyresources/article/doi/10.1115/1.4032729/444232/Physicochemical-Characterization-and-Pyrolysis. Acesso em: 22 maio 2020.

VANREPPELEN, K.; VANDERHEYDEN S.; KUPPENS, T.; SCHREURS S., YPERMAN J.; Carleer, R. Activated carbon from pyrolysis of brewer’s spent grain: Production and adsorption properties. **Waste Management & Research**, London, v. 32, n. 7, p. 634-645, jul. 2014. DOI: https://doi.org/10.1177/0734242X14538306. Disponível em: https://journals.sagepub.com/doi/10.1177/0734242X14538306. Acesso em: 20 fev.2020.

VIEIRA, A. C.; SOUZA, N. M.; BARICCATTI, R. A.; SIQUEIRA, J. A. C.; EDUARDO, C.; NOGUEIRA, C. Caracterização da casca de arroz para geração de energia. **Varia Scientia Agrárias**, [*S. l.*], v. 3, n. 1, p. 51-57, 2013. Disponível em: https://e-revista.unioeste.br/index.php/variascientiaagraria/article/view/6100. Acesso em: 10 fev.2020.

WANG, T.; ZHAI, Y.; ZHU, Y.; LI, C.; ZENG, G. A review of the hydrothermal carbonization of biomass waste for hydrochar formation: Process conditions, fundamentals, and physicochemical properties. **Renewable and Sustainable Energy Reviews**, Oxford, v. 90, p. 223-247, jul. 2018. DOI: https://doi.org/10.1016/j.rser.2018.03.071. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S1364032118301618. Acesso em: 18 maio 2020.

XU, L.; ZHOU, Y. P.; TANG, L. J.; WU, H. L.; JIANG, J. H.; SHEN, G. L.; YU, R. Q. Ensemble preprocessing of near-infrared (NIR) spectra for multivariate calibration. **Analytica Chimica Acta**, Amsterdam, v. 616, n. 2, p. 138-143, jun. 2008. DOI: https://doi.org/10.1016/j.aca.2008.04.031. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0003267008006971. Acesso em: 22 jun. 2020.