Physicochemical characterization of agro-industrial residues for second-generation ethanol production

Caracterização físico-química de resíduos agroindustriais para produção de etanol de segunda geração

Caracterización fisicoquímica de residuos agroindustriales para la producción de etanol de segunda generación

Abstract

Ethanol production from renewable sources, such as lignocellulosic materials, is already underway in several countries. The interest in the technology stems from concerns about global warming and the environmental impacts of solid waste disposal. Moreover, the conversion of agro-industrial wastes into ethanol is a value-adding strategy. This study aimed to evaluate the physicochemical characteristics of three lignocellulosic materials—rice straw bran, sugarcane bagasse, and corn peel bran—and determine, on the basis of these analyses, their suitability as feedstocks for second-generation ethanol production. Physicochemical characterization included the determination of particle size, moisture, ash, total solids, water activity, crude fat, protein, total extractives, soluble and insoluble lignin, holocellulose, cellulose, hemicellulose, and total carbohydrates. Rice straw bran is composed of 38.33% cellulose and 19.73% hemicellulose, sugarcane bagasse is composed of 27.09% cellulose and 5.61% hemicellulose, and corn peel bran is composed of 55.75% cellulose and 12.93% hemicellulose. The characterization showed the high concentration of cellulose in the residue of the corn peel bran. The results indicate that the three biomasses are suitable raw materials for biofuel production.

Keywords: Lignocellulosic; Rice straw bran; Sugarcane bagasse; Corn peel bran; Bioethanol.

Resumo

A produção de etanol a partir de fontes renováveis, como materiais lignocelulósicos, já está sendo produzido em vários países. O interesse pela tecnologia decorre da preocupação com o aquecimento global e os impactos ambientais do descarte de resíduos sólidos. Além disso, a conversão de resíduos agroindustriais em etanol é uma estratégia de agregação de valor. Este estudo teve como objetivo avaliar as características físico-químicas de três materiais lignocelulósicos - farelo de palha de arroz, bagaço de cana-de-açúcar e farelo de casca de milho - e determinar, com base nessas análises, sua adequação como matéria-prima para a produção de etanol de segunda geração. A caracterização físico-química incluiu a determinação de granulometria, umidade, cinzas, sólidos totais, atividade de água, gordura bruta, proteína, extrativos totais, lignina solúvel e insolúvel, holocelulose, celulose, hemicelulose e carboidratos totais. O farelo da palha de arroz é composto por 38,33% de celulose e 19,73% de hemicelulose, o bagaço de cana é composto por 27,09% de celulose e 5,61% de hemicelulose e o farelo de casca de milho é composto por 55,75% de celulose e 12,93% de hemicelulose. A caracterização evidenciou a alta concentração de celulose no
resíduo do farelo da casca do milho. Os resultados indicam que as três biomassas são matérias-primas adequadas para a produção de biocombustíveis.

Palavras-chave: Lignocelulósicos; Farelo de palha de arroz; Bagazo de cana-de-açúcar; Farelo de casca de milho; Bioetanol.

Resumen
La producción de etanol a partir de fuentes renovables, como los materiales lignocelulósicos, ya está en marcha en varios países. El interés en la tecnología proviene de las preocupaciones sobre el calentamiento global y los impactos ambientales de la eliminación de desechos sólidos. Además, la conversión de desechos agroindustriales en etanol es una estrategia de valor agregado. Este estudio tuvo como objetivo evaluar las características fisicoquímicas de tres materiales lignocelulósicos—salvado de paja de arroz, bagazo de caña de azúcar y salvado de cáscara de maíz—y determinar, a partir de estos análisis, su idoneidad como materia prima para la producción de etanol de segunda generación. La caracterización fisicoquímica incluyó la determinación del tamaño de partícula, humedad, cenizas, sólidos totales, actividad de agua, grasa cruda, proteína, extractos totales, lignina soluble e insoluble, holocelulosa, celulosa, hemicelulosa y carbohidratos totales. El salvado de paja de arroz está compuesto por un 38,33% de celulosa y un 19,73% de hemicelulosa, el bagazo de caña de azúcar está compuesto por un 27,09% de celulosa y un 5,61% de hemicelulosa, y el salvado de cáscara de maíz está compuesto por un 55,75% de celulosa y un 12,93% de hemicelulosa. La caracterización mostró la alta concentración de celulosa en el residuo del salvado de cáscara de maíz. Los resultados indican que las tres biomassas son materias primas adecuadas para la producción de biocombustibles.

Palabras clave: Lignocelulósicos; Salvado de paja de arroz; Bagazo de caña de azúcar; Salvado de cáscara de maíz; Bioetanol.

1. Introduction

Agro-industries generate large volumes of waste and spend considerable amounts of money with solid waste disposal. The conversion of agro-industrial residues into high added value products, such as second-generation ethanol, is a solution to this costly problem (Paula et al., 2011; Sudha et al., 2015). However, plant residues are complex matrices, and thorough characterization is required to determine their suitability as raw materials for bioethanol production (Mitra, 2015).

Brazil has a large agricultural sector and produces tones of agro-industrial residues per year, the majority of which is used as animal feed or for household energy production in cogeneration systems. Nevertheless, there are concerns about the environmental impacts associated with the improper disposal of agro-industrial wastes (Santos et al., 2012). New policies and procedures have been adopted for handling and processing solid wastes with the aim of recovering, recycling, and converting wastes into value-added products (Gombert & Maris, 2015; Jan et al., 2017).

According to FAO, the United States and Brazil remain the two largest ethanol producers, the world biofuel projections for ethanol from 119.3 (2016) to 128.4 million litres (2025). A report, Biofuels Annual, by the United States Department of Agriculture (USDA) estimated that Brazilian ethanol production in 2020 at 31.35 billion liters, a decrease of 16 percent relative to the revised figure for 2019 (37.38 billion liters), mainly because sugar-ethanol plants are diverting more sugarcane towards sugar production.

Second-generation ethanol is produced from agro-industrial biomass (Raele et al., 2014). These lignocellulosic materials are abundant and low cost. Unlike sugar- and starch-based substrates, lignocellulosic materials can be used for ethanol production without impacting food supplies (Bahmani et al., 2016). Among the components mainly by cellulose, hemicellulose and lignin, due to the recalcitrant structure they need more process steps to release access to carbohydrates. Industries and researchers across the world have been faced with the challenge of reducing ethanol production costs (UDOP, 2017).

This study aimed to determine the physicochemical properties of three agro-industrial residues—rice straw bran, sugarcane bagasse, and corn peel bran—and evaluate their potential as raw materials for second-generation ethanol production.
2. Material and Methods

Biomass samples were kindly donated by Brazilian agro-industries. Corn peel bran, a by-product of starch processing, was provided by Cargill Incorporated (Uberlândia-MG, Brazil). Steam-exploded sugarcane bagasse was provided by the Sugarcane Technology Center - CTC (Piracicaba - SP, Brazil). And ground rice straw bran was supplied by Cocal Ltda (Uberlândia-MG, Brazil). The samples did not require any pre-treatment before analysis, according to National Renewable Energy Laboratory (NREL) guidelines. All analyses were performed in triplicate. In the Figure 1 the aspect of the agroindustry residues are presented. In the present study, methodological supports were based on Pereira et al. (2018). Thus, materials and methods used are set out below.

Figure 1 - Aspect of the agroindustrial residues of (a) rice straw bran, (b) sugarcane bagasse and (c) corn peel bran, respectively.

![Residues](image)

Source: Authors.

2.1 Particle Size Analysis

The particle size distribution is used to characterize the particle size of a material, since materials with identical average diameters can have different distributions. Particle size distribution (granulometric distribution) was determined by sieving 50 g of sample through 10 to 35 mesh (1.68 mm - 420 µm) Tyler standard sieves placed on a vibratory sieve shaker for 10 to 20 min and until a constant mass determined by analytical balance. After sieving, the mass of material retained in each sieve was determined (Gomides, 1997).

2.2 Determination of Extractives

To avoid interferences with later analytical steps, it is necessary to remove non-structural material from biomass prior to analysis. Thus, the content of extractives in the biomass samples was determined by Soxhlet extraction according to the NREL method (Sluiter et al., 2008a). Approximately 4.0 g of sample were placed in a round-bottom flask on a heating mantle. Successive extractions were performed for 6 h with ultrapure water and for 16 h with anhydrous ethanol using 190.0 mL of solvent. Was adjusted the heating mantles to provide a minimum of 4-5 siphon cycles per hour to water and of 6-10 siphon cycles per hour to ethanol extractions. The solvent was evaporated, separated and stored, at the end of each extraction. The extracted solids were transferred to a cellulose paper filter in a Buchner funnel and washed with approximately 100.0 mL of anhydrous ethanol. The samples were oven dried for 24 h at 40 ± 2 °C, and the total extractives content was calculated.
2.3 Determination of Structural Carbohydrates and Lignin

The constituents the biomass samples, carbohydrates and lignin, must be measured as part of a comprehensive biomass analysis. Carbohydrates can be structural or non-structural. Structural carbohydrates are bound in the matrix of the biomass, while non-structural carbohydrates can be removed using extraction or washing steps.

Structural carbohydrates, cellulose and hemicellulose, and lignin were analyzed following the NREL method (Sluiter et al., 2012). Extractives-free biomass samples (0.25 g) were placed in test tubes and received the addition of 3.0 mL of 72% (m/m) sulfuric acid. The system was incubated in a water bath at 30 ± 2°C for one hour. Manual agitation was performed every 5 min. Stirring is essential to ensure even acid to particle contact and uniform hydrolysis. The mixture was diluted with 80.0 mL of ultrapure water, autoclaved for one hour at 121°C. After cooling the hydrolyzates near room temperature, filtered through a sintered glass crucible, with previously measured mass in an analytical balance, using a vacuum pump. The sample retained in the crucible was oven dried at 105 ± 2°C until a constant mass for the determination of the acid insoluble lignin fraction.

Acid soluble lignin was determined in the filtrate, as well as carbohydrates. To acid soluble lignin, a 1.0 mL aliquot was diluted with ultrapure water in 100.0 mL flasks, to bring the absorbance into the range of 0.7–1.0, and absorbance was determined by ultraviolet spectrophotometry at 240 nm. The acid soluble lignin content was calculated according to Equations (1) and (2):

\[
\% \text{Acid Soluble Lignin} = \frac{A \times V_{\text{filtrate}} \times D}{E \times M \times D}
\]

\[
D = \frac{V_{\text{sample}} + V_{\text{filtration solvent}}}{V_{\text{sample}}}
\]

Where \(A\) is the UV-Vis absorbance of the sample at appropriate wavelength, \(V_{\text{filtrate}}\) is the volume of the filtrate, \(D\) is the dilution factor, \(E\) is the absorption coefficient of the sample, \(m\) is the mass of the sample (mg), and \(p\) is the pathlength of the cuvette (cm).

The hydrolyzed liquor was utilized to determination carbohydrates, was transferred an approximately 20 mL aliquot of each liquor to a 50 mL Erlenmeyer flask, and neutralized with calcium carbonate to pH 5.5–6.0, then decant and filtered with 0.22 μm filter. This filtrate was used for the determination of sugars by high performance liquid chromatography (HPLC) on a Shimadzu LC-20A Prominence chromatograph equipped with Suplecogel K column and a refractive index detector. The mobile phase was 15 mM dibasic potassium phosphate, the flow rate was set at 0.5 mL/min, the oven temperature was set at 85 °C, and the injection volume was 10 μL. The sugar content was determined using calibration standards and Equation (3):

\[
\% \text{Sugar} = \left( \frac{C_{\text{HPLC}} \times F \times V_{\text{filtrate}}}{m} \right) \times 100
\]

where \(C_{\text{HPLC}}\) is the sugar concentration determined by HPLC (mg/mL), \(F\) is the conversion factor of 0.88 for C-5 sugars (xylose and arabinose) or the correction factor of 0.90 for C-6 sugars (glucose, galactose, and mannose), \(V_{\text{filtrate}}\) is the volume of filtrate, and \(m\) is mass of sample in milligrams free extractives.

2.4 Holocellulose, α-cellulose and hemicellulose, determination

The holocellulose is generally used to refer to carbohydrates totals present in a plant cell. The α-cellulose indicates undegraded, higher molecular mass cellulose content in pulp; the β-cellulose indicates a degraded cellulose, and the γ-cellulose consists mainly of hemicellulose (Ranby, 1952; Ziaie-Shirkolae et al., 2007). The main technique used in the determination of
holocellulose consists of the oxidation of lignin in an acidic medium, and for the determination of the α-cellulose content is the determination of the holocellulose fraction that is not dissolves in the solution of sodium hydroxide (Morais et al., 2010).

The experimental procedure was an adaptation by Morais et al. (2010), holocellulose were prepared by treatment of the biomass with sodium chlorite under acidic conditions, extractives-free sample (4.0 g) was added to a 1.0 L Erlenmeyer flask containing 110.0 mL of ultrapure water, and added 3.0 mL of concentrated glacial acetic acid, 22.0 mL of sodium acetate 20%, and 9.0 mL of sodium chlorite (40%). The system was heated at 75 ± 2 °C under constant stirring for 1 h, and Erlenmeyer flask capped with a vapor collection system. The reagents were added slowly until a white precipitate was formed. The precipitate was cold and filtered in a system containing sintered glass funnel connected in a kitasato flask and vacuum pump. The filter mass was previously measured in an analytical balance. The precipitate collected in the funnel washed with 500.0 mL of ultrapure water until the proximity of neutrality, after whit 10.0 mL of acetone, and another washing with ultrapure water. The funnel-holocellulose was oven dried at 105 ± 2 °C for 18 h, until constant mass, and determined the mass the holocellulose.

α-Cellulose and hemicellulose were determined in the powder obtained for analysis of holocellulose. The sample, 1.0 g, was placed in a mortar and added 15.0 mL of 17.5% (m/v) sodium hydroxide solution and allowed to rest for 2 min. Then, the sample was crushed for 8 min, received the addition 40.0 mL of ultrapure water, and transfer the content, quantitatively, to the sintered glass funnel (the mass was previously measured) and precipitate washed with ultrapure water until the proximity of neutrality. Posteriorly was oven dried at 105 ± 2 °C for 18 h until constant mass. Was determined the mass the resulting material, and the data were used to calculate the content of α-cellulose and hemicellulose.

2.5 Determination of Total Solids

Biomass can contain large and varying amounts of moisture, which can change quickly when exposed to air. Thus, the results of chemical analyses of biomass samples are typically reported on a dry mass basis. Total solids determination was carried out according to Sluiter et al. (2008b). Prior to the analysis, aluminum dishes were oven dried at 105 ± 2 °C for 4 h. Then, 0.5 g of sample was uniformly spread onto a dish and placed in an infrared moisture analyzer set at 105 ± 2 °C. The sample was analyzed until the change in mass was less than 0.05% per minute, defined as constant mass. Moisture content was calculated from the percentage of total solids according to Equation (4):

\[ \%\text{Moisture} = 100\% - \%\text{Total solids} \]  

(4)

2.6 Determination of Water Activity (aw)

The water activities (aw) indicates the intensity of the forces that join the water with other components and, consequently, a water available for the growth of microorganisms, so that they can carry out reactions and biochemical (Ordoñez et al., 2005). Water activity was determined in 0.5 g of sample using a water activity meter (AQUALAB). The ambient temperature was 28.7 °C.

2.7 Ash determination

The amount of inorganic material in biomass, structural or extractable, should be measured as part of the total composition. Structural ash is inorganic material that is bound in the physical structure of the biomass. Extractable ash is inorganic material that can be removed by washing or extracting the material. These can be the result of soil remaining in the biomass.
Thus, the ash content was determined according to Sluiter et al. (2008c). Ashing crucibles containing 2.0 g of sample were kept on a heating system until smoke was no longer produced. The crucibles were placed in a desiccator containing desiccant to cool. Were, then calcined in a muffle furnace at 575 ± 5°C for 24 h. After cooling, was determined mass the crucibles, and the ash content was calculated using Equation (5).

\[
\text{Ash} = \frac{\text{Sample mass before calcination} - \text{Sample mass after calcination}}{\text{Sample mass before calcination}} \times 100
\]  

(5)

Ash- The inorganic residue left after dry oxidation at 575°C.

2.8 Protein determination

Biomass used as a feedstock for conversion to fuels contain protein and other nitrogen containing materials. The Kjeldahl method is widely used to measured nitrogen content of the biomass sample and the protein content is estimated using an appropriate Nitrogen Factor (NF). Thus, protein content was determined according to Hames et al. (2008) by the Kjeldahl method. The method consists of three steps: digestion, distillation, and titration. In the first step, 1.0 g of homogenized sample, 1 g of catalyst, and 5 mL of concentrated sulfuric acid were added to Kjeldahl tubes. The tubes were placed in a block digester at ambient temperature (25 ± 2 °C). The temperature was increased by 50 °C every 20 min until it reached 400 ± 5 °C. The digestion end-point was defined when the solution became liquid and translucent, and the brownish smoke stopped being released. The tubes were allowed to cool at room temperature.

The distillation step started with the addition of 30 mL of distilled water to the digested samples. The contents of the tubes was homogenized, the pH was raised using sodium hydroxide solution (50% (m/v)), and flasks were placed in the Kjeldahl distillation equipment. An Erlenmeyer flasks containing 25 mL a of boric acid indicator solution (4% (m/v)) was placed at the other end of the distiller. The digested system was distilled until the distillate started to turn green.

The distillate was titrated with standard solution of hydrochloric acid (0.01 mol L⁻¹) to a until the color change. Protein content was calculated using Equations (6) and (7):

\[
\%\text{Nitrogen compounds} = \frac{F \times 0.0014 \times 100 \times \frac{V}{M}}{m}
\]  

(6)

\[
\%\text{Protein} = \%\text{Nitrogen compounds} \times \text{NF}
\]  

(7)

Where F is the correction factor for the standard solution of hydrochloric acid (0.01 mol L⁻¹), V is the volume of titrant that was necessary to reach the titration endpoint, M is the molarity of the titrant, NF is the conversion factor used to estimate protein content from measured nitrogen content, and m is the mass of the sample.

2.9 Crude fat determination

Crude fat was determined by Soxhlet extraction according to the AOAC method (1995). First, 2.5 g of sample was placed in a round-bottom flask containing 190 mL of petroleum ether. The system was exhaustively extracted for 6 h at 60 ± 2 °C. The solvent was evaporated and stored, and the sample was oven dried at 80 ± 2 °C for 8 h to ensure complete removal of residual solvent. The flask was allowed to cool to room temperature, in desiccator containing desiccant, and determined mass. The percentage of crude fat was calculated according to Equation (8):
3. Results and discussion

3.1 Particle size distribution

The particle size distribution of biomass grinds is shown in Figure 2. Note that rice straw bran and sugarcane bagasse exhibited a more uniform particle size distribution. Most of the rice straw bran sample was retained in no. 35 sieve; that is, the particles had a diameter of less than 420 µm. The sugarcane bagasse sample was mainly retained in no. 10 sieve (1.68 mm). Corn peel bran showed a non-uniform particle size distribution. About 42% of the sample was retained in no 35 sieve (420 µm).

![Figure 2 - Particle size distribution of sugarcane bagasse, rice straw bran and corn peel bran, respectively.](image)

Particle size directly affects the contact area between reagents and biomass, and can influence later processes, enzymatic saccharification and microbial fermentation, in the production of lignocellulosic ethanol.

3.2 Chemical Characteristics

Table 1 shows the chemical composition of the studied residues, extractives, cellulose, hemicellulose, lignin, and ashes. The removal of non-structural material from biomass is important to avoid interference in later analytical steps. The sugarcane bagasse and corn peel bran, greater extractive content, 18.70 and 12.82% respectively, when compared with the rice straw bran (12.82%), the results are in accordance with the characteristics of residues characterized and those obtained by other authors (Table 2).
Table 1 - Chemical characterization of biomass to produce second generation ethanol.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Extratives (%)</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
<th>Ashes (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice Straw Bran</td>
<td>5.82±2.73</td>
<td>38.33±0.96</td>
<td>19.73±0.96</td>
<td>19.01±0.83</td>
<td>7.99±0.17</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>36.40±1.83</td>
<td>31.09±2.99</td>
<td>28.61±2.99</td>
<td>12.30±1.34</td>
<td>2.70±0.06</td>
</tr>
<tr>
<td>Corn Peel Bran</td>
<td>12.82±0.06</td>
<td>55.75±2.40</td>
<td>12.93±2.40</td>
<td>9.84±0.22</td>
<td>3.47±0.17</td>
</tr>
</tbody>
</table>

Source: Authors.

Table 2 – Extratives compositions in % of biomass.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Extratives (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice husk</td>
<td>3.10</td>
<td>Morais et. al., 2010</td>
</tr>
<tr>
<td>Rice husk</td>
<td>4.08</td>
<td>Mourtzinis et. al., 2016</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>31.76</td>
<td>Narron et. al., 2017</td>
</tr>
<tr>
<td>Corn Straw</td>
<td>11.60</td>
<td>Ogeda and Petri, 2010</td>
</tr>
<tr>
<td>Corn cob</td>
<td>18.00</td>
<td>Ogeda and Petri, 2010</td>
</tr>
<tr>
<td>Corn Straw</td>
<td>17.22</td>
<td>Panaro et. al., 2015</td>
</tr>
</tbody>
</table>

Source: Authors.

The cellulose content (Table 1) of rice straw bran (38.33%) and sugarcane bagasse (27.09%) were similar to those reported in the literature (Table 3). Cellulose content in corn peel bran (55.75%), however, was higher than that found in other studies for corn straw and cob. No data on the cellulose content of corn peel bran were found in the literature, as this residue, obtained from starch production, is used principally as animal feed.

Table 3 – Cellulose, hemicellulose and lignin composition in % of biomass.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice straw</td>
<td>29.20 – 34.70</td>
<td>23.00 – 25.90</td>
<td>17.00 – 19.00</td>
<td>Prasara and Gheewala, 2017</td>
</tr>
<tr>
<td>Rice straw</td>
<td>44.00</td>
<td>20.10</td>
<td>19.00</td>
<td>Raele et. al., 2014</td>
</tr>
<tr>
<td>Rice straw</td>
<td>42.54</td>
<td>24.51</td>
<td>9.16</td>
<td>Rastogi and Shrivastava, 2017</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>38.80</td>
<td>29.40</td>
<td>21.70</td>
<td>Santos et. al., 2010</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>46.86</td>
<td>27.50</td>
<td>26.70</td>
<td>Sasaki et al., 2016</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>25.00 – 45.00</td>
<td>28.00 – 32.00</td>
<td>15.00 – 25.00</td>
<td>Prasara and Gheewala, 2017</td>
</tr>
<tr>
<td>Corn Straw</td>
<td>36.70</td>
<td>34.20</td>
<td>14.00</td>
<td>Morais et. al., 2010</td>
</tr>
<tr>
<td>Corn cob</td>
<td>35.40</td>
<td>26.90</td>
<td>18.00</td>
<td>Morais et. al., 2010</td>
</tr>
<tr>
<td>Corn Straw</td>
<td>41.18</td>
<td>16.31</td>
<td>14.14</td>
<td>Silva et. al., 2015</td>
</tr>
<tr>
<td>Corn Straw</td>
<td>47.22</td>
<td>22.15</td>
<td>12.77</td>
<td>Panaro et. al., 2015</td>
</tr>
</tbody>
</table>

Source: Authors.

A biomass with high cellulose content presents potential feedstock for bioethanol production, just as delignification is essential to increase the yield of enzymatic hydrolysis and alcoholic fermentation (Abraham et al., 2016; Cai et al., 2016; Silva...
et al., 2015). The results obtained suggest that biomass evaluated in the present study can be satisfactorily used as raw materials for the production of second-generation ethanol, because of their high cellulose and hemicellulose contents.

The biomass samples had a low concentration of ash, similar to that of other biomass samples reported in the literature (Table 4). A low ash content is desirable for biomass conversion to bioethanol and application in energy generation systems (Filho and Juliani, 2013).

Table 4 – Ashes composition in % of biomass.

<table>
<thead>
<tr>
<th>Ashes (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice husk</td>
<td>17</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>1.61</td>
</tr>
<tr>
<td>Corn Straw</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>0.64</td>
</tr>
</tbody>
</table>

Source: Authors.

The ashes lower content may be considered an advantage, because during the pretreatment the biomass containing salts solubilize in the hemicellulose and cellulose hydrolysates. This increase in the concentration of ions leads to an increase in the osmotic pressure in the medium, hindering the alcoholic fermentation (Silva et al., 2015).

3.3 Carbohydrate Composition

The carbohydrate composition of rice straw bran, sugarcane bagasse, and corn peel bran is presented in Table 5. The presence of glucose and xylose indicates that cellulose and hemicellulose were degraded during delignification (Islam et al., 2017; Lee et al., 2017).

Table 5 - Monosaccharide concentration resulting from hydrolysis.

<table>
<thead>
<tr>
<th></th>
<th>Rice Straw Bran (%)</th>
<th>Sugarcane bagasse (%)</th>
<th>Corn Peel Bran (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>40.69±1.60</td>
<td>43.35±4.00</td>
<td>51.58±1.60</td>
</tr>
<tr>
<td>Fructose</td>
<td>5.35±0.70</td>
<td>6.84±0.20</td>
<td>8.59±0.70</td>
</tr>
<tr>
<td>Xylose</td>
<td>4.94±0.10</td>
<td>6.84±0.20</td>
<td>8.59±0.70</td>
</tr>
<tr>
<td>Arabinose</td>
<td>3.35±0.00</td>
<td>-</td>
<td>4.43±0.30</td>
</tr>
<tr>
<td>Saccharose</td>
<td>-</td>
<td>1.45±0.10</td>
<td>-</td>
</tr>
<tr>
<td>Cellobiose</td>
<td>-</td>
<td>1.30±0.09</td>
<td>-</td>
</tr>
</tbody>
</table>

Source: Authors.

Table 6 shows that the carbohydrate composition of the studied residues was similar to that of other samples reported in the literature. Some monosaccharides, mostly pentoses, are more difficult to ferment to fuel ethanol than hexoses such as glucose (Vassilev et al., 2010). The physicochemical characterization of these residues suggests that they can be submitted to enzymatic or chemical hydrolysis for the release of sugars and subsequent fermentation for biofuel production.
### Table 6 - Carbohydrate Composition in % of monosaccharides.

<table>
<thead>
<tr>
<th>Carbohydrate</th>
<th>Glucose</th>
<th>Xylose</th>
<th>Arabinose</th>
<th>Cellobiose</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice straw</td>
<td>32.83</td>
<td>12.50</td>
<td>7.35</td>
<td>-</td>
<td>Sudha et al., 2015</td>
</tr>
<tr>
<td></td>
<td>34.20</td>
<td>19.30</td>
<td>2.00</td>
<td>-</td>
<td>Szczersowski et al., 2014</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>36.74</td>
<td>20.30</td>
<td>1.80</td>
<td>-</td>
<td>Vieira et al., 2013</td>
</tr>
<tr>
<td></td>
<td>42.30</td>
<td>20.90</td>
<td>-</td>
<td>-</td>
<td>Zambom et al., 2008</td>
</tr>
<tr>
<td>Corn free of extractives</td>
<td>42.60</td>
<td>25.80</td>
<td>13.70</td>
<td>-</td>
<td>Zheng et al., 2017</td>
</tr>
<tr>
<td>Corn</td>
<td>45.40</td>
<td>22.70</td>
<td>2.30</td>
<td>-</td>
<td>Zheng et al., 2017</td>
</tr>
<tr>
<td>Corn cob</td>
<td>37.90</td>
<td>29.00</td>
<td>2.80</td>
<td>-</td>
<td>Zheng et al., 2017</td>
</tr>
</tbody>
</table>

Source: Authors.

### 3.4 Total Solids, Moisture Content, and Water Activity

The total solids, moisture content, and water activity of the biomass samples are presented in Table 7. These parameters are directly associated with microbial development (Romão, 2015) and can indicate the chemical, physical, and microbial stability of the biomass (Cavalcante et al., 2018). Different microorganisms require different values of $a_w$ (which ranges from 0 to 1) for growth. Fungi can grow at an $a_w$ of 0.70, yeasts at 0.80, and bacteria at 0.90. Microbial development is unlikely at $a_w$ values of 0.20–0.50 (Morais et al., 2010).

<table>
<thead>
<tr>
<th>Biomass Type</th>
<th>Total Solids (%)</th>
<th>Moisture (%)</th>
<th>$a_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice Straw Bran</td>
<td>93.08±2.15</td>
<td>6.92±2.15</td>
<td>0.391±0.05</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>57.29±3.88</td>
<td>42.71±3.88</td>
<td>0.822±0.03</td>
</tr>
<tr>
<td>Corn Peel Bran</td>
<td>90.91±1.43</td>
<td>9.09±1.43</td>
<td>0.437±0.03</td>
</tr>
</tbody>
</table>

Source: Authors.

The residue composition and the pre-treatment used can influence the moisture content of a biomass. Vieira et al. (2013) reported that the moisture content of rice husks was 7.9–10% and of corn cob was 16.93%. Sugarcane bagasse has a moisture content of around 50% (Manochio et al., 2017). In this study, the moisture contents of the samples were lower than those presented in the literature. These results do study indicate important information about properties, storage and handling criteria for biomass.

### 3.5 Crude Fat and Protein Contents

Crude fat and protein contents are presented in Table 8. The results of this study were similar to those reported by other authors. Moongngarm et al. (2012) found a crude fat content of 17.59% in rice bran. A crude fat content of 15.3% was observed in brown rice straw bran in a study by Chaud et al. (2009). Carvalho et al. (2006) characterized sugarcane bagasse and found a crude fat content of 0.07%. Zambom et al. (2008) reported that ground corn had a crude fat content of 3.59%.
Table 8 - Composition of Fat and Protein in biomass.

<table>
<thead>
<tr>
<th></th>
<th>Fat (%)</th>
<th>Protein (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice Straw Bran</td>
<td>17.45±3.43</td>
<td>0.68±0.04</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>0.59±0.14</td>
<td>-</td>
</tr>
<tr>
<td>Corn Peel Bran</td>
<td>3.32±0.13</td>
<td>7.31±0.03</td>
</tr>
</tbody>
</table>

Source: Authors.

The protein content of sugarcane bagasse was also similar to that reported in other studies. Carvalho et al. (2006) observed a protein content of 2.32% in sugarcane bagasse. Zambom et al. (2008) studied the composition of ground corn and observed a crude protein content of 8.38%, similar to that of corn peel bran in the present study. Kunrath et al. (2010) found a protein content of 15.5% in rice straw bran, similar to our results. However, Chaud et al. (2009) reported a protein content of 1.54% in rice straw bran. This difference can be due to the type of rice evaluated, the climatic and soil conditions in which the rice was grown, and the time of harvest.

4. Conclusions

The physicochemical characteristics of agro-industrial residues can determine their suitability for application in value adding processes. Provides important information such as biomass properties, theoretical yields and issues related to large scale industrial operations. The results of this study suggest that rice straw bran, sugarcane bagasse, and corn peel bran are potential feedstocks for the production of second-generation ethanol, because of their high cellulose and hemicellulose levels and a significant amount of monosaccharides, mainly glucose and xylose, released after hydrolysis. Brazil’s large agro-industrial sector can benefit greatly from using these residues for bioethanol production, in the management of waste, enabling applications and valuing agro-industrial by-products.

In future studies and research, it is suggested to use agroindustry biomasses characterized in the production of enzymes and as a substrate for cellulosic ethanol production.

Acknowledgements

This study was supported by the Minas Gerais State Research Foundation, Brazil (FAPEMIG), under project code FAPEMIG (TEC-APQ-02489-16 e TEC-APQ-02079-16). The authors are also gratefully to the Cane Technology Centre (CTC), Brazil, and cereal and food processing industries, Brazil.

References


