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Mass balance and water demand in the alkaline pretreatment process of the main brewing residuel

Balanço de massa e demanda hídrica no processo de pré-tratamento alcalino do principal resíduo cervejeiro

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ABSTRACT

Alkaline pretreatment is one of the most effective processes in lignin removal for different types of lignocellulosic materials. However, the generation of a large amount of black liquor with a high excess of hydroxyl ions (OH-), in addition to the wastewater generated in the biomass washing steps, are some of the main problems with using this type of pretreatment. This work aims to show, through a case study, the water consumption required to carry out this type of pretreatment. Brewer's spent grain (BSG) was used as lignocellulosic material to carry out alkaline pretreatment with 4% NaOH and to quantify the water used in the process. A global mass balance during the BSG delignification process allowed identifying a global recovery percentage of 87.92% of cellulose, 84.56% of hemicellulose and 87.63% of lignin of the total material fed into the delignification process. For quantifying the main components present in the studied BSG, it was necessary to characterize the washing water of the solids obtained in the pretreatment. At the end of the process, approximately 0.50 g of cellulose, 0.71 g of hemicellulose and 0.97 g of lignin were lost in relation to the grams fed, initially in the delignification process. The water demand during the process was 131.2 mL per g of dry material.

Keywords:

Lignocellulosic material, characterization, black liquor, Biotechnological processes, Brewers' spent grain.

RESUMO

O pré-tratamento alcalino é um dos processos mais eficazes na remoção de lignina para diferentes tipos de materiais lignocelulósicos. Porém, a geração de grande quantidade de licor negro com elevado excesso de íons hidroxila (OH-), além dos efluentes gerados nas etapas de lavagem da biomassa, são alguns dos principais problemas da utilização desse tipo de pré-tratamento. Este trabalho tem como objetivo mostrar, através de um estudo de caso, o consumo de água necessário para a realização deste tipo de pré-tratamento. O resíduo de cerveja foi utilizado como material lignocelulósico para realizar o pré-tratamento alcalino com NaOH 4% e quantificar a água utilizada no processo. Um balanço de massa global durante o processo de deslignificação BSG permitiu identificar um percentual de recuperação global de 87,92% de celulose, 84,56% de hemicelulose e 87,63% de lignina do material total alimentado no processo de deslignificação. Para quantificar os principais componentes presentes no resíduo estudado, foi necessário caracterizar a água de lavagem dos sólidos obtidos no pré-tratamento. Ao final do processo, foram perdidos aproximadamente 0,50 g de celulose, 0,71 g de hemicelulose e 0,97 g de lignina em relação aos gramas alimentados, inicialmente no processo de deslignificação. A demanda de água durante o processo foi de 131,2 mL por g de material seco.

Palavras-chave:

Material lignocelulósico, caracterização, licor negro, processos biotecnológicos, bagaço de malte.

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1 INTRODUCTION

The growing concern about the scarcity of oil reserves, including the need to preserve the environment, are the main factors leading to the search for alternative renewable sources for the production of sustainable (Souza; Silvestre, 2022). Accordingly, the concept of the biorefinery which is based on traditional oil refineries, in which a single raw material can generate numerous products minimizing waste turns out to be an interesting alternative. Because, similarly, biorefineries can use biomasses of vegetable origin in order to produce compounds of high added value for the cosmetic, pharmaceutical, food, animal feed and even health (Vernès *et al*., 2019). In this context, in recent years, a considerable amount of bioenergetic research has been directed to the characterization of biomass, to pretreatment, to thermochemical and biochemical conversion, and to the revaluation of biofuels. This is because the production of second-generation biofuels (2G) from abundant lignocellulosic biomass can provide sustainable energy without compromising food security (Gnansounou *et al*., 2015; Nanda *et al*., 2015).

One of the main biomasses generated by the brewing industry is brewer's spent grain (BSG), generally intended for the use of animal feed. This application does not consume all the residue, just as it is not profitable for this industry (Lynch *et al.*, 2016). The BSG is the most abundant brewing by-product, corresponding to around 85% of total by-products generated, and it may consist of the residues from malted barley, or those from malted barley and adjuncts (nonmalt sources of fermentable sugars), such as wheat, rice, or maize added during mashing (Reinold, 1997).

The chemical composition of BSG varies according to barley variety, harvest time, malting and mashing conditions, and the quality and type of adjuncts added in the brewing process (Santos *et al*.,2003), BSG is considered as a lignocellulosic material rich in protein and fiber, that is primarily composed of cellulose (17–25%), hemicelluloses (25–35%), protein (15–24%), lignin (8–28%), and lower amounts of lipids (10%). (Gupta *et al*., 2010; Robertson *et al*., 2010; Aliyu; Bala, 2011).

In this way, this biomass could be used to produce glucose, giving rise to production in the biorefinery scheme (conversion of biomass into a wide range of biomaterials, bioproducts, and/or bioenergy, such as second-generation ethanol and/or other value-added products) (Ortiz and Oliveira, 2016). Even more, when the production of beer by in 2016 showed Brazil as the world's third-largest beer producer with 13.3 billion liters, exceeded only by the United States of America with 22.1 billion and China with 41.4 billion (Godoi *et al*., 2019), and with an estimated production of around 30 million tons of BSG in 2012 (Niemi *et al*., 2012).

In order for the release of glucose to occur, it is necessary to break down the polymers constituting the biomass through a pretreatment process, separating the cellulose from the lignin, which interferes with the enzymatic hydrolysis process of the cellulose into glucose (Karagöz *et al*., 2012). The pretreatment objectives are basically, to remove lignin and hemicellulose; reduce cellulose crystallinity and increase material porosity (Sun; Cheng, 2002).

The alkaline pretreatment digests lignin and makes holocellulose accessible for hydrolysis. Generally, sodium, potassium, calcium and ammonium hydroxides are used in this process (Rao *et al*., 2016). Studies by Yang *et al*., (2016), confirm that the NaOH solution was efficient in dissolving lignin, causing the lignocellulosic biomass to swell, leading to an increase in the internal surface area under relatively mild conditions, thus improving the hydrolysis enzyme of lignocellulosic biomass. A fundamental step in the production of bioproducts or biofuels from lignocellulosic materials is cellulose hydrolysis.

The hydrolysis of pretreated lignocellulosic residues can be carried out by the action of different acids or cellulolytic enzymes. In acid hydrolysis, which can be carried out with either concentrated or diluted acid, the material is hydrolyzed by the action of acids, under certain conditions of temperature and pressure, and solid-liquid ratio.

The enzymatic hydrolysis of lignocellulosic materials, on the other hand, is a process known and studied for presenting specificity of the reaction, absence of secondary reactions, absence of formation of secondary products, and reaction in mild conditions that they do not require high pressures and temperatures or corrosive environments for the equipment (Sun *et al*., 2016; Pratto *et al*., 2020;).

This hydrolyzate could later be fermented by yeasts to obtain bioethanol or biobuthanol (Lechon et al., 2005; Luo et al., 2020). Therefore, this work aimed to collect mass balance data from the alkaline pretreatment of BSG, as well as to quantify the consumption of water and energy in this process in order to obtain glucose for the production of bioproduct.

2 MATERIALS AND METHODS

2.1 Raw material

The brewer's spent grain used in the experiments was yielded by brewery located in Aparecida de Goiânia, State of Goiás (Brazil) (see Table 1).

2.2 Alkaline pretreatment

For the delignification process, 30 g of dry BSG were weighed and added to a solution of 4% sodium hydroxide (obtained of Neon), in a proportion of 1:10 (mass/volume) and added to an autoclavable glass bottle. The material was homogenized and placed in an Stermax autoclave of 30 liters and 1500 w at 121ºC for 30 minutes. After the end of the pretreatment, the material was filtered in a vacuum filtration system with the Ionlab vacuum pump model VAC 29 of 1/2 HP and qualitative filter paper. The black liquor obtained after filtration was measured in terms of weight and volume. The solid fraction was washed with water to neutral pH, as many of the cellulolytic enzymes present optimal conditions for hydrolysis at acidic pH. The raw pulp of the BSG was dried at room temperature (see Figure 1).

2.3 Chemical characterization of solid material

The determination of structural carbohydrates, lignin, ash, and extracts was carried out according to the rules of the National Renewable Energy Laboratory (obtained of Halogenn) (Sluiter *et al*., 2008; Gouveia *et al*., 2009). Dry BSG (0.3 g) and 3 mL of 72% sulfuric acid were placed in pressure tubes and placed in a water bath at 30 ° C for 60 minutes, being constantly homogenized. After that period, 84 mL of ultrapure water was added to the tubes and conducted to the Stermax autoclave at 121 ° C and 1 atm for 60 minutes. The hydrolyzed samples were filtered in Gooch crucibles previously dried in an oven at 105 ° C for 24 hours. The hydrolyzed liquid was used for High-Performance Liquid Chromatography (HPLC) analysis to determine carbohydrates; and spectrophotometer for the determination of soluble lignin. The quantification was carried out in the Agilent HPLC (model 1260 Infinity) equipped with a quaternary pump, degasser, autosampler and oven, with Bio-Rad Aminex HPX-87H column (300 x 7.8 mm, 9 µm particle size. (see Figure 1).

2.4 Determination of ash and insoluble lignin

Gooch's crucibles (item 2.3) containing the filtrate were placed in a muffle previously programmed to determine lignin. Equations 1 and 2 were used to calculate the ash content and the percentage of insoluble lignin.

$$\%\,Ash\ content = \frac{M_{c2} - M_{c3}}{Mc2 - Mc1} x100 \qquad eq.(1)$$

$$\%\,Insoluble\ lignin = \frac{(Mc2 - Mc1) - (Mc3 - Mc1)}{MS} x100 \qquad eq.(2)$$

Where Mc1 is empty crucible mass (g); Mc2 is kiln-dried sample mass together with the crucible (g); Mc3 is a sample after passing through the muffle together with the crucible (g); MS is dry mass of the initial sample (g).

2.5 Determination of soluble lignin

The collected hydrolyzed liquids (item 2.3) were analyzed using a visible UV spectrophotometer and the absorbances were read at a wavelength of 240 nm. Equation 3 was used to determine the concentration of soluble lignin in the hydrolyzate:

$$\%\,Soluble\ lignin = \frac{UVabs\ x\ Volume_{filtered}\ x\ Dilution}{\varepsilon\ x\ Dry\ mass}\ x\ 100 \qquad eq.(3)$$

Where UVabs is average absorption of UV-Visible for the sample at wavelength 240 nm; Volume filtrate is equivalent to 87 mL (3 mL of 72% sulfuric acid + 84 mL of ultrapure water); ε is the biomass absorptivity at a specific wavelength.

2.6 Determination of carbohydrates, organic acids and inhibitors

The aliquots were used to determine the structural carbohydrates and organic acids, initially the samples were centrifuged at 14000 rpm for 10 minutes in the Kasvi K14-4005 centrifuge order to separate the residual solid particles from the filtration. 0.7 mL samples were analyzed on HPLC under the following conditions: Aminex HPX.87 H column with pre-column, RID detector, 0.01 ml injection volume, 0.6 mL/minute mobile phase, column temperature and detector 45 ° C and run time 60 minutes.

2.7 Determination of extractives

The method used to determine the extracts present in the BSG was based on the NREL nº10 "Determination of Extractives in Biomass" (Sluiter *et al*. 2008). Samples of 10 g of BSG previously ground and dried in extraction cartridges were placed to be extracted in a Soxhlet extractor using 200 mL of 99% ethyl alcohol together with 200 mL of distilled water. The extraction ends when the solvent around the extraction cartridge becomes colorless. The cartridges were dried in an oven at 105 ° C until constant mass. The quantification of extractables content is described in Equation 4.

$$\%\,Extractives = \frac{M_b - M_f}{M_b} \times 100 \qquad eq.(4)$$

Where *Mb* is dry BSG mass (g); *Mf* is BSG mass free of extracts (g).

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2.8 Determination of proteins

An Elementary Analyzer CHN Perkin Elmer 2400 Serie II was used for the determination of carbon, hydrogen, nitrogen, sulfur and oxygen content in organic compounds and their presence in any inorganic compound. The pretreated biomass was ground and sieved and the particles of size 80 mesh were used in the determination of proteins. For operation in CHN mode, Acetanilide (BDH - organic analytical standard) was used as a standard for calibration. The values were obtained in the percentage of nitrogen in the sample. The percentage of proteins is calculated, according to Equation 5.

$$\%\, Proteins = \frac{\frac{\%\, Nitrogênio\ \times\ M_a}{100} \times 6.25}{M_a} \times\ 100 \qquad eq.(5)$$

Where Ma is the mass of the inserted sample (g).

2.9 Chemical characterization of black liquor

The xylose monomers and glucose oligomers present in the liquor collected after pretreatment were identified by the HPLC method. The black liquor was subjected to pH correction for a range between 2 and 5 (ideal range for acid characterization of this material). In 5 mL of liquor, 0.174 mL of 72% sulfuric acid were added and autoclaved at 1 atm and 121 ° C in pressure tubes for 1 hour. The contents were centrifuged for 5 minutes at 14,000 rpm. The collected supernatant was dried in an oven at 105 ° C overnight until constant weight values were obtained at the time they were weighed. For calculating the percentage of cellulose and hemicellulose present in the liquor, the amount of recovered biomass (rb) was considered, discounting the masses of sodium hydroxide and sulfuric acid used to correct the pH, according to Equation 6.

$$Recovered\ Biomass = MTlicor - Mh - Mac \qquad eq.(6)$$

Where *MTlicor* is the total mass of liquor (g); *Mh* is the mass of sodium hydroxide (g); *Mac* is a mass of sulfuric acid used to correct pH (g). With the determination of the sugars in HPLC, it was possible to obtain the composition of the macromolecules according to the respective conversion factors, from Equation 7.

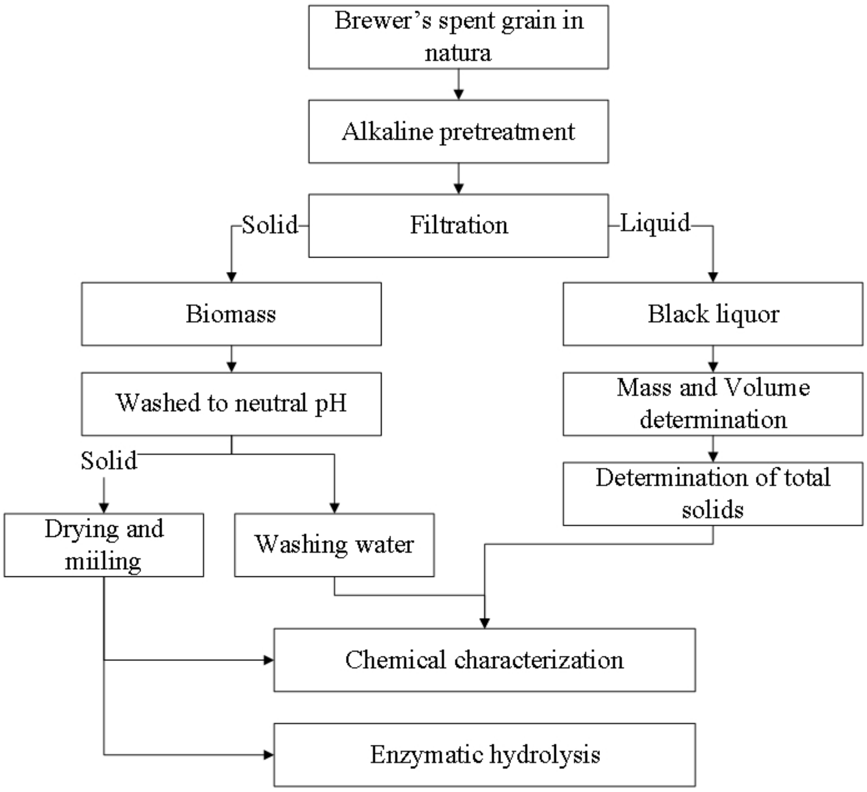
$$\%Macromolecul = \sum \frac{\left(\frac{o.oo5174\ x(Cm\ x\ f)x\ VT}{5}\, x\, \frac{Vr}{VL}\right)}{rb\ x\ 100} \qquad eq.(7)$$

Where *Cm* is sugar concentration (glucose, xylose, etc.) (g/L); f is a factor for converting sugar into cellulose or hemicellulose; *VT* is the total volume used in pH correction (volume of liquor + volume of acid) (mL); *Vr* is the total volume recovered in the filtration of the pretreated cake (mL); *VL* is the volume of liquor used to correct pH (mL); *rb* is recovered biomass (g).

3 RESULTS AND DISCUSSION

In order to obtain a material with a higher cellulose content, the Brewer's spent grain *in natura* was subjected to an alkaline pretreatment process. A sample of the BSG processing and when the material characterizations were performed is shown in Figure 1. In addition, the chemical compositions of *in natura* and pretreated BSG obtained after characterization processes are shown in Table 1.

Figure 1. Summary of brewer's spent grain characterization



Source: authors (2023)

Table 1. Chemical composition of Brewer's spent grain (BSG) *in natura* and pretreated.

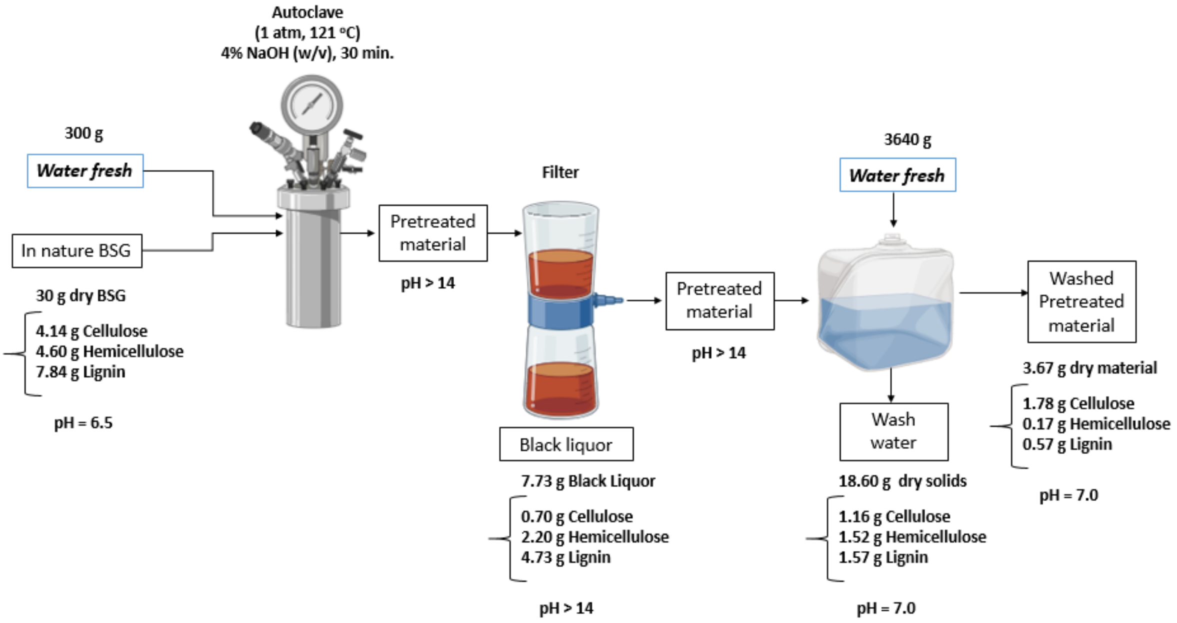
Component	Material (% dry base)		Material (g dry base)	
	In natura	Pretreated	In natura	Pretreated
Cellulose	13.79 ± 0.43	48.40 ± 1.92	4.14 ±0.14	1.78 ± 0.32
Hemicellulose	15.32 ± 0.57	4.74 ± 0.30	4.60 ±0.19	0.17 ± 0.04
Lignin	26.11 ± 1.20	15.58 ± 0.63	7.83 ±0.39	0.57 ± 0.10
Proteins	20.24 ± 1.43	3.95 ± 0.13	6.07 ±1.20	ND
Extractives	20.88 ± 0.67	ND	6.26 ±0.84	ND
Ash	2.05 ± 0.21	0.11 ± 0.08	0.62 ±0.15	ND
Total	83.47 ± 5.92	72.78 ± 3.06	25.04 ±2.91	3.67 ± 0.52

ND: Not determined.

Source: authors (2023)

In order to identify the flow of the main constituents of biomass (cellulose, hemicellulose, and lignin) during the processing stages, a mass balance was carried out in each of the stages involved. The alkaline pretreatment process showed a 8.4% yield, this means that, of the 30 g of raw material dry that entered the autoclave (Figure 2), and after going through all the stages of the pretreatment, the characterization of the solid and liquid fractions of the global process (cake and black liquor, respectively), including washing water, allowed the quantification of 2.52 g of solid material at the end of the process, the rest of the material was solubilized, a part of the material was identified in the washing water, while another in the black liquor. The masses of the respective components at each stage of the process, as well as the volumes of freshwater used and the pH of the filtrates are given in Figure 2.

Figure 2. Flow chart of the separation processes for the main components of Brewer's spent grain.



Not identified

Source: authors (2023)

From the overall balance presented in Figure 2, it is possible to observe that 1.78 g of the cellulose present in the raw material were maintained in the pre-treated material, while 2.36 g of the initial cellulose were solubilized during the alkaline pretreatment. From the solubilized material it was possible to identify 97.88% of the cellulose found in the black liquor, washing water and in the washed pre-treated material. Likewise, the global quantification of the process allowed us to identify that the identification percentage of cellulose in relation to the raw bagasse fed is 87.92%, thus resulting in a loss in the total quantification of the material during the process of 12%.

In the case of lignin, the delignification process led to the removal of 92.73% of the lignin fraction present in the fresh material fed to the process. In fact, delignification allowed an increase in the g cellulose/g lignin ratio, which grew approximately 5.9 times after the process, going from an initial value of 0.52 g cellulose/g lignin to 3.12. g of cellulose / g of lignin at the end of the process, these results reaffirm the data obtained in the research carried out by YANG, et al., (2016), in which they show that the use of a NaOH solution is efficient in removing the lignin, thus leaving the purest cellulose for subsequent enzymatic hydrolysis.

Regarding the inputs used during the process, such as the demand for water and sodium hydroxide, the quantities needed for the delignification process showed that for each gram of cellulose processed, approximately 2.9 g of NaOH and 951.2 g of water must be spent, the latter being the most alarming, as there is a worldwide concern with water consumption that keeps growing, according to a publication of the British newspaper, The Guardian, humans use about 4,600 km3 of water per year, 70% of which goes to agriculture, 20% to industry and 10% to families. Emphasizing that the global demand has increased six times in the last 100 years and continues to grow at a rate of 1% per year (The Guardian, 2018).

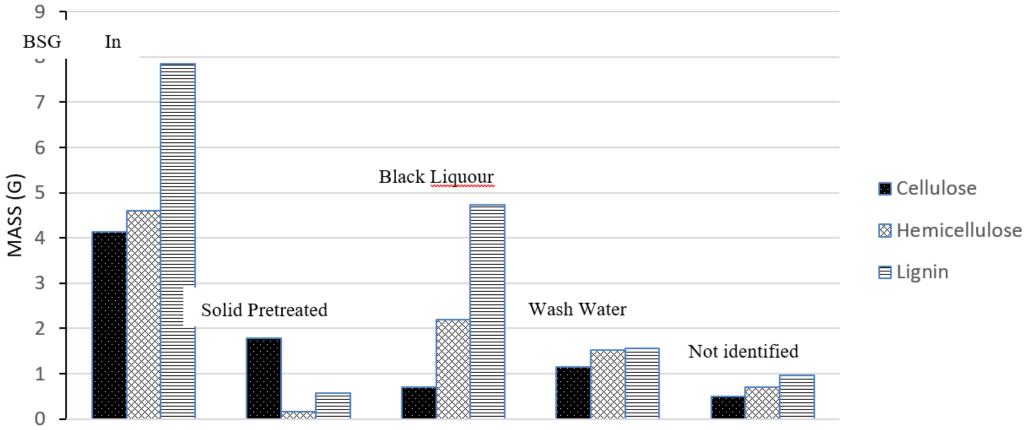
Therefore, for industrial use of this process, it will be necessary to reduce the consumption of this substance, opting for its reuse, through treatment in different stages of the process, not only to reduce its use but also to recover NaOH and of the cellulose and hemicellulose fractions still present in these process waters, the latter fraction being mainly found in black liquor and washing water.

In the case of hemicellulose, at the end of the process, it was possible to identify 0.17 g still present in the solid material after delignification, while 3.72 g were solubilized in black liquor and washing water, in this case the percentage of identification of this fraction was a little larger when compared to cellulose, totaling 96.30% of the initial mass. It was also possible to verify that the amount of hemicellulose solubilized during the delignification process was greater when compared to cellulose. This type of behavior occurs because this group of biopolymers ends up being insoluble in water and soluble in alkaline solutions (Silva *et al*., 1998; Garcia *et al*., 2000; Oliveira *et al*., 2010).

The other component analyzed in the mass balance per component is lignin, in this case 0.57 g of material still present in the pre-treated material was quantified, with the remainder of the lignin being solubilized during the delignification process, with a solubilization percentage of 60.33% in black liquor and 20.02% in washing water. To determine the percentage of total solubilization, which was 80.36%, it was necessary to recover and quantify the wash water to identify total lignin, as well as cellulose and hemicellulose. In general terms, the removal of lignin and hemicellulose by this type of pretreatment was highly efficient with percentages greater than 90% for the components, these results are expected, as this type of pretreatment not only breaks the bonds between lignin and carbohydrates , but also the structure of lignin; due to the increase in the internal surface, due to swelling and the decrease in the degree of polymerization and crystallinity, this effect depends on the lignin content of the materials and the operational conditions of the process, such as temperature (Chang *et al*.,1998;; Carvalheiro *et al*., 2008;; Sánchez; Cardona, 2008; Kumar *et al*., 2009; Galbe; Zacchi, 2012).

However, the possible loss of cellulose and therefore fermentable sugars and the production of inhibitory compounds must be taken into account to optimize pretreatment conditions (Alvira *et al*., 2010), since in strong alkaline concentrations dissolution, peeling of groups terminals, alkaline hydrolysis and degradation and decomposition of dissolved polysaccharides can occur (Hendriks; Zeeman, 2009). Finally, the lack of closure of the mass balance can be attributed to the degradation of sugars during pretreatment, the removal of volatile sugar degradation products during the evaporation process and also to physical losses that occur during washing of the pretreatment material obtained during alkaline pretreatment. For a better analysis of the 3 main components present in the BSG, Figure 3 presents each one separately and its distribution between the solid and liquid phases after the alkaline pretreatment process.

Figure 3. Recovery of the main components in the pretreatment solid and liquid fractions based on the content of the raw material (black bars), solid fractions (dotted bars) and liquid fractions (striped bars).



Source: authors (2023)

In Figure 3 it is possible to observe how the cellulosic fraction is mainly retained in the solid material, which favors the process, but there is still a great loss of this component in the washing water, with about 35.51% of cellulose when compared to the raw material fed to the process, so a more efficient and low-cost additional process is necessary to allow the recovery of that part of cellulose lost in the liquid fraction. However, for the hemicellulose and lignin fractions, these components are preferably in the liquid fraction with a percentage of 90.56% for lignin and 67.61% for hemicellulose distributed between the washing water and the black liquor.

Finally, an approach in the context of biorefinery can enable the use of lignocellulosic residues, through alkaline pretreatments, since the biorefinery uses different areas, such as bioengineering, polymer chemistry, food science, and agriculture, for the bioconversion of biomass in bioproducts such as biofuel, cosmetics, food and health industry products, among others (Kaparaju, 2009; Zhang *et al*., 2011; Dávila *et al*., 2019; Gomes *et al*., 2021).

4 FINAL CONSIDERATIONS

Despite the low concentration of cellulose (about 14%) present in the BSG used in this study, this by-product turns out to be attractive for the production of biofuels and bio-products with higher added value, due to the presence of not only cellulose but also of the hemicellulose and lignin, components that turn out to be important in the production of biomolecules. In addition, BSG is produced in large quantities and in breweries around the world, making it an abundant and easily accessible raw material for different economies.

The use of alkaline pretreatment using NaOH for the delignification of the material proved to be an effective process for the separation of the main components of BSG, increasing the final concentration of cellulose to 48% and reducing the concentration of lignin from 26% to 15%. However, the high consumption of sodium hydroxide in this type of pretreatment turns out to be the main challenge, being important to search for a method for its reuse or recovery, an alternative for this would be the integration with other equipment and processes in the biorefinery context, which would not only allow its recovery, but also the use of hemicellulose and lignin fractions for the production of chemical inputs, materials, food, feed, among others.

Finally, the mass balances show that there are losses of material in the process, due to the degradation of carbohydrates, removal of volatile by-products during evaporation in the delignification and washing of the obtained solid fractions, losses that must be considered when performing an increase of scale. Thus, increasing the recovery of the material while minimizing its losses it is essential to make the pretreatment stage feasible for these important changes, such as changes in the evaporators. And recycling in the washing process must be considered.

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