Advanced Energy Conversion Materials
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UNIVERSAL WISER PUBLISHER

Research Article

Organoenergetic Investigation on the Potential of Industrial Brewers' Spent Grain Valorization for Biogas Production

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Received: 7 June 2024; **Revised:** 30 August 2024; **Accepted:** 2 September 2024

Abstract: Cameroon is a high country producer and consumer of beer in Africa which has various breweries generating a large amount of brewer spent grain (BSG) yearly. This study was designed to investigate the potential use of spent grains derived from the Cameroonian brewing industry as a viable and sustainable energy source for biogas production. A comprehensive proximate analysis was performed, focusing on key physicochemical parameters including moisture content, acidity level, ash content, and the proportions of proteins, carbohydrates, and fats, thereby enabling the derivation of their energy value to determine the organoenergetic profile. Physicochemical characterization of the spent grains revealed a pH of 5.6, moisture content of 8%, and ash content of 9.8% at 450 °C for 2 h using a muffle furnace. The organic composition included a high iron content of 194.2 mg/100 g, an organic matter content of 99%, a total organic carbon (TOC) content of 57.39%, a total nitrogen content of 3%, and a nitrogen-carbon ratio of 19.13%. In addition, the spent grains exhibited substantial concentrations of total protein (18.75%), crude fiber (3.6%), lipids (8.7%), and carbohydrates (51.15%), with an energy value of 14.97 MJ/kg. Moreover, the chemical oxygen demand (COD) was determined to be 3,880 mg/kg, while the lower calorific value (LCV) was 19.76 MJ/kg, resulting in a COD/TOC ratio of 86.03. These findings showed that the spent grain from Cameroonian brewery has a significant organ energetic potential based on its components and physicochemical properties, thereby highlighting their suitability as a valuable resource for biogas generation.

***Keywords*:** brewing waste valorization, proximate analysis, organoenergy

Nomenclature

AC	Ash content (%)
BSG	Brewer spent grain
C/N	Carbon-to-nitrogen ratio
COD/TOC	Chemical oxygen demand on total organic carbon
LCV	Lower calorific value (MJ/kg)

DOI: https://doi.org/10.37256/aecm.5220245114

TN	Total nitrogen (%)
E	Energy MJ/kg
DM	Dry matter (%)
OM	Organic matter (%)
KSCN	Potassium thiocyanate
BSG	Brewer spent grain
CH_4	methane (%)
VFAs	Volatile fatty acids
AFS	Ammonium Ferrous Sulphate
V_t	Volume of SFA required for distilled water to draw
V_e	Volume of SFA required for sample printing
TS	Test socket

1. Introduction

The current policy of countries in the world and Cameroon in particular tends to limit the pollution of energy sources. The constraints of introducing circular economy concepts into industrial production encourage research into recoverable raw materials. Biogas, and therefore the principles of production dating back to the mid-nineteenth century, has been returning to the world stage as a source of renewable energy of natural origin for approximately fifteen years [1]. In these times of searching for alternative energy sources to fossil resources, the integration of biogas into the energy landscape affects political, economic, and environmental aspects. From a strategic point of view, the recovery of organic residues from brewing industries is part of the requirements of the circular economy in connection with sustainable development. In addition, industrialization and increased consumption are putting increasing pressure on natural resource reserves. This pressure leads to resource scarcity due to the abusive exploitation of resources. This pressure can be reduced by redirecting residual materials for energy production [2].

Brewing producers are also among those companies that generate organic waste. The production of beer requires more or less starchy raw materials such as maize, malt, cassava, and wheat. This beer production in breweries generates by-products and organic residual matter including spent grains, representing approximately 85% of the total secondary products [3, 4]. The latter results from the extraction of fermentable sugars while heating a mixture of crushed malted grains and water during a step called stuffing. This allows the activation of enzymes contained in malted grains and the conversion of starch into fermentable sugars [5]. The mixture is then filtered to remove the grains, i.e. the remaining solid, insoluble matter from the grains, including proteins and lipids [6, 7]. The sweet filtered liquid obtained is a must. It is mixed with yeast to convert sugars into alcohol and produce beer. The spent grains removed from the process are a residual material of high humidity for which management solutions must be chosen.

The most frequent use of these grains is as feed for livestock, particularly for feeding pigs. However, little attention has been given to these residual organic materials to obtain products with high added value. Given the fact that Cameroon is one of the largest producers and consumers of beer in Africa ahead of Ethiopia, these grains become an interesting raw material to study, given their availability at low prices. To this end, the reflection is oriented toward the best solution allowing the recovery of this waste.

In the case of the reclamation of the latter, different authors have proposed different uses for these residual materials. For example, it is used as an animal feed, additive in the production of building blocks, bioethanol production, enzyme production, lactic acid, xylitol, and biorefinery options, among others [3, 8, 9]. The determination and analysis of the physicochemical composition of brewer's grains, which have potential for human consumption, were evaluated. The humidity was determined by oven drying at 105 °C for 24 h. The calcination of the samples at 550 °C allowed the production of ash. Proteins, fats, crude fiber, carbohydrates, and energy were obtained by analytical standards following the protocol used by Lutz [10]. Various investigations have been carried out from an experimental point of view to determine options for the development of spent grains. The exploitation of spent grains for energy production is all the more interesting because it also intervenes in the preservation of the environment [4, 9].

As such, the possibility of recovering energy from brewer's grains by anaerobic digestion and anaerobic fermentation, in search of economic and environmental advantages, was analyzed from an experimental point of view

[11]. The authors found that anaerobic digestion of brewer's grains is an alternative to energy recovery. The prediction of the anaerobic yield of biogas from spent grains involves the elementary adjustment of certain substances, such as sludge, wastewater, certain specific organic wastes, and chemical pre-treatment.

Brewer spent grain (BSG) appears to be an important starting substrate for biogas production because it is affordable and accessible and its components have high value. As such, several investigations have been conducted on the use of BSG as a substrate for biogas generation. This application is reported to be particularly well suited to obtaining thermal energy in breweries with minimal environmental damage [12]. However, BSG contains a large amount of lignin, cellulose, and hemicellulose, which are difficult to degrade in anaerobic, mostly due to the presence of degradation products, such as phenolic compounds, which cause process inhibition [13]. To solve these limitations, researchers have suggested an anaerobic co-digestion approach i.e. digestion of a combination of two or more different substrates is carried out aiming at enhancing the effectiveness of the process [12]. However, it has been demonstrated that stable biogas production from brewery-spent grain as a mono-substrate is possible by applying a long-term process [13].

The most important parameters in the biogas production process are mold, C/N ratio, and pH. Studies on the physicochemical characterization of brewed spent grains have shown that they contain, on average, 70.6% to 81.3%, 7.1 to 26.5; and 3.8 to 6.9 moisture, C/N ratio and pH, respectively [14]. However, these values are not adequate for sufficient biogas production. Indeed, efficient biogas production requires, on average, 60 to 65%, 20 to 30, and 5.5 to 7.5 moisture ratio, C/N ratio and pH, respectively. Methods for optimizing the efficient production of biogas from spent grains, such as those based on the use of anaerobic bacteria cultures, have been proposed [15].

The physicochemical composition of spent grains varies depending on the barley varieties, the time of harvest, the malting and brewing conditions, and the amount and type of additives incorporated into the brewing process. There are few data available indicating the properties of local spent grains. A database of the physicochemical properties of locally spent grains would enable industry and scientists to consider more effective decision-making.

This study aimed to experimentally determine the organ energetic concentration of brewers from the brewing industry in Cameroon for integrated biogas production. Samples of fresh grains were collected, dried, and characterized to determine their physicochemical parameters, organic composition, and energy value. The characteristic values obtained will allow, among other things, the evaluation of the methanogenic potential of these spent grains. The proposed experimental study and the following results offer a very useful database for the valorization of these important and abundant residues.

2. Material and methods

2.1 *Material*

Spent grain is the main material used in this study. The spent grain was collected from the brewing industry established in Bafoussam, Western Cameroon. The chemicals used for this study were nitric acid (HNO_3), potassium thiocyanate (KSCN), sulfuric acid (H_2SO_4) 1 M, salicylic acid ($C_7H_6O_3$), sodium hydroxide (NaOH), potassium dichromate ($K_2C_2O_7$), mercury sulfate ($HgSO_4$), and ammonium ferrous sulfate, known as AFS ($(NH_4)_2Fe(SO_4)_26{\cdot}H_2O$). All the chemicals were of analytical grade, with a purity of 99.5%, and were purchased from Merck Group, United Kingdom.

2.2 *Collection of raw material*

The raw material from industrial beer processing residues was collected at a brewing company (Figure 1a). Approximately 2 kg of spent grain was collected and dried at room temperature (30 ± 3) °C for 5 days. The dried spent grain sample was subsequently characterized (Figure 1b).

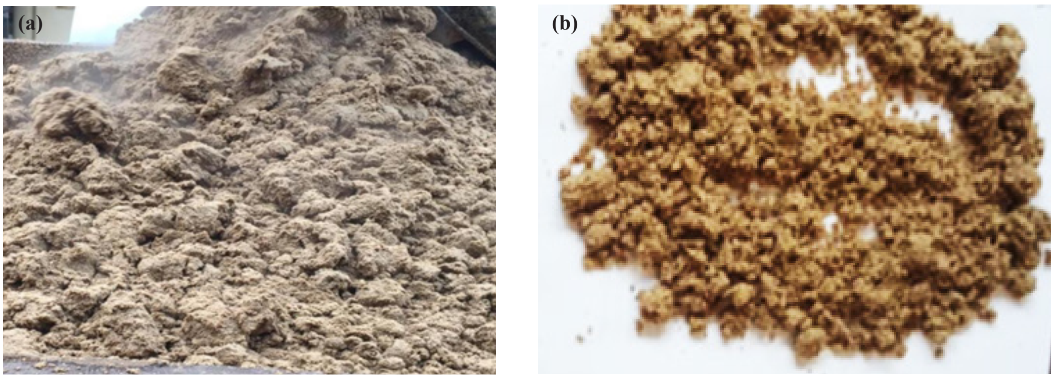

Figure 1. (a) Raw material (spent grain) from the brewing industry; (b) air-dried spent grain made available for testing

2.3 *Analysis of physicochemical parameters*

2.3.1 *Determination of dry matter and moisture content*

A 10 g sample of the air-dried spent grain was weighed. The samples were dried in an oven at 105 °C until a relatively constant weight was obtained. The spent grain dry matter (*DM*) was determined according to Eq. 1 [16].

$$DM\,(\%) = \frac{Final\ mass \times 100}{Initial\ mass} \tag{1}$$

The *MC* % was then deduced from Eq. 2:

$$MC\ (\%) = 100 - DM \tag{2}$$

2.3.2 *Determination of acidity*

The acidity of the spent grain sample was assessed using a pH meter. The dried spent grain sample was diluted in distilled water to obtain 10% (w/v) spent grain solutions. The resulting mixture was then filtered through a Whatman N1 filter device. The acidity was then measured using a pH meter (8200/8200 M, GOnDO Electronic CO., Ltd, Taiwan).

2.3.3 *Determination of AC*

One gram of each spent grain sample per test was introduced into a porcelain crucible and calcined in a Carbolite Eurotherm muffle furnace at 450 °C for 2 h. The ash content (*AC*) was then estimated by Eq. 3 [17].

$$AC(\%) = \frac{Final\ mass \times 100}{Initial\ mass} \tag{3}$$

2.3.4 *Determination of iron (Fe) content*

Determining the iron in the spent grain was carried out as previously described with some modifications [18]. The spent grain ash was briefly treated with 10 ml of 1 M nitric acid (HNO_3) for 30 min and then cooled and filtered through the Whatman N1 filter paper. The Fe content was quantified by mixing 5 mL of the spent grain solution in 1 mL of 5% potassium thiocyanate (KSCN). The resulting mixture was left to rest for 10 min. The residual absorbance was measured with a UV-visible spectrophotometer (Model N600, Manufacturer by Shanghai Yoke Instrument Co., Ltd., China) at 420 nm. The standards were processed according to the same protocol used for the samples. The iron concentration (mg/100 g) of the sample was obtained using a linear regression of concentrations concerning the absorbance of the standards. The calibration curve and the calculation of concentrations, expressed in mg/100 g, are approximate.

2.4 *Determination of organic compounds*

2.4.1 *Determination of organic matter and organic carbon*

The levels of organic matter and organic carbon in the spent grain were determined as previously described with slight modifications [18, 19]. To measure the content of matter and organic carbon, 1 g of sample (m_1) was introduced into a porcelain crucible and calcined in a Carbolite Eurotherm muffle furnace at 550 °C for 2 h. The mass of the crucible + sample assembly (m_2) was measured. The OM% was determined using Eq. 4.

$$OM\ (\%) = \frac{(m_1 - m_2)\times 100}{m_1} \tag{4}$$

Organic carbon can be estimate for waste materials according to the standard (NF44-161) as a function of organic carbon content using the Eq. 5 [19-21]:

$$TOC\ (\%) = \frac{OM}{1.725} \tag{5}$$

Where, *OM* is the organic matter and *TOC* is the total organic carbon.

2.4.2 *Determination of macromolecule content*

Macromolecules (proteins, crude fibers, carbohydrates, and fats) are organic molecules. The determination of the macromolecule content of spent grain makes it possible to deduce its energy value and its ability to produce biogas.

2.4.3 *Determination of nitrogen and total protein*

The determination of the proteins consisted of the complete prior mineralization of nitrogen by a mixture of concentrated 1 M H_2SO_4 and heated 1 M $C_7H_6O_3$ at 350 °C. The mixture was distilled by steam entrainment; the distillate was then titrated using a solution of 0.01 M H_2SO_4. The percentages of nitrogen (% *N*) and total protein were approximated using Eqs. 6 and 7, respectively.

$$N\ (\%) = \frac{(Vacide - V_0)\times 14}{100} \tag{6}$$

Where V_0 is the volume of the control sample.

$$Protein\ (\%) = N \times 6.25 \tag{7}$$

2.4.4 *Determination of total fiber content*

The total fiber content was determined. In a beaker containing 0.255 M H_2SO_4, 1 g of the sample test (*ST*) was introduced. The mixture was boiled for 30 min and then filtered. NaOH (0.313 M) was added to the product, and the mixture was boiled again for 30 min. After filtration, the residue was washed three times with 5 ml of hot distilled water and then twice with acetone (5 ml). The resulting insoluble sample was dried at 105 °C for 8 h and weighed (M_1). This dry residue was incinerated at 550 °C for 3 h, after which the ashes were weighed (M_2). The % of fibers was calculated according to Eq. 8.

$$Fibres\ (\%) = \frac{(M_1 - M_2) \times MS \times 100}{ST} \tag{8}$$

Where *MS* is the dry matter and *ST* is the mass of the sample.

2.4.5 *Determination of lipid content*

The total lipid level was determined according to the BIPEA (1976) method used by Adou et al. [22]. Fat was extracted using hexane, and the dried residue was weighed after the solvent had evaporated [23]. One gram of the sample was then introduced into a cellulose capsule and continuously extracted by boiling in hexane. The fat in the solvent returned to the flask in successive spills because of the siphoning effect in the lateral bend. Only when the solvent evaporates, does the fat accumulate in the flask until the extraction is complete. Once the extraction was complete, the hexane was evaporated using a rotary evaporator, and the fat was then weighed. The total lipid content was measured by Eq. 9.

$$Lipids\ (\%) = \frac{Fatmass \times 100}{Sample\ Mass} \tag{9}$$

The carbohydrate content of the spent grain was obtained by arithmetic calculation as previously described from the contents of *water*, *ash*, *protein*, *fiber*, and *fat* presented by Eq. 10 [22].

$$Carbohydrates = 100 - (protein + fat + fibre + ash + water\ content) \tag{10}$$

2.4.6 *Determination of the E value*

The *E* value of the spent grain sample was calculated according to Coleman's standard formula, using the Atwater and Rosa coefficients presented by Eq. 11 [23].

$$E = \frac{[(protein + fat) \times 4 + (fat \times 9)]}{1} \tag{11}$$

2.4.7 *Determination of COD*

COD was determined according to the protocol described above [24, 25]. A total of 25 ml of spent grain solution, 25 ml of 0.25 M $K_2C_2O_7$, 75 ml of concentrated 1 M H_2SO_4 and 1 g of $HgSO_4$ were added to a Pyrex flat-bottomed flask. An ascending amount of refrigerant was then added to the flask, and the mixture was heated to 148 °C for 2 h. At the same time, an identical process was carried out on 25 ml of distilled water as a blank. After cooling, the refrigerants were rinsed with approximately 150-200 ml of distilled water. The contents of each balloon were then decanted into Erlenmeyer flasks to which a few drops of ferroin (colored indicator) were added. The resulting colored solution was titrated with $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (AFS) and the volumes of AFS required for the turn were recorded. The COD was then estimated by Eq. 12.

$$COD(mg/l) = \frac{(Ve - Vt) \times 8,000 \times N}{V} \tag{12}$$

Where *Vt* is the volume of AFS required for titration of distilled water, *Ve* is the volume of AFS required for titration of the sample, *V* is the volume in ml of the test portion and *N* is the normality of the SFA solution used.

2.5 *Determination of the LCV*

The lower calorific value was determined by the ASTM D240 standard combustion method [26, 27]. The gross energy of the samples was measured using a bomb calorimeter, particularly a C5000 adiabatic calorimeter (IKA®-Werke, Staufen, Germany). The sample was placed into a bomb calorimeter, and automated ignition inside the calorimeter was allowed under closed conditions. The equipment was connected to a computer, and the system software was used to determine the total LCV per sample after the complete ignition of the sample.

2.6 *Data processing*

The information collected during the field investigations was analyzed and processed using Microsoft Excel 2016 and SPSS (Statistical Package, v27.0.1) software. The processing of the information and the synthesis of the data were applied to produce contingency tables in a suitable format, which were exported for further analysis and appropriate processing.

3. Results and discussion

3.1 *Physicochemical characteristics of spent grain*

The physicochemical characteristics of the malted grain samples at pH, AC, MC, DM, and Fe concentrations of 5.6, 9.8%, 8%, 92%, and 194.2 mg/100 g, respectively, are presented in Table 1. When analyzing the data, 57.39% and 3% were obtained for TOC and TN, respectively. A comparison of the data obtained in this study with those from previous studies [28, 29], revealed that TOC and TN values varied from approximately 17.48 to 57.39% and from 2.4 to 4.3%, respectively. Deviations approaching 4.39% of the approximate value and 1.025% were found for TOC and TN [3]. The protein and total crude fiber contents were 18.75% and 3.6%, respectively, which are consistent with the results of Thiago et al. [28]. Musaida et al. [29-31] also determined the total protein and crude fiber contents and reported values between 2.4 and 24% for protein and 3.3% for crude fiber. The values of protein and total crude fiber agreed with those found in the respective studies by Thiago et al. [28] and Musaida et al. [30, 32], who also determined total protein and crude fiber and found values between 2.4 and 24% for protein and 3.3% for crude fiber. The proteins contained in brewers' grains are thought to have interesting properties for controlling inflammation [33]. The iron content of the brewers' grains proposed in this study is close to that proposed by [34]. The very high organic matter content of 99% obtained in the present study makes these spent grains a potential ingredient for anaerobic digestion. This value is 29% higher than that found by Amir et al. [35]. According to studies conducted by Joncer et al. [36], the OM% concentration in the substrates is important for the operation of the plant as well as for the prediction of the quantities of biogas produce.

The aim is to exploit the data obtained from the characterization of malting grains to assess the concentration of organic and energetic matter to predict the quantities and qualities of the biogas from which it is derived.

pH is an important chemical parameter for anaerobic digestion, and for optimal anaerobic digestion, the pH should be neutral, i.e., between 6.5 and 8.5 [40]. The decrease in pH is generally due to the accumulation of volatile fatty acids or dehydrogenizes, which can lead to acidification in an anaerobic digestion plant, which contributes to the inhibition of the anaerobic digestion process. Therefore, it is very important to monitor the pH, which can be adjusted if necessary, by injecting NaOH to neutralize the digester environment. The values obtained for the pH, ash content, moisture content, and dry matter content agreed with the data obtained in similar studies. These values are similar to those of Matia [38] and Thiago [28], who approximated pH values of 5.8 and 5, respectively. Jane [41] proposed a pH value of 5.5 for malting grains made of 100% malt, indicating that these values are favorable for anaerobic digestion. Indeed, good anaerobic digestion requires a pH between 5.5 and 7.5, which corresponds effectively to the pH value (5, 6) obtained for our spent grain sample. However, pH adjustment through the use of anaerobic microbial cultures is necessary to increase the amount of methane produced [15].

Table 1. Physicochemical composition of spent grain and comparison with relevant studies

pH	AC (%)	MC (%)	DM (%)	Fe (mg/100 g)	References
5.6	9.8	8	92	194.2	This study
-	10. 96	5.05	-	-	[37]
5.8	-	-	-	-	[38]
5.41	3.8	82.6 ± 0.10	-	-	[28]
-	11.9 ± 1.1	5.8 ± 1.0	-	-	[29]
-	4.05	72.32	-	187.6	[34]
-	3.76 ± 1.23	78.23 ± 1.45	-	-	[10]
-	2.4-4.6	58	-	-	[30]
-	11-46	77-85	-	-	[39]
-	3.303 ± 0.048- 4.290 ± 0.018	2.178 ± 0.030- 4.353 ± 0.109	-	-	[36]

Previous work carried out on different samples of wheat (100%), sorghum (100%), malt (100%), malted barley (80%), and malted maize (20%) showed deviations in physicochemical characteristics ranging from 2.4 to 46% and 2.178 to 5.8% for AC and MC, respectively [28, 30, 37]. In other studies, values of 2.3 to 7.9% and 76.8% were found for AC and MC, respectively [41, 42]. The variability of these data indicates that the chemical composition varies depending on the initial composition of the raw material producing the spent grains, the malting and brewing conditions, and the quality or type of additives used in the brewing process. The AC (9.8%) obtained in the tested sample is favorable for use as a substrate in biogas production. Indeed, it has been reported that an ash content of 10% is characteristic of a relatively acceptable fraction of the methanogenic elements of spent grain [41, 42]. The MC of the spent grain sample used in this study was 8%. This high level of MC is suitable for biogas production efficiency. Indeed, the high level of MC enhances microbiological growth that contributes to biogas production [43].

3.2 *OM, TOC, TN, and C/N ratio*

The results of the OM, TOC, and TN characterization of the brewers' grains are presented in Table 2. OM, total organic carbon (TOC), total nitrogen (TN), and the C/N ratio of the brewing grain were 99, 57.39, 3, and 19.13%, respectively. Values of 57.39% and 3% were obtained for TOC and TN, respectively, when analyzing the data. A comparison of the data obtained from this study with those from the literature [28, 29] revealed that the values of TOC and TN vary from approximately 17.48 to 57.39% and from 2.4 to 4.3%, respectively. Deviations approaching 4.39% of the approximate value and 1.025% were found for TOC and TN [3].

The very high organic matter content of 99% in this study makes these spent grains a potential ingredient for anaerobic digestion. This value is higher than that reported in the literature [29], and the work done by Panjicko et al. [35]. According to previous studies [40], the OM concentration in the substrates is important for the operation of the plant as well as for the prediction of the quantity of biogas produced. This quantity also depends on the TOC value and is also assessed by the magnitude of the COD. As a result, the OM of the spent grain studied in this study is significant and predicts that a significant amount of biogas will be produced.

The C/N ratio is important for anaerobic digestion. A relatively low or too high C/N ratio affects system performance. Spent grain, which has a C/N ratio of approximately 19, is considered to be a relatively suitable ratio as confirmed by studies by previous studies in the specific context of anaerobic digestion [30, 34]. The C/N ratio of 19.13 obtained in this study demonstrates the methanogenic potential of the raw material tested.

Table 2. Comparison of the composition of OM, TOC, and TN and the C/N ratio of spent grain with earlier studies

OM (%)	TOC (%)	TN (%)	C/N Ratio	References
99	57.39	3	19.13	This study
-	53	3.81	13.81	[37]
-	47.5-45.5	2.9-2.4	16.4-19	[38]
-	52.3 ± 09	4.3 ± 04	12.1	[28]
-	41.6	-	-	[29]
-	17.48	3.46	5.06	[34]
-	51.20	3.63	14.11	[30]

3.3 *Macromolecule content and energy value*

Table 3 presents the results of the characterization of the total protein, crude fiber, fat, carbohydrate, and energy contents of the brewers' grains. The spent grain samples tested contained 18.75% and 3.6% total protein and crude fiber, respectively. These values are close to those reported in similar studies, i.e., 2.4 to 24% and 3.3% for total protein and crude fiber, respectively [28, 30, 32]. The values of protein and total crude fiber are close to those found in similar studies [10, 32]. The protein concentration in the spent grain sometimes depends on the type of cereal used, the nature of the adjuvants, and the milling and brewing conditions. The values of total protein and crude fiber depend on these parametric variations.

Table 3. Macromolecular composition and energy value of spent grain in comparison with earlier studies

Total Protein (%)	Crude fiber (%)	Fats (%)	Carbohydrates (%)	Energy (MJ/kg)	References
18.75	3.6	8.7	51.15	14.97	This study
26.9					[28]
4.89 ± 0.29	4.19 ± 0.56	2.67 ± 0.68	1.89 ± 1.21	109.23 ± 4.23	[10]
15-31	-	-	-	-	[30]
20	-	-	-	-	[39]
22.217 ± 0.050-30.236 ± 0.133	-	9.470 ± 0.534-13.105 ± 0.314	50.683 ± 0.442-60.190 ± 1.692	-	[36]

The fat and carbohydrate contents obtained for the spent grains studied are relatively high compared with those in the literature. These data indicate that brewers' grains are mainly a favorable fibrous material for microbiological conditioning, as described in the studies of Joncer [36] as well as those of Salihu et al. and Sumato et al. [3, 9]. The energy obtained is relatively high at 14.97 MJ/kg compared with that reported by Sideney et al. [10]. These data indicate that the spent grain studied is mainly a material containing a relatively high organic matter content and energy potential characterized by the amount of protein, carbohydrate, and lipid.

3.4 *COD, COD/TOC ratio and LCV*

As presented in Table 4, the values obtained for the COD, COD/TOC ratio, and LCV were 3,880 mg/kg, 86.03%, and 19.764 MJ/kg, respectively. The COD of the spent grain studied was relatively high at 3,880 mg/kg. This quantity also makes it possible to measure the concentration of organic matter in the waste, which is a relatively high value of the organic matter content of the spent grain in this study. The COD/TOC ratio of 86.03 in this study reflects the characteristics of the organic matter present in this spent grain. The susceptibility to oxidation is proportional to the organic matter content [34]. The LCV is 19.764 MJ/kg which is within the reported range. Indeed, the calorific value of BSG amounts to approx. 18-20 MJ/kg [12] makes it an interesting raw material for energy production in the process of combustion [44].

Table 4. COD, COD/TOC ratio, and LCV of the spent grain in comparison with earlier studies

COD (mg/kg)	COD/TOC ratio	LCV (MJ/kg)	References
3,880	86.03	19.764	This study
1,164	-	-	[38]
1,092,000 ± 220	-	-	[28]
-	-	12.6	[29]
-	-	18.70	[34]
-	-	20	[30]
-	-	18.64	[39]

The value of the LCV obtained in this study is high compared to the earlier findings [29, 34, 39] but close to the value reported by Lee et al. [30]. Notably, the LCV is a parameter for evaluating the energy potential of any biomass resource [30, 34].

4. Conclusion

This study aimed to characterize the physicochemical properties of Cameroonian brewers' grains and to analyze their organic and energetic concentrations. The dehydrated brewers' grains studied have a high water content (8%), which characterizes these grains as a material that favors microbiological growth, requiring a few days to deteriorate and produce biogas. A high organic load was also observed in their composition (TOC around 50%), with a high COD (> 2,000 $mg \cdot kg^{-1}$), and a lower calorific value of 19.764 $MJ \cdot kg^{-1}$, which corresponds to microbial origins. Nevertheless, the pH value obtained for this study is lower than the normal range (6.5 and 8.5) as defined in the literature for optimal operation of biométhanisation. However, pH adjustment using anaerobic bacterial cultures would be necessary to increase the quantity of methane to be produced. These results show that Cameroonian brewers' grains have significant organo-energy potential, based on their components and physicochemical properties, thus highlighting their relevance as a potential resource for biogas production. It can be concluded that the brewers' grains tested have significant methanogenic potential. The need to reduce the time taken by the raw material from the brewing industry to the analysis laboratory is one of the conditions for optimizing the results. We could also consider characterizing and analyzing certain parameters used to monitor the operation of the biométhanisation process, such as volatile fatty acids (VFA), which are needed to determine the rate of degradation of organic matter. To optimize and increase the potential for biogas production, it will be essential to analyze the rate of lignocellulosic matter. Therefore, additional analyses need to be performed prior to implementing the use of this spent grain as a substrate for biogas generation. However, based on its physicochemical characteristics and components, its successful use for biogas generation can be anticipated.

Credit author contribution

ZMY: Methodology, Formal Analysis BN: Writing- Original Draft, NH: Writing-Review and Editing, SM: Conceptualization, SLK: Formal Analysis, DB: Supervision and Project Administration.

Acknowledgments

This study benefited from the technical support of Koloko Brice Landry of the Quality Control Laboratory of Agri-food, Parapharmaceutical and Cosmetic Products from the University Institute of Technology of Douala (IUT) and Njuhou Saliou, Pountounynyi Paul Duclair.

Conflict of interest

The authors declare no competing financial interest.

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