|  |  |
| --- | --- |
| cetlogo ***CHEMICAL ENGINEERING TRANSACTIONS***  ***VOL. 92, 2022*** | A publication of  aidiclogo_grande |
| The Italian Association  of Chemical Engineering  Online at www.cetjournal.it |
| Guest Editors: Rubens Maciel Filho, Eliseo Ranzi, Leonardo Tognotti  Copyright © 2022, AIDIC Servizi S.r.l. **ISBN** 978-88-95608-90-7; **ISSN** 2283-9216 | |

Charcoal produced with brewing malt residue, development and characterization

Ghiovani Z Ranieroa, Julia C Zanchetab, Jaqueline G B Januáriob, Claudia C F Monteiroc,d, Antonio R G Monteiroa\*

a Post graduation program in Food Science, Universidade Estadual de Maringa, Av Colombo, 5790, Maringa, PR, Brazil

b Department of Food Engineering, Universidade Estadual de Maringa, Av Colombo, 5790, Maringa, PR, Brazil

c CIAUD, Research Centre for Architecture, Urbanism and Design, Lisbon School of Architecture, Universidade de Lisboa, Rua Sá Nogueira, Polo Universitário do Alto da Ajuda, 1349-063 Lisboa, Portugal

d Department of Design, Universidade Estadual de Maringa, R Afonso Pena, 130, Cianorte, PR, Brazil

\* argmonteiro@uem.br

In South America, almost 2 billion litres of beer were produced in 2019 by small and medium-sized breweries, generating approximately 150 thousand tons of malt residue per year. If, on the one hand, large breweries use the waste from the brewing process to generate energy for their own factories, on the other hand, many of small and medium-sized breweries do not have an adequate destination for their waste. The unfeasibility is mainly since each of these breweries individually produces low volumes of waste. At the same time, briquets for energy generation in boilers have relatively low added value, which is only justified when produced in large quantities.

In this context, this research aimed to develop and characterise charcoal for use in barbecue grills produced from malt residue from the brewing process.

To produce charcoal from brewing residue, pre-gelatinised corn was initially made by extrusion, in an IMBRA RX50 single screw extruder (INBRAMAQ, Ribeirão Preto, SP). Soon after extrusion, expanded corn ground it in a hammer mill with a smaller than 0.7 mm particle size. The pre-gelatinised was mixed with the brewer's residue in the proportions established in the experimental design and passed through a cold extruder M-10 (Braesi, Curitiba, Brazil) followed by drying in an oven time and temperature according to the experimental design. The briquet obtained subsequently underwent the pyrolysis process at 180°C for 3 hours in a muffle.

Once the charcoal is ready, all treatments established in the experimental planning, as well as conventional charcoal and commercial briquet charcoal (as standard), were analysed using the methods of Universal testing machine (model DL1000, EMIC, São José dos Pinhais, Brazil) in compression mode, Calorific power value by C-200 calorimeter (IKA, Staufen, Germany), density by seed displacement, acceptance by sensorial analysis and Colour by Minolta Chroma Meter CR-400 colourimeter.

The statistical analysis of the results obtained showed that the charcoal produced with brewer's residue and pre-gelatinised corn in the proportion of 95:5 presented adequate results. It enabled both good mechanical strength and a high calorific value when compared to the standard.

It was possible to conclude that charcoal produced with brewer's residue and pre-gelatinised corn had characteristics similar to conventional charcoal. Since the process used is of low installation cost and low energy consumption, the product proved viable to add value to the residue from small and medium breweries.

1. Introduction

The food industry is responsible for a large amount of waste. The improper disposal of this waste results in environmental problems due to the high organic load of the chemical composition of these materials. In this context, the brewing industry stands out, which includes stages of processing and fermentation of vegetable raw material, such as barley, hops and other grains used as adjuncts, generating different by-products (Mathias et al., 2014).

The brewing process involves several stages, leading to the fermentation of the sugars contained in the malt and its conversion into alcohol and carbon dioxide by the yeast after the use of the malt. The three main brewing industry wastes include brewer's spent grain, hot trub, and residual brewer's yeast. Proper management of these wastes may bring economic benefits and help to protect the environment from pollution caused by their excessive accumulation (Rachwal et al., 2020).

According to Monteiro et al. (2019) one of the biggest challenges for brewing industries, in special the small and medium, is making a good destination for their solid wastes.

The proper management of this waste can bring economic benefits and help protect the environment from pollution caused by its excessive accumulation. However, disposing of this waste is a problem for producers, on environmental issues, but possible reuse in other processes and products.

Malt cake is the main by-product of the brewing industry, accounting for about 85 % of the total by-products generated.  After the moisture stage and the exhaustion of the ground malt grains, the soluble compounds of interest, to make the sugar available for fermentation. Moreover, bagasse plays an important role as a filter (Aliyu et al., 2011).

This residue is a lignocellulosic material containing about 17 % cellulose, 28 % non-cellulosic polysaccharides, chiefly arabinoxylans, and 28 % lignin.  BSG is available in large quantities throughout the year, but its main application has been limited to animal feeding (Mussatto et al., 2006).

Other applications of this waste have been studied and used by industry, with the objective of reducing production costs and adding value to products. As the production of energy by direct burning or by biogas production via anaerobic fermentation, the production of charcoal, use as adsorbent material in chemical treatments, substrate for the cultivation of microorganisms and bioproducts by fermentation and support for cell immobilisation (Aliyu et al., 2011).

Malt cake is a good material for sorption and processing in activated carbon. Another way is to use it as a crude fuel after hydrothermal carbonisation or as a raw material for anaerobic digestion (Gomes et al., 2019).

Wood when subjected to a heat source (thermal energy) goes through the drying and carbonisation processes of its main components: hemicellulose, cellulose, and lignin. As the wood decomposes and generates the fumes of carbonisation (gases and vapours), the coal is formed by the concentration of carbon, which in its elemental value begins with 50 % of the wood, volatilises part with oxygen and hydrogen and, what is fixed, reaches the concentration demanded by blast furnaces around 75 % (2 %), when it reaches temperatures between 3500 and 3800 °C (CGEE, 2015).  In the manufacture of briquette, the raw materials used can be sawdust, wood wool, rice husk, corn straw, cobs, sugarcane bagasse, cotton husk, coffee husk, among others.

The briquette manufacturing process goes through the stages of grinding and sorting the coal, mixing the binder, pressing, and drying the briquettes. One of the most critical steps in the process is the addition of the binder. The ground charcoal is transported to the mixer where it receives a percentage of agglutinating water (pregelatinized starch). The proportion of this binder is a function of the coal particle size and the final quality desired for the briquette (Fontes et al., 1984).

In countries like Brazil, Uruguay and Argentina, barbecue consumption is a tradition and a form of socialisation. Generally, barbecue is prepared at home in traditional barbecue grills that use charcoal, which is obtained through wood pyrolysis. This coal has an added value much higher than the briquets that large industrial companies use, making it viable for production on smaller scales.

The use of corn starch as a binder improves the quality of briquettes, by increasing the density and mechanical resistance (Martins et al., 2016).

Corn flour, when going through the extrusion process, has its modified amylaceous structure, improving the absorption and solubility of water, that is, the changes cause the gelatinisation of starch facilitating the development of products. Moreover, this type of flour is a benefit for technological development, providing the reduction of industrial losses with the use of by-products that were previously not used, and through the process can be used to produce pre-flour gelatinised (Gomes, 2019).

Pregelatinized maise flour, due to its Physico-chemical characteristics, has binding power, and for this reason, it is an excellent alternative to participate in the agglomeration of malt cake particles.

The development and characterisation of coal produced with brewing malt residue, using pregelatinized corn flour, was the objective of this study, aiming at an alternative to reuse the malt residue generated by brewing, since made a high-value product.

**2. Material and methods**

2.1 Materials

For obtaining ground and standardised beer residue, the used malt residue was supplied by a small local brewery (Maringa, PR, Brazil), after the mashing process of a pure malt lager the resulting residue was dried in an oven at 70 °C with air circulation for 48 hours, the grinding was done in a mill and separated into three different granulometry (3.5-6, 6-14, 14-28) and later stored in polypropylene bags until the moment of use.

To obtain the milled corn extrudate, corn grits provided by Nutrimilho (Maringa, PR, Brazil) was used, it was extruded according to Nakagawa et al. (2019) using IMBRA RX50 single screw equipment (INBRAMAQ, Ribeirão Preto, SP, Brazil) 50 mm diameter and 200 mm length. The die plate had two holes of 3 mm diameter, and extrusion parameters were 20 A of motor amperage, the feed rate of 12 g/s and a screw speed of 90 rpm. Afterwards, the extrudates were ground, and the 60-80 mesh fraction was separated and later stored in polypropylene bags until use.

2.2.1 charcoal briquet production

To prepare the charcoal briquet, 20 g of distilled water, beer residues and extruded ground corn were mixed in the proportions and granulometric according to 22 experimental design shown in Table 1, the central point (treatment 5 was made in triplicate).

The mixed raw materials were pelletised in a pasta extruder M-10 (Braesi, Curitiba, Brazil). The palettized material were transferred to greenhouses at 70 °C for 3 hours to lose the moisture. The dry material was inserted in a 180 °C muffle for 3 hours to pyrolyze, in a no oxygen environment.

Table 1: Experimental design of the charcoal briquet process

|  |  |  |  |
| --- | --- | --- | --- |
| Treatment | Malt waste (g) | Extruded maise (g) | The particle size of malt waste (mash) |
| T1 | 95 | 5 | 14 – 28 |
| T2 | 95 | 5 | 3.5 – 6 |
| T3 | 85 | 15 | 14 – 28 |
| T4 | 85 | 15 | 3.5 – 6 |
| T5 | 90 | 10 | 6 – 14 |

2.3 Charcoal Characterization

To characterise the charcoal, was made a density, tensile strength, Colour, and calorific power for the five treatments made according to experimental design and with a commercial charcoal briquet (C1) as well as commercial charcoal made by Acacia Negra wood (C2) as controls.

**2.3.1 Density**

The density was measured according to Nakagawa et al. (2019) with modifications. To measure the volume, a 300 mL container was used, where 20 g of each treatment of charcoal briquets or the controls was added, and the volume was completed with corn seeds. Seed displaced was measured by checking its volume using a 100 mL graduate tube. To measure the mass, an analytical balance was used. To density was calculated according to Equation (1).

(1)

2.3.2 Tensile strength

The mechanical resistance was analysed for five treatments using a Universal testing machine (model DL1000, EMIC, São José dos Pinhais, Brazil). Each sample was loaded by 100 kgf at 1 mm\*s-1, with probe angled at 135 ° and analysed according to Monteiro et al. (2019). The control samples do not measure because they had different shapes when compared with the treatments.

**2.3.3 Calorific power**

The calorific power was measured by a C-200 calorimeter (IKA, Staufen, Germany), with Saletnik et al. (2021) parameters.

**2.3.4 Colour**

The Colour was evaluated using a Minolta Chroma Meter CR‐400 colourimeter with D65 illuminate as the reference, with readings in three-point each sample for each treatment. Results were expressed by the CIELAB system, with values of L \*, a \* and b \* whose L \* values. The five treatments were evaluated as well as the two controls.

**2.3.5 Appearance**

The appearance of the materials was made according to Monteiro et al. (2019) in the Sensory Analysis Laboratory of UEM by 21 untrained tasters, using individual booths. All five samples and two controls had been presented simultaneously, coded with random numbers, along with the evaluation sheet. In order to evaluate the overall acceptability of appearance, we used the 5-point structured hedonic scale where 5 represented the maximum score 'liked extremely' and 1, the minimum score 'disliked extremely'. The evaluation of the hedonic scale is converted into numerical scores and statistically analysed to determine the difference in the degree of preference between the samples. The tasters were asked the differences that can make a choice.

**2.3.6 Statistical Analysis**

All data were treated statistically from the analysis of variance (ANOVA) with subsequent analysis of the Tukey tests' means at 5 % probability and correlation test. The statistical tests were made by software Sisvar 5.6 (Monteiro et al., 2019).

**4.** **Results and discussion**



T1

T2

T3

T4

T5

C1

C2

*Figure 1. The Picture of the five charcoals made according to 5 treatments and two controls*

Figure 1 presents a photo of the five treatments and the two controls used. Both in the colour tests, it was not possible to identify a significant difference between the treatments and the standards, as found by Gerd et al. (2017). However, the black Colour of the samples does not allow the visualisation of any discrepancies from the raw materials.

The appearance analysis made it possible to observe that all the samples had a good evaluation. However, the samples with larger granulometry (T2 and T4) had a significantly worse assessment. According to the information from the tasters, this was mainly due to the non-homogeneity of the final product. Therefore, data sample colour and acceptance are shown in table 2.

Table 2. Appearance of the formulations: Colour e appearance

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample | L\* | Colour  a\* | b\* | Appearance |
| T1 | 5.517095 | 0.51871 | 16.88837 | 3.71a |
| T2 | 5.220671 | 0.05838 | 16.14036 | 3.30ab |
| T3 | 4.709036 | -0.39597 | 13.68250 | 4.06a |
| T4 | 5.687904 | 0.54517 | 16.86298 | 3.04b |
| T5 | 5.057122 | -0.52571 | 15.00975 | 3.99a |
| C1 | 4.508457 | -0.26838 | 13.49015 | 4.09a |
| C2 | 5.064476 | -0.47824 | 14.89436 | 3.82a |

Means with different letters in the same column are significantly different (*P* < 0.05).

Table 3 presents the results of the physical characteristics of treatments and controls. It was possible to observe that the density of the samples varied a lot, and the samples with greater granulometry had a lower density. This was expected as compaction during pelleting should occur less efficiently in larger particulate systems. All treatments had a significantly higher density than the charcoal tested, but when compared to commercial briquet, only one had a higher density.

According to Somerville and Jahanshahi (2015) temperature and compression in pyrolysis could change de density of the vegetal charcoal because it reduced the porosity of the material. They found higher values in density because they use a high compression in the pyrolysis process to make charcoal to be used as an industry energy supply. In this research, the same conditions were used in all treatments with low compression were used to make barbecue charcoal.

The higher density of the material can, on the one hand, be a factor that facilitates the transport of the material. Still, on the other hand, very high densities can make it challenging to start a fire in the material.

As for the mechanical resistance of the materials, it was possible to observe that the samples with greater granulometry presented less resistance than the sample with lower granulometry. Therefore, it was impossible to measure the control samples because they have different formats from the treatments, making comparisons unfeasible.

In terms of calorific value, as expected, there was no significant difference between all treatments and the control samples since all materials are predominantly composed of cellulose. The results found were higher than the results from Carnaje et al. (2018), probably because the were a moisture difference between both.

The burning of the material should be influenced mainly by the calorific value and density. Materials with lower density tend to release heat with more incredible speed, which may not be interesting for the product's purpose. On the other hand, the charcoal used as a control must present a different behaviour from the briquets because their cells have different connecting structures.

Table 3. The charcoal briquet characterisation

|  |  |  |  |
| --- | --- | --- | --- |
| Treatment | Density  (kg/m3) \* 10-3 | Tensile Stench (N) | Calorific power  (J/kg) \* 10-6 |
| T1 | 1.21f | 573c | 21.4a |
| T2 | 0.62c | 273a | 21.9a |
| T3 | 0.91d | 674c | 22.4a |
| T4 | 0.49b | 327ab | 22.1a |
| T5 | 1.02de | 490bc | 21.6a |
| C1 | 1.10ef | - | 21.9a |
| C2 | 0.36a | - | 22.4a |

Means with different letters in the same column are significantly different (*P* < 0.05).

5. Conclusions

The results obtained made it possible to conclude that the production of briquet with residue from the brewing process using pre-gelatinized corn was viable. However, the formulation with 95 % of residue and 5 % of extruded with fine grinding showed auspicious characteristics and at the same time had a lower production cost due to the use of less corn.

In future works, analyses of the composition of the smoke generated by the burning of this material should be carried out to verify the possible formation of undesirable compounds.

Acknowledgements

This work is financed by national funds through FCT - Fundação para a Ciência e a Tecnologia, I.P., under the Strategic Project with the references UIDB/04008/2020; and UIDP/04008/2020 and by Conselho Nacional de Desenvolvimento Científico e Tecnológico. Brazil (CNPq project n 303597/2018-6), CAPES and Fundação Araucária / Paraná.

References

Aliyu S., Bala M., 2011, Brewer's spent grain: A review of its potentials and applications. African Journal of Biotechnology, v. 10, n. 3, p. 324-331.

Carnaje N.P., Talagon R.B., Peralta J.P., Shah K., Paz-Ferreiro J., 2018, Development and characterisation of charcoal briquettes from water hyacinth (Eichhornia crassipes)-molasses blend, PLOS ONE, 13(11), e0207135.

CGEE - Centro de Gestão e Estudos Estratégicos, 2015, Modernização da Produção. Vegetal no Brasil: Subsídios Para Revisão do Plano Siderurgia, Centro de Gestão e Estudos Estratégicos, Brasília, Brasil. <https://www.cgee.org.br/documents/10195/734063/Carvao\_Vegetal\_ WEB\_02102015\_10225.PDF/a3cd6c7c-5b5b-450a-955b-2770e7d25f5c?version=1.3> acessed in 19/01/2022.

Fontes P.J.P., Quirino W.F., Pastore J.R.F., Filgueiras S.M.S., 1984, Aglutinante para briquetagem de carvão vegetal, Laboratório de Produtos Florestais, Departamento de Pesquisas, Instituto Brasileiro de Desenvolvimento Florestal, Brasília, Brasil, 1–5.

Gerd W., Acosta J.C., Elster C., 2017, Evaluation of uncertainties for CIELAB color coordinates. Color Research and Application, 42: 564-570

Gomes A.C.G., Lima M.C.P.M., Caliari M., D.G., Alves D.G., Machado A., Egea M.B., Martins K.R.B., 2019, Application of Pregelatinized Meal of Rice and Sorghum in the Preparation of Instant Soups: Centesimal Characterization, Technological, Microbiological and Sensory Quality, Current Nutrition and Food Science, v. 15, p. 10.2174/157340.

Martins M.P., Benício E.L., Dias Júnior A.F., Almeida R.B., Carvalho A.M., Yamaji F.M., 2016, Produção e avaliação de briquetes de finos de carvão vegetal compactados com resíduo celulósico proveniente da indústria de papel e celulose, Revista Árvore, v. 40, p. 173-180.

Mathias T.R.S., Mello P.P.M., Servulo E.F.C., 2014, Caracterização de resíduos cervejeiros, XX Congresso Brasileiro de Engenharia Química, Blucher Chemical Engineering Proceedings, v 1, Pages 3805-3812, ISSN 2359-1757T.

[Monteiro C.C.F.](https://www-scopus.ez79.periodicos.capes.gov.br/authid/detail.uri?authorId=56504764300), [Malavazi B.](https://www-scopus.ez79.periodicos.capes.gov.br/authid/detail.uri?authorId=57209271150), [Mendes M.P.](https://www-scopus.ez79.periodicos.capes.gov.br/authid/detail.uri?authorId=57194691136), [Paschoarelli L.C.](https://www-scopus.ez79.periodicos.capes.gov.br/authid/detail.uri?authorId=6507022094), [Clifford M.](https://www-scopus.ez79.periodicos.capes.gov.br/authid/detail.uri?authorId=7004955062), 2019, [Biomaterial based on brewing waste and vegetable resin: Characterization and application in product design](https://www-scopus.ez79.periodicos.capes.gov.br/record/display.uri?eid=2-s2.0-85067107771&origin=resultslist&sort=cp-f), [Chemical Engineering Transactions](https://www-scopus.ez79.periodicos.capes.gov.br/sourceid/19600161818?origin=resultslist), 75, pp. 475–480.

Mussatto S.I., Dragone G.R., Roberto I.C., 2006, Grãos gastos de cervejeiros: geração, características e aplicações potenciais, Journal of cereal Science, v. 43, n. 1, 1-14.

[Nakagawa A.](https://www-scopus.ez79.periodicos.capes.gov.br/authid/detail.uri?authorId=57209273161), [Mendes M.P.](https://www-scopus.ez79.periodicos.capes.gov.br/authid/detail.uri?authorId=57194691136), [Raniero G.Z.](https://www-scopus.ez79.periodicos.capes.gov.br/authid/detail.uri?authorId=57194688611), [Monteiro C.C.F.](https://www-scopus.ez79.periodicos.capes.gov.br/authid/detail.uri?authorId=56504764300), [Monteiro A.R.G.](https://www-scopus.ez79.periodicos.capes.gov.br/authid/detail.uri?authorId=24464461100), 2019, [The use of waxy starch and guar gum in total substitution of vegetable oil in extruded snack aromatisation](https://www-scopus.ez79.periodicos.capes.gov.br/record/display.uri?eid=2-s2.0-85067100631&origin=resultslist&sort=cp-f), [Chemical Engineering Transactions](https://www-scopus.ez79.periodicos.capes.gov.br/sourceid/19600161818?origin=resultslist),  75, pp. 283–288.

Rachwał K., Waśko A.., Gustaw K, Polak-Berecka M., 2020, Utilization of brewery wastes in food industry, PeerJ 8:e9427, https://doi.org/10.7717/peerj.9427.

Saletnik B., Bajcar M., Saletnik A., Zaguła G., Puchalski C., 2021, Effect of the Pyrolysis Process Applied to Waste Branches Biomass from Fruit Trees on the Calorific Value of the Biochar and Dust Explosivity, Energies, 14(16):4898. https://doi.org/10.3390/en14164898.

Somerville M., Jahanshahi S., 2015, The Effect of Temperature and Compression during Pyrolysis on the Density of Charcoal Made from Australian Eucalypt Wood, Renewable Energy, 80, 471-78.