Rice Husk as a Source for Lightweight Flameless Heat-Energy Carbon Briquettes

K. Zhumakhan¹,², Ye. Tileuberdi³*, M. Biysenbayev², Ye. Ongarbayev¹, K. Zhanbekov³, N. Godbert⁴*, K. Tastambek¹,⁵, C. Oliviero Rossi⁶

¹Al-Farabi Kazakh National University, 71, al-Farabi ave., Almaty, Kazakhstan
²LLP Scientific and Production center «Zhalyn», 11, Pavlodarskaya st., Almaty, Kazakhstan
³Abai Kazakh National Pedagogical University, 13, Dostyk ave., Almaty, Kazakhstan
⁴MAT_InLAB (Laboratorio di Materiali Molecolari Inorganici), Centro di Eccelenza CEMIFCAL, LASCAMM CR-INSTM della Calabria, Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, 87036 Arcavacata di Rende (CS), Italy
⁵M. Auezov South Kazakhstan University, 5, Tauke khan ave., Shymkent, Kazakhstan
⁶Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Cubo 14D, 87036, Arcavacata di Rende (CS), Italy

# These authors contributed to this work equally.

* E-mail: er.tileuberdi@gmail.com, nicolas.godbert@unical.it
Abstract

Herein we present a new method for producing fuel briquettes from rice husk, which can be used both individually or in combination. The designed briquettes are light-weighted and characterized by a flameless combustion that do not emit toxic substances during burning. These new briquettes were shaped from amorphous carbon obtained by carbonization of rice husks that was carried out in an inert atmosphere (N₂/Ar) at the temperature 450 °C, followed by desilication using caustic soda for 2 hours and demineralization using nitric acid for 2 hours. To the thus obtained raw material, carboxymethyl cellulose (CMC) used as biobinder was added to form the briquettes and bind the carbon-based materials. In order to obtain briquettes of suitable hardness for all purposes (ca. 30 MPa of briquette strength), 20% of biobinder was necessary. Oxygenating reagents (NaNO₃ and NH₄NO₃) were also added to ensure high performant briquette flameless combustion. Based on the fact that these briquettes are mainly carbon-based materials with the containing 70-90% and therefore are characterized with a rather light overall weight during 30-38 g.

Keywords: Activated carbon; rice husk; pores; fuel briquette; combustion; specific surface area.
1. Introduction

Global energy demand will be expected to double by the middle of the 21st century. This is due to the global economic growth, sustainable urbanization, as well as the increased demand for other energy-dependent services (mobility, shelter, heat, light, etc.). Among all energy sources, solid biomass is becoming a sustainable alternative towards the worldwide reduction of emitted CO$_2$.[1-2] Being plant-based, biomass has the advantage of releasing during combustion the amount of carbon dioxide the plant took from the atmosphere during its lifecycle, with the benefit of avoiding the emission of harmful secondary compounds usually released by the burning of coal and other fossil fuels. Furthermore, on an industrial point of view, the equipment designed for utilizing conventional fossil fuels can also be used for biomass, only requiring slight alterations and thus preventing significant investments in new apparatus and/or infrastructures.[3-6]

Millions of tons of crop waste materials are produced from agricultural and industrial processes every year,[7] and although they could be of use for fiber reinforcement of cementitious materials, their high tenacity, low bulk density and high transportation costs limit their use in this field, thus resulting most often in their final disposal through burning.[8]

The efficient recycling of agricultural waste would therefore be twofold: i) reduce the CO$_2$ emission during waste disposal, ii) allow a decrease in the continuous consumption of combustible fossil fuels. However, a major issue in recycling agricultural wastes, including waste materials such as rice husks, coffee husks, coconut husks, nut shells, and cotton stalks resides in the difficulty to store them, due to their low density, large volume and high humidity thus requiring the development of efficient solid biomass pretreatment processes. Several pretreatments methods
have been investigated in order to achieve high energy and high quality solid biofuels, that spam from densification technologies such as biomass pelleting and briquetting to torrefaction for the production of biochars and hydrothermal carbonization for the preparation of hydrochars.\[9\]

In this regard, briquetting is at the moment the most preferred method since it remains the easiest, highly reliable and more economic pathway to reduce the total volume of biomass by \textit{ca.} 90\% that is achieved through densification. For these reasons, biomass briquettes are already becoming a dominant source of cooking and heating energy for people in developing countries and accounts for about 14\% of total global energy use.\[1-3\] Indeed, the use of briquettes through compaction technology is one of the technologies in development for domestic heating and electricity production in China.\[10\] Briquette production processes include collection and transportation, drying, size reduction and densification. The compaction process mainly increases the bulk density, reduces processing and labor costs, improves thermal properties of agricultural waste, as well as combustion.\[11\] Compact waste in the form of briquettes can take different shapes and sizes, such as cylindrical or rectangular with a hole in the middle. A number of compaction systems are used in briquette production, including hydraulic piston presses, mechanical piston and frame presses, roller presses, hand presses, and screw extruders.\[9, 12-13\] A detailed review of energy briquette manufacturing processes and various associated briquetting machines was recently reported by Marrero \textit{et al.}, to which interesting readers are referred.\[14\] In most cases, briquettes are cylindrical in shape with a diameter ranging from 18 to 55 mm and a length from 10 up to 100 mm. Smaller sizes of cylindrical briquettes are typically from 3 to 27 mm in diameter and 3 to 31 mm in length.\[15-17\]
Thermochemical conversion technologies using briquettes include combustion, gasification and pyrolysis. However, combustion is the most developed and widely used process for such utilization due to its low costs and high reliability.18-19 Globally, briquette energy remains an important component of renewable energy. This is the achievement of sustainable energy for heat supply, reducing the impact on the environment, creating bioeconomies, reducing dependence on fossil fuels, improving the quality of life in rural and urban areas, and producing various biofuels.20-22

Therefore, improving briquette technology to meet the need for thermal energy in order to increase the combustion properties of energy briquettes and reduce the emission of greenhouse gases, nitrogen and sulfur gases during combustion is a key step that still requires to be developed. More specifically, the development of a briquette machine, a briquette plant, a biomass briquette plant for the production of agro-waste briquettes must be regarded as a highly relevant topic of nowadays research to offer sustainable solutions to reduce gas emission and long-term preserved the environment.23-24

Herein, carbon material obtained from the carbonization of rice husk was used for the production of energy briquettes. Desilication and demineralization steps allowed to obtain porous briquettes with high efficiency in oxidant absorption thus allowing the production of flameless, highly energetic and light weighted materials for easy to carry heating sources utilizable both indoors than outdoors.25-26 The briquettes prepared herein to be used as solid fuel and based on carbon and activated rice husk were obtained from 40-75 mass % of plant residues. These samples are lighter in weight and less smoky than the briquettes so far reported and reviewed above. The
proposed briquettes can be used for environmentally friendly heating of premises in domestic conditions, as well as for outside and portable cooking devices without impairing the organoleptic properties of food. Thus the proposed briquettes can also be used by a multitude of diverse users (from military units, explorers and tourists…) that are working in areas where a constant supply of fuel is needed and is usually highly difficult to access to.

2. Experimental section

2.1 Material preparation

Obtaining carbon materials from rice husks was carried out on a carbonization pilot. The production capacity of the designed pilot is 5 kg of carbon materials per hour, and its technological scheme is shown in Fig. 1. This unit is equipped with a reactor designed to operate continuously as a conveyor thanks to the rotation of the screw, which conveys the rice husks from the loading zone to the further heated carbonization chamber, allowing to collect at the end of the screw axis the carbonized rice husk.[27]
Fig. 1 Schematic version of the plant for obtaining carbon materials from rice husks.

To insure efficient thermal energy combustion, the thus produced carbon material was mechanically activated and crushed to 100 micron-size rubbles in a ball mill. To the resulting fine black powder was added Carboxymethyl cellulose (CMC), used as organic binder in order to form the desire briquettes. After mixing with the binder, small-sized briquettes (average dimension: h=5 cm, d= 4.5 cm, and 30-38 g in weight) were prepared in JC-70 vacuum extruder as shown in Fig. 2.
The small-sized briquette samples were activated at 850 °C in the CO₂ stream at atmospheric pressure and in a second step, were treated with NaOH and HNO₃ solutions to perform the desilication and demineralization processes respectively in order to obtain a rich carbon content and porous material. In particular, the desilication process was carried out by extraction process using caustic soda for 2 hours. The process of demineralization was carried out in a glass container within a tank that was equipped with a spiral electric heater connected to a current source. The top of the tank was equipped with a reflux condenser to avoid leakage of nitric acid fumes. The demineralization process includes the following steps: The sorbent was placed in a container
and poured with a mixture of a concentrated solution of nitric acid (3%) and the mixture was heated to boiling point for 4 hours and left to cool down overnight to insure complete demineralization; the remained acid solution was drained by decantation prior to transfer the sorbent in a new container to proceed to several washes with boiling distilled water loads until neutral pH was finally reached.

To further improve the efficiency of the produced carbon briquettes, NaNO\textsubscript{3} and NH\textsubscript{4}NO\textsubscript{3} were finally used as oxidizing components for their ability to release a large amount of oxygen during thermal decomposition. The oxidants were adsorbed under vacuum by immerging the carbon briquettes, used as adsorbent, in either a NaNO\textsubscript{3} aqueous solution or a NH\textsubscript{4}NO\textsubscript{3} aqueous solution (Fig. 3). The solutions were prepared by dissolving in 100 ml of distilled water either 5 g of NaNO\textsubscript{3} or 5 g of NH\textsubscript{4}NO\textsubscript{3}, and the briquette samples were immerged and placed in a vacuum dryer at a temperature of 150 °C for 2 hours. This process ensures overall good adsorption of the oxidants within the pores of the briquette samples. Finally, the samples were taken out and dried in a drying cabinet at a temperature of 150 °C for 2 hours.
2.2 Material characterization

The specific surface area, specific volume and pore size of the thus produced briquettes were determined by the 3H-2000PS1 automatic analyzer. The specific surface area was measured using the single-point and multi-point Brunauer-Emmett-Teller (BET) method, as well as the Langmuir method for low-temperature adsorption of liquid nitrogen. The elemental composition of the samples was determined by energy-dispersive spectroscopy on an EDAX ametek instrument, morphological structure of samples analyzed by Scanning Electron Microscope (SEM), and thermal decomposition of samples tested by Differential thermal analysis (DTA) and thermogravimetric analysis (TG).
3. Results and discussion

Small-sized briquettes bonded with organic binders were prepared by briquetting the mixture in a JC-70 vacuum extruder at a fixed minimum pressure of 100 MPa. The strength characteristics of the carbon briquettes were investigated by computerized electronic universal testing machine WDW-50E, and the results are reported in Table 1. Results clearly evidenced the role of the binder content onto the strength of the resulting briquette. First, without any biobinder, the carbon material remains under an agglomerated form, too brittle to stand on its own, so that no briquettes can be formed. With an increasing amount of binder, at the same operating pressing pressures, the briquettes become more resistant to compression and wear. In particular, when the content of biobinder was increased from 10 to 30%, the wear resistance increases from 7.2 to 7.9% at a compressive pressure of 100 MPa, and the compressive strength increased from 18.1 up to 79.2 MPa.

Table 1. Strength of small size briquettes

<table>
<thead>
<tr>
<th>Composition of the prepared briquettes, %</th>
<th>Briquette strength</th>
</tr>
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<tbody>
<tr>
<td>Carbon, %</td>
<td>Biobinder, %</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>
In order to obtain briquettes strong enough and of suitable hardness for all purposes (ca. 30 MPa of briquette compressive strength\[^{[20]}\]), a 20% w/w ratio of biobinder was necessary. This composition was consequently used thereafter for the production of all briquettes.

The elemental contents of the porous carbon material obtained from the dried rice husk by the isothermal carbonization process was compared with the elemental contents of the activated briquette (Table 2). The carbonization process was carried out by pyrolysis in an inert atmosphere (N\(_2\)/Ar) at the temperature 450 °C. The elemental contents of the sample shows that the material consists of 88.2% carbon (C) and 7.5% oxygen (O), as well as 4.3% of other elements including Si, K, Fe, Na and Mg.

Table 2. Characteristics of carbonized rice husk and activated briquettes.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Elemental composition, %</th>
<th>Specific surface area, m(^2)/g</th>
<th>Specific pore volume, cm(^3)/g</th>
<th>Pore size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonized rice husk</td>
<td>88,20 7,50 4,30</td>
<td>281,90</td>
<td>0,12</td>
<td>0,79</td>
</tr>
<tr>
<td>Activated briquette</td>
<td>91,06 7,04 1,90</td>
<td>514,50</td>
<td>0,23</td>
<td>0,75</td>
</tr>
</tbody>
</table>

Activation of small-sized briquettes was carried out using carbon dioxide at a temperature of 850 °C, with an activation time of 60 minutes under 0.01 l/min pressure of CO\(_2\). The set-up used
for this activation is reported in Fig. 4. The elemental contents of the sample shows that the material consists of 91.06 % carbon (C) and 7.04 % oxygen (O).

According to these data, the activation of the briquette does not have a high impact onto its chemical composition being almost identical both the content of carbon and oxygen before and after activation. Note that the total amount of other elements decreases down to 1.90 % after activation of briquette. This reduction can be rationalised in taking into account that most of these elements were settled on the surface of the briquettes, flying away as dusty powders during the activation process at high temperature. However, activation has a high impact onto the Specific surface as well as the specific pore volume. Indeed, both parameters are nearly twice their original values passing from 514.5 m²/g for the specific surface and 0.12 cm³/g for the specific pore volume for the activated briquettes with respect to 281.90 m²/g and 0.12 cm³/g respectively before activation. Noteworthy, the pore size remains almost identical. These results can be interpreted as an overall increase of the porosity of the material, mostly derived from the opening of the pores during activation. A deeper insight onto the morphological variations brought by activation is given by observation through SEM microscopy.
Morphological structure of carbonized rice husk and activated briquette were studied by scanning electron microscope (SEM) and representative images are presented in Fig. 5. Before activation (Fig. 5A and 5B), the sample shows a granular morphology made of assembled aggregates at low magnification while on a 5 micron scale, the cellulose walls dispersed in all aggregates are clearly visible (Fig. 5B). After activation, the structure of the briquette is more homogeneous. All aggregates have been fused creating an overall smooth, highly compact structure that still present large holes and depressions. At higher magnification, the complete absence of cellulose walls is clearly evident (Fig. 5D) as well as the overall increased of compacity of the material.
As a result of using CO$_2$ as an activating agent for the briquette activation process, carbon materials with characteristic porous structure, open surface morphology and texture were obtained as shown by SEM images (Fig. 5 C, D). The presence of macropores on the surface of the obtained materials ensures the transport of the adsorbent throughout the whole material, while the micropores identified through measurements of specific surface area, specific volume and pore size by porosimetry (Table 2) allow the insertion of the absorbent within the briquette. As adsorbent, NaNO$_3$ and NH$_4$NO$_3$ were used as oxidants for their known properties to promote flameless combustion of high heating power.
To study the kinetics ruling the combustion of the briquettes and to quantified the amount of absorbed oxidising agent, thermogravimetric analysis (TG) and Differential thermal analysis (DTA) were carried out under inert atmosphere. Samples were submitted to an increase of temperature at a scan rate of 10 °C/min. Due to the intrinsic nature of the compound, measurements were performed in triplicate to ensure reproducibility of the data. No significant deviations were observed between the repetition scans.

TG and DTA analyses were carried out to the activated briquette without adding oxidants. However, in this case, no signs of chemical decomposition or changes in energy difference were recorded.

After oxidation by NaNO₃ or NH₄NO₃ of the activated briquettes, the TG/DTA dramatically change their profiles. Indeed, thermal decomposition of absorbed oxidizing components initiates at 380 °C for oxidant NaNO₃ (Fig. 6A) and 400 °C for oxidant NH₄NO₃ (Fig. 6B) and goes through a continuous endothermic reaction until their complete decomposition which takes place in both cases at 420°C (considering the minimum reached on the DTA curves). Indeed, it is known that oxidant modified briquettes have the ability to release a large amount of oxygen during combustion. NaNO₃ or NH₄NO₃ oxidizers undergo a continuous endothermic reaction until complete thermal decomposition.
Fig. 6 Diagram of the thermal decomposition of a small-sized briquette with added oxidants NaNO$_3$ (A) and NH$_4$NO$_3$ (B) under inert atmosphere

Usually, when sodium nitrate is heated above 380°C, it decomposes with the release of oxygen and sodium nitrite:

$$2 \text{NaNO}_3 \rightarrow 2 \text{NaNO}_2 + \text{O}_2$$

Instead, thermal decomposition of ammonium nitrate can occur in different ways depending on the temperature, for example, at a temperature below 200 °C, the following chemical reaction occurs:

$$\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2 \text{H}_2\text{O}$$
while, it detonates at temperatures above 350 °C:

$$2 \text{NH}_4\text{NO}_3 \rightarrow 2 \text{N}_2 + 4 \text{H}_2\text{O} + \text{O}_2$$

Interestingly in both cases, the overall weight loss relative to the amount of oxidising agent is relatively low, of ca. 0.8% for the briquettes oxidised by NaNO₃ and 1.2% for briquettes oxidised by NH₄NO₃. Although the decomposition temperature of the two differently oxidised briquettes are identical (420°C), from the DTA curves (Fig. 6), it is clearly evidenced by the width of the registered peak that the decomposition process is slower in the case of NaNO₃ with respect to NH₄NO₃.

Analysis of the open air combustion of small-sized briquettes was carried out in a special set-up as shown in the Fig. 7. According to the experimental results, thermal decomposition of the oxidizing agent NaNO₃ and NH₄NO₃ takes place completely at about 400 °C. Therefore, the results of burning in a propane gas flame given at a speed of 200 l/min in a chamber for testing horizontal and vertical flammability for 30 seconds were considered. During combustion temperature was continuously monitored by placing a thermal probe within the core of the briquette.

![Fig. 7 open air combustion of heat-energy small-sized flameless carbon briquettes](image)
For the activated briquettes (Fig. 8, black line), the flame temperature was raised up to 305 °C in 5 minutes and complete burning takes place rapidly over a period of only ten minutes. For the briquettes oxidised by NaNO₃ (Fig. 8, red line), in the same conditions, the oxidised briquette still shows a rapid increase of temperature flame in the 5 first minutes however reaching much higher temperature of ca. 515°C. Nevertheless, combustion is still taking place and the temperature of the flameless combustion still increases at a slower rate for further 35 minutes reaching a maximum of 922°C. At this point, combustion still goes on for further 40 minutes accompanied by a slow and constant decrease of temperature over time.

![Graph showing temperature profiles](image)

**Fig. 8** Briquette combustion in open air: Temperature profiles as a function of time.
The temperature vs. time plots during combustion in air are reported in Fig. 8. Measurements were performed onto the activated briquettes before and after oxidation for direct comparison. Measurements were also performed in triplicate to insure reproducibility of the data, and no significant variations were observed between the repetitions.

Finally, the combustion of the briquette oxidised by NH$_4$NO$_3$ (Fig. 8, blue line), show a similar profile than that observed for the NaNO$_3$ oxidised briquette, with the differences that higher temperature is reached in the first five minutes (ca. 580°C), the maximum temperature is reached earlier (30 minutes after ignition) but reaching almost the same temperature maximum (913°C). The combustion continues over a longer period with respect to the NaNO$_3$ oxidised briquettes since the overall combustion in this case lasts for 90 minutes while after 80 minutes the NaNO$_3$ briquette was completely burnt. Mass changing of briquette samples before and after burning are presenting in table 3. The weight of the studied samples was between 30-37 g. The existence of this slight difference in mass can be reconducted to the conditions of cutting the briquette samples in the extruder and the drying processes during the addition of oxidizers to the briquettes. However, in any case, this variation does not have any adverse effect on the phenomena observed during combustion.
Table 3. Mass of briquette samples before and after burning.

<table>
<thead>
<tr>
<th></th>
<th>Briquette mass (g)</th>
<th>Ash mass after burning, (g)</th>
<th>Mass fraction of ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated briquette</td>
<td>37,3797</td>
<td>35,2902</td>
<td>94,4</td>
</tr>
<tr>
<td>NaNO₃ Oxidized briquette</td>
<td>34,5571</td>
<td>6,4220</td>
<td>17,5</td>
</tr>
<tr>
<td>NH₄NO₃ Oxidized briquette</td>
<td>30,9073</td>
<td>5,4450</td>
<td>18,5</td>
</tr>
</tbody>
</table>

Noteworthy, oxidation of the activated briquettes allows to neatly reduce the amount of residual ash after combustion. Indeed, the average mass of the briquettes produced is between 30-38 grams. The ash content of the briquettes without any additives was 94.4%, while for briquettes embedded with oxidizing agents (NaNO₃ and NH₄NO₃), the ash residue is drastically reduced. This must be attributed to the higher temperature combustion and longer burning time being both observed for the se briquettes. Consequently, the ash content for these latter ones drop down to 17-18%.

4. Conclusions

Herein we have developed a new method for the preparation of rice husk based flameless briquettes of high heating capacity. Carboxymethyl cellulose used as biobinder was employed to insure the compactness of the briquettes with a 20 % w/w amount ratio as optimised composition for binding to occur. The obtained briquettes are light weighted (maximum 40 g) and are characterised by the reaching of high combustion temperature over a long period of time. The best
performances were given by using NH₄NO₃ as absorbed oxidising agent. In this case, with only 1.2% in weight of oxidising agent, the maximum registered temperature of the briquette during combustion was 913°C, with a combustion taking place during 90 minutes. Noteworthy, already ca. 500°C are reached in the first 5 minutes of combustion. With such features and characteristics, we are confident that the results herein presented prove that production of solid fuel from recycling agricultural wastes can be achieved to produce briquettes with high energy value that could be employed to reduce worldwide CO₂ emission and therefore preserve the environment on a long term basis.

**Supporting information**

Available at

**Conflict of interest**

There are no conflicts to declare.

**Reference**


