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Valorisation of rice husks and bean straws through fuel pellets production: an experimental and modelling approach

Valorización de cascarilla de arroz y paja de frijol mediante la producción de pellets combustibles: un enfoque experimental y de modelado

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Abstract

Worldwide, some agricultural wastes represent an environmental problem due to their high volumes, slow degradation, and inadequate disposal. Due to this, the valorization of agricultural wastes has been reported in the literature, being the production of biofuels a promising option. In a previous study, rice husks were proposed to produce fuel pellets, but they did not fulfill the ISO 17225-6 standard due to its elevated ash content; thus, it remains as an opportunity area its mix with other wastes available in the same region. In Mexican states where rice is produced also bean is cultivated, whose residues are not used and have an elevated content of volatile solids. Therefore, the objective of this research is to produce fuel pellets from mixtures of rice husks and bean straws, with the objective of satisfying ISO 17225-6 standard. For this, the densification was carried out using three levels of moisture content and mixing ratios of the biomasses. Based on the experimental data, optimal densification conditions were found through a response surface analysis. Results show that fuel pellets produced from bean straw (90%) and rice husk (10%) with 15.0% of moisture content fulfill ISO 17225-6 standard. At these conditions, fuel pellets have calorific power of 3,645.78 kcal/kg, 6.98 ash, 9.76% final moisture, 610.78 kg/m^3 bulk density, and 99.51% durability.

Keywords: fuel pellets, biomass, waste valorisation, bean straw, rice husks.

Resumen

A nivel mundial, algunos residuos agrícolas constituyen un problema de contaminación debido a los altos volúmenes en los que son producidos, su lenta degradación, así como inadecuada disposición. Por ello, los esfuerzos de la comunidad científica se han centrado en su revalorización, siendo una alternativa promisoria su conversión hacia biocombustibles. En un trabajo previo, se estudió la producción de pellets combustibles de cascarilla de arroz; sin embargo, éstos no cumplían con las propiedades establecidas en la norma ISO 17225-6. Por ello, se requiere mezclar la cascarilla de arroz con otros residuos disponibles en la misma región. En los estados de México donde se produce arroz también se cultiva frijol, cuyos residuos no son utilizados y contienen altas cantidades de sólidos volátiles. Por ello, en este trabajo se propone la producción de pellets combustibles a partir de cáscara de arroz y paja de frijol, con el objetivo de satisfacer la norma ISO 17225-6. La densificación se realizó utilizando tres niveles de contenido de humedad y proporciones de mezcla de las biomasas. Con base en los datos experimentales, se optimizaron las condiciones de densificación mediante un análisis de superficie de respuesta. Así, los pellets combustibles elaborados con paja de frijol (90%) y cáscara de arroz (10%) con humedad del 15.0% cumplen con la norma ISO 17225-6 respecto del poder calorífico (3,645.78 kcal/kg), cenizas (6.98%), humedad (9.76%), densidad aparente (610.78 kg/m^3) y durabilidad (99.51%).

Palabras clave: pellets combustibles, biomasa, valorización de biomasas, paja de frijol, cascarilla de arroz.

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1 Introduction

In spite of variations in the oil price as well as changes in the commercial dynamic, most of the economic sectors had exhibited growth until 2019; this fact is supported on the constant increment of the worldwide growth domestic product until that year, in which a value of 87.608 trillion USD was reached (WB, 2021). However, this indicator drops to 84.705 trillion USD (WB, 2021) as consequence of the pandemic derived from the quick propagation of SARS-CoV-2. When the virus began to disseminated around the world social isolation measures were implemented, which changed consumption patterns, causing disturbs in the supply chains.

Therefore, the International Energy Agency, along with the World Bank, developed a Sustainable Recovery Plan in 2020 (IEA, 2021). In this plan, two scenarios are proposed: the quick scenario, where the 2019's productivity level is reached in 2021, and the late scenario, where those levels are reached in 2022 (IEA, 2021). The main difference between both scenarios is the investment in key sectors related with renewable energy, sustainable biofuels, energetic efficiency and low carbon technologies; moreover, the valorisation of residues is highlighted as a win-win situation, since the pollution problem due to its inadequate disposal is solved at the same time that value-added products and/or biofuels are produced. This work is focused on the valorisation of agricultural residues for the production of renewable fuels in México.

Agricultural residues are materials generated from the direct consumption of primary products or from their industrialization; these wastes are no longer useful for the process that generated them, but they are susceptible to be transformed to other products with economic value. Worldwide, agriculture produces the vast amount of residues every year, being many of them untreated and underutilized (Sadh *et al*., 2018). It is important to highlight that around 1.3 billion kg per year of biomass residues from different food crops are generated in the world (Martínez-Guido *et al*., 2021). In Mexico, in 2014, 75.73 million tons of dry matter were produced from 20 different food crops (Saval, 2012). However, recently, it has been reported the annual production of 1,673.03 million tons of residues just considering some edible crops (sugarcane, maize, sorghum, wheat and citrus) and forest activities (Tauro *et al*., 2018); this represents a significant increase of agricultural residues in México. Among the main agricultural products cultivated in Mexico, corn, beans, wheat, rice, sorghum, sugar cane and oilseeds stand out; some of these harvest residues are used as forage (SAGARPA, 2015), but most of them has not use. It is important to mention that the scientific community has focused their efforts in the development of revaluation of agricultural wastes; for this, the use of these wastes has been proposed for removal of metals from effluents (Romero-González *et al*., 2007; Salazar-Pinto *et al*., 2020), and substrates for fungus cultivation (Vargas-Solano *et al*., 2021). In spite that these proposals are not in the industrial implementation step, they constituted a solid base to achieve it.

In particular, the residues of rice production represent an opportunity area, due to the amounts in which are generated. In 2020, 276,386 tons of rice were produced in Mexico (SIAP, 2021); nevertheless, according to the Secretariat of Agriculture and Rural Development the rice production will increase in 15% at the end of 2021 (SADER, 2021). The increasing in rice production is of great relevance for México, since it is one of the main agricultural products. With the increasing in rice production, the residues will also grow; in particular, the rice husk constitutes approximately 20% by weight of the grain (Sierra Aguilar, 2010). According to Goodman (2020), only ~20% of rice straw is used for practical purposes, such as production of construction materials, paper, fertilizers and animal feed. Nevertheless, in most Asian countries, farmers resort to open burning, resulting in severe air pollution, and soil degradation, due to its hard degradation, high silica contents, and low specific weight (Khan, 2015; Shukla *et al*., 2022). In particular, the burning releases harmful gases like carbon monoxide (CO), polycyclic aromatic hydrocarbons, volatile organic compounds, nitrous oxides (NO), suspended particulate matter, which contributes to global greenhouse gases (Sharma *et al*., 2020). However, rice husk contains about 75% organic volatile matter, which imply a good biomass reactivity (Khan *et al*., 2012); thus, the use of these agricultural residues to produce fuel pellets can transform a problem into an opportunity, and new forms of bioenergy can be generated (Pradhan *et al*., 2018). However, one of the main disadvantages of the direct use of agricultural wastes as fuel is its low physical and energy density. For this reason, the densification process is of great importance in the use of wastes as a raw material for the production of biofuels, in particular fuel pellets (Arias Ortíz and

Meneses Cruz, 2016).

Fuel pellets are the most popular solid biofuels, since they have a high potential to meet the energy requirements associated with population growth; these type of solid biofuels can be used to generate electricity and/or heat that can be utilized in domestic kitchens, boilers and power plants (Torres, 2008; Castellano *et al*., 2015). According to standard ISO 17225-6, fuel pellets are defined as densified biofuel made from grinded or milled biomass with or without additives and unitized as cylinders, usually diameter < 25 mm, random length and typically 3.15 mm to 40 mm with broken ends, obtained by mechanical compression (ISO, 2021). The densification of biomass into a pellet decreases its humidity content, improves its calorific value, facilitates storage and handling during distribution (Kusumaningrum and Sofyan-Munawar, 2014), and reduce CO_2 emissions (Nishiguchi and Tabata, 2016). Fuel pellets can be produced with residues derived from agricultural, forestry and industrial activities. In particular, agricultural wastes represent a promising raw material to produce fuel pellets since they contain lignin, which act as a binder during the densification process; in addition, these wastes have high carbon contents, which is directly related to the calorific power.

The production of fuel pellets from agricultural waste has attracted the attention of the scientific community. Several studies have been conducted of the effects of raw material composition and pelletization conditions on the properties of fuel pellets. Regard the raw materials, it has been reported the use of different types of woody and non-woody biomass to produce fuel pellets (Berastegui *et al*., 2017). Among these biomasses it can be listed corn stubble, wheat straw, sorghum stalk (Theerarattananoon *et al*., 2011), tomato crop residues (Celma *et al*., 2012), mix of potato pulp with wheat husks (Obidziński, 2014), coffee residues (Aguas and Villarreal, 2016), corn stover (Tumuluru *et al*., 2020), coffee residues with pine sawdust (Jeguirim *et al*., 2014), and wood (Tumuluru *et al*., 2016), among others. Regard the variables involved in the pelletization process, the most studied are moisture content and particle size of the biomass, as well as the temperature and pressure of the densification (Stelte *et al*., 2011). It is important to mention that the production of fuel pellets from agricultural wastes will generate a new product that can be commercialized by farmers. Thus, additional incomes can be obtained, improving the profitability of the crop production. In particular, some studies are reported for the use of waste from rice crops for the production of fuel pellets.

Rice straw pellets are the main type of solid biomass fuels, and they are currently used as a bioenergy resource in many countries, mainly in China (Shan *et al*., 2016). In 2014, Ishii and Furuichi reported the influence of operating parameters on the quality of rice straw pellets. They found that rice straw pellets achieved calorific power of 12 MJ/kg, with durability major than 95%. Said *et al* (2015) studied the quality of fuel pellets made from rice straw using starch as an additive. According to its results, the best durability was 99.31%, which was obtained with biomass with 17% of moisture content. However, the combustion of these pellets showed significant problems, due to their high ash content (around 16%) and low calorific value (around 3,400 kcal/kg), which reduces the possibility of being used in domestic heating (Ríos-Badrán *et al*., 2020). Later, Chen *et al* (2022) reported the effect of torrefaction on the quality of rice husk and rice straws. Based on their results, the calorific power of the rice straws (1236.84 kg/m^3) and rice husks (1277.50 kg/m^3) were improved as result of the pretreatment. Subsequent studies reported that mixing of different types of biomass materials was very useful to improve the properties of the pellets from non-compatible feedstocks (Pradhan *et al*., 2018). A mixture of bamboo and rice straw was used to improve the properties of the rice straw fuel pellets (Liu *et al*., 2013); in that study, the aim was to optimize the proportions of rice husk and bamboo to achieve the highest calorific value of the fuel pellets. It was found that the pellets manufactured with a mixing ratio (3:2) of bamboo and rice straw, contained less than 8.0% moisture and a calorific value greater than 17,500 J/g (4,182.60 kcal/kg). In other study, Iftikhar *et al* (2019) proposed the use of crow dung to improve quality properties of fuel pellets produced with mixtures of wheat straw and rice husk. Based on their results, the calorific power increase to 19.13 MJ/kg, and the ash content was reduced in 52%, respect to the fuel pellets produced with mixtures of wheat straw and rice husk. In the same line, Fadimatou *et al*. (2021) reported the use of arabic gum to improve the quality of rice husk pellets. The results exhibited a higher calorific power of 18.79 MJ/kg with a water content of 7.97%. Moreover, Brand *et al*. (2021) performed a study to analysis the quality of pellets produced with different blends containing rice husk, rice straw, rice husk ash, and *Pinus spp*. shavings. They found that the blends affect the moisture content for densification, but they do not have an impact on mechanical durability. In particular, the inclusion of rice straw improves the physical properties of the fuel pellets, while its calorific power is improved with the use of *Pinus spp*. shavings. Thus, the mix of different biomass materials is an effective way to optimize the properties of solid biomass fuels.

In Mexico, just one study for the production of fuel pellets made from rice husk as well as a mixture of rice husks and wheat straw was carried out. Those results suggested that the mixture of these biomasses improve the quality and combustion characteristics of the pellets when a mixture is used in a 50:50 ratios with 21% of moisture content, obtaining pellets with a calorific value of 15.44 MJ/kg (3,688.26 kcal/kg) (Ríos-Badrán *et al*., 2021). However, in the Mexican states where rice is cultivated low or none wheat is produced. This implies that in order to implement this solution wheat straw must be transported for long distances, which could make unviable this valorisation strategy since the establishment of local or regional supply chains is desirable (Martínez-Guido *et al*., 2019; Martínez-Guido *et al*., 2021).

Therefore, it is necessary to analyze other raw materials that can be mixed with rice husks, in order to use them for the production of a fuel pellets, which can be utilized in the same rice production or commercialized; this will improve the profitability of rice production, through the revaluation of this waste, at the same time that a pollution problem is solved. Another important aspect is that the potential biomasses to be mixed must be cultivated in the same region or state, in order to avoid its transportation for long distances (Martínez-Guido *et al*., 2019; Martínez-Guido *et al*., 2021). According to the Agri-food and Fisheries Information Service (SIAP, 2021), the Mexican states where rice is cultivated are Campeche, Chiapas, Colima, Guerrero, Jalisco, México state, Michoacán, Morelos, Nayarit, Tabasco, Tamaulipas and Veracruz. In these states, other crops are produced; among them, the bean crop highlights. It is important to mention that beans are the second agricultural product cultivated in México. So, elevated amounts of this residue are available without a value-added used; as reference, the bean production was 228,322 tons per year, considering only the states of Campeche, Chiapas, Colima, Guerrero, Jalisco, Mexico state, Michoacán, Morelos, Nayarit, Tabasco, Tamaulipas and Veracruz (SIAP, 2021). It has been reported that the bean straw contains high carbon content, high volatile matter content, and low ash content (Villa Gomez *et al*., 2020). Indeed, Okot *et al*. (2019) reported the production of briquettes considering bean straw and well as mixtures of bean straw with maize cob. According to the authors, bean straw briquettes of high quality are achieved at low pressures and large particle sizes. Thus, considering these properties of bean straw, the mix of rice husks and bean straw can be useful to generate fuel pellets that satisfy the standard ISO 17225-6; this mix will allow to utilize these residues widely produced in México to produce bioenergy and solve the associated pollution problem.

Therefore, the production and characterization of fuel pellets from rice husks and bean straw is proposed in this work. In order to achieve this objective, the proportion of biomasses was determined as well as the moisture content that allows obtaining fuel pellets that comply with the standard ISO-17225-6 (ISO, 2021); for this, experimental and modelling of response surface analysis has been performed. The article is organized as follows. Section 2 presents the material and methods used for the experimentation tests, and well as the modelling derived from those data. Later, the obtained results are discussed in Section 3, while the conclusions are given in Section 4.

2 Methodology

2.1 Experimental methodology

2.1.1 Collection of biomass

According to Mexican Government (2019), the rice and bean production was 226,000 ton and 1.1 million tons, respectively. These crops along with corn and wheat are the four main basic grains produced in México. The rice husk was collected in the municipality of Ezequiel Montes, Querétaro (20° 39’ 48” North, 99° 53’ 54” West), while the bean straw was obtained in the municipality of El Carmen, Hidalgo (20°22’31”N 99°39’02”W); the specific production of these crops in these states is not available, mainly because the producers are dispersed and the production areas are small and medium. Both residues were generated in the cultivation of 2019, and were collected around 50 kg of each biomass directly from the producer; so, there is no information about the time that the biomass stayed in the field or it was stored. The biomasses were processed as soon as they arrived at the laboratory.

2.1.2 Biomasses characterization

The characterization of the biomasses includes the determination of the proximal analysis (water, ash and volatile matter content), elemental analysis (carbon, nitrogen content), as well as the measurement of the calorific value and the moisture content. It is important to mention that the biomasses were characterized after they were crushed. Next, information about each determination will be provided.

Regard the proximal analysis, the moisture content was determined using the reported Hach method (AOAC, 2002). In this method, the samples are heated at 100 °C for 2-4 h until constant weight of the biomass is reached. The loss weight is reported as moisture content. On the other hand, the ASTM D 1102-84 method was used to obtain the ash content (ASTM, 2007); for this, the samples are heated at 800 °C for 10 h to achieve calcination, and once cooled down, the samples weight is reported as ash content. The volatile matter content was determined with the reported Hach method (Hach, 2015); for this, the samples are heated at 550 °C, measuring each 30 min the samples weight until samples weight is constant. For the elemental analysis, the carbon content was calculated by the loss on ignition method (Tabatabai, 1996), which consisted on the calcination of the sample at 375 °C by 16 h. Total nitrogen was determined using the Kjeldahl technique from Hach (Method 8075), through digestion to determine the amount of generated nitrogen compounds by spectrophotometry (HACH DR6000) at 460 nm wavelenght (Hach, 2015). On the other hand, for the determination of the calorific value, approximately 1 g of ground and sieved sample of each biomass was weighed in order to generate a tablet through the use of a manual press (Parr 2811). The tablets obtained, as well as the fuel pellets from each treatment, were introduced into the isoperibolic calorimeter Parr 6200 where combustion begins until the value of the calorific value is obtained (NOM, 1976).

2.1.3 Production of fuel pellets

Before the densification, both biomasses were grinded to reduce the particle size. Subsequently, an ALCON sieve with an opening of 0.42 mm was used to homogenize the size of the samples. In order to obtain the pellets, the raw materials were mixed until a homogeneous texture was obtained; then, with the help of the hygrometer smart sensor, model AR991, the moisture content of each treatment was measured and the pellets were densified. The pellets were produced on a roller pelletizer with a Magne Tek 5 HP motor with an 8 mm diameter die. It is important to mention that the pelletizer machine performs the densification but the pressure and temperature cannot be adjusted, the fuel pellets obtained were stored in resealable bags, and they were characterized according to the analyses described in subsection 2.1.2. In addition, the determination of the diameter and length of the fuel pellets was carried out using a Mitutoyo digital 200 mm vernier. To determine the mechanical durability, the ASTM D3038-93 (ASTM, 2004) standard was used with slight modifications, which are described next. The weight of the fuel pellet was measured; later, the fuel pellet was dropped from a 1.85 m height. As result, the fuel pellet is fractionated, and the weight of all the pieces was recorded; the major weight is considered the final pellet weight. Finally, the impact resistance is calculated by the difference in the weights of the fuel pellet before and after the impact. The individual density was determined by measuring the mass and volume of one pellet; for this, the diameter and length were measured with a Mitutoyo digital 200 mm vernier, and the weight of the fuel pellet was determined with a balance Precisa model 321. The bulk density is calculated by determining the mass of the pellets that a container of known volume contains; its units can be kg/m^3.

In order to find the optimal conditions to densify the raw materials, it was proposed an experiment design of two factors, each one with three levels as follows. The first factor is moisture content with three levels: 10%, 15% and 20%. The second factor is the biomass proportion (rice husks:bean straws) with three levels: (75:25), (50:50), (25:75).

2.1.4 Statistical analysis

All the experiments were realized by triplicate; the results are expressed as means ± standard deviation. The JMP v.8.0 software and the Tukey-Kramer test were used to identify significant differences between samples. The significance level was set at $p<0.05$.

2.2 Modelling of response surface

With the data generated from the experimental design, the JMP Software was used to perform the response surface analysis. Based on the results of the characterization, the analysis was carried out considering the variables that do not comply with the parameters established in the standard. In order to obtain the model of the response surface, a limit between 10-15% of moisture content and a biomass mixture with 0-40% bean straw were specified.

Based on the optimal conditions, it was performed an analysis considering the rice and bean production in the Mexican states of Campeche, Chiapas, Colima, Guerrero, Jalisco, México state, Michoacán, Morelos, Nayarit, Tabasco, Tamaulipas and Veracruz (SIAP, 2021). Considering the crop production, the wastes were estimated as well as the potential energy produced.

3 Results and discussion

In this section, the discussion of the obtained results will be presented. First, the characterization of the rice husks, Figure 1, and bean straws, Figure 2, is presented. Later, the characterization of the produced pellets is described, along with an analysis of the fulfillment of its properties according to standard ISO 17225-6 (ISO, 2021). Finally, with the experimental data the response surface is showed, allowing the identification of moisture content and biomasses mixture proportion that satisfy the standard ISO17225-6 (ISO, 2021).

Figure 1. Rice husks.

Table 1. Results of the characterization of rice husk and bean straw.

	Rice husk	Bean straw
% Moisture	5.58±0.11	6.45±0.14
% Ashes	18.99±0.12	6.59±0.21
% Volatile matter	74.42±0.05	86.18±0.09
% Carbon	46.93±0.03	54.27±0.02
% Total nitrogen	0.41±0.03	0.57±0.04
Calorific power (MJ/kg)	13.51±0.99	16.89±0.26

Figure 2. Bean straws.

3.1 *Characterization of the biomass*

The results obtained from the characterization of the rice husk and bean straw residues are presented in Table 1. From Table 1, it can be seen that the low moisture determined in rice husk and bean straw with 5.58% and 6.45%, respectively, reveals that the fuel pellets will have a rapid combustion; so, its calorific value will be high, since not so much energy will be wasted in the evaporation of the water. The ash content is another important variable, since it represents all the material that is not burned; a greater quantity of ash in the biomass negatively affects the calorific value. In this work, the rice husk showed a high ash content (18.99%), unlike the bean straw where a value of 6.59% was obtained; therefore, the mixture of both biomasses in the production of fuel pellets would increase the potential of the rice husk to be used as a raw material to produce solid biofuels. On the other hand, the volatile matter content is of vital importance in the combustion rate; the values for this variable were 74.42% and 86.18% for rice husk and bean straw, respectively, which shows that they burn very easily. Carbon content indicates the mass remaining after the release of volatile compounds, excluding ash and moisture. The carbon content in rice husk was 46.93%, while for bean straw it was 54.27%; these values are similar to those previously described in the literature, where 50.9% is reported in the carbon content of wood residues such as pine (Kijo-Kleczkowska *et al*., 2016), and 47.71% in bamboo (Liu *et al*., 2014). Moreover, a high nitrogen content is not desirable since NOx emissions would occur; these emissions are of great concern for environmental measures. The total nitrogen content in rice husk was 0.41%, while the nitrogen content in bean straw was 0.57%. Finally, the calorific power is the amount of energy, in the form of heat, that the pellet can release per unit of mass from its combustion or burning. In reported works, values of 16.1 MJ/kg have been obtained for olive fruit branches, 15.4 MJ/kg for orange fruit branches (Fernández-Puratich *et al*., 2014), 13-16 MJ/kg for cocoa husks, and corn stalks with a calorific value of 13-15 MJ/kg (Núñez *et al*., 2012). The results obtained for rice husks and bean straw were 13.51 and 16.89 MJ/kg, indicating that these are a potential source of energy.

3.2 *Production and characterization of fuel pellets*

The results of the determination of the chemical, physical and energy tests for the characterization of pellets with initial moisture content of 10%, 15% and 20% are presented in Tables 2, 3 and 4, respectively. In each table, there are included the three proportions of biomasses, as well as the referenced values established in the standard ISO 17225-6 (ISO, 2021). It is important to mention that ISO 17225 determines the quality classes and technical specifications of solid biofuels produced from herbaceous biomass, fruit biomass, aquatic biomass, biomass blends and mixtures (ISO, 2021). Moreover, ISO 17225 provides classification principles for solid biofuels, which allows efficient trading of biofuels, good understanding between seller and buyer, as well as a tool for communication with equipment manufacturers (ISO, 2021). Hence, compliance with the standard is of great importance.

From these tables it can be observed that regard the volatile matter content, this showed significant statistical differences between the different mixing ratios. The content of volatile material in the samples was higher for those treatments with higher bean straw content. Although there is no comparison parameter in the standard, it is known that volatile matter participates in the biomass combustion process, directly affecting yield and physical stability (Tauro *et al*., 2018). Moreover, it can be observed that the fuel pellets made with 25% rice husk and 75% bean straw exhibited a higher content of volatile matter, total carbon and nitrogen compared to the other treatments; this is consistent for all the moisture content values. On the other hand, fuel pellets with 75% rice husk and 25% bean straw exhibited high ash values, due to the silica content from the rice husk; this is also consistent for all the moisture values.

Respect the final moisture content there were significant statistical differences between the different initial moisture contents, while there were no significant differences between the different mixing proportions; here, initial moisture content is referred to that contained in the biomass previous to its densification. The average values for fuel pellets with an initial moisture of 10% and 15% were 7.76% and 9.98%, respectively.

Table 2. Proximal, elemental and energetic characterization of rice husk and bean straw pellets with an initial moisture content of 10%.

Proportion rice husks: bean straw	**75:25:00**	**50:50:00**	**25:75**	**ISO 177225-6 (ISO, 2021)**
Proximal and elemental characterization				
Moisture (%)	7.76±0.65^a	7.45±0.51^a	8.07±0.84^a	≤10
Volatile matter (%)	75.06±0.58^c	81.31±0.87^b	86.14±1.03^a	-
Ashes (%)	16.05±0.90^a	12.99±0.26^b	10.94±0.32^c	≤7
TOC (%)	42.50±0.65^c	45.26±0.09^b	46.86±0.05^a	-
TNC (%)	0.45±0.01^c	0.49±0.01^b	0.54±0.01^a	≤0.7
Energetic characterization				
Calorific power (MJ/kg)	14.36±0.08^a	14.48±0.47^a	14.57±0.10^a	≥14.5
Physical determinations				
Diameter (mm)	8.05±0.03^a	8.01±0.03^a	7.91±0.19^a	6-8
Length (mm)	15.03±1.59^a	14.38±2.82^a	11.84±1.43^a	15-40
Individual density (g/cm^3)	0.80±0.03^a	0.89±0.08^a	0.76±0.04^a	-
Bulk density (kg/m^3)	625.28±5.91^a	621.33±3.53^a	622.73±9.63^a	≥600
Durability (%)	66.87±4.75^b	79.43±6.32^a	71.68±4.14^b	≥97.5

The values are expressed as means ± SD of two independent experiments. Different letters express significant differences (p<0.05) by row using Tukey-Kramer's Test. TOC: total organic carbon; TNC: Total nitrogen content.

Table 3. Proximal, elemental and energetic characterization of rice husk and bean straw pellets with an initial moisture content of 15%.

Proportion rice husks: bean straw	**75:25:00**	**50:50:00**	**25:75**	**ISO 177225-6 (ISO, 2021)**
Proximal and elemental characterization				
Moisture (%)	9.66±0.59^{a}	10.3±0.76^{a}	9.98±0.65^{a}	≤10
Volatile matter (%)	77.12±0.92^{c}	79.14±0.63^{b}	83.00±0.30^{a}	-
Ashes (%)	16.08±0.32^{a}	12.85±0.15^{b}	9.78±0.29^{c}	≤7
TOC (%)	42.76±0.04^{c}	45.08±0.09^{b}	47.24±0.69^{a}	-
TNC (%)	0.47±0.01^{b}	0.50±0.01^{ab}	0.51±0.01^{a}	≤0.7
Energetic characterization				
Calorific power (MJ/kg)	14.08±0.28^{a}	13.91±0.25^{a}	14.07±50.20^{a}	≥14.5
Physical determinations				
Diameter (mm)	8.01±0.01^{a}	7.99±0.04^{a}	7.97±0.11^{a}	6-8
Length (mm)	24.59±0.67^{a}	25.04±0.78^{a}	24.12±1.59^{a}	15-40
Individual density (g/cm^3)	1.15±0.07^{a}	1.21±0.05^{a}	1.18±0.03^{a}	-
Bulk density (kg/m^3)	610.14±3.70^{a}	610.10±5.35^{a}	613.27±4.09^{a}	≥600
Durability (%)	99.53±0.41^{a}	99.74±0.08^{a}	99.75±0.05^{a}	≥97.5

The values are expressed as means ± SD of two independent experiments. Different letters express significant differences (p<0.05) by row using Tukey-Kramer's Test. TOC: total organic carbon; TNC: Total nitrogen content.

Table 4. Proximal, elemental and energetic characterization of rice husk and bean straw pellets with an initial moisture content of 20%.

Proportion rice husks: bean straw	**75:25:00**	**50:50:00**	**25:75**	**ISO 177225-6 (ISO, 2021)**
Proximal and elemental characterization				
Moisture (%)	12.43±0.56^{a}	14.02±0.87^{a}	13.60±1.14^{a}	≤10
Volatile matter (%)	76.12±3.03^{b}	81.01±0.58^{a}	85.02±0.42^{a}	-
Ashes (%)	16.54±0.36^{a}	12.39±0.38^{b}	8.79±0.14^{c}	≤7
TOC (%)	42.37±0.38^{c}	45.85±0.02^{b}	48.08±0.64^{a}	-
TNC (%)	0.44±0.01^{b}	0.49± 0.01^{a}	0.52±0.01^{a}	≤0.7
Energetic characterization				
Calorific power (MJ/kg)	12.89±0.17^{a}	12.63±0.01^{a}	12.41±0.29^{b}	≥14.5
Physical determinations				
Diameter (mm)	8.02±0.06^{a}	8.06±0.01^{a}	8.00±0.02^{a}	6-8
Length (mm)	26.56±2.57^{a}	25.65±2.10^{a}	24.75±1.59^{a}	15-40
Individual density (g/cm^3)	1.24±0.06^{a}	1.26±0.04^{a}	1.24 ±0.03^{a}	-
Bulk density (kg/m^3)	577.99±6.22b	588.37±7.99ab	600.54±6.19a	≥600
Durability (%)	99.91±0.08^{a}	99.74±0.12^{a}	99.55±0.04^{a}	≥97.5

The values are expressed as means ± SD of two independent experiments. Different letters express significant differences (p<0.05) by row using Tukey-Kramer's Test. TOC: total organic carbon; TNC: Total nitrogen content

The fuel pellets obtained showed moisture contents of less than 10%, as indicated by the standard ISO 177225-6 (ISO, 2021), while the fuel pellets made with initial moisture of 20% have moisture content above the standard.

On the other hand, the ash content showed statistically significant differences between the different proportions of biomass in the mixture. The standard ISO 17225-6 (ISO, 2021) specifies a maximum ash content of 7.0% for class A and 10.0% for class B. The ash content of the samples is less than 10% in pellets with 75% of bean straw. The values suggest that they can be classified within class B for this mixing ratio.

It is also observed that there are significant differences in the carbon content between treatments of different proportions of biomass. Pellets made from rice husks and bean straw in a 25:75 ratio showed a higher carbon content; although this parameter is not established in the standard it is important, since high fixed carbon contents are associated with high calorific power (Forero-Nuñez *et al*., 2015). Regard the nitrogen content, significant differences are also observed between treatments of different biomass proportions. The standard ISO 17225-6 (ISO, 2021) specifies a content ≤ 0.7, so the different treatments are within the established.

The calorific power showed statistical differences between the different moistures percentages used, while there were no statistical differences between the different mixtures. It is observed that an increase in the amount of initial moisture in the biomass cause a reduction in the calorific value, due to the fact that having high moisture values would imply that part of the heat is initially consumed in the evaporation of water; so, the fuel pellets with an initial humidity of 20% exhibited the lowest energy content. The standard ISO 17225-6 (ISO, 2021) indicates ≥ 14.5 MJ/kg, which means that only treatment with 25% rice husk and initial moisture of 10.0% was within the established with a value of 14.57 MJ/kg.

Regarding the physical analyzes, it is observed that there were no statistical differences between the different proportions of mixtures. The standard specifications regarding the diameter is 6-8 mm; so, the values for all treatments are close to the upper value established. Concerning the length, values are observed in a range of 23.01 mm to 28.05 mm for the different treatments with 15% and 20% moisture, respectively; both treatments complying with the specifications of the standard ISO 17225-6 (ISO, 2021), which determines lengths between 15 mm and 40 mm. For moistures of 10%, an average value of 14.65 mm was determined; so, it does not comply with what is established.

It is observed that when increasing the moisture content of the pellets there is a higher individual density, which is explained by the presence of water, since it has a higher density than dry biomass; then, the greater the amount of water in the pellet, the greater its unit density (Harun and Afzal, 2016).

On the other hand, the standard ISO 17225-6 (ISO, 2021) specifies that the bulk density must be at least 600 kg/m^3; thus, treatments with 10% and 15% initial moisture are within the standard with 623.11 kg/m^3 and 610.17 kg/m^3, respectively. It is shown that at high moisture content values, the bulk density of the fuel pellets decreases; for instance, with a moisture content of 20.0%, lower bulk densities were obtained with an average value of 588.97 kg/m^3.

Figure 3. Fuel pellets obtained with 15% of moisture content, 25% of rice husk and 75% of bean straws.

Finally, the standard ISO 17225-6 (ISO, 2021) specifies that the mechanical durability must be ≥ 97.5. The average durability for treatments with 15% and 20% moisture was 99.67 and 99.73, respectively; so, both treatments are within the standard. Figure 3 shows the fuel pellets obtained with 15% of moisture content, 25% of rice husk and 75% of bean straws.

As it can be observed, the biomass properties affect the quality of the produced biofuel. The calorific power depends mainly on the amount of fixed carbon, as well as the volatile material present in biomass; that is, at higher values of fixed carbon and volatile material it can be expected a higher calorific power (Rodríguez-Romero *et al*., 2022). However, a high content of volatile matter does not guarantee a high calorific power, since some components of the volatile matter are transformed into non-combustible gases (CO_2 and H_2O) (Özyuğuran and Yaman, 2017). On the other hand, the ash content affects negatively to calorific power; the higher the ash content, the lower the calorific power (Rodríguez-Romero *et al*., 2022). Moreover, ash content could cause fouling, slagging and corrosion inside the combustion equipment (ISO, 2021); due to this, the ash content must be as minimum as possible. It is important to mention that a high ash content depends on many factors, such as composition of the biomass, characteristics of the soil where it is cultivated, biomass contamination during handling, storage and transportation, the use of inorganic additives, or their processing by chemical treatments (Vassilev *et al*., 2010). Therefore, the analysis of these variables as well as the fulfillment of

ISO 17225 standard is important to achieve the quality of fuel pellets; in this way, fuel pellets can be used in specially designed appliances for residential, small commercial and public buildings as well as industrial energy generation applications (ISO, 2021).

3.3 Modelling of response surface

The modelling of the response surface was carried out mainly of ash and calorific value, since these variables showed values outside the established according to the standard. It was determined that the use of raw material with 14-15% of initial humidity and a mixture of biomass with 90% bean straw and 10% rice husk would allow to obtain pellets with a calorific value of 3,645.78 kcal/kg (15.25 MJ/kg), 6.98-7% ash, 9.76% final moisture, 610.78 kg/m^3 bulk density, and 99.51% durability. The rest of the parameters evaluated in the standard will be met; these parameters are length, diameter, and nitrogen content. The percentage of volatile matter and carbon are similar to those reported for other study biomass. The response surface model shown in Figure 4 was obtained. The compliance with the ISO 17225-6 standard is important to the commercialization of the fuel pellets; otherwise, the quality of the fuel products can cause malfunctions in the devices where they are used.

Equations 1 and 2 show the mathematical model obtained for the prediction of calorific power and ash content, respectively:

$$\begin{aligned}
&13.8153471412412 - 0.9723858509723 \times \frac{\text{Rice husk (\%)} - 50}{50} - 0.5516671525528 \times \frac{\text{Moisture content} - 10}{10} \\
&+ \left(\frac{\text{Rice husk (\%)} - 50}{50}\right) \times \left[\left(\frac{\text{Moisture content} - 10}{10}\right) \times 0.3826329239873\right] \\
&+ \left(\frac{\text{Rice husk (\%)} - 50}{50}\right) \times \left[\left(\frac{\text{Rice husk (\%)} - 50}{50}\right) \times 1.95553496046862\right] \\
&+ \left(\frac{\text{Moisture content} - 10}{10}\right) \times \left[\left(\frac{\text{Moisture content} - 10}{10}\right) \times (-1.0916644218739)\right]
\end{aligned} \tag{1}$$

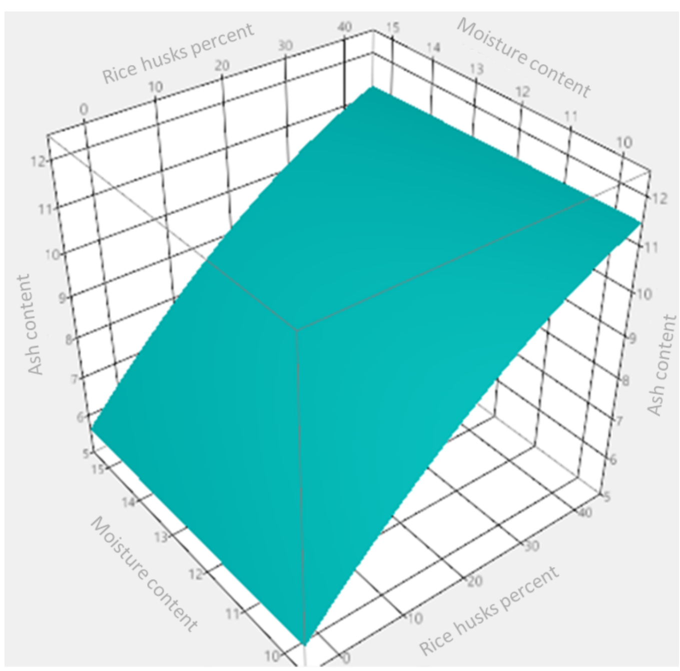

Figure 4. Response surface design.

$$13.557516983986 + 6.2396108073604 \times \left(\frac{\text{Rice husk (\%)} - 50}{50}\right) - 0.9882242804807 \times \left(\frac{\text{Moisture content} - 10}{10}\right)$$
$$+ \left(\frac{\text{Rice husk (\%)} - 50}{50}\right) \times \left[\left(\frac{\text{Moisture content} - 10}{10}\right) \times 0.90300832893897\right]$$
$$+ \left(\frac{\text{Rice husk (\%)} - 50}{50}\right) \left[\left(\frac{\text{Rice husk (\%)} - 50}{50}\right) \times (-1.1975412172851)\right]$$
$$\left(\frac{\text{Moisture content} - 10}{10}\right) \times \left[\left(\frac{\text{Moisture content} - 10}{10}\right) \times 0.16119245094502\right] \quad (2)$$

Table 5. Rice and bean production in Mexican states (Sierra-Aguilar, 2010; Silva Hernández *et al*., 2020; SIAP, 2021).

State	Rice production (ton)	Rice wastes (ton)	Bean production (ton)	Bean straw (ton)
Campeche	62,303	12,460.60	833	733.04
Chiapas	634	126.8	61,182	53,840.16
Colima	19,014	3,802.80	4	3.52
Guerrero	2,360	472	14,149	12,451.12
Jalisco	8,959	1,791.80	9,682	8,520.16
Mexico state	99	19.8	4,089	3,598.32
Michoacán	30,055	6011	3,089	2,718.32
Morelos	8,839	1,767.80	1,233	1,085.04
Nayarit	88,876	17,775.20	100,820	88,721.60
Tabasco	7,421	1,484.20	1,959	1,723.92
Tamaulipas	14,040	2808	2,318	2,039.84
Veracruz	33,784	6,756.80	28,964	25,488.32

Table 6. Rice and bean fuel pellets that can be generated.

State	Bean straw (ton)	Rice wastes (ton)	Fuel pellets (ton)	Energy (TJ)
Campeche	733.04	81.45	733.04	11.18 (0.23%)
Chiapas	53,840.16	5,982.24	53,840.16	821.06 (7.04%)
Colima	3.52	0.39	3.52	0.05 (0.0007%)
Guerrero	12,451.12	1,383.46	12,451.12	189.88 (1.66%)
Jalisco	8,520.16	946.68	8,520.16	129.93 (0.28%)
Mexico state	3,598.32	399.81	3,598.32	54.87 (0.10%)
Michoacán	2,718.32	302.04	2,718.32	41.45 (0.16%)
Morelos	1,085.04	120.56	1,085.04	16.55 (0.19%)
Nayarit	88,721.60	9,857.96	88,721.60	1,353.00 (23.30%)
Tabasco	1,723.92	191.55	1,723.92	26.29 (0.22%)
Tamaulipas	2,039.84	226.65	2,039.84	31.11 (0.10%)
Veracruz	25,488.32	2,832.04	25,488.32	388.70 (1.13%)

The prediction of the calorific power (R^2: 0.81) and ash content (R^2: 0.99) regard the experimental data exhibited a good fit. Moreover, the variance analysis reports values from error mean square of 0.439 and 0.200 for calorific power and ash content, respectively.

Now, the potential energy production in Mexican states where rice and bean are cultivated will be estimated. Table 5 shows the rice production in all Mexican states (SIAP, 2021), as well as the estimation of the rice husks based on data reported by Sierra-Aguilar (2010); also, in the same table the bean production (SIAP, 2021) and bean straw (Silva Hernández *et al*., 2020) estimation in those states is shown.

From Table 5, it can be observed that the major amount of rice husk is generated in Nayarit, Campeche, Veracruz and Colima. On the other hand, the bigger production of bean straw is generated in Nayarit, Chiapas, Veracruz and Guerrero. However, the proportions of each type of wastes are different, and they need to be adjusted in order to produce fuel pellets considering the optimal conditions found previously. Thus, it is assumed that all bean straws can be used for the production of fuel pellets considering a yield of 90%; so, based on that, it can be used the amount of wastes indicated in Table 6. Considering the calorific power obtained for these pellets (15.25 MJ/kg), it can be produced the amount of energy indicated in Table 6, where the number between parenthesis represent the percentage that can be supplied with these fuel pellets respect the total energy consumption of each state (SIE, 2021).

According to Table 6, it can be observed that in Nayarit is possible to produce 23.30% of the total energy consumed in the state, while in Chiapas this percentage is 7.04%. In Guerrero and Veracruz, the potential contribution is 1.66% and 1.13%, respectively. It is expected that the energy produced in each state will be economically viable; in the worst-case scenario, the biomasses can be produced in one extreme of the state, and the energy required in the other extreme. In these cases, the extreme points in straight line inside each state are at not more than 291 km (Nayarit), 386 km (Chiapas), 450 km (Guerrero), and 735 km (Veracruz); these distances were obtained using Google Maps. It is important to mention that these distances are considered as the worst-case scenario, since the location of specific cultivation zones is not available from the database selected. If this is the case, according to the conclusions of the study of Tauro *et al*. (2018), in Nayarit, Chiapas and Guerrero, the best transportation alternative is by truck, while in Veracruz the better option is train. Specific locations of the cultivation zones could bring more information to determine the optimal supply chain. In the other states, the amount of energy produced is small, and the cost-benefit could not be so attractive. However, in those states the valorization of these residues allows to generate energy with reduced carbon dioxide emissions, and diminish its dependence of fossil fuels. It has been observed that during pandemics the waste to energy industry is highly immune to the perturbations (Mikulčić *et al*., 2021).

At the same time, the total amount of bean straw and 40.38% of the total amount of rice husk, generated in the selected states, are removing from the crop fields, avoiding a pollution problem, and generating a renewable solid biofuel. Nevertheless, it is important to consider other residues in order to use the total wastes derived from rice production.

Conclusions

The use of rice husk and bean straw in the production of fuel pellets was presented; in order to obtain the maximum calorific power, moisture content and biomass proportions were established as control factors. The results indicated that pellets made from 25% rice husk and 75% bean straw at 15% initial moisture met the standards set by ISO 17225-6, with respect to final moisture content, nitrogen content, diameter, length, bulk density and durability; however, the ash content and calorific value are outside the established values. Due to the high ash content, waste disposal problems can arise. According to the response surface analysis, it was determined that the use of raw material with 15.0% initial humidity and a biomass mixture with 90% bean straw and 10% rice husk would allow obtaining fuel pellets that meet all the specifications established by ISO 17225-6 standard. Moreover, it is possible to use the 40% of the total wastes derived from rice production, in the selected states, along with the total amount of bean straw, to generate 3,064.08 TJ of renewable energy; however, the most promissory alternatives for application are located in Nayarit, Chiapas, Guerrero and Veracruz states. It is important to mention that the specific amount of produced bioenergy will depend on the particular physicochemical composition of the wastes; this composition varies according the variety crop, soil composition and cultivation conditions. The conversion of rice husk and bean straw to fuel pellets is an effective option to reduce the environmental problems associated with inadequate waste disposal; also, the revaluation of these agricultural wastes contribute to expanding and diversifying the renewable energy market, reducing dependence on non-renewable fuels.

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