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Evaluation of Four Types of Kilns Used to Produce Charcoal from Several Tree Species in Mexico

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Abstract: Charcoal production is an activity that dates back over the years. The objective of the study was to determine the temperature and heating ramp in industrial carbonization processes using different kiln types and to quantify its impact on yield and quality of charcoal from different firewood species. The selection of sites, kiln types, and species investigated was based on those with highest production in Mexico. Brazilian beehive kilns using *Arbutus xalapensis*, *Quercus durifolia*, and *Quercus sideroxyla* species were analyzed; modified Brazilian beehive kilns with *Pithecellobium dulce* and *Tamarindus indica*; Argentine half-orange kilns with *Quercus magnoliifolia* and *Q. sideroxyla*, industrial metal kilns with *Brosimum alicastrum*, *Vitex gaumeri*, *Manilkara zapota*, and *Pouteria unilocularis*. The process time, temperature, heating ramp, production yield, and quality of charcoal produced were determined. Data were analyzed in a completely random statistical design. The industrial type kilns showed the highest production yield (>35%), and the Brazilian beehive kilns obtained the longest carbonization time (>240 h). On the other hand, the modified Brazilian beehive kilns obtained the best energetic characteristics (>75% fixed carbon and <16% volatile material). A carbonization process with a slow heating ramp (<1 °C min^{-1}) and temperatures of 500–600 °C can generate a charcoal with export quality.

Keywords: bioenergy; thermochemical conversion; solid biofuel; biofuels; masonry kiln; industrial kiln

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1. Introduction

Energy demand and greenhouse gas emissions have increased globally, and primary energy demand has increased from 8737 to 14,485.75 million tons petroleum equivalent (Mtoe) from 1990 to 2019, while carbon dioxide emissions were from 20,511 to 33,621 million tons of carbon dioxide (Mt CO_2) on the same period [1]. Energy generation is the main contributor to climate change, accounting for about 60% of global greenhouse gas (GHG) emissions. One of the sustainable development goals (SDG 7 affordable and clean energy) is the production of clean energy, and the reducing energy production from fossil sources by 2030 [2]. In order to achieve the above, biomass is a crucial alternative because it is a renewable resource that can be developed in a sustainable way, has favorable environmental properties, does not generate net carbon dioxide emissions, has a low sulfur content, and provides a significant economic contribution to producers [3–5].

Charcoal production is considered an ancestral activity, with the earliest records dating back more than 30,000 years [6–8]. Although there are new alternatives for energy generation, charcoal is, for many people, the main source of cooking [9]; this preference is based on ease of storage, high calorific value, low cost, and because it is more durable than firewood [10]. Preference in industrial use is due to low sulfur content, a high proportion of carbon:ash, relatively low and unreactive inorganic impurities, specific pore structure with a large surface area, and low smoke emissions [3], although a common problem in the use of charcoal is its great variability of physical and chemical properties [11].

The world's largest charcoal producers are Brazil, Nigeria, Ethiopia, India, and China, while Indonesia, Paraguay, Argentina, Somalia, and Myanmar are the largest exporters; however, the countries with the greatest impact in terms of volume imported are Germany, Japan, Republic of Korea, China, and Belgium [12]. Mexico produces 760,000 t (23.9 PJ/year) of charcoal per year. The value of national production is approximately $568 million dollars (the year 2018). The income of producers who sell at the edge of the gap is 32% of this value [13].

Biomass pyrolysis, as carbonization is called, is defined as the thermal decomposition of the organic matrix of biomass in inert atmospheres at high temperatures and in the absence of oxygen, which produces oil, charcoal, condensable, and non-condensable gaseous products [14,15]. The quality of the charcoal depends on the experience of the operators, the technology used (kiln characteristics), the temperature and process time, the species, and the physical conditions of the firewood [16]. Despite the global importance of charcoal, physical and chemical knowledge of the species used and the charcoal produced is limited [17].

Regarding kilns to charcoal production, these vary in their dimensions and therefore in the production capacity, materials of which they are built, the form, the number of chimneys, the mechanization, the process control levels, and the heat source for heating the wood [16]. Traditional ovens are pit and parva, and these have the simplest technologies. Therefore, they represent the most common ovens for charcoal processing, and an advantage of this type of kiln is that carbonization can be carried out at the place where the wood is cut, so the investment in its transport is minimal. Some of the drawbacks of these ovens are that they must be monitored throughout the process and have higher emissions of greenhouse gases (GHG), which is tired and dangerous for the producer. A problem to consider is that charcoal tends to get dirty and its production depends largely on good weather conditions [18]. On the other hand, masonry kilns are built in areas that have a medium or long-term forestry plan, they must be located at a midpoint where the availability of the raw material is located, the ground must be wide to have a storage yard, have roads with access to van and trailer, the ground must contain low humidity, and be firm and compact. These types of have a main door that opens to load the raw material and unload charcoal. After loading, the door is closed and sealed with bricks and mud. Vents around the base of the oven are used to control air infiltration and thus temperature [19]. This type of furnace uses external heating and recirculates the gas emitted during carbonization, thus obtaining higher yields than the other types of kilns.

Traditional pit and parva kilns have the disadvantage of producing largely brittle, dirty charcoal with a high percentage of burning, ash, and moisture, so they are not considered good quality [18,20]. Bustamante et al. [21] reported that charcoal produced in the upper part of the furnace has the best energy characteristics (lower content of volatile material, as well as higher content of fixed carbon and calorific value when evaluated the quality of charcoal from *Quercus sideroxyla* charcoal produced in a Brazilian beehive kiln at different levels).

In Mexico there is a lack of regulations regarding charcoal quality; additionally, various production technologies are used, but consumers value the product empirically [22]. However, when it is necessary to assess the quality of charcoal, international standards are used [23], such as DIN 51749, EN 1860-2, GOST 7657-84, DIN 51749, EN 1860-2, GOST 7657-84 [24], and FAO [25]. Among the quality requirements, the standards indicate that the fixed carbon content must be between 65 and 78%, volatile material < 25%, ash content < 10%, and moisture content < 10%, and strictly require values of 75%, 14%, 3%, and 6%, respectively. Low contents of moisture, volatile material, and ash, and high contents of fixed carbon and calorific value, have been related to processing temperatures of 400 to 1200 °C in Brazilian beehive-type kilns; on the other hand, production yield is an important aspect to evaluate. This depends on the type of wood (origin and size of specimens), moisture content of the wood, type of kiln, heating ramp, and largest carbonization temperature. Generally, efficient charring requires approximately five tons of wood to produce one ton of charcoal [3,20].

Further, there is limited information that relates the parameters of the carbonization process with the quality and yield of charcoal using different technologies and species of firewood, so the objective of this study is to monitor and evaluate the charcoal production process in four types of kilns used in Mexico, as well as to relate the temperatures and heating rates of each process with the yield and physicochemical characteristics of charcoal, considering technologies and firewood species.

2. Materials and Methods

2.1. Sites of Study

The sites, kiln types, and species were selected considering the states with the highest charcoal production in Mexico, quality reports, production yield and use, and the importance of the species [18,21,26–28]. The selected sites are presented in Figure 1, while the information related to the four types of kilns, location, and firewood species is shown in Table 1.

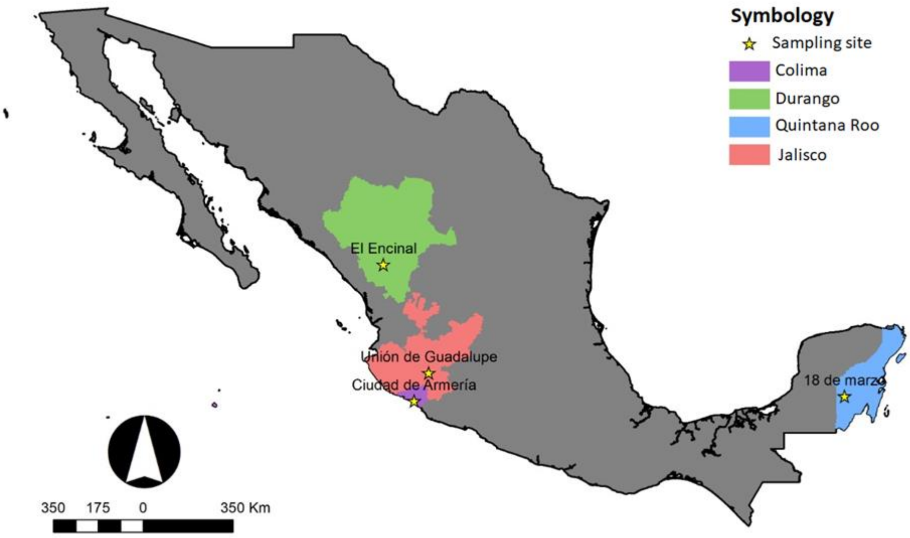

Figure 1. Location of the sites selected to analyze the charcoal production process in Mexico.

2.2. Description of Kilns

2.2.1. Brazilian Beehive Kiln

The Brazilian kiln is in El Encinal, Durango (Figure 1). In this site the vegetation type is classified as coniferous forest, where firewood species of the *Quercus* and *Arbutus* genus are used for charcoal production. The kiln is made of masonry, has a diameter of 5 m, height of 2.35 m, a dome of 1.85 m high, and a hole in the upper part, which is used to light the kiln. It also has a door of 1.50 and 2.00 m wide and high, through which the firewood is loaded into the oven and the charcoal is unloaded. There are twenty vents systematically distributed on the kiln walls, eight of which are in the middle part of the kiln and twelve in the lower part. The kiln has a capacity of forty cubic meters of firewood and estimated production of 6 tons of charcoal in each process (Figure 2). The kiln is lit from the top of the dome, adding leaves and thin branches for easy ignition, and after about 3 to 4 h of ignition the trench is closed for fire distribution. The burning occurs in a descending manner, so the color of the smoke generated by the holes is the signal used by the handlers of this type of oven, when a blue color of smoke is observed, they proceed to close the holes and thus make the fire descend to the bottom of the oven, finally, when the blue color of the smoke is observed by the lower vents, they proceed to seal the oven and cover it with mud mixture to help its subsequent cooling. This procedure is the same for masonry kilns.

Table 1. Description of four kiln types, location, and firewood species used for charcoal production.

Kiln Type	Total Capacity (m^3)	Coordenates Latitude and Longitude (°)	State	Community	Firewood Species
Brazilian beehive	40.00	23.7147–105.0670	Durango	El Encinal	*Arbutus xalapensis* (Madrone), *Quercus durifolia* (white oak) *y Quercus sideroxyla* (red oak)
Modified Brazilian beehive	12.00	18.9338–104.0082	Colima	Ciudad de Armería	*Pithecellobium dulce* (Guamúchil) *y Tamarindus indica* (Tamarindo)
Argentine half-orange	16.00	19.9288–103.4382	Jalisco	Unión de Guadalupe	*Quercus magnoliifolia* (white oak) *y Quercus sideroxyla* (red oak)
Industrial metal	5.20	19.0735–88.8074	Quintana Roo	18 de Marzo	*Brosimum alicastrum* (Ramón), *Vitex gaumeri* (Yaxnic), *Manilkara zapota* (Zapote), *Pouteria unilocularis* (Zapotillo)

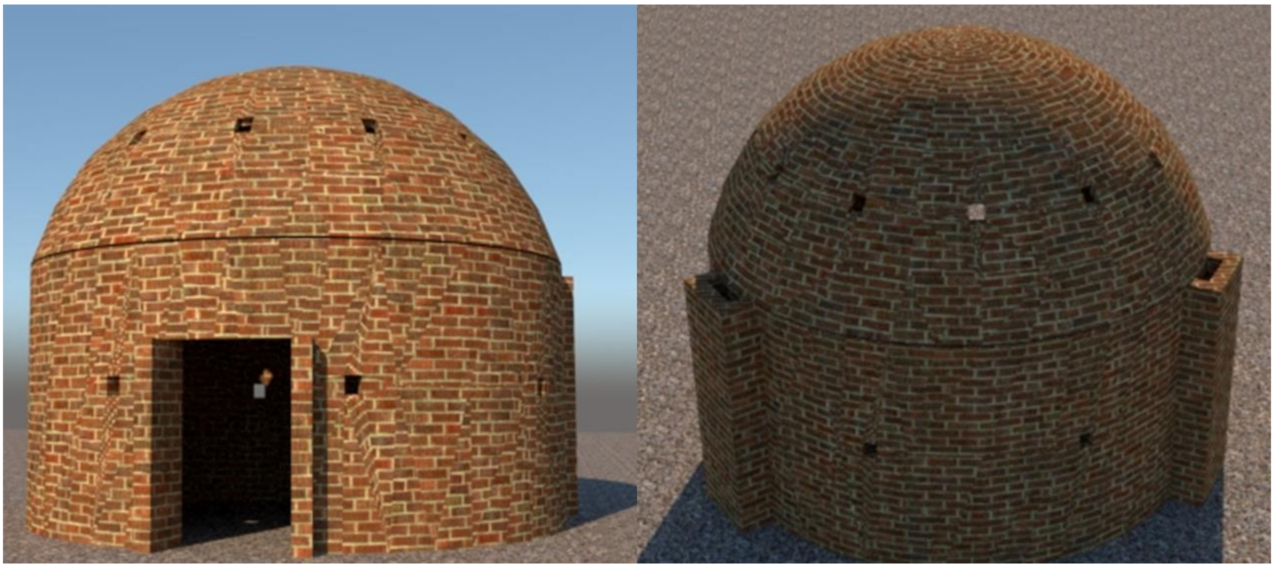

Figure 2. Design of a Brazilian beehive type kiln.

2.2.2. Modified Brazilian Beehive Kiln

The modified Brazilian kiln is in Armería, Colima, and the vegetation type of this site is tropical deciduous forest; however, the charcoal production is based on *Pithecellobium dulce* and *Tamarindus indica* species extracted for the use of land change for papaya and coconut production. The kiln is masonry type, and has a diameter of 3.4 m, height of 1.6 m, and one dome of 60 cm. The door is 80 cm wide and 1.25 m high, through which the wood is loaded and the charcoal is unloaded. It also has a chimney, and three vents at the top and four at the bottom. The kiln capacity is twelve cubic meters of firewood and the estimated production is 2.5 tons of charcoal in each process (Figure 3). This kiln does not have an ignition hole, and for this reason the ignition is made through the upper part of the door, and after about 3 h the hole is sealed for the distribution of the fire. The control of fire is the same as mentioned above.

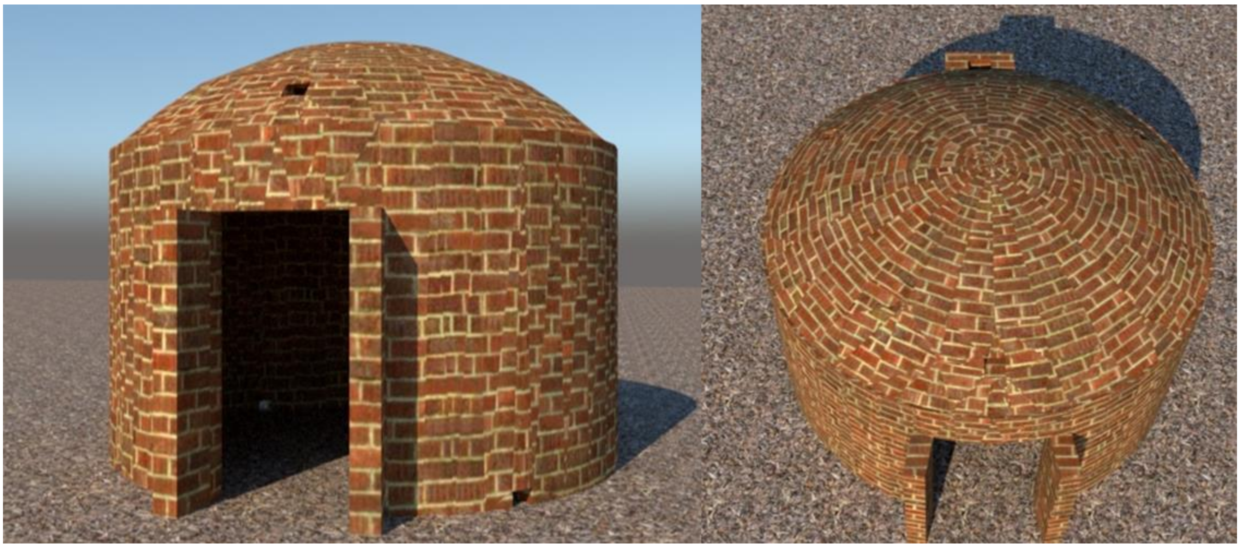

Figure 3. Design of a modified Brazilian beehive type kiln.

2.2.3. Argentinian Half-Orange Kiln

The Argentine half-orange kiln is in Unión de Guadalupe, Jalisco, with a predominant vegetation type, *Quercus* Forest, used for charcoal production. The kiln is made of masonry and has a diameter of 5 m and 3 m height. The door is 1 m width and has a height of 1.60 m. This type of kiln does not have a chimney but presents twenty-six vents distributed at five levels, three at 2.8 m high, five at 2.0 m high, five at 1.20 m high, five at 0.5 m, high, and eight at ground level. The kiln is fired from the top of the entrance. The kiln capacity is sixteen cubic meters of firewood, and the estimated production is 3 tons of charcoal in each process (Figure 4). The kiln was turned on through the upper part of the door, and after about three hours the hole was sealed.

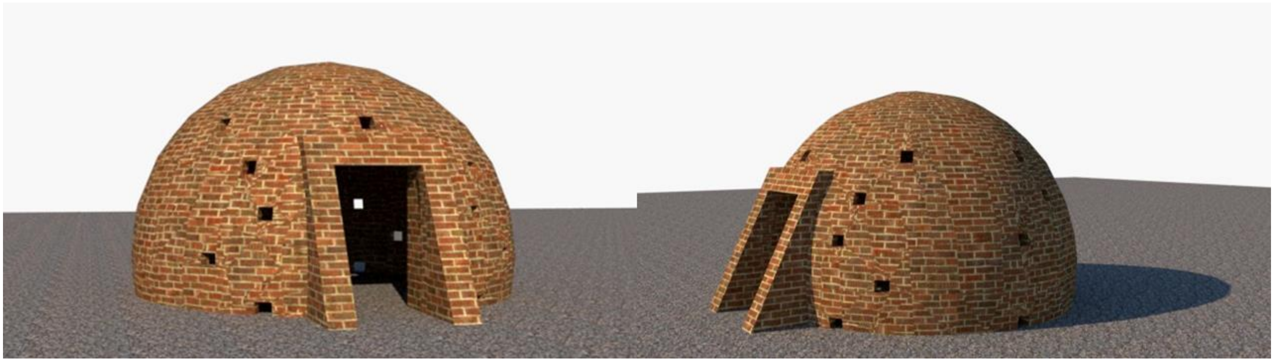

Figure 4. Design of an Argentinian half-orange kiln.

2.2.4. Metallic Industrial Type Kiln

The industrial metal kiln is 18 de Marzo, Quintana Roo, with a predominant vegetation type of tropical evergreen forest where there are more than sixty tree species. The kiln is metallic, and the container has a diameter of 1.30 m and 1.50 m height. Once this container is loaded with firewood, it is placed with a polyplast in a container covered with brick and metal, measuring 1.80 m diameter and 1.51 m height. The system consists of a connection of four kilns, and all need to be loaded to start the production process. The kilns are lit by external fire, and firewood is placed under each kiln until it reaches the exothermic process (>280 °C). For this reason, it is important that the firewood has the lowest possible moisture content, otherwise the ignition is difficult. The capacity of each kiln is 1.30 cubic meter of firewood, with an estimated production of 250 kg, reaching one ton of production in the system in each process (Figure 5).

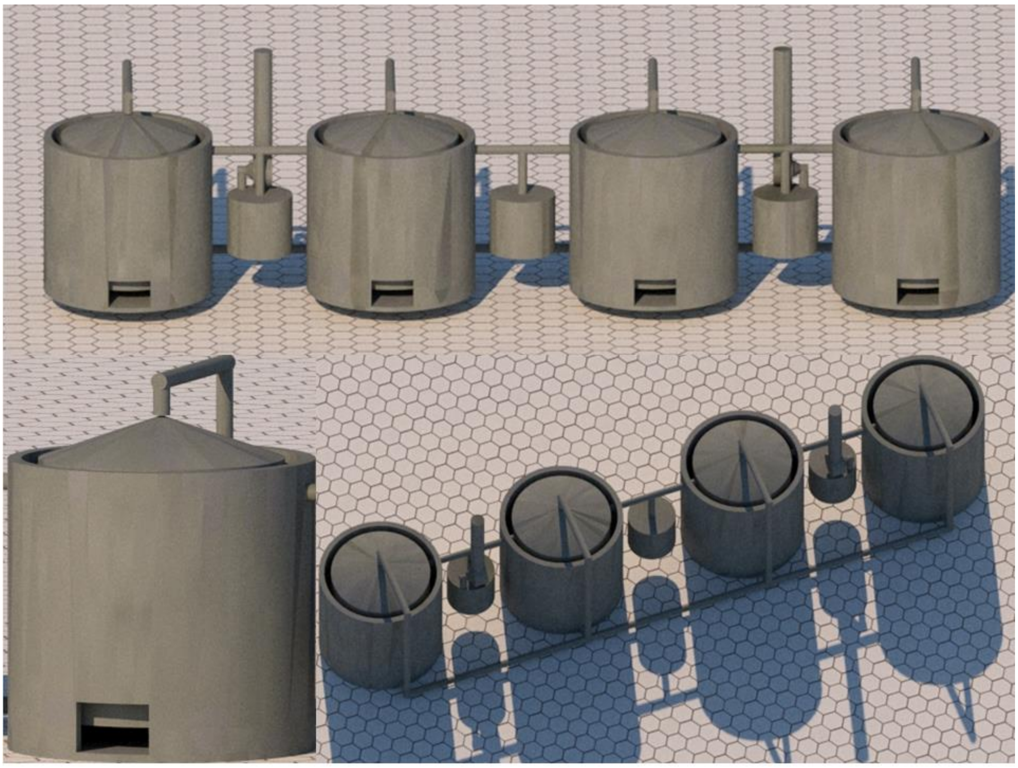

Figure 5. Design of a metallic industrial kiln.

2.3. Samples Preparation

Three firewood samples of each species were randomly selected for each burning and kiln type. The sample size was from 10 to 20 cm wide and approximately 60 cm long. In each type of kiln, three burns were conducted with the three repetitions of each firewood species. The volume and weight of firewood for each burn were measured before and after the pyrolysis process to determine the production yield [5]. Table 2 presents the physical and chemical characteristics of firewood of the species used for charcoal production.

Table 2. Chemical composition, density and moisture content of the biomass used for conversion to charcoal.

Species	Biomass Origin	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Moisture Content (%)
Madrone	Durango	52.92 ± 1.45	14.11 ± 1.98	20.41 ± 0.94	34.05 ± 14.21
White oak		44.34 ± 1.91	16.16 ± 2.64	19.58 ± 1.08	50.40 ± 5.03
Red oak		47.55 ± 1.86	16.29 ± 1.12	19.82 ± 1.30	43.86 ± 8.85
Guamúchil	Colima	57.40 ± 4.05	10.69 ± 1.34	22.44 ± 0.68	91.97 ± 3.22
Tamarindo		60.78 ± 2.22	11.52 ± 1.47	19.58 ± 0.72	22.13 ± 6.56
White oak	Jalisco	59.98 ± 0.45	13.30 ± 0.52	17.79 ± 1.08	34.60 ± 9.27
Red oak		54.75 ± 3.47	14.06 ± 1.33	20.79 ± 1.93	37.34 ± 6.13
Ramón	Chetumal	64.55 ± 0.39	8.44 ± 0.34	22.62 ± 0.77	10.75 ± 1.23
Yaxnic		64.03 ± 0.88	5.55 ± 0.46	22.90 ± 1.01	11.55 ± 1.00
Zapote		60.59 ± 0.93	12.16 ± 0.31	21.69 ± 1.23	12.46 ± 2.30
Zapotillo		63.60 ± 1.39	8.23 ± 1.32	23.84 ± 0.91	11.16 ± 0.74

The chemical composition of the biomass was determined using the ANKOM method (2005) which calculates neutral detergent fiber (FDN), acid detergent fiber (FDA), and lignin (L). Symbol ± shows standard deviation.

2.4. Carbonization Process Monitoring

In the thermal degradation of lignocellulosic biomass from broadleaf firewood, five phases have been identified: the first occurs during the change of ambient temperature (25 to 30 °C) to 100 °C, where the ignition of the kiln is ensured. In phase two, the temperature rises from 100 to 200 °C, which allows for the complete evaporation of the moisture present in the firewood. For phase three, the temperature rises from 200 to 280 °C, where hemicellulose degradation takes place and CO_2 is emitted as a combustion product. Phase four goes from 280 °C to the kiln's maximum heating point (>400 °C), during which cellulose is degraded and lignin breaks down; CO_2 and CH_4 emissions also occur, and condensable and non-condensable volatile material is produced, while firewood is transformed into charcoal. Finally, phase five is characterized by the cooling of the kiln [15,20,28–34].

The identification of each phase described above was made by recording the temperature inside the kilns during carbonization using thermocouples type k 5m and an Extech thermometer (VIR50). The thermocouples were placed in the center of the kiln, and the temperature was recorded for one to three hours during the entire process. For the masonry kilns, carbonization was considered complete once the fire reached the lower vents, while in the metal kiln the process was considered finished after twelve hours of burning.

2.5. Charcoal Characterization

2.5.1. Charcoal Yield

The yield (m^3 ton^{-1}) was obtained by relating the volume (m^3) of each firewood sample to the mass (t) of the same charred sample according to Equation (1) developed by Garcia [35].

$$Y = \frac{V}{m} \quad (1)$$

where:

Y = Yield
V = Volume of sample
m = Mass of pyrolyzed sample

2.5.2. Physicochemical Analysis

The moisture content, volatile material, fixed carbon, and ash content of the charcoal were determined according to the international standard ASTM D 1762-84 [36]. Three charcoal samples of each firewood species, burn, and kiln were introduced in a SM 300 cutting mill at a speed of 1500 rpm and sieved for five minutes at a speed of 100 rpm in an AS 200 analytical sieve, separating the particle size of 850 µm (20 mesh) and using the remaining material <420 µm (mesh > 40).

2.5.3. Mass Yield

The mass yield was determined by relating the mass of charcoal (kg) to the mass of biomass (kg) according to Equation (2) by Basu [37].

$$MY = \frac{MC}{MGB} * 100 \quad (2)$$

where:

MY = Mass yield
RM = Mass yield
MGB = Mass of green biomass (kg)
MC = Mass of charcoal (kg)

2.6. Higher Heating Value

The higher heating value of charcoal was determined with an automatic iso-peribolic calorimetric pump model AC600 Leco, according to UNE-EN 18125 [38].

2.7. Statistical Analysis

The data of the variables determined for charcoal were statistically analyzed as a completely randomized experimental design. It was considered as three burns with three replicates per burn and firewood species. Two to four firewood species in each type of kiln were studied (Table 2).

Shapiro and Kolmogorov–Smirnov normality tests were performed for all variables, as well as variance heterogeneity tests. ANOVA and Tukey's mean comparison tests were also performed for normally distributed data, whereas data of variables that did not meet the assumption of normality ($p > 0.05$) were analyzed using Kruskal–Wallis tests and Duncan's comparison with a significance of $\alpha = 0.05$. In addition, a principal component analysis (PCA), which is a multivariate analysis used to simplify the data set and identify correlated variables, was integrated with fourteen variables that interact during charcoal production and are influenced by physicochemical quality. The FactorMineR v2.4 package was developed [39]. All calculations were developed using the packages and functions of the Rstudio® statistical system.

3. Results

3.1. Description of the Carbonization Process

3.1.1. Brazilian Beehive Kiln

The carbonization process showed variations in the total time, time of each phase, and maximum temperature reached (Figure 6). Burn 1 presented the shortest carbonization time with 120 h up to phase 4, and a maximum temperature of 450 °C; burn 2 presented the longest carbonization time with 170 h because it had problems with ignition (90 h in phase 1). Burn 3 presented more homogeneous heating ramps among its phases; it also presented the highest carbonization temperature (600 °C). The slowest heating ramps were seen in phase 1, while the fastest occurred in phase 4 for all burns (Table 3).

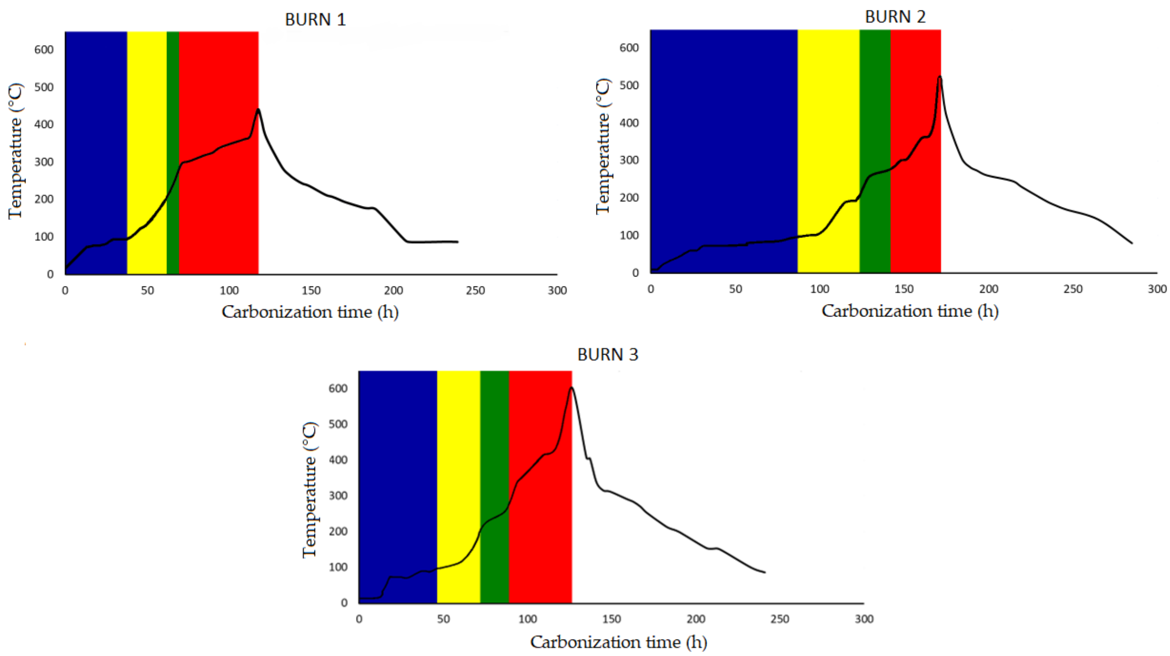

Figure 6. Heating ramps during carbonization in three burnings of Brazilian beehive kilns. Blue color = phase 1, yellow color = phase 2, green color = phase 3, red color = phase 4, white color = phase 5. This carbonization process includes the following species: Madrone, White oak, and Red oak.

Table 3. Burning time and heating ramps on each phase during carbonization in Brazilian beehive kilns.

Burn	Phase 1		Phase 2		Phase 3		Phase 4	
	Time	R	Time	R	Time	R	Time	R
1	38	0.04	22	0.08	10	0.13	48	0.06
2	93	0.02	28	0.06	23	0.06	27	0.15
3	48	0.03	23	0.07	17	0.08	40	0.13

Time = elapsed time in Phase (h), R = heating ramp (°C/min).

3.1.2. Modified Brazilian Beehive Kiln

The burning time and maximum temperature in each burn showed variations (Table 4, Figure 7). Burning 1 showed the longest carbonization time (167 h until phase 4), due to ignition problems, remaining in phase 1 > 60 h. Phase 2 represented the second longest duration since the humidity of the Guamúchil firewood was high (>90%) and this firewood species was mostly placed in the upper part of the kiln; phase 4 was 39 h long and the maximum temperature was 420 °C. Burn 2 was the fastest, with a carbonization process of 65 h until the end of phase 4; in addition, this phase had the longest duration (28 h), with a maximum temperature of 580 °C (Table 4). On the other hand, burn 3 presented the highest temperature (596 °C), which presented a fast ignition (4 h) and had the longest drying time (61 h) and 27 h in phase 4; due to the above-mentioned conditions, it can be considered as the best carbonization process of this type of kiln (Figure 7).

Table 4. Burning time and heating ramps on each phase during carbonization in modified Brazilian beehive kiln.

Burn	Phase 1		Phase 2		Phase 3		Phase 4	
	Time	R	Time	R	Time	R	Time	R
1	66	0.02	54	0.03	10	0.13	39	0.07
2	4	0.32	22	0.08	13	0.10	28	0.20
3	4	0.32	61	0.03	2	0.67	27	0.20

Time = elapsed time in Phase (h), R = heating ramp (°C/min).

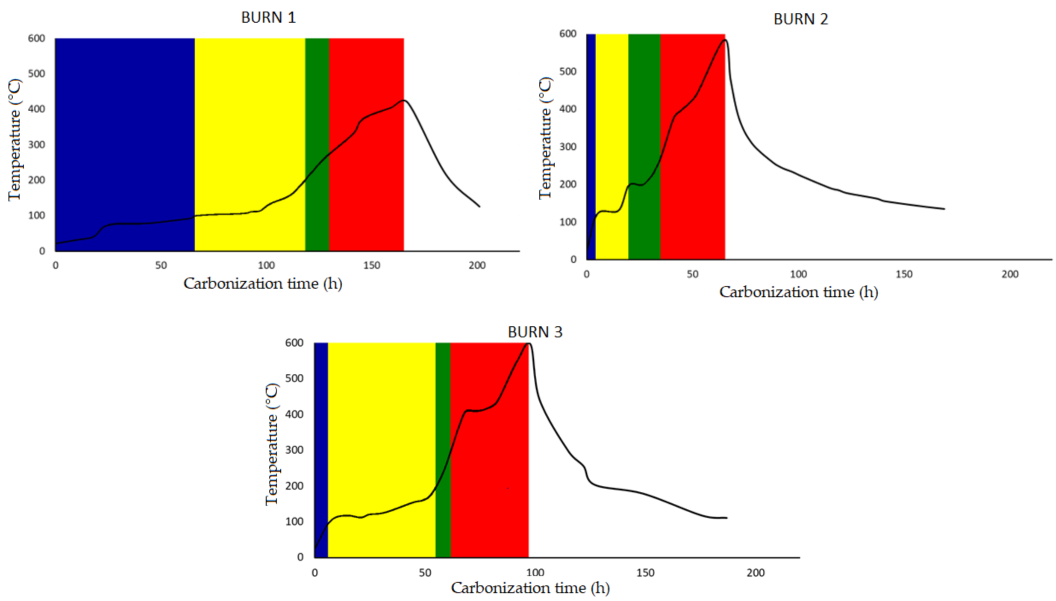

Figure 7. Heating ramps during carbonization in three burnings of modified Brazilian beehive kilns. Blue color = phase 1, yellow color = phase 2, green color = phase 3, red color = phase 4, white color = phase 5. This carbonization process includes the following species: Guamúchil and Tamarindo.

3.1.3. Argentine Half-Orange Kiln

The burning time and maximum temperature showed differences (Figure 8). Burn 1 presented a maximum temperature of 432 °C, with a time of 92 h until the end of phase 4. On the other hand, burn 2 presented the highest temperature (660 °C) and carbonization time (103 h until the end of phase 4), finally, burn 3 had the lowest time and temperature (75 h until the end of phase 4 and 403 °C). Burn 2 represented the best process with respect to heating ramps, with a fast ignition (0.14 °C min^{-1}) and a slow and long-lasting ramp in stage 4 (0.08 °C min^{-1}) (Table 5).

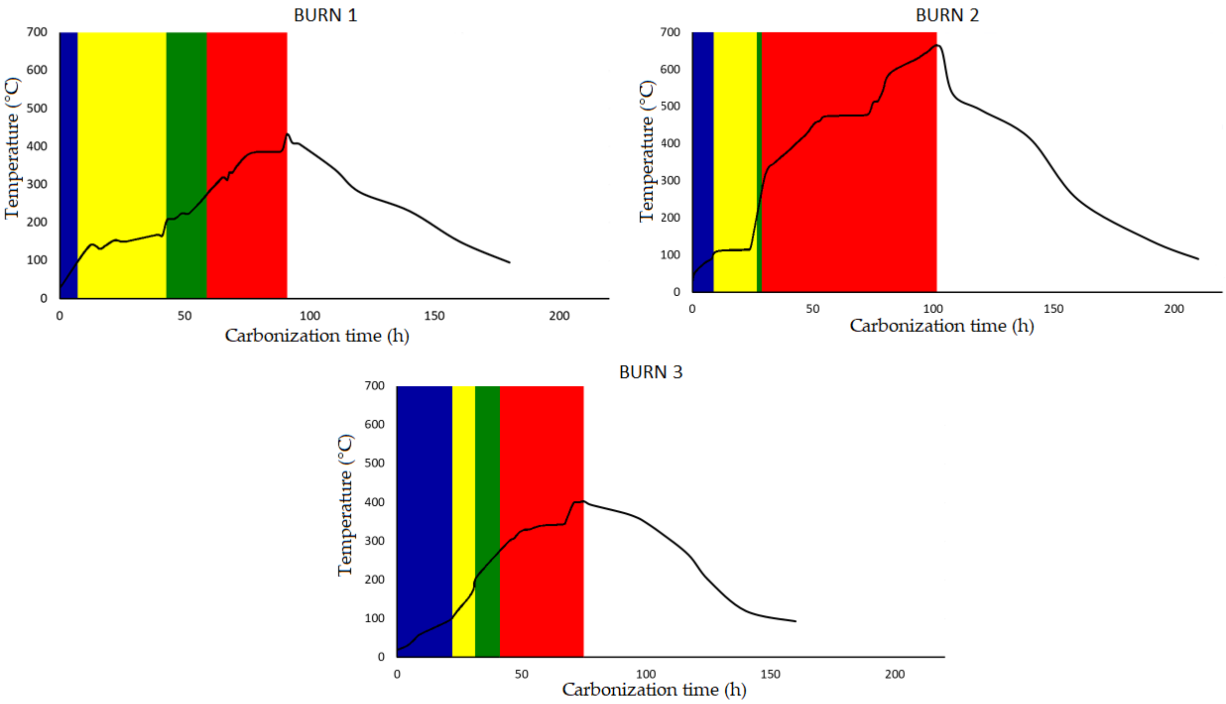

Figure 8. Heating ramps during carbonization in three burnings of Argentine half-orange kilns. Blue color = phase 1, yellow color = phase 2, green color = phase 3, red color = phase 4, white color = phase 5. This carbonization process includes the following species: White oak and Red oak.

Table 5. Burning time and heating ramps on each phase during carbonization in an Argentine half-orange kiln.

Burn	Phase 1		Phase 2		Phase 3		Phase 4	
	Time	R	Time	R	Time	R	Time	R
1	10	0.13	43	0.04	3	0.44	13	0.22
2	9	0.14	19	0.09	2	0.67	73	0.08
3	22	0.06	10	0.17	11	0.12	34	0.03

Time = elapsed time in Phase (h), R = heating ramp (°C/min).

3.1.4. Industrial Metal Kiln

The carbonization process among burns showed variations in total time, time of each phase, and maximum temperature (Figure 9). Burn 3 presented the longest carbonization time (11 h), as well as the highest temperature (498 °C); on the other hand, burn 2 presented a longer drying time, shorter carbonization time (7 h), and lower temperature (310 °C), while burn 1 showed a longer time in the ignition phase (3 h). The heating ramps in this type of kiln were more homogeneous. Even so, they showed that burner 3 presented the best process, maintaining the longest burning time in phase 4 (Table 6).

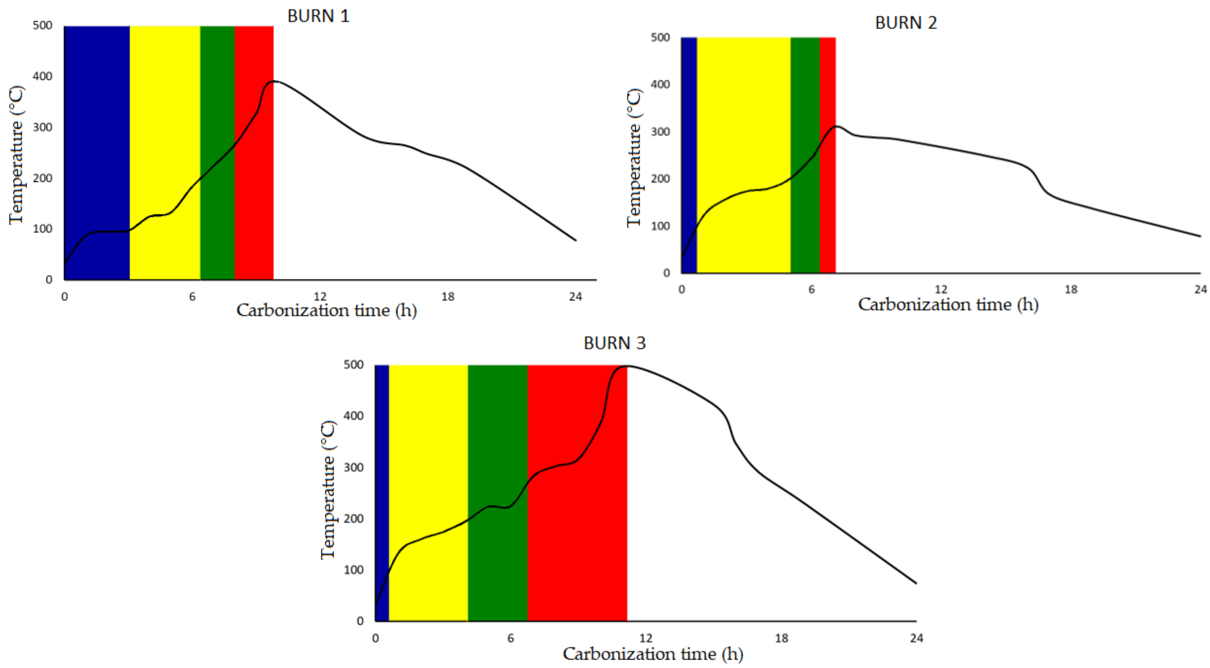

Figure 9. Heating ramps during carbonization in three burnings of industrial metal kilns. Blue color = phase 1, yellow color = phase 2, green color = phase 3, red color = phase 4, white color = phase 5. This carbonization process includes the following species: Ramón, Yaxnic, Zapote, and Zapotillo.

Table 6. Burning time and heating ramps per phase during carbonization in industrial metal kilns.

Burn	Phase 1		Phase 2		Phase 3		Phase 4	
	Time	R	Time	R	Time	R	Time	R
1	3	0.56	3	0.56	2	0.67	3	0.62
2	1	1.67	4	0.42	2	0.67	1	0.50
3	1	1.67	4	0.42	2	0.67	5	0.93

Time = elapsed time in Phase (h), R = heating ramp (°C/min).

3.2. *Yield*

3.2.1. Brazilian Beehive-Type Kiln

This type of furnace, having a large storage capacity (40 m^3), tends to have a cooling time of 15 days, and to make this process faster the operator adds water. Due to this, the charcoal tends to crumble, and for this reason the test tubes were not recovered in their entirety, preventing the performance analysis. The yield in this kiln type was determined by relating the firewood loading capacity to the number of sacks of charcoal produced in each burn. There was an estimated consumption of 7 to 9 m^3 of firewood to produce one ton of charcoal, so the estimated yield is 20%.

3.2.2. Modified Brazilian Beehive kiln

Firewood consumption (m^3 ton^{-1}) for charcoal production in burn 1 showed a consumption of 8.20 m^3 ton^{-1}, with a yield of 21.24%, while consumption in burn 2 was 8.89 m^3 ton^{-1} and a yield of 18.56%. Finally, burn 3 presented a consumption of 8.73 m^3 ton^{-1} and 18.57% yield. The yield with the species of Guamúchil and Tamarindo in the three burns did not present significant statistical differences ($p > 0.05$, Tukey). It was used from 8 to 10 m^3 of firewood to produce one ton of charcoal; the yield did present significant statistical differences ($p < 0.05$, Tukey). The Tamarindo firewood species, in the burn 1, had the highest yield (23%), while the Guamúchil, in burns 2 and 3, had the lowest yield (<20%) (Figure 10).

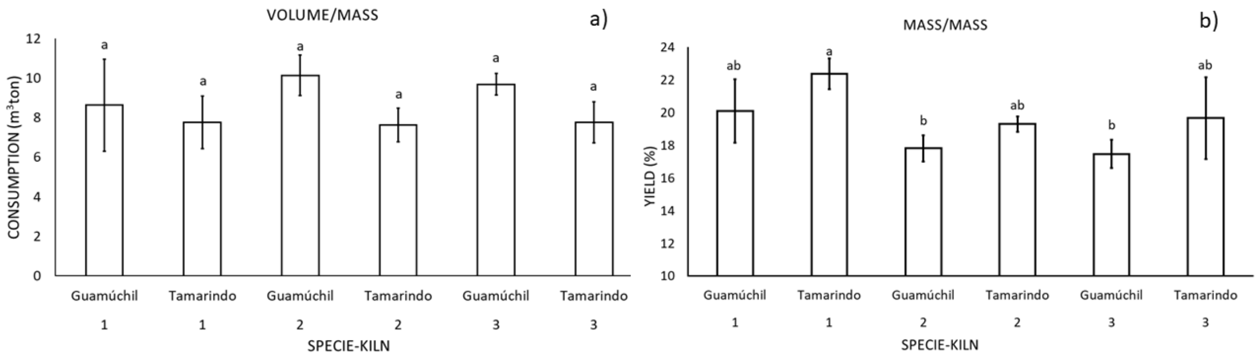

Figure 10. (**a**) Firewood consumption, and (**b**) charcoal production yield in modified Brazilian beehive kilns. Values with the same letter are statistically equal, according to Tukey test ($p \geq 0.05$).

3.2.3. Argentinian Half-Orange Kiln

There were significant statistical differences in firewood consumption and mass yield ($p < 0.05$, Tukey test) (Figure 11). Burn 1 had an average consumption and yield of 5.07 m^3 ton^{-1} and 30.38%, while burn 2 had the highest firewood consumption and lowest mass yield (6.19 m^3 ton^{-1} and 24.43%), finally, burn 3 had a consumption of 5.12 m^3 ton^{-1} and a yield of 30.30%. The white oak species from burn 2 required the greatest volume of firewood to produce one ton of charcoal (6.37 m^3 ton^{-1}), while the white oak from burn 1 required the least volume of firewood (4.74 m^3 ton^{-1}). Considering the above, the white oak from burn 1 obtained the highest percentage of mass yield (32.25%), while the two species from burn 2 had the lowest yield (23.96 and 24.10%, respectively).

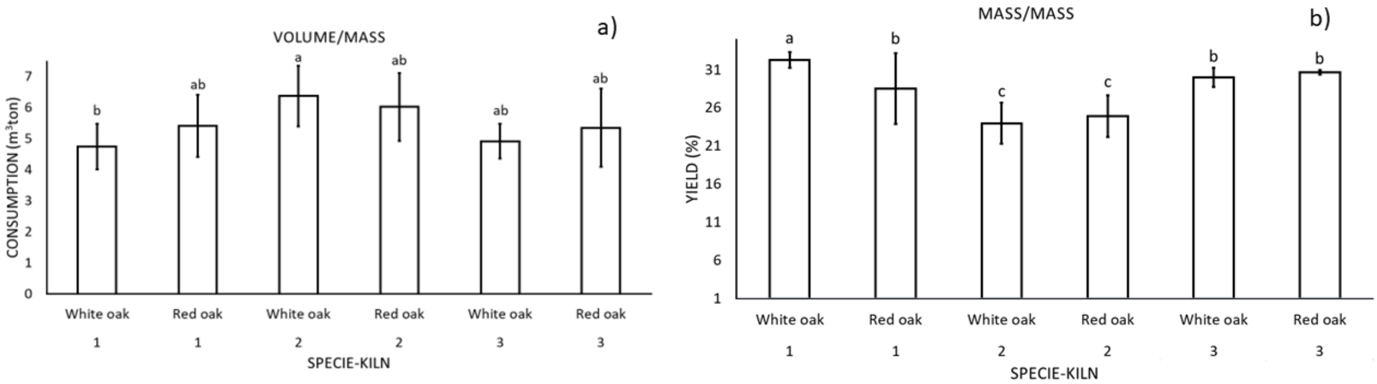

Figure 11. (**a**) Firewood consumption and (**b**) charcoal production yield in Argentine half-orange kilns. Values with the same letter are statistically equal, according to Tukey test ($p \geq 0.05$).

3.2.4. Metallic Industrial Kiln

There were significant statistical differences in firewood consumption and mass yield ($p < 0.05$). Burn 1 had a consumption of 4.84 m^3 ton^{-1} and a yield of 38.85%, burn 2 had a consumption of 5.09 m^3 ton^{-1} and a yield of 36%, and burn 3 had a consumption of 5.37 m^3 ton^{-1} and a yield of 33.55%. The Ramón species from burn 3 had the highest firewood consumption to produce one ton of charcoal (6 m^3 ton^{-1}), while the Zapote species from burn 1 had the lowest firewood consumption (4 m^3 ton^{-1}). In relation to yield, the Ramón species from burn 3 had the lowest mass yield (28%), while the Zapote species from burn 3 had the highest value (45%). The Ramón species behaved similarly in the 3 burns, being the one with the lowest production. In addition, it was identified that the species Yaxnic, Zapote, and Zapotillo from burn 1 obtained the highest charcoal production yield (Figure 12).

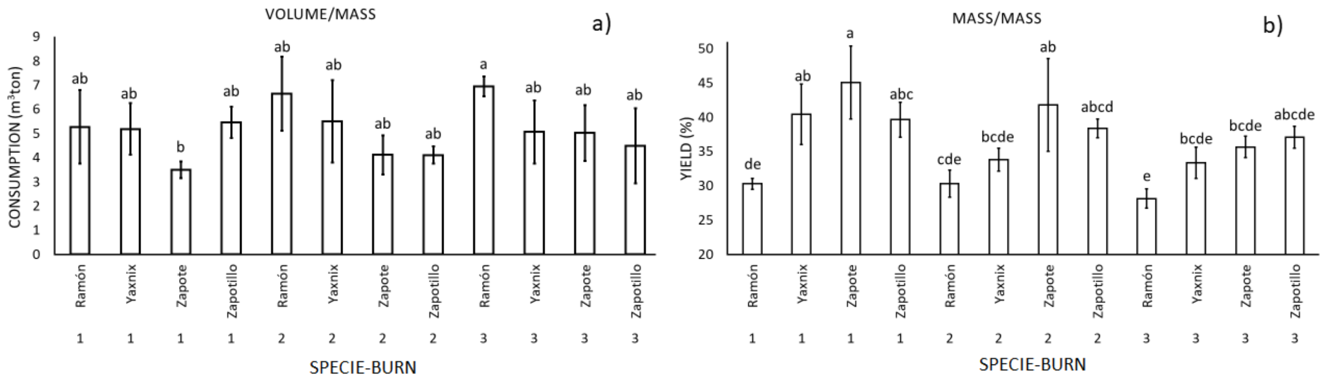

Figure 12. (**a**) Firewood consumption and (**b**) charcoal production yield in industrial metal kilns. Values with the same letter are statistically equal, according to Tukey test ($p \geq 0.05$).

3.3. Proximal Analysis of Charcoal

3.3.1. Brazilian Beehive-Type Kiln

The proximate analyses showed significant statistical differences ($p < 0.05$, Kruskal–Wallis). The highest moisture content was found in White oak from burn 2 (2.68%), while Madrone had the lowest percentage (1.98%). The volatile material content showed two statistical groups, and the Red oak species from burns 1 and 2 presented the lowest percentage (16.44 and 17.58%, respectively), while the rest of the species did not have significant statistical differences ($p > 0.05$). The highest percentage of fixed carbon was found in the Red oak species from burn 1 (78.15%), and the highest ash content was found in the Red oak species from burn 2 (4.27%), while the Madrone from burn 1 had the lowest percentage (1.57%) (Table 7).

Table 7. Proximate analysis of charcoal produced in Brazilian beehive kilns.

BURN	SPECIE	MC	VM	FC	ASH
1	Madrone	1.98 ± 0.26^{ab}	20.68 ± 2.15^{a}	75.47 ± 2.20^{b}	1.57 ± 0.45^{e}
	White oak	2.08 ± 0.12^{c}	20.62 ± 1.86^{a}	74.82 ± 2.00^{b}	2.49 ± 0.16^{bc}
	Red oak	1.95 ± 0.09^{cd}	17.58 ± 0.56^{b}	78.15 ± 0.43^{a}	2.33 ± 0.09^{cd}
2	Madrone	1.69 ± 0.29^{d}	21.67 ± 6.69^{a}	74.76 ± 7.00^{b}	1.88 ± 0.57^{de}
	White oak	2.68 ± 0.17^{a}	18.76 ± 5.65^{a}	75.76 ± 5.16^{b}	2.80 ± 1.22^{bc}
	Red oak	2.03 ± 0.38^{c}	16.44 ± 8.45^{ab}	77.26 ± 8.25^{b}	4.27 ± 0.72^{a}
3	Madrone	2.49 ± 0.34^{ab}	20.95 ± 2.15^{a}	74.48 ± 2.59^{b}	2.08 ± 0.25^{de}
	White oak	2.67 ± 0.15^{ab}	20.45 ± 0.72^{a}	74.35 ± 0.77^{b}	2.53 ± 0.10^{b}
	Red oak	2.44 ± 0.19^{b}	20.10 ± 0.24^{a}	75.11 ± 0.61^{b}	2.35 ± 0.47^{cd}

MC = moisture content (%), VM = volatile material (%), FC = fixed carbon (%), ASH = ash content (%). Values with the same letter are statistically equal, according to Kruskal–Wallis ($p \geq 0.05$).

3.3.2. Modified Brazilian Beehive Kiln

Significant statistical differences were found ($p < 0.05$, Kruskal–Wallis). The three burns presented moisture content < 10%, volatile material < 17%, fixed carbon > 74%, and ash content < 11%, and the burn 3 presented the best percentages. Guamúchil from burn 2 had the highest moisture content (7.33%), while Tamarindo from burn 3 had the lowest percentage (0.69%). The highest percentage of volatile material was found in both species in burn 1 (16.62 and 16.71%, respectively), while Guamúchil from burn 2 had the lowest value (7.88%). The lowest fixed carbon content was found in both species from burn 1, while Tamarindo from burn 3 had the highest percentage (84.21%). Finally, the ash content was higher in Guamúchil in the three burns (6.89, 10.41, and 8.10%, respectively), while Tamarindo had the lowest percentage (4.88, 5.46, and 5.40%, respectively) (Table 8).

Table 8. Proximate analysis of charcoal produced in modified Brazilian beehive kilns.

BURN	SPECIE	MC	VM	FC	ASH
1	Guamúchil	2.01 ± 0.21 [c]	16.62 ± 1.10 [a]	74.47 ± 1.76 [c]	6.89 ± 0.87 [a]
	Tamarindo	1.98 ± 0.08 [c]	16.71 ± 0.71 [a]	76.43 ± 1.18 [c]	4.88 ± 0.95 [b]
2	Guamúchil	7.33 ± 1.10 [a]	7.88 ± 0.67 [d]	74.38 ± 5.38 [c]	10.41 ± 3.83 [a]
	Tamarindo	3.46 ± 0.93 [b]	9.48 ± 3.58 [bc]	81.61 ± 3.58 [b]	5.46 ± 1.14 [b]
3	Guamúchil	0.89 ± 0.07 [d]	10.60 ± 0.50 [b]	80.40 ± 1.26 [b]	8.10 ± 1.16 [a]
	Tamarindo	0.69 ± 0.06 [e]	9.70 ± 0.57 [c]	84.21 ± 0.94 [a]	5.40 ± 0.68 [b]

MC = moisture content (%), VM = volatile material (%), FC = fixed carbon (%), ASH = ash content (%). Values with the same letter are statistically equal, according to Kruskal–Wallis ($p \geq 0.05$).

3.3.3. Argentinian Half-Orange Kiln

There were significant statistical differences ($p < 0.05$, Kruskal–Wallis). Burn 2 presented the best energetic characteristics in both species; lower volatile material content (<20%) and higher percentage of fixed carbon (>75%); on the other hand, the Red oak species of burn 2 presented the lowest moisture and volatile material content, higher fixed carbon, and ash content (1.04, 10.20, 82.12, and 6.62%, respectively) (Table 9).

Table 9. Proximate analysis of charcoal produced in Argentine half-orange kilns.

BURN	SPECIE	MC	VM	CF	ASH
1	White oak	1.50 ± 0.59 [b]	20.79 ± 10.00 [ab]	73.66 ± 9.68 [bc]	4.03 ± 0.95 [bc]
	Red oak	2.00 ± 0.28 [a]	25.14 ± 0.39 [a]	69.53 ± 0.44 [c]	3.30 ± 0.76 [c]
2	White oak	1.53 ± 0.40 [bc]	19.18 ± 5.90 [b]	75.16 ± 6.44 [b]	4.14 ± 1.12 [b]
	Red oak	1.04 ± 0.14 [c]	10.20 ± 2.45 [c]	82.12 ± 1.84 [a]	6.62 ± 1.49 [a]
3	White oak	1.99 ± 0.99 [a]	22.08 ± 0.43 [b]	72.24 ± 0.67 [bc]	3.74 ± 0.36 [bc]
	Red oak	1.94 ± 0.05 [a]	22.02 ± 0.95 [b]	71.99 ± 1.55 [b]	4.03 ± 0.82 [b]

MC = moisture content (%), VM = volatile material (%), FC = fixed carbon (%), ASH = ash content (%). Values with the same letter are statistically equal, according to Kruskal–Wallis ($p \geq 0.05$).

3.3.4. Metallic Industrial Kiln

There were significant statistical differences ($p < 0.05$, Kruskal–Wallis). Charcoal production from burn 3 presented the best energy characteristics, low moisture content (<3%), low ash content (<8%), higher fixed carbon content (>72%), and lower volatile material (<23%). Yaxnic and Zapotillo species from burn 3 obtained the highest percentage of moisture (2.79 and 2.88%, respectively), while Ramón had the lowest percentage (1.52%); in addition, burn 1 presented the highest percentage of volatile material (32.71%) and burn 3 presented the lowest (11.13%). Zapotillo from burn 1 had the lowest fixed carbon content (61.30%), while Ramón had the best value (79.20%). The highest percentage of ash was obtained by Zapotillo from burn 2 and Ramón from burn 3 (6.73 and 8.15%, respectively), while Yaxnic from burn 3 presented the lowest value (2.81%) (Table 10).

3.4. Higher Heating Value

The higher heating value presented significant statistical differences ($p < 0.05$), and the species used in the masonry kilns had the highest values. The charcoal produced on burns 2 and 3 with the Brazilian beehive kiln had the highest heating value in its three species (>30 MJ kg^{-1}); on the contrary, the higher heating value of the species produced with the industrial metallic kiln presented the lowest heating value (<31 MJ kg^{-1}). In addition, oak species presented the highest heating value in both technologies (Table 11).

Table 10. Proximate analysis of charcoal produced in industrial metal kilns.

BURN	SPECIE	MC	VM	FC	ASH
1	Ramón	2.17 ± 0.22 bcd	32.71 ± 4.42 a	61.39 ± 4.39 hi	3.73 ± 0.55 ef
	Yaxnic	1.85 ± 0.34 d	22.66 ± 2.68 efg	70.56 ± 2.02 c	4.93 ± 1.65 bc
	Zapote	1.91 ± 0.08 d	28.94 ± 2.80 bc	64.39 ± 3.35 fgh	4.76 ± 0.53 bcde
	Zapotillo	2.12 ± 0.04 bcd	31.43 ± 2.24 ab	61.30 ± 1.66 i	5.15 ± 0.83 bc
2	Ramón	2.04 ± 0.26 cd	31.22 ± 2.59 ab	63.55 ± 2.21 ghi	3.18 ± 0.69 fg
	Yaxnic	2.40 ± 0.25 b	26.57 ± 2.33 d	66.39 ± 3.60 ef	4.64 ± 1.69 bcd
	Zapote	2.41 ± 0.13 b	27.97 ± 2.04 cd	65.23 ± 3.60 efg	4.38 ± 1.70 cde
	Zapotillo	2.12 ± 0.20 bcd	23.40 ± 2.01 e	67.75 ± 1.54 de	6.73 ± 0.63 a
3	Ramón	1.52 ± 0.11 e	11.13 ± 0.87 h	79.20 ± 0.59 a	8.15 ± 1.25 a
	Yaxnic	2.79 ± 0.09 a	21.57 ± 1.44 fg	72.83 ± 0.89 ab	2.81 ± 0.80 g
	Zapote	2.36 ± 0.18 bc	23.45 ± 2.87 ef	68.91 ± 2.95 cd	5.28 ± 0.91 b
	Zapotillo	2.88 ± 0.30 a	20.57 ± 0.76 g	72.52 ± 0.63 b	4.03 ± 0.16 de

MC = moisture content (%), VM = volatile material (%), FC = fixed carbon (%), ASH = ash content (%). Values with the same letter are statistically equal, according to Kruskal–Wallis ($p \geq 0.05$).

Table 11. Heating value (MJ kg^{-1}) of charcoal produced in four types of kilns.

KILN TYPE	BURN	SPECIE	HHV	MINIMUM HHV	MAXIMUM HHV
Brazilian beehive	1	White oak	30.64 ± 0.08 gh	30.55	30.70
	2		30.61 ± 0.23 gh	30.44	30.88
	3		31.33 ± 0.52 ef	30.74	31.69
	1	Red oak	31.81 ± 0.12 cd	31.67	31.89
	2		33.09 ± 0.22 a	32.85	33.26
	3		31.92 ± 0.40 cd	31.53	32.32
	1	Madrone	30.80 ± 0.21 g	31.67	31.03
	2		32.89 ± 0.22 ab	32.85	33.12
	3		32.05 ± 0.28 bc	31.53	32.35
Modified Brazilian beehive	1	Guamúchil	29.08 ± 0.24 jk	28.82	29.28
	2		27.07 ± 0.25 mn	26.79	27.27
	3		30.07 ± 0.14 i	29.95	30.23
	1	Tamarindo	29.29 ± 0.14 j	29.15	29.43
	2		31.41 ± 0.13 f	31.32	31.55
	3		31.68 ± 0.04 de	31.65	31.72
Metallic industrial	1	Ramón	29.10 ± 0.21 jk	28.86	29.26
	2		27.87 ± 0.21 lm	27.63	28.01
	3		31.36 ± 0.20 f	31.23	31.59
	1	Yaxnic	30.48 ± 0.18 hi	30.31	30.66
	2		30.40 ± 0.29 hi	30.17	30.72
	3		30.56 ± 0.50 gh	30.00	30.97
	1	Zapote	23.89 ± 0.16 opq	23.75	24.06
	2		25.88 ± 0.61 mno	25.30	26.51
	3		22.41 ± 0.18 q	22.20	22.55
	1	Zapotillo	23.47 ± 0.33 pq	23.12	23.78
	2		24.03 ± 0.19 op	23.84	24.21
	3		25.35 ± 0.18 no	25.15	25.51
Argentinian half-orange	1	White oak	31.67 ± 0.16 def	31.53	31.84
	2		32.26 ± 0.27 abc	31.96	32.47
	3		29.11 ± 0.31 j	28.76	29.30
	1	Red oak	29.31 ± 0.24 j	29.12	29.58
	2		29.21 ± 0.10 j	29.13	29.32
	3		28.77 ± 0.35 kl	28.36	28.99

HHV = heating value (MJ kg^{-1}). Values with the same letter are statistically equal, according to Kruskal–Wallis ($p \geq 0.05$).

3.5. Principal Component Analysis

Showing the correlation analysis of 14 variables studied, it was observed that the heating ramp of the carbonization phases was negatively correlated with the fixed carbon content and calorific value, while the fixed carbon production yield was positively correlated with the volatile material and the fast-heating ramps. The correlation with the fixed carbon was negative (Table 12). Principal components (PC) 1 and 2 explained 69% of the total variance. PC 1 accounted for 50.4% of the variance and included phases 2, 4, 1, and 3, cellulose, lignin, yield, volatile material, wood moisture, heating, fixed carbon, and hemicellulose; PC 2 accounted for 18.6% of the variance and consisted of ash content, wood moisture, fixed carbon, cellulose, moisture content, hemicellulose, yield, and volatile material (Figure 13).

Table 12. Sperman correlation analysis of 14 variables representative of the carbonization process.

Variable	MC	VM	ASH	FC	HHV	YIELD	MCB	Stage1	Stage2	Stage3	Stage4	HEM	CEL	LIG
MC	1	0.12	−0.18	−0.3	−0.21	0.23	−0.061	0.12	0.21	−0.27	0.21	−0.088	−0.005	0.2
VM	0.12	1	−0.31	−0.9	−0.47	0.76	−0.51	0.4	0.63	0.35	0.38	−0.26	0.35	0.4
ASH	−0.18	−0.31	1	0.073	−0.42	−0.37	−0.11	0.42	0.11	0.45	0.33	−0.57	0.47	0.35
FC	−0.3	−0.9	0.073	1	0.66	−0.76	0.47	−0.49	−0.65	−0.36	−0.47	0.42	−0.43	−0.53
HHV	−0.21	−0.47	−0.42	0.66	1	−0.5	0.27	−0.54	−0.53	−0.49	−0.38	0.53	−0.44	−0.59
YIELD	0.23	0.76	−0.37	−0.76	−0.5	1	−0.64	0.55	0.8	0.47	0.61	−0.26	0.37	0.46
MCB	−0.061	−0.51	−0.11	0.47	0.27	−0.64	1	−0.63	−0.65	−0.55	−0.61	0.51	−0.71	−0.47
Stage1	0.12	0.4	0.42	−0.49	−0.54	0.55	−0.63	1	0.74	0.83	0.79	−0.76	0.8	0.68
Stage2	0.21	0.63	0.11	−0.65	−0.53	0.8	−0.65	0.74	1	0.58	0.57	−0.52	0.61	0.61
Stage3	−0.27	0.35	0.45	−0.36	−0.49	0.47	−0.55	0.83	0.58	1	0.62	−0.71	0.75	0.58
Stage4	0.21	0.38	0.33	−0.47	−0.38	0.61	−0.61	0.79	0.57	0.62	1	−0.68	0.71	0.68
HEM	−0.088	−0.26	−0.57	0.42	0.53	−0.26	0.51	−0.76	−0.52	−0.71	−0.68	1	−0.91	−0.74
CEL	−0.005	0.35	0.47	−0.43	−0.44	0.37	−0.71	0.8	0.61	0.75	0.71	−0.91	1	0.61
LIG	0.2	0.4	0.35	−0.53	−0.59	0.46	−0.47	0.68	0.61	0.58	0.68	−0.74	0.61	1

MC = Moisture content (%), MCB: Wood moisture content MV = Volatile material (%), FC = Fixed carbon (%), ASH = Ash content (%), HHV = Heating value, CEL = Cellulose, Lig = Lignin, HEM = Hemicellulose.

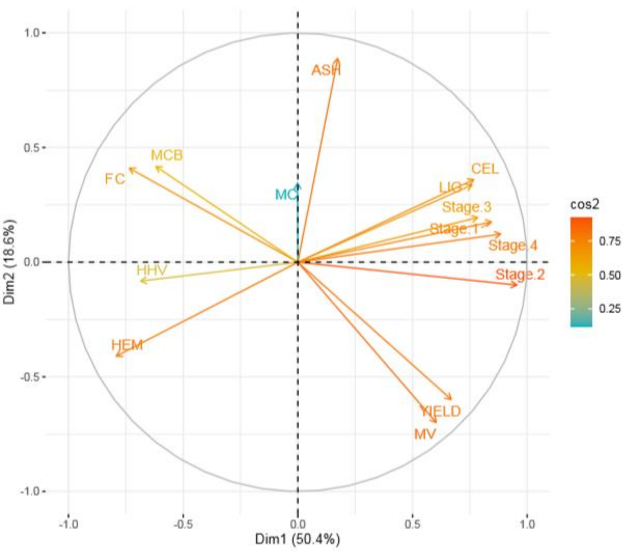

Figure 13. Principal Component Analysis (PCA), representing the two main components. MC = moisture content (%), MCB: wood moisture content MV = volatile material (%), FC = fixed carbon (%), ASH = ash content (%), HHV = Heating value, CEL = Cellulose, Lig = Lignin, HEM = Hemicelulosa.

The charcoal made in the modified Brazilian beehive kilns was grouped in the quadrant with the highest fixed carbon content and moisture content of the firewood. On the other hand, the charcoal made in the Argentine half-orange kilns was grouped in the highest-level of the highest heating value and hemicellulose in the firewood, and the charcoal made in the Brazilian beehive kilns was also grouped with the Argentine half-orange kilns, which were influenced by oak's species. Finally, the charcoal produced in the metal kiln was grouped with the highest production yield, but also with the highest content of volatile material (Figure 14).

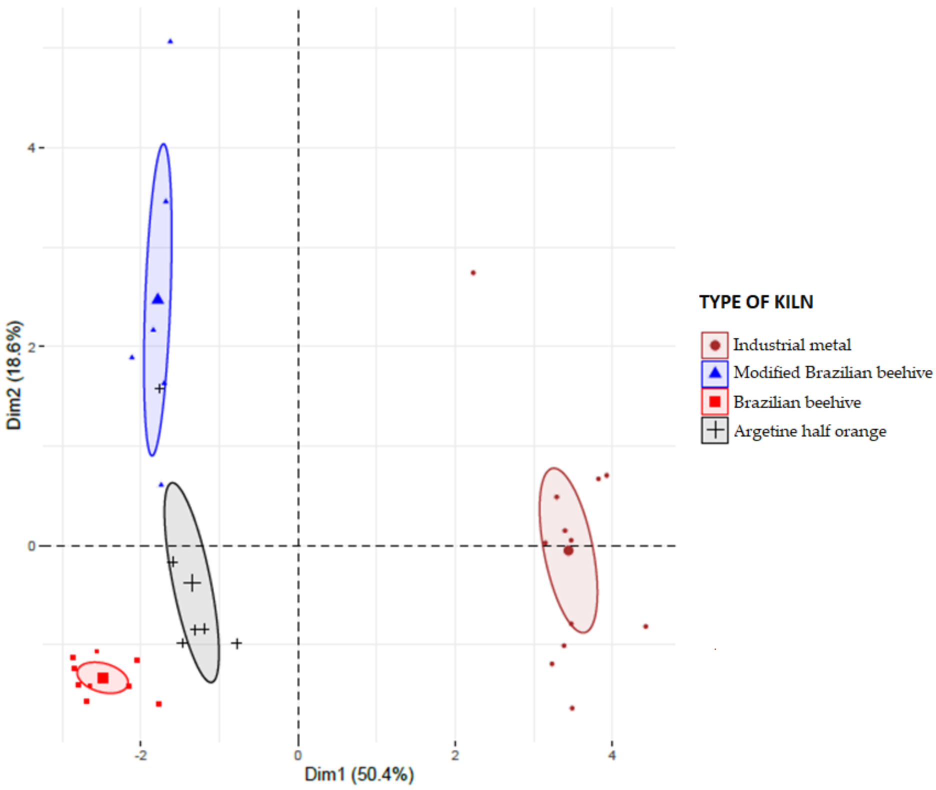

Figure 14. Grouping of the variable's representative of the carbonization process.

4. Discussion

4.1. Carbonization Conditions

The study of the carbonization process with different types of species and kilns showed that carbonization time is related to several factors, among them the kiln type and capacity. That is why the greater the volume of firewood loaded in the kiln, the longer the carbonization time. Another factor is the moisture content of the firewood; in particular, this increases the time for phases 1 and 2, which correspond to kiln ignition, drying of the firewood, and decomposition of the hemicellulose. Therefore, if the aim is to reduce the carbonization time, firewood with low moisture content (<30%) should be used, which coincides with Pyshyev et al. [40]. On the other hand, phase 3, where cellulose and hemicellulose remnants react, was the shortest, regardless of the type of kiln used. For their part, Pyshyev et al. [40] considered that the most important phase during the charcoal production process is phase 4, since it represents a change in the energy process, changing from an endothermic phase (<280 °C) to an exothermic one (>280 °C), a phase in which the remnants of hemicellulose and cellulose are minimal, as established by Chen et al. [41] and Pereira et al. [34]. Therefore, the component that carbonizes in this phase is lignin as a result of its elemental structure and is composed of a high percentage of carbon and low oxygen content. The temperature required to promote its reaction is high, as was shown by Stefanidis et al. [42]. This is consistent with Basile et al. [43], who say that the decomposition of hemicellulose and cellulose is complete at 400 °C, so that from that temperature the remaining compound is converted into charcoal.

In relation to the maximum process temperature, the results are consistent with Rodrigues and Braghini [44] and Oyebanji and Oyedepo [4], who point out that the higher the process temperature, the higher the quality of the charcoal generated, because it has a lower content of volatile material, but with a low yield, as was presented in burn 3 of the Brazilian kiln, burn 3 of the modified Brazilian kiln, burn 2 of the Argentine half-orange kiln, and burn 3 of the industrial metallic kiln. Finally, the cooling phase, which is minimally considered in the literature, has a duration similar to the carbonization time when carried out in a natural way, while if water is added, its duration will be shorter, but with high risks of obtaining a brittle charcoal of lower quality Arias-Chalico [45], as occurred in the burnings of the Brazilian kiln, where it was not possible to recover all the specimens due to the added water.

The lowest yield was observed when the temperature in the carbonization process increases (>450 °C) and the duration of phase 4 is longer, as was monitored in the masonry kilns used in this research, while Massuque et al. [46] mentioned that this range (400 to 450 °C) is the most important for producing charcoal for domestic use; on the other hand, Pyshyev et al. [40] mentioned that for carbonization maintained at the lower temperature of phase 4, charcoal presents the best performance, is easy to ignite, but still presents considerable amounts of tar, so for a quality product with low emissions and a content of >75% fixed carbon, carbonization should be performed above 500 °C.

The best conditions to produce charcoal were presented with the metallic kiln using Ramón, Yaxnic, Zapote, and Zapotillo firewood species. Abreu et al. [47] mentioned that firewood density is positively correlated with charcoal production when the objective is to have a higher stiffness. In addition, they had higher lignin content compared to species from other sites, but the process control was not optimal, leaving only burn 3 as acceptable. In addition to the above, this is attributed to the lack of experience, and it is necessary to train operators as it is the technology with the greatest benefits in charcoal production. The metal industrial kiln is technologically the most modern, so it presents an improvement in its system of reuse of gases and vapors, loading and unloading system, and rapid cooling and use of resistant materials, as suggested by Rodrigues and Braghini [16].

4.2. Yield

The highest charcoal production yields occurred in the metallic kiln, showing values of 30 to 45%, which is closely related to the high content of volatile material contained in the carbon produced by this type of furnace; on the other hand, the lowest yields occurred in the Brazilian kiln and modified Brazilian kiln, which could be influenced by the percentage of moisture in the firewood (>30%). According to Canal et al. [5], the moisture content of the firewood does not influence the quality of the charcoal, as was observed with the Guamúchil firewood, but it influences the yield and the emissions released into the environment, since high moisture on the firewood will require a greater consumption of firewood to achieve carbonization. In addition, it is mentioned that masonry kilns have a yield of around 30% in their best scenarios, which is like Bailis et al. [48], Pereira [34], and Pyshyev et al. [40], who state that traditional kilns with low technology result in low yield and low charcoal quality. This is to be "considered" because most of the world's charcoal production is done with low technology.

4.3. Physicochemical Analysis

Kilns with a slow ramp (<1 °C min^{-1}) produced charcoal of good quality, and the final temperature observed was similar to that recommended by Kan et al. [15], who mentioned that the ideal temperature is from 400 to 550 °C. One of the most widely used standards for categorizing charcoal is EN 1860-2 [49], which is applicable to most European countries (Jelonek et al.) [8]. This stated for export and consumption purposes, and fixed carbon should be ≥75%, ash ≤ 8%, moisture content ≤ 8%, while volatile material is not considered, but if the assumption that the proximate analysis should add up to 100% is applied, it should be ≤16%, as could be seen in the in the correlation analysis of the four types of kilns. There was a strong negative correlation between the volatile material and the fixed carbon (−0.9), while it was positive with the production yield (0.76), which proves that the shorter time of phases 2 and 3 the volatile material content tends to be high, because the removal of oxygen bonds is involved in these phases. Given the above values, the carbonized species in the Brazilian beehive and modified Brazilian beehive kilns meet these requirements, which both species in burn 2 used in Argentine half-orange also meet; for its part, the tropical species used in the metal-type kiln, the Ramón in burn 3, meets these requirements. However, there are also other classifications for domestic use, as mentioned by Antal and Grønli [6], which, for domestic purposes, establish that the percentage of acceptable fixed carbon is ≥65% and volatile material ≤ 30%. Therefore, if followed for this use, the species used in this research are suitable, except for Ramón in burn 1 and 2, as well as Zapotillo from burn 1. Costa et al. [50] mention that charcoal for domestic use presents a great variation in quality because in most kilns the process is difficult and often an inadequate raw material is used, generating a heterogeneous product.

4.4. Principal Component Analysis

The volatile material content presented a high and negative correlation with fixed carbon, which agrees with Missio et al. [51]. The increase of temperature in the carbonization process causes the breakdown of the structural components of firewood (cellulose, hemicellulose, and lignin), while water, CO, CO_2, and other gases (VM) are removed from the firewood.

The PCA in this work represented 69% of the variance by including 14 study variables and satisfactorily obtaining a classification of the different kilns used. Roque et al. [52] evaluated the similarity between biomass and charcoal for energy purposes. In their study, two principal components were presented to explain 72.3% of the accumulated variance of the data and to obtain a classification; on the other hand, Costa et al. [50] performed a PCA with the maximum number of twelve principal. In this analysis, no clear groups were formed with respect to charcoal producers, which may be due to the lack of variables during the carbonization process, such as the absence of information on temperature; on the contrary, in this research it is considered, and that is why the different classifications are made.

5. Conclusions

The charcoal carbonization process clearly presents five phases, when keeping a heating ramp < 1 °C in all phases until a final temperature > 500 °C, will favor carbonization, generating a quality product for domestic consumption and complying with export quality parameters (>75% fixed carbon, <8% ash, and <8% humidity).

The firewood moisture content < 30% will favor the carbonization process time, making phases 1 and 2 shorter and thereby increasing the charcoal production yield.

The kilns Brazilian beehive-type, modified Brazilian beehive-type, Argentinian half-orange, and metallic industrial used for charcoal production are capable of producing a product suitable for domestic use, although it is advisable to use kilns that do not exceed 20 m^3 of firewood capacity, since as the size of the kiln increases, control of the kiln becomes more complicated, thus increasing the time of phase 5 and even using water for cooling, which results in a product with friability and homogeneous quality.

Different plant species and different technologies, from different regions analyzed, demonstrated the potential to produce acceptable quality charcoal, given appropriate burning conditions as analyzed. Based on this research, it is suggested that more analyses of different kilns and species be carried out on an industrial scale, with temperature monitoring and homogenization of the firewood.

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References

1. IEA. Data and Statistics. 2019. Available online: https://www.iea.org/data-and-statistics (accessed on 1 June 2020).
2. UN. 7 Affordable and Clean Energy, Goal 7- Ensure Access To Affordable, Reliable, Sustainable and Modern Energy. 2019. Available online: https://www.un.org/en/chronicle/article/goal-7-ensure-access-affordable-reliable-sustainable-and-modern-energy-all (accessed on 6 December 2019).
3. Demirbas, A. Sustainable charcoal production and charcoal briquetting. *Energy Sources Part A* **2009**, *31*, 1694–1699. [CrossRef]
4. Oyebanji, J.A.; Oyedepo, S.O. Compositional and experimental investigation of the effect of reactor temperature on softwood and hardwood pyrolysis. *World J. Eng.* **2018**, *15*, 21–26. [CrossRef]
5. Canal, W.D.; Carvalho, A.M.M.; Figueiró, C.G.; Carneiro, A.D.C.O.; Fialho, L.D.F.; Donato, D.B. Impact of wood moisture in charcoal production and quality. *Floresta E Ambient.* **2020**, *27*, 1–7. [CrossRef]
6. Antal, M.J.; Grønli, M. The art, science, and technology of charcoal production. *Ind. Eng. Chem. Res.* **2003**, *42*, 1619–1640. [CrossRef]
7. Oaks, R. Making Charcoal and Biochar A Comprehensive Guide. Ramsbury, Marlborough Wiltshire SN8 2HR. 2018. Available online: http://www.crowood.com (accessed on 12 October 2022).
8. Jelonek, Z.; Drobniak, A.; Mastalerz, M.; Jelonek, I. Environmental implications of the quality of charcoal briquettes and lump charcoal used for grilling. *Sci. Total Environ.* **2020**, *747*, 25. [CrossRef] [PubMed]
9. Nabukalu, C.; Gieré, R. Charcoal as an energy resource: Global trade, production and socioeconomic practices observed in Uganda. *Resources* **2019**, *8*, 183. [CrossRef]
10. Sangsuk, S.; Buathong, C.; Suebsiri, S. High-energy conversion efficiency of drum kiln with heat distribution pipe for charcoal and biochar production. *Energy Sustain. Dev.* **2020**, *59*, 1–7. [CrossRef]
11. Francisco, A.; Junior, D.; Pompeu, R.; Álison, E.; Aécio, S.; Sousa, D. Investigating the pyrolysis temperature to define the use of charcoal. *Eur. J. Wood Wood Prod.* **2020**, *78*, 193–204. [CrossRef]
12. FAO. *The Charcoal Transition: Greening The Charcoal Value Chain To Mitigate Climate Change And Improve Local Livelihoods*; FAO: Rome, Italy, 2017.
13. Arias-Chalico, T. Situación Actual Y Escenarios Para El Desarrollo De Biocombustibles Sólidos En México Hacia 2024 Y 2030. 2018. Available online: http://rembio.org.mx/newsite/wp-content/uploads/2020/11/Situacion-actual-y-escenarios-para-el-desarrollo-de-biocombustibles-solidos-en-Mexico.pdf (accessed on 22 January 2022).
14. Surup, G.R.; Trubetskaya, A.; Tangstad, M. Charcoal as an alternative reductant in ferroalloy production: A review. *Processes* **2020**, *8*, 1432. [CrossRef]
15. Kan, T.; Strezov, V.; Evans, T.J. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. *Renew. Sustain. Energy Rev.* **2016**, *57*, 1126–1140. [CrossRef]
16. Rodrigues, T.; Junior, A.B. Charcoal: A discussion on carbonization kilns. *J. Anal. Appl. Pyrolysis* **2019**, *143*, 16. [CrossRef]
17. Freddy, Z.J.; Joseph, Z.M.; Benoit, N.; Evariste, F.F.; Ruben, M.; Maximilien, N.; Bernard, B.A. Physicochemical and hygroscopic properties of charcoals produced from residues of two tropical woods from Cameroon. *Int. J. Coal Prep. Util.* **2022**, 1–24. [CrossRef]
18. Arias-Chalico, T. Carbón Vegetal en México Consumo, Mercados y Productores. Naturaleza y Desarrollo NYDE AC. Available online: https://kipdf.com/carbon-vegetal-en-mexico_5ae745e67f8b9a18528b45c6.html (accessed on 15 February 2022).
19. Kajina, W.; Junpen, A.; Garivait, S.; Kamnoet, O.; Keeratiisariyakul, P.; Rousset, P. Charcoal production processes: An overview. *J. Sustain. Energy Environ.* **2019**, *10*, 19–25.
20. FAO. Métodos Simples Para Fabricar Carbón Vegetal. 1983. Available online: http://www.fao.org/docrep/x5328s/x5328s00.htm (accessed on 1 March 2022).

21. Bustamante-García, V.; Carrillo-Parra, A.; González-Rodríguez, H.; Ramírez-Lozano, R.; Corral-Rivas, J.; Garza-Ocañas, F. Evaluation of a charcoal production process from forest residues of Quercus sideroxyla Humb., & Bonpl. in a Brazilian beehive kiln. *Ind. Crop. Prod.* **2013**, *42*, 169–174. [CrossRef]
22. Carrillo-Parra, A.; Foroughbakhch-Pournavab, R.; Bustamante-García, V. Calidad del carbón de Prosopis laevigata (Humb. & Bonpl. ex Willd.) M.C. Johnst. y Ebenopsis ebano (Berland.) Bar-neby & J.W. Grimes elaborado en horno tipo fosa. *Rev. mex. de cienc. Forestales* **2013**, 62–71. Available online: https://www.scielo.org.mx/scielo.php?script=sci_arttext&pid=S2007-11322013000300007 (accessed on 5 February 2022).
23. Ngangyo-Heya, M.; Foroughbahchk-Pournavab, R.; Carrillo-Parra, A.; Rutiaga-Quiñones, J.G.; Zelinski, V.; Pintor-Ibarra, L.F. Calorific value and chemical composition of five semi-arid mexican tree species. *Forests* **2016**, *7*, 58. [CrossRef]
24. Petrović, S.; Glavonjic, B. Standards and Certificates for Charcoal and Charcoal Briquettes in the Function of Harmonization of their Quality and Market Development. In Proceedings of the Development Trends in Economic and Management in Wood Processing and Furniture Manufacturing, Kozina, Slovenia, 9 June 2011; Faculty of Forestry University of Belgrade: Beograd, Serbia, 2011. Available online: https://www.researchgate.net/publication/352120554_STANDARDS_AND_CERTIFICATES_FOR_CHARCOAL_AND_CHARCOAL_BRIQUETTES_IN_THE_FUNCTION_OF_HARMONIZATION_OF_THEIR_QUALITY_AND_MARKET_DEVELOPMENT (accessed on 1 December 2022).
25. FAO. Industrial Charcoal Making-Quality Contrôle of Charcoal and by Products. 1985. Available online: http://www.fao.org/3/x5555e/x5555e.pdf (accessed on 3 March 2022).
26. García-Quezada, J.; Musule-Lagunes, R.; Carrillo-Ávila, N.; Carrillo-Parra, A. Tipo de hornos para la producción de carbón vegetal en México. In *Optimización De Los Procesos De Extracción De Biomasa Sólida Para Uso Energético*, 1st ed.; Programa Iberoamericano De Ciencia Y Tecnología Para El Desarrollo (CYTED): Cambridge, UK, 2021; Volume 1, pp. 293–321.
27. De la Cruz-Montelongo, C.; Gamboa, J.H.; Sánchez, I.A.O.; Saucedo, J.C.R.; Serna, R.R.; Carrillo-Parra, A. Caracterización energética del carbón vegetal producido en el Norte-Centro de México. *Madera Y Bosques* **2020**, *26*, 13. [CrossRef]
28. Manals, E.; Penedo, M.; Giralt, G. Análisis termogravimetrico y térmico diferencial de diferentes biomasas vegetales. *Tecnol. Química vol.* **2011**, *31*, 180–190.
29. Oliveira, A.C.; Carneiro, A.D.C.O.; Pereira, B.L.C.; Vital, B.R.; Carvalho, A.M.M.L.; Trugilho, P.F.; Damásio, R.A.P. Otimização da produção do carvão vegetal por meio do controle de temperaturas de carbonização. *Rev. Árvore* **2013**, *3*, 557–566. [CrossRef]
30. Vilela, A.D.O.; Lora, E.S.; Quintero, Q.R.; Vicintin, R.A.; Souza, T.P.D.S.E. A new technology for the combined production of charcoal and electricity through cogeneration. *Biomass Bioenergy* **2014**, *69*, 222–240. [CrossRef]
31. Montoya, J.I.; Colombiano, I. *Pirólisis Rápida De Biomasa*; Universidad Nacional de Colombia: Bogotá, Colombia, 2014.
32. Wang, S.; Luo, Z. Biomass components and characteristics. In *Pyrolysis of Biomass*; Walter de Gruyter: Berlin, Germany, 2016; p. 32. [CrossRef]
33. Dhyani, V.; Bhaskar, T. A comprehensive review on the pyrolysis of lignocellulosic biomass. *Renew. Energy* **2018**, *129*, 695–716. [CrossRef]
34. Pereira, E.G.; Fauller, H.; Magalhães, M.; Guirardi, B.; Martins, M.A. Potential use of wood pyrolysis coproducts: A review. *Environ. Prog. Sustain. Energy* **2022**, *41*, e13705. [CrossRef]
35. Elyounssia, K.; Blinb, J.; Halim, M. High-yield charcoal production by two-step pyrolysis. *J. Anal. Appl. Pyrolysis* **2010**, *87*, 138–143. [CrossRef]
36. ASTM. Standard Test Method for Chemical Analysis of Wood Charcoal. 2021, pp. 1–2. Available online: https://www.astm.org/d1762-84r21.html (accessed on 1 September 2022).
37. Basu, P.; Rao, S.; Dhungana, A. An investigation into the effect of biomass particle size on its torrefaction. *Can. J. Chem. Eng.* **2013**, *91*, 466–474. [CrossRef]
38. *UNE-EN 18125*; Biocombustibles Sólidos Determinación Del Poder Calorífico. INTECO: Bruck, Austria, 2018.
39. Lê, S.; Josse, J.; Rennes, A.; Husson, F. FactoMineR: An R Package for Multivariate Analysis. 2008. Available online: http://www.jstatsoft.org/ (accessed on 11 February 2022).
40. Pyshyev, S.; Miroshnichenko, D.; Malik, I.; Contreras, A.B.; Hassan, N.; ElRasoul, A.A.; Carbosur, C.M.F. State of the art in the production of charcoal: A review. *Chem. Chem. Technol.* **2021**, *15*, 61–73. [CrossRef]
41. Chen, W.; Chen, Y.; Yang, H.; Li, K.; Chen, X.; Chen, H. Investigation on biomass nitrogen-enriched pyrolysis: Influence of temperature. *Bioresour. Technol.* **2018**, *249*, 247–253. [CrossRef]
42. Stefanidis, S.D.; Kalogiannis, K.G.; Iliopoulou, E.F.; Michailof, C.M.; Pilavachi, P.A.; Lappas, A.A. A study of lignocellulosic biomass pyrolysis via the pyrolysis of cellulose, hemicellulose and lignin. *J. Anal. Appl. Pyrolysis* **2014**, *105*, 143–150. [CrossRef]
43. Basile, L.; Tugnoli, A.; Cozzani, V. Influence of macrocomponents on the pyrolysis heat demand of lignocellulosic biomass. *Ind. Eng. Chem. Res.* **2017**, *56*, 6432–6440. [CrossRef]
44. Rodrigues, T.; Junior, A.B. Technological prospecting in the production of charcoal: A patent study. *Renew. Sustain. Energy Rev.* **2019**, *111*, 170–183. [CrossRef]
45. Arias-Chalico, T. Manual De Operación Del Horno De Ladrillos Con 8 A 12 Chimeneas Metálicas Para Leña De Encino; Naturaleza y Desarrollo A.C. pp. 1–7. Available online: http://nyde.org.mx/wp-content/uploads/MANUAL-DE-OPERACION-DEL-HORNO-RABO-QUENTE-con-8-a-12-CHIMENEAS.pdf (accessed on 6 December 2022).
46. Massuque, J.; De Assis, M.R.; Loureiro, B.A.; Matavel, C.E.; Trugilho, P.F. Influence of lignin on wood carbonization and charcoal properties of Miombo woodland native species. *Eur. J. Wood Wood Prod.* **2021**, *79*, 527–535. [CrossRef]

47. De Abreu Neto, R.; De Assis, A.A.; Ballarin, A.W.; Hein, P.R.G. Effect of final temperature on charcoal stiffness and its correlation with wood density and hardness. *SN Appl. Sci.* **2020**, *2*, 1020. [CrossRef]
48. Bailis, R.; Rujanavech, C.; Dwivedi, P.; Vilela, A.D.O.; Chang, H.; de Miranda, R.C. Innovation in charcoal production: A comparative life-cycle assessment of two kiln technologies in Brazil. *Energy Sustain. Dev.* **2013**, *17*, 189–200. [CrossRef]
49. *UNE-EN 1860-2*; Aparatos, Combustibles Sólidos Y Sustancias De Encendido Para El Asado En Barbacoas. INTECO: Bruck, Austria, 2005.
50. Costa, A.; Ramalho, F.; Costa, L.; Trugilho, P.; Hein, P. Classification of commercial charcoal for domestic use by near infrared spectroscopy. *Biomass Bioenergy* **2019**, *127*, 105280. [CrossRef]
51. Missio, A.L.; Mattos, B.D.; Gatto, D.A.; De Lima, E.A. Thermal Analysis of Charcoal from Fast-Growing Eucalypt Wood: Influence of Raw Material Moisture Content. *J. Wood Chem. Technol.* **2014**, *34*, 191–201. [CrossRef]
52. Lima, M.D.R.; Patrício, E.P.S.; Junior, U.D.O.B.; de Assis, M.R.; Xavier, C.N.; Bufalino, L.; Trugilho, P.F.; Hein, P.R.G.; Protásio, T.D.P. Logging wastes from sustainable forest management as alternative fuels for thermochemical conversion systems in Brazilian Amazon. *Biomass Bioenergy* **2020**, *140*, 105660. [CrossRef]