FEDERAL UNIVERSITY OF SÃO CARLOS
SOROCABA CAMPUS
GRADUATE PROGRAM IN MATERIAL SCIENCES

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BINCHOTAN CHARCOAL AS A RENEWABLE SOURCE FOR PARTIAL REPLACEMENT OF CALCINED PETROLEUM COKE IN THE ALUMINUM INDUSTRY

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Thesis submitted to the Graduate Program in Material Sciences in partial fulfillment of the requirements for the degree of Doctor of Material Sciences.

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DEDICATION

To my grandparents.

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RESUMO

PEREIRA, Lucas Clarindo. Carvão binchotan como fonte renovável para substituição parcial de coque calcinado de petróleo na indústria do alumínio. 2024. Tese (Doutorado em Ciência dos Materiais) – Universidade Federal de São Carlos, Sorocaba, 2024.

Os materiais de origem fóssil são utilizados na indústria de alumínio há muitas décadas, porém causam grandes impactos ambientais. A utilização de biomateriais pode contribuir com a redução destes impactos. A indústria de alumínio utiliza coque calcinado de petróleo e piche de alcatrão na produção dos anodos de carbono, que atuam como redutores químicos e condutores elétricos durante o processo de eletrólise da alumina. Este trabalho avaliou a substituição parcial do coque calcinado de petróleo por carvão binchotan, visando a produção de anodos de carbono. O uso do binchotan se deu por ser um tipo de carvão caracterizado por apresentar alto teor de carbono, alta densidade e baixa resistividade elétrica. O estudo foi realizado em parceria com uma empresa produtora de alumínio, o que permitiu o uso de materiais, metodologias e equipamentos que são aplicados nos anodos de carbono convencionais. A revisão bibliográfica (Capítulo 1), aborda os conceitos ligados à biomassa, aos processos de redução e a origem, as características e o processo de produção do carvão binchotan. No Capítulo 2 consta a caracterização dos materiais. Amostras de carvão binchotan foram analisadas e comparadas com o coque calcinado de petróleo. Foram realizadas as seguintes análises: análise imediata, composição química, microscopia eletrônica de varredura e espectroscopia por energia dispersiva (MEV-EDS), espectroscopia no infravermelho por transformada de Fourier (FTIR), termogravimetria, densidade, poder calorífico, resistividade elétrica e difração de raios-X (DRX). O carvão binchotan apresentou alto teor de carbono e baixo teor de cinzas, mas os valores observados no coque foram melhores. Uma maior porosidade foi observada no carvão binchotan por meio da análise das imagens do MEV. O comportamento térmico dos materiais foi similar, assim como os espectros de FTIR. A densidade do coque foi maior que a do carvão binchotan e o poder calorífico apresentou valores similares. O carvão binchotan apresentou uma resistividade elétrica maior do que o coque de petróleo. Os padrões de DRX evidenciaram a presença de grafita nos materiais, com maior intensidade no coque. Em geral, as propriedades do coque calcinado de petróleo foram melhores do que as do carvão binchotan, porém os resultados indicaram que uma substituição de pequenos percentuais seria viável. A produção de anodos de carbono com adição de carvão binchotan está descrita no Capítulo 3. Os anodos foram produzidos em escala laboratorial, substituindo 1% e 3% de coque calcinado de petróleo por carvão binchotan. As amostras foram analisadas pela composição química, densidade aparente, resistência mecânica, reatividade com CO_2 e resistividade elétrica. Os dados obtidos foram comparados com um padrão de referência industrial. Todos os resultados foram considerados aceitáveis, sugerindo ser possível realizar a substituição parcial do coque calcinado de petróleo pelo carvão binchotan. Do ponto de vista técnico, a adição de pequenos percentuais de carvão binchotan nos anodos de carbono se mostrou viável.

Palavras-chave: Biomassa. Carvão Branco. Carbono. Biocoque. Bioanodo.

ABSTRACT

PEREIRA, Lucas Clarindo. Binchotan charcoal as a renewable source for partial replacement of calcined petroleum coke in the aluminum industry. 2024. Thesis (Doctorate in Materials Science) – Federal University of São Carlos, Sorocaba, 2024.

Fossil-based materials have been used in the aluminum industry for many decades but cause major environmental impacts. The use of biomaterials can help to reduce these impacts. The aluminum industry uses calcined petroleum coke and coal tar pitch in carbon anode production, and the anodes act as chemical reducers and electrical conductors during the alumina electrolysis process. This work evaluated the partial replacement of calcined petroleum coke with binchotan charcoal, aiming at the production of carbon anodes. Binchotan was used because it is a type of charcoal characterized for showing high carbon content, high density, and low electrical resistivity. The study was carried out in partnership with an aluminum production company, which allowed the use of materials, methodologies, and equipment that are applied in conventional anodes. The literature review (Chapter 1) addresses concepts related to biomass, reduction processes, the origin, characteristics, and production process of binchotan charcoal. The materials characterization is in Chapter 2. Samples of binchotan charcoal were analyzed and compared to calcined petroleum coke. The following analyses were performed: proximate analysis, chemical composition, scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS), Fourier-transform infrared spectroscopy (FTIR), thermogravimetry, density, higher heating value, electrical resistivity, and X-ray diffraction (XRD). Binchotan charcoal showed high carbon content and low ash content, but these values were better in coke. Analyzing the SEM images, a higher porosity was observed in binchotan charcoal. The thermal behavior was similar in all the materials, as were the FTIR spectra. The density of the coke was higher than that of the binchotan charcoal and the results of higher heating values were similar. Binchotan charcoal showed an electrical resistivity higher than petroleum coke. The XRD patterns were similar and showed the presence of graphite in the materials, with higher intensity in coke. In general, the properties of calcined petroleum coke were better than those of binchotan charcoal, although the results indicated that a replacement of small percentages would be feasible. The production of carbon anodes with the addition of binchotan charcoal is described in Chapter 3. The anodes were produced on a laboratory scale, replacing 1% and 3% of calcined petroleum coke with binchotan charcoal. The samples were analyzed by chemical composition, apparent density, mechanical strength, CO_2 reactivity, and electrical resistivity. The obtained data was compared with an industrial reference standard. All the results were considered acceptable, suggesting that it is possible to make a partial substitution of calcined petroleum coke for binchotan charcoal. From a technical point of view, the addition of small percentages of binchotan charcoal in the carbon anodes proved to be viable.

Keywords: Biomass. White Charcoal. Carbon. Biocoke. Bioanode.

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LIST OF ABBREVIATIONS AND ACRONYMS

AJ	Anode with the addition of binchotan charcoal made in Japan
AM	Anode with the addition of binchotan charcoal made in Myanmar
Al_2O_3	Alumina / Aluminum oxide
BJ	Binchotan charcoal made in Japan
BM	Binchotan charcoal made in Myanmar
CBA	Companhia Brasileira de Alumínio (Brazilian Aluminum Company)
CO_2	Carbon dioxide
CO_2e	Carbon dioxide equivalent
DTG	Derivative thermogravimetry
EDS	Energy dispersive spectroscopy
FTIR	Fourier-transform infrared spectroscopy
HHV	Higher heating value
ITA	Instituto Tecnológico de Aeronáutica (Aeronautics Institute of Technology)
ppm	parts per million
SEM	Scanning electron microscopy
TGA	Thermogravimetry / Thermogravimetric analysis
UFSCar	Universidade Federal de São Carlos (Federal University of São Carlos)
VBD	Vibrated bulk density
XRD	X-ray Diffraction

SUMMARY

INTRODUCTION

There is a constant search for different supplies and energy sources among many industries and sectors. From an environmental point of view, great attention is given to fossil materials due to a direct relationship with gas emissions, mainly carbon dioxide (Fan; Friedmann, 2021).

Fossil materials have been used for many decades. Many technological evolutions happened with their application, resulting in lower costs and/or better properties, in comparison to other sources. Although it is a non-renewable source, the shortage of this kind of resource should not occur in a short time, on the other hand, the environmental impacts are a current problem and can rapidly increase (Cheng et al., 2020).

Besides the partial or total substitution by renewable sources, studies aiming for a better use of resources and the reduction of environmental impacts are also made. The criteria change around the world, according to the laws and incentives of each country or the agreement to which they are signatories. The most prominent sustainable energy sources with the potential to be used are hydro, wind and solar power, nuclear, and biomass, each one having its particularities, costs, and risks. Biomass has as an additional advantage the possibility of being used as feedstock in other applications (Brough; Jouhara, 2020; Saevarsdottir; Kvande; Welch, 2020).

The biomass can be used in natura or after processing. When it is used for energy generation, by burning, a compensation of the greenhouse gas emissions can happen due to the carbon dioxide capture that occurs during the growing of trees and agricultural plantations (Fan; Friedmann, 2021; Saba; El Bachawati; Malek, 2020).

High contents of carbon are required in several applications that use fossil materials, for example, solid fuels, in this case, the biomass needs to be processed to achieve comparable properties. These materials can also be used in the ironmaking process and the production of carbon anodes for the aluminum industry (Cheng et al., 2020; Fan; Friedmann, 2021; Senanu; Solheim, 2021).

Traditionally, carbon anodes are produced by mixing calcined petroleum coke and coal tar pitch, and present properties such as high mechanical resistance, low electrical resistivity, and low reactivity (Glastonbury et al., 2020; Ozturk et al., 2018). The biomass application in the production of the carbon anodes used in aluminum production has been studied, aiming to reduce the use of fossil materials and their emissions (Amara et al., 2022; Lu et al., 2021; Senanu; Solheim, 2021).

It is estimated that aluminum production is responsible for about 2% of global carbon dioxide emissions (Saevarsdottir; Kvande; Welch, 2020). Some research lines aim for the partial replacement of the calcined petroleum coke with charcoal to reduce the dependence on non-renewable sources and to minimize environmental impacts (Ratvik; Mollaabbasi; Alamdari, 2022).

To be used, the biomaterials have to show properties that are similar to those of fossil materials and not compromise the quality of the final product. Because of this, it is necessary to select specific biomasses and use mechanical, chemical, or thermal processes for modification and adequacy of the characteristics. For this purpose, binchotan charcoal shows characteristics that seem suitable for the application of carbon anodes in the aluminum industry.

Binchotan charcoal is produced from a high-density type of Japanese oak and through a specific process of carbonization. (Fujimoto, 2023; Itani; Kishimoto, 2018). This kind of charcoal is made using a slow pyrolysis process at low temperatures, followed by an increase in temperature at the end. It shows high carbon content, high density, good adsorption capacity, and good electrical properties (Chia et al., 2014; Win; Ni; Aye, 2020).

The selection of this material was made based on a technical point of view, and although availability and price are important for industrial applications, the traditional charcoal produced in Brazil did not seem to match the requirements to be used in carbon anodes.

Studies related to the use of binchotan charcoal as a substitute for calcined petroleum coke in carbon anode production in Brazil were not found in the technical literature. The general objective of this study was to evaluate the use of binchotan charcoal as a substitute for small percentages of calcined petroleum coke in carbon anode production used in aluminum production. The expected results should confirm that it is possible to replace small percentages of calcined petroleum coke with binchotan charcoal.

The specific objectives of this study were:

- Evaluate the chemical, physical, and mechanical properties of binchotan charcoal samples;
- Compare the properties of calcined petroleum coke with those of binchotan charcoal;
- Analyze the properties of carbon anodes produced with binchotan charcoal on a laboratory scale;
- Compare the properties of the anodes produced with binchotan charcoal with a reference standard.

CHAPTER 1 – LITERATURE REVIEW

1.1. Biomass and Fossil Materials

Vegetable and organic matter from plants, trees, agricultural wastes, manure, and organic residues is considered biomass. This organic matter carries accumulated energy from biochemical transformations and can be used to generate heat, by direct burning, to produce electricity in thermal power plants replacing fossil fuels (Barros, 2019; Nakashima et al., 2017).

Biomass can be used as an energy source or raw material in the production of supplies and final products, being a renewable resource with great availability, however, the variability and the material characteristics must be considered (Cheng et al., 2020).

Another biomass application is soil nutrient replenishment, adding value to agricultural wastes, and avoiding improper disposal. For this purpose, the biomass can be used in natura or after the pyrolysis process, being converted into a biochar. It differs from charcoal due to its application and to the pyrolysis parameters. The use of biochar aims the soil amendment, increasing the content of organic carbon, improving water retention, neutralizing the pH, among others (Cheng et al., 2020; Mansor et al., 2018; Nakashima, 2020).

In the burning processes, the biomass can be used in natura, as firewood or residues, or in the form of charcoal or briquette, aiming to improve its properties (Saba; El Bachawati; Malek, 2020). During the burning many gases and residues are also produced, with a prevalence of carbon dioxide. In the case of biomass, CO_2 is absorbed during the growth of the plants, resulting in a reduction of CO_2 emissions at the end of the cycle (Fan; Friedmann, 2021).

The fossil materials have, naturally, higher carbon contents than the biomasses which need additional processes to change their characteristics, like pyrolysis (Cheng et al., 2020). In some applications, carbon is also necessary for chemical reactions, such as oxygen reduction in the iron smelting process or in the aluminum electrolysis process (Fan; Friedmann, 2021; Senanu; Solheim, 2021).

The main source of carbon in these processes is coke, which fulfills the technical requirements and has several well-developed processes; on the other hand, it is a non-renewable material and largely responsible for carbon dioxide emissions. The coke can be obtained as a byproduct of coal or from petroleum fractions (Huang; Kocaefe; Kocaefe, 2018; Petrobras, 2019).

The processing of petroleum fractions originates the green petroleum coke. The name green petroleum coke is due to the fact that the product has not yet undergone any thermal decomposition process. In Brazil, it is produced by the Petrobras (Petróleo Brasileiro S.A.) in two grades: fuel/metallurgical grade coke and anode grade coke. Part of the green petroleum coke is destined for calcination and is used in carbon anode production for the aluminum industry. (Petrobras, 2019).

Carbon anodes are typically produced using a mixture of calcined petroleum coke and coal tar pitch, in proportions of about 70% (coke) and 30% (pitch). The percentages can vary according to the characteristics of the raw materials. The process parameters and it is common to add butts and recycled anodes to formulate the coke mass, which is called dry aggregate. Coal tar pitch is a by-product of coal, at room temperature is a solid material but after heating, it becomes viscous and acts as a binder for the coke particles (Hussein et al., 2017; Lu et al., 2021; Ozturk et al., 2018).

1.2. Iron Smelting

The characteristics and properties of the biomasses used in aluminum and pig iron smelting are different, although similar terms are used, like bio-carbon, biocoke, and bio-coal. The materials have particularities and are not always interchangeable. In the aluminum industry, the term biocoke is generally applied to designate the charcoal used as a substitute for petroleum coke.

Good mechanical strength and high calorific value (higher heating value) are important requirements in iron pig smelting, due to the necessity to withstand loads and generate heat (Florentino-Madiedo; Díaz-Faes; Barriocanal, 2020). On the other hand, in the aluminum smelting process materials with high fixed carbon content and high density are sought, which favors the production of anodes with the electrical conductivity required for the electrolysis (Huang; Kocaefe; Kocaefe, 2018).

The main raw material in steel alloy and iron castings is pig iron, whose production demands a great amount of iron ore and coke. In Brazil, part of the iron pig production is made with biomass, replacing the coke with charcoal and making the production more sustainable, but the final product has a substandard quality in comparison with the conventional (Fan; Friedmann, 2021).

Another solution that has been developed is the partial replacement of coke with biocoke, produced from different biomasses, by the application of pressure and heat (Tamio et al., 2013). Biocoke is characterized by not having a loss of mass during its processing, creating a uniform material, with low moisture, high density, and excellent mechanical strength (Barros, 2019; Tagami-Kanada et al., 2021).

More than 70% of the global production of pig iron is made in blast furnaces by smelting iron ore, which contains metallic iron. The blast furnace is a type of vertical furnace that can operate for consecutive months and its temperatures can overcome 1500 °C. Loads of iron ore, coke, and limestone are added on the top of the furnace, each one having a specific function: the iron ore contains the desired metal; the coke generates heat by burning and acts as a reducing agent of iron; the limestone provides elements for the chemical reduction (Fan; Friedmann, 2021).

Biocoke can replace a small part of the metallurgical coke in pig iron production and higher proportions can be reached with the development of new processes and equipment, without compromising the costs and the quality of the production. Despite the current high availability, coke is a non-renewable source and its reserves can reach a critical point in the future, along with the environmental problems due to pollution it is evident the importance of studying and developing alternatives (Barros, 2019; Mansor et al., 2018).

From an environmental point of view, the insertion of biomass in this production chain can bring great benefits to companies that are seeking to become more sustainable (Adrados et al., 2015; Cheng et al., 2020).

For an effective application of biocoke, the material needs to satisfy some technical requirements and its thermal, physical, chemical, and mechanical properties must be appropriate and compatible with those of metallurgical coke. It is difficult to reproduce laboratory results on an industrial scale, considering the real size of the production, which is of the order of tonnes. Several studies are still necessary and those must considerate the particularity of each location, such as type and amount of available biomass, the distance between industrial plants, sources of supply, applied technologies, environmental regulations, volume and costs of production (Cheng et al., 2020; Fan; Friedmann, 2021; Mansor et al., 2018).

1.3. Briquettes and Biocokes

Briquetting is a process used for the densification of different materials, applying compressive loads with or without the use of heating. The result is a homogeneous product (briquette), energetically efficient, easier to transport and store, and that can have different shapes (Bokov et al., 2020; Saba; El Bachawati; Malek, 2020; Yustanti et al., 2019).

The industrial production of biomass briquettes is made by compression with hydraulic pistons or by extrusion. As wood replacers, the biomass briquettes have a large application due to the similarity of their characteristics, furthermore, the processing is easier to control (Nakashima et al., 2017; Saba; El Bachawati; Malek, 2020; Šooš et al., 2018). The biocokes are produced similarly to briquettes, applying pressure, but the use of heating (> 200 ºC) is necessary (Mansor et al., 2018; Tamio et al., 2013).

In addition to the difficulties related to the parameters control on an industrial level, the process on a large scale needs to deal with a crucial item: the feedstock variability, due to the different types of biomasses and their compositions. Moisture and granulometry can vary considerably among different biomasses, but they must be in a certain range of values to produce the biocoke, which demands energy consumption and specific processes, increasing the costs. Other parameters like pressure and temperature must be adjusted according to the biomasses (Florentino-Madiedo; Díaz-Faes; Barriocanal, 2020; Tagami; Ida, 2019; Yustanti et al., 2019).

Mansor et al. (2018), listed the characteristics for a good solid fuel: i) high calorific value: which means that the fuel must generate a great amount of heat during the burning; ii) moderate ignition temperature: a low-value results in the risk of starting a fire during storage or transportation and a high-value makes the burning more difficult; iii) low moisture content: the moisture affects directly the calorific value, the higher the moisture content the lower the calorific value; iv: low content of noncombustible matter: part of the not burned material remains in the form of ashes and complete combustion is always desired; v) inert products post-combustion: the burning residues should be as much inert as possible to avoid excessive pollution; vi) high availability and low cost: to keep the production affordable, the feedstock must be highly available and the process simple and reproducible; vii) easy to transport and store: these steps demand more processes and can generate more gas emissions and/or increase the costs.

A comparison between different cokes, made from coal, and biocokes exemplifies how the biomasses variability influences the biocokes properties. The calorific value of coal coke is about 30 $MJ.kg^{-1}$, while in the biocokes this value can vary between 18 and 31 $MJ.kg^{-1}$ depending on the biomass. The fixed carbon content of coke is near 90% and for biocoke, the values are in the range of 80–90%. The mechanical strength is around 20 MPa for the coke and can reach values higher than 100 MPa in some biocokes (Florentino-Madiedo; Díaz-Faes; Barriocanal, 2020; Mansor et al., 2018; Nakashima et al., 2017; Yustanti et al., 2019).

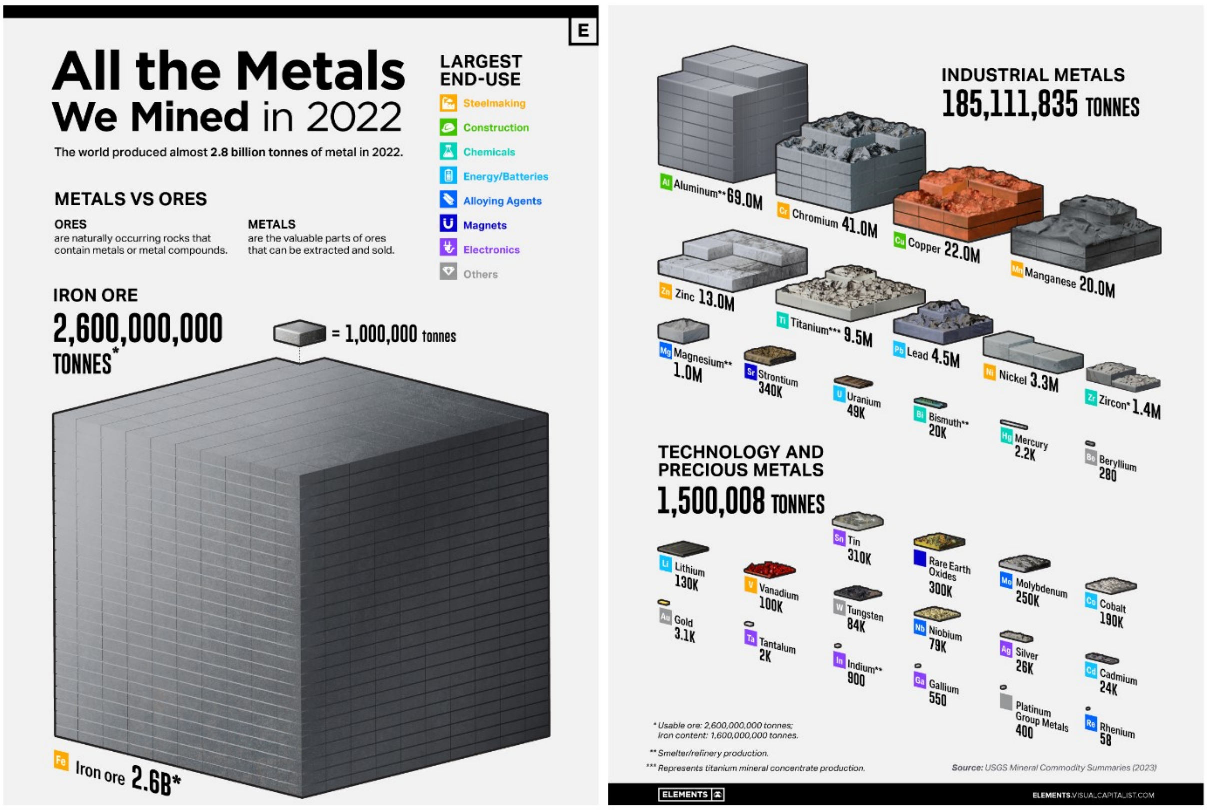
1.4. Aluminum Electrolysis

Aluminum is the most abundant metal in the Earth's crust, corresponding to approximately 8% of the mass of Earth's crust. It is rarely found in its metallic form due to its high oxygen affinity, which originates alumina (aluminum oxide). Among the lightweight metals and their alloys, aluminum is the most produced, with a wide variety of applications and many properties (Brough; Jouhara, 2020; Venditti, 2021).

Aluminum is a highly durable, versatile, and totally recyclable metal. Its recycling allows a reduction in energy consumption above 90% in comparison to primary production (Brough; Jouhara, 2020; Saevarsdottir; Kvande; Welch, 2020).

The infographic below (Figure 1) was based on data from the USGS (United States Geological Survey) and compiles information about some metals and ores mined in 2022. The production of ores is always higher because of the natural existence of the elements in the form of oxides. Approximately 98% of the mined iron ore is used in the production of steel and cast iron, indicating that those are the most produced metals in the world. Among all the metals, aluminum had the second highest production (Venditti, 2023).

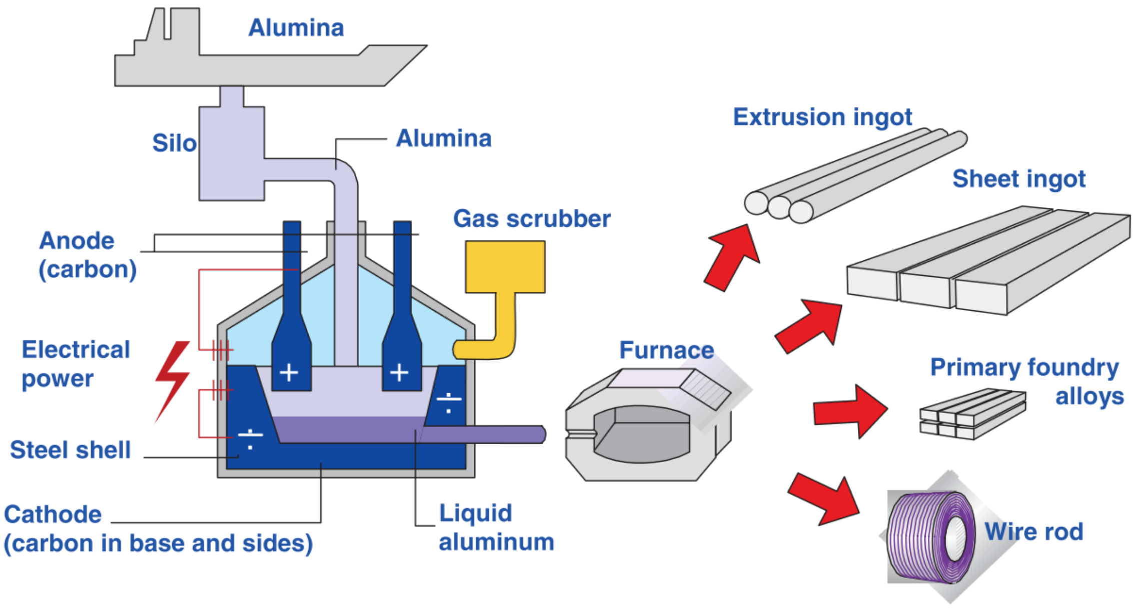
Figure 1 – Metals mined in 2022.



Source: Venditti (2023).

Aluminum production can be divided into primary and secondary. The primary production processes are bauxite mining, alumina refining, aluminum reduction (electrolysis), and casting. The secondary production includes the manufacturing of final products, the mechanical processing, and the aluminum recycling process. Figure 2 shows a flowchart of the aluminum production process (Brough; Jouhara, 2020; Kvande; Drabløs, 2014).

Figure 2 – Aluminum production processes.



Source: Kvande; Drabløs (2014).

To obtain the metallic aluminum, the alumina (Al_2O_3) is reduced by the Hall-Héroult process (Sequeira, 2020), in which the anodes provide the necessary carbon for the following reaction:

$$\mathbf{2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2}$$

Other materials, besides the alumina, are added to the process and more reactions occur inside the electrolytic cell so that the gas emission is not restricted to carbon dioxide (CO_2), although this one is used as the main indicator of greenhouse gas emissions (Edwards, 2015; Ozturk et al., 2018).

An estimation of the greenhouse gas emissions in primary aluminum production is in Figure 3. The data is presented in tonnes of CO_2 equivalent (CO_2e) per tonne of primary aluminum produced and was reported by the International Aluminum Institute (IAI) as part of a life cycle assessment (LCA) of the process, using inventory data and estimations over the years. The emissions were evaluated in a study cradle-to-gate, considering the impacts from the origin of the raw materials to the end of the primary aluminum production and, therefore, excluding the effects of the metal secondary processing, its use, and the recycling/disposal (IAI, 2023).

Figure 3 – CO_2e emissions in primary aluminum production.

Period		Electricity-Indirect	Perfluorocarbon (PFC) - Direct	Process (CO2)-Direct	Ancillary Materials-Indirect	Thermal Energy-Direct/Indirect	Transport-Indirect	Total-Cradle to Gate
	tonnes of CO2e per tonne of primary aluminium							
2022	Mining	0.00			0.00	0.04		0.04
	Refining	0.3			0.4	1.7	0.2	2.6
	Anode Production	0.0		0.1	0.6	0.1		0.9
	Electrolysis	8.9	0.8	1.5	0.1		0.2	11.4
	Casting	0.0			0.0	0.1		0.1
	Primary Aluminium	9.3	0.8	1.6	1.2	1.8	0.4	15.1

Source: IAI (2023).

Considering the indicated steps, the electrolysis presented a higher impact due to the electricity generation, followed by the alumina refining and the anode production, whose main impact came from the raw materials; similar results were also reported by Yang et al. (2019). It is noticeable that the utilization of renewable sources for energy generation, mainly electricity, can drastically reduce the environmental impacts since about 73% of CO_2e emissions are related to energy generation. Considering the materials involved in the process, the higher impacts are concentrated in alumina refining and carbon anode production (IAI, 2023).

To produce 1 kg of aluminum, roughly, 2 kg of alumina, 0.45 kg of carbon, and 14 kWh of electricity are consumed (Kvande; Drabløs, 2014). On a global scale, the use of fossil sources for energy generation still is the majority, predominantly coal. In places where the electrical matrix utilizes renewable sources, the environmental impacts can be minimized and the actions that aim to reduce emissions are turned in the direction of other processes, like alumina refining and anode production (Edwards et al., 2022; Saevarsdottir; Kvande; Welch, 2020).

The electricity generation by hydropower enables a cleaner process and reduces significantly the greenhouse gas emissions from aluminum production (Edwards et al., 2022; Yang et al., 2019). Several efforts are still necessary to make the production more sustainable, this can be done by changes in the electrical matrix in the places with predominantly utilization of non-renewable sources, by the implementation of new technologies in pollution treatment, or by the application of new materials like those made from biomass (Amara et al., 2022; Mann et al., 2019; Saevarsdottir; Kvande; Welch, 2020).

The primary aluminum production in Brazil, published by the Brazilian Aluminum Association for the years 2020 and 2021, is in Figure 4.

Figure 4 – Primary aluminum production in Brazil.

		Production Capacity		Production per Plants	
Producers	Location	2020	2021	2020	2021
Albras - Alumínio Brasileiro S.A. (1)	Barcarena (PA)	460	460	378.9	426.9
Companhia Brasileira de Alumínio (2)	Alumínio (SP)	450	450	306.2	344.8
Total		$\boxed{910}$	$\boxed{910}$	$\boxed{685.1}$	$\boxed{771.7}$

Notes: Effective Production capacity as at December 31 each year.
(1) *Prebaked* technology.
(2) Soderberg technology.

Source: Primary Aluminum Producers
Unit: 1000 tons

Source: Adapted from ABAL (2022).

There was an increase in the production of approximately 12.6% year-over-year and both listed companies still could increase their production. Concerning the carbon anodes, it is important to highlight the difference in the technology employed by each company: Prebaked anodes were used by the Albras (Alumínio Brasileiro S.A.) and Soderberg anodes by the Brazilian Aluminum Company (Companhia Brasileira de Alumínio – CBA). For the years 2022 and 2023, this association also reported a total production of 810.9 and 1021.7 tonnes, respectively, showing an increase in the total production in Brazil (Abal, 2023).

Soderberg anodes are a type of continuous anode, that demands a constant addition of raw materials during the electrolysis process due to the anode consumption. The added material provides carbon to the reaction and is gradually baked due to the heat inside of the cell and to the electric current passage. The Prebaked anodes are externally manufactured, i.e. the baking is made in a specific process and outside the electrolysis cell. With the consumption, after some weeks, the used anodes are changed by new ones (Brough; Jouhara, 2020; Ratvik; Mollaabbasi; Alamdari, 2022; Sequeira, 2020).

The use of Soderberg anodes was predominant in the aluminum industry for many years, being reduced over the years and replaced by prebaked anodes due to limitations related to energy efficiency, operational costs, and CO_2e emissions. The costs involved in changing the technology, from Soderberg to prebaked anodes, are high and the industrial plants that still use Soderberg anodes have invested in new technologies and automated pre-existing processes. These changes aim to increase energy efficiency, reduce emissions and environmental impacts, improve operational control, and reduce manual handling activities (Barber; Tabereaux, 2014; Brough; Jouhara, 2020; Mann et al., 2021).

1.5. Bioanodes

The aluminum reduction process also utilizes coke, more specifically in the production of the carbon anodes that are used in the electrolysis process for dissolving the alumina (aluminum oxide). In this process, the metallic aluminum is extracted using electrochemical reactions and the carbon anode acts as a reducing agent and an electrical conductor (Amara et al., 2021; Sequeira, 2020).

Carbon anodes are produced from a mixture of calcined petroleum coke (≈ 70%) and coal tar pitch (≈ 30%), forming a paste that is molded into the desired shape and heated in a process known as baking. The coke used to produce anodes undergoes a calcination process to improve its properties. In general, the pitch is obtained by the distillation of the coal tar and acts as a coke particle binder, forming an anode with good thermal and mechanical resistance, low electrical resistivity, and low air and CO_2 reactivity (Glastonbury et al., 2020; Ozturk et al., 2018).

The calcination, performed in the green petroleum coke, is a thermic process that aims to increase the fixed carbon content by reducing the contents of volatile matter and moisture, producing a material with high density, electrical conductivity, and mechanical strength (Petrobras, 2019).

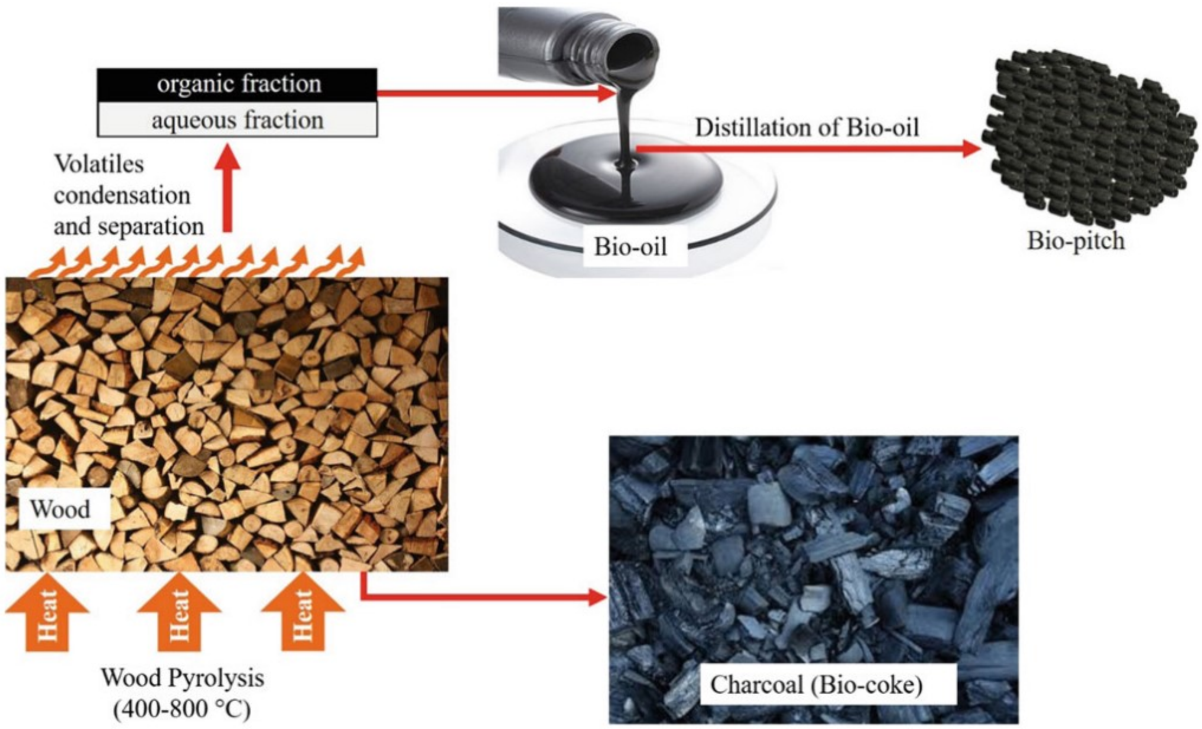
The aluminum industry has faced problems dealing with greenhouse gas emissions, which are increasing as both demand and production of aluminum rise. The production of alumina and carbon anodes and the electrolysis process release CO_2, as well as electricity generation, mainly when fossil sources are used. Worldwide, it is estimated that the production of aluminum contributes to approximately 2% of all CO_2e emissions (Saevarsdottir; Kvande; Welch, 2020).

To try to reduce the emission of greenhouse gases and to add value to biomass residues, part of the coke used in the anodes can be replaced with biocoke (charcoal) made from wood or similar sources (Amara et al., 2021; Monsen; Ratvik; Lossius, 2010). The term bioanode refers to the carbon anodes made with the addition of biomaterials, like charcoal.

Several studies indicate that it is possible to use biomass in carbon anode production, replacing a small part of the coke or the pitch. The biocoke can be made from bio-oil or charcoal, being necessary to use a heat treatment with high temperatures. It is also possible to use the bio-oil to produce the biopitch, to then replace part of the coal tar pitch (Elkasabi; Boateng; Mullen, 2016; Hussein; Picard; Alamdari, 2021a; Senanu; Solheim, 2021).

These biomaterials (biocoke and biopitch) are shown in Figure 5 with a simplified sequence of the processes used to obtain them, the wood pyrolysis for the biocoke and the bio-oil distillation for the biopitch.

Figure 5 – Biocoke and biopitch.



Source: Senanu; Solheim (2021).

To employ charcoal (biocoke) as a raw material in the production of carbon anodes some characteristics must be achieved, such as high carbon content (over 90%), high density, and the presence of fine particles that lead to a low electrical resistivity, these parameters are alike to those of the anodes produced with calcined petroleum coke (Huang; Kocaefe; Kocaefe, 2018).

Many challenges related to the use of biomass have been addressed in the literature because the quality and performance of the biomaterials tend to be inferior to the fossil materials unless they are submitted to some processing that allows their application in aluminum production. The most promising scenarios seem to be those in which there is a partial introduction of biomass in the fossil base already used. These strategies deemed the substitution of the fossil binder for a biomaterial or the addition of small amounts of biocoke in the production of the anodes (Ratvik; Mollaabbasi; Alamdari, 2022; Senanu; Solheim, 2021).

In addition to the possibility of having a new carbon source, minimizing the risk of feedstock scarcity, and reducing the environmental impacts associated with CO_2 emissions, biomass also has the technical advantage of having a lower sulfur content when compared with coal tar pitch and the different types of coke made from fossil sources (Adrados et al., 2015; Senanu; Solheim, 2021).

Research has been conducted in different places, seeking to find better solutions, and the most advanced ones have cooperation between industries and universities. Canada is a prominent country in this field, as it is one of the biggest aluminum producers in the world and it also has top universities and large companies involved in research and development in this area of interest (Amara et al., 2022; Regal, 2021).

In the literature are found studies reporting the use of biomass in the production of bioanodes, either biocoke or biopitch. In general, what is noticed is the decrease of the carbon anode properties with the increase of the biomass content. In the case of biocoke, this content is typically under 5%. There is still a lot of research to be done until this alternative becomes industrially feasible from a technical and financial point of view because a large modification of equipment tends not to be viable in established plants (Saevarsdottir; Kvande; Welch, 2020).

Huang; Kocaefe; Kocaefe (2018) produced biocokes calcined at high temperatures, obtaining a material with high carbon content and a microstructure similar to that of the calcined petroleum coke. To compare with a standard anode that utilizes petroleum coke, anodes with the addition of the biocokes were produced and the results showed that a replacement of 3% in the fine fraction resulted in anodes with similar properties.

Ozturk et al. (2018) investigated the modification of the calcined petroleum coke with chemical additives to improve the wettability between the coke and the pitch. The modification of coke with additives improved the properties of the anodes produced in the study; an improvement in the mechanical properties, in addition to a reduction in the electrical resistivity and the reactivity with CO_2 and air, was noted. This kind of modification has a great advantage, the possibility to be employed in established plants because the properties of the material were improved without the necessity to change the parameters of the process.

Studies about the chemical modification of the biomass used in the production of the anodes can be found as well. According to Amara et al. (2021), the addition of the biocoke can hinder the anode properties, however, it is possible to do a modification with chemical additives, making the material more suitable for anode production. The authors used an additive of generic class phenyl-alkyl-aldehyde, adding 3% and 4%, to improve the biocoke properties. The results showed that the modification was effective and the wettability between the biocoke and the pitch improved, which also improved the bioanode properties.

In the work of Sommerseth et al. (2020), different contents of charcoal were added to the carbon anodes produced on a laboratory scale. The charcoal was made with different heat treatments and submitted to acid-washing with sulfuric acid. The acid-washing reduced the metallic impurities and the increase of the temperatures in the heat treatments decreased the porosity, but the anodes did not achieve the same industry standard, indicating deterioration of the quality due to the use of biomaterials.

The work of Lu et al. (2020) approaches the synthesis of a biopitch obtained from bio-oil under different conditions of extraction. The authors also made a characterization of the physical and chemical properties aiming to discover the proper conditions for anode production. In comparison to the coal tar pitch, the studied biopitch samples displayed lower levels of substances considered health and environmental hazards.

Lu et al. (2021) carried out studies utilizing biopitch modified with biochar, aiming to improve the properties of the biopitch used in carbon anode production. The results showed that 9% of biochar as an additive can be beneficial to formulate anodes and reduce the general consumption of biopitch.

A material that shows good characteristics for these applications is the so-called white charcoal, also known as binchotan charcoal. This type of charcoal is made by slow pyrolysis at low temperatures followed by a high increase in the temperature at the end of the carbonization process. Afterward, the charcoal is removed from the furnace to be cooled in a mixture of sand, earth, and ashes (Chia et al., 2014; Miura, 1931; Pijarn et al., 2021; Win; Ni; Aye, 2020).

The binchotan charcoal shows high fixed carbon content, low volatiles content, and high density because it is made from hardwoods; has good properties of adsorption/absorption, exhibits a high level of porosity, and has electrical properties that favor conductivity. Binchotan charcoal can be used as a water purifier, dehumidifier, radio frequency shielding, electromagnetic wave absorber, and room deodorizer, it can also be employed in electronic components and the medical field, among other applications (Chia et al., 2014; Win; Ni; Aye, 2020).

The work of Kwon et al. (2018) brings information about the production of white charcoal with a secondary system used for thermotherapy, aiming to minimize the environmental problems that come from the fine dust and the gases generated in the furnaces. Win; Ni; Aye (2020) used bamboo samples to produce white charcoal in a laboratory and compared its physicochemical properties with those of commercial samples made from wood, the authors verified that bamboo can also be used to produce white charcoal and they can show high absorption capacity due to the abundance of porous of the material.

Pijarn et al. (2021) made a comparison between black charcoal (common) and white charcoal (binchotan) in the treatment of effluents. The results confirmed that white charcoal has higher thermal stability and higher carbon content, and an SEM-EDS (scanning electron microscope with energy dispersive spectroscopy) analysis showed that binchotan is highly porous, which allows its use as activated charcoal. The charcoal was produced with different biomasses, using a special furnace and reaching temperatures above 1000 °C.

The use of biomass as a substitute for calcined petroleum coke or coal tar pitch is currently in the research and development stage, given the many challenges that still need to be overcome in order to meet the demands of an industrial scale. However, it is a valid alternative that has the potential to help reduce the carbon footprint of aluminum production (Ratvik; Mollaabbasi; Alamdari, 2022).

1.6. Material Characterizations

The biomass in natura and its processed products, like charcoal, biocoke, biopitch, and bioanode, must be characterized to evaluate if the material characteristics are suitable to the proposed applications and how their properties can be changed. Different analyses are described in the literature for the characterization of the biomass in natura, the biocoke and biopitch, and the bioanode.

1.6.1. Biomass in natura

Proximate analysis: it is a characterization performed in most of the studies related to biomass: fixed carbon, volatile matter, and ash content.

Chemical analysis of constituents: different methods can be employed to obtain the contents of extractives, cellulose, and lignin. These components influence the biomass heating value and can be used as a binder when submitted to high temperatures.

Granulometry: sieves with different openings are used for size classification. Several tests require a specific granulometry, normally indicated in the standard procedures, and the processing of the biomass is also influenced by this parameter.

Ultimate analysis: allows the identification of the chemical elements present in the sample: carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O).

Density: is given by the ratio of mass to volume, can affect the properties and applications of the material, as well as the storage, the logistics, and the equipment used for the processing of the biomass. According to the analysis methodology, the densities can be subdivided into bulk, apparent, and real density.

Calorific value (heating value): indicates the amount of energy that the material contains and is influenced mainly by the contents of carbon and hydrogen. The calorific value is divided into higher, lower, and useful heating values; the last two are calculated based on the contents of hydrogen and moisture, respectively.

Thermogravimetric analysis and differential scanning calorimetry: thermogravimetry enables the analysis of the thermal behavior of the material over time and with the increase of the temperature. The decomposition of the components and other events are characterized by the loss of mass and the analysis is made in a controlled atmosphere, which can be inert or oxidizing. Differential scanning calorimetry also provides information about the material thermal behavior, according to the absorption and the release of heat, making it possible to analyze transformations and calculate the specific heat of the samples.

1.6.2. Biocoke and Biopitch

Overall, the analyses employed for the biomass in natura can also be used for the processed products; the briquettes and the charcoal can be included in this section in addition to the biocoke and the biopitch that have applications related to the smelting of iron and aluminum.

Mechanical strength: represents the capacity that the material has to withstand the load application and can be dynamically or statically measured, using for example compressive and/or flexural strength testing.

Scanning electron microscope and energy dispersive spectroscopy (SEM/EDS): these techniques are employed in the assessment of the morphology and in the semiquantitative analysis of the main elements that are present in the sample.

Brunauer–Emmet–Teller method (BET): this method utilizes nitrogen adsorption to analyze the surface area, the porosity volume, and the total pore size.

Electrical resistivity: some methods can also measure other electrical properties, like inductance and capacitance. The materials must present low values of electrical resistivity because it affects the energy consumption during the electrolysis and therefore the production costs. In some studies, the measure of the electrical conductivity, which is the reciprocal of the resistivity, is reported.

Reactivity: it is a parameter traditionally used to measure the quality of the materials employed as reducers, and the reactivities with air and CO_2 are analyzed. Thermal treatments, like calcination, can improve the properties of the material and reduce its reactivity.

Wettability: it is typically characterized by the sessile drop test, measuring the contact angle of the drop. The wettability is an indicator of the quality of the mixture and the homogeneity of the paste used for anode production. To analyze the interaction between the coke and the pitch a heating system with a controlled atmosphere is required during the test.

Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction: with infrared spectroscopy, it is possible to identify the different functional groups that are present in the samples, because the appearance of new bonds can affect other properties. The X-ray diffraction makes it possible to analyze the material structure and identify if it is predominantly amorphous or crystalline.

Coking value: indicates the amount of coke that remains after the carbonization of the pitch and the release of the volatiles. Pitches with a high coking value are desirable since this makes it possible to produce anodes with higher density and lower porosity.

1.6.3. Bioanode

Many of the analyses previously cited are also performed in the bioanodes, mainly the tests of electrical resistivity, density, mechanical strength, and reactivity with air and CO_2. Some characterizations are made both in the green anode and in the baked anode, i.e. before and after the calcination.

Calcination: in the absence of a specific furnace, the laboratory anodes can be calcined in the same equipment that is used in the thermogravimetric analysis, allowing the control of the heating rate and the use of an inert atmosphere. In some works, calcination is described as the baking process of the carbon anodes, in which the volatile matter is removed due to the high temperatures employed.

Coefficient of thermal expansion: a minimum value of this coefficient is desired to enhance the anode strength and to avoid the formation of cracks during the electrolysis process. This parameter is affected by many aspects, such as the raw materials, thermal treatment, size of particles, and others.

1.7. Binchotan Charcoal

There are few academic texts and scientific papers about binchotan charcoal. In the Japanese language, it is possible to find some archives, newsletters, and books that approach the production and use of this type of charcoal.

It is possible to find videos, that show the production process of binchotan charcoal, and texts that explain what it is and how this kind of charcoal is made (Fujimoto, 2023; NHK, 2022; Sumikobo, 2023). In general, these contents were made by producers and their apprentices, governmental entities, journalists, binchotan enthusiasts, companies related to the food business, and sellers of the binchotan charcoal and its byproducts.

Some information was obtained in 2023 from Kishu Binchotan Memorial Park, a museum dedicated to the binchotan located in the city of Tanabe, Wakayama Prefecture, Japan. The characters of Japanese writing (*kanji, hiragana, and katakana*) were indicated in the text, aiming to help with searches and to explain some terms and concepts.

1.7.1. Origin and Characteristics

Binchotan charcoal, also known as bincho-charcoal or white charcoal, received this name because of a producer of the region of Wakayama Prefecture, in Japan, which traded this type of charcoal at the end of the 17th century. The term Binchotan (備長炭) came from the name of this producer, ***Bi**cchuya* ***Cho**zaemon* (**備**中屋**長**左衛門), and the word ***Tan*** (炭), which can also be read as *Sumi* and means charcoal (Fujimoto, 2023; Kishu-Binchotan, 2018). The terms *Hakutan* and *Shirosumi* (白炭), which means white charcoal, can also be used (Wakayama-Ken, 2023).

During the Edo Period (1603~1867) the Prefecture of Wakayama was called Kishu and for this reason, the binchotan charcoal produced in that region was known as Kishu-Binchotan to be differentiated from the other varieties made in other locations (Fujimoto, 2023; Narumiya, 2023). In this period the binchotan charcoal produced in Kishu was widely appreciated for its qualities, such as high calorific value, long burning time, and water purification capacity. It became so valuable that the producers traded pieces of binchotan as payment (Kishu-Binchotan, 2018; Magali, 2016).

At first, the binchotan was only found in Kishu but some charcoal makers moved to other regions of Japan, like Tosa and Hyuga, beginning the production of binchotan charcoal in those locations. Tosa was the name of the current Prefecture of Kochi and Hyuga is now the Prefecture of Miyazaki (Fujimoto, 2023; Nishikidori, 2020). Until now this type of charcoal is indicated with the name of those regions as a reference of quality, so the three main white charcoal made in Japan are the Kishu-binchotan from Wakayama Prefecture, the Tosa-binchotan from Kochi Prefecture, and the Hyuga-binchotan from Miyazaki Prefecture (Fukushima, 2022; Sumikobo, 2023).

The binchotan charcoal of better quality is made from a specific type of oak known as Ubame oak (*Quercus phillyraeoides*) or Ubamegashi (ウバメ樫). The character 樫 (*kashi* or *gashi*) means oak in Japanese, while ウ (*u*) バ (*ba*) メ (*me*) are the characters that represent the term ubame. The characters ガシ (*gashi*) and カシ (*kashi*) can also be used to refer to the word oak (Fujimoto, 2023; Kishu-Binchotan, 2018). To describe the term ubame it can also be used the characters 姥目 or 馬目, both are read as *ubame*. In Japanese, 姥 (*uba*) means elderly woman, 馬 (*uma*) means horse, and 目 (*me*) means eye so that *ubame* can mean elderly woman's eye or horse's eye, which is a reference to the buds of the trees that resemble wrinkly eyes (Fujimoto, 2023). The character 芽 (*me*) means bud or sprout, so to describe this type of oak the character 姥芽樫 (*ubamegashi*) can also be used.

The excellent quality of the binchotan charcoal does not depend only on the technology applied in its production, but also on the fact that Ubamegashi is used as raw material. This kind of evergreen tree is an extremely hard species that grows mainly in the coastal region. The Ubamegashi has slow growth and takes more than 20 years for a tree to be able to produce charcoal with good quality (Itani; Kishimoto, 2018; Minabe-Kanko, 2023; Narumiya, 2023).

This type of oak has been used in charcoal production for several years. It is a medium-sized tree with high density, that sinks when put in the water and generally grows in hilly areas that are difficult to access, making the wood harvest more challenging than with other species (Midorinoshima, 2023; Minabe-Kanko, 2023). The fibers of Ubamegashi are dense and hard, which does not allow its use as a building material or in woodworking products but makes it suitable to produce charcoal, being the best material for binchotan charcoal production (Narumiya, 2023; Sumikobo, 2023).

According to Abe et al. (2012), the basic density of Ubamegashi (*Quercus phillyraeoides*) was the highest among 14 species of the genus *Quercus*. The authors analyzed the radial variation of the basic density of 35 wood samples from 14 species of *Quercus*. The basic density of the samples was less than 0.80 $g.cm^{-3}$ for all species except Ubamegashi, which presented a density of 0.80 $g.cm^{-3}$ or more.

Even though the binchotan is traditionally made from the *Quercus phillyreoides* (Ubamegashi), in some cases other types of Japanese oak can also be used, like the *Quercus glauca* and the *Quercus salicina*, if the other steps of the process are maintained (NHK, 2022; Tanagokoro, 2009).

The production of binchotan charcoal begins with the wood harvest, which is made by hand, although chainsaws are used to help in the process. Heavy machinery cannot access the places that are characterized as hilly areas (Fujimoto, 2023; Kishu-Binchotan, 2018). Instead of cutting the entire tree, only the thicker trunks and branches are selected and cut. Small trees are left to grow and the remaining sprouts can be cut off in 10 or 15 years, in this way the forest will not be depleted (Stuart-Wolff, 2023; Sumikobo, 2023).

The Ubamegashi is a species of tree characterized by having a winding shape. Because of this, the trunks and branches used to produce charcoal need to be manually straightened to allow better packing of wood inside the kiln, reducing the gaps. It is necessary to make small cuts and insert wedges to straighten the wood, which is later grouped in bundles. The thickest trunks are split in half to maintain a better regularity of sizes (Minabe-Kanko, 2023; Narumiya, 2023).

The binchotan charcoal made from Ubamegashi presents high fixed carbon content (greater than or equal to 90%) and a refinement degree between 0~2 degrees (Kishu-Binchotan, 2018). The refinement degree refers to the degree of carbonization of charcoal and measures the electrical resistivity of the charcoal surface, it is ranked on a scale from 0 to 9 degrees, where a lower number indicates better and harder charcoal (Kwon et al., 2018).

The binchotan is a hard material, characterized by emitting a metallic sound when struck, and can even be used to produce wind chimes and xylophones. In comparison with conventional charcoal (black charcoal), the binchotan (white charcoal) shows a greater burning capacity and, besides being harder to catch fire, it has a steady long-lasting burning. It also shows as a great advantage a low production of ashes (Narumiya, 2023; Wakayama-Ken, 2023). Binchotan is also considered a type of activated charcoal, showing an excellent adsorption capacity. Based on this principle, the particles responsible for unpleasant smells and tastes will adhere to the charcoal surface, helping in the purification of the air or the water, for example (Midorinoshima, 2023).

A high-quality binchotan charcoal tends to present the following characteristics: its cross section exhibits a shiny surface, the pieces of charcoal release little dust when touched, binchotan sounds like metal when is hit, the place of origin is plainly indicated (Tanagokoro, 2009; Win; Ni; Aye, 2020).

1.7.2. Production Process

The production process of binchotan charcoal is similar to other types of charcoal, consisting of a controlled burn with low oxygen, which allows the extraction of the moisture of the material and prevents the charcoal from being burned into ashes. The biggest difference in binchotan production is at the end of the process (Fujimoto, 2023).

At the end of the process of making the black charcoal (conventional), the mouth of the kiln is closed and the air is blocked to extinguish the fire, when the kiln is cooled down the charcoal is removed. At the end of the carbonization of binchotan (white charcoal), the mouth of the kiln is opened and the air is pumped into the kiln, the charcoal and the volatile matter catch fire and the impurities are eliminated (Tanagokoro, 2009; Wakayama-Ken, 2023).

According to the volume of the production, the whole process takes from 10 to 20 days, from the cutting of the wood until the end of the carbonization. In general, the producers stack the wood vertically inside the kiln and manage all the processes based on the color and the scent of the smoke released from the kiln (Minabe-Kanko, 2023; Stuart-Wolff, 2023).

A special fig-shaped kiln is commonly used and the bundles of wood need to be stacked in an orderly and tight way. Typically, these kilns can withstand high temperatures and are large enough for a person to be able to walk inside. Once the wood is stacked the kiln is lit using light firewood, which burns quickly (Fujimoto, 2023; Magali, 2016).

In some kilns, the size of the mouth only allows a person to enter and the filling process must be done while the kiln is still warmed from the previous batch. In this case, the use of tools and special techniques are required, making the activity more difficult because the trunks are heavy and the surroundings are smoldering. These traditional techniques continue to be passed down from generation to generation, demanding ability and experience from the charcoal makers (Narumiya, 2023; Okuno; Onitsuka; Hoshino, 2020).

After being lit the kiln is gradually closed, leaving only small holes to allow the passage of air to feed the fire. The burning occurs slowly and with low temperatures due to the small airflow, removing moisture from the wood over several days. During this step, white smoke will be released from the chimney and when it ceases the wood will become charcoal. The charcoal maker manages the conditions of the batch by the smell and the color of the smoke, without using thermometers or other apparatus (Fujimoto, 2023; Minabe-Kanko, 2023).

At this point, a common charcoal would be made by closing the kiln and extinguishing the fire due to the oxygen suppression Then the charcoal would be left to cool down, but to produce binchotan an additional step is necessary, this final process is called refining or activation. In Japanese, this process is called ねらし (*nerashi*). Instead of closing the kiln and extinguishing the fire, the mouth of the kiln is open and the airflow is gradually increased. A faster airflow could burn the charcoal into ashes and a slower one may not be enough for the process to be done properly (Fujimoto, 2023; Midorinoshima, 2023; Narumiya, 2023).

When the kiln is opened, the flood of oxygen increases the temperature to a scorching level and the internal atmosphere of the kiln begins to show a white-hot appearance (Stuart-Wolff, 2023). This part of the process can take up to 48 hours, when the temperature exceeds 1000 °C, burning the remaining components, increasing the carbon content, and transforming the charcoal into a denser and harder material (Sumigen, 2023). The intense heat also eliminates many impurities present in the charcoal, that volatilize and create a huge quantity of micropores, increasing significantly the surface area of the material. In this way, the adsorption capacity increases, and the material becomes capable of adhering to and neutralizing several substances, which makes it possible to use the binchotan as activated charcoal (Itani; Kishimoto, 2018; Morihata, 2023).

The charcoal maker has to remove the hot charcoal from the kiln using a long iron rake, pulling out a pile of glowing pieces of charcoal to be subsequently cooled (Narumiya, 2023; Stuart-Wolff, 2023). The glowing binchotan being removed from the kiln is shown in Figure 6, the process was performed in the Kishu Binchotan Memorial Park.

Figure 6 – Removal of the binchotan from the kiln.

(Kishu Binchotan Memorial Park)

Source: The author.

The hot charcoal is then covered with a wet mixture of sand and ash to be gradually cooled; this mixture leaves white marks on the charcoal surface, hence the name white charcoal. The binchotan is considered the best example of white charcoal (Tanagokoro, 2009; Wakayama-Ken, 2023).

Most of the wood is consumed during the production process of the binchotan charcoal and its yield is typically around 10%, without considering the firewood burned at the beginning as fuel (Fujimoto, 2023; Sumigen, 2023). The charcoal yield can be defined as the percent mass of solid residue that remains after the carbonization, the value varies according to the species of the tree and to the operational parameters, such as temperature and residence time (Kim; Kang, 2015). The typical shrinkage of binchotan charcoal is shown in Figure 7, comparing a piece of binchotan with the Ubame oak. The material suffers a great reduction in its diameter and almost none in its length.

Figure 7 – Shrinkage of binchotan in comparison with Ubame oak.

(Kishu Binchotan Memorial Park)

Source: The author.

Binchotan production is time-consuming, requires a lot of skills, and is considered a tiring activity that not everyone is capable of doing, however, it has survived and has been passed down through generations. The charcoal makers that work with the binchotan were trained for several years to develop the required skills to produce the best possible product (Fujimoto, 2023; Magali, 2016).

1.7.3. Usages and Heritage

Due to its properties and because it is made by experts, binchotan charcoal is highly valued, being sold in different grades. In general, the binchotan is graded according to the following items: brand; place of origin; species of the tree used, which influences density and strength; shape regularity; size of the pieces, diameter, and length (Wakayama-Ken, 2023).

The cost depends on these items and it is usually more expensive for denser and bigger pieces, with circular shapes and greater homogeneity. The Kishu-binchotan and the Tosa-binchotan made from Ubamegashi are among the most valued and wanted ones (Fujimoto, 2020).

The binchotan charcoal is mostly used for cooking, to grilling meats and seafood, because it has thermal stability, burns for a long time, produces little smoke, and does not release odors in the food (Minabe-Kanko, 2023; Narumiya, 2023). It is also said that can emit far-infrared rays, favoring fast and uniform cooking and preserving texture and aroma, as well as maintaining the umami flavor of some foods, which is highly prized in Japanese cuisine. Besides its use as a fuel for grilling food, in some locations of Japan is possible to taste a menu that uses binchotan as an ingredient, mixed with noodles or desserts (Henderstein, 2016; Kishu-Binchotan, 2018).

Due to its other non-fuel properties, binchotan charcoal can also be used as activated charcoal, employed as a room deodorizer and dehumidifier, electromagnetic wave absorber, and water or air purifier, reducing the use of chemical and harmful substances (Miki et al., 2003; Minabe-Kanko, 2023). After being used, the pieces of charcoal can be applied for soil amendment, which helps to aerate the soil, improving microbial activity and creating a healthier environment for the plants to grow. In this way, the use of binchotan charcoal nearly generates no waste (Morihata, 2023; Tanagokoro, 2009).

Many applications of the binchotan are also found in the cosmetics industry, in hygiene, and in beauty products. The charcoal can be ground to a powder and mixed with products like shampoos, toothpaste, scrub towels, soaps, and face and eye masks (Henderstein, 2016; Morihata, 2023).

Every industry that depends on nature must be carefully operated to avoid the excessive use of resources, which could impair the entire industry. The same occurs with the binchotan charcoal, the producers rely 100% on natural resources that are only available in specific places and because of this, they have learned over the years how much wood they can harvest per year to preserve the forests and the binchotan industry (Fujimoto, 2023).

Binchotan production is labor-intensive. Human touch is necessary to recognize the differences that exist in each tree, to cut only the appropriate trunks and branches, to adjust the parameters of the carbonization, and to convert the Ubamegashi from a simple hardwood into a high-quality charcoal. The producers are deeply concerned about how to create a high-quality and sustainable product, at the same time they care about the heritage and how to pass their knowledge to the next generations (Henderstein, 2016).

Okuno; Onitsuka; Hoshino (2020) carried out a case study in Minabe Town, Wakayama Prefecture – Japan, using virtual reality in the teaching and learning process of the traditional techniques and skills used in the production of binchotan charcoal, to contribute to the preservation of those techniques. Two other methods were used for comparison, a video made with a fixed-point camera and a text material that included photographs. The people involved in the experiment had to study the process using the three methods, perform the techniques, and answer questionnaires. The results showed that, in comparison with the video and the text material, virtual reality was more efficient and comprehensive in promoting the understanding of the main points of the techniques and skills. However, the practical performance of the skills could not be mastered because it depends on practice and experience.

The basic processes for making the binchotan can be learned in a few years, but mastering and perfecting the production can take decades. Achieving a level where it is possible to become independent and make money demands the acquisition of land, equipment, and supplies (Henderstein, 2016; Wakayama-Ken, 2023). In the past, only old people were involved in this industry, but now this has been changing and younger people are also participating and undertaking in this field (Fukushima, 2022).

Generally, it is noticed that people have a harmonious relationship between work, nature, family, and traditions, so it is common to see different generations of the same family producing binchotan charcoal (NHK, 2022). The binchotan is actively present in the life of the people in many aspects and it is made by the sensibility and the ability of skilled producers (Sumikobo, 2023). These producers are more than traditional artisans, they are keepers of the forest, carefully selecting the trunks to be used, trying to keep the trees healthy, and working collectively to prevent the Ubamegashi exploration beyond its limits (Henderstein, 2016).

In Japan, a good part of the Tosa-binchotan is produced in the region of Muroto City, in Kochi Prefecture, where is possible to find new producers and apprentices of the traditional techniques. With the dedication of these people and the support of the city, this industry has been kept alive in the region (Fukushima, 2022; Sumigen, 2023). In Wakayama Prefecture, most part the Kishu-binchotan is made in the cities of Minabe and Tanabe, where there are museums about the binchotan charcoal and is possible to learn about the history, the tools that are used in the production, to see products made from binchotan and sometimes to visit the nearby charcoal makers and experience the removal of the charcoal from the kiln (Kishu-Binchotan, 2018; Minabe-Kanko, 2023). The technology used in the production of the Kishu-binchotan was designated as an intangible cultural property of Wakayama Prefecture in 1974. (Wakayama-Ken, 2023).

It is also possible to find white charcoal made in other countries of Asia, such as Malaysia, Myanmar, and Korea, where the use of oak is mentioned as raw material but more precise information is hard to find.

A price comparison made on the websites of Amazon USA and Amazon Japan (Feb/2023) showed that there exists a great difference in the prices of binchotan charcoal, according to the place of origin, the package size, the recommended application (for cooking or purification). The prices of 1 kg of binchotan in Japan ranged from US$ 8.00 to US$ 20.00 for cooking applications (as fuel) and from US$ 40.00 to US$ 80.00 to be used as a water purifier. Outside Japan, the prices were higher, on the order of two times or more for similar products.

From an economical point of view, binchotan charcoal seems to be more expensive than other types of charcoal. At least when the comparison is made based only on the price of 1 kg and considering the low yield of its production (around 10%). For reference, on the website of Mercado Livre in Brazil, the prices of 1 kg of eucalyptus charcoal for barbecue (Feb/2023) ranged from US$ 1.50 to US$ 3.50. However, a more elaborate analysis should be considered because the properties and applications of each type of charcoal are different and often cannot be exchanged.

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CHAPTER 2 – EVALUATION OF BINCHOTAN CHARCOAL AS AN ALTERNATIVE TO CALCINED PETROLEUM COKE

Abstract: The aluminum industry uses petroleum coke to produce carbon anodes, which act as chemical reducers and electrical conductors during the electrolysis of alumina in the Hall-Héroult process. The use of renewable sources, such as charcoal, could replace coke and reduce the impacts caused by fossil materials. In this study, binchotan charcoal samples were characterized and compared with calcined petroleum coke, aiming to use them in anode production. The coke and the binchotan were characterized by proximate analysis, chemical composition, scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS), Fourier-transform infrared spectroscopy (FTIR), thermogravimetry, density, higher heating value, electrical resistivity, and X-ray diffraction (XRD). The binchotan charcoal showed high fixed carbon content (> 91%) and low ash content (< 1.7%). The typical elements of the materials were identified, and using SEM, a high porosity was noted in the charcoal. The thermal behavior of both materials was alike and was noted that charcoal is more influenced by moisture. The FTIR spectra were similar too, suggesting the absence of heteroatoms and chemically active groups. The coke density was higher than charcoal and the results of higher heating value were similar. The charcoal showed an electrical resistivity three times higher than coke and the XRD patterns showed the presence of graphite in the samples, with higher intensity on coke. The results indicated that binchotan has the potential for a partial replacement of coke in the aluminum industry.

Keywords: Biomass. Aluminum. Carbon. Electrolysis. Biocoke.

CARACTERIZAÇÃO DO CARVÃO BINCHOTAN COMO ALTERNATIVA AO COQUE CALCINADO DE PETRÓLEO

Resumo: A indústria do alumínio utiliza o coque petróleo na produção dos anodos de carbono, que atuam como redutores químicos e condutores elétricos durante a eletrólise da alumina no processo Hall-Hérault. O uso de fontes renováveis, como o carvão vegetal, pode substituir o coque e auxiliar na redução dos impactos causados pelos materiais fósseis. Neste estudo, amostras de carvão vegetal binchotan foram caracterizadas e comparadas com o coque calcinado de petróleo, visando sua aplicação na produção de anodos. O coque e o binchotan foram caracterizados via análise imediata, composição química, microscopia eletrônica de varredura e espectroscopia por energia dispersiva (MEV-EDS), espectroscopia no infravermelho por transformada de Fourier (FTIR), termogravimetria, densidade, poder calorífico, resistividade elétrica e difração de raios-X (DRX). O carvão binchotan apresentou alto teor de carbono fixo (> 91%) e baixo teor de cinzas (< 1,7%). Os elementos característicos de cada material foram identificados e por meio do MEV foi observada uma alta porosidade no carvão. O comportamento térmico dos dois materiais foi semelhante e verificou-se que o carvão está mais sujeito à umidade do ambiente. Os espectros de FTIR também foram parecidos, sugerindo a ausência de heteroátomos e grupos quimicamente ativos. A densidade do coque foi maior que a do carvão e o poder calorífico apresentou valores similares. O carvão apresentou uma resistividade elétrica três vezes maior que o coque e os padrões de DRX evidenciaram a presença de grafita nos materiais, com maior intensidade no coque. Os resultados indicaram que o binchotan tem potencial para uma substituição parcial do coque na indústria do alumínio.

Palavras-chave: Biomassa. Alumínio. Carbono. Eletrólise. Biocoque.

2. INTRODUCTION

The increase in demand and aluminum production leads to higher levels of greenhouse gas emissions, creating new challenges related to sustainability. In the industry of aluminum, many processes generate carbon dioxide, such as the production of alumina and carbon anodes, and electricity generation, which is one of the most critical processes because the use of fossil sources is a majority worldwide. All around the world is estimated that aluminum production is responsible for almost 2% of carbon dioxide emissions (Saevarsdottir; Kvande; Welch, 2020).

The aluminum industry uses calcined petroleum coke to produce the carbon anodes, which act as reducing agents and electrical conductors during the electrolysis of the alumina (aluminum oxide) in the Hall-Héroult process, used to obtain the metallic aluminum. To reduce the emissions and add value to the biomass and its residues, part of the petroleum coke can be replaced with charcoal made from wood or similar sources. In this case, charcoal is known as biocoke (Amara et al., 2021).

Several studies indicate that it is possible to use biomass in the production of carbon anodes for the aluminum industry, replacing part of the coke or the coal tar pitch. Using thermal treatments with high temperatures the biocoke can be obtained from charcoal or bio-oil; the bio-oil can also be used to produce biopitch (Elkasabi; Boateng; Mullen, 2016; Hussein; Picard; Alamdari, 2021a; Senanu; Solheim, 2021).

To be used in the production of the anodes, the charcoal needs to reach some characteristics, for example, high carbon content, high density, and low electrical resistivity, which are some of the main parameters shown by the anodes produced with calcined petroleum coke (Huang; Kocaefe; Kocaefe, 2018).

The use of biomass as a carbon source reduces the risks of feedstock scarcity and decreases the environmental impacts related to greenhouse gas emissions. Furthermore, it is a material with low sulfur contents in comparison with fossil materials (Adrados et al., 2015; Senanu; Solheim, 2021).

Several studies can be found reporting the use of biocoke and biopitch in the production of carbon anodes. In general, a decrease in the anode quality is noticed with the increase of biomass content, being lower than 5% for biocokes. These alternatives need more study to be technical and financially feasible because changes that require equipment are harder to implement in industrial plants that already exist (Saevarsdottir; Kvande; Welch, 2020).

One material with the potential to be applied in the production of carbon anodes is binchotan charcoal, also known as white charcoal. This kind of charcoal is produced from hardwoods using slow pyrolysis, initiating at a low temperature, and followed by a great increase in temperature at the end of the carbonization. At the end of the process, the charcoal is removed from the furnace and cooled down in a mixture of earth, sand, and ashes (Chia et al., 2014; Miura, 1931; Pijarn et al., 2021).

This chapter aimed to characterize samples of binchotan charcoal and to compare its properties with those of calcined petroleum coke, to evaluate the possibility of its use in the production of carbon anodes in the aluminum industry.

2.1. Materials and Methods

2.1.1. Materials

Commercial samples of binchotan charcoal and calcined petroleum coke were used, and the sample preparation followed specific standards and methods for each characterization test. Two binchotan charcoals from different producers were used, one made in Japan and another in Myanmar, and both were made from Ubame oak (*Quercus phillyraeoides*). The coke samples were provided by the Brazilian Aluminum Company (CBA – Companhia Brasileira de Alumínio) and were part of the production line of carbon anodes of the company. In this work, the binchotan charcoal samples are identified by the abbreviation BM, made in Myanmar, and BJ, made in Japan. The term biocoke, when used in this study, refers to binchotan charcoal.

2.1.2. Characterizations

The characterizations were: proximate analysis, chemical composition, scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), bulk and vibrated bulk density, higher heating value, electrical resistivity, and X-ray diffraction (XRD). The tests were performed in the Bioenergy and Biomass Laboratory of the Federal University of São Carlos (UFSCar – Sorocaba, Brazil), in the Chemical Laboratory of the Paste Room of the Brazilian Aluminum Company (CBA – Companhia Brasileira de Alumínio), in the laboratories of the Department of Manufacturing Processes and Materials of the Aeronautics Institute of

Technology (ITA – Instituto Tecnológico de Aeronáutica, Brazil), and in the company Celqa Technical Analyses, Brazil.

2.1.3. Proximate Analysis

The proximate analysis was performed in the UFSCar – Sorocaba. The analysis of binchotan charcoal was based on the ASTM D1762, being obtained the contents of moisture, volatile matter, and ash. For coke, the analyses were based on the standards ASTM D3173 (moisture), ASTM D3175 (volatile matter), and ASTM D3174 (ash). The fixed carbon content was calculated by the difference between 100% and the contents of volatile matter and ash. All the analyses were repeated three times. A mass of approximately 1 ± 0.1 g was used in each test and a grain size between 35 and 60 mesh (425 µm – 250 µm) for the binchotan charcoal and grain size < 60 mesh (< 250 µm) for the coke. Porcelain crucibles with 30 mL, pre-heated in a muffle furnace at 750 ºC for 15 min, a desiccator for cooling the samples, and a scale with precision of 0.0001 g were used.

To obtain the moisture content of the binchotan and the coke, the samples were kept in a drying oven at 105 °C until constant weight, the results were reported on a dry basis. The volatile matter contents of the binchotan and the coke were obtained in a muffle furnace heated at 950 °C. The analysis of the ash content of the binchotan was made with the sample inside the muffle furnace at 750 °C for 6 hours, for the coke the temperature was 950 °C and a dwell time of 5 hours.

2.1.4. Chemical Composition

The chemical composition was obtained for both samples of binchotan charcoal, using two different techniques. The analysis based on Methodology IN 037 of MAPA (2017) was performed in the company Celqa and provided the carbon (C) contents using redox volumetry. The analysis with X-ray fluorescence was performed in the CBA based on the NBR 15964, using the equipment Axios Minerals of Panalytical, and the contents of sulfur (S), phosphorus (P), sodium (Na), vanadium (V), iron (Fe), silicon (Si), calcium (Ca), nickel (Ni) and chlorine (Cl) were obtained. The sulfur content was also consulted in the literature because it has typically a low value and shows a minimal variation in biomass. The data of the calcined petroleum coke were indicated according to the company history and the supplier information.

2.1.5. Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM-EDS)

The binchotan and coke samples were analyzed in the UFSCar – Sorocaba, using an SEM of the brand Hitachi, model TM 3000. Different grain sizes and magnifications (60x, 500x, and 2000x) were used to perform the morphological analysis by backscattered electrons detection. The analysis with EDS used an acceleration voltage of 15 kV and a magnification of 60x, and different parts of the samples were examined to perform a semiquantitative analysis of the materials.

2.1.6. Fourier-transform Infrared Spectroscopy (FTIR)

The analyses of the binchotan and the coke were performed in the UFSCar – Sorocaba with a spectrometer Cary 630 of the brand Agilent, using a small mass of the materials with grain size < 60 mesh (< 250 μm). The samples were directly placed in the equipment reader and before each scan, a blank analysis was performed to avoid interferences between the materials. The spectra (Attenuated Total Reflectance – ATR) were evaluated in a range of wavenumber between 650 and 4000 cm^{-1} and the scanning was repeated two times.

2.1.7. Thermogravimetric Analysis (TGA)

The thermogravimetric analyses of the binchotan and the coke were performed in the equipment Pyris 1 TGA of the brand Perkin Elmer, in the UFSCar – Sorocaba. A mass of approximately 8 mg of each material, with grain size < 60 mesh (< 250 μm), was used. The test parameters were: temperature range from 50 °C to 900 °C, heating rate of 20 $°C.min^{-1}$, inert atmosphere of nitrogen (N_2), and gas flow of 20 $mL.min^{-1}$.

2.1.8. Bulk and Vibrated Bulk Density

The bulk density of the binchotan and the coke was obtained in the UFSCar – Sorocaba, being calculated by the ratio of mass to volume. A glass beaker of 25 mL was used as a reference for the volume and a scale with a precision of 0.001 g was used for the weighing. The samples were dried in a drying oven at 90 °C for 4 hours and different grain sizes were used to obtain better material representativeness.

The vibrated bulk density (VBD) test was performed in the CBA, based on the ASTM D7454, and using the equipment VBDD of the brand STAS. All the analyses were repeated three times. The samples were ground to a grain size between 20 and 35 mesh (850 µm – 425 µm), and a volume of about 100 mL was necessary for the analysis. The vibration and the sample feeding were controlled by the equipment, after reaching a given volume the process was automatically stopped, and the sample was weighed, the density was calculated by the ratio of mass to volume.

2.1.9. Higher Heating Value

To measure the higher heating value a calorimeter IKA C200 was used. Approximately 0.5 g of dried material was used and the inner vessel was filled with oxygen (O_2) with a pressure of 30 bar. The analyses were performed in the UFSCar – Sorocaba, based on the standards ASTM D5865 and EN 14918, and the materials were ground to a grain size between 35 and 60 mesh (425 µm – 250 µm) for the binchotan and < 60 mesh (< 250 µm) for the coke. The results were indicated directly in the equipment and the tests were repeated two times.

2.1.10. Electrical Resistivity

The electrical resistivity of the binchotan and the coke was obtained with a piece of equipment developed by the company R&D Carbon, model RDC-147, following the ISO 10143 standard. Each test used 15 g of material with a grain size between 12 and 16 mesh (1.40 mm – 1.00 mm), providing the electrical resistivity values directly in the equipment. The tests were performed in the CBA and repeated three times.

2.1.11. X-ray Diffraction (XRD)

The X-ray diffraction analyses of the binchotan and coke samples were made in an Empyrean diffractometer from Panalytical, in the ITA. The samples, with a grain size < 60 mesh (< 250 µm), were placed directly in the equipment holders and leveled, the scanning was repeated two times. The test parameters were: Cu Kα radiation, a voltage of 30 kV, a current of

15 mA, and a range of 2θ between 5° and 100°. The interlayer spacing (d_{002}) was determined from Bragg's law, and the crystallite sizes (L_c and L_a) were calculated using Scherrer's equation. The following equations were used:

$$d_{002} = \lambda / (2\sin\theta)$$
$$L_{c\ (002)} = 0.89\lambda / (\beta\cos\theta)$$
$$L_{a\ (100)} = 1.84\lambda / (\beta\cos\theta)$$

Where:
λ: wavelength of Cu Kα radiation (0.15406 nm)
θ: angular location of the peak maximum
β: peak width at FWHM (full-width half maximum)

2.2. Results and Discussion

In the analyses in which repetitions were made, the presented values are indicated by the average and the standard deviation.

2.2.1. Proximate Analysis

The results of the proximate analysis are listed in Table 1, presenting the contents of moisture, volatile matter, ash, and fixed carbon for the samples of binchotan and coke.

Table 1 – Proximate analysis of binchotan charcoal and coke.

Sample	Moisture [%]	Volatile Matter [%]	Ash [%]	Fixed Carbon [%]
Charcoal BM	10.48 ± 0.03	6.97 ± 0.71	1.12 ± 0.03	91.91 ± 0.68
Charcoal BJ	9.82 ± 0.02	6.98 ± 0.82	1.65 ± 0.06	91.37 ± 0.87
Coke	0.09 ± 0.03	1.65 ± 0.18	0.30 ± 0.02	98.06 ± 0.20

Source: The author.

Both samples of binchotan charcoal (BM and BJ) showed close results, with low ash content and high fixed carbon content, values above 90%. Similar results for fixed carbon were found in other researches, with values ranging from 85% (regular charcoal) to 95% (binchotan charcoal) (Chia et al., 2014; Mansor et al., 2018). The calcined petroleum coke showed lower ash and volatile matter contents than those of the binchotan charcoal, and hence, a higher fixed carbon value, above 98%.

The moisture can be easily removed from the materials along the processing, demanding more attention to the binchotan charcoal due to its greater capacity to absorb moisture from the environment. The volatile matter is released during the production of the anodes. There are no worries related to the obtained results, approximately 7% for the binchotan and 1.6% for the coke.

2.2.2. Chemical Composition

The results of the chemical composition are listed in Table 2, the data of the coke was provided by the CBA and was included for comparison.

Table 2 – Chemical composition of binchotan charcoal and coke.

Sample	C [%]	S [%]	P [ppm]	Na [ppm]	V [ppm]	Fe [ppm]	Si [ppm]	Ca [ppm]	Ni [ppm]	Cl [ppm]
Charcoal BM	87.2	0	127	735	0	101	639	0	0	0
Charcoal BJ	88.2	0	179	607	0	50	341	0	1	0
Coke	> 99	0.61	< 5	60	228	69	99	—	—	—

Source: The author.

As well as in the proximate analysis, the carbon (C) contents of both samples of binchotan charcoal were close, around 87–88%. These values were slightly lower than the fixed carbon contents, which was expected considering the use of different techniques and can be seen in other works (Pijarn et al., 2021). The indicated value for the coke (> 99%) was reported by the supplier, being slightly higher than the result obtained in the proximate analysis (98%).

Phosphorous (P) is not commonly found in coke. Nonetheless, the phosphorous (P) was analyzed because it is a contaminant in the aluminum electrolysis process, and can cause a reduction in the current efficiency of the electrolysis cell (Al-Mejali et al., 2016; Edwards, 2015). The concentration of phosphorous in the cell is slowly reduced, prolonging the residence time in the electrolytic bath and increasing the negative effect on current efficiency. A possible reason for this is the fact that phosphorous gas is produced at the cathode, and most of it is oxidized in the bath or at the anode. Although it is difficult to quantify the influence of phosphorous on current efficiency, a reduction of about 1% for each 100 ppm of phosphorous is normally accepted. The phosphorous can also reduce the corrosion resistance of the aluminum and make the metal more brittle (Al-Mejali et al., 2016). The samples of binchotan charcoal showed contents under 200 ppm, which can be considered low because at first the coke replacement is made in a small percentage, but this element needs to be tracked when biomass is used.

The sulfur (S) content in biomasses and charcoals is low, values lower than 0.1% were reported in several works (Adrados et al., 2015; Amara et al., 2021; Coutinho; Rocha; Luengo, 2000; Hussein et al., 2017; Surup et al., 2020). The lower value presented by biocokes can help reduce pollution because sulfur is always present in coke, with values < 1% (low-sulfur content) and up to > 4% (high-sulfur content) (Amara et al., 2022; Edwards, 2015; Petrobras, 2019).

Calcium (Ca) and silicon (Si), along with potassium (K), are commonly found in charcoal samples (Pijarn et al., 2021; Senanu; Solheim, 2021), and the contents of Ca and Si need to be tracked when charcoal is used. Iron (Fe) and silicon act as contaminants in the process and can increase the impurities in the produced aluminum. The silicon also hinders the current efficiency of the process and can lead to higher consumption of energy during the electrolysis (Al-Mejali et al., 2016). As well as other impurities, sodium (Na), vanadium (V), and calcium act as a catalyst in the reaction that occurs between the anode and the CO_2, it can also affect the interaction between the coke and the pitch (Huang et al., 2016b; Ratvik; Mollaabbasi; Alamdari, 2022). Even though calcium was not observed in this analysis, it is important to always verify this element. Considering the other elements, the contents showed by the binchotan charcoal were very low or nonexistent.

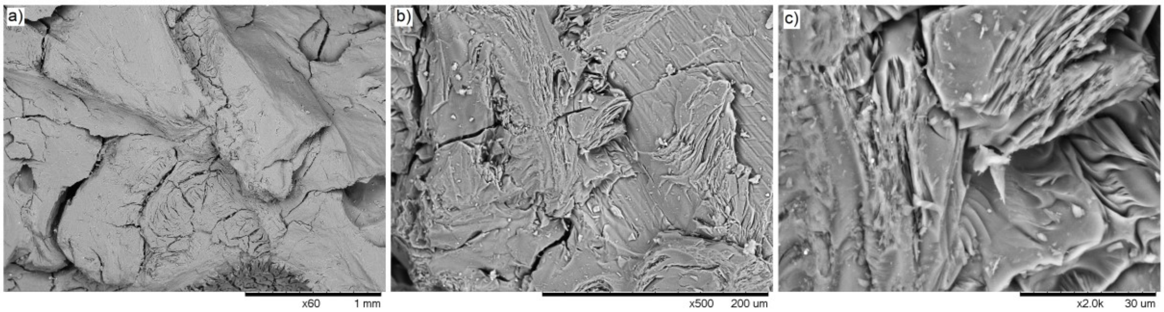
Regarding the proximate analysis and the chemical composition, both the samples of binchotan charcoal showed suitable results to be used in the production of carbon anodes. However, some elements need to be tracked, like phosphorous, silicon, and sodium. More information concerning the impacts of the chemical composition can be obtained with the analysis of CO_2 reactivity in the carbon anodes produced with biocoke. Usually, the biomaterials are more reactive (Adrados et al., 2015; Senanu; Solheim, 2021).

2.2.3. Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM-EDS)

The SEM micrographs of a coke particle are shown in Figure 8, with a magnification of 60x, 500x, and 2000x. For the binchotan samples magnifications of 60x, 500x, and 2000x were also used and the micrographs are shown in Figures 9 and 10, with a grain size between 35 and 60 mesh and < 100 mesh¸ respectively.

Figure 8 – SEM of a coke particle.

a) magnification of 60x, b) magnification of 500x, c) magnification of 2000x.

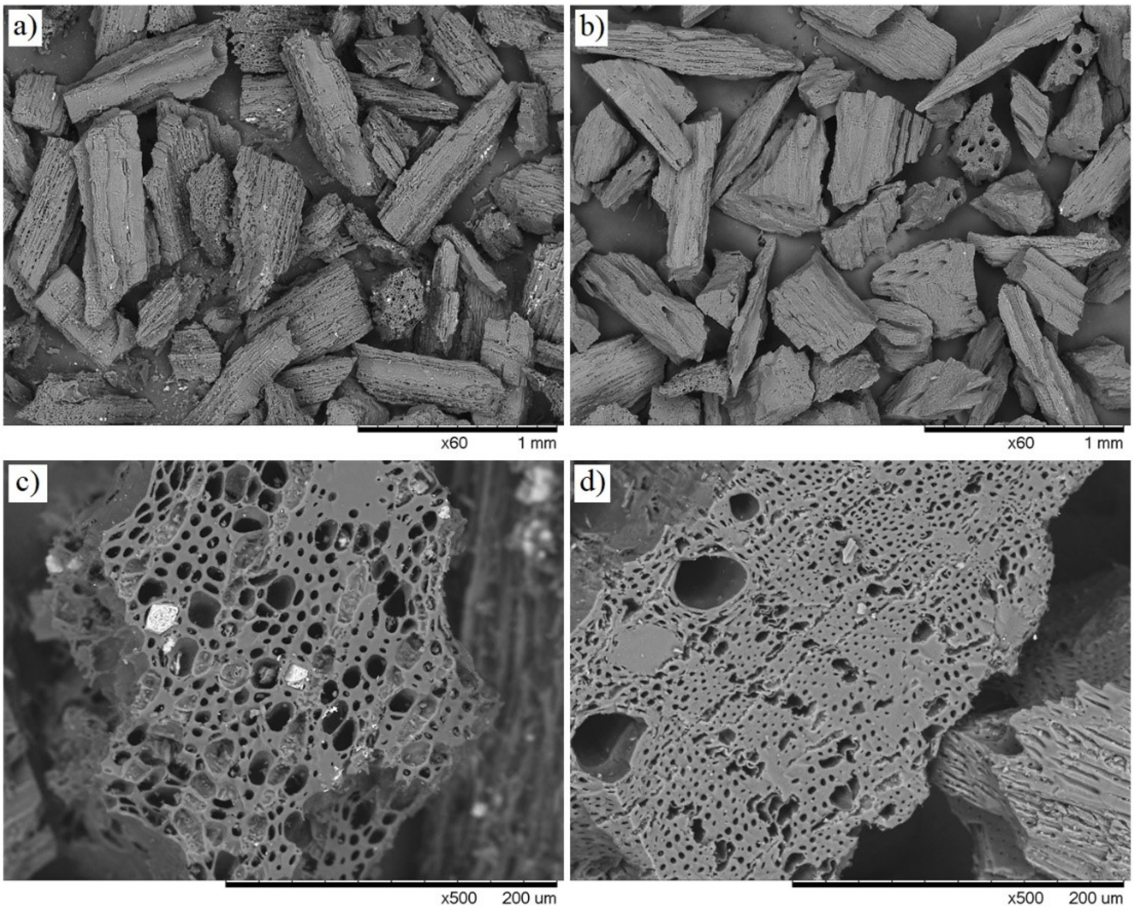


Source: The author.

Figure 9 – SEM of binchotan charcoal, grain size between 35 and 60 mesh.

a) BM magnification of 60x, b) BJ magnification of 60x,

c) BM magnification of 500x, d) BJ magnification of 500x.



Source: The author.

It is noticeable the difference in the porosity of calcined petroleum coke (Figure 8) and binchotan charcoal (Figure 9). Even in a lower magnification, it is possible to see the great quantity of porous in the particles of binchotan, which contributes to the adsorption properties presented by the binchotan charcoal (Chia et al., 2014; Mansor et al., 2018; Pijarn et al., 2021).

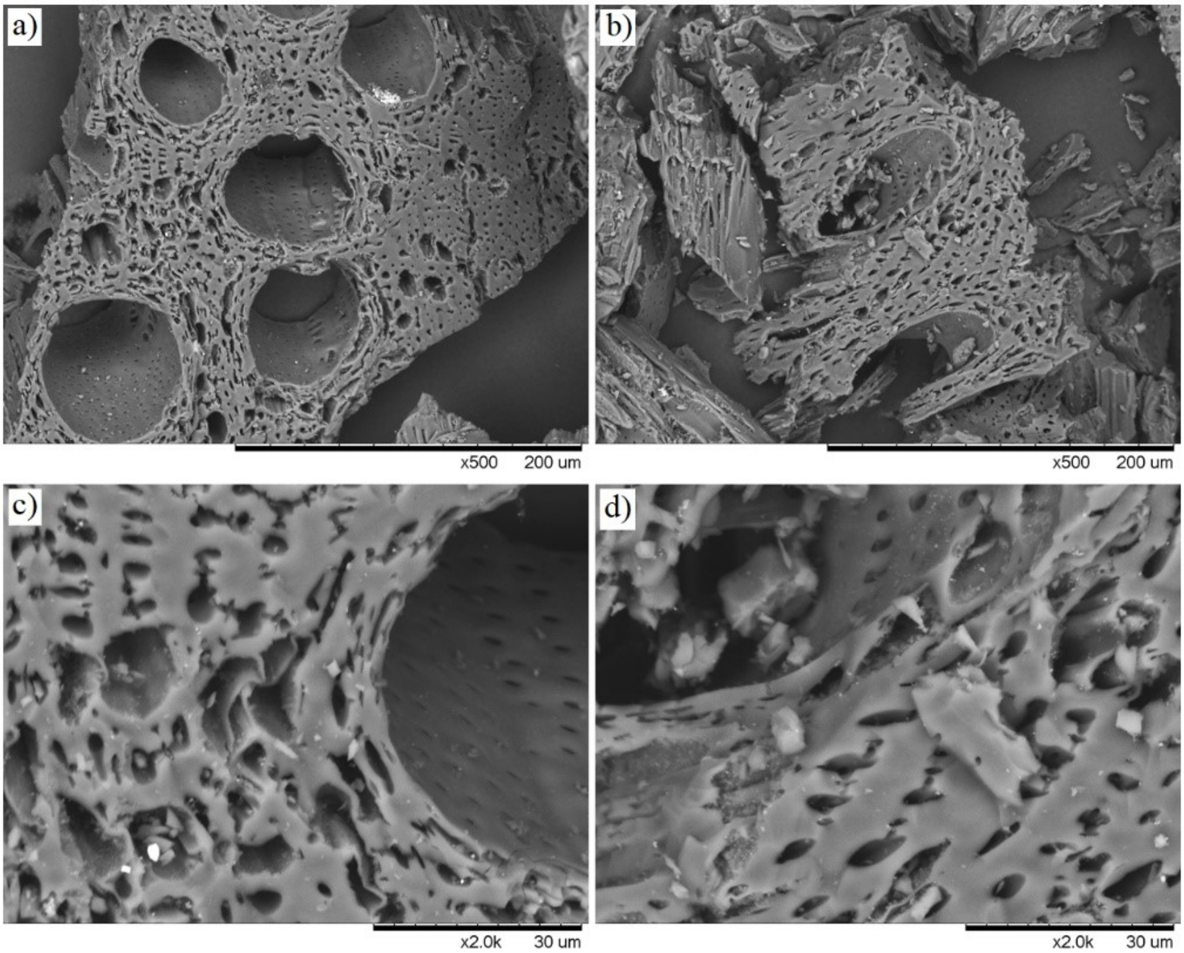
During the production of the carbon anodes, the coal tar pitch acts as a binder for the coke particles, filling the larger porous too (Hussein; Picard; Alamdari, 2021a; Lu et al., 2021). With the use of biocoke, this behavior is also expected and the higher porosity should not be a problem, although may be necessary to do an adjustment in the parameters of the anode production or an analysis of the wettability between the charcoal and the pitch (Senanu; Solheim, 2021; Sommerseth et al., 2020).

The addition of biocoke in the carbon anode production is usually made with fine fractions, using a small grain size (Amara et al., 2021; Huang; Kocaefe; Kocaefe, 2018). Considering this point, samples were analyzed using a smaller grain size and a higher magnification (Figure 10), aiming to verify the porosity. The structure noticed in charcoals is usually similar to the structure of the wood that was used, but some change can occur during the pyrolysis due to the carbonization parameters, such as the heating rate and the final temperature (Kwon et al., 2018; Santos et al., 2020). It was possible to notice the existence of vessels larger than 50 microns and the presence of porous smaller than 10 microns, similar to what was reported in the work of Pijarn et al. (2021).

Figure 10 – SEM of binchotan charcoal, grain size < 100 mesh.

a) BM magnification of 500x, b) BJ magnification of 500x,

c) BM magnification of 2000x, d) BJ magnification of 2000x.



Source: The author.

Besides the high porosity observed, the mechanical strength of the binchotan charcoal seems not to be impaired, which could be noticed during the preparation of the samples and because of the high density measured (section 2.2.6).

The main elements detected by the energy dispersive spectroscopy (EDS) are listed in Table 3, the elements with high content were listed and the remaining were indicated as others because the percentage was very small. In the EDS analysis, the selected elements are listed proportionally, always totaling 100%.

Table 3 – Elements detected with EDS.

(acceleration voltage of 15 kV and magnification of 60x)

Element	Charcoal BM [%]	Charcoal BJ [%]	Coke [%]
C	89.50	91.93	95.11
O	8.67	6.94	3.99
K	1.17	0.58	—
S	—	—	0.47
Ca	0.47	0.32	—
Al	—	—	0.20
Others	0.19	0.23	0.23

Source: The author.

The elements with higher contents in the samples of binchotan were carbon (C) and oxygen (O). It was expected due to the high fixed carbon content previously analyzed and the fact that oxygen is reported as one of the main elements in biomass samples. Furthermore, the oxygen content is typically smaller in the coke (Adrados et al., 2015; Huang; Kocaefe; Kocaefe, 2018).

Small amounts of potassium (K) and calcium (Ca) were found in the binchotan samples, which are elements usually found in charcoal (Pijarn et al., 2021; Senanu; Solheim, 2021). A small quantity of sulfur (S) and aluminum (Al) was observed in the coke. The presence of aluminum is not a problem and the sulfur was already expected because is commonly found in coke and is also used to rank the quality of these materials (Amara et al., 2022; Petrobras, 2019).

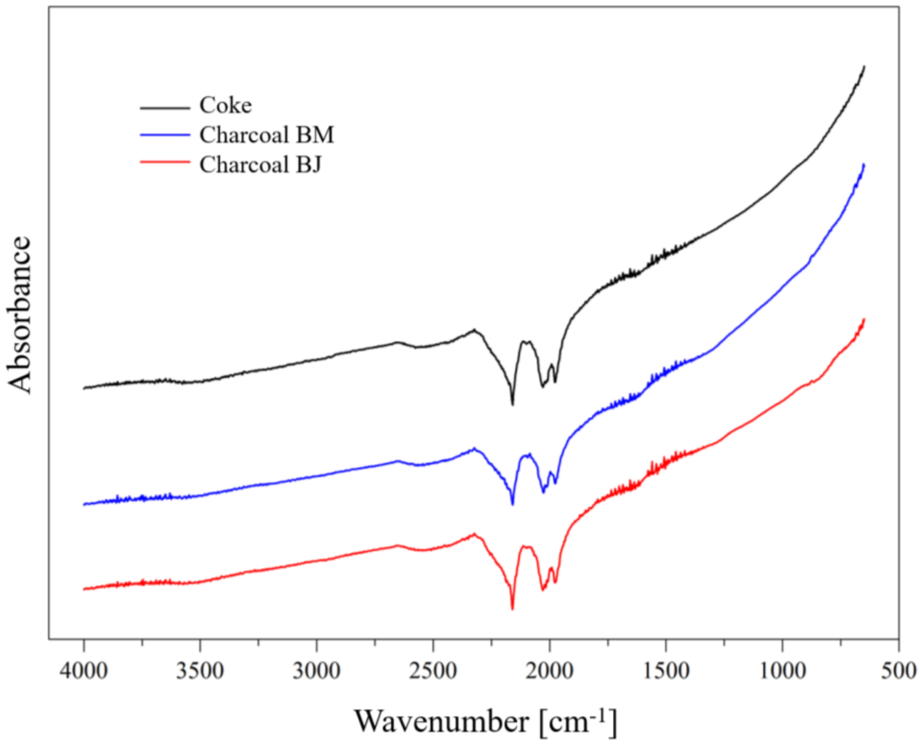
The carbon contents observed with EDS were close to those found in the chemical composition and close to the fixed carbon contents obtained in the proximate analysis. The EDS analysis is not recommended for accurate elemental quantification, especially for elements with low molecular weight. However, the technique can help to do a quick analysis of charcoal samples and identify the materials with higher carbon contents, which is a requirement to be used in the anodes.

2.2.4. Fourier-transform Infrared Spectroscopy (FTIR)

The FTIR spectrum obtained for the samples of binchotan charcoal and coke is shown in Figure 11. Two analyses were made with each material and the obtained results were very similar, because of this the first analysis was randomly chosen to be presented.

Figure 11 – FTIR spectrum of binchotan charcoal and coke.

(range of wavenumber between 650 and 4000 cm^{-1})



Source: The author.

The spectra of the binchotan and the coke were similar, with only small differences in the intensity along the spectrum. In the work of Huang; Kocaefe; Kocaefe (2018) the FTIR spectra of coke and biocoke showed similarity between the wavenumbers 500 and 3000 cm^{-1}. In the range between 3200 and 3500 cm^{-1} a huge difference was noticed, which was attributed to the presence of heteroatoms and chemically active groups and could result in a higher reactivity in the carbon anode.

Some of the main functional groups found in the materials used in the carbon anode production (coke, biocoke, pitch, and biopitch) are listed in Table 4, the data were compiled from the literature.

Table 4 – Functional groups of the materials used in carbon anodes.

Wavenumber [cm^{-1}]	Functional Group	Assignment
3600 – 3800	O–H	Free moisture, Phenol, Carboxylic acid
3200 – 3600	NH/OH	Secondary amine, OH Stretching
3000 – 3100	CH, C=C	C–H Stretching, Aromatic C=C
2800 – 2900	CH	Aliphatic C–H
2700 – 2950	C≡C, C=C, and C–C	Aliphatic groups
2200	C≡C	C≡C
1799	C=O	C=O
1740 – 1700	C=O	C=O Stretching
1431 – 1505	C=C	C=C Stretching vibrations
1200 – 1275	C–O	Stretching in phenols
1126	–O–	Esters C–O, Ether, COOH
700 – 900	Substitution	Substitution of the aromatic ring
600 – 860	C–H	Stretching of aromatic groups

Source: (Huang et al., 2016c; Hussein et al., 2020; Lu et al., 2020; Ozturk et al., 2018; Syarif et al., 2020)

The FTIR results showed that the most representative bands were concentrated in the range between 1500 and 2500 cm^{-1}, where the functional groups attributed to C=C, C=O, and C≡C bonds are present. It is important to emphasize that the absence of sharper peaks does not mean that a certain functional group is missing, this can occur when the quantity of that group is low or due to a detection limit of the equipment used in the analysis (Huang et al., 2016c).

The resemblance between the spectra of the coke and the binchotan can be an indicator of a good interaction of these materials with the coal tar pitch. These interactions are influenced by thermal treatments and by the composition of the materials (Huang et al., 2016c) and can have an impact on carbon reactivity (Syarif et al., 2020). More information about this interaction can be obtained with the wettability analysis of the pitch, which is generally made using the sessile drop test (Ozturk et al., 2018).

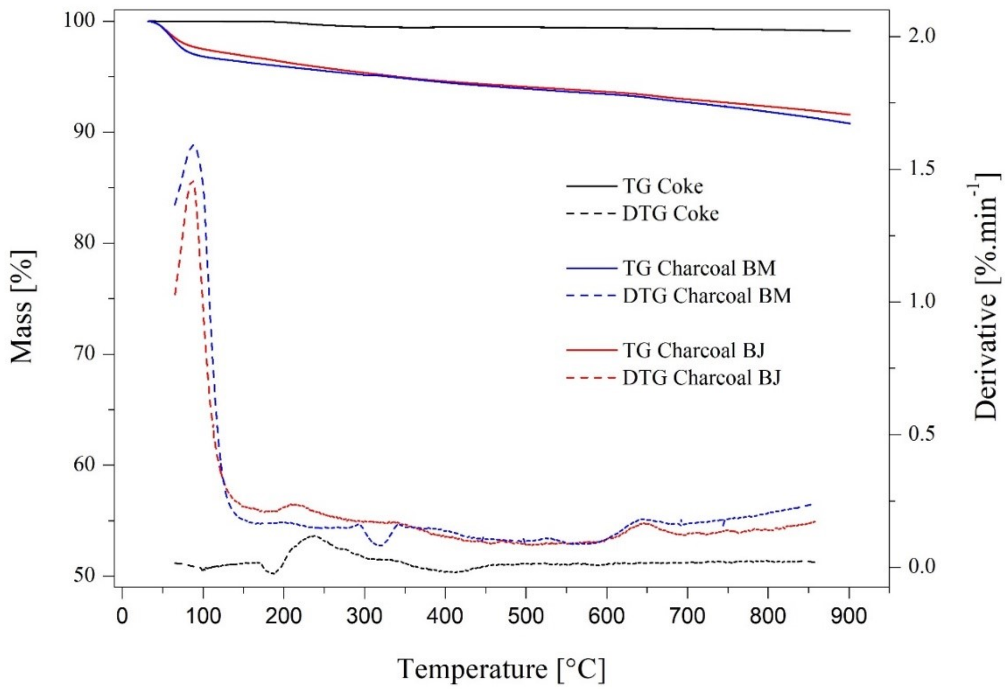
2.2.5. Thermogravimetric Analysis (TGA)

From the data obtained in the thermogravimetric analysis, the TGA (thermogravimetry) and DTG (derivative thermogravimetry) curves were plotted (Figure 12). With the TGA curves was possible to verify the mass loss during the increase in temperature. The DTG curves indicate the mass variation as a function of time, allowing the identification of thermal events and the temperature range in which they occur.

The materials were dried before the analysis, but it was noticed that the binchotan charcoal samples absorbed moisture from the environment before the beginning of the test, as reported by Cheng et al. (2020). This effect was evidenced by the mass variation in the TGA curve and by the peak around 100 °C in the DTG curve, subsequently, there was an almost constant loss of mass, which can be attributed to the release of the volatile matter. With the coke, a small decrease of mass was observed, without influences of the moisture.

Figure 12 – TGA and DTG curves of binchotan charcoal and coke.

(temperature range from 50 °C to 900 °C, heating rate of 20 °C.min^{-1}, inert atmosphere of nitrogen (N_2), and gas flow of 20 mL.min^{-1})



Source: The author.

The mass variations noticed in the thermogravimetric analysis (TGA) are listed in Table 5, indicating the mass loss at 100 °C and the total mass loss. The percentage indicated as the volatile matter was calculated by the difference between the total mass loss and the mass loss at 100 °C, which was considered as the moisture absorbed by the samples.

Table 5 – Mass variations in the TGA of binchotan charcoal and coke.

Sample	Mass loss at 100 °C [%]	Total mass loss [%]	Volatile matter [%]
Charcoal BM	3.19	9.22	6.03
Charcoal BJ	2.52	8.43	5.91
Coke	0.01	0.88	0.87

Source: The author.

In the proximate analysis, the volatile matter content (7%) of the binchotan was close to the observed in the thermogravimetric analysis (6%). For the coke, the volatile matter content was < 2% in the proximate analysis and < 1 % in the thermogravimetric analysis. A slight variation between analyses is expected and acceptable, because of the different parameters of each technique.

Considering these analyses was noticed the carbon stability under a temperature of up to 900 °C in an inert atmosphere since most of the mass loss can be attributed to the volatile matter. Regarding the control of the temperature and the shielding atmosphere, thermogravimetry could also be used in the production and calcination of biocokes with temperatures above 1000 °C (Amara et al., 2021; Huang et al., 2016a; Huang; Kocaefe; Kocaefe, 2018).

2.2.6. Bulk and Vibrated Bulk Density

The results of the analyses of bulk and vibrate bulk density (VBD) are in Table 6.

Table 6 – Densities of binchotan charcoal and coke.

(VBD = vibrated bulk density)

	Bulk density [$g.mL^{-1}$]			**VBD [$g.mL^{-1}$]**
Sample	**35 – 60 *mesh***	**< 60 *mesh***	**< 100 *mesh***	**20 – 35 *mesh***
Charcoal BM	0.40 ± 0.01	0.43 ± 0.01	0.58 ± 0.02	0.555 ± 0.001
Charcoal BJ	0.68 ± 0.02	0.65 ± 0.02	0.70 ± 0.05	0.733 ± 0.002
Coke	———	0.84 ± 0.02	———	0.820 ± 0.001

Source: The author.

The vibrated bulk density is the standard test used to evaluate the calcined petroleum coke, but requires specific equipment, because of this a simpler bulk density analysis was made to verify if the obtained values could be used for sample comparison. The bulk density of the binchotan charcoal was made using three different grain sizes since this was the material with more interest in the characterization.

Considering the binchotan samples, the bulk density obtained with a grain size < 100 mesh was closer to the results of the vibrated bulk density than the others. For coke, the values were also close, even though a unique grain size had been used. Based on these results it is noticed that is possible to use bulk density, which does not require specific equipment, to evaluate charcoal samples, the density is an important parameter for its use in carbon anodes.

Comparing the results of the vibrated bulk densities, the value obtained for the charcoal BJ (0.73 g.mL^{-1}) was close to the petroleum coke (0.82 g.mL^{-1}), whereas the lower value was obtained for the charcoal BM (0.55 g.mL^{-1}). The values of the vibrated bulk density were indicated by the equipment during the analysis. However, it needs to be considered that the binchotan charcoal samples had an average moisture of 10%, so the density of these samples is smaller than indicated in the analysis.

Besides the lower density of the binchotan charcoal in comparison with the coke, these biomaterials showed values close to other charcoals reported in similar studies, with values varying between 0.41 and 0.67 g.mL^{-1} (Adrados et al., 2015; Cheng et al., 2020; Hussein et al., 2017; Kwon et al., 2018).

2.2.7. Higher Heating Value

The results of the higher heating value (HHV) of the samples of binchotan charcoal and coke are in Table 7. The calorimeter provided the values in J.g^{-1} and those were converted to MJ.kg^{-1} and kcal.kg^{-1} to make easy the comparison with other materials.

Table 7 – Higher heating value (HHV) of binchotan charcoal and coke.

(0.5 g of material, inner vessel filled with oxygen (O_2) with a pressure of 30 bar)

	Charcoal BM	Charcoal BJ	Coke
HHV [MJ.kg^{-1}]	31.8 ± 0.01	31.3 ± 0.02	33.0 ± 0.04
HHV [kcal.kg^{-1}]	7604 ± 2	7476 ± 5	7886 ± 10

Source: The author.

The contents of carbon and hydrogen in the materials have a direct influence on the HHV (Barros, 2019), the similarity of the obtained values can be explained by the high carbon content of the binchotan and the coke.

A higher heating value (HHV) between 31 and 32 $MJ.kg^{-1}$ for the binchotan charcoal and 33 $MJ.kg^{-1}$ for the calcined petroleum coke were obtained. Several results of HHV were reported in similar works: between 25.4 and 28.2 $MJ.kg^{-1}$ for samples of charcoal (Cheng et al., 2020); around 33.9 $MJ.kg^{-1}$ for the white charcoal (binchotan) (Kwon et al., 2018); from 35.2 $MJ.kg^{-1}$ for the green petroleum coke (Petrobras, 2019); of 29.3 $MJ.kg^{-1}$ for metallurgical coke (Adrados et al., 2015); varying from 27.1 $MJ.kg^{-1}$ to 31.6 $MJ.kg^{-1}$ for biocokes produced with different biomasses (Mansor et al., 2018).

The production and use of carbon anodes in the aluminum industry do not require the burning of the material, although the analysis of this parameter was important for the characterization of charcoal. The results of the higher heating values and the density indicated the possibility of using binchotan charcoal as an alternative to metallurgical coke (studies are needed to confirm). In this case, the material must fulfill three requirements: provide energy to the process, act as a reducing agent providing carbon to the reaction, and withstand the loads inside the furnace (Adrados et al., 2015; Barros, 2019; Mansor et al., 2018).

2.2.8. Electrical Resistivity

The values of the electrical resistivity and the electrical conductivity of the samples of binchotan charcoal and coke are in Table 8. The conductivity was indicated to help the comparison with other samples and techniques because it is the reciprocal of the resistivity.

Table 8 – Electrical resistivity and conductivity of binchotan charcoal and coke.

	Charcoal BM	Charcoal BJ	Coke
Resistivity [μΩ.m]	1248 ± 6	1350 ± 5	442 ± 7
Conductivity [$S.m^{-1}$]	801	741	2262

Source: The author.

The binchotan charcoal resistivities were lower than 1400 μΩ.m and the coke result was lower than 450 μΩ.m, consequently, the electrical conductivities were higher than 700 $S.m^{-1}$ for the binchotan charcoals and 2200 $S.m^{-1}$ for the coke.

The values of the electrical resistivity of the binchotan charcoal were higher than those of the coke, about three times, but in comparison with other studies, the results were notably better. Although the charcoal BM showed a lower density than the charcoal BJ, its resistivity was also lower, which indicates a slightly better electrical property. The production of carbon anodes with these samples can allow the evaluation of the impact of these parameters and which one is the most critical, helping the selection of materials.

Surup et al. (2020) evaluated samples of coal, coke, and charcoal and confirmed that heat treatment with high temperatures can significantly decrease electrical resistivity. However, the reported values were of the order of 10 mΩ.m, much higher than those obtained in this study. In the work of Mansor et al. (2018), the electrical conductivity of samples of biocoke was reported to vary from 0.2 to 0.3 $S.m^{-1}$, lower than those obtained with the binchotan charcoal which was above 700 $S.m^{-1}$. In the work of Hussein; Picard; Alamdari (2021a), the electrical resistivity of the calcined coke was 750 μΩ.m, exceeding the value obtained with the coke in this study (< 450 μΩ.m).

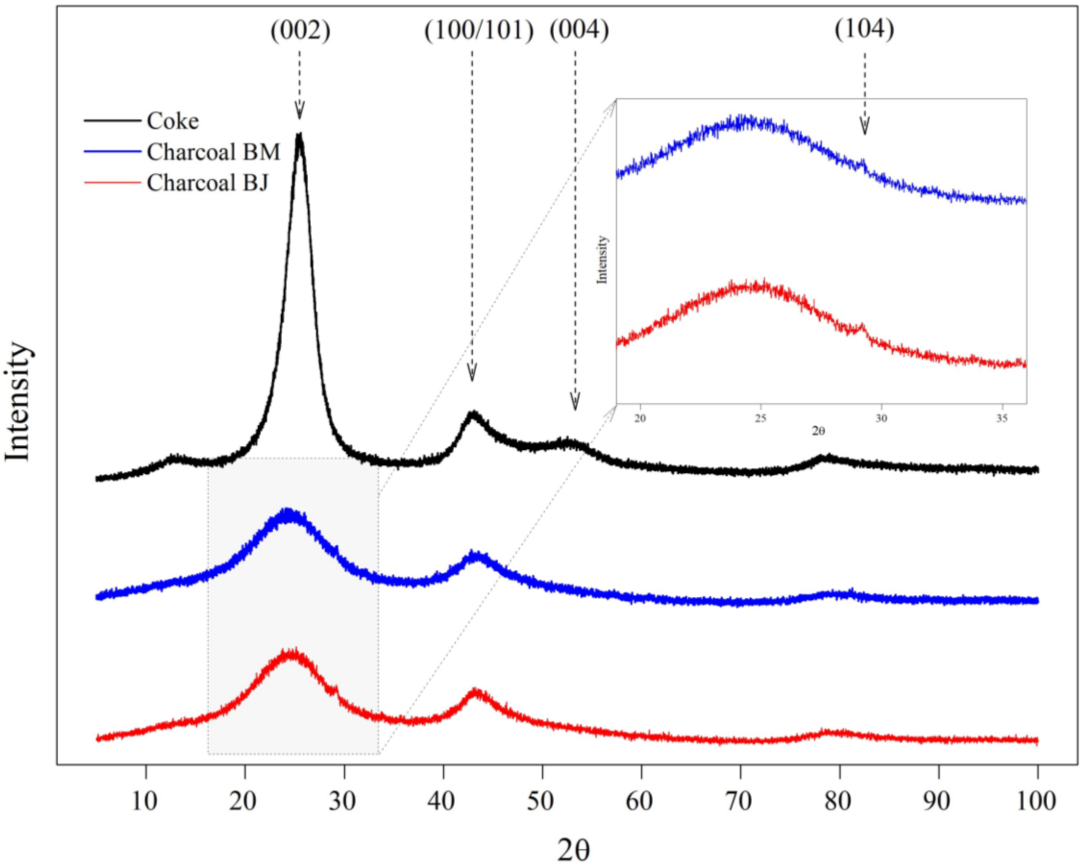
Binchotan charcoal has a good capacity to conduct electricity because of its structure, being able to be used as electrodes in batteries and capacitors (Chia et al., 2014; Syarif et al., 2020). Electrical resistivity is an important parameter in carbon anodes, due to its direct impact on energy consumption and operational costs, as a result, lower values of resistivity are desired (Amara et al., 2022; Huang; Kocaefe; Kocaefe, 2018; Ozturk et al., 2018).

2.2.9. X-ray Diffraction (XRD)

The X-ray diffraction patterns obtained for the samples of binchotan charcoal and coke are in Figure 13. Two scans were made with each material and the obtained results were very similar, because of this the first scan was randomly chosen to be presented. With the binchotan, the patterns were very close and both samples showed peaks in similar regions to coke, but with lower intensity as observed in the plane (002).

Figure 13 – X-ray diffraction patterns of binchotan charcoal and coke.

(Cu Kα radiation, voltage of 30 kV, current of 15 mA, range of 2θ between 5° and 100°)



Source: The author.

In the coke, the diffractions observed close to 25° and 53°, planes (002) and (004), are attributed to structured carbon materials (Ismagilov; Popova; Sozinov, 2021). The peak in (002), also present in binchotan, is attributed to the presence of graphite layers and is often noticed in carbonaceous materials, including the coal tar pitch used in the anode production (Chia et al., 2014; Coutinho; Rocha; Luengo, 2000; Hussein; Picard; Alamdari, 2021b).

The peaks indicated in planes (110/101), around 43°, are also attributed to the presence of graphite (Hussein; Picard; Alamdari, 2021b; Miki et al., 2003). In the samples of binchotan charcoal, the smaller peak around 29° is characteristic of the calcite ($CaCO_3$) plane (104), which appears in the white charcoal (binchotan) due to its processing with high temperature and fast cooling (Chia et al., 2014; Pijarn et al., 2021).

The X-ray diffraction parameters, interlayer spacing (d_{002}), and crystallite sizes (L_c and L_a), for the samples of binchotan charcoal and coke are shown in Table 9.

Table 9 – X-ray diffraction parameters of binchotan charcoal and coke.

Sample	d_{002} [nm]	$L_{c\ (002)}$ [nm]	$L_{a\ (100)}$ [nm]
Charcoal BM	0.367	0.666	1.617
Charcoal BJ	0.364	0.712	1.488
Coke	0.350	2.197	1.285

The interlayer spacing (d_{002}) of the coke was 0.35 nm and for the binchotan, the values were over 0.36 nm. The samples presented values larger than that of the graphite (0.335 nm), which suggests a random combination of graphitic and turbostratic stacking (Hussein; Picard; Alamdari, 2021b; Lu et al., 2021). For the binchotan samples, the L_a parameter exceeded L_c by more than two times, the difference between this parameter for the coke was lower, with the crystallite size L_c being higher than the L_a. The higher the difference between L_c and L_a, the more the material tends to be characterized as having an anisotropic crystallite shape (Ismagilov; Popova; Sozinov, 2021).

The higher crystallite size (L_c) of coke was expected since the peak in the diffractogram was much sharper than that of the binchotan charcoals. A higher L_c is also related to a lower electrical resistivity (Hussein; Picard; Alamdari, 2021a), which was verified before. According to Huang et al. (2016b), the parameter (L_c) is an indicator of the crystalline structure of the material. In the same work, the authors reported the crystallite size (L_c) of the biocoke before and after the calcination, with values rising from 0.23 to 1.04 nm. The maximum temperature used for the calcination was 1200 °C. The binchotan charcoal presented intermediate values, close to 0.7 nm. A possible reason for this result is the fact that white charcoals (binchotan) reach temperatures near 1000 °C at the end of the carbonization process. This may start the graphitization of the material, leading to higher crystallinity and lower values of electrical resistivity, as seen in the previous section.

According to Coutinho; Rocha; Luengo (2000), the effect of graphitization in electrodes produced with charcoal and submitted to treatments between 900 °C and 2700 °C was noticed, and the X-ray diffraction patterns evidenced the evolution of graphitic structures. Huang et al. (2016b) showed that the microstructures of coke and biocoke are highly influenced by calcination, which increases the crystallinity of the material and starts the graphitization of the carbon. Besides the heat treatment, electrochemical processing can also modify the crystallography of the materials. In the work of Syarif et al. (2020), samples of binchotan charcoal were submitted to treatments with different chemical solutions, resulting in the appearance of new peaks and an increase of intensity in the regions of crystalline structure.

The results can help the analysis of carbon anodes produced with biocoke, allowing the comparison of the diffraction patterns of the raw materials (coke and binchotan) with those obtained after producing the anodes. The anode production involves thermochemical transformations due to the mixture with coal tar pitch and due to the calcination (thermal treatment).

2.3. Summary of results

Two samples of binchotan charcoal were characterized and compared to calcined petroleum coke, to analyze their properties and evaluate the possibility of using binchotan charcoal in the production of carbon anodes in the aluminum industry. The main results were:

- Proximate analysis: the binchotan showed high fixed carbon content and low ash content, but the coke showed better results;
- Chemical composition: the binchotan charcoal showed suitable results to be used in the production of carbon anodes, but some elements need to be tracked because the charcoal has a tendency to be more reactive than the petroleum coke;
- Scanning electron microscopy (SEM): a high porosity was observed in the binchotan charcoal even with a higher magnification and a smaller grain size, this characteristic contributes to the adsorption capacity of the binchotan;
- Fourier-transform infrared spectroscopy (FTIR): the FTIR spectra of the binchotan charcoal and the coke were very similar, suggesting the absence of heteroatoms and chemically active groups;
- Thermogravimetric analysis (TGA): the results of both materials were alike, carbon stability was noticed, and the binchotan charcoal was shown to be more influenced by moisture;
- Higher heating value (HHV): the HHV results were similar, which can be explained by the high carbon content of the binchotan charcoal and the calcined petroleum coke;
- Density: the density of calcined petroleum coke was higher than that of binchotan charcoal, but in comparison to other biomaterials, the binchotan showed a high density;
- Electrical resistivity: binchotan showed an electrical resistivity three times higher than that of coke. However, the results of both materials were notably lower in comparison with other studies;

- X-ray diffraction (XRD): The XRD patterns showed the presence of graphite in both materials, with a higher intensity in the petroleum coke.

2.4. Conclusions

The calcined petroleum coke showed better properties than the binchotan charcoal. A total replacement is difficult without the necessity of changes in the process of carbon anode production. However, the use of binchotan charcoal, in smaller proportions, seemed to be feasible as a coke substitute. The results of this work motivate novel studies approaching the addition of different contents of binchotan charcoal in the carbon anodes and the characterization of its efficiency.

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CHAPTER 3 – ADDITION OF BINCHOTAN CHARCOAL IN THE PRODUCTION OF CARBON ANODES

Abstract: Carbon anodes are produced by the mixture of calcined petroleum coke and coal tar pitch, forming a paste that is cooked lately. The addition of biomass in the anodes could help reduce greenhouse gas emissions and minimize the use of non-renewable sources. In this work, carbon anodes were produced with the addition of 1% and 3% of binchotan charcoal, replacing part of the petroleum coke. Binchotan is a type of Japanese charcoal, characterized by having a high density, good electrical properties, and a high carbon content. The bioanodes were evaluated with the following analyses: chemical composition, apparent density, mechanical strength, CO_2 reactivity, and electrical resistivity. The tests were performed based on a methodology that is used in the aluminum industry and the results were compared with an international reference. All the values were considered adequate, indicating that it is possible to replace small percentages of calcined petroleum coke with binchotan charcoal. Technically, binchotan charcoal seemed feasible to be applied in carbon anodes produced on a laboratory scale and has the potential to be used in the aluminum industry.

Keywords: Biomass. Coal Tar Pitch. Calcined Petroleum Coke. Soderberg. Bioanode.

ADIÇÃO DE CARVÃO BINCHOTAN NA PRODUÇÃO DE ANODOS DE CARBONO

Resumo: Os anodos de carbono são produzidos a partir de uma mistura entre coque calcinado de petróleo e piche de alcatrão, formando uma pasta que é posteriormente cozida. A adição de biomassa nos anodos pode auxiliar na redução das emissões de gases do efeito estufa e minimizar a dependência de fontes de carbono não renováveis. Neste trabalho foram produzidos anodos de carbono com adição de 1% e 3% de carvão vegetal binchotan, substituindo parte do coque de petróleo. O binchotan é um tipo de carvão japonês, caracterizado por apresentar alta densidade, boas propriedades elétricas e alto teor de carbono. Os bioanodos foram avaliados conforme as seguintes análises: composição química, densidade aparente, resistência mecânica, reatividade com CO_2 e resistividade elétrica. Os ensaios foram realizados com base em uma metodologia usada na indústria do alumínio e os resultados foram comparados com uma referência internacional. Todos os valores foram considerados adequados, indicando ser possível substituir pequenos percentuais de coque calcinado de petróleo pelo carvão vegetal binchotan. Tecnicamente, o carvão binchotan se mostrou viável para ser aplicado nos anodos de carbono produzidos em escala laboratorial e com potencial para ser aplicado na indústria do alumínio.

Palavras-chave: Biomassa. Piche de Alcatrão. Coque Calcinado de Petróleo. Soderberg. Bioanodo.

3. INTRODUCTION

Aluminum is the most abundant metal in the Earth's crust, composing approximately 8% of the mass of the planet. It is rarely found in its metallic form due to a great affinity with oxygen, which gives origin to alumina. Among the lightweight metals and their alloys, aluminum is the most produced one, having a wide variety of applications and several properties (Brough; Jouhara, 2020; Venditti, 2021).

To produce 1 kg of aluminum, roughly 2 kg of alumina, 0.45 kg of carbon, and 14 kWh of electricity are consumed. In countries where the electrical matrix utilizes renewable sources, the environmental impacts can be reduced, and more sustainable efforts are focused on other processes, such as alumina refining and anode production (Kvande; Drabløs, 2014; Saevarsdottir; Kvande; Welch, 2020).

In general, the carbon anodes are produced from a mixture of calcined petroleum coke (≈ 70%) and coal tar pitch (≈ 30%), forming a paste that is molded in the desired shape and baked afterward. The coal tar pitch acts as a coke particle binder, forming an anode with good properties: high thermal and mechanical resistance, low electrical resistivity, and low reactivity (Glastonbury et al., 2020; Ozturk et al., 2018). Calcination, made in petroleum coke, is a thermic process that aims to increase the fixed carbon content by reducing the contents of volatile matter and moisture, producing a material with high values of density, electrical conductivity, and mechanical strength (Petrobras, 2019).

Studies related to the challenges of biomass use in the aluminum industry have been addressed in the literature. Biomass tends to be inferior to fossil materials and it is necessary to use treatments to improve their properties. The most promising strategies seem to be those in which it is made a partial replacement of the fossil materials, introducing small amounts of biocoke in the production of the anodes (Ratvik; Mollaabbasi; Alamdari, 2022; Senanu; Solheim, 2021).

The addition of biomass in the anodes helps to reduce the emissions of greenhouse gases and minimize the dependency on fossil materials as carbon sources (Adrados et al., 2015; Senanu; Solheim, 2021). The increase of the biomass content, in the form of biopitch or biocoke (charcoal), tends to reduce the carbon anode properties. The replacement is made with low percentages and there is still a lot of research to be done until this alternative becomes industrially feasible (Saevarsdottir; Kvande; Welch, 2020).

Binchotan charcoal is produced from a high-density type of Japanese oak and through a specific process of carbonization. Because of this, the material shows high density, good electrical properties, and a high fixed carbon content, in addition to low production of ashes and a good adsorption capacity, being typically used for cooking or as activated charcoal (Fujimoto, 2023; Itani; Kishimoto, 2018).

This chapter aimed to analyze the properties of carbon anodes made on a laboratory scale with the addition of binchotan charcoal, to evaluate the replacement of small percentages of the calcined petroleum coke.

3.1. Materials and Methods

The bioanode production and the analyses of the samples were performed based on the recommendations of the company R&D Carbon for the evaluation of Soderberg paste for aluminum application (R&D Carbon, 2012). The R&D Carbon is one of the biggest suppliers of solutions and an international reference in the field of carbon anodes. Providing support, supplies, and equipment for different types of analyses of carbon material that are used in the aluminum industry, following the appropriated international standards (R&D Carbon, 2023).

3.1.1. Materials

Carbon anodes were produced on a laboratory scale with the addition of binchotan charcoal. Two samples of binchotan from different producers were used, one made in Japan and another in Myanmar. The calcined petroleum coke and the coal tar pitch, used as raw material for carbon anodes, were provided by the Brazilian Aluminum Company (CBA – Companhia Brasileira de Alumínio). In this work, the anodes produced with the addition of binchotan charcoal are identified by the abbreviation AM (binchotan made in Myanmar), and AJ (binchotan made in Japan). The term bioanode, when used in this work, refers to a carbon anode produced with the addition of binchotan.

At first, a dry aggregate (blend) with calcined petroleum coke and binchotan was made, using binchotan proportions of 1% and 3%. The addition of binchotan was made in the finer fraction of the dry aggregate, in which the predominant granulometry is < 200 mesh (< 74 μm). This blend was mixed with coal tar pitch to form the Soderberg paste, also called green paste, in a proportion of 66.5% (blend) and 33.5% (pitch). The coke and pitch contents of the mixture were the same as those used by the company at the time and a total mass of 7 kg of green paste was produced with each type of binchotan.

To produce the carbon anodes, this paste was put into a metallic mold with a cylindrical shape and baked in the RDC-165 furnace from R&D Carbon. A given pressure was applied over the paste to guarantee a density level similar to the real process, and the temperature was gradually increased following different heating rates, until reaching 1000 °C. This process is known as anode calcination and can take up to 3 days, considering the cooling time. According to R&D Carbon (2012), the laboratory anodes produced under these conditions show chemical and physical properties that are similar to those of industrial carbon anodes.

Subsequently, test specimens were produced for characterization, extracting cylinders of 50 mm diameter from the center of the anodes, to eliminate the ends and the outer layers that could have suffered reactions during the calcination due to the contact with the air and the walls of the mold. The lengths of the samples varied from 50 to 130 mm, depending on the analysis. The samples were produced in duplicate.

3.1.2. Characterizations

The characterizations were: chemical composition, apparent density, mechanical strength (flexural and compressive), CO_2 reactivity, and electrical resistivity.

All the tests were performed in the Chemical Laboratory of the Paste Room of the CBA, and the R&D Carbon apparatus that was used is identified by the company code (RDC-XXX), along with the corresponding standard.

3.1.3. Chemical Composition

The chemical composition was obtained with X-ray fluorescence, based on the NBR 15964, and using the equipment Axios Minerals of Panalytical. The contents of sodium (Na), silicon (Si), calcium (Ca), vanadium (V), iron (Fe), copper (Cu), sulfur (S), nickel (Ni), magnesium (Mg), and phosphorus (P) were obtained.

3.1.4. Apparent Density

The apparent density was calculated by the ratio of mass to volume, based on ISO 12985-1 (baked anode) and ISO 12985-2 (green paste). The green paste density was obtained using an Archimedes balance; the mass was determined by weighing and the volume by the

Archimedes principle, immersing the sample in water and measuring the resulting force. To obtain the baked anode density, a scale for weighing and an analog caliper for measuring the samples with Ø 50 x 130 mm were used.

3.1.5. Mechanical Strength

To determine the mechanical strength, compressive strength, and flexural strength tests were performed. The analyses were made based on the standards ISO 18515 (compressive strength) and ISO 12986-1 (flexural strength). To obtain the compressive strength, the RDC-144 apparatus was used, and a load was applied until the breaking point of a sample with Ø 50 x 50 mm. The flexural test was performed using the RDC-187 apparatus and a sample measuring Ø 50 x 130 mm. The analysis was performed by the three-point method, where a load was applied in the center of the sample until the failure.

3.1.6. CO_2 Reactivity

The CO_2 reactivity was analyzed with the RDC-146 furnace, where a sample with Ø 50 x 60 mm was exposed to a saturated atmosphere of carbon dioxide (CO_2) for 7 hours and under a temperature of 960 ºC. After cooling, the sample was weighed and tumbled using the RDC-181 apparatus to remove any loose particles. The test was performed based on ISO 12988-1 and the result was presented by the amount of residual sample.

3.1.7. Electrical Resistivity

The electrical resistivity of the anode was determined based on ISO 11713 and using the RDC-150 apparatus. A sample measuring Ø 50 x 130 mm was placed between two plates, a constant electrical current of 1 A was applied, and the voltage drop was measured. As the sample dimensions are known, the electrical resistivity can be obtained by calculations.

3.2. Results and Discussion

The results were compared with a reference standard, data from the R&D Carbon company (R&D Carbon, 2006), and a range of values that are acceptable for carbon anodes produced with calcined petroleum coke was indicated.

3.2.1. Chemical Composition

The results of the chemical composition are in Table 10, along with the reference values for comparison.

Table 10 – Chemical composition of the bioanodes.

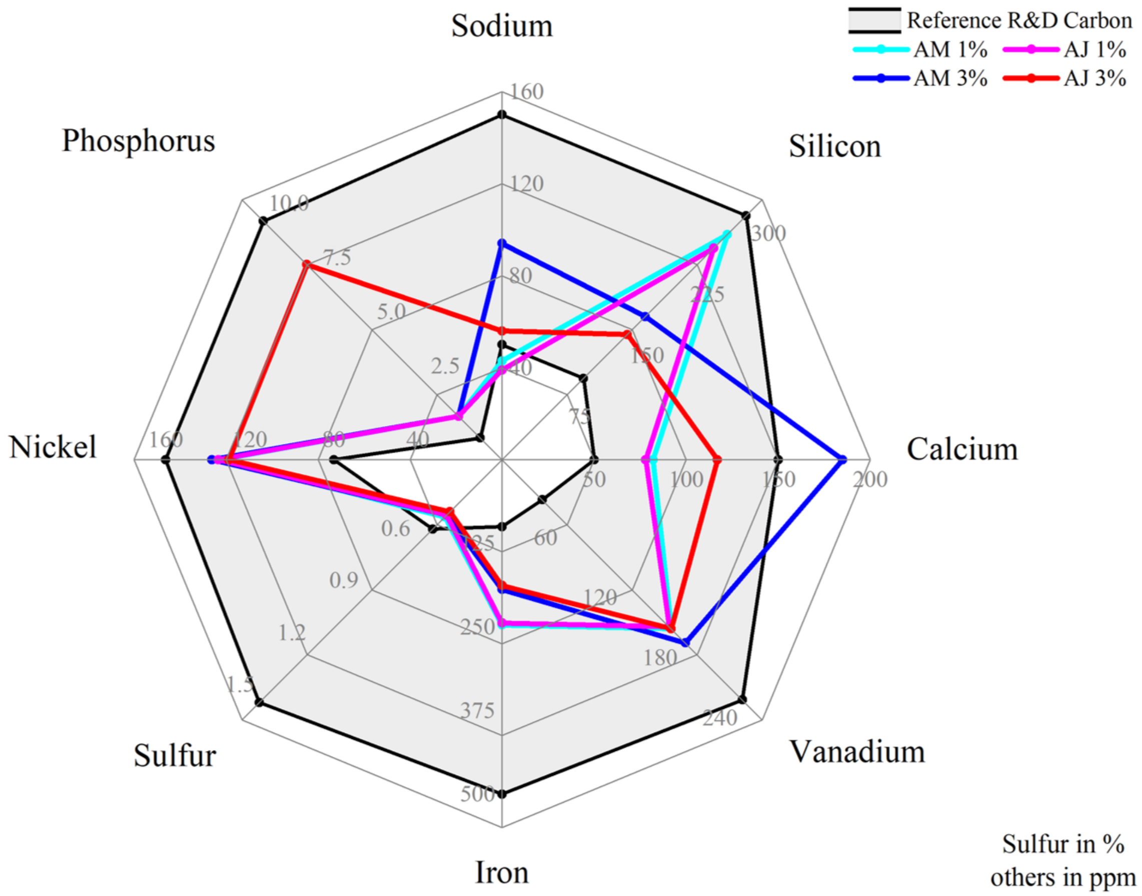
	Bioanode AM 1%	Bioanode AJ 1%	Reference R&D Carbon	Bioanode AM 3%	Bioanode AJ 3%
Na [ppm]	43	39	50 – 150	94	56
Si [ppm]	277	260	100 – 300	176	154
Ca [ppm]	82	78	50 – 150	185	117
V [ppm]	169	167	40 – 240	183	169
Fe [ppm]	247	244	100 – 500	194	188
Cu [ppm]	3	3	—	3	3
S [%]	0.43	0.42	0.5 – 1.5	0.42	0.4
Ni [ppm]	134	135	80 – 160	138	130
Mg [ppm]	9	8	—	6	4
P [ppm]	1	1	0 – 10	1	8

Source: The author.

Most of the values were within the recommended range. For some elements, the difference was not significant, as in the sodium (Na) content of the bioanodes with 1% of charcoal (< 50 ppm), the content of calcium (Ca) of bioanode AM 3% (185 ppm), and in the sulfur (S) contents of all samples (≈ 0.42%). A reference value for copper (Cu) and magnesium (Mg) was not provided, however, the results were very low (< 10 ppm).

A comparison of the main elements analyzed is shown in Figure 14, making it evident that the bioanodes presented mostly satisfactory results. Copper and magnesium were not included due to the absence of a reference value, and the recommended range is indicated by the gray region.

Figure 14 – Comparison of the main elements of the bioanodes.



Source: The author.

No tendency was noted in the results given the increase in the charcoal content, from 1% to 3%. Some elements showed higher values with the increase of the charcoal content, others showed a reduction, and there were also those in which the variation was zero or practically null.

Regarding the chemical composition, the bioanodes produced with the addition of binchotan charcoal showed acceptable values on a laboratory-scale production. For large-scale experiments, it is necessary to track the elements that exhibited deviation from the recommended range, as well as the elements that typically have a higher concentration in charcoal, such as sodium, silicon, calcium, and phosphorus.

3.2.2. Apparent Density

The results of the apparent density of the green paste and the baked bioanodes are listed in Table 11.

Table 11 – Densities of the bioanodes.

	Green Density [g.mL^{-1}]		Baked Density [g.mL^{-1}]	
Charcoal Content	1%	3%	1%	3%
Bioanode AM	1.575	1.563	1.440	1.460
Bioanode AJ	1.576	1.568	1.480	1.480
Reference R&D Carbon	1.520 – 1.590		1.390 – 1.470	

Source: The author.

The green and baked densities of the bioanodes showed adequate values in comparison with the reference. The baked density of the bioanode AJ was slightly above (0.7%) the recommended range, but it can be considered acceptable. Regarding the samples and the contents, the green density of the bioanodes with 1% was slightly higher than with 3%. There was no difference between the use of the binchotan from Myanmar and Japan. In the baked density, a bigger difference was observed between the samples, with a slightly higher value for the bioanode made with binchotan from Japan.

The addition of binchotan charcoal was made in the finer fraction of the dry aggregate. The use of a coarser granulometry can have an influence on the density and the other properties. It is necessary to re-evaluate the density if the parameters change. A high density is desirable because it contributes to the reduction of resistivity and prolongs the anode life, increasing the energy efficiency and carbon availability during the aluminum electrolysis (Ratvik; Mollaabbasi; Alamdari, 2022). On the other hand, a too-high density can cause breakage in the anode due to the release of volatile matter during the baking process (Amara et al., 2022).

3.2.3. Mechanical Strength

The results of the mechanical strength analysis, obtained by compressive and flexural tests are in Table 12. These analyses are important to evaluate the mechanical behavior and the thermal shock resistance of the carbon anodes. Low mechanical strength, as well as the presence of cracks, can be detrimental to the anodes performance and even lead to their breakage. Very high values are indicative of brittle materials that are more sensitive to temperature variation (R&D Carbon, 2023).

Table 12 – Mechanical strength of the bioanodes.

	Compressive [MPa]		Flexural [MPa]	
Charcoal Content	1%	3%	1%	3%
Bioanode AM	29.91	29.13	7.52	8.93
Bioanode AJ	30.11	30.21	8.78	9.03
Reference R&D Carbon	19.6 – 34.3		6 – 10	

Source: The author.

All the results obtained in the mechanical strength analysis were adequate and within the recommended range. The compressive strength values of the bioanodes were close; only the AM 3% sample showed a value slightly lower than the others. Regarding the flexural strength, the samples with 1% of binchotan showed values a little lower than those with 3%, and the bioanodes AJ reached slightly bigger results.

The mechanical behavior in carbon anodes with charcoal observed in the studies of Hussein et al. (2017) and Huang; Kocaefe; Kocaefe (2018) demonstrated that the increase of the charcoal content leads to a decrease in the strength, but with contents up to 3%, the changes were lower and acceptable. The results showed that the addition of up to 3% of binchotan charcoal did not cause negative impacts on the mechanical resistance of the anodes produced on a laboratory scale.

3.2.4. CO_2 Reactivity

The results of the CO_2 reactivity test are in Table 13. The results were indicated in percentage and refer to the amount of material that remained after the analysis. Thus, a lower value indicates a higher reactivity, resulting in greater consumption of the anode.

Table 13 – CO_2 reactivity of the bioanodes.

	CO_2 reactivity [%]	
Charcoal Content	1%	3%
Bioanode AM	93.7	87
Bioanode AJ	93.9	90.1
Reference R&D Carbon	80 – 92	

Source: The author.

All the bioanodes showed satisfactory results, indicating that the wear caused by the CO_2 reactivity was not impaired by the addition of the binchotan charcoal. The samples with 1% of binchotan showed a lower reactivity, with values slightly above the reference itself. In general, charcoal is more reactive than petroleum coke (Amara et al., 2021; Huang; Kocaefe; Kocaefe, 2018; Monsen; Ratvik; Lossius, 2010). The increase in the charcoal content tends to increase the CO_2 reactivity. This tendency was observed in the bioanodes with 3% of binchotan.

A high reactivity can lead to higher net anode consumption, increasing the electrical resistivity during the electrolysis, reducing the energy efficiency of the process, and increasing the CO_2 emissions of aluminum production.

As well as charcoal, coal tar pitch is usually more reactive than calcined petroleum coke. In this case, a high reactivity results in greater consumption of the binder matrix, causing the phenomenon known as dusting. This phenomenon is characterized by the detachment of coke particles due to the loss of structural integrity of the anode (Huang; Kocaefe; Kocaefe, 2018). The occurrence of dusting causes an increase in the electrical resistivity of the electrolysis process. According to Ozturk et al. (2018), the theoretical amount of carbon needed to produce 1 kg of aluminum is about 0.33 kg. However, other reactions of carbon with air and CO_2, occur and more than 0.40 kg of carbon is consumed for every 1 kg of aluminum produced. Because of this, anode reactivity is related to excess anode consumption and higher greenhouse gas emissions.

3.2.5. Electrical Resistivity

The properties of the carbon anodes are strongly affected by the properties of the coke. In such a way that the electrical resistivity of the anode is associated with that of coke and, by extension, with its density too. These parameters are indicative of high-quality materials, and anodes that show proper values of density and electrical resistivity contribute to enhancing the energy efficiency of the process (Ratvik; Mollaabbasi; Alamdari, 2022). The results of electrical resistivity and conductivity are in Table 14. The conductivity was indicated to help the comparison with other studies because it is the reciprocal of the resistivity.

Table 14 – Electrical resistivity and conductivity of the bioanodes.

	Electrical Resistivity [μΩ.m]		Conductivity [$kS.m^{-1}$]	
Charcoal Content	1%	3%	1%	3%
Bioanode AM	64.5	67	15.50	14.93
Bioanode AJ	66.2	61.5	15.11	16.26
Reference R&D Carbon	68 – 76		13.16 – 14.71	

Source: The author.

The bioanodes electrical resistivities were below the reference values, consequently, the electrical conductivities were also higher than the reference. However, the results were considered acceptable because they indicate that the samples have good electrical properties. According to Amara et al. (2021), a low value of resistivity is wanted during the aluminum electrolysis process due to its influence on energy consumption and production cost.

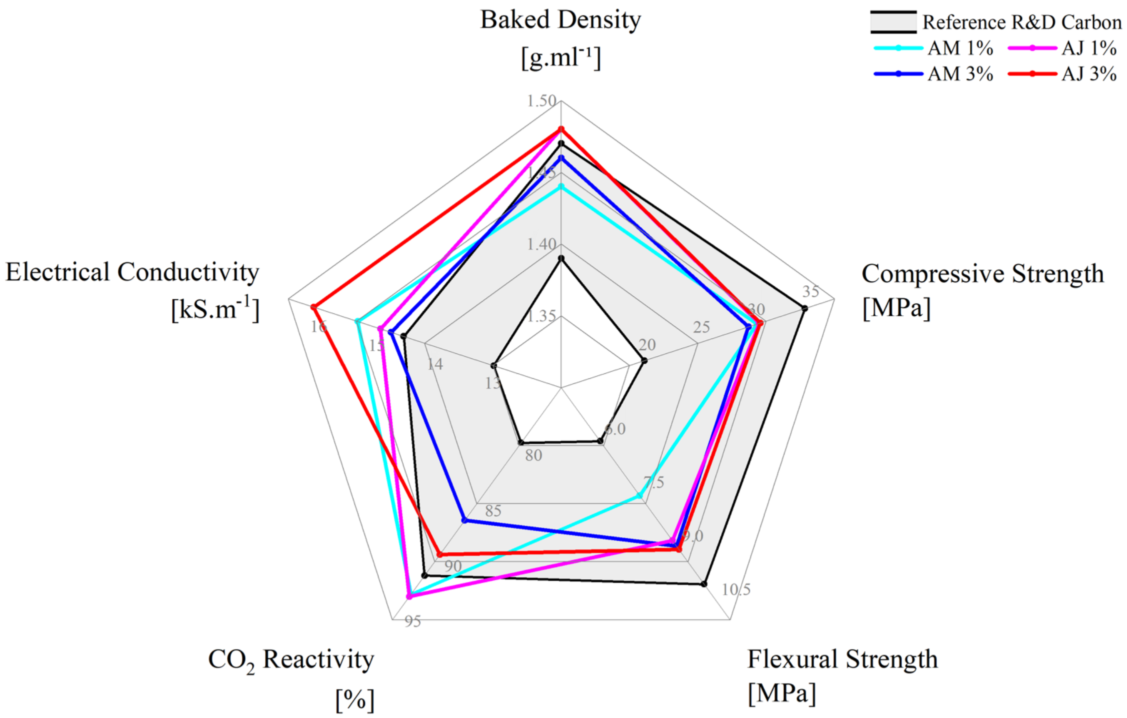
The bioanode AM 1% showed an electrical resistivity lower than the bioanode AM 3%. For the sample AJ, the lower value of resistivity was obtained with 3% of binchotan (61.5 μΩ.m), which was also lower than the others. It is important to highlight that fine particles of charcoal were used to replace the calcined petroleum coke. If the grain size or the content of charcoal were changed, the standard recipe of the anode needs to be re-evaluated to adjust the pitch content employed, which could lead to a change in the mechanical and electrical properties (Hussein et al., 2017).

Similar to coke, the bioanode properties are also affected by the charcoal properties. The high values of density noticed in the bioanodes and the fact that binchotan is a kind of charcoal with high density and good electrical conductivity, the results of the electrical properties tests were expected to be adequate, as was seen in this analysis.

3.2.6. Binchotan Charcoal

Considering the results obtained in this study, it is evident that binchotan charcoal has the potential to be used in many technological applications. A summary of the results of the properties analyzed in the bioanodes is in Figure 15, comparing the different contents of binchotan charcoal with the recommended range of values, indicated by the gray region.

Figure 15 – Comparison of the properties of the bioanodes.



Source: The author.

As previously discussed, the values that deviated from the reference did not compromise the results, such as the higher electrical conductivity of all bioanodes and the higher values of baked density and CO_2 reactivity of some samples.

The laboratory tests provided valid information to analyze the characteristics of carbon anodes produced with the addition of binchotan charcoal. However, large-scale tests may present different values, given the possibility of a greater variation in the parameters due to the use of larger equipment and a greater variation in the characteristics of the feedstocks. More tests are needed, with different scales and different contents of charcoal, to validate the use of binchotan charcoal as a partial substitute for the calcined petroleum coke in the aluminum industry.

Another advantage of the use of binchotan is the fact that a commercial sample can be used in natura, i.e., the material does not need any modification or treatment. Only the mechanical processing used to adjust the granulometry was required to formulate the green paste.

It is important to note that the content of the coal tar pitch used to form the anode paste influences the final quality of the carbon anode. Hussein et al. (2017) and Hussein; Picard; Alamdari (2021) verified that the increase in pitch content in the formulation of the anode with the use of biomass led to an increase in density and mechanical strength, as well as a decrease in electrical resistivity. This could be attributed to a better bonding of the coke particles due to a greater availability of the binder.

There is an amount of pitch that is considered ideal. The pitch demand must be enough to bond the coke particles, fill free spaces, and allow the pitch expansion during the baking, preventing excessive shrinkage or expansion and the formation of cracks or porosity in the structure of the carbon anode. A low pitch content hinders the formation of the anode paste, resulting in anodes with low density and lack of homogeneity. High-pitch contents led to a drop in the baked density due to a greater loss of mass during the baking, which increases the porosity (Ratvik; Mollaabbasi; Alamdari, 2022). Modifications in the pitch contents are mainly required when there is a decline in the quality of the raw materials. Just as can happen with petroleum coke, the commercial samples of binchotan charcoal are also susceptible to quality variability.

The use of biomass in the production of carbon anodes is one of the alternatives being studied to try to reduce CO_2 emissions from aluminum production. Another alternative that is being implemented and has great potential is the use of inert anodes as a substitute for prebaked anodes. The inert anode is not carbon-based, so the CO_2 is not released from the reaction during aluminum electrolysis. Two projects have gained attention in this type of technology: the Elysis project, developed by a partnership between the companies Alcoa and Rio Tinto and expected to be commercialized in 2024; and the company US Rusal, which is currently testing on an industrial scale (Brough; Jouhara, 2020; Ratvik; Mollaabbasi; Alamdari, 2022).

However, the replacement by inert anodes is not simple in companies that employ the Soderberg technology of continuous anodes; it is necessary to modify the infrastructure and change equipment. In this case, the addition of biomass to carbon anodes becomes an even more appealing alternative, even if it is done in small percentages.

Considering the large volume of petroleum coke that is used in the aluminum industry, even the addition of just 1% of charcoal can be beneficial to this field. According to Edwards et al. (2022), the best electrolytic cells in the world can achieve a net carbon consumption of approximately 395 kg per ton of aluminum, but in reality, this value is typically between 400 – 450 kg. This carbon comes from the mixture of coke and pitch used in the anode and, based on a generic recipe with 70% of coke and 30% of pitch, it can be estimated that an average of 298 kg of calcined petroleum coke is used per ton of primary aluminum. For a replacement from 1% to 3% of charcoal, would be needed between 2.98 kg and 8.94 kg of charcoal for every 1 ton of aluminum produced. In 2021, 345 thousand tonnes of primary aluminum were produced in Brazil using Soderberg technology (Abal, 2023). Considering this volume, about 1028 to 3084 tonnes of charcoal would be necessary for a substitution of 1% to 3% of coke.

The real impact that the addition of charcoal can have on carbon emissions needs to be analyzed through a life cycle assessment (LCA). The carbon demand in the aluminum industry is high, so an analysis of the feasibility of using binchotan charcoal on a large scale must also consider the costs involved, the logistics, and its production capacity. In the case of binchotan, the charcoal yield is around 10% and the growth time of the trees is over 20 years (Fujimoto, 2023; Narumiya, 2023).

From a technical point of view, the results indicated that binchotan charcoal had the necessary characteristics to be used as a substitute for calcined petroleum coke in the production of carbon anodes on a laboratory scale. Based on this data, new studies can be carried out to find other sources of biomass that can be used and that meet the demands of the aluminum industry. One of the determining factors in this case is the proximity of the charcoal production site to the aluminum production plant.

3.3. Summary of results

Carbon anodes were produced on a laboratory scale with the addition of 1% and 3% of binchotan charcoal, as a partial substitute for calcined petroleum coke. Different properties were analyzed in the bioanodes and the main results were as follows:

- Chemical composition: The majority of the values were within the recommended range. In the few elements that showed deviation, the difference was not significant.
- Apparent Density: Both green and baked densities were adequate, and no considerable difference was found between the samples or the contents.
- Mechanical Strength: Compressive and flexural strength were analyzed and the results were within the recommended values, regardless of the charcoal content used.

- CO$_2$ reactivity: The increasing of binchotan content led to an increase in reactivity, as expected, but all the results were under the reference values.
- Electrical resistivity: The bioanodes exhibited low electrical resistivity, indicating that binchotan addition was not detrimental to the electrical properties.

3.4. Conclusions

The physicochemical characteristics presented by the carbon anodes produced with the addition of binchotan charcoal were within an acceptable range of the international standard values. Given the great volume of primary aluminum production, even the use of only 1% of charcoal in the production of the anodes could have a big impact on the emissions of greenhouse gases. Also, it is a starting point in the study of materials that can reduce the dependence on non-renewable sources. These results evidenced that, from a technical point of view, the addition of small percentages of binchotan charcoal seemed to be feasible. However, more studies to evaluate the economic and logistical feasibility of using charcoal and similar sources are still necessary.

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4. GENERAL CONCLUSIONS

Different strategies have been used to reduce CO_2 emissions from aluminum production, such as the modernization of industrial plants, the use of renewable sources for energy generation, the development of technologies and equipment more efficient, and the use of more sustainable materials, like biomass, which can be used as a partial substitute for the raw materials that are used in the production of carbon anodes.

The addition of binchotan charcoal to replace part of the calcined petroleum coke in the formulation of carbon anodes was addressed on a laboratory scale. The results showed that binchotan can be used in small percentages without causing major deteriorations of the properties of the anodes. The physical, chemical, and mechanical properties of the samples were characterized and compared with information and materials commonly used in the aluminum industry. The results of the analyses provided data for comparison with other studies and also evidenced the potential that binchotan charcoal has to be used in other technological applications.

Some of the analyses were performed using methodologies and equipment from an aluminum producer, which allowed a more realistic evaluation since the same tests were performed with calcined petroleum coke. Binchotan charcoal presented the main characteristics required to be used in carbon anodes, such as high density, high carbon content, and low electrical resistivity. Although the values of these items were not as good as those of calcined petroleum coke, the results were similar to or higher than those of other charcoals found in the literature.

Given the volume of charcoal that would be necessary to meet the demand of the aluminum industry, the use of binchotan on a large scale would also need to be evaluated in terms of its production and the costs involved. Technically, the binchotan charcoal proved to be adequate and its use did not require any kind of additional treatment, only mechanical processing, so its addition in the carbon anodes would imply few modifications to the existing aluminum production process.

As a suggestion for future studies, the following topics could be addressed:

- Production of carbon anodes with the addition of higher contents of binchotan;
- Characterization of Brazilian charcoals based on the methodology used in this work;
- Production of white charcoal using Brazilian woods of higher density;
- Life cycle assessment of aluminum production using binchotan charcoal.