applied sciences

Article

Partial Replacement of Petroleum Coke with Modified Biocoke during Production of Anodes Used in the Aluminum Industry: Effect of Additive Type

Belkacem Amara [1], Duygu Kocaefe [1,*], Yasar Kocaefe [1], Dipankar Bhattacharyay [2], Jules Côté [3] and André Gilbert [4]

[1] UQAC Research Chair on Industrial Materials (CHIMI), Department of Applied Sciences, University of Quebec at Chicoutimi (UQAC), Chicoutimi, QC G7H 2B1, Canada; belkacem.amara1@uqac.ca (B.A.); yasar_kocaefe@uqac.ca (Y.K.)
[2] School of Applied Sciences, Centurion University of Technology and Management, Bhubaneswar 752050, Odisha, India; dipankar.bhattacharyay@cutm.ac.in
[3] Aluminerie Alouette, Sept-Îles, QC G4R 5M9, Canada; jcote@alouette.qc.ca
[4] Boisaco Inc., Sacré-Cœur, QC G0T 1Y0, Canada; agilbert@boisaco.com
* Correspondence: duygu_kocaefe@uqac.ca

Abstract: In order to reduce greenhouse gas (GHG) emissions, biocoke modified with different additives was used to replace part of the petroleum coke. Previously, a number of researchers attempted to manufacture anodes using biocoke. However, the majority of these efforts were unsuccessful because the quality of the anodes deteriorated with this replacement. The deterioration was due to the weak interactions between the pitch and biocoke compared to those between the pitch and petroleum coke. In this study, a chemical modification of biocoke was carried out using three additives (i.e., A(1), A(2), and A(3)) with the aim of improving biocoke–pitch interactions to prevent the deterioration of anode quality. The results of this study showed that biocoke–pitch interactions improved when the biocoke was modified with A(1) and A(3). The anodes containing biocoke modified with these two additives had properties similar to those of the standard anode (i.e., without biocoke). The utilization of additive A(2) did not show the same trend.

Keywords: carbon anodes; modified biocoke; coke; pitch; additive types; aluminum production

check for updates

Citation: Amara, B.; Kocaefe, D.; Kocaefe, Y.; Bhattacharyay, D.; Côté, J.; Gilbert, A. Partial Replacement of Petroleum Coke with Modified Biocoke during Production of Anodes Used in the Aluminum Industry: Effect of Additive Type. *Appl. Sci.* **2022**, *12*, 3426. https://doi.org/10.3390/app12073426

Academic Editors: Antonio Di Bartolomeo and Gaind P. Pandey

Received: 17 February 2022
Accepted: 24 March 2022
Published: 28 March 2022

1. Introduction

Aluminum is produced from alumina (Al_2O_3) electrolytically using carbon anodes. Anode production in Canada is approximately 1.5 million tons per year [1]; around 0.44 tons of carbon is consumed and approximately 2 tons of CO_2 (equivalent) is generated per ton of aluminum [1,2]. It is desired that anodes have high density, low electrical resistivity, and low air and CO_2 reactivities. They should also have good mechanical properties [3], which are important since anodes have to withstand different manipulations while they are placed in and removed from the baking furnace and the electrolysis cell. High-density anodes contain more carbon available for aluminum production. They also have lower porosity so that air and CO_2 cannot penetrate easily into the interior of the anode and react with carbon. High-density anodes have lower electrical resistivity, which decreases the energy consumption due to the Joule effect. Thus, the utilization of good-quality anodes decreases the cost, emission of GHGs, and power and carbon consumption, hence, increasing aluminum production.

The quality of the raw materials and the operating parameters of the different processes (mixing, compacting, cooling, and baking) used during the production of anodes influence the anodes' properties [4]. A carbon anode is composed mainly of petroleum coke and coal tar pitch [5]. Unfortunately, the quality of these raw materials is continuously deteriorating [6].

Along with the aluminum industry, the forest industry is considered one of the most important industries in Quebec and in Canada. Canada has 9% of the world's forests [7] and is ranked first in pulp and paper production. However, their use has declined significantly due to the advances in digital media [8]. As a result, the forest industry wants to diversify its activities by emphasizing the development of new and innovative products. The utilization of biocoke, produced via the pyrolysis of wood residue, to replace a part of petroleum coke, which is one of the major raw materials needed in anode production, could be a great opportunity for the wood industry. It is inexpensive, sulfur-free, renewable, abundant, and freely available [9]. During anode production, biocoke also produces CO_2, just like petroleum coke. However, wood is a renewable material. The CO_2 produced during biocoke production does not contribute to GHG emissions because a similar amount of CO_2 is used by trees during photosynthesis to produce O_2. Thus, the partial replacement of petroleum coke with biocoke would potentially reduce the GHG emitted during carbon anode production [10]. Since biocoke is not wetted well by pitch, it does not enter into the pores of biocoke, which is highly porous. This significantly decreases the density of an anode. Consequently, the addition of biocoke deteriorates the properties of an anode as reported in the literature [9,11–16]. It was suggested that only a part of the fine fraction of coke should be replaced by biocoke, since the effect of the porosity is much less for this fraction. In addition, during the calcination of biocoke, the number of heteroatom-rich functional groups (i.e., C–N/C–O/C–S, C–O/CSO_2, and COOH) present on the biocoke surface decreases [9]. The heteroatoms facilitate the interactions of coke/biocoke with pitch. Therefore, the decrease in heteroatoms decreases the interactions of biocoke with pitch [11]. Earlier, our carbon research group at UQAC (Research Chair on Industrial Materials (CHIMI)) modified petroleum coke using additives to improve the weak interaction of calcined biocoke with pitch [17]. The results showed that two of the six additives used enriched the surface of coke and, thus, improved the interaction of coke with pitch. In addition, there were a number of attempts to modify the biocoke as reported in the literature. Hussein et al. [15] reported that good-quality anodes were produced with acid-treated biocoke. However, the utilization of acid (HCl) has harmful effects on health and the environment, which was not considered in the study. There is no other study reported in the literature that claims to have produced anodes using modified biocoke without deteriorating their properties, except the work of the authors of the present study. Elkasabi et al. [18] concluded that good-quality anodes can be produced using biocoke based on the average properties of a calcined mixture of non-modified biocoke and coke without producing any anodes. This is not reliable unless the effect of using this mixture on anode properties are tested.

The research group of the authors (CHIMI) was the first to modify biocoke using environmentally friendly additives and produce anodes with properties similar to those of industrial anodes. They have published numerous articles on this subject; most other published studies obtained anodes with deteriorated properties as mentioned above.

The first study carried out by the authors of the current article was on the wettability of non-modified biocoke by coal tar pitch. This study showed that biocoke is well-wetted by pitch. In addition, biocoke's anisotropic and lamellar structure is suitable for partially replacing the coke used in anode production [9]. Then, they studied the interaction mechanism of three different pitches with non-modified biocoke. The FTIR and XRD analyses of biocoke indicated that the surface functional groups can form covalent and hydrogen bonds with pitch, and the crystalline length of biocoke increases with increasing pyrolysis temperature [11].

In their next study, anodes were made using biocoke, and the particle size of the biocoke to be used in anode production was established as less than 45 µm [13]. Biocoke is very porous, which decreases the anode density. Therefore, the particle size of biocoke should be small, and only the fine fraction of petroleum coke should be partially replaced by biocoke to eliminate the large pores and reduce the porosity effect.

In the following study, the anodes were produced using a different coke than the one used in the previous study. However, the results were not as good. The only difference between this study and the previous one was the type of coke used, since the biocoke and the pitch were the same. This shows that not all cokes can be directly replaced with biocoke, because the surface chemical composition of biocoke and its compatibility with pitch are very important. Thus, biocoke was modified with an environmentally friendly additive, which significantly improved the anode's properties. They were similar to those of the anodes manufactured without biocoke [16]. This result showed that the utilization of chemically modified biocoke in anode production results in good-quality anodes.

Subsequently, the effect of the coke type on the properties of anodes' containing biocoke was investigated in more detail. Anodes were produced with three different cokes. The pitch, biocoke, and the additive were the same as the ones used in previous studies. This study showed that any type of coke can be replaced with the modified biocoke, and good-quality anodes can be obtained. However, one type of additive was used in this study [19].

Finally, the effect of additive type was also investigated, which was the subject of the current paper. For this study, three environmentally friendly additives were identified, and the results are presented. There are no other studies that have investigated the effects of different parameters of biocoke utilization on anode production in such detail. Thus, the current paper constitutes the last part of a group of novel studies that the authors of this article have carried out.

2. Materials and Methods

2.1. Materials

In this study, petroleum coke, biocoke, butts, green and baked anode rejects (dry aggregate), and pitch (binder) were used as raw materials to produce carbon anodes. Biocoke was produced from wood chips. The same raw materials were used for all the anodes. Only the additives were different. Anode raw materials were supplied by Aluminerie Alouette, whereas the wood chips (65% black spruce and 35% fir) were supplied by Boisaco Inc., Sacré-Cœur, QC, Canada.

Biocoke is produced in the carbon laboratory at the UQAC (CHIMI), Chicoutimi, QC, Canada by heating wood chips up to 1100 °C under a nitrogen atmosphere at a heating rate of 7 °C/h. Different heating rates were tested. In the range of heating rates used, this parameter did not have a significant difference on anode quality. However, a heating rate of 7 °C/h, which resulted in slightly better-quality biocoke, and consequently slightly better-quality anodes, was used. Moreover, biocoke was kept at the maximum temperature for eight hours (holding time). The biocoke modification was carried out using three different additives that were obtained from Alfa Aesar: A(1), A(2), and A(3). Table 1 presents the abbreviations for the additives and biocokes used. In order to respect the confidentiality agreement between the research group and its partners, the names of the additives are not disclosed.

Table 1. Additives and biocokes used in this study.

Abbreviation	
UMBC	Unmodified biocoke
BCM-A(1)	Biocoke modified with 3% A(1)
BCM-A(2)	Biocoke modified with 3% A(2)
BCM-A(3)	Biocoke modified with 3% A(3)

2.2. XPS

The surface functional groups of coke and biocokes were determined using X-ray photoelectronic spectrometry (Kratos Axis Ultra DLD) at the University of Sherbrooke. CasaXPS software (version 2.3.23) was used for the data analysis. The sample area was

300 µm × 700 µm. The passing energy (PE) and the deviation were 160 and 1 eV, respectively, which helped to determine the percentage of contamination. C1s was analyzed with high-resolution spectra obtained with 20 eV PE and a 0.05 eV pitch size.

2.3. Wettability

Wettability (contact angle) is a measure of the degree of interaction between a solid and a liquid (the solid was unmodified or modified biocoke, and the liquid was pitch in this case). The dynamic contact angles were measured using the sessile-drop method. The pitch and coke/biocoke were placed in their respective crucibles. The fine solid particles were packed to form a bed. The particle size of biocoke was 45 µm. The pitch crucible was positioned above the coke/biocoke crucible. All were heated to 170 °C under a nitrogen atmosphere in a furnace. After this temperature was reached, a drop of pitch was placed on the bed by applying a slight gas pressure to the line going to the pitch crucible. The change in contact angle, which is the angle at the triple point (i.e., interface of biocoke, pitch, and nitrogen) with time (dynamic contact angle) was measured by capturing images of the pitch drop at different times using a data acquisition system. The FTA.32 software was used to analyze the images. The lower the contact angle, the better the wettability. The details of the equipment are given elsewhere [4].

2.4. Laboratory Anode Production

Anodes were produced in the laboratory under conditions similar to those used in the industry. Preheated dry aggregate was mixed with liquid pitch in an intensive mixer in desired proportions to produce anode paste. This paste was vibro-compacted to produce green anodes. These were cored: four cores, 50 mm in diameter and 130 mm in height were obtained from each anode. Then, the cores were baked to 1100 °C followed by 8 h of holding time.

In this study, five anodes were produced. Biocoke modification was performed using three different additives: A(1), A(2), and A(3). Based on a previous study by the authors, 3% of the petroleum coke was replaced with biocoke, since this percentage of biocoke utilization resulted in anodes with properties similar to those of the standard anode [13]. Anodes were identified as given in Table 2. "B" and "A" represent biocoke and additive, respectively. Their percentages are given right after. For example, B3A(1)3 indicates that 3% of the petroleum coke was replaced with biocoke that was modified with 3% additive A(1).

Table 2. Composition of the anodes.

Anode	Percent Biocoke (%)	Additive	Percent Additive (%)
B0-A(0)0 *	0	0	0
B3-A(0)0	3	0	0
B3-A(1)3	3	1	3
B3-A(2)3	3	2	3
B3-A(3)3	3	3	3

* Standard anode.

2.5. Measurement of Anode Properties

The different properties of the anodes were measured from the anode cores. The standards used were ASTM D5502-00 [20] (density before and after baking), ASTM D6120-97 [21] (electrical resistivity before and after baking), ASTMD6559-00a [22] (air reactivity), ASTM-D6558-00a [23] (CO_2 reactivity), and ISO 12986-1:2014 [24] (bending strength).

3. Results and Discussion

3.1. Density

As was mentioned previously, five anodes were manufactured under conditions similar to those used in industry. The standard anode (i.e., B0-A(0)0) did not contain any biocoke or additive. It was used as a reference anode. Subsequently, four anodes containing modified or unmodified biocoke were manufactured (one anode with unmodified biocoke and three anodes with modified biocokes, see Table 2).

The addition of 3% unmodified biocoke resulted in a decrease in both green and baked anode (i.e., B3-A(0)0) densities compared to those of the standard anode (i.e., B0-A(0)0) as shown in Figure 1. This decrease was due to the low density and the non-wettability of biocoke by pitch [9]. This has also been reported by other researchers. Monsen et al. [16] found that the density of the charcoal (biocoke) was much lower than that of the petroleum coke due to the fact of its porous structure. In addition, the open pores of the biocoke were not filled when it was mixed with pitch. Consequently, this decreased the anodes' density and unfavorably affected other anode properties. The densities of green and baked anodes containing biocoke modified with additives A(1) and A(3) (i.e., B3-A(1)3 and B3-A(3)3) approached those of the standard anode. Modification of biocoke with A(2) resulted in a significant decrease in anode densities (i.e., B3-A(2)3).

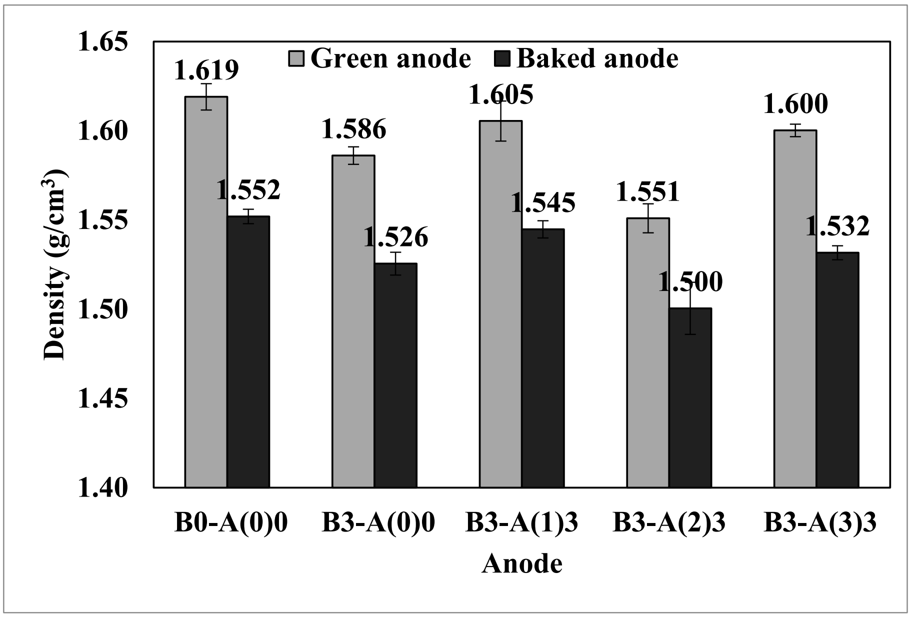

Figure 1. Densities of the green and baked anodes produced without biocoke (standard) and with unmodified and modified biocoke.

Biocoke has high porosity, and pitch cannot penetrate into the pores, since it does not wet well the biocoke. Figure 2 presents the contact angles of unmodified biocoke and biocokes modified using three additives. As can be seen from this figure, the biocoke modified with A(1), followed by the one modified with A(3), had the lowest contact angles, which means that pitch wetted these modified biocokes better than it wetted the unmodified biocoke. The contact angle of the biocoke modified with A(2) was the highest. Its wettability by pitch decreased even in comparison to the wettability of the unmodified biocoke.

Table 3 presents the XPS analysis results. The increase in the density of anodes manufactured with biocoke modified with additives A(1) and A(3) was due to the fixation of additional functional groups (i.e., C–O, C=O, and COO/COON) on the surface of the modified biocokes obtained from the convolution of the C1s peak. This improved the wettability of biocoke by pitch as shown in Figure 2. As can be seen from Table 3, some of the C=C groups of biocoke modified with A(2) and A(3) converted to C–C. The aromaticity (presence of C=C) groups increased the C/H ratio, which is an indication of higher density [5]. This conversion was lower for A(3), which resulted in a slight decrease in the wettability of biocoke modified with this additive compared to that of the biocoke modified with A(1). The amount of C=C of biocoke modified with A(3) was lower than that of the unmodified biocoke but higher than that of the biocoke modified with A(2). It seems the decrease in the C=C group of biocoke modified with A(3) was compensated by an increase in oxygen-containing (heteroatoms) surface functional groups. It is well known that heteroatoms increase the wettability by facilitating the formation of hydrogen [11,25,26] and covalent [26] bonds between pitch and coke/biocoke. However, the transformation of a C=C groups to a C–C group was quite high for A(2). Thus, the green and baked anodes containing biocoke modified with this additive (i.e., B3-A(2)3) had the lowest density. Table 3 also presents the total percentages of different elements including those present in C1s, O1s, and S2p 3/2 peaks. The presence of heteroatoms, such as O, N, and S, are important for the wettability of modified and non-modified biocokes by pitch. This facilitates the penetration of pitch into the pores of biocoke, which has a highly porous structure and, thus, helps increase the anode's density. It can be seen that the total oxygen percentage of the modified biocokes was higher than that of the unmodified biocoke.

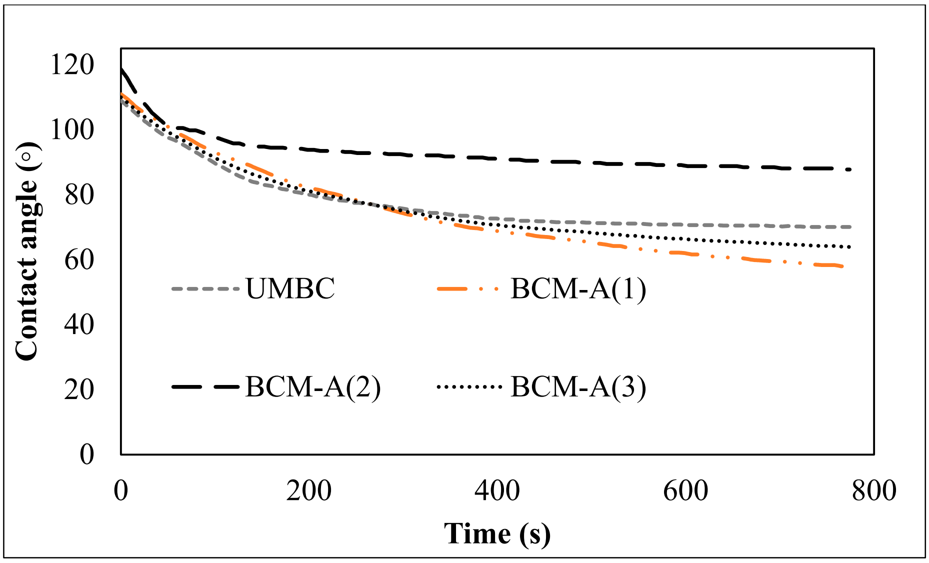

Figure 2. Contact angles of the modified and unmodified biocokes.

3.2. Electrical Resistivity

The specific electrical resistivities of green and baked anodes are given in Figure 3. Replacing 3% of the coke with unmodified biocoke increased the electrical resistivity of the green anode compared to that of the standard anode. However, the increase in the resistivity of the corresponding baked anode was not significant. In addition, the change in the resistivity of the anodes produced with biocoke modified using A(1) and A(3) was quite small, both for green and baked anodes. Modifying the biocoke with A(3) even decreased the resistivity of the green anode (i.e., B3-(A3)3) slightly compared to the resistivity of the standard anode. This was not the case for the corresponding baked anode. The quality of coke used in anodes is decreasing. Industry-mixes cokes of different origin to obtain a mixture, which contains a reasonable amount of impurities that affect the reactivity of coke [6]; thus, blending at the industrial scale results in the non-homogeneity of the coke. Slight changes in properties are expected, even if they are produced under similar conditions and using the same raw materials. On the other hand, the resistivities of the anode containing biocoke modified with A(2) were high both for green and baked anodes (i.e., B3-A(2)3). Use of anodes with high electrical resistivity increases power consumption during electrolysis. These results can be explained based on the anode's density. Anodes with low density have high resistivities, since they are more porous compared to high-density anodes. Air in the pores of low-density anodes increases the resistivity. The enrichment of the surface functional groups of biocoke with the additives increases the wettability of biocoke by pitch, thus facilitating the penetration of pitch into the pores. Consequently, this lowers the electrical resistivity (Figure 2 and Table 3).

Table 3. Atomic percentages of the coke, pitch, and unmodified/modified biocokes.

Sample	Carbon C1s Components (%)					
	Aromatic	Aliphatic	Ether Alcohol	Carbonyl	Carboxyl, Imide, Ester	Amine, Epoxy
	C=C	C–C	C–O	C=O	COO/COON	CN
UMBC	89.8	0	1.5	1.2	1.2	-
BCM-A(1)	88.3	0	1.7	2.2	2.2	-
BCM-A(2)	56.24	25.43	5.41	1.7	2.07	-
BCM-A(3)	73.06	9.82	4.82	2.09	1.34	
Pitch	66.1	25.8	0.9	0.4	0.4	0.5
Coke	89.4	4.9	1.1	1	0.9	-
Simple	Atomic Percentage					
		Heteroatoms				
	C (%)	O (%)	S (%)	N (%)	K (%)	
UMBC	93.8	4.9	0.1	-	1.1	
BCM-A(1)	91.9	6.3	-	-	1.2	
BCM-A(2)	92.41	7.59	-	-	-	
BCM-A(3)	92.18	7.82	-	-	-	
Pitch	94.8	3.6	0.1	2.2	-	
Coke	97.3	2.5	0.2	-	-	

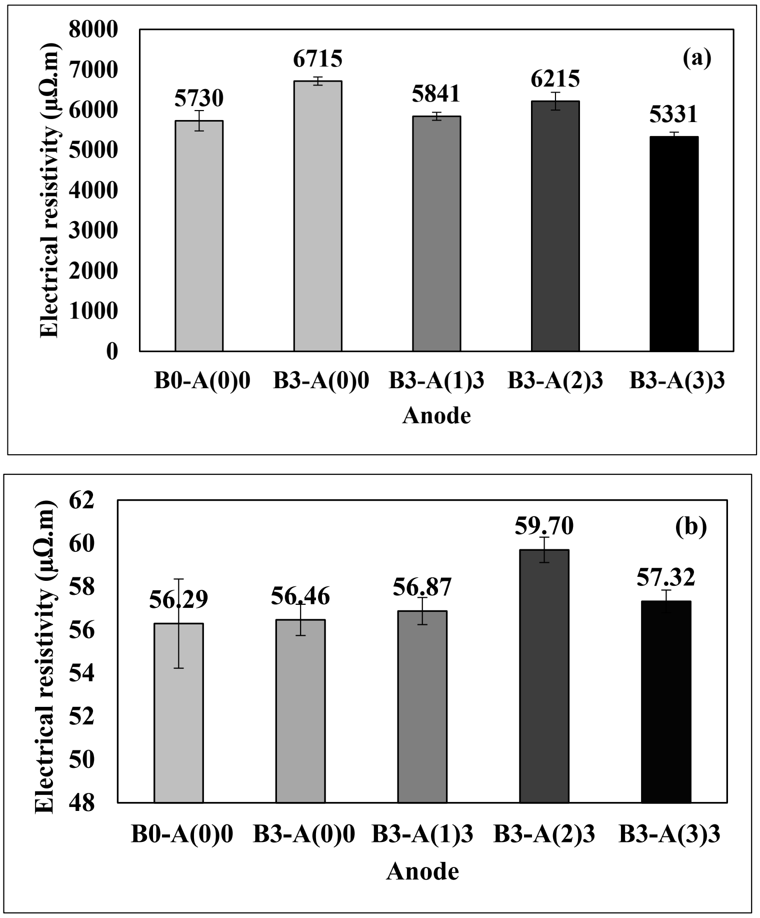

Figure 3. Electrical resistivity of the anodes before (**a**) and after (**b**) baking.

3.3. Air and CO_2 Reactivities

3.3.1. Air Reactivity

During the production of aluminum, air can infiltrate from the top of the electrolysis cells and react with the anode top and sides in spite of the presence of the anode cover. This reaction produces CO_2, which results in the overconsumption of the anode [3,27–30], because carbon consumed by this reaction cannot be used to produce aluminum (carbon loss). Air reactivity results are given in Figure 4 for all anodes. As shown in this figure, air reactivity generally increased with increasing anode density for anodes containing 3% unmodified and modified biocoke (i.e., B3-A(0), B3-A(2), and B3-A(3)), with the exception of B3-A(1)3. These results are in agreement with the literature [5,30], which states that air reactivity is a surface reaction. A higher density provides a greater surface for reaction. The air reactivity of the anode B3-A(1)3 did not seem to fit this trend. This type of behavior is quite common when heterogeneous industrial materials are used. In general, the addition of biocoke (modified or unmodified) reduced the air reactivity. Modification of biocoke with A(1) decreased the air reactivity the most.

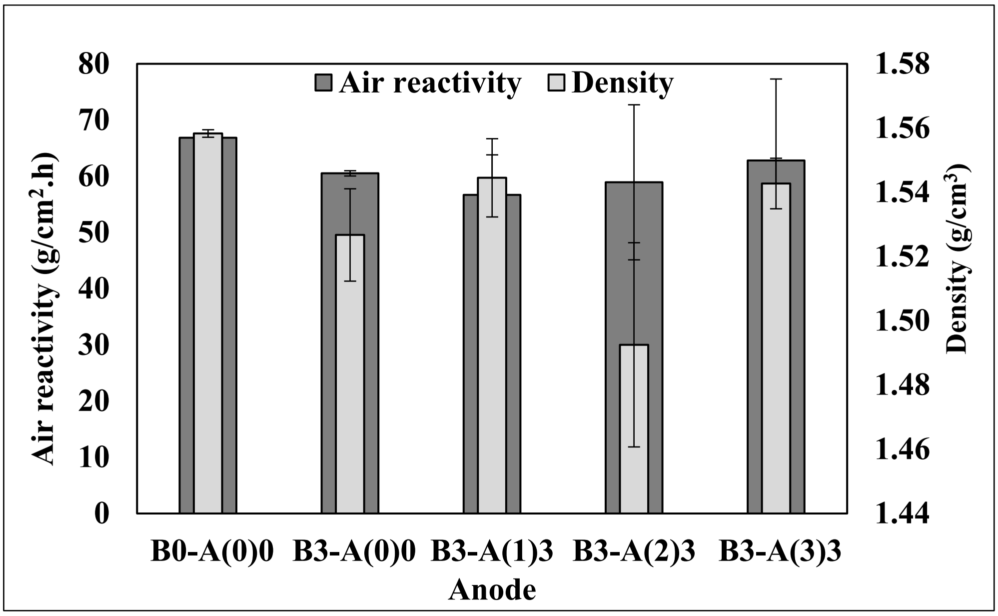

Figure 4. Air reactivity of the anodes.

3.3.2. Carbon Dioxide (CO_2) Reactivity

Carbon dioxide (CO_2) is produced during the electrolysis due to the reaction of oxygen in alumina with the anode's carbon. The produced carbon dioxide infiltrates into the pores of the anode and reacts with the carbon, producing carbon monoxide (CO) [27]. This is called the Boudouard reaction ($CO_2 + C \rightarrow 2CO$). This side reaction consumes carbon that otherwise could be used to produce aluminum [3,27–29]. The CO_2 reactivities of the anodes are presented in Figure 5. The addition of biocoke and additives increases the CO_2 reactivity compared to that of the standard anode. This might be due to the lower densities (higher porosities) of the anodes containing biocoke, which permits the diffusion of CO_2 into the interior of the anode and/or possibly the impurities present in biocoke. Anodes containing biocoke modified with A(1) had the highest CO_2 reactivity (i.e., B3A(1)3). Among the anodes containing biocoke, the utilization of A(3) presented the lowest reactivity (i.e., B3-A(3)3). This is in agreement with the XPS results. Biocoke modified with A(3) had the highest and biocoke modified with A(1) had the lowest oxygen content (heteroatom), which increased the wettability of biocoke by pitch and, hence, improved the properties.

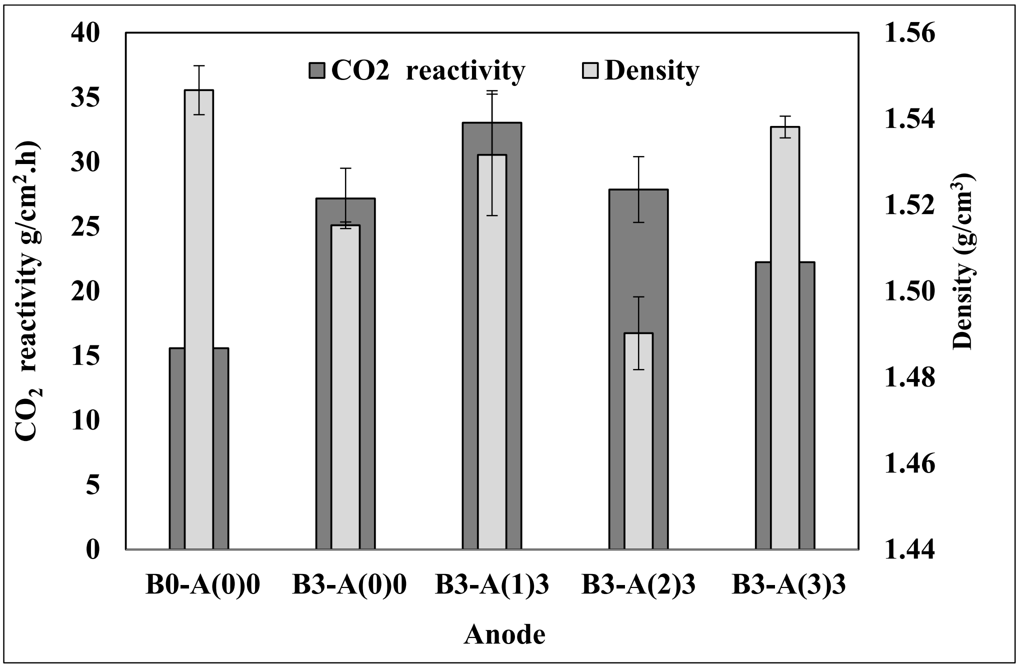

Figure 5. CO_2 reactivity of anodes.

3.4. Bending Strength

The bending strength indicates if an anode can withstand manipulations during its placement and removal in and out of the baking furnace as well as the electrolysis cell. The results are given in Figure 6. As can be seen from this figure, the modification of biocoke with A(1) and A(3) (i.e., B3-A(1)3 and B3-A(3)3) increased the bending strength of the anodes compared to that of the standard anode (i.e., B0-A(0)0), whereas the modification of biocoke with A(3) reduced it (i.e., B3-A(3)3). This is in agreement with the wettability and the XPS results explained previously.

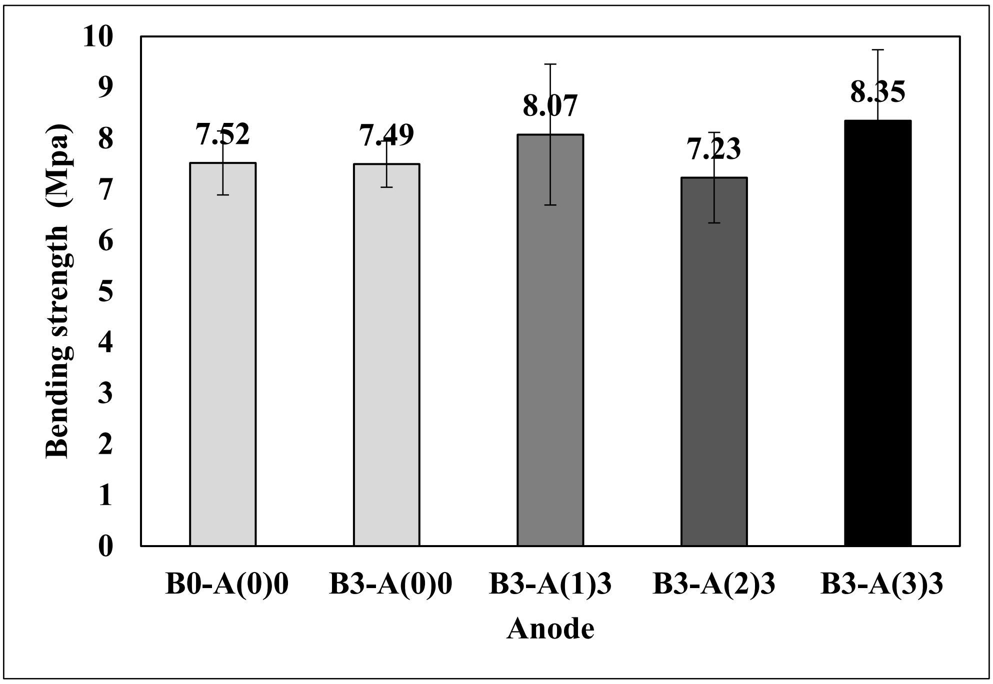

Figure 6. Bending strength of the anodes.

4. Conclusions

The use of biocoke is one possible solution to reduce greenhouse gas emissions during the production of aluminum, but its use deteriorates the properties of anodes. Modification of biocoke with a chemical additive improved the interaction of biocoke with pitch and helped maintain the properties of carbon anodes with the exception of CO_2 reactivity. In this study, three additives were used for biocoke modification. The interaction of each additive with biocoke brought changes on the surface, either by enriching the surface functional groups and transforming the existing ones shown by the XPS results. Only additives A(1) and A(3) improved the interaction of biocoke with pitch. The opposite effect was observed for additive A(2). The modification of biocoke with the additives A(1) and A(3) led to the production of anodes that had the most properties close to those of the standard anode or even better in some cases.

However, it may not be possible to maintain all properties of the anodes. In this case, the CO_2 reactivities of the anodes slightly increased. It must be noted that although the CO_2 reactivities were slightly higher than that of the standard anode, they were significantly lower than that of the anode made with unmodified biocoke. However, the advantages of reducing GHG emissions and associated carbon taxes as well as the disadvantage of an increase in CO_2 reactivity should be evaluated together via an economic analysis. In addition, this study was carried out using 3% biocoke and 3% additive. Different combinations of these percentages should also be studied. Moreover, the wood chips used to produce biocoke were a mixture of black spruce and fir. The preliminary chemical analysis by XRF of biocoke showed that it had a high calcium and phosphorous content. Calcium affects the reactivity of the anode, while phosphorous decreases the current's efficiency; thus, it is controlled strictly in the plant. The utilization of different species might improve the results. Since the reactivities were affected by the presence of some impurities, the impurity content of the wood chips and their effect on the air and CO_2 reactivities must also be studied.

Author Contributions: Investigation, B.A.; Conceptualization, D.K., Y.K. and B.A.; Supervision, D.K., Y.K. and D.B.; Methodology, D.K., Y.K. and B.A.; Writing, B.A.; Review and Editing, D.K. and Y.K.; Validation, D.K., Y.K. and B.A.; Formal Analysis, B.A., D.K., Y.K. and D.B.; Project Administration, D.K.; Resources, J.C. and A.G.; Funding Acquisition, D.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Fonds de Recherche du Québec—Nature et Technologies (FRQNT, grant no: 2019-GS-260252), Aluminerie Alouette (AAI), Boisaco Inc., and the University of Quebec at Chicoutimi (UQAC). The principal investigator was D.K.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to acknowledge the financial and technical support from FRQNT, AAI, Boisaco Inc., and the UQAC.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Saevarsdottir, G.; Halvor, K.; Barry, J.W. Aluminum production in the times of climate change: The global challenge to reduce the carbon footprint and prevent carbon leakage. *JOM* **2020**, *72*, 296–308. [CrossRef]
2. Aluminium Association of Canada. Une Intensité de GES Figurant par les plus Basses au Monde. 2018. Available online: https://aac.metrio.net/indicators/environnement/emissions/emissions_ges (accessed on 10 December 2021).
3. Charette, A.; Kocaefe, Y.S.; Kocaefe, D. *Le Carbone dans l'Industrie de l'Aluminium*; Les Presses de l'Aluminium: Chicoutimi, QC, Canada, 2012.
4. Amara, B. Effet du Soufre sur la Réactivité des Anodes en Carbone. Ph.D. Thesis, Université du Québec à Chicoutimi, Chicoutimi, QC, Canada, 2017.
5. Hulse, K.L. *Anode Manufacture: Raw Materials, Formulation and Processing Parameters*; R & D Carbon Ltd.: Sierre, Switzerland, 2000.

6. Edwards, L.; Backhouse, N.; Darmstadt, H.; Dion, M.J. Evolution of Anode Grade Coke Quality. In *Light Metals*; Springer: Cham, Switzerland, 2012; pp. 1207–1212.
7. The 2020 State of Canada's Forests Annual Report: An Overview 2020. Available online: https://www.nrcan.gc.ca/2020-state-canadas-forests-annual-report-overview/22925 (accessed on 2 February 2022).
8. Overview of Canada's Forest Industry. Available online: https://www.nrcan.gc.ca/our-natural-resources/forests-forestry/forest-industry-trade/overview-canadas-forest-industry/13311 (accessed on 2 February 2022).
9. Huang, X.; Kocaefe, D.; Kocaefe, Y.; Bhattacharyay, D. Wettability of bio-coke by coal tar pitch for its use in carbon anodes. *Colloids Surf. A Physicochem. Eng. Asp.* **2016**, *490*, 133–144. [CrossRef]
10. Burgess, J.M. Biomass and renewables as alternative energy sources andreductants in the minerals industry. *Fremantle* **2004**, *2004*, 9–13.
11. Huang, X.; Kocaefe, D.; Kocaefe, Y.; Bhattacharyay, D. Interaction of bio-coke with different coal tar pitches. *Fuel* **2016**, *179*, 179–192. [CrossRef]
12. Huang, X.; Kocaefe, D.; Bhattacharyay, D.; Kocaefe, Y.; Morais, B. Characterization of carbon anode materials by image analysis. In *Light Metals*; Springer: Cham, Switzerland, 2016; pp. 859–864.
13. Huang, X.; Kocaefe, D.; Kocaefe, Y. Utilization of Biocoke as a Raw Material for Carbon Anode Production. *Energy Fuels* **2018**, *32*, 8537–8544. [CrossRef]
14. Hussein, A. A Bio-Coke for Anode Production and the Manufacturing Method Thereof. Master's Thesis, Université Laval, Québec City, QC, Canada, 2014.
15. Hussein, A.; Fafard, M.; Ziegler, D.; Alamdari, H. Effects of Charcoal Addition on the Properties of Carbon Anodes. *Metals* **2017**, *7*, 98. [CrossRef]
16. Monsen, B.E.; Ratvik, A.P.; Lossius, L.P. Charcoal in anodes for aluminium production. In *Light Metals*; Springer: Cham, Switzerland, 2010; pp. 929–934.
17. Ozturk, S.; Kocaefe, D.; Bhattacharyay, D.; Kocaefe, Y.; Morais, B. Modification of coke by different additives to improve anode properties. *Fuel* **2018**, *211*, 102–109. [CrossRef]
18. Elkasabi, Y.; Yetunde Omolayo, Y.; Spatari, S. Continuous calcination of biocoke/petcoke blends in a rotary tube furnace. *ACS Sustain. Chem. Eng.* **2021**, *9*, 695–703. [CrossRef]
19. Amara, B.; Kocaefe, D.; Kocaefe, Y.; Bhattacharyay, D.; Côté, J.; Gilbert, A. Effect of Coke Type on the Partial Replacement of Coke with Modified Biocoke in Anodes Used in Primary Aluminum Production. In *Light Metals*; Springer: Cham, Switzerland, 2022; pp. 818–825.
20. *An American National Standard, ASTM D5502-00 (2005)*; Standard Test Methodes for Apparent Density by Physical Measurements of Manufactured Anode and Cathode Carbon Used by the Aluminium Industry. American National Standards Institute: New York, NY, USA, 2010.
21. *An American National Standard, ASTM D6120-97 (2007)*; Standard Test Method for Electrical Resistivity of Anode and Cathode Carbon Material at Room Temperature. American National Standards Institute: New York, NY, USA, 2010.
22. *An American National Standard, ASTM D6559-00 (Reapproved 2005)*; Standard Test Method for Determination of TGA Air Reactivity of Baked Carbon Anodes and Cathode Blocks. American National Standards Institute: New York, NY, USA, 2010.
23. *An American National Standard, ASTM D6558-00 (Reapproved 2005)*; Standard Test Method for Determination of TGA CO_2 Reactivity of Baked Carbon Anodes and Cathode Blocks. American National Standards Institute: New York, NY, USA, 2010.
24. *ISO 12986-1: 2014*; Carbonaceous Materials Used in the Production of Aluminium—Prebaked Anodes and Cathode Blocks—Part 1: Determination of Bending/Shear Strength by the Three-Point Method. International Organization for Standardization: Geneva, Switzerland, 2014.
25. Suriyapraphadilok, U. Characterization of Coal- and Petroleum-Derived Binder Pitches and the Interaction of Pitch/Coke Mixtures in Pre-baked Carbon Anodes. Ph.D. Thesis, Pennsylvania State University, State College, PA, USA, 2008; 354p.
26. Kocaefe, D.; Sarkar, A.; Das, S.; Amrani, S.; Bhattacharyay, D.; Sarkar, D.; Kocaefe, Y.S.; Morais, B.; Gagnon, M. Review of different techniques to study the interactions between coke and pitch in anode manufacturing. In *TMS Light Metals*; Springer: Cham, Switzerland, 2013; pp. 1045–1050.
27. Hume, S.M. *Anode Reactivity: Influence of Raw Material Properties*, 2nd ed.; R & D Carbon Ltd.: Sierre, Switzerland, 1999.
28. Kuang, Z.; Thonstad, J.; Sørlie, M. Effects of additives on the electrolytic consumption of carbon anodes in aluminium electrolysis. *Carbon* **1995**, *33*, 1479–1484. [CrossRef]
29. Sørlie, M. Effect of sulphur on anode reactivity and electrolytic consumption. In *Light Metals*; Springer: Cham, Switzerland, 1994; pp. 659–665.
30. Amara, B.; Faouzi, F.E.; Kocaefe, D.; Kocaefe, Y.; Bhattacharyay, D.; Côté, J.; Gilbert, A. Modification of biocoke destined for the fabrication of anodes used in primary aluminum production. *Fuel* **2021**, *304*, 121352. [CrossRef]