CB05 - Impact of Heating Rate on Biocoke and Carbon Anode Quality

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Abstract

The aluminum industry is actively working towards sustainable production practices and reducing the emission of greenhouse gases (GHG). One source of GHG emissions in the industry is the variation in raw material quality used in carbon anode recipes. Carbon anodes used in aluminum electrolysis are composed of petroleum coke, coal tar pitch, recycled anodes, and butts. In order to reduce GHG, a group of researchers succeeded to replace a part of petroleum coke with biocoke. Biocoke is produced through the pyrolysis of wood chips at temperatures similar to those reached during anode baking, around 1100 ºC. This study focuses on investigating the impact of different heating rates during the pyrolysis of wood on the properties of biocoke and corresponding anodes produced.

First, the chemical characterization of biocokes were carried out using the X-ray photoelectron spectrometry (XPS) to assess the potential differences in surface functional groups depending on the heating rates. In addition, the wettability of biocokes by coal tar pitch was measured using the sessile-drop test to determine the influence of heating rates on biocoke/pitch interactions. Subsequently, laboratory-scale anodes were produced, and some of their properties (baked density, electrical resistivity, air and CO_2 reactivities, and bending strength) were measured and compared with those of standard anodes. The XPS analysis, the wettability test results, and the comparison of the anode properties indicated the most favorable heating rates. The biocoke produced under the best conditions had to be chemically modified to attain the anode properties similar to those of standard anodes. The article describes the details of the work done and the results of the study.

Keywords: Greenhouse gas emissions, Carbon anode, Anode properties, Raw materials, Heating rates, Biocoke, Additives

1. Introduction

Aluminum industry plays a vital role in Canada's economy, particularly in Quebec, which alone produces 90 % of the nation's aluminum production [1]. Ranked as the fifth largest global producer of aluminum, Canada stands out by leading in the production of environmentally-friendly aluminum [2]. This achievement is attributed to the industry's utilization of renewable and sustainable energy sources, primarily hydroelectric power instead of relying on fossil fuels.

The aluminum is produced electrolytically via Hall-Héroult process by the dissociation alumina to separate aluminum. In Canada, approximately 1.5 mt of anodes are produced annually [3]. Through this process, about 0.44 t t C/t Al is consumed, resulting in the emission of approximately 2 t CO_2 equiv./t Al [3, 4]. The aluminum industry remains dedicated to achieving sustainable production and reducing greenhouse gas (GHG) emissions. Anodes must meet certain requirements including high density, low electrical resistivity, low air and CO_2 reactivities as well as favorable mechanical properties [5].

Efforts are underway in the aluminum industry to achieve the above objectives to minimize GHG emissions. Raw materials used in carbon anode recipes are significant contributors to GHG emissions. Anode quality is closely linked to the quality of these raw materials [5, 6]. Carbon anodes used in aluminum electrolysis are composed of petroleum coke, coal tar pitch, recycled anodes, and butts. The quality of the raw materials, particularly petroleum coke and coal tar pitch, has been deteriorating, leading researchers to explore alternative options. Biocoke has emerged as a potential substitute. It is produced through the pyrolysis of wood chips at temperatures similar to those reached during anode baking, around 1100 ºC. Biocoke offers advantages such as lower cost compared to petroleum coke and low sulfur content. Incorporating biocoke into the carbon anode recipe can reduce the impact of anodes on the environment by reducing GHG emissions. Some researchers studied the biocoke pyrolysis, its structure, and properties. They found that it has an anisotropic and lamellar structure similar to the petroleum coke, but did not produce anodes [6, 7, 8]. Others produced biocoke by calcining wood residue together with petroleum coke in a rotary furnace. They concluded that the general properties of the mixture (percent anisotropy, porosity, crystallite thickness (Lc), and trace element concentrations) were suitable for anode production [9]. However, they did not produce any anode containing biocoke and compare its quality with the standard anode. Therefore, it is not possible to conclude the effect of biocoke on the anode quality from the above studies.

Some studies are carried out on the replacement of a part of petroleum coke with biocoke to reduce GHG emissions. Elkasabi et al. [10, 11] produced coke from bio-oil and produced anodes. Only the electrical resistivity of the anodes was measured which was around 100–200 μΩm. This value seems high because the average electrical resistivity of industrial anodes is around 55–60 μΩm. No conclusion can be withdrawn from these studies without measuring other anode properties and comparing them with those of the standard anodes. In majority of the studies on the quality of anodes containing biocoke, a decline was observed in all anode properties due to the low density (high porosity) and poor mechanical properties of biocoke [12, 13]. One study carried out by Huang et al. [14] demonstrated that replacing 3 % of the very fine coke particles by biocoke did not degrade the anode quality.

Inadequate interactions (low wettability) between pitch and biocoke can be the cause of the inferior quality of anodes when a part of the coke is replaced with biocoke. This is due to the low concentration of compatible surface functional groups of coke and pitch on the surface of biocoke. These groups play a crucial role in promoting the bonding and facilitating the interactions between biocoke and pitch, thus they promote good wettability. Good wettability allows pitch to penetrate into the pores of biocoke/coke and fill the gaps present among these particles, resulting in denser anodes. During the pyrolysis of wood, many chemical functional groups are removed as volatile matter, depleting the presence of these groups on the surface of the biocoke. To enhance the interaction between biocoke and pitch, the authors of this article have modified the biocoke. They studied the effect of modification, coke and additive types as well as the biocoke pyrolysis temperature on the quality of anodes [15-18]. This article focuses on the heating rate of biocoke production. Exploring the use of biocoke produced at higher heating rates could potentially reduce the energy and time required for biocoke production while maintaining its viability as a coke replacement.

2. Materials and Methods

2.1 Materials

Anode raw materials (coke, pitch, recycled anodes, and butts) were provided by Aluminerie

Alouette and the wood chips (a mixture of 65 % black spruce and 35 % fir) by Boisaco Inc., two industrial partners of the project. Table 1 and Table 2 show the properties of the petroleum coke and the coal tar pitch, respectively.

Biocoke is produced by the pyrolysis of wood chips as is, which are the product of first transformation, about 2-2.5 inches in size) under nitrogen atmosphere in the carbon laboratory of the UQAC Research Chair on Industrial Materials (CHIMI). The temperature is gradually increased to 1100 °C using a predetermined heating rate (HR). In this study, four different heating rates (HR1 < HR2 < HR3 < HR4) were used. The modification of biocoke was carried out using an additive (Alfa Aesar). This additive is non-toxic, affordable, and does not contaminate the metal. Table 3 shows the heating rates used in the production of each biocoke.

Table 1. Petroleum coke properties.

Property		Value
Real density (g/cm^3)		2.06
Bulk density (g/cm^3)		0.89
Ash (wt%)		0.2
Moisture (wt%)		0.2
Impurities	S (wt%)	3.34
	Si (ppm)	100
	Fe (ppm)	200
	V (ppm)	340
	Ni (ppm)	200
	Ca (ppm)	100
	Na (ppm)	80

Table 2. Coal tar pitch properties.

Property		Value
Density at 20 °C (g/cm^3)		1.32
Softening point °C		119.6
Quinoline-insolubles (wt%)		6.9
Toluene insoluble (wt%)		29.1
Beta resin (wt%)		22.2
Coking value (wt%)		59.1
Impurities	Ca (ppm)	34
	Fe (ppm)	192
	Na (ppm)	111
	Pb (ppm)	144
	S (wt%)	0.47
	Si (ppm)	132
	Zn (ppm)	241
Viscosity at 150 °C (mPa s)		8420
Viscosity at 170 °C (mPa s)		1390
Viscosity at 190 °C (mPa s)		370

Table 3. Biocokes used in the study.

Abbreviation	
BCHR1	Unmodified biocoke produced using the heating rate of HR1
BCHR2	Unmodified biocoke produced using the heating rate of HR2
BCHR3	Unmodified biocoke produced using the heating rate of HR3
BCHR4	Unmodified biocoke produced using the heating rate of HR4
BCMHR2	Modified biocoke produced using the heating rate of HR1

2.2 XPS

X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD) analysis is a quantitative method that allows the determination of the surface composition. This analysis provides valuable information, including the percentages of different atoms and various functional groups. In this study, all the analyzed samples (coke, pitch, modified and unmodified biocokes) were finely ground to powder. This analysis was conducted at the University of Sherbrooke. The sample area was 300 x 700 µm and the sample thickness was 10 nm. The pass energy (EP) used for all the samples was 160 eV, with a 1 eV interval to determine the contamination percentage. High-resolution spectra were obtained using 20 eV pass energy and a step size of 0.05 eV to analyze C1s. The analysis was performed using CasaXPS software (version 2.3.23).

2.3 Wettability Tests

The measurements of contact angles between biocokes produced at four different heating rates and pitch were carried out using the sessile-drop method. A graphite crucible containing pitch was utilized. It was placed on top of a bed consisting of biocoke particles smaller than 45 µm. The pitch crucible and the sample bed were placed in a furnace and heated to 170 °C under a nitrogen atmosphere. After reaching the target temperature, the small opening of the crucible aligned directly above the bed. A slight pressure was applied to the inlet of the pitch crucible using nitrogen gas to push a drop of pitch to fall onto the top of the bed. The contact angle formed between the pitch drop and the biocoke bed was continuously monitored with a camera connected to a computer. The acquired images of the drop were analyzed using the FTA.32 software. This allowed the determination of dynamic contact angle. Each experiment was repeated at least three times.

For each experiment, the contact angles were carefully determined by calculating the average of measurements obtained from two different sides of the drop. To ensure the accuracy and reliability of the results, multiple repetitions of each experiment were conducted. This approach allowed for a comprehensive evaluation of the contact angle, minimizing potential errors and increasing the confidence in the obtained data.

2.4 Laboratory Anode Production

Laboratory-scale anodes were produced without biocoke (standard) as well as with unmodified and modified biocokes. The production conditions for these anodes were similar to those employed in the industry. The process involved preheating the raw materials followed by the mixing of dry aggregates (coke/biocoke, butts, and rejected anodes) and the pitch in specific proportions using an intensive mixer to produce anode paste at 170 °C. This paste was then vibrocompacted to obtain green anodes of 10 kg at this temperature. From each green anode, four cores measuring 50 mm in diameter and 130 mm in height were extracted. These cores were subsequently baked at a temperature of 1100 °C.

In this study, four anodes were produced using one coke and one pitch. The aim was to replace a part of coke with biocoke without deteriorating the anode quality. One of the anodes was the standard anode (no biocoke). Two anodes were made with the unmodified biocoke that was produced using heating rates HR2 and HR4. The last anode was fabricated with the modified biocoke which was produced at the heating rate of HR2. Table 4 shows the composition of each anode. Modified biocoke is designated as MOD and unmodified biocoke is designated as UNMOD in this table.

According to the previous study conducted by the authors, a substitution of 3 % fresh petroleum coke with biocoke was implemented. This specific percentage of biocoke utilization was determined to yield anode properties that were comparable to those of the standard anode [14]. The percentage of additive used for the modification was 3 % of biocoke which was also based on the previous studies [15-18].

Table 4. Anode composition.

Anode	Biocoke (%)	Additive (%)
Std*	0	0
HR2-UNMOD	3	0
HR4-UNMOD	3	0
HR2-MOD	3	3

*Std: Standard anode made only with petroleum coke (no biocoke and no additive).

2.5 Anode Properties

Once the cores were baked, the density (from the weight and the volume of the cores, 4 repetitions), electrical resistivity (four-point method, 4 repetitions), air and CO_2 reactivities (thermogravimetry, 1 sample each) and the flexural strength (three-point method with universal testing machine, 1 sample) of the baked cores were measured according to the following standards: ASTM D5502-00, ASTM D6120-97, ASTMD6559-00a, ASTM-D6558-00a, and ISO 12986-1:2014.

3 Results and Discussion

The wettability tests were carried out to investigate the interactions between unmodified biocokes produced at different heating rates with pitch. Contact angle indicates the level of interaction between a solid and a liquid. A lower contact angle signifies a better interaction between pitch and biocoke while a contact angle above 90° indicates that pitch does not wet biocoke [19]. The results indicated that as time progressed, the contact angles decreased, indicating improved wetting as the pitch spreads on the biocoke bed surface and penetrates into the bed. The complete wetting (zero contact angle) was not reached. The wettability results are shown in Figure 1. The results showed that the biocokes BCHR2 and BCHR4 exhibited lower contact angles, indicating better wetting, compared to biocoke BCHR1 and biocoke BCHR3. The biocoke BCHR2 (lowest contact angle obtained with unmodified biocoke) was wetted by pitch better than the biocoke BCHR4. As it can be seen from this figure, the modification of the biocoke decreased the contact angle further (BCMHR2).

These results can be explained with the XPS results presented in Table 5. These results revealed that the amounts of heteroatom-containing functional groups (total percentage of oxygen- and nitrogen-containing groups: C-O, C=O, COO/COON) found in BCHR2 and BCHR4 (3.9 % and 3.8 %, respectively) were higher than those found in BCHR1 and BCHR3 (2.5 % and 3.5 %, respectively). Heteroatoms (O, N, and S containing groups) play a significant role in enhancing the wettability (forming bonds). The wettability is related to the interaction of functional groups on the pitch surface with those on the surface of biocoke. Increase in functional groups increases the possibility of these interactions. Based on these results, BCHR2 and BCHR4 were used in production of anodes. It can also be seen from Table 5 that the modified biocoke BCMHR2 has the most heteroatoms showing that the modification increased the possibility of bonding between biocoke and pitch. The interaction mechanism between the biocoke and the additive was not studied in detail. The differences are probably due to the contact time between the additive and the biocoke at different temperatures and the reactions taking place at those temperatures.

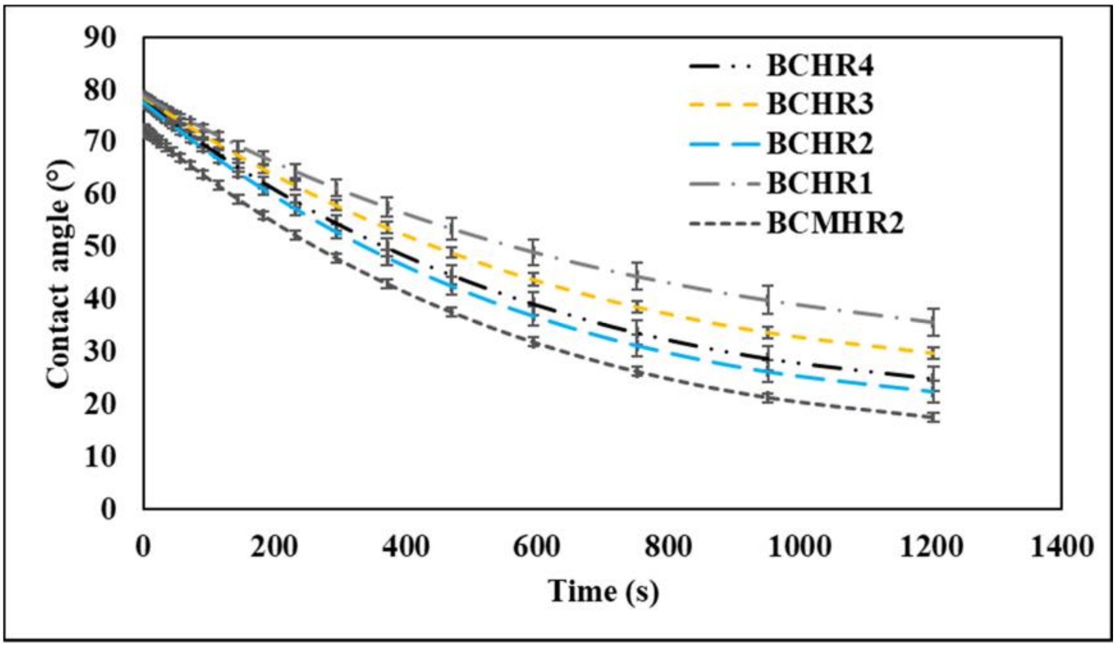

Figure 1. Measured contact angles of biocoke/pitch systems.

Table 5. Percentage of different components of biocokes (unmodified biocoke, modified biocoke), coke, and pitch.

Sample	Carbon C 1s components (%)					
	Aromatic	**Aliphatic**	**Ether alcohol**	**Carbonyl**	**Carboxyl, imide, ester**	**Amine, epoxy**
	C=C	C-C	C-O	C=O	COO/COON	CN
BCHR1	91.1	-	0.7	0.9	0.9	-
BCHR2	89.8	-	1.5	1.2	1.2	-
BCHR3	90.9	-	1.1	1.2	1.2	-
BCHR4	91.0	-	1.0	1.4	1.4	-
BCMHR2	88.3	-	1.7	2.2	2.2	-
Pitch	66.1	25.8	0.9	0.4	0.4	0.5
Coke	91.1	0	1.7	0.7	0.7	-

Simple	Atomic percentage				
		Heteroatoms			
	C (%)	**O (%)**	**S (%)**	**N (%)**	**K (%)**
BCHR1	94.1	4.9	-	-	1.0
BCHR2	93.8	4.9	0.1	-	1.1
BCHR3	94	4.7	0.1	-	1.2
BCHR4	93.3	5.2	-	-	1.3
BCMHR2	91.9	6.3	-	-	1.2
Pitch	94.8	1.3	0,1	2.2	-
Coke	94.8	3.6	0.9	0.7	-

3.1 Density

As shown in Figure 2, the density of baked anodes decreased with the addition of unmodified biocoke compared to that of the standard anodes. The decrease in density of anodes containing biocoke is due to the low density of biocoke [6]. The bulk density of biocoke used during this study was 0.45 g/cm^3 whereas that of the petroleum coke was 0.89 g/cm^3. The results also indicated that the density of the anode made with unmodified biocoke produced using the heating rate HR4 is lower than that of the anode containing unmodified biocoke produced using the heating rate HR2. These results can be explained with the interaction between biocoke and pitch (wettability). The presence of heteroatoms facilitates the biocoke/pitch interactions; thus, improves wetting. Table 5 shows that BCHR2 has more heteroatoms than BCHR4. Thus, the biocoke produced at HR2 was modified with 3 % additive to further enhance the biocoke properties, which again increased the number of heteroatoms attached to the surface of modified biocoke BCMHR2 compared to those of the unmodified biocokes. Thus, biocoke modification improved the density due to better biocoke/pitch interactions, consequently, better wetting. The density of the anode (HR2-MOD) containing modified biocoke was higher than that of the anode containing unmodified biocoke (HR2-UNMOD) produced using the heating rate of HR2.

The increase in the density of anode manufactured with biocoke modified with additive is due to the fixation of additional functional groups (C-O, C=O, and COO/ COON) on the surface of the modified biocoke as presented in XPS results (Table 5). This improves biocoke/pitch interactions, thus wettability. The pitch penetrates better into the biocoke which results in higher anode density.

Improved density means that more carbon is available for the aluminum production. This increases the anode life and the aluminum production.

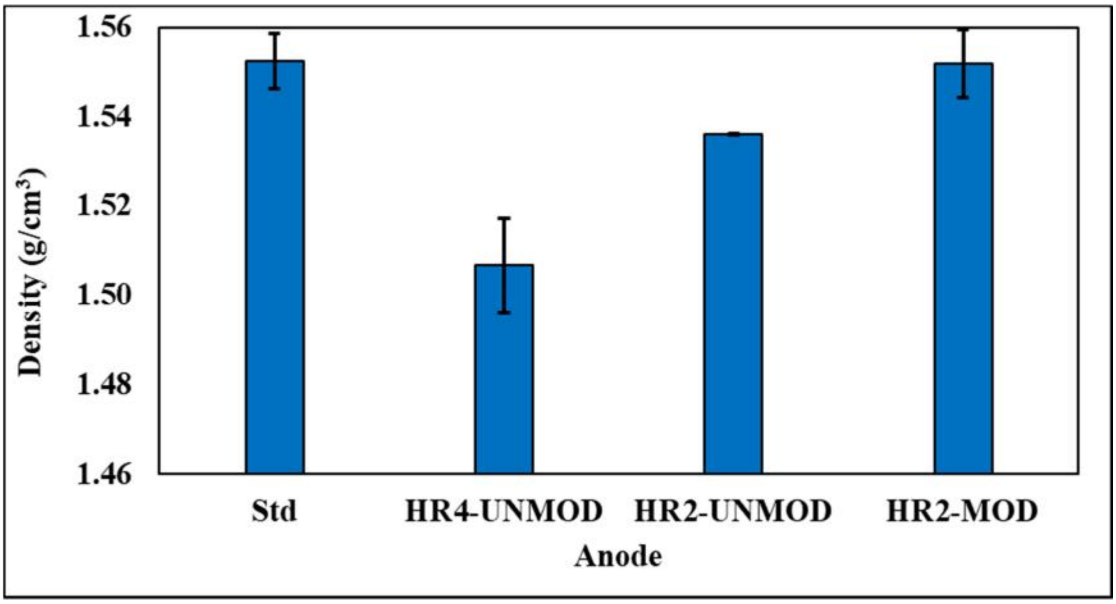

Figure 2. Densities of baked anodes.

3.2 Electrical Resistivity

The results of the electrical resistivity measurements for the baked anodes are given in Figure 3. Replacing 3% of coke with unmodified biocoke increased the electrical resistivity of baked anode (HR4-UNMOD and HR2-UNMOD) compared to that of the standard anode. It is also shown that the electrical resistivity of the anode made with biocoke produced using the heating rate of HR2 is lower than that of anode made with biocoke produced using the heating rate of HR4 (HR4-

UNMOD). These results can be explained with the interactions between biocoke and pitch (wettability).

The utilization of modified biocoke produced at the heating rate of HR2 in the anode production (HR2-MOD) decreased the electrical resistivity compared to that of the anode containing unmodified biocoke (HR2-UNMOD) and became similar to that of the standard anode. This is due to the functional groups grafted onto the surface of biocoke during modification, which increases the wettability of biocoke. This was shown by the XPS test results as mentioned previously.

Increasing density decreases the anode pores and result in lower electrical resistivity. Low electrical resistivity decreases the power requirement during the electrolysis, thus reduces the cost and emissions.

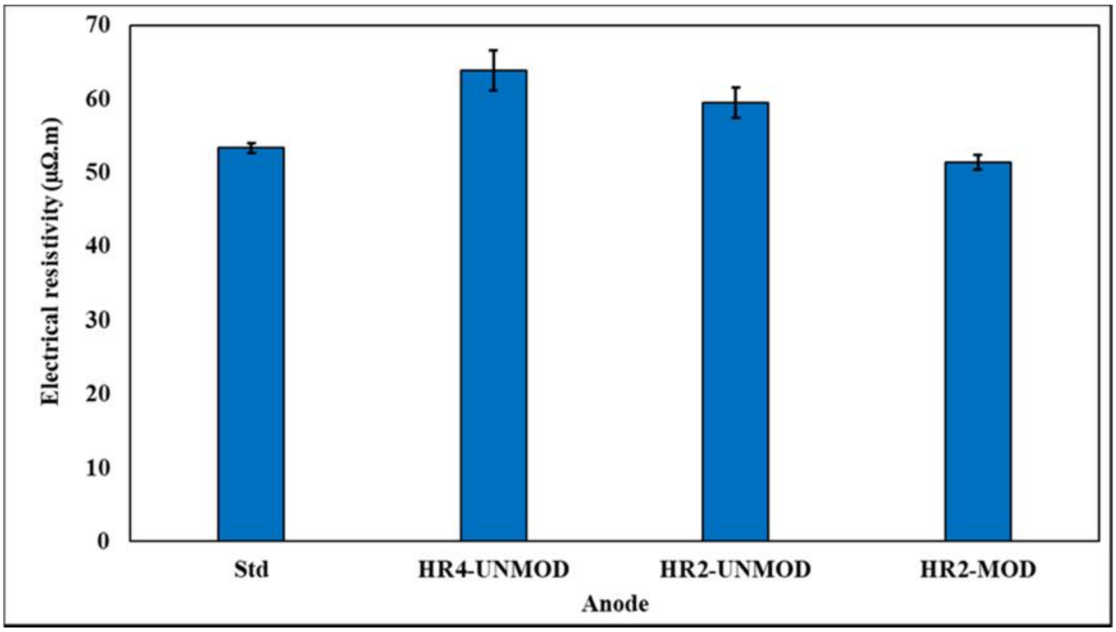

Figure 3. Electrical resistivity of baked anodes.

3.3 Bending strength

The three-point bending tests were carried out to measure the flexural strength of the anodes. Figure 4 presents the results. It can be seen from this figure that the addition of unmodified biocoke (HR4-UNMOD and HR2-UNMOD) decreased the bending strength of resulting anodes. It is also shown that the bending strength of the anodes made with biocoke produced at HR2 is higher compared to those of the anodes containing biocoke produced using the heating rate HR4. The results indicate that the bending strength of the anodes made with modified biocoke (HR2-MOD) is higher than that made with unmodified biocoke (HR2-UNMOD). Furthermore, it is worth noting that the bending strength of the anodes made with modified biocoke (HR2-MOD) is even higher than that of the standard reference anode. This is due to the functional groups added onto the surface of biocoke during modification, which increased the wettability of biocoke. These results can be explained with the wettability and the XPS results as presented in Figure 1 and Table 1. Good bending strength is needed to assure the structural integrity of the anodes during handling.

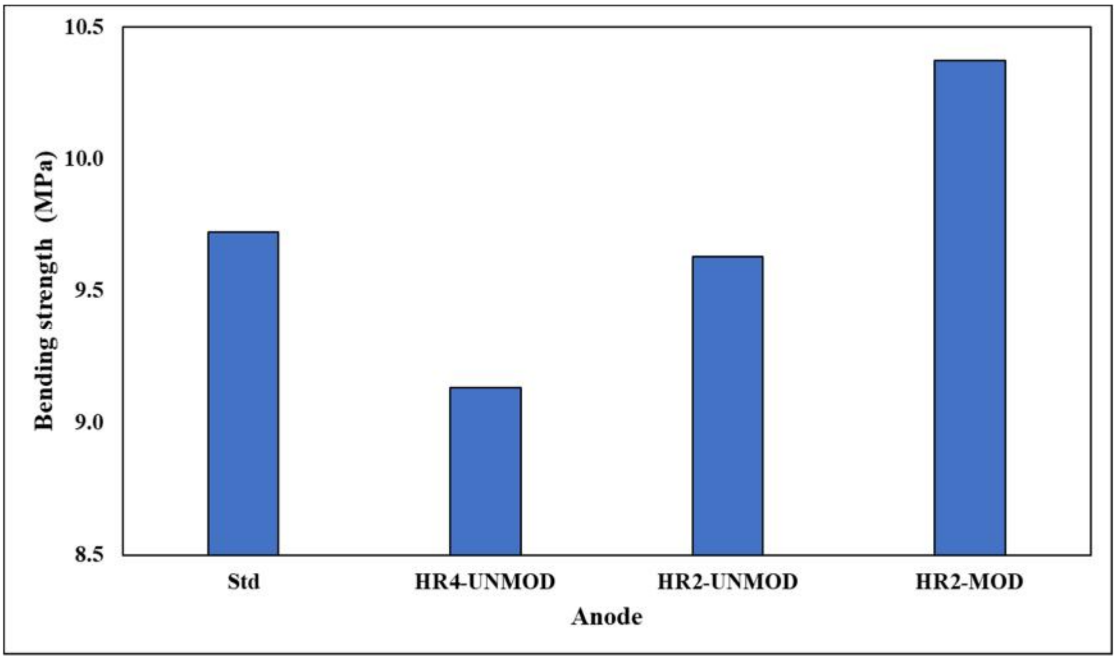

Figure 4. Bending strength of baked anodes.

3.4 Air and CO_2 Reactivities

➢ **Air Reactivity**

During the electrolysis, the air infiltrating from the top of the cell reacts with anode carbon, which results in the overconsumption of carbon [19, 20-22]. The effects of heating rate and the modification of biocoke on air reactivity were investigated. The results of these tests are presented in Figure 4. They show that the higher the density is, the lower the air reactivity is. The air reactivity of the anode made with modified biocoke produced using heating rate of HR2 is the lowest.

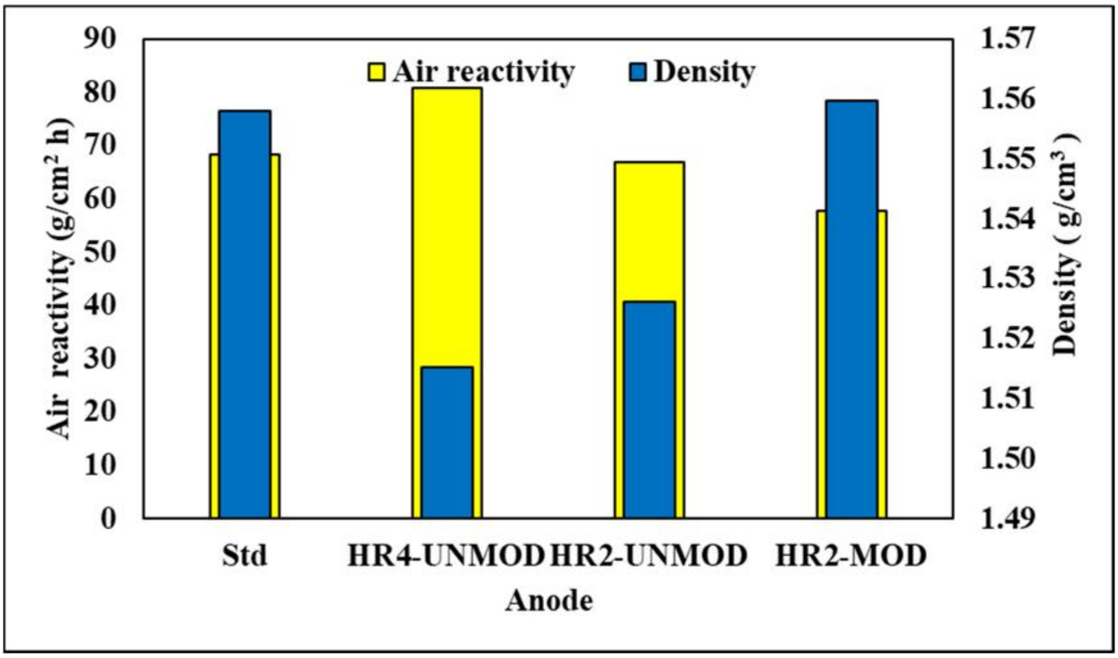

Figure 5. Air reactivity of all the anodes.

- **CO_2 Reactivity**

Carbon dioxide (CO_2) is produced during the electrolysis due to the reaction of oxygen in alumina with anode carbon. Produced carbon dioxide infiltrates into the pores of the anode and reacts with the carbon producing carbon monoxide (CO) [22]. This is called the Boudouard reaction ($CO_2 + C \rightarrow 2CO$). This side reaction leads to the consumption of carbon that could have been used for aluminum production [5, 20-22]. Figure 6 displays the CO_2 reactivities of the anodes. The CO_2 reactivity of anodes made with biocoke produced at heating rates of HR2 and HR4 (HR4-UNMOD and HR2-UNMOD) was higher compared to that of standard anode. However, the modification of biocoke with additive decreased the CO_2 reactivity. This is due to the decrease in porosity with increasing anode density. The CO_2 reactivity is diffusion controlled. The diffusion of the CO_2 into the interior of the anode, hence its contact with anode carbon, decreases as the porosity decreases. A similar trend was observed for standard anodes by Lu at al. [23]. The CO_2 reactivity was higher for all cases compared to that of the standard anode. This might be due to crack formation during anode baking.

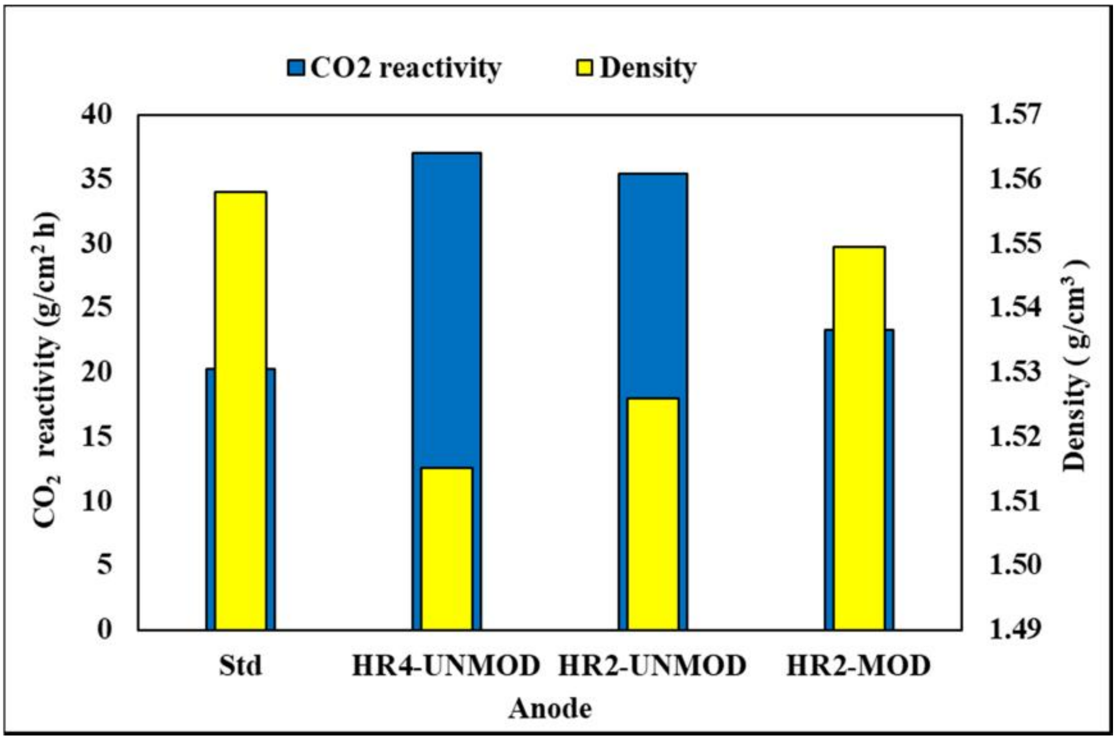

Figure 6. CO_2 reactivity of all the anodes.

4 Conclusions

One of the problems facing the aluminum industry is the degradation of the raw materials that make up the anode and increasing greenhouse gas (GHG) emissions. The use of biocoke is a possible solution to reduce GHG emissions for the aluminum production, but its use alters anode properties. Biocoke production conditions play a major role on anode properties. In this study, the focus is on the heating rate used during the biocoke pyrolysis.

Heating rates HR2 and HR4 resulted in the best biocoke/pitch interactions (increased wettability) as shown by the XPS and wettability results. As discussed in Section 3 (Table 5), these biocokes have a higher percentage of heteroatom-containing (O and N) groups. For anode production, biocokes produced with HR2 and HR4 were used. The results of the anode properties demonstrated that the quality of the anode containing the biocoke produced at heating rate HR2 is better than that the anode produced with the biocoke prepared at heating rate HR4. The modification of biocoke, produced using the heating rate of HR2, with 3 % additive successfully increased anode properties by increasing the surface functional groups of biocoke as shown by XPS results.

Utilization of wood chips to produce biocoke and their subsequent utilization in anode production benefits two major industries of Quebec and Canada, aluminum and wood. It decreases GHG emissions produced during aluminum production, thus decreasing the carbon imprint. It also adds value to the residue of wood industry, hence contributing to circular economy practices.

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