Effect of Wood Type on Biocoke Wettability by Coal Tar Pitch

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Abstract

One of the major challenges for the aluminum industry is the greenhouse gas (GHG) emissions generated both during the manufacture of carbon anodes and during the electrolysis. The aluminum industry is actively pursuing sustainable production practices and reducing greenhouse gas (GHG) emissions. Carbon anodes used in aluminum electrolysis are composed of petroleum coke, coal tar pitch, recycled anodes and butts. In order to reduce GHG emissions, several solutions have been proposed, including the partial replacement of petroleum coke by biocoke in carbon anodes. Biocoke is obtained by pyrolysis of wood chips around 1 100 ºC, similar to the maximum temperature reached during anode baking. Our research group succeeded in replacing part of the petroleum coke with biocoke modified with additives without affecting the anode properties. However, only one source of wood chips was used in the biocoke production.

The objective of this study was to investigate how the choice of wood type for biocoke production and the modification of the produced biocoke influence its wettability by coal tar pitch. In this work, five different wood species were used to produce biocokes which were then modified using an additive. The type of wood species was the only difference among the five unmodified biocoke samples. They were all produced under the similar conditions. The wettabilities of unmodified and modified biocokes by the pitch were measured using the sessile-drop method. The wettability plays a major role in the penetration of pitch into the pores of biocoke particles as well as the biocoke bed, a critical factor in producing high-quality anodes. The best wood species among the ones studied were identified for use in future anode production.

Keywords: Anode, Wood species, Biocoke, Wettability, Additive

1. Introduction

Aluminum is one of the most used metals in various fields such as aeronautics, construction or even in everyday life. It is electrolytically produced from alumina (Al_2O_3) in the presence of a carbon source (anode) using electrical energy [1]. During this process, about 0.44 tonne of carbon is consumed and about 2 tonnes of CO_2 equivalent per tonne of aluminum is produced [2, 3]. Thus, even if the Canada produces the greenest aluminum in the world [3], there is still GHG emissions. Aluminum industry is aiming to further reduce these emissions to achieve more sustainable aluminum production.

Carbon anodes are composed of petroleum coke, butts, rejected anodes (baked and green) used as dry aggregate and coal tar pitch used as binder. Among these, the coke is the raw material, which is used in high quantities compared to the other raw materials [1]. It is important that the pitch penetrates into the pores of the coke particles and empty spaces between the particles. During baking, pitch carbonizes forming pitch-coke which binds the aggregate particles together resulting in good quality anodes. The anode quality has the outmost importance for overcoming many challenges the aluminum industry is facing with respect to issues related to carbon loss, energy use, cell performance, and production cost, especially for high amperage cells.

To reduce the GHG emissions using different raw materials and maintaining the anode quality at the same time is very challenging [7-16]. Utilization of biocoke to partially replace the petroleum coke as an alternative raw material has not been successful, because it results in deterioration of anode quality [7, 8, 11-16]. This decline is due to the highly porous nature of biocoke and its weak interactions with pitch. Researchers have been working on improving the properties of coke and pitch by chemical modification making use of additives and surfactants [5, 6]. The researchers of the Research Chair on Industrial Materials (CHIMI) modified the biocoke and successfully replaced 3 % of the coke with this raw material without affecting the anode quality [7-16]. Biocoke is a carbon material produced from biomass (wood chips, sawmill dust, etc.). It is inexpensive, renewable, and available [18]. The partial replacement of petroleum coke by biocoke, produced from wood residue, has the potential of reducing the production cost and the GHG emissions.

In 2018, a study carried out by the researchers of CHIMI recommended the utilization of small biocoke particles (45 µm) to reduce the effect of biocoke porosity on the anode quality [11]. It was found that the replacement of 3 % of o petroleum coke by the biocoke did not lead to degradation of the anode properties for the given raw materials. In another study, they tested the effect of the biocoke percentage on the anode quality. This time, the size reduction of biocoke particles was not enough to maintain the anode quality. The difference between this study and the previous one was the type of petroleum coke used. As it is well-known, the coke quality changes from one supplier to another as well as the coke blending. To enhance the wettability of biocoke by pitch so that it can be used with different types of cokes, the surface of the biocoke was chemically modified using an additive [12]. It was found that anodes manufactured with 3 % biocoke modified with 3 % additive, in general, had better properties than those manufactured with unmodified biocoke for different types of coke [14]. In order to determine additive to be used for the modification of biocoke, an investigation was carried out using different additives. The results showed that not all selected additives improved the biocoke-pitch interactions [15]. In addition, other studies were carried out to improve the quality of the biocoke used in anode production. The effect of heating rate used during biocoke production [16] and the final pyrolysis temperature [13] on the quality of the anodes were studied.

In all of the above studies, only one type of wood was used to produce biocoke. This article focuses on the utilization of various types of species for the production of biocoke in order to investigate the impact of wood type used on the biocoke-pitch interactions, and effect of its eventual utilization on the anode quality were investigated. For this purpose, the modification of five different biocokes with an additive and the measurement of the wettability of unmodified and modified biocokes by pitch were carried out. Additive chosen as the best additive during the previous study [15] was used. In general, the correlation between the wettability of biocoke/coke by the pitch and the quality of green anode is very good [19]. Thus, the wettability test is a useful tool for preselecting the suitable species for the biocoke production. If the best type of wood is determined to produce biocoke, it might be possible to increase the percentage of petroleum coke replaced in the anode which would decrease the GHG emissions further.

The wettability test is used to assess the level of interactions between coke and pitch. The measure of the wettability is the contact angle, which is the angle formed between the solid (biocoke) and liquid (pitch) phases when a pitch drop is placed on biocoke bed (see Figure 1). It is affected by several parameters such as the porosity of the solid (both particle and bed porosity), the compatibility of surface functional groups present on the biocoke and pitch surfaces. A contact angle greater than 90° indicates that the liquid/solid system is non-wetting. If the contact angle is less than 90°, the liquid (pitch) is considered to wet the surface of the solid (coke/biocoke). The lower the contact angle is, the better the wettability is.

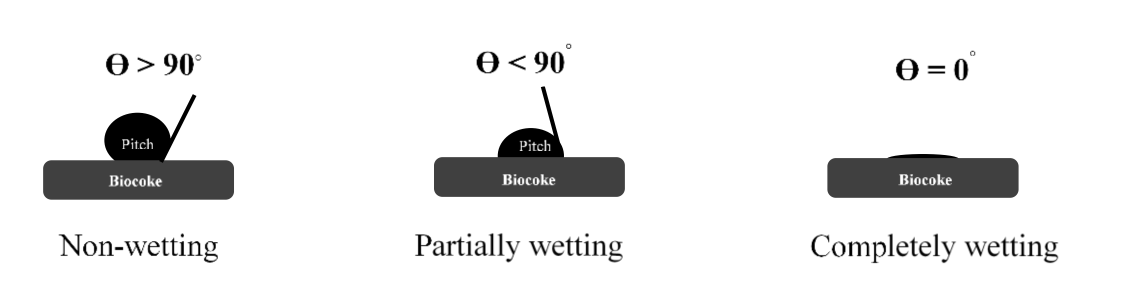

Figure 1. Wettability of a solid (biocoke) by liquid (pitch) determined [18].

2. Materials and Methods

2.1 Materials

The materials used were five different types of wood chips, an industrial petroleum coke, butts, rejected anodes, and an industrial coal tar pitch. The pitch properties are presented in Table 1.

The five different biocokes (BC1, BC2, BC3, BC4, and BC5) were produced from the five different types of wood chips in the carbon laboratory of CHIMI, by pyrolyzing the wood chips under nitrogen atmosphere. The temperature was gradually increased with a predetermined heating rate [16] until 1100 °C is reached [13]. The wood type was the only difference among the samples.

The modification of the biocoke was carried out using an additive, which is a member of the generic class of alkyl-phenyl-aldehydes (Alfa Aesar). It is non-toxic, low cost, and it does not contaminate neither the anode nor the produced aluminum. The percentage of the additive used was set at 3 % based on the previous studies of the authors of this article [15]. The abbreviations of the different types of biocoke used in this study are presented in Table 2.

Table 1 . Coal tar pitch properties.

Property		Value
Density at 20 °C (g/cm^3)		1.32
Softening point (°C)		119.6
Quinoline-insoluble (% m/m)		6.9
Toluene insoluble (% m/m)		29.1
Beta resin (% m/m)		22.2
Coking value (% m/m)		59.1
Impurities	Ca (ppm m/m)	34
	Fe (ppm m/m)	192
	Na (ppm m/m)	111
	Pb (ppm m/m)	144
	S (% m/m)	0.47
	Si (ppm m/m)	132
	Zn (ppm m/m)	241
Viscosity at 150 °C (mPa·s)		8 420
Viscosity at 170 °C (mPa·s)		1 390
Viscosity at 190 °C (mPa·s)		370

Table 2. Biocokes used in the study.

Abbreviation	
BC1	Biocoke 1
BC2	Biocoke 2
BC3	Biocoke 3
BC4	Biocoke 4
BC5	Biocoke 5
MBC1	Modified Biocoke 1
MBC2	Modified Biocoke 2
MBC3	Modified Biocoke 3
MBC4	Modified Biocoke 4
MBC5	Modified Biocoke 5

2.2 Wettability Tests

The sessile-drop method was used for the wettability measurements. During the tests, a drop of pitch was placed on the biocoke bed and the evolution of the contact angle was monitored over time. The biocoke and pitch samples were first ground. The ground pitch is placed in a graphite crucible containing a small hole. The ground biocoke (45 µm in size) is put in another graphite sample crucible placed just below the hole of the pitch crucible. The system is heated to 170 °C under nitrogen atmosphere. This temperature is similar to the mixer temperature where pitch and coke first comes into contact in the carbon plants. At this temperature, the pitch is in liquid form. A drop of pitch is deposited on the bed by applying a slight pressure with nitrogen to the crucible containing the liquid pitch. The images of pitch drops were recorded at predetermined time intervals and analyzed using the dpiMAX software to obtain the dynamic contact angles. Each contact angle was determined as the average of the angle measurements taken on both sides of the drop. Each experiment is repeated several times to ensure the reliability of the results. Figure 2 shows the experimental set-up used for the wettability test.

Figure 2. Sessile-drop system for wettability measurements at UQAC.

3. Results and Discussion

During this study, the wetting experiments were carried out using a coal tar pitch and five unmodified as well as five modified biocokes prepared under the same pyrolysis conditions. Change of contact angle with time was followed during the experiments.

Figures 1 to 7 present the measured average contact angles as a function of time for each test carried out. The final images showing the shape of the pitch drop on the bed of each biocoke (before and after modification) are also illustrated in these figures. Table 3 shows the values of the final contact angles before and after modification of each biocoke.

Based on the results (see Figures 1 to 7), weak interactions (relatively high contact angles) were observed between pitch and all the unmodified biocokes. Similar results were also reported in the literature [9, 10, 12]. These results are explained by the low content of heteroatom containing surface functional groups (COOH, C-N/C-O/C-S, and C-O/CSO_2) on the biocoke surface, which are eliminated during pyrolysis [9]. Heteroatoms (groups containing O, N, and S) play a significant role in the bond formation between biocoke and pitch, thus significantly affect the wettability. The wettability is related to the interactions of the functional groups on the surface of the pitch with those on the surface of the biocoke. If these groups are compatible, they form bonds. Thus, pitch can penetrate better into the biocoke.

The modification of biocoke using an additive increases the functional groups present on the biocoke surface. Thus, the number of compatible groups on biocoke and pitch surfaces increase. Therefore, the possibility of bond formation between the biocoke and pitch augments, which in turn increases the wettability. This was shown in another publication of the authors [15]. Based on the results obtained for the unmodified biocokes, BC1 was wetted the most by the pitch shown by its lowest contact angles among the biocokes in this group. The order of the final contact angles from the lowest (best wetted) to highest (least wetted) is BC1 < BC2 < BC4 < BC3 < BC5 (see Table 3). Pitch does not penetrate into Biocoke 5 (BC5) at all.

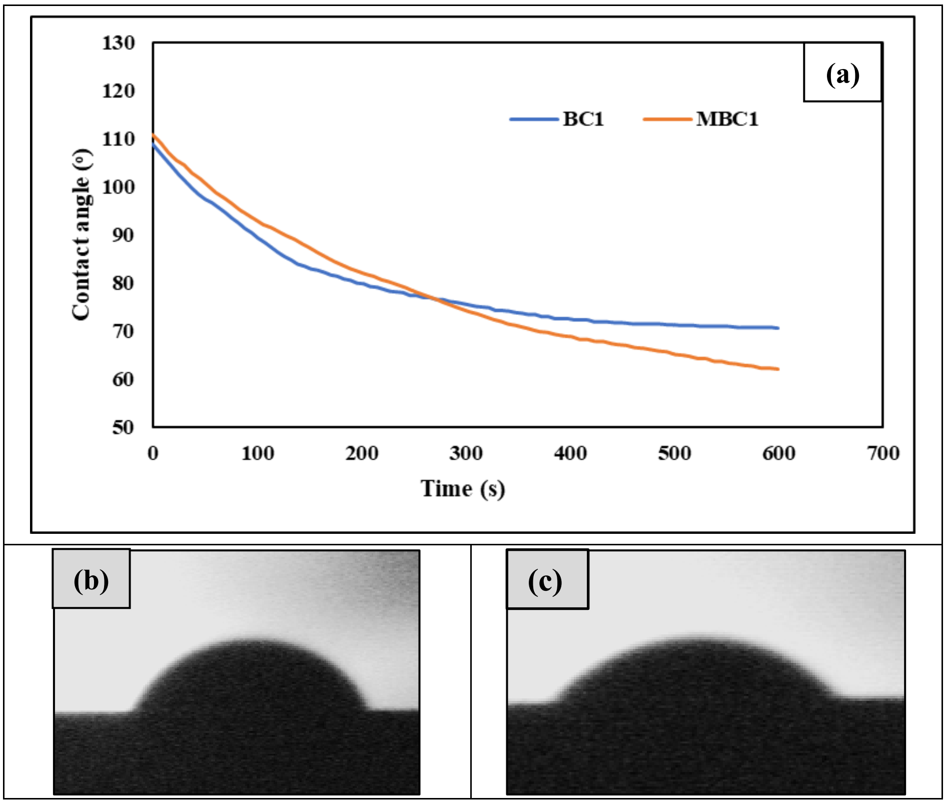

Figure 3. Evolution of contact angles (a) and (b), (c) final contact angles of BC1 and MBC1.

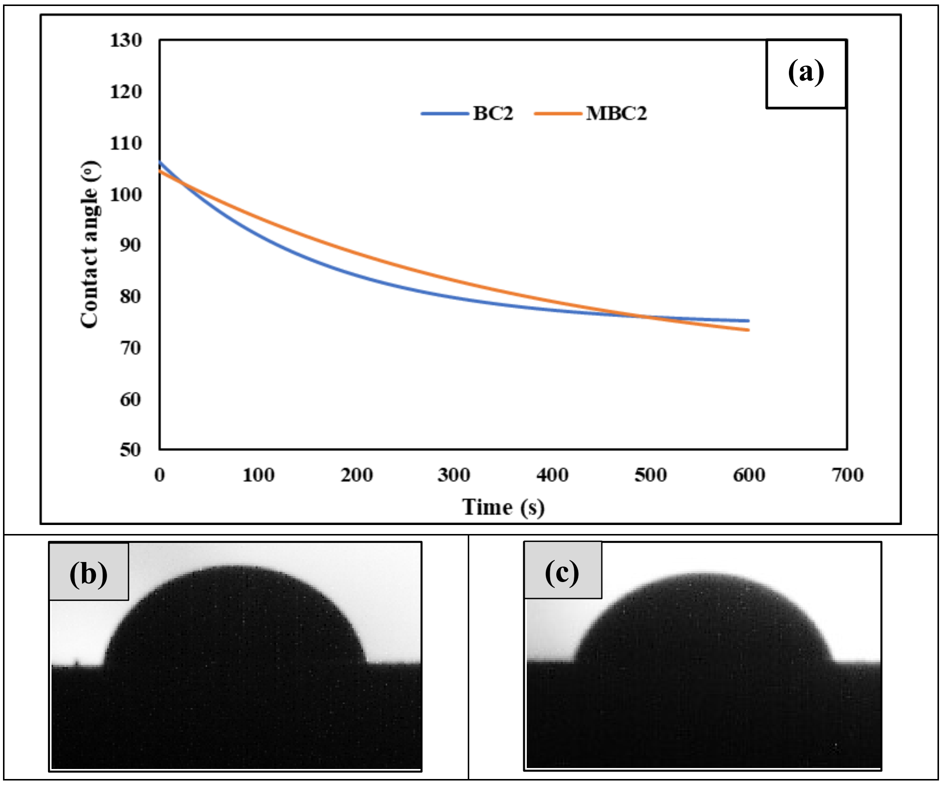

Figure 4. Evolution of contact angles (a) and (b), (c) final contact angles of BC2 and MBC2.

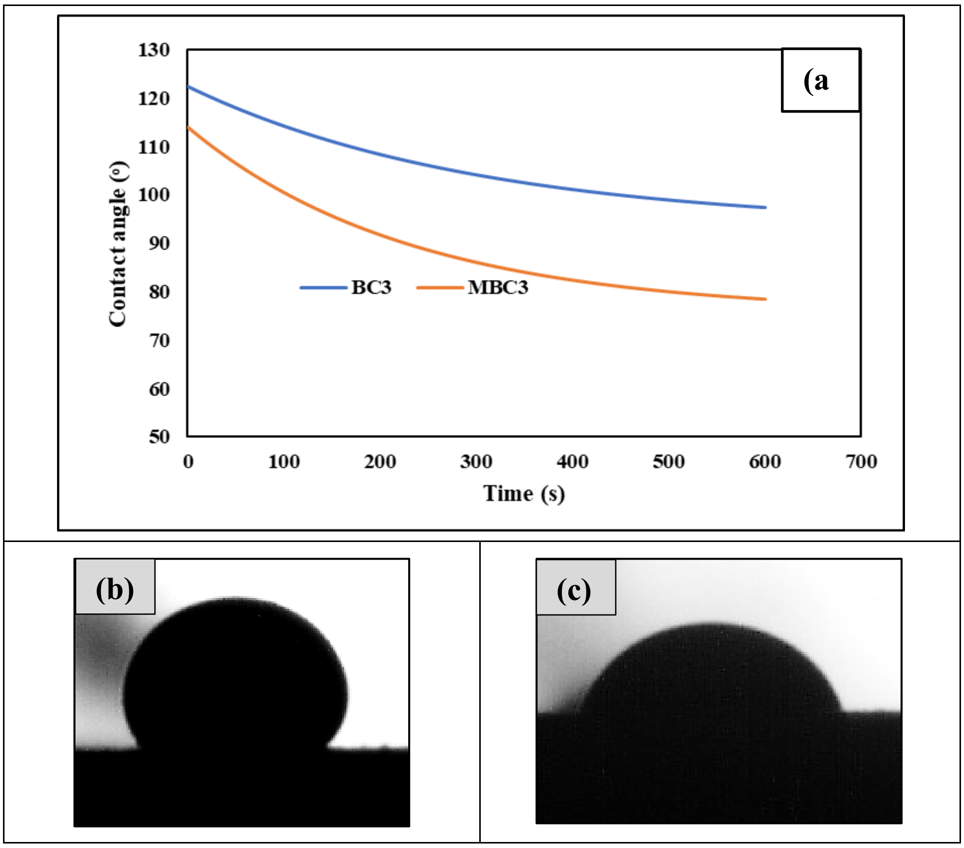

Figure 5. Evolution of contact angles (a) and (b), (c) final contact angles of BC3 and MBC3.

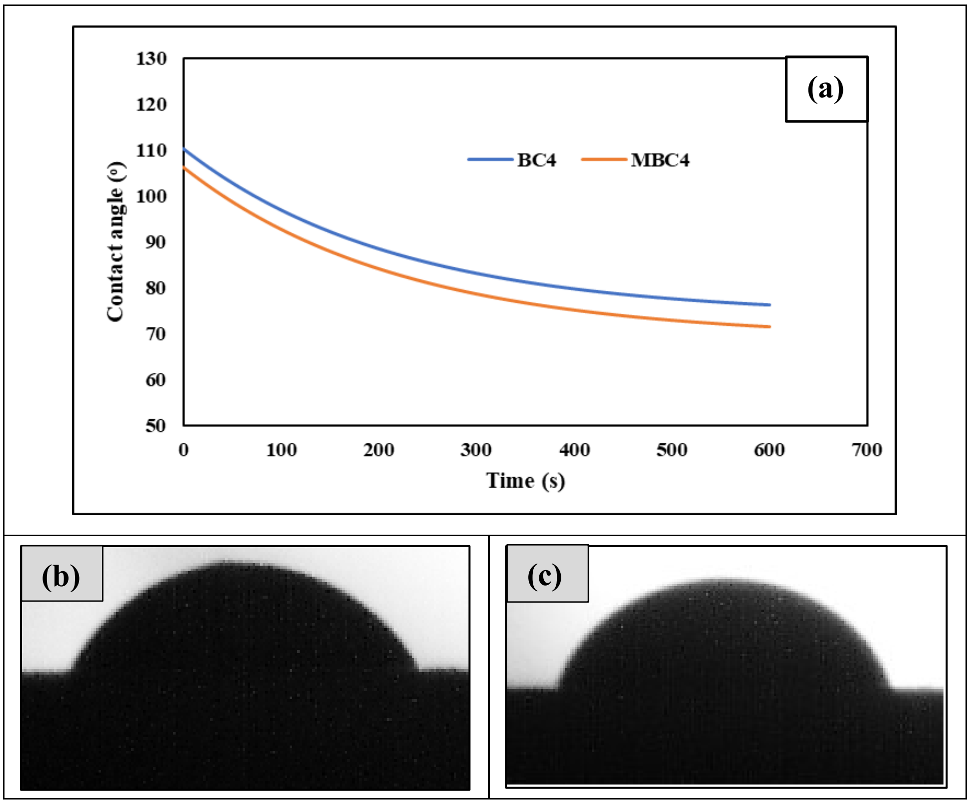

Figure 6. Evolution of contact angles (a) and (b), (c) final contact angles of BC4 and MBC4.

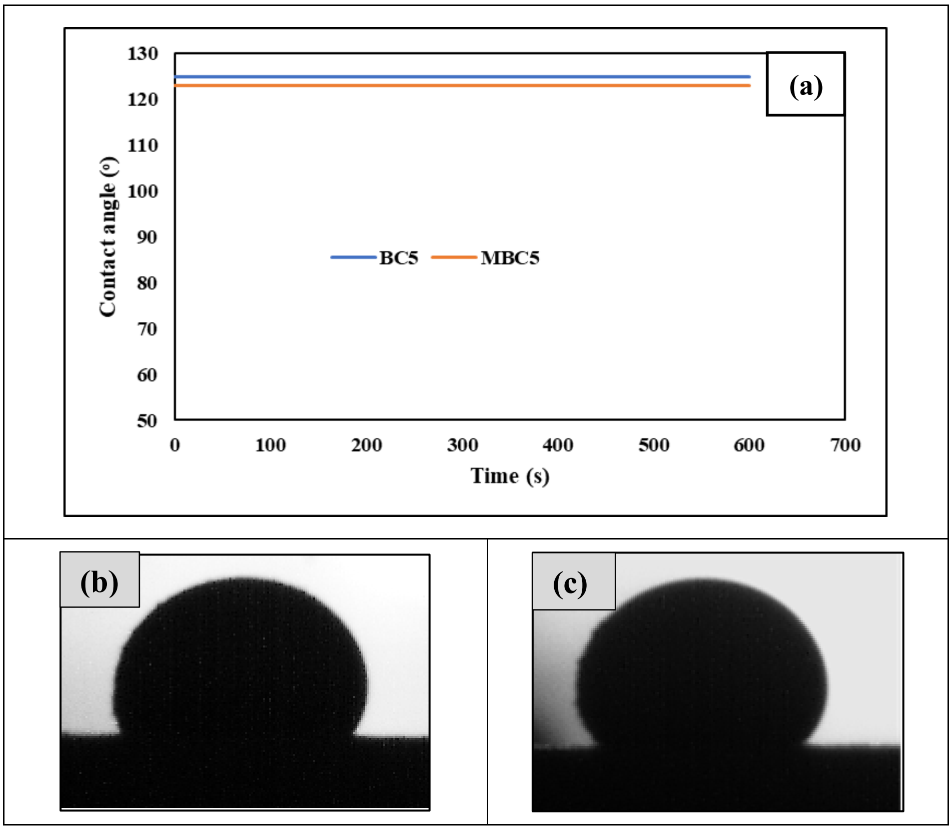

Figure 7. Evolution of contact angles (a) and (b), (c) final contact angles of BC5 and MBC5.

Table 3. Final contact angle of the biocokes before and after modification.

Simple	Before modification		After modification	
	Contact angle (°)		Contact angle (°)	
	Initial	Final	Initial	Final
BC1	109	71	110	61
BC2	106	75	104	73
BC3	122	98	114	78
BC4	110	76	106	71
BC5	125	125	123	123

Modification did not improve the wettability of Biocoke 2 (MBC2) and modified Biocoke 5 (MBC5) (see Figures 4, 7 and Table 3). For Biocoke 1 modified with 3 % additive (MBC1), the final contact angle decreased from 71° to 61°. MBC3 displayed the highest reduction of 20° in the final contact angle compared to that of unmodified biocoke (BC3), decreasing from 98° to 78°. The contact angle of Biocoke 4 modified with 3 % additive (MBC4), decreased slightly (by 5°), from 76° to 71°. This shows that MBC1, MBC3, and MBC4 were wetted better by the pitch compared to their unmodified counterparts: BC1, BC3 and BC4, respectively. The contact angles of MBC2 and MBC5 were not affected by the modification.

The results show that Biocoke 1 exhibited the lowest contact angle both before and after chemical modification, implying better pitch penetration into both unmodified (BC1) and modified Biocoke 1 (MBC1) compared to all the other unmodified and modified biocokes. Accordingly, among the various biocokes obtained from different types of wood chips, the partial replacement of petroleum coke with modified Biocoke 1 (MBC1) is the best choice to be used in anode production among the wood types tested.

4. Conclusions

The efficiency of aluminum production is influenced by several factors, one of which is the quality of carbon anodes. The quality of the anodes is influenced in turn by the raw materials used in their production. In order to reduce GHG emissions coming from the anodes, biocoke was chosen to partially replace some of the petroleum coke because it is low cost, renewable, and available.

Previous studies demonstrated that biocoke interacts poorly with pitch. That is to say, coal tar pitch poorly wets biocoke and consequently does not penetrate into its pores and between the particles. This decreases the anode quality. Modifying biocoke increases the pitch/biocoke interactions (bond formation and hence wettability). Partially replacing petroleum coke with biocoke decreases the GHG emissions since it is a renewable bio-sourced material.

Wettability test is an effective tool to predetermine the suitability of biocoke-pitch pairs. Because, if pitch wets the biocoke, this indicates that there is bond formation between them. Consequently, increasing wettability leads to better quality anodes. Among the five biocokes made with wood chips of different species, the best (lowest) contact angle is that of biocoke BC1. The modification of biocoke has improved the wettability of biocokes MBC1, MBC3, and MBC4 in different extents. Even if the greatest reduction in the contact angle was observed for biocoke MBC3, biocoke MBC1 had the lowest contact angle. The BC5 was the least suitable biocoke to be used in anodes. Thus, the results show that the species type used to produce biocoke plays an important role on the suitability of biocoke for the anode production.

5. Acknowledgements

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6. References

1. André Charette, Yasar Kocaefe and Duygu Kocaefe, Le carbone dans l'industrie de l'aluminium. *Les presses de l'aluminium*, Canada, 2012.
2. Gudrun Saevarsdottir, Halvor Kvande and Barry Welch, Aluminum production in the times of climate change: The global challenge to reduce the carbon footprint and prevent carbon leakage, *JOM*, vol. 5, no. 1 2020, 296–308.
3. Aluminium Association of Canada,] faits saillant environnement, Rapport DD, 2023; Available from: https://developpementdurable.aluminium.ca/indicators/environnement/hl-environnement/ind_highlights_environnement
4. Sheralyn Hume, Markus Meier, *Anode reactivity: influence of raw material properties*, 2nd Edition., Sierre, Suisse, R & D Carbon, xi, 1999, 433 pages.
5. Julie Bureau et al., Modification des propriétés du brai de goudron de houille utilisé dans la fabrication des anodes, *Can. J. Chem. Eng.*, 96 (2) 2018, 545–553.
6. Sena Ozturk et al., Modification of coke by different additives to improve anode properties, *Fue*l 211 2018, 102–109.
7. Asem Hussein, *A bio-coke for anode production and the manufacturing method thereof*, Ph.D. Thesis, Université Laval, Québec, Canada, 2014.
8. Asem Hussein et al., Effects of charcoal addition on the properties of carbon anodes, *Light Metals* 7(3), 2017, 1–9,.
9. Xianai Huang et al., Wettability of bio-coke by coal tar pitch for its use in carbon anodes, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2016, 490: p. 133–144
10. Xianai Huang et al., Interaction of bio-coke with different coal tar pitches, *Fuel*, 2016. 179: p. 179–192.
11. Xianai Huang, Duygu Kocaefe and Yasar Kocaefe, Utilization of Biocoke as a Raw Material for Carbon Anode Production, *Energy and Fuels*, 32(8), 2018, 8537–8544,
12. Belkacem Amara et al., Modification of biocoke destined for the fabrication of anodes used in primary aluminum production, *Fuel*, 304, article 121352, 2021.
13. Belkacem Amara et al., Partial replacement of coke with biocoke: effect of biocoke production temperature on anode quality, *Light Metals*, 2023, 1089–1094.
14. Belkacem Amara et al., Effect of coke type on the partial replacement of coke with modified biocoke in anodes used in primary aluminum production, *Light Metals*, 2022, 818–825
15. Belkacem Amara et al., Partial replacement of petroleum coke with modified biocoke during production of anodes used in aluminum industry: Effect of additive type, *Applied Sciences*, 12 (7), article 3426, 2022.
16. Belkacem Amara, Duygu Kocaefe and Yasar Kocaefe, Impact of Heating Rate on Biocoke and Carbon Anode Quality, *Proceedings of the 41st International ICSOBA Conference*, Dubai, 5 - 9 November 2023, 1035–1046.
17. Yaseen Elkasabi, Yetunde Omolayo and Sabrina Spatari, Continuous calcination of biocoke/petcoke blends in a rotary tube furnace. *ACS Sustainable Chem. Eng*., 9, 2021, 695–703.
18. Belkacem Amara, *Utilisation du biocharbon dans la production des anodes en carbone*, Ph.D. Thesis, Université du Québec à Chicoutimi, Quebec, Canada, 2022.

19. Duygu Kocaefe et al., Effect of pitch modification on anode properties: Effect of additive type, *ACS Omega*, 8, 2023, 25467-25477.