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 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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