Bio-pitch Improvement for Coal Tar Pitch Replacement in Pre-baked Anodes

Marie Aimee Tuyizere Flora[1], Guillaume Gauvin[2], Simon Laliberté-Riverin[3], Thierry Ollevier[4], Julien Lauzon-Gauthier[5] and Houshang Alamdari[6]

1. Ph. D. Student
2. Research Professional
3. Postdoctoral Fellow
6. Professor

Department of Mining, Metallurgical and Materials Engineering, Laval University, Québec, Canada

Aluminium Research Center – REGAL, Québec, Canada,

4. Full Professor

Department of Chemistry, Laval University, Québec, Canada

5. Research Engineer

Alcoa Corporation, Continuous Improvement Smelting Technology, Québec, Canada,

Corresponding author: marie-aimee.tuyizere-flora.1@ulaval.ca

Abstract

The bio-pitch (BP) derived from biomass pyrolysis oil has the potential to replace coal tar pitch (CTP) as a binder in pre-baked anodes for aluminium smelting. Replacing CTP by BP would have the advantages of reducing the emissions of carbon dioxide and carcinogenic polycyclic aromatic hydrocarbons during anode baking. However, the oxygenated functional groups in BP induce high mass loss during its carbonization into bio-coke, causing a reduction of BP coking value (CV) to less than 45 wt.% and high anode porosity. It is suggested in this study to introduce additives to bio-oil before processing it into BP to increase the CV of BP. Bio-oil blends from 0 wt.% to 30 wt.% of fine particles of calcined petroleum coke (fine CPC) were heat treated to form hybrid bio-binders (HBBs). The heat treatment was done in air up to 180 °C with a 0.5 °C/min heating rate, and 1 h soaking time. The mass loss, CV, softening point, and viscosity of bio-binder samples (BP and HBBs) were quantified and compared with CTP. It was found that the mass loss of HBBs decreases during carbonization when fine CPC is added. As a result, the CV of HBB increases with fine CPC addition. A CV higher than 45 wt.%, nearly that of CTP (50-65) wt.%, was obtained for HBB with (18-30) wt.% of fine CPC. The softening point of bio-binders is lower than that of CTP (110 °C), and their viscosity is lower than that of CTP between (145−178) °C. In addition, the introduction of fine CPC between (5 -18) wt.% causes an unexpected decrease in softening point and viscosity in comparison to BP. This phenomenon may be due to the activation of fine CPC during bio-oil blend heat treatment. Further experiments on HBB are planned to understand HBB characteristics compared to CTP.

Keywords: Heat treatment, Bio-pitch, Petroleum coke, Hybrid bio-binders.

1. Introduction

The carbon anode plays the role of an electrical conductor during aluminium smelting. Between 400 kg and 450 kg of carbon is consumed to produce 1 t of aluminium, resulting in the emission of 1.5 t of CO_2, considering the electricity used for smelting comes from hydropower [1, 2]. The carbon anodes are made with fossil fuels, so increased aluminium demand leads to increased greenhouse gas emissions [3, 4]. In response to incentives to lower their carbon footprint, aluminium smelters have been welcoming new green technologies for low emissions in their production processes [5]. The aluminium industry roadmap is to reduce emissions by (30–35) % by 2030 towards a net zero emissions target by 2050 [4, 5]. In order to reach those goals, innovative research in the aluminium industry is extended to developing a suitable, ecological, and sustainable anode [3, 4].

The conventional binder in anode formulation, coal tar pitch (CTP), releases polycyclic aromatic hydrocarbons (PAHs) during anode baking [6-8]. These substances are considered to be carcinogenic to the human being and harmful to the environment [1, 7-9]. In addition, the consumption of carbon anodes during aluminium smelting emits CO_2. For those reasons, the research on anode binders produced from sustainable sources [10-12], i.e., bio-pitch, has been gaining interest [6, 13].

The bio-pitch (BP) is extracted from biomass pyrolysis oil (bio-oil), which is typically derived from lignocellulosic biomass through fast pyrolysis at (500-550) °C in the absence of air [14-18]. A complex mixture of bio-oil yields up to 70 wt.% of the net amount of feedstock [16, 17, 19]. It is an acidic dark-brown viscous liquid with a smoky odor [18, 19]. Biochar and non-condensable volatiles are also produced during biomass fast pyrolysis. Bio-oil contains more than 400 oxygenated hydrocarbons such as phenolics, ketones, aldehydes, organic acids, alcohols, sugars, hydrocarbons, and other compounds [14, 17, 19-21].

BP exhibited encouraging characteristics comparable to those of CTP such as low softening point, relatively low viscosity at mixing temperature, good wettability with calcined petroleum coke [22-24], and low emissions of PAHs when BP is baked [6]. However, the oxygenated functional groups in bio-pitch molecular structure cause a mass loss of 67 wt.% on average, when BP is carbonized into bio-coke [6, 13]. The typical oxygen content in BP is (20-30) wt.% [6, 23]. This reduces the coking value (CV) of the bio-pitch to less than 45 wt.% [13, 22, 23], which is problematic for having a quality anode that could exhibit low porosity and lower reactivity with air and CO_2 [15]. A quality binder is expected to have a CV at least greater than 45 wt.% [9]. The typical range of CV for CTP is between (55-60) wt.% [2, 23]. The CV of CTP is dependent on its aromaticity, and it is also an indicator of the amount of PAHs it contains [9]. This means that the higher the percentage of PAHs, the higher the CV [9]. BP contains little PAHs, however, it typically contains appreciable amounts of oxygen and exhibits low CV. New strategies are therefore needed to increase its CV to render it as a suitable binder for anode manufacturing.

It has been shown that the modification of bio-pitch by introducing fine particles of calcined petroleum coke (fine CPC) in bio-oil during its heat treatment could potentially address the issue encountered with bio-pitch of low CV [23, 25]. As CPC has practically no volatiles, its addition to the bio-oil may reduce the oxygen content and the mass loss of the mixture and increase the CV of the corrected bio-pitch. Hussein [23] developed a BP through pyrolysis that exhibited a CV lower than 45 wt.%, low softening point (lower than 100 °C), and relatively low viscosity. Lu [25] added biochar in bio-oil from 0 wt.% up to 9 wt.% to produce a modified BP through vacuum distillation. The bio-pitch CV of 29.2 wt.% was increased by 27.4 % when a higher fraction of biochar was added. The softening point increased but remained lower than 100 °C, and the viscosity increased with a decrease in wettability of the calcined coke with a modified BP [25]. The aim of this work is to produce an anode binder with a CV higher than 45 wt.% and to find the maximum amount of fine CPC which can be added to the bio-pitch without degrading its other properties, i.e., rheological properties. To achieve that, fine CPC was introduced in bio-oil in different amounts of (0-30) wt.%. The mass losses after heat treatment and carbonization were quantified. The measurements of the coking value, the softening point, and viscosity were also carried out by applying standard methods.

and starts to increase again with the continuous addition of fine CPC up to 30 wt.%. The HBBs show a Newtonian behavior for shear rates above 10 s^{-1}, and the viscosity is generally constant with a shear rate increase.

From these observations, we demonstrated that the SP and viscosity follow the same trend while increasing the fine CPC content of the HBB. The BP could be improved into HBB as it exhibits increased CV. Surprisingly, the mass loss of bio-pitch in the presence of fine CPC particles is slightly higher than that of pure bio-pitch. It is hypothesized that the fine CPC may be activated by bio-oil compounds during heat treatment. Thus, active sites may be created on the fine CPC surface and enable its reactivity with bio-oil during heat treatment. Further characterization of HBB samples is required to confirm the existence of the activation phenomenon of fine CPC and to enhance our understanding of the interactions between fine CPC and BP.

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7 References

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