A Study of Volatiles Emitted During Bio-Oil Upgrading to Bio-Pitch

Simon Laliberté-Riverin[1], Marie Aimée Tuyizere Flora[2] and Houshang Alamdari[3]
1. Postdoctoral Fellow
2. Ph. D. Student
3. Professor
Aluminium Research Center, REGAL, Department of Mining, Metallurgical and Materials Engineering, Laval University, Quebec, Canada
Corresponding author: simon.laliberte-riverin@gmn.ulaval.ca
https://doi.org/10.71659/icsoba2025-el004

Abstract

Replacing coal-tar pitch in carbon anodes with a binder derived from biomass is an active research topic. The development of such a binder, known as bio-pitch, could help the aluminium industry in reducing its carbon footprint. However, this technology has not yet been demonstrated on an industrial scale. Bio-pitch is produced through the upgrading of wood pyrolysis oil (bio-oil), either by heat treatment or distillation. More knowledge about the mechanisms of bio-oil upgrading is required to produce binders that meet industrial requirements. In this work, we analyzed the volatiles evolved during the heat-treatment of bio-oil up to 250 °C. The temperature, mass loss, and composition of the volatiles were monitored simultaneously using a thermogravimetric analysis setup coupled with a quadrupole mass spectrometer. Time series data was collected on ion abundance for mass-to-charge ratios of 1–150. The data was deconvoluted using principal component analysis, to reconstruct the mass spectra of desorbed species and link them with their emission profiles. It was found that a group of water-rich compounds, containing acids and oxygenates, starts vaporizing around 100 °C, and that another group of compounds containing heavier molecules can be detected after reaching 150 °C. This information could be used to fine-tune bio-oil heat-treatment processes.

Keywords: Carbon anodes, Bio-pitch, Mass spectrometry, Thermogravimetric analysis, Principal component analysis.

1. Introduction

The term “bio-pitch” designates a solid, thermoplastic material, originating from the pyrolysis of biomass. It is usually obtained after upgrading of the pyrolytic oil, or “bio-oil”, which is, along with biochar and biogas, a coproduct of biomass pyrolysis [1]. There has been interest in recent years into considering bio-pitch as a potential substitute for coal-tar pitch in pre-baked anodes [2]. Such a substitution could potentially reduce the fossil CO_2 emissions associated with coal-tar pitch production, anode baking and carbon consumption in electrolysis cells [3]. However, this technology is not currently ready for industrial production.

Reports about lab-scale anodes made with bio-pitch state a baked apparent density similar [4] or slightly inferior [5] to that of coal-tar pitch-based anodes, similar electrical resistivity [4], and slightly higher air and CO_2 reactivities [4]. Bio-pitch contains oxygenated compounds which make its chemical composition much different from that of coal-tar pitch, the latter containing mainly heterocyclic and polycyclic aromatic hydrocarbons [6]. The presence of oxygenated compounds in bio-binders hinders mesophase formation, causing the baked microstructure to be isotropic with a low L_c [4, 7]. In addition, the oxygenated compounds are volatilized during baking, leaving behind a low fixed carbon content or low coking value product [4].

Anode paste needs to be mixed and formed at a temperature higher than the softening point of the binder, but the binder needs to solidify at room temperature to facilitate handling of the anodes. Upgrading of bio-oil to bio-pitch is done to remove water and relatively light compounds and give the binder the desired thermoplastic properties. Upgrading can be done by heat treatment [4, 7], vacuum distillation [8], or flash distillation [9]. The upgrading conditions, mainly time and temperature, control the softening point, the coking value and the viscosity of the binder as well as its wettability to calcined petroleum coke. However, these properties are interrelated and difficult to tune independently [8].

The optimal temperatures reported for bio-oil upgrading are close to 180 °C. Ideally, a higher heat-treatment temperature would be needed to increase the coking value, but a higher temperature causes cross-linking of oxygenated functional groups, and a corresponding increase of viscosity and loss of thermoplastic properties and wettability to coke [10]. A more detailed understanding of heat-treatment kinetics could help to fine-tune the heat-treatment conditions and ultimately obtain better quality binders.

In this work, a bio-oil sample is put in a reactor and subjected to simulated heat-treatment conditions. The mass loss is monitored continuously with an analytical balance, while the evolved volatiles are analyzed with an online quadrupole mass spectrometer. Deconvolution of the time evolution of mass spectrometry data with principal component analysis reveals insights on the volatile evolution kinetics.

2. Materials and Methods

2.1 Bio-Oil

The bio-oil used in this work was produced by vacuum pyrolysis [11] of spruce wood chips (Pyrovac, Saint-Lambert-de-Lauzon, Québec, Canada). The bio-oil has a water content of 18 wt.% and an oxygen level of 30.5 wt.% (dry basis) [12].

2.2 Test Setup and Test Conditions

The reactor, Figure 1, comprises a vertical steel cylinder inside a vertical tube furnace (3210 Series, Applied Test Systems, Butler, PA, USA). The top of the cylinder is closed by a blind flange which contains two type K thermocouples and an open hole. On top of the setup, there is a box in which the volatiles coming out of the hole in the top flange are extracted. A balance with a precision of ±0.01 g (Model ML802T, Mettler-Toledo, Greifensee, Switzerland) is placed on top of the box. The sample (8 g) is put in a glass test tube in a wire mesh basket suspended on a hook under the balance via a steel rod that passes through the hole in the top flange of the cylinder. The weight is recorded continuously on a computer through a USB connection.

A connection on the side of the vertical steel cylinder is used as a continuous sampling point. The sample is brought to the spectrometer via a capillary transfer line, heated to 300 °C to prevent volatile condensation throughout the process. The sample is analyzed at 30 s intervals for mass-to-charge ratios (m/z) between 1 and 150 with a quadrupole mass spectrometer (Calypso DS, In Process Instruments, Bremen, Germany). The spectrometer is equipped with an electron impact ion source, a Faraday cup and an electron multiplier. Air or argon is injected through a connection at the bottom of the cylinder and is controlled to 5 L/min with a mass flow controller (SLA5850S, Brooks Instruments, PA, USA). It should be mentioned that the upgrading of bio-oil to bio-pitch is normally done in air. The tests in Ar were done to determine if there was any reaction between air and bio-oil.

could potentially achieve this by fine-tuning the heat-treatment conditions, for example by modulating the heating rate or adding isothermal steps. The results also did not show a significant effect of the amount of oxygen in the atmosphere on the kinetics of heat-treatment, hinting that conducting the heat-treatment in air is a sound approach. Nevertheless, the results shown in this work are qualitative. It was not possible to determine the mass lost with each of the groups of compounds. More detailed studies would be required to further improve the heat-treatment conditions.

5. Conclusions

In the present work, we used a coupled thermogravimetric–mass spectrometric setup to study the volatiles emitted during the heat-treatment of bio-oil to bio-pitch. It was shown that two groups of compounds are volatilized at different temperatures during the heat-treatment of bio-oil to bio-pitch. The first group is rich in water, acids and other oxygenated compounds with molar mass < 75 g/mol and boiling points of 100 °C to 150 °C (PC2). It starts evaporating around 100 °C, and evaporation peaks around 200 °C. The second group (PC1) contains heavier oxygenated compounds (> 75 g/mol) with boiling points higher than 160 °C. Vaporization of those compounds starts around 150 °C, and most likely peaks slightly higher than the maximum test temperature.

The presence of oxygen in bio-binders has undesirable effects, such as limiting the achievable coking value of the binder. Since the compounds in PC2 have higher oxygen content than those in PC1, a possible strategy to improve the quality of binders would be to design new heat-treatments to maximize the removal of oxygen in PC2, while keeping as much carbon as possible in the binder, by minimizing volatilization of PC1. The methodology proposed in this paper can help these further developments by monitoring the vaporized species in a high level of detail.

6. Acknowledgements

This project was funded by Alcoa and the Natural Sciences and Engineering Research Council of Canada, NSERC (Alliance-Avantage-2020-557053). Part of the research presented in this work was financed by the Fonds de recherche du Québec – Nature et technologies, through the Aluminium Research Centre – REGAL (FRQNT-2024-RSMA-340932). S. Laliberté-Riverin thanks the Fonds de recherche du Québec for the postdoctoral fellowship (FRQNT-B3-357820, https://doi.org/10.69777/357820). The mass spectrometer used in this work was provided by InProcess Instruments and Isomass Scientific Inc. The bio-oil was provided by Pyrovac inc.

7. References

1. Anthony V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass and Bioenergy, Vol. 38, 2012, 68–94. https://doi.org/10.1016/j.biombioe.2011.01.048
2. Samuel Senanu and Asbjørn Solheim, Biocarbon in the Aluminium Industry: A Review, Light Metals 2021, 649–656. https://doi.org/10.1007/978-3-030-65396-5_87
3. Bernard Osei, Simon Laliberté-Riverin, and Houshang Alamdari, A Cradle-to-Gate Life Cycle Assessment of Pre-baked Carbon Anode Production; A Case Study in Quebec, Proceedings of the 42nd International ICSOBA Conference, Lyon, Oct. 2024, TRAVAUX 53, 807–829.
4. Asem Hussein, Donald Picard, and Houshang Alamdari, Biopitch as a Binder for Carbon Anodes: Impact on Carbon Anode Properties, ACS Sustainable Chemistry & Engineering, Vol. 9, No. 12, (2021), 4681–4687. https://doi.org/10.1021/acssuschemeng.1c00618

5. Nooshin Baastani et al., Effect of Mixing and Pressing Parameters on the Properties of Biopitch-Based Lab-Scale Carbon Anodes for Use in the Hall-Héroult Electrolytic Cell, Light Metals 2024, 804–814. https://doi.org/10.1007/978-3-031-50308-5_101
6. André Charette et al., Experimental and kinetic study of volatile evolution from impregnated electrodes, Fuel, Vol. 69, No. 2, (1990), 194–202. https://doi.org/10.1016/0016-2361(90)90173-N
7. Gøril Jahrsengene et al., Bio-Binders and Their Carbonization and Interaction with Petroleum Coke During Baking, Light Metals 2022, 883–889. https://doi.org/10.1007/978-3-030-92529-1_116
8. Ying Lu et al., Synthesis and Characterization of Bio-pitch from Bio-oil, ACS Sustainable Chemistry & Engineering, Vol. 8, No. 31, (2020), 11772–11782. https://doi.org/10.1021/acssuschemeng.0c03903
9. Yaseen Elkasabi et al., Flash Distillation of Bio-Oils for Simultaneous Production of Hydrocarbons and Green Coke, Industrial & Engineering Chemistry Research, Vol. 58, No. 5, (2019), 1794–1802. https://doi.org/10.1021/acs.iecr.8b04556
10. Ying Lu et al., Properties of Bio-pitch and Its Wettability on Coke, ACS Sustainable Chemistry & Engineering, Vol. 8, No. 40, (2020), 15366–15374. https://doi.org/10.1021/acssuschemeng.0c06048
11. Christian Roy, D. Morin, and F. Dubé, The biomass Pyrocycling process, Proceedings of the International Conference on Gasification and Pyrolysis of Biomass, Stuttgart, 1997, 9–11.
12. Marie Aimee Tuyizere Flora et al., Bio-pitch improvement for coal-tar pitch replacement in pre-baked anodes, Proceedings of the 41st International ICSOBA Conference, Dubaï, Oct. 2023, TRAVAUX 52, 1047–1059.
13. The SciPy Community, SciPy documentation. Accessed: Apr. 28, 2025. [Online]. Available: https://docs.scipy.org/doc/scipy/index.html
14. James M. Thompson, Mass Spectrometry. Pan Stanford Publishing Pte. Ltd., 2018. https://doi.org/10.1201/9781351207157
15. Scikit-learn, User Guide, https://scikit-learn.org/stable/user_guide.html (Accessed on 29 April 2025).
16. Tobias M. Richter et al., Evaluation of PTR-ToF-MS as a tool to track the behavior of hop-derived compounds during the fermentation of beer, Food Research International, Vol. 111, (2018), 582–589. https://doi.org/10.1016/j.foodres.2018.05.056
17. NIST, NIST Chemistry Webbook, SRD69, https://doi.org/10.18434/T4D303. (Accessed on 29 April 2025).
18. Anja Oasmaa and Dietrich Meier, Pyrolysis liquids analyses - The results of IEA-EU round robin, Fast Pyrolysis of Biomass: A Handbook, Vol. 2, CPL Press, 2002, 41–58.
19. Javier Ordonez-Loza et al., An investigation into the pyrolysis and oxidation of bio-oil from sugarcane bagasse: Kinetics and evolved gases using TGA-FTIR, Journal of Environmental Chemical Engineering, Vol. 9, No. 5, (2021), 106144. https://doi.org/10.1016/j.jece.2021.106144