# Production of Bio-Binders from Pyrolysis Condensates and its Interaction with Calcined Petroleum Coke

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**Abstract**



Bio-based binders are suggested as a viable alternative to fossil-based coal tar pitch (CTP) binders in carbon anodes for aluminium production. In this study, upgrading of bio-condensates from pyrolysis of Norwegian spruce wood is done by slow heat treatment in small scale. Condensates were subjected to a heating rate of 0.5 °C/min with maximum temperature varying from 160 to 180 °C and holding time at maximum temperature varied from 1 to 3 hours. The produced materials were then subjected to a wetting test using an optical dilatometer, to observe the interaction between the binder and calcined petroleum coke during heating. The contact angle development between coke and binder varied between the different binder materials, ranging from good wetting for some samples to no wetting at all for other samples. Some results were more difficult to interpret; to confirm interaction between coke and binder in these cases, µCT imaging and light microscopy were applied to the samples after the wetting test. The imaging methods confirms the major differences between wetting and non-wetting behaviour observed in the original test, and also reveals that some of the bio-materials have relatively good interaction between coke and binder even without perfect wetting appearance during the wetting test. The imaging techniques are shown to be suitable methods to observe the interactions between coke and binders with different wetting ability. Many of the bio-binders produced seem to have a good wetting ability towards calcined petroleum coke, and are thus viable as an alternative to fossil-based binders in anodes.

**Keywords:** Green aluminium production, Bio-binders, Coke/binder interactions, Optical imaging.

## 1. Introduction

The pre-baked anodes used in the Hall-Hérault process to produce aluminium consists of calcined petroleum coke (CPC) and recycled anode butts as filler material, and coal tar pitch (CTP) as binder material. CTP consists mainly of aromatic homo- and heterocyclic hydrocarbons, and is the main source of polycyclic aromatic hydrocarbon (PAH) emissions during the baking process. PAH are human carcinogens and damaging to the environment, and CTP is classified as particularly hazardous material by the European Chemical Agency (http://echa.europa.eu/). Implementing alternative binders to reduce binder toxicity, while retaining the good binder qualities needed for the anode manufacturing, is therefore of high interest for the industry.

Pitch derived from biomass, or more specifically, wood, is proposed as a viable alternative to coal tar pitch. Depending on the source and production parameters, sulfur-free bio-pitches with significantly lower PAHs can be produced. However, it is important to characterize the physical and chemical properties of the material and compare these to the coal tar pitch properties, and the interactions between the binder and the coke, to determine if bio-based binders indeed can replace conventional pitch in anode manufacturing.

The bio-binder needs to uphold several important properties for further application, including coking value, softening point, low alkali content and good wetting properties to coke grains. The main challenge identified regarding use of bio-binders in anode production is the low coking value (compared to CTP). In addition, vaporisation of binder during the baking process may be intensive and result in a less dense anode.

The earliest work on upgrading bio-oil to bio-pitches was based on eucalyptus woods [1-4], showing the ability to produce materials with varying softening point and coking value by changing the production parameters. European wood-tar as precursor for binders for electrodes (not optimised for aluminium production) has also been investigated, where the produced electrodes had high compression strength despite somewhat high porosity of the electrodes [5]. This is an indication of good interactions between filler and binder materials.

The most recent works originating at Laval University have looked into production of bio-pitches for use in pre-baked anodes in aluminium production, using both slow heating at atmospheric pressure [6] and using heating under vacuum [7, 8]. Both methods have been able to produce a variation of pitches based on the production parameters, and specific care was done to confirm the wetting abilities [9]. The results showed enhanced penetration of some bio-pitches, likely due to the low viscosity, surface tension, lack of quinoline insolubles (QI) particles and presence of active surface functional groups. Anodes made from these bio-pitches have also shown to demonstrate the same density as CTP based anodes, indicating that the enhanced wetting ability of the bio-materials is feasible to mitigate the effects of low coking value. The impact on carbon anode properties has also been thoroughly reported [10], where the comparable properties again was attributed to the good adhesion between coke and bio-pitch, resulting in a volume shrinkage that likely reduced the distance between coke particles. These works show that even with somewhat different properties, most importantly the coking value, anodes with good behaviour have been produced at lab-scale using bio-pitches, and this is indeed a viable alternative to fossil-based binders.

In this work, binders produced from pyrolysis of Norwegian spruce wood were investigated for its ability to wet CPC. Additional methods than previously reported are computed tomography and light microscopy with polarised light, which have been utilised to get a better understanding of the actual interactions between the coke and binder during such a test, also demonstrating its usefulness for investigations of this type of samples.

## 2. Experimental

In the current study, pyrolysis was conducted using an apparatus comprising of a vertical tubular fixed bed reactor, a condenser and a gas monitoring system. The sample was placed inside a basket in the reactor tube which was heated by an electrical furnace with three heating zones, each with a temperature controller giving different heating rates and holding times. Nitrogen gas ($N_2$) was purged from the bottom of the tube at a controlled rate, sweeping volatiles and gases into a condensation system. The condensable volatiles and gases passed through a condenser and cooled down to 50 °C degrees, to be collected in a tank. In this work, spruce woodchips were charged into the tubular reactor that was further sealed and assembled with the other components of the system. The system was then purged with $N_2$ for 1 hour with a steady flow rate of 2 L/min as carrier gas to sweep away residual air. After the purging step, the woodchips were further heated to a temperature of 450 °C with a heating rate of 10 °C /min and maintained at this temperature for 60 min before gradual cooling (with $N_2$ flow) until reaching 50 °C. More on this method can be found elsewhere [11]. In this study, the condensed liquid product consisting of heavy tars and contact angle between the coke and binder materials, as well as with µCT and light microscopy techniques. Although the water content in these materials may prove problematic during baking of anodes, good bonding between the coke and binder might be more determining on the material's final properties and result in dense anodes suitable for aluminium production. µCT and light microscopy using polarized light is shown to provide good insight on the interactions between coke and binder and is suggested to use on baked materials as well. The result in this study strengthens the proposal of using bio-carbons in aluminium production, to reduce the use of fossil-based carbons.

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