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

lighter oil fractions was collected and stored in a refrigerator before the upgrading process to achieve binder-materials. Due to the high amount of water in this fraction, the material is further referred to as bio-condensate, or just condensate (rather than bio-oil which tend to have a lower water content). The exact water content of the condensate was analysed by volumetric Karl Fischer titration.

The production of bio-binders from the bio-condensates was done on a small scale: 5.5-7.5 g condensate was placed in an alumina crucible and heated in a muffle furnace. The heating rate was held constant at 0.5 °C/min throughout the experiments, while the maximum temperature (160-180 °C) and holding time (1-3 hours) at this temperature was varied. The produced binder was removed from the crucible and further analysed.

One small part of solid binder material was placed on a bed of coke particles (<250 μm), and heated with a heating rate of 2.5 °C/min up to 400 °C. A Misura ODHT optical dilatometer (Expert System Solutions, Italy) was used to capture the behaviour of the interaction between coke and binder, including softening of the material, formation of droplet, and possible wetting or non-wetting by observing the contact angle during the experiment. The contact angle was extracted from the recorded video with respect to temperature and plotted. The behaviour of the produced bio-binders was compared to that of a regular coal tar pitch with Mettler softening point of 129 °C.

After the wetting test, the samples were investigated using micro X-ray computed tomography (μCT) to inspect the wetting between the binder and the coke powder. The μCT used is an XTek/Nikon XT H 225 ST instrument. Lastly, some of the samples were investigated by optical microscopy (regular and polarized light) to have a final confirmation on the interaction between the binder and the coke after the wetting test. The samples were embedded in Epofix epoxy (Struers) under vacuum and cut after curing. The cut samples were re-embedded in epoxy and polished. The polished surface was mapped using a motorized Leica DMI8 microscope, assembling image mosaics of up to 96 images.

3. Results and Discussion

3.1 Production of Bio-Binder

By Karl Fischer titration the condensate was found to have 50 wt% water. This is significantly higher than most bio-oils investigated for binder purposes, and the resulting yield was reflectively low (26-31 %). The condensate was somewhat fractionated after storage time and needed to be mixed thoroughly before the extraction of sample before the heat treatment.

Several parallel and separate experiments were done by heating multiple crucibles up to 160 °C and holding time 1 hour (>10 crucibles total, 6 experiments). For these parameters, the average yield was 30.6% ± 0.9%. Some correlations to the amount of sample in each crucible were observed; a smaller crucible with less condensate resulted in a lower yield. Since there is no stirring during the heat treatment, this is likely an effect of different convection in the liquid, while it can also be an effect of the inhomogeneous bio-condensate. Larger sample size and better homogeneity of original bio-condensate should reduce this effect, while stirring during production would also be needed for a bigger batch.

Single or double experiments were done at longer holding times (1.5-3 hours) and different maximum temperatures (170 °C and 180 °C). As expected, a higher temperature or longer holding time decrease the yield (Figure 1). Assuming the same variation for all parameter combinations as the 1 h 160 °C, the most significant differences were between 160 and 180 °C and 1 hour holding time, and 1 and 3 hours holding time for 160 °C. The sample treated to 160 °C for 2 hours

appears to be an outlier and the result may be explained by inhomogeneous sample or sample size. Whether or not the larger weight loss influenced the interactions with the CPC by removing important chemical fractions was then investigated further.

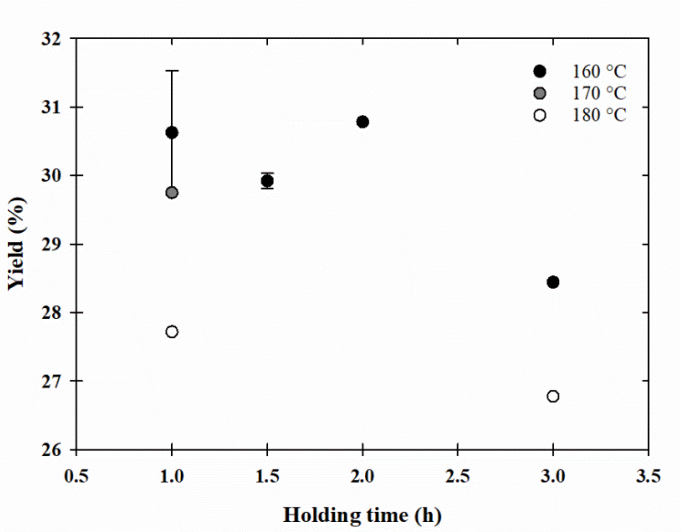

Figure 1. The yield after the heat treatment.

3.2 Wetting towards CPC

The wetting test revealed that changing the different production parameters resulted in materials that appeared to wet the CPC to a varying degree. The behaviour also reflected the yield, indicating that at some point the densification of the tar went too far, and interactions between coke and binder is non-existent (this behaviour was also reported by [6, 9]). Looking at the materials heated for 1 hour in Figure 2, the extremes can be observed. The binder produced at 160 °C completely wets the coke between 140 and 156 °C, while the one produced at 180 °C, after forming a liquid droplet at the top of the coke, simply keeps its shape until it starts to swell above 200 °C.

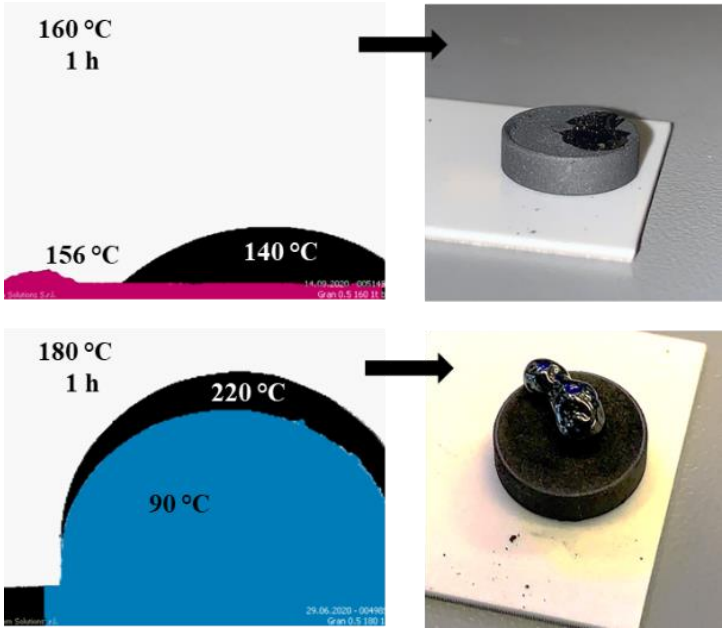

Figure 2. Examples of the behaviour of the samples near the end of the experiment, and after the experiment, of one sample that wetted the coke (top) and did not wet the coke (bottom).

The results from tracking the contact angle are presented in Figure 3 for the different holding times for the 160 °C temperature, and holding time 1 hour for the different maximum temperatures in Figure 4. The starting angle for all but the one heated to 180 °C, is 120-140°, and similar to the one for CTP.

The results reveal that compared to CTP, the produced bio-binders all achieve droplet form at a lower temperature, signifying a lower softening point (SP). The lower SP and good wetting at low temperatures may be positive for the anode production process, allowing mixing to be done at lower temperature than what is currently used (although CTP is fabricated with a variation of softening points), given that the low coking value usually reported for these bio-materials is not problematic for the anodes (as reported by [10]).

Otherwise, the following results were observed:

- The binders produced at 160 °C, 1 h and 1.5 h behaves similarly and appears to completely wet the coke based on the contact angle development.
- The behaviour of the 160 °C, 2 h and 3 h indicates that the coke is not wetted completely; the contact angle decreases similarly as the others but flattens out around 200 °C, contact angles 45° and 80° respectively.
- The two 170 °C 1 h optical dilatometer tests gave some variation (same produced material). In both cases there seems to be some interaction with the coke at lower temperature, but one appeared to almost reach full wetting at 200 °C, while the other did not.
- The binder produced at 180 °C did not appear to wet the coke at all, the contact angle was constant at 90° throughout the experiment.
- Increasing the maximum temperature appears to give a larger effect than increasing the holding time with 0.5 h.

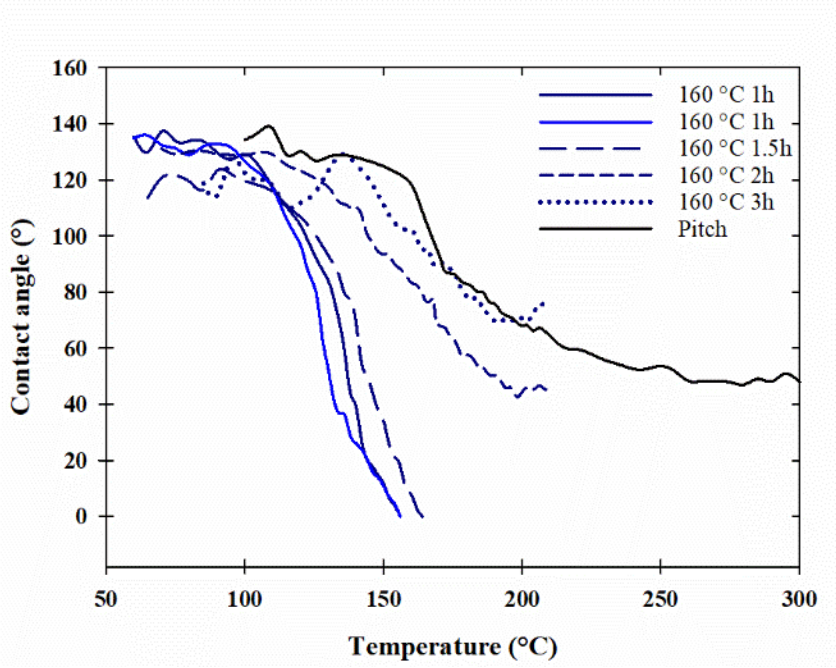

Figure 3. Contact angle between binder and CPC with a bio-binder with varying holding time at 160 °C, and comparison with CTP (heating rate 2.5 °C/min).

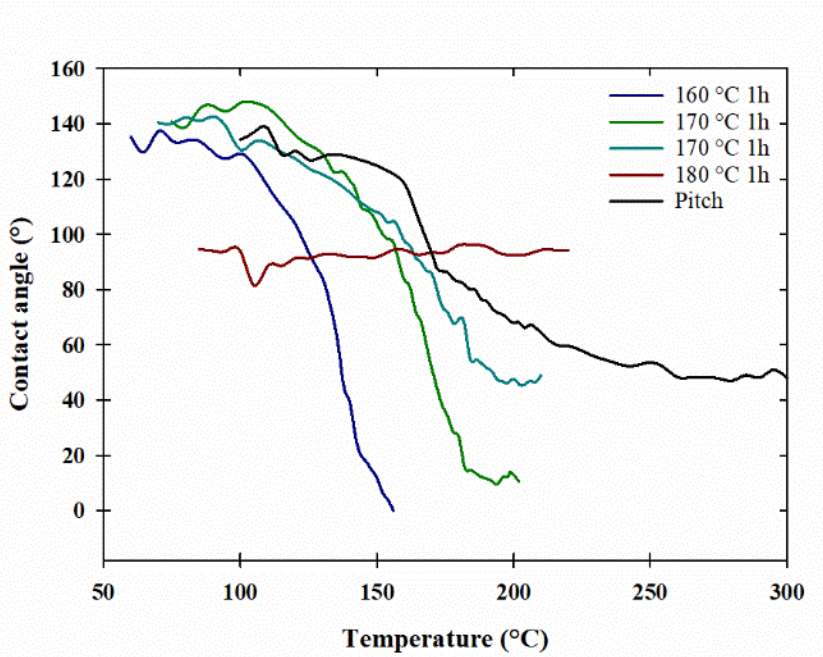

Figure 4. Contact angle between binder and CPC with a bio-binder with varying maximum temperature, and comparison with CTP (heating rate 2.5 °C/min).

Using these parameters during the wetting test, the CTP appear to not reach complete wetting as the angle levelled out like several of the produced bio-binders (although at higher temperatures for CTP than the produced bio-binders). For this reason, although the test gives a good indication of completely non-wetting materials (like the one heated to 180 °C), some uncertainty about the actual interaction during the optical dilatometer test was present. Since the CTP behaved like some of the bio-binders that did not appear to wet the coke completely, these observations are not necessarily an indication that it is not usable as binder, especially as the industrial mixing process is very different than the laboratory testing environment. Having identical temperature of coke and binder before and through the mixing process might prove successful for these materials as well. Additionally, some swelling of the binder was observed when the temperature was higher than the production temperature (usually observed over 200 °C, similar to what can be seen in Figure 2). This might indicate that the contact angle behaviour may be a temperature effect (heating rate) rather than bad wetting. Further investigations with imaging methods were thus needed.

3.3 X-ray µCT after Wetting

X-ray µCT was done on most samples from the optical dilatometry experiments to inspect the wetting between the binder and the coke powder. An example of results on the binder produced at 160 °C and 1 hour holding time is presented in Figure 4. The sample has wetted the coke well and formed a mix of coke and binder as a flat disk, with some shrinkage after cooling.

The following observations are made for the other binders, with some examples in Figure 5.

- The CTP has penetrated the coke partially, and there is a sharp boundary between the pitch and the coke after cooling (Figure 5).
- The sample produced with 160 °C max temperature and 1.5 h holding time has wetted the coke well and formed a mix of coke and binder as a flat disk, with some shrinkage after cooling, similar to the one held for only 1 hour at the same temperature.

- For the 160 °C 2 h sample we see similar behaviour as for CTP; the binder has penetrated the coke partially and there is a sharp boundary between the pitch and the coke after cooling. The sample has attached to the edge of the graphite crucible and expanded due to volatile formation (Figure 5).
- The binder produced at 160 °C 3 h lies as a drop on top of the coke, expanded from volatile formation. There is only partial wetting (Figure 5).
- The 170 °C 1 h parallel that appeared to have partial wetting, is similar to the spruce 160 °C 2 h and pitch samples (Figure 5). The other parallel from this batch, which based on the wetting angles wetted better, was not investigated.
- The binder produced at 180 °C 1 h lies as a loose drop on top of the coke, an appeared to be have expanded due to volatile formation. There is no wetting at all.

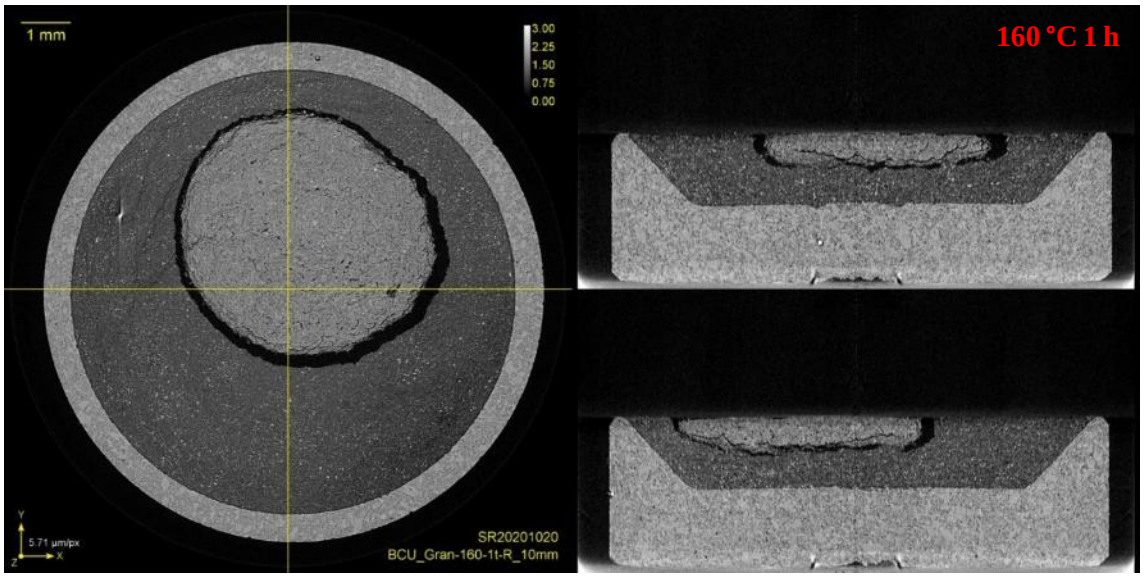

Figure 4. µCT visualization of the coke bed and binder after the wetting test. This bio-binder was produced by heating slowly to 160 °C with a holding time of 1 hour.

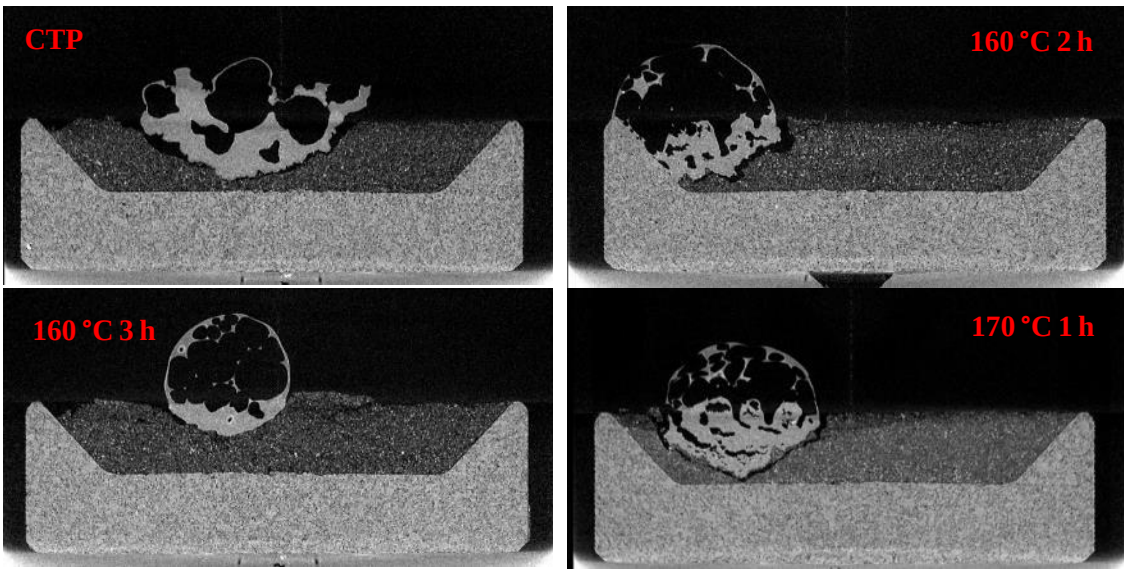

Figure 5. µCT side-view of some of the samples after the wetting test.

To summarize the investigations using µCT, the samples that appeared to wet the coke very well looking at the contact angle between coke and binder were confirmed to have a good interaction

with the coke, making a mix of coke and binder. However, the µCT method does not provide sufficient X-ray absorption contrast between coke carbon and binder carbon to confirm if this was also the case for the materials that ended up as a blob on top of the coke.

3.4 Optical Microscopy after Wetting

Since it was unclear from the µCT images whether there are coke grains inside the binder blobs for most of the tests (with the exception of the samples that ended up like disks, produced at 160 °C 1 and 1.5 h), light microscopy was chosen to further investigate samples from some of the tests. Three samples from the wetting test (optical dilatometry) using bio-binders produced at 160 °C 1 h, 2 h and 170 °C 1 h, were investigated together with the CTP sample. For the CTP the blob floated on top of the epoxy, so the image does not show the coke bed. There is a considerable amount of coke grains inside the pitch. For the sample 160 °C 1 h the binder blob is fully dispersed with coke grains, confirming good wetting. For the binder produced at 160 °C 2 h the blob has many coke grains inside the lower part (below the coke bed surface). The bubbly layer above the surface has just a few coke grains embedded. The binder blob has detached a bit from the coke bed due to the buoyancy effect from the epoxy. The 170 °C 1 h is like the 160 °C 1 h sample, with some coke grains in the lower part.

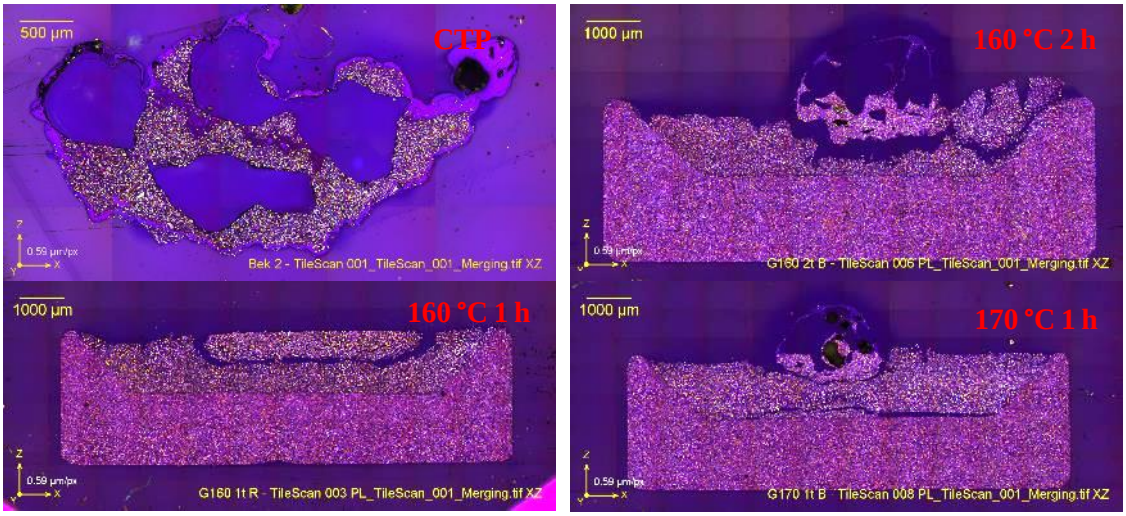

Figure 6. Optical microscopy image of pitch and three bio-binders after the wetting test.

It is worth noticing from these optical microscopy images that also the samples where the binder just appeared as a blob on top of the coke bed has partially wetted the coke, as there are plenty of coke grains inside the binder. So, the binder appears to have wetted the coke initially, then expanded to a droplet due to the volatiles escaping during the heat treatment. In an anode manufacturing context, where the grains are fully mixed with the binder before the heat treatment, also these "heavier" binders might work well. It is recommended to investigate this further by observing how the structure evolves during the carbonization at anode baking temperatures.

3.5 Applicability of Bio-Binders in Anodes

It appears that the binders based on bio-materials in this study were able to interact sufficiently well with CPC, in several cases showing superior wetting ability compared to regular CTP. Questions on whether a test with a temperature gradient is suitable to analyse the behaviour that would occur during industrial mixing at constant temperature can be raised, however it appears that using additional imaging methods reveals good interaction for most of the binders produced. Other parameters in this type of test, like coke bed packing and pitch size, might also affect the

wetting curve and give conflicting results, and the imaging methods show the true interactions. Since there is plenty of coke grains inside the binders in all cases where some change in contact angle was observed, an argument can be made that keeping both coke and pitch at the mixing temperature before mixing and compaction will likely give green anodes with well-wetted coke grains for these materials.

Despite the difference in the type of wetting test utilized at Laval [6, 9], where the test is done at constant temperature and the contact angle is evaluated over time, the results in our test appear to be comparable to their work, mainly with respect to the maximum temperature that is effective to produce pitches that have good wetting towards CPC. At certain test temperatures, references [6, 9] reported that the good wetting abilities of the studied bio-binders completely disappeared, similar to what we observed for the samples heated to 180 °C in the current work. The non-wetting sample from Laval had significantly higher average molecular weight and viscosity than all the others that showed good wetting properties, but had similar main chemical composition (C/H/O) [9]. For the current work, the tested condensates were treated at different temperatures with certain holding time. It could result in a similar change of physical-chemical properties of treated condensates as binder with different wetting properties. For example the large polymerization difference could result in varying functional groups and the much higher viscosity than what is ideal for pitches.

In this work, the results indicates that the bio-binder samples produced at a maximum temperature of 160 °C and holding time of 1 h and 1.5 h gave the best wetting properties. Compared to the CTP several of the other samples heated also gave an appearance of sufficiently good wetting (as confirmed with imaging methods). As expected, increasing heating temperature and holding time decreased the yield of binder from the condensate, which appeared to increase the softening point as well. Using certain production parameters, binders that can wet the coke completely at similar or lower temperatures as CTP can be produced. It can be questioned if it is necessary to produce a new binder material with correlating softening point as CTP; from an end-use perspective for use in carbon anodes it can be beneficial to reduce the mixing temperature if the softening point of the binder is lower, as this will save energy. It may however result in other problems during baking.

Since bio-binders have a significantly lower coking value than CTP, it is easy to disregard them as useful for anode production as it should result in a more porous anode. However, industrial or pilot-scale production of anodes would be needed to confirm this; several pilot-scale anodes based on bio-pitches produced at Laval appeared to have good density, revealing that this was in fact not a problem because of high shrinkage of the anodes. The good properties of the anodes were assumed to be because of the excellent wetting ability of bio-based pitches [9, 10]. However, the binders produced in our study is produced from bio-condensates and might contain more water than those (i.e., bio-oil) produced from different biomasses and using different production technologies. This may give other problems during baking than with anodes made of binders originating from more traditional bio-oil; there might be a point where the positive effects of the wetting abilities of the biomaterials is negated by the high loss in volatiles during baking. More investigations need to be done to understand how much volatiles can be present in the bio-binders for them to be suitable for anodes, and how to optimize a process to produce these based on start-materials with different amounts of water.

4. Conclusion

In this work, biomaterials based on pyrolysis of Norwegian spruce woods have been upgraded to materials that appear to have a variable degree of wettability towards calcined petroleum coke. Some of the materials had excellent wetting properties, shown by observing the rapid change in

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.

5. Acknowledgements

This research was funded by Research Council of Norway grant number 294679 (BioCarbUp). The authors would like to acknowledge the use of the μCT laboratory of the X-ray Physics Group at NTNU, part of the National Infrastructure NEXT, funded by NTNU, the Norwegian Research Council, and European program INFRAIA (90659800).

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