Bio-Binders and its Carbonization and Interaction with Petroleum Coke during Baking

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Abstract
To reduce the carbon footprint in aluminium production, bio-based binders are suggested to replace some or all coal tar pitch in the carbon anodes. In this study, bio-binders based on Norwegian spruce and birch woods were produced in a laboratory set-up, which were studied in terms of wetting properties towards petroleum coke. The binders were mixed with petroleum coke and baked to three different temperatures. Graphitization of the binders were investigated on pure carbonized binders by XRD. Optical light microscopy was used to investigate the structures and interactions between coke and binder after baking. The bio-based binders appeared to adhere well to the coke particles, indicating excellent wetting behaviour during mixing. The optical structure of the carbonized bio-binder seemed to be affected by strain due to shrinkage of the bio-binder around the coke grain boundaries.

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

1. Introduction

Aluminium is produced in the Hall-Héroult process, a process that consumes 0.4-0.5 kg carbon when producing 1 kg Al, at the same time producing CO_2 gas, which has a negative impact on the world climate ("greenhouse effect", global warming). The carbon comes from the consumable pre-baked anodes. The carbon anodes act as both conductors of the electricity and reductants in the process and are normally made from calcined petroleum coke (CPC), recycled anode butts and coal tar pitch (CTP). These materials are mixed at temperatures depending on the softening point (SP) of the CTP, producing an anode paste that is further formed and pressed before baking at 1250 °C. All the constituents are currently fossil-based and implementing bio-based carbon materials in anodes is suggested to cope with both the future availability of materials and reducing the carbon footprint of aluminium production.

A possible alternative to CTP is binder derived from thermal conversion of woody biomass materials. Literature suggests that materials with suitable properties for anode manufacturing may be produced by changing the heat treatment parameters when upgrading the more traditional bio-oils (one of the products from wood pyrolysis), first investigated for eucalyptus wood [1-4]. Comparisons with CTP have been in focus in later literature, where bio-binders with viscosity close to that of traditional CTP have been produced, showing excellent wetting properties towards coke particles [5]. These binders are less harmful for people and environment, as they are considered renewable, and have almost none of the polycyclic aromatic hydrocarbons (PAHs) found in regular CTP (carcinogenic) and are very low in sulfur content, making them very interesting for the aluminium industry.

Although bio-binders have been shown to have good wetting properties and can be produced with different softening points (similar to CTP), the main challenge identified is the low coking value (CV, often in the range 30-40 %) compared to that of CTP (55-65 %). During the carbonization process of the binder during anode baking, volatiles escape from the anodes and leave a certain porosity in the structure. With the low coking value, anodes made from bio-pitches have been assumed to be less dense, have larger possibility of other imperfections like cracks, and not

conduct electricity as well as anodes made from CTP. However, recent work has shown that laboratory anodes made from bio-pitches actually can have comparable density and electrical conductivity to laboratory anodes made from CTP [6]. The explanation for this behaviour is still being investigated but the main reason can be assumed to be the good adhesion between bio-based binder and the coke particles.

A research group at Laval University have thoroughly worked through the possibilities of changing the production parameters to achieve different binder properties [7-9], with special focus on evaluating the wetting properties [5]. Enhanced penetration of some bio-pitches was observed, likely because of low viscosity and surface tension, lack of quinoline insoluble (QI) particles and presence of active surface functional groups (C-O/C=O, O-C-O/O-C=O). Some bio-pitches had, however, been treated at too high temperatures. This resulted in a much higher average molecular weight, which again led to a material with high viscosity which did not wet the coke. The heat treatment is therefore extremely important to produce suitable bio-pitches, but the exact parameters needed to produce the most optimum binders likely depend on initial raw material source (like tree type) and water content of the initial bio-oil.

Initial tests showed that pilot anodes made of bio-binders that had good wetting properties, also had comparable densities to similarly made CTP based anodes [5], which indicated that despite the lower coking value this did not affect the anode properties in a negative way. This was investigated in detail [6] and was indeed explained by the good adhesion between coke and bio-pitch. The laboratory anodes made with bio-pitch had a much larger volume shrinkage than the ones made with CTP during baking, which likely reduced the distance between the coke particles and increased the density. The bio-pitch and CTP anodes had similar specific electrical resistivity and compression strength as well. The comprehensive work shows that, although with some major differences from CTP (mainly CV), anodes with good properties were produced at lab-scale using bio-pitches, indicating its viability for replacing fossil-based binders.

In this work, binders produced from lab-scale pyrolysis of Norwegian spruce and birch woods were investigated and compared to CTP and a bio-pitch made from a more traditional bio-oil like the ones used otherwise in literature (which are produced by fast pyrolysis and using fractional condensation to separate out most of the water). The materials were investigated for wetting properties towards CPC. To better understand what occurs during the baking process, carbonization to different temperatures was also performed, and the materials investigated with X-ray diffraction (XRD). Finally, binders were mixed with CPC and the paste went through a heat treatment cycle similar to that during anode baking. The resulting baked materials were investigated with optical light microscopy to evaluate the resulting anode structure.

2.   Experimental

Pyrolysis was conducted using an apparatus comprising of a vertical tubular fixed bed reactor, a condenser and a gas monitoring system. A sample was placed 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. Control and monitoring of the temperatures in the reactor used were enabled by three pairs of thermocouples along the length of the tubular reactor. 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 gas passed through a condenser and cooled down to 50 °C degrees, to be collected in a tank. The non-condensable fraction of the products further flowed through two filters to remove entrained particulates. In this work, pre-dried spruce (or birch) wood chips 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 flowrate of 2 L/min as carrier gas to sweep away residual air. After the purging step, the wood chips were further heated to a given pyrolysis temperature, with a heating rate of 10 °C/min, and maintained at this temperature for 60 min before gradual cooling

(with contributed N_2 flow) until reaching 50 °C. Staged pyrolysis was also possible, where the material was held on each step temperature for 60 min. The condensed liquid products consisting of heavy tars and lighter oil fractions were collected and stored in a refrigerator before further upgrading to achieve binders. Further details of the experimental setup for the pyrolysis stage are provided in [10]. Due to the high amount of water in the condensed fraction, the materials produced by this method are further referred to as bio-condensate, or just condensate. The exact water content of the condensates was analysed by volumetric Karl Fischer titration. Condensates were upgraded by placing 5.5-7.5 g in an alumina crucible and heating them in a muffle furnace. The heating rate for this upgrading was held constant at 0.5 °C/min for all experiments.

First, condensates from spruce wood, pyrolysis temperature 450 and 500 °C, and birch wood with pyrolysis temperature 500 °C were heated to 160, 170 and 180 °C, respectively, and held at the maximum temperature for 1 hour. The produced binder was removed from the crucible and further analysed for wetting properties. The wetting test consisted of placing one small part of solid binder material on a bed of coke particles (<250 µm) and heated with a heating rate of 2.5 °C/min up to 400 °C. The behaviour of the interaction between coke and binder, including softening of the material, formation of droplets, and possible wetting or non-wetting, was done by observing the contact angle during the experiment by use of a Misura ODHT optical dilatometer (Expert System Solutions, Italy). 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.

In the second part of the study, the production of all bio-based binders was done by heating in the muffle furnace up to 160 °C and using a holding time for 1 h. The condensate from spruce wood produced at 450 °C, and a condensate originating from birch wood where the pyrolysis was staged first to 350 then 500 °C were used. Additionally, a more traditional bio-oil, with much lower water content than the condensates, was studied for comparison purpose. The CTP mentioned above was also studied, resulting in four different binder materials. Each binder was mixed with CPC, either a "coarse" fraction (0.5-1 mm, 30 wt% binder) or a "fine" fraction (<0.250 mm, 50 wt% binder) at ~150 °C (CTP at a slightly higher temperature due to higher SP). The crucibles were then placed in a container and covered with packing coke and placed in a furnace for the baking. The same type of baking cycle found in [6] was chosen. The temperature was increased to 150 °C (60 °C/h), then to 650 °C (20 °C/h), and finally to the maximum baking temperature (50 °C/h), and this temperature was maintained for 20 h. Three different maximum temperatures were chosen, 900, 1100 and 1300 °C, respectively. Pure binders were also included, to investigate and compare the carbonization. At the end of the heat treatment, the furnace was switched off, allowing the samples to cool down to the room temperature.

X-ray diffraction (XRD) was used to investigate the degree of carbonization of the binders. This is assessed by measuring the crystallite height (L_c), which is calculated according to the ISO 20203 standard method. This is based on the Scherrer equation, using a constant of 0.89. The samples were crushed to a powder and packed into a "zero background" silicon single crystal sample holder, with a shallow groove of 10 mm width. The XRD scans were done on a Bruker D8 Focus instrument, using a fixed slit size of 1.0 mm. The Scherrer equation was calculated using curve-fitting functions available in the Bruker DIFFRAC EVA software.

The optical microscopy was done using a motorized Leica DMI8 microscope, combining multi-focus stacks into image mosaics. The samples were imaged using reflective light, passing through crossed polarizers and a lambda filter. This gives interference colours, according to the degree of crystallinity (double refraction) and angular orientation of the crystallites (optical domains). The samples for optical microscopy were prepared by embedding the heat-treated coke/binder mixture in EpoFix epoxy (Struers) under vacuum and then cut and polished after curing. The polished surface was mapped using a motorized Leica DMI8 microscope, assembling image mosaics of

12x16 = 192 images using the Leica LAS-X software as provided by the manufacturer. Each of the images in this mosaic was acquired as a stack of images taken at multiple focus depths, from which a best focus image was calculated by the software.

3. Results and Discussion
3.1 Production of Bio-Binder
The condensates were inhomogeneous and fractionated, and required vigorously mixing. This resulted in some variation in the Karl Fischer titration results and can explain some of the discrepancies after the upgrading. The birch condensates contained 40-45 wt% water and those produced from the spruce wood had 50-55 wt%. The pyrolysis temperature influenced the water content for the same tree type. The spruce condensate produced during carbonisation to 450 °C had lower water content (50 wt%) than the one heated to 500 °C (55 wt%), which could be due to the additional 50 °C temperature increase resulting in relatively more H_2O than other condensables. The condensates are all starting with a significantly higher water content than most bio-oils investigated for binder purposes (e.g., the bio-oil from majority of the studies at Laval had <10 wt% water) and this was very apparent when comparing with the appearance of the bio-oil used for the study.

Fig. 1 shows the yield of residues for condensate samples heated for 1 h at different temperatures. An apparent correlation between yield and upgrading temperature is observed. For three studied condensates there is a decrease in the yield with higher upgrading temperature. The spruce condensate from the pyrolysis at 450 °C have several parallels, especially at 160 °C (as materials treated in this way was prepared for the second part of this study) showing an average yield of 30.9 ± 0.9 wt%. For 170 °C and 180 °C only two parallels were run, but assuming a standard deviation around 1 wt% there is a definite decrease with increasing heat treatment temperature. The two parallels at 180 °C were quite different, showing that the relative decrease in the yield from 160 to 180 °C was 4 % and 16 %. Then looking at the other two materials, where only one parallel was run for each upgrading temperature, the same type of decrease is observed. There is a relative change in yield of 9 % from 160 to 180 °C for these two materials.
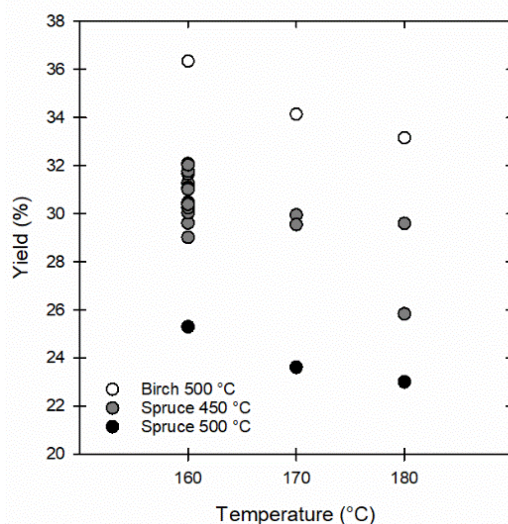

Fig. 1 – The yield for three different condensate materials heated to three different temperatures and held for 1 h.

There is also a clear difference between the materials depending on the water content in the condensates, as the yield decrease with higher water content. This is as expected, given that all three condensates consist of approximately the same chemical compounds and the major

difference is in the water retained in the condensate. If materials produced by the same parameters have the same binder properties was the focus for the further analysis.

3.2   Wetting Test

The binders produced by heating the three abovementioned condensates to 160, 170 and 180 °C, respectively, for 1 h were all investigated for their ability to interact with CPC. The results are presented in Fig. 2. All the bio-binders tended to swell above 200 °C, which is why the contact angle is not tracked above this temperature. This temperature is significantly higher than would be relevant during mixing of pitch and coke during anode production and should not be a problem for the actual fabrication of green anodes. It may however prove problematic during baking. The CTP used in this study had a Mettler softening point at 129 °C, which is higher than for the bio-based binders as they achieved droplet form at a temperature below 100 °C. With higher heat treatment temperature of the condensates the solid binder formed a droplet on top of the CPC at a higher temperature, confirming the higher softening point for these and the ability to fine-tune this property with variable production parameters, as observed in other works [3, 7].

Previous work from the authors have confirmed the interactions between the binder and coke after this test using optical light microscopy and computed tomography [11]. Materials that reached 0-20° contact angle was confirmed to wet the coke well, forming a uniform mix of coke and binder. Materials where the contact angle reached a constant value in the 20-80° range partially wetted the coke and can be assumed to have good binder properties given proper mixing conditions. Materials where the contact angle did not decrease significantly after forming a droplet did not interact with the coke at all.
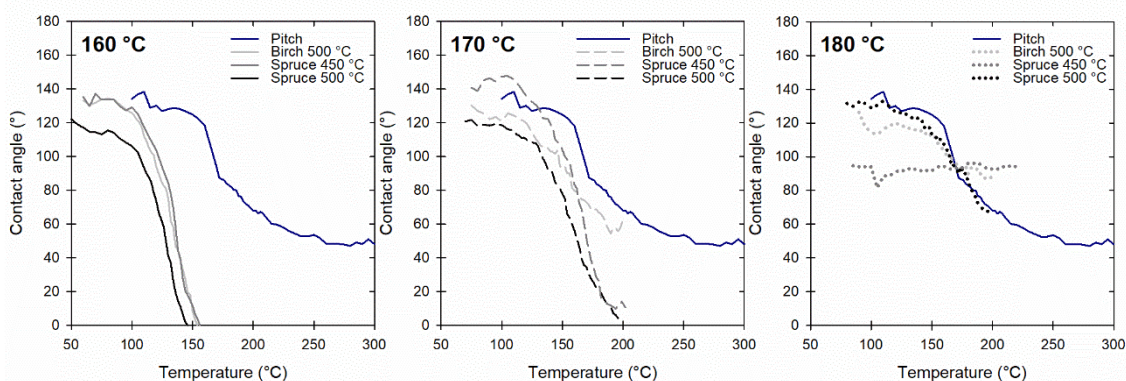

Fig. 2 – Contact angle between the binders and CPC with upgrading of three different condensates to 160, 170 and 180 °C with holding time of 1 h, and comparison with CTP (heating rate 2.5 °C/min).

For the materials produced at 160 °C all three bio-binders appeared to behave similarly. The three binders reached a contact angle of 0° around 150 °C, indicating complete wetting of the material. The small variations between them are insignificant, although the binder originating from the condensate with highest water content, the spruce pyrolyzed at 500 °C, did appear to wet the coke at a bit lower temperature than the other two. This indicates that the water content could be a deciding factor to choose production parameters. A slightly higher temperature or holding time might have produced a material with similar behaviour as the other two, because the same amount of water and light fractions would have been allowed to evaporate during the upgrading.

Both spruce samples with upgrading temperature of 170 °C completely wetted the coke, while the birch sample gave partial wetting. This could also be explained by the lower water content of the birch condensate, and that some of the heavier chemicals that give good binding properties

have started to evaporate in this sample during the identical heat treatments. All three may be suggested to be used as binder. However, for the samples upgraded at 180 °C, two of the samples does not appear to wet the coke, indicating that they have reached the stage where the average molecular weight rapidly increases and produce a material that no longer interacts favourably with the coke (similar to [5]). The last sample, the spruce produced at 500 °C and with the largest portion of water in the condensate, follows the CTP behaviour, which was shown to give partial wetting [11].

For the spruce produced at 450 °C the contact angle did not change at all for the material upgraded with 180 °C, and the binder investigated for the wetting test in Fig. 2 correlate to the parallel in Fig. 1 with the lowest yield (relative change of 16 % from the average yield at 160 °C). It can be questioned if the other parallel at this temperature, which had much lower reduction in yield, would have behaved similarly or had some partial wetting, as it is likely that this has more of the lighter fractions remaining in the produced material. These differences are explained by the inhomogeneity of the condensate. Similar to what has been reported previously [5, 7], some parameters clearly resulted in materials which does not wet CPC at all and are unusable as replacement of CTP, and for these materials this is likely around 180 °C, given a holding time of 1 h.

Due to the similar wetting behaviour of all materials when heated to 160 °C for 1 h, this temperature was chosen for the further analysis. One spruce condensate (450 °C) and one birch condensate (staged pyrolysis, 350-500 °C, were chosen based on quantity needed for all parallels in this part of the study) and a regular bio-oil were upgraded in this way. This birch-sample was confirmed to behave in the same way and at similar temperatures as the materials in Fig. 2, while the bio-oil based binder had the same behaviour but at significantly lower temperatures. The low water content in the bio-oil resulted in yields around 77-81% after the initial heat treatment, similarly high values as what has been observed for other bio-oils with low water content [9]. The bio-oil would likely need a higher temperature or longer holding time to end up with identical properties as the ones discussed previously. This may not, however, be necessary, as the softening point often vary between regular CTP as well, and all three binders appeared to wet the coke suitably. It is unknown how the differences may affect the anode properties. These three bio-binders, in addition to CTP, was therefore further analysed after high temperature treatment with respect to carbonization and interactions with CPC during baking.

3.3 Carbonization

The weight loss for the binders carbonized to 1100 °C and 1300 °C are presented in Table 1 (Note that for 900 °C the results were somewhat contaminated). The weight loss is higher for the spruce than the birch, and both increased with the temperature. The weight loss for the bio-oil was the same for these two temperatures, and in the lower range of the loss for the bio-condensate. CTP had a much smaller weight loss, but a larger difference between the two temperatures than the others. This shows the high volatile fraction in the bio-materials, which again questions their use as binders.

Table 1 – Weight loss for the binders during heat treatment.

Material	Weight loss at 1100 °C (%)	Weight loss at 1300 °C (%)
Spruce	78	86
Birch	68	77
Bio-oil	71	71
CTP	31	49

Fig. 3 shows an example comparing XRD scans of all binders heat-treated to 1300 °C. The CTP has developed a narrow peak (high L_c value), while the bio-binders have much wider peaks (low

L_c value). The amount of reflected X-rays is also lower for the bio-binders, so these have a lower signal-to-noise ratio. The scans are normalised for comparison purposes. There is no significant difference in the peak shape of the bio-binders, they are all similarly broad.
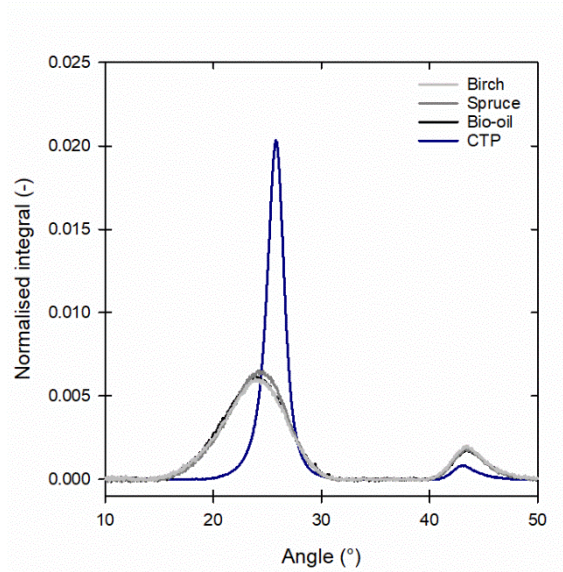

Fig. 3 – Example XRD scans at 1300 °C

Table 2 and Fig. 4 shows a comparison of the calculated L_c values. The L_c increases with increasing baking temperatures for all binders, but the increase is relatively small for the bio-binders. For the CTP the increase is large. This implies that the bio-binders are hard to carbonize; they retain a relatively amorphous structure with increasing baking temperature.

Table 2 – Calculated L_c values

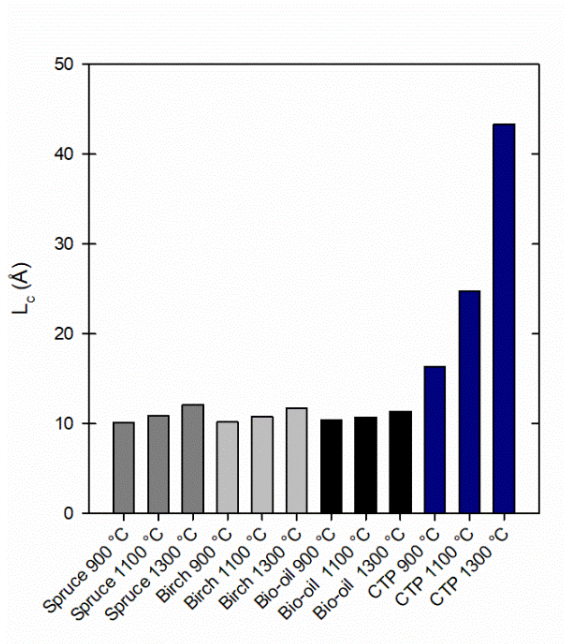| Material	L_c 900 °C (Å)	L_c 1100 °C (Å)	L_c 1300 °C (Å)
Spruce	10.1	10.9	12.1
Birch	10.2	10.8	11.7
Bio-oil	10.4	10.7	11.4
CTP	16.3	24.8	43.3

Fig. 4 – L$_c$ values for all binders.

3.4 Coke and Binder Interactions during Baking (optical)
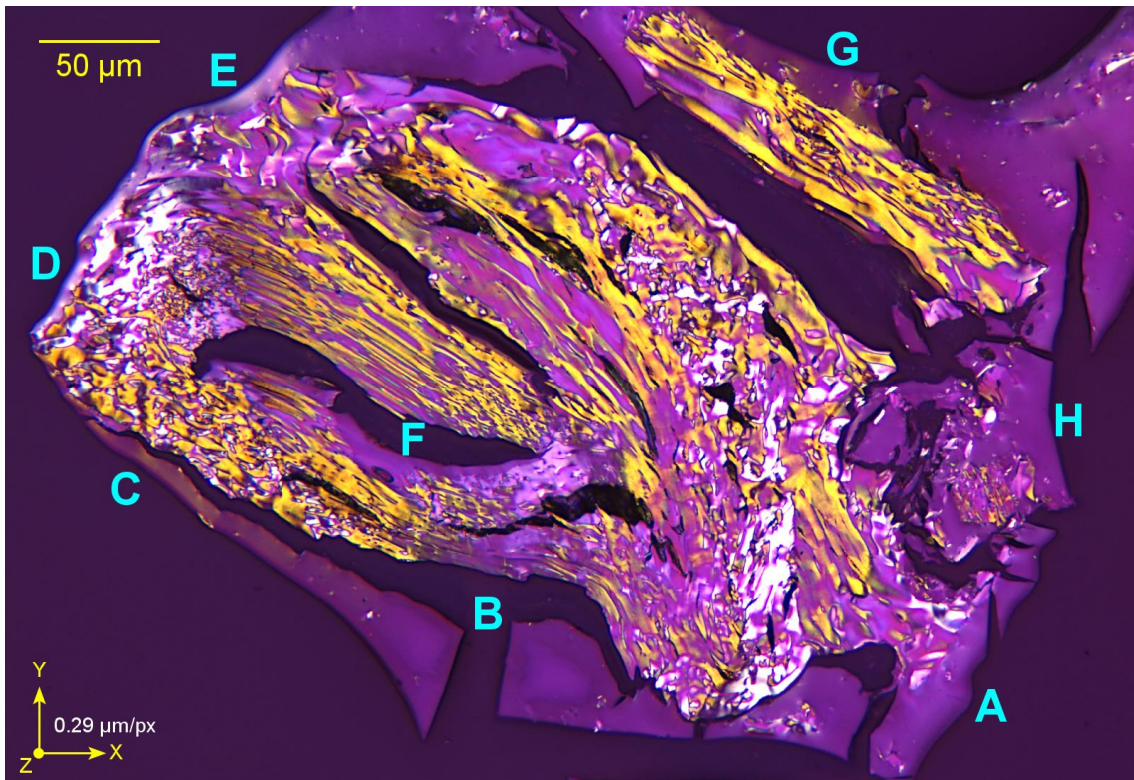

Fig. 5 – Optical image of a coke grain covered by bio-binder (0.5-1 mm coke grain mixed with bio-binder from spruce, heat treated to 1300 ℃).

Fig. 5 shows a representative image of a coke grain with bio-binder (spruce, 1300 ℃) attached to most of its surface. The colours in this image are due to interference from the double refraction

of the carbon surface when viewed in crossed polarizers and shows both the degree of carbonization and the angle of the graphitic layers in the structure. The brighter the saturation of the colour, the higher the degree of carbonization. The colour is yellow/orange when the angular direction of the graphitic layers is northwest to southeast (NW-SE) and cyan/bright blue when the direction is southwest to northeast (SW-NE). The colour is purple if the graphitic angle is parallel to the surface, or the carbon is amorphous. The dark purple areas are the surrounding epoxy, while the brighter purple smooth areas surrounding the colourful coke grain is the baked bio-binder.

The following features can be observed in Fig. 5:
- The bio-pitch wets the coke grain perfectly at the convex parts (A, D, E, G, H) of the grain surface
- The bio-pitch has detached from the coke grain at the concave parts (B) of the grain surface
- There is a slight development of an anisotropic structure of the pitch several places (A, C, D, E, G). The colour of this anisotropy follows the direction of the stretched binder layer, it is orange in the NW-SE oriented parts (C, G) and bluish in the SW-NE oriented parts (A, D, E). This indicates that the anisotropy develops from strain due to the baking shrinkage of the bio-binder around the coke grain. It does not follow the structure of the coke: In area D, the coke structure has a NW-SE orientation (orange), but the bio-binder structure follows the SW-NE orientation of the grain surface
- The bio-binder has partially filled some pores (F) with perfect wetting of the pore wall in the lower facing part

The observations shown here were found to be common for all combinations of bio-binder type and baking temperatures. With the limited amount of bio-binder available in the cut surface of the samples, no trend could be detected. This corresponds to the small variation found between the bio-binders in the XRD data. It appears that these pastes, which have not been fabricated to full anodes, behave the same independently from the investigated parameters.

The good wetting behaviour observed in the wetting test (Fig. 2) for the binders fabricated from bio-materials are upheld during high temperature heat treatment, resulting in good adhesion of binder to coke discussed in other literature [6] being visually observed in this study. It confirms that the good wetting for bio-binders is the likely cause for the good anode properties (density, SER) achieved when producing pilot anodes with bio-based binders rather than with CTP and are thus promising for the future use of this material in anode fabrication.

4.   Conclusions

Bio-binders fabricated from the collected heavy tars and light oil fractions during pyrolysis of woods were upgraded through heat treatment to materials with binder properties. The wetting properties towards CPC changed when increasing the upgrading temperature, and the excellent wetting behaviour achieved when upgrading the condensates at 160 °C was completely lost for some materials when increasing the upgrading temperature to 180 °C. No obvious differences were observed between binders originating from birch or spruce condensates and bio-oil with respect to wetting and carbonization, and the bio-based binders are more difficult to carbonize than CTP under the same conditions. XRD measurements show that all bio-materials develop lower L_c values than CTP during baking, with little increase at higher baking temperatures. Optical microscopy confirms that the bio-binders wet the CPC particles well, and the use of these types of binders in anode production is indeed promising.

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