

CB06 - Bio-pitch Improvement for Coal Tar Pitch Replacement in Pre-baked Anodes

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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 CO₂, 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 CO₂. 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 CO₂ [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.

2. Experimental Work

2.1 Raw Materials

Bio-oil used in this work was supplied by Pyrovac Inc. (Québec, Canada). It was extracted from spruce wood biomass. Table 1 shows the elemental composition of the bio-oil (analyzed by an elemental analyzer - Perkin Elmer 2400 Series II in CHNS mode) on a wet basis. The oxygen content was calculated by difference. The water content of the bio-oil was measured using the Karl Fischer titration method according to the standard ASTM E203. A Metrohm Titrando 890 was used with the HYDRANAL™ Composite 5K titrating agent (without methanol).

Table 1. Bio-oil elemental analysis and water content.

| Chemical element | C | O | H | S | N |
|---|------|------|-----|------|-------|
| Wet basis (wt.%) | 60.0 | 30.5 | 8.6 | <0.5 | < 0.5 |
| Dry basis (normalized from 82 to 100 %) | 73.2 | 17.6 | 8.0 | <0.6 | < 0.6 |
| Water content (wt.%) | 18.0 | | | | |

The bio-oil is not chemically stable as it changes over time [17, 19]. This is due to the presence of some molecular species which contain unsaturated compounds such as olefins, aldehydes, and ketones that polymerize slowly [16, 17]. The bio-oil used for bio-pitch syntheses in previous research had typical oxygen content greater than 20 wt.% [6, 15, 22].

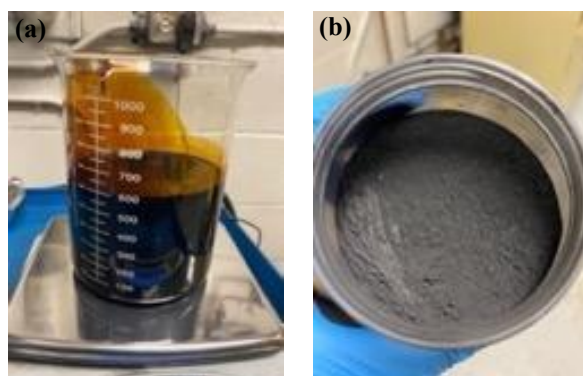


Figure 1. Raw materials: (a) Bio-oil and (b) Fine calcined petroleum coke.

The second raw material was the fine calcined petroleum coke (fine CPC), mainly composed of carbon (98 wt.%) and sulfur (1.49 wt.%) [22, 23]. The fine CPC was produced through ball milling of dry CPC, provided by Alcoa Corporation (Québec, Canada). The fine CPC was ball-milled to reach a Blaine Number (BN) of 5000, having a particle size range of (0.4–239) μm . A Mastersizer 2000 (Malvern instrument, UK) was used to characterize the particle size distribution of fine CPC. The fine CPC was then added into bio-oil at different proportions to make bio-oil blends as presented in Table 2.

Table 2. Proportions of fine CPC particles in bio-oil during heat treatment.

| Total mass of bio-oil blend (g) | 950 | | | | | |
|-----------------------------------|-----|-----|------|------|------|------|
| Fine CPC mass in the blend (wt.%) | 0 | 5.0 | 10.0 | 18.0 | 25.0 | 30.0 |

CTP, provided by Alcoa Corporation (Québec, Canada), was used as a reference sample. The CTP is mainly composed of carbon (92.49 wt.%), oxygen (2.37 wt.%), hydrogen (4.10 wt.%), and nitrogen (1.04 wt.%) [6, 23]. It also contains Fe (279 ppm), Ca (109 ppm), Na (53 ppm), S (0.66 wt.%) and Si (420 ppm) in a minor quantity [6, 23].

2.2 Bio-binder Production

Bio-oil blends containing different fine CPC, as indicated in Table 2, were heat treated. The resulting materials were called hybrid bio-binders (HBB). The term “bio-pitch” is used only to designate the binders obtained by the heat treatment of bio-oil alone. Thus, both HBB and BP are categorized under bio-binders.

Bio-oil was first agitated in a bulk container (24 L). A fraction of fine CPC was added in a 1000 ml glass beaker containing a bio-oil fraction and agitated manually for 5 min. A glass beaker containing around 950 g of bio-oil blend was placed in an open-top crucible furnace (Lindberg, 56610C, Riverside, MI, USA) for heat treatment (Figure 2). A mechanical stirrer was used for continuous agitation during heat treatment. The temperatures of the bio-oil and furnace were recorded *via* a data acquisition system (DT85 Series 2, Australia), and a collecting system was installed to capture volatiles.

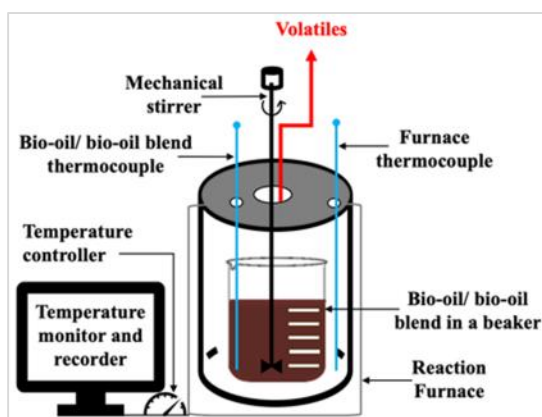


Figure 2. Set up of bio-oil heat treatment under atmospheric environment.

The heat treatment was carried out under an atmospheric environment by heating up to 180 °C with a heating rate of 0.5 °C/min, and 1 h of soaking time. The soaking temperature and soaking time are two crucial factors for producing quality pitch. The soaking temperature plays a role in the control of the cracking reactions and the soaking time influences the polymerization and condensation reactions [9].

2.3 Bio-binder Characterization

The mass loss after heat treatment, the coking value (CV), the softening point (SP), and the viscosity at 145 °C, 155 °C, 165 °C, and 178 °C were measured for the produced hybrid bio-binders. The results were compared to reference samples of BP and CTP.

The mass loss after heat treatment was calculated according to Equation 1 and Equation 2:

$$m_{BOB} = m_{BO} + m_{fCPC} \quad (1)$$

$$L_{AP} = \frac{m_{BOB} - m_{BB}}{m_{BOB}} \text{ (wt.\%)} \quad (2)$$

where:

m_{BOB} Bio-oil blend mass, g

m_{BO} Bio-oil mass, g

m_{fCPC} Fine CPC mass, g

L_{AP} Mass loss after heat treatment, wt.%

m_{BB} Final bio-binder mass, g

The coking value (CV) was quantified as per modified ISO 6998:1997. Each sample of bio-binder was crushed into small particles of size less than 1 mm. For each bio-binder, three samples of 1 g each were weighed in porcelain crucibles with lids. The crucibles were covered with packing coke to prevent bio-binder oxidation. They were carbonized at 550 °C for 2 h inside a muffle furnace (MTI corporation, KSL-1500X, Richmond, CA, United States). Equation 3 was used to determine the CV.

$$CV = \frac{m_{BC}}{m_{BB}} \text{ (wt.\%)} \quad (3)$$

where:

CV Coking value, wt.%

m_{BC} Bio-pitch coke mass, g

Thus, mass loss after carbonization (L_{AC}) was quantified as expressed in Equation 4:

$$L_{AC} = (100 \% - CV) \text{ (wt.\%)} \quad (4)$$

The total cumulative mass loss (L_{TC}) was calculated as expressed in Equation 5:

$$L_{TC} = \frac{m_{BOB} - m_{BC}}{m_{BOB}} \text{ (wt.\%)} \quad (5)$$

It should be emphasized that the cumulative mass loss represents the sum of the mass losses occurred during two steps, i.e., converting bio-oil to bio-pitch and carbonizing bio-pith to coke.

In order to assess the coking value of the bio-pitch within the HBB, we also calculated the corrected coking value by removing the mass of fine CPC from the HBB mass. We assumed that fine CPC does not decompose below its calcination point of 1250 °C [2], thus it does not contribute to the mass loss. The coking value of the bio-pitch within the carbonized HBB is obtained from Equation 6. This parameter, if different from the CV of the bio-pitch, may indicate the effect of fine CPC on the heat treatment process of the bio-pitch.

$$CCV = \frac{m_{BC} - m_{fCPC}}{m_{BB} - m_{fCPC}} \text{ (wt.\%)} \quad (6)$$

Softening point: The measurement was taken using ISO 5940-2:2007 standard ring-and-ball method. Each sample of bio-binder was crushed into small particles of size less than 5 mm, and 20 g of each sample were heated at 150 °C in a crucible furnace (FE3D). The viscous liquid was poured into the two rings of a ring-and-ball apparatus, which were set into a 1000 ml beaker containing 600 ml of glycerol, supplied by Fischer Scientific, New Jersey, USA. The beaker was placed on a heating plate and the temperature was increased at a rate of 5 °C/min until the softening point was observed. A thermocouple was immersed in the glycerol to read temperature.

Viscosity: A Discovery Hybrid Rheometer (DHR-3, TA Instruments, New Castle, USA), equipped with two 40 mm Peltier parallel steel plates, was used to measure the rheological properties of bio-binder samples. A gap of 1 mm was set between the plates. For each sample, the viscosity measurements were performed at 145 °C, 155 °C, 165 °C, and 178 °C with shear rates of (1-100) s⁻¹. The measurement of CTP was carried out at 165 °C, and 178 °C with the same shear rates.

3 Results

Table 3 shows the formulation of bio-binders. Fine CPC amounts of 0 wt.%, 5.0 wt.%, 10.0 wt.%, 18.0 wt.%, 25.0 wt.% and 30.0 wt.% were added to bio-oil prior to heat treatment to obtain different HBB samples.

Table 3. Bio-binders formulation.

| Sample | Bio-oil (wt.%) | CPC (wt.%) | Heating rate (°C/min) | Soaking temperature (°C) | Soaking time (h) |
|------------|----------------|------------|-----------------------|--------------------------|------------------|
| BP | 100 | 0 | 0.5 | 180 | 1 |
| HBB-5 CPC | 95 | 5 | 0.5 | 180 | 1 |
| HBB-10 CPC | 90 | 10 | 0.5 | 180 | 1 |
| HBB-18 CPC | 82 | 18 | 0.5 | 180 | 1 |
| HBB-25 CPC | 75 | 25 | 0.5 | 180 | 1 |
| HBB-30 CPC | 70 | 30 | 0.5 | 180 | 1 |

As observed in Figure 3. **Bio-binder samples:(a) BP, (b) HBB-5 CPC, (c) HBB-10 CPC, (d) HBB-18 CPC, (e) HBB-25 CPC, and (f) HBB-30 CPC**, all bio-binders are solid and look carbonaceous as their parent materials. All HBB demonstrated a sticking behavior at room temperature, after being crushed into small particles. A more pronounced tendency to stick was observed on HBB-10 CPC and HBB-18 CPC samples.

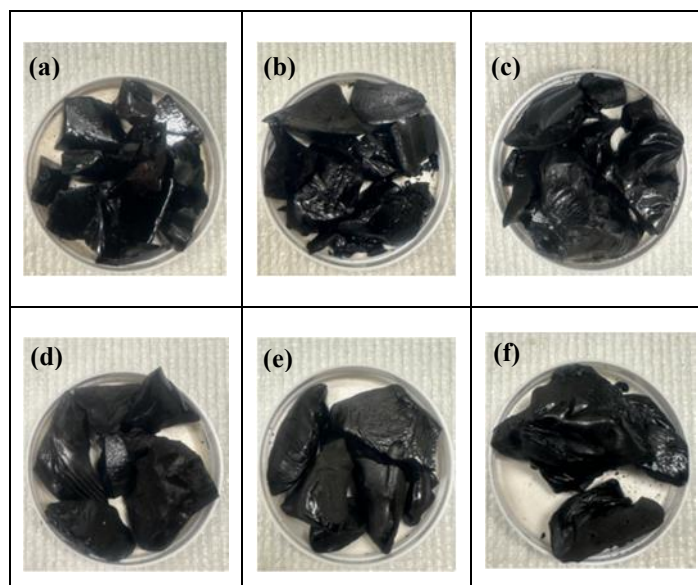


Figure 3. Bio-binder samples:(a) BP, (b) HBB-5 CPC, (c) HBB-10 CPC, (d) HBB-18 CPC, (e) HBB-25 CPC, and (f) HBB-30 CPC.

Figure 4 shows the mass loss of the samples after heat treatment (a), after baking (b), and the cumulative mass loss. It can be observed that the mass losses monotonically decrease as the fraction of CPC increases. This was expected, since the CPC does not contribute to the mass loss. However, compared to the BP, the mass loss of HBB-5 CPC after pyrolysis is slightly higher (Fig 4-a). This observation was unexpected. The same sample exhibits lower mass loss in the subsequent carbonization step (compared to BP) and its cumulative mass loss is slightly lower than that of BP (Fig. 5-c).

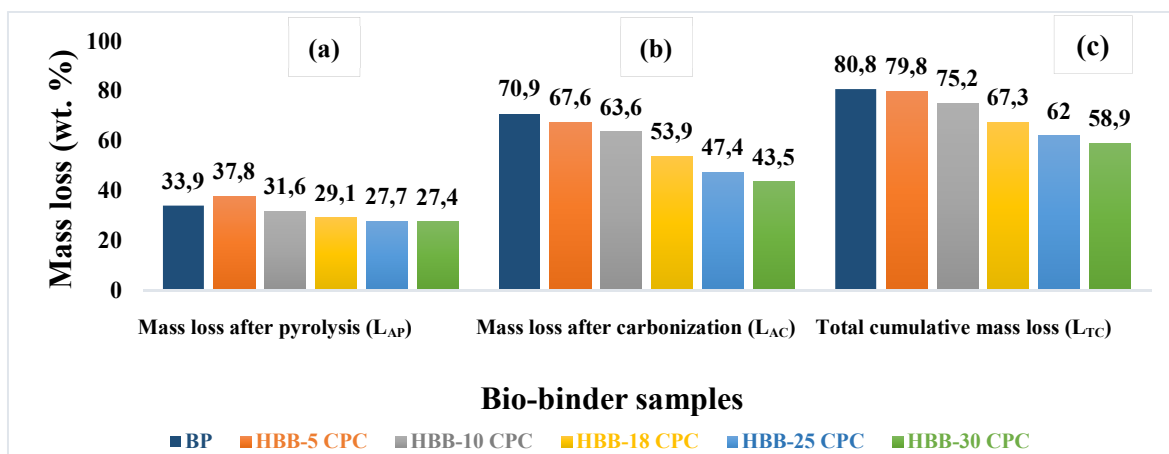


Figure 4. Mass loss of (a) bio-oil and bio-oil blend samples after heat treatment, (b) bio-binder samples after carbonization, and (c) cumulative of the samples.

We also plotted the CV values of BP, HBBs, and CTP samples with standard deviation as presented in Figure 5. It should be noted that this CV value corresponds to the mass loss after carbonization and not the total cumulative mass loss. A high CV was observed in all HBBs compared to BP, and HBB-30 CPC exhibited the highest CV. The CV of all bio-binders is still lower than that of CTP. A High CV greater than 45 wt.% is observed in HBB-18 CPC, HBB-25 CPC, and HBB-30 CPC samples.

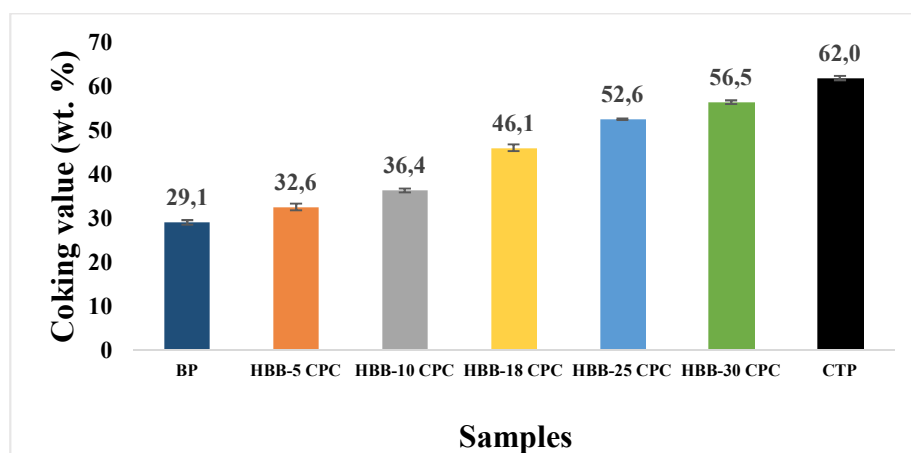


Figure 5. Coking value of bio-binder and CTP samples.

Assuming that there is no mass change of fine CPC in HBB compared to its mass after heat treatment (or before carbonization), one may expect that the corrected coking value of HBBs (which shows the coking value when the contribution of fine CPC is subtracted) be the same as that of the pure BP, i.e., 29.1 %. Surprisingly, we observe that this corrected coking value is systematically lower in HBB samples, indicating that the BP at the vicinity of CPC exhibits slightly higher mass loss during carbonization. This may be due to several factors including the fact that fine CPC may catalyze the BP gasification during carbonization (more details are discussed in Section 4).

The error of each measurement was estimated by considering three measurements of the CV per each sample. Type A and type B error analysis was applied to determine combined standard deviation of each measurement. According to the repeatability method in the ISO 6998:1997, the uncertainty error between the corrected coking values shouldn't be more than 1.0 % (mass).

According to the estimated errors in Table 4, the uncertainty errors for samples are within the acceptable limit.

Table 4. Corrected coking value (CCV) of bio-pitch alone in hybrid bio-binder.

| Samples | BP | HBB-5 CPC | HBB-10 CPC | HBB-18 CPC | HBB-25 CPC | HBB-30 CPC |
|------------|-------------|--------------|--------------|--------------|--------------|--------------|
| CCV (wt.%) | 29.1 ± 0.79 | 28.96 ± 0.84 | 27.92 ± 0.75 | 27.74 ± 0.79 | 28.25 ± 0.58 | 25.97 ± 0.92 |

The t-statistical test was carried out to determine the differences in CCV by estimating the p-value in Table 5. The difference in the CCV of BP and HBB-5 CPC is not statistically significant. The differences between the CCV of BP and HBB-10 CPC, BP and HBB-18 CPC, BP and HBB-25 CPC, BP and HBB-30 CPC are statistically significant.

Table 5. Statistical comparison of corrected coking value (CCV) between BP and HBB.

| Sample | BP and HBB-5 CPC | BP and HBB-10 CPC | BP and HBB-18 CPC | BP and HBB-25 CPC | BP and HBB-30 CPC |
|---------|------------------|-------------------|-------------------|-------------------|-------------------|
| p-value | 0.07 | 0.04 | 0.04 | 0.006 | 0 |

Figure 6 shows that BP and all HBB samples have softening point lower than that of CTP (110 °C). One may expect that by adding solid fine CPC in bio-pitch, its softening point increases monotonically. Interestingly, we observe a decrease of SP for HBB up to 18 wt.% of fine CPC addition. When the amount of fine CPC additive increased beyond 25 wt.%, the SP of HBB samples starts increasing to reach a value higher than that of BP, with a maximum of 80.5 °C for HBB-30 CPC, which is still much lower than 110 °C.

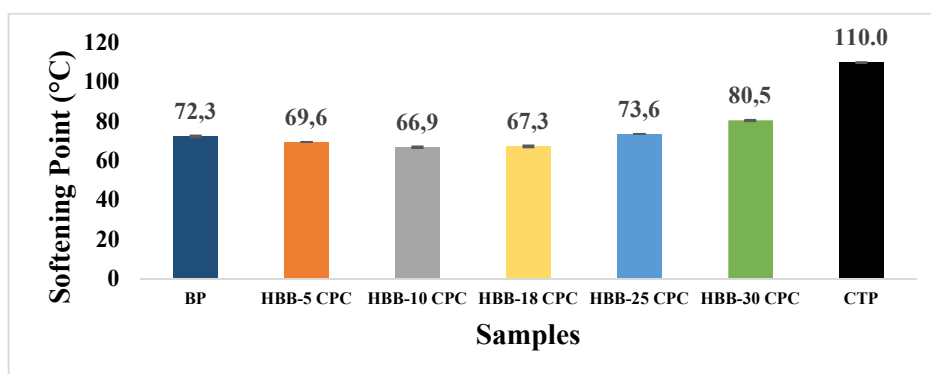


Figure 6. SP of bio-binder and CTP samples.

The viscosity of the samples is presented in Figure 7. Again, one may expect that the addition of solid fine CPC in bio-pitch increases its viscosity. However, we observe a decrease of viscosity from that of BP with increasing the amount of fine CPC from zero up to 10 wt.%. For example, at 145 °C, the viscosity decreases from 3.3 Pa.s for BP, to a minimum of 0.7 Pa.s for HBB-10 CPC. Beyond 10 wt.% of fine CPC, the viscosity starts to increase and at 25 wt.% fine CPC, the viscosity of the sample (2.6 Pa.s) is still lower than that of BP. The viscosity increased to 5.4 Pa.s for HBB-30 CPC and exceeded that of BP. To some extent, the same behavior was observed for other temperatures. The difference between the viscosity of the BP and the minimum viscosity of HBB is reduced as the temperature increases. The viscosity of CTP was higher than that of all other samples (BP and HBBs).

As we can observe in Figure 7, the viscosity of BP decreased significantly with the rise in temperature from 145 °C up to 178 °C. Compared to BP, the effect of temperature on viscosity for HBB containing 5 wt.% and wt.10 % fine CPC is much lower. For all HBBs, the viscosity slightly decreased with the increase in temperature from 145 °C up to 165 °C, and there was no significant reduction of viscosity between 165 °C and 178 °C. The viscosity of CTP decreased with an increase in temperature from 165 °C up to 178 °C.

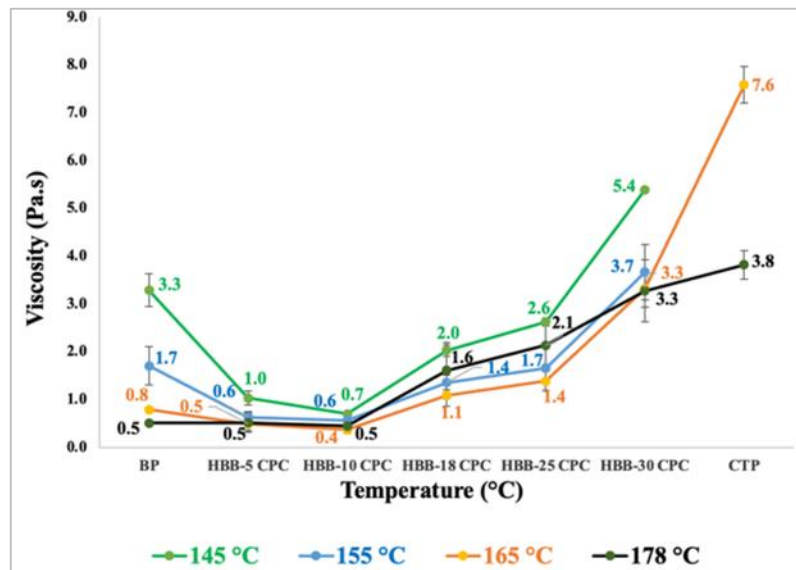


Figure 7. Viscosity of bio-binder and CTP samples at 145 °C, 155 °C, 165 °C and 178 °C.

The viscosity of HBBs, especially with a high amount of fine CPC, shows shear thinning behavior between 1 s⁻¹ and 10 s⁻¹ (Figure 8. Viscosity versus shear rate of samples at (a) 145 °C, (b) 155 °C, (c) 165 °C, and (d) 178 °C.). Beyond 10 s⁻¹, the viscosity remains constant with an increase in shear rate, demonstrating a Newtonian fluid behavior. The viscosity of CTP also shows shear thinning behavior in all shear rates at 165 °C and 178 °C. It should be emphasized that the viscosity of CTP at temperatures lower than 165 °C was not measured because of the expected high viscosity out of acceptable range.

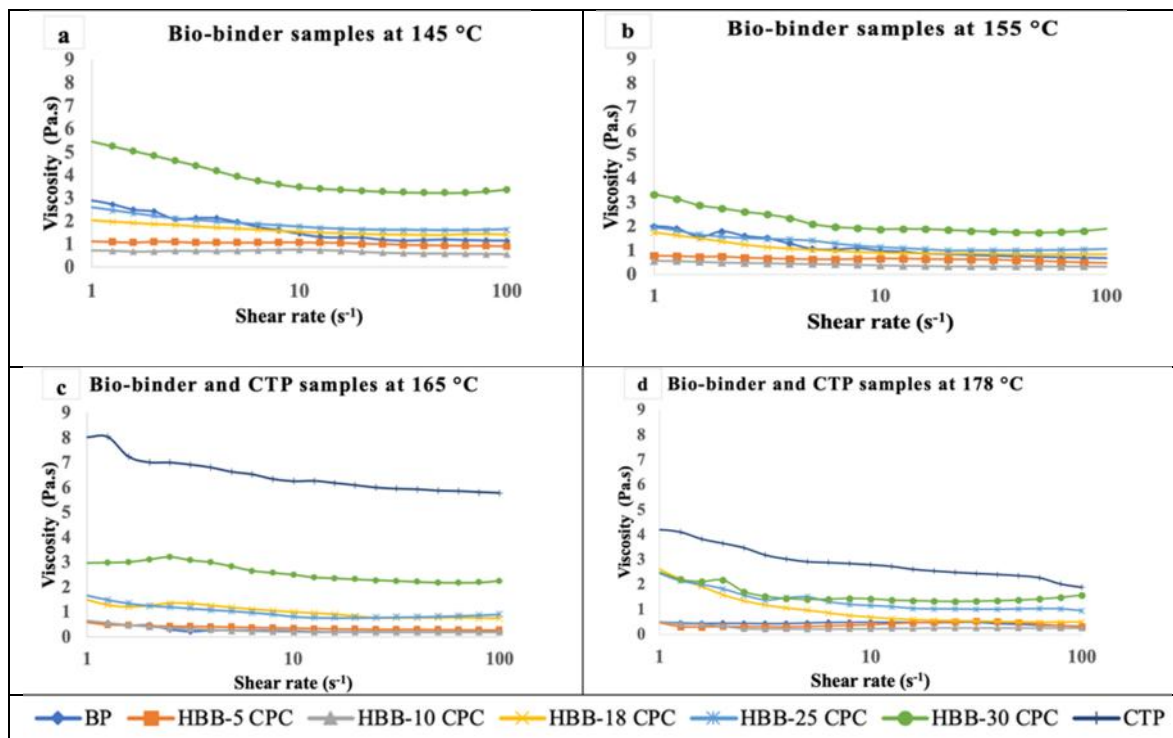


Figure 8. Viscosity versus shear rate of samples at (a) 145 °C, (b) 155 °C, (c) 165 °C, and (d) 178 °C.

4 Discussion

It was shown in Section 3 that the CV of all HBB samples is higher than that of the pure BP, but the corrected CV (the CV of BP alone) of all HBBs is lower than that of the pure BP. Compared to BP, the sticking behavior was observed on all HBB samples at room temperature, especially the HBB sample with fine CPC between (10-18) wt.%. Compared to BP, a low SP was observed on HBB samples with fine CPC between (5-18) wt.%. A low viscosity, for instance at 145 °C, was also observed for HBB samples with fine CPC fraction between (5-25) wt.%, compared to BP.

Since the introduction of fine CPC in bio-oil aimed to improve the coking value of HBB, a decrease in the corrected CV of BP was not expected. Furthermore, a linear increase of SP and viscosity with a fine CPC amount increase was also expected [25, 26]. The deviation of the obtained results from the expected results for HBB samples is possibly explained by the activation or functionalization phenomena occurring during the heat treatment of a bio-oil blend.

Activation refers to the creation of reactive sites on the carbon surface through the formation and development of the surface area, porosity, and functional groups [27, 28]. Activation is performed with the use of physical and chemical techniques in the presence of acid or basic medium [27, 28]. Activated carbons (AC) are defined by their high surface area (above 500 m²/g) which makes them interesting for industrial applications such as catalyst support or direct catalysts [27-30]. Referring to previous work, green petroleum coke can be oxy-cracked into activated coke in the presence of KOH at temperatures ranging between (170-230) °C [27, 31]. Sulfur and inorganic matter are released, which leads to the creation of active sites, new pores (mesopores and micropores), and reactive oxygenated functional groups [29, 31]. About half of the green petroleum particles had their size decrease after treatment with alkalis (KOH and NaOH); thus activated surface area was created [29]. The functional groups created, as reported in the literature, are carboxylic, carbonyl, phenolic, and sulfonic functions [31].

Functionalization refers to the application of organic linker molecules composed of oxygenated or amino functional groups on the surface of a carbonaceous material [32, 33]. The functionalization is done through oxidative chemical reactions whereby chemical bonds are formed between carbon and the functionalizing agents [32, 33]. As a result, oxygenated functional groups of carboxylic acids, ketones, alcohols, and ester groups are formed at the end of the oxidized structure [32]. The technique frequently used to functionalize carbon is to add an acidic solution such as HNO₃ and H₂SO₄ [32]. Both activation and functionalization mechanisms have similar effects on increasing surface area and creating pores and functional groups on the carbon structure.

Since bio-oil is acidic, it is hypothesized that it may activate or functionalize fine CPC during heat treatment. Thus, it introduces oxygenated functional groups on the surface of fine CPC. Fine CPC would react with bio-oil, lose some mass, and have active sites created on its surface because of the removal of carbon and sulfur atoms in the form of carbon oxides or sulfur oxides, respectively. The activated carbon is known to absorb moisture because of the presence of functional groups on its surface [29]. The reason for HBB sticking behavior may be due to the presence of heteroatoms (O, N, S) that may cause the increase of functional groups and moisture content in HBB through activation [27, 30]. A low corrected CV may be due to the fine CPC that catalyzes BP during carbonization, and this resulted in increased volatiles in the BP. This is when the computation of corrected CV based on the assumption that fine CPC mass remained constant. If carbon activation occurs, the lost mass could come partly from the fine CPC.

The lower SP of all HBB samples compared to CTP is due to the presence of BP with low SP. During activation, the fine CPC may adopt some amorphous structure on its surface, in addition

to the BP microstructure which is amorphous in its nature [23]. As a result, activated fine CPC would become compatible with reactive BP due to the amorphous [23] and hydrophilic [30, 32, 33] behavior shared. The more amorphous carbon becomes, the more reactive it gets [34] and the more the rate of changing from solid to liquid state occurs [34], which is a possible explanation for the reduction in SP with the addition of fine CPC. An alternative explanation stems from the moisture content present on the surface of activated fine CPC which may also change the structural and physical behavior of BP in HBB samples. Nevertheless, it is not known yet which one of the two possible explanations is more likely to cause the SP reduction.

The chemistry on the surface of bio-binders is different from that of CTP because it has O-containing functional groups. The viscosity of a heated HBB depends on the volume fraction of the solids and the arrangement of individual solid particles [35]. The low viscosity of HBB samples compared to BP may be explained by the fact that the fine CPC may react with the BP and thus change its rheological behavior [35]. When the solid amount in the binder is high, the shear layers that were initially aligned can be distorted and disoriented, thus viscosity increases [35, 36].

The fact that the bio-binders demonstrate lower SP and viscosity, a good wettability of the bio-binder on calcined coke is expected. This may permit HBB to flow smoothly between calcined coke surfaces and penetrate in calcined coke pores easily during the mixing to make anode paste. On the other side, it may be inconvenient for a very thin flow of the bio-binder when heated as this wouldn't permit it to make stable and strong bonds with calcined coke surfaces during mixing. It has been reported that a substantial increase in pitch (CTP) fluidity prevents adhesive forces between the binder and calcined coke [37].

To be able to select optimized HBB samples, it is needed to carry out wettability tests to study the interactions between each of the HBB and calcined coke while making anode paste. Since HBB is a new material and little has been reported in the literature on the relevant topic, the fine CPC contribution to HBB quality should be further investigated by defining the best and specific way to characterize its CV. This would be achieved by testing the activation of fine CPC particles through measurement of their specific surface area, pores size, and morphology to characterize their microstructure.

5 Conclusions

In the current work, bio-oil and bio-oil containing different fractions of fine CPC additive were heat treated into solid bio-pitch (BP) and hybrid bio-binder (HBB), respectively. The mass losses of bio-oil and bio-oil blends after heat treatment were characterized. The mass loss of HBB after carbonization, the coking value, the softening point, and the viscosity were also measured and compared with BP and CTP. The main conclusions are:

- Compared to BP, HBB exhibits lower mass loss both during heat treatment and after carbonization.
- The fine CPC of (5-30) wt.% in HBB samples increases the CV to (32.6-56.5) wt.%, compared to BP (which has a CV of 29.1 wt.%). The HBBs containing more than 18 wt.% fine CPC showed a CV greater than 45 %.
- All bio-binders have a lower CV, compared to CTP (which has a CV of 62 wt.%). The highest CV value obtained for HBB is about 9 % less than that of CTP.
- The softening point of HBB seems first to decrease by increasing fine CPC content up to 10 wt.%, then starts to increase. Compared to CTP, which has a SP of 110 °C, all bio-binders have lower SP.
- All bio-binders have a viscosity lower than that of CTP at all temperatures. The viscosity of HBB generally decreases below that of BP by increasing the fine CPC amount up to 10 wt.%

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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