Biocarbon in the Aluminium Industry: A Review

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Abstract

Reduced fossil carbon footprint is currently a hot topic in the metalproducing industries. Replacement of fossil carbon with bio based equivalents is thus an important topic also for the primary aluminium industry. Several challenges related to biocarbon have been discussed in the literature as the quality and performance of carbon materials made from bio based sources tend to be inferior to the fossil based materials, unless they undergo expensive treatments for adaptation to the aluminium industry. The most likely successful scenario appears to be a gradual introduction of biocarbon into the fossil based carbon materials already being used. Strategies being considered include replacement of the fossil binder material with a bio based binder as well as introducing small amounts of bio-coke in the production of carbon anodes and ramming paste. The current paper reviews research works on candidate bio based carbon materials in the aluminium industry. Sustainability of biocarbon with respect to availability is also discussed.

Introduction

The production of aluminium metal via the Hall-Héroult process leads to high CO_2 emissions. Apart from bauxite mining, alumina production, and power generation, it is estimated that about 2.2 tonnes of CO_2 equivalents per tonne of aluminium is emitted in the anode production, the electrolysis process, and the foundry. Theoretically, 1.22 t CO_2/t Al is related to the carbon consumption during the electrolysis process, as displayed by Reaction 1 [1].

$$\frac{1}{2}Al_2O_3 + \frac{3}{4}C = Al(l) + \frac{3}{4}CO_2$$
(1)

In practice, the CO₂ evolution in the electrolysis is about 1.5 t CO₂/t Al due to excess carbon consumption caused by loss in current efficiency, air burn, Boudouard reaction, and dusting. Data from the International Aluminium Institute (IAI) showed that ca. 64 million tonnes of aluminium was produced in 2019 [2]. This translates into ca. 140 million tonnes of CO₂ equivalent emissions from the production process with 98 million tonnes coming from the electrolysis process due to carbon consumption, as stated by Monsen et. al [1]. Currently, fossil carbon is the main form of carbon employed in the industry. The CO₂ emissions from the fossil carbon poses an environmental challenge to the aluminium industry, as CO₂ is a greenhouse gas responsible for global warming. This challenge is further highlighted by the commitment

made by industrialized countries to reduce their fossil CO_2 footprints through the Paris Agreement [3]. Thus, the aluminium companies are expected to decrease their CO_2 footprint to stay competitive.

As discussed in the literature, the use of bio based carbon can reduce fossil CO₂ emissions and the consequent global warming [1, 3, 4]. The reduction in emissions is explained by the fact that the CO₂ emitted by the bio based carbon material is at least partly balanced by the CO₂ absorbed during the growth period, thereby resulting in reduced CO₂ emissions [5]. Of course, this requires that the bio based carbon material source is renewable and sustainable to ensure that there is constant regeneration to take up the emitted CO₂. Beside the reduction in CO₂, it is also expected that the use of bio based carbon in making materials such as the carbon anode and ramming paste provides a green and clean alternative to the harmful substances emitted during the baking process, such as PAH (polyaromatic hydrocarbons) [6].

Different types of bio based carbon materials are currently being tried and tested in the aluminium industry. The most common are bio-pitch and charcoal. While there is no doubt that the use of biocarbon in the aluminium industry will reduce the CO_2 emissions, there exist some challenges. The most important obstacles relate to the technical performance of biomaterials during the electrolysis process, the availability, and the sustainability of the materials. The purpose of this paper is to discuss the introduction of bio based materials in the aluminium industry, including the challenges and possible solutions as well as the availability and sustainability of candidate materials.

Bio-pitch

Bio-pitch is derived from the bio-oil obtained from wood pyrolysis processes, such as charcoal production [7]. The bio-oil is obtained by condensing the volatiles released during slow pyrolysis, which typically occurs around 400-500 °C for eucalyptus wood [7-10] and up to 800 °C for sawdust briquettes from coniferous and deciduous wood [11]. The condensed volatile is collected and then separated into an aqueous fraction and an organic fraction, which is the biooil. The bio-oil component is about 7 wt% of the initial mass of wood and it is further distilled to separate it into different fractions. Bio-pitch is a distillation residue containing ca. 50 wt% of the initial bio-oil [7]. Figure 1 shows the bio based carbon materials that can be derived from wood pyrolysis and used in the aluminium industry.

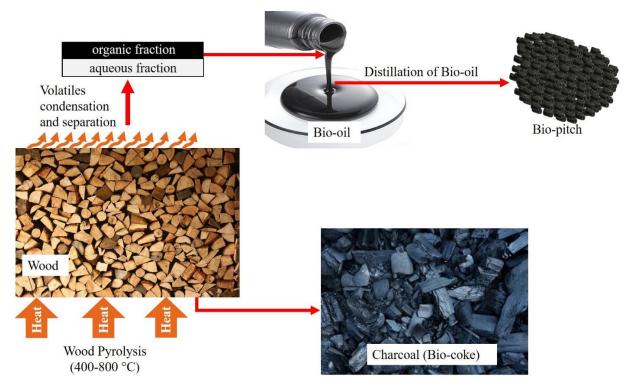


Fig.1 Basic flow chart for bio based carbon materials derived from wood pyrolysis.

As a result of high oxygen content, bio-oil is highly sensitive to heat treatment when compared to coal tar and petroleum, so the maximum temperature employed for the distillation of bio-oil to produce bio-pitch is kept around 270 °C as compared to ca. 360 °C for the fossil based coal tar and petroleum pitches [12]. Typical biomass sources for the production of bio-pitch include deciduous wood, coniferous wood, and eucalyptus [13]. It appears that the biomass source, as well as the distillation techniques employed to produce the bio-pitch, determines its properties [8, 13]. For example, the bio-pitch produced from deciduous wood sawdust has low toxicity and high graphitizability when compared to pitch produced from coniferous wood [13]. According to Pasa et al. [8]. the properties of bio-pitch derived from eucalyptus wood depend on the processes used for the recovery and particularly on the distillation conditions. It is, for example, reported that bio-pitches with different softening points can be produced depending on the final temperature and pressure during the distillation process. The distillation processes mentioned include steam distillation, vacuum distillation and flash distillation [8].

Like the coal tar pitch used in the aluminium industry, bio-pitch is characterized by such properties as softening point (SP), ash content, residual carbon or coking value, quinoline insoluble (QI), toluene insoluble, etc. Additionally, a property referred to as acetone insoluble (AI), which generally relates to the degree of polymerization, is also used [12]. In order to replace the fossil based coal tar pitch binder currently being used in the aluminium industry, it is very important that bio-pitch possesses similar or better properties than the coal tar pitch (CTP). CTP is the binder of choice for the industry, despite the harsh chemical environment (PAH generation) created during baking, because of its favourable physicochemical properties. A summary of important properties for the coal tar pitch used in the industry is given in Table 1

Table 1 Important properties of the coal tar pitch used for anode manufacture in the aluminium industry [14, 15].

Property	Typical range
Softening point Mettler [°C]	110-115
Quinoline insoluble [%]	4-16
Toluene insoluble [%]	26-36
Viscosity at 160 °C [mPas]	1200-4000
Real density in water [kg/dm ³]	1.30-1.33
Coking value [%]	56-62
Water content [%]	0.0-0.2
Fractionated distillation at 0-360 °C [%]	3-6
Elemental XRF:	
Sulfur (S) [%]	0.4-0.7
Sodium (Na) [ppm]	50-250
Zinc (Zn) [ppm]	100-500
Ash content [%]	0.1-0.3

Several techniques have been employed by various researchers to characterize bio-pitch. Techniques such as elemental analysis, infra-red (IR) spectroscopy, proton and carbon-13 nuclear magnetic resonance (¹³CNMR) in solutions and in solid state, high resolution size exclusion chromatography (HRSEC), gel permeation chromatography (GPC), softening point (SP), acetone insoluble content (AI) and residual carbon content (RC), rheological studies, scanning electron microscopy (SEM), etc. have been used [7, 10, 16, 17]. Results from some of these analyses suggest that bio-pitch is more oxygenated and less aromatic than their fossil pitch counterparts, presenting higher H/C and O/C ratios, which makes them more reactive [16]. Moreover, the chemical structures of bio-pitch differ from that of the coal tar pitch [7, 18]. Studies of the chemical structure of bio-pitch derived from eucalyptus wood suggest it constitutes mainly phenolic, guaiacyl and syringyl based

polymers (types of lignin), which have low aromaticity and high O/C atomic ratio as mentioned earlier. This is argued to result from lignin degradation during wood pyrolysis [7]. Studies of coal tar

pitch, on the other hand, show a chemical structure consisting of compounds of higher aromaticity and high H/C atomic ratios [18]. Figure 2 shows the chemical structures of the two pitch materials.

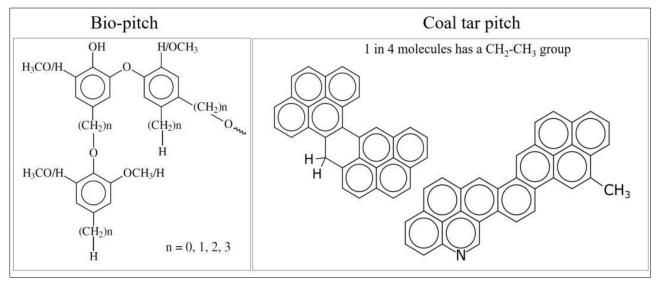


Fig. 2 Chemical structures of bio-pitch derived from eucalyptus wood and coal tar pitch [7, 18]

Furthermore, investigations by Prauchner et al. [16] showed that important properties such as softening point, degree of polymerization, viscosity and thermal stability were affected by heat treatment times and temperatures. This provides the opportunity to manipulate the properties of the bio-pitch to resemble that of the fossil based coal tar pitch currently being employed in the industry. Characteristics of the bio-pitch derived from coniferous wood sawdust (bio-pitch A), and deciduous wood sawdust (bio-pitch B), and coal tar pitch was analysed by Lis et al. [11], and the results are given in Table 2

Table 2 Characteristics of bio-pitch and coal tar pitch [11].

Property	Bio-pitch A	Bio-pitch B	Coal tar pitch			
Coking value [%]	28.7	33.7	54.1			
Softening point Mettler [°C]	82.9	83.8	103.3			
Quinoline insoluble [%]	0.4	0.4	6.3			
Ash content [%]	0.07	0.05	0.13			
Total PAH content [µg/g]	322	235	126298			

As stated earlier, the successful implementation of bio-pitch as a binder for traditional carbon materials employed in the aluminium industry will be determined by its technical suitability, which should be at least comparable with coal tar pitch. As discussed by Prauchner et al. [16], it is possible to adjust the important properties of bio-pitch such as viscosity, softening point and thermal stability to make it more applicable in manufacturing of carbon materials. The following section will highlight some of the investigations made to make bio-pitch applicable as a suitable binder in the aluminium industry.

Lu et al. [13, 19] studied the physical and chemical properties of bio-oil and bio-pitch that could be used as a binder for carbon anode production in the aluminium industry. Three bio-pitches were made by heat treatment of three different bio-oils derived from softwood (coniferous wood) and hardwood (deciduous wood) from different parts of Canada. Characterization techniques similar to the ones used by previous researchers [7, 10, 16, 17] were used to determine properties such as density, softening point, coking value, quinoline insoluble, molecular weight, viscosity, chemical groups, surface composition, and microstructures. Results from the analysis of the three bio-pitches (BP-1, BP-2, and BP-3) as compared to coal tar pitch (CTP) are summarized in Table 3.

Table 3 Properties of bio-pitch prepared, analysed and compared with coal tar pitch by Lu et al. [13].

Property	BP-1	BP-2	BP-3	CTP	
Yield [wt%]	70.8	57.9	48.7	NA	
Softening point Mettler [°C]	74.6	125.3	124.5	110.0	
Density helium [g/cm ³]	1.29	1.25	1.36	1.35	
Quinoline insoluble [wt%]	0.19	0.07	0.49	15.9	
Coking value [wt%]	39.43	35.27	45.30	65.24	
Molecular weight [g/mol]	517.6	515.9	554.3	126.5	
Viscosity [Pa·s]:					
166 °C	0.55	151.24	91.89	8.54	
178 °C	0.40	59.14	35.25	2.81	
190 °C	0.23	33.25	26.42	1.74	

Other results from the analysis by Lu et al. [13, 19] confirmed the bio-pitch as being more oxygenated and having more active chemical functional groups than coal tar pitch. It was argued by the researchers that this could influence the wettability between bio-pitch and the coke particles during anode manufacturing. Consequently, it is evident that more work needs to be done on the bio-pitch before it can replace the coal tar pitch, especially when considering the chemical functionality, coking value, softening point, wettability, and viscosity.

Hussein et al. [20], also from the same research group as Lu et al. [13], prepared bio-pitch samples by heating bio-oils supplied by a local producer. The bio-pitch samples were prepared by heating the bio-oil to three different temperatures (160 °C, 180 °C and 200 °C) at different heating rates (fast and slow heating rates) and soaking times. In addition to the usual characterization techniques used by previous researchers that has been mentioned already, Hussein et al. [20] analysed the wettability of calcined petroleum coke by the bio-pitch using a video-based optical contact angle measuring system. Results from their analysis showed that bio pitch could exhibit wettability values comparable to that of coal tar pitch. In agreement with the observation by Prauchner et al. [16], it was observed from the heat treatments that the softening points varied based on the temperatures and heating rates. The bio-pitch samples heated slowly to higher temperatures showed relatively higher softening points than the rest. This was proposed to result from lower molecular weight species having enough time to evaporate, leaving behind the higher molecular weights with a corresponding higher softening point. Lower softening point is said to be disadvantageous to the manufactured anode, as the binder is likely to exhibit viscoelastic behaviour at room temperature, affecting the mechanical stability of the formed anode. Higher softening point, on the other hand, is also detrimental, as the bio-pitch would not be able to melt and bind the coke particles homogeneously at the appropriate mixing temperatures. Furthermore, it was observed that heat treatment to higher temperatures at slower rates increased the coking value as well as the quinoline insoluble. These enhancements in coking value and quinoline insoluble were assumed to be due to polymerization reactions responsible for the precipitation of solid carbon. The coking value of bio-pitch is observed to be far lower than that of coal tar pitch, even for the heat-treated bio-pitch samples, and this is attributed to the high aromatic nature of coal tar pitch relative to the high concentration of aliphatic and oxygen-containing compounds. Low coking value has the detrimental effect of causing high porosity within the baked anode since most of the bio-pitch would disappear as volatiles during the carbonization process. Quinoline insoluble particles are assumed to play an important role during the carbonization process of coal tar pitch during anode baking, as they help in refining the carbon structure of the carbonized coal tar pitch [21]. This refined carbon structure can be assumed to contribute positively to the mechanical strength of the final carbon anode. Thus, it is important to investigate the effects of QI on the structure of the baked anode. However, not enough work has been done in this area [20].

Currently, one area where the use of bio-pitch could gain ground is the manufacture of the so-called clean or eco-friendly ramming paste, which is used as a sealant during the construction of the carbon cathode section of the electrolysis cells [6]. The shift to a more environmentally friendly ramming paste is mainly motivated by the PAH emissions in the pot rooms during the baking of the ramming paste before start-up of the electrolysis cells. Report from Allard et. al. [6] shows that these eco-friendly pastes do not affect regular operations in any harmful way. Molasses are mentioned as a possible source for the bio based binder for ramming paste. It is, however, stated that the use of such binders could result in harder and glass-like isotropic cokes [22].

Bio-Coke (Charcoal)

Bio-coke or charcoal is the product obtained after wood pyrolysis [7]. The motivation to use this material is the same as for the biopitch discussed in previous paragraphs, which is to use a renewable material with the potential of reducing the CO₂ footprint. Additionally, studies have shown that the bio-coke displays anisotropic and lamellar structures similar to that of petroleum coke [23]. Despite the advantage of being renewable and consequently contributing to a balanced CO₂ emission, the use of bio-cokes or charcoal as a raw material in the aluminium industry comes with certain challenges. Challenges relating to mechanical strength, CO₂ reactivity, porosity, density, electrochemical consumption, purity, etc. have been mentioned in the literature [1, 3, 4, 23]. The larger porosity of bio-coke (charcoal) relative to the petrol coke currently used in the industry is displayed in Figure 3 below. To gain more knowledge about bio-coke in order to deal with the challenges aforementioned, several studies have been conducted by various researchers over the years.

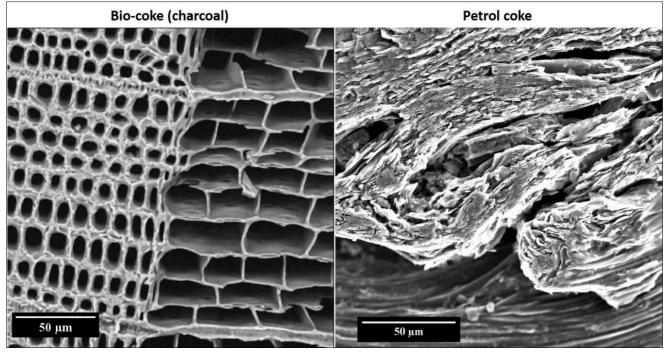


Fig.3 SEM images showing the microscopic structures of bio-coke (charcoal) and petrol coke [1].

Monsen et al. [1] studied charcoal made from three different wood types using microscopy and elemental analysis to analyse the porosity and purity levels. Pilot anodes were also made using coal tar pitch, petroleum coke and charcoal. The charcoal was used as a substitute for the coke fines. Results from their investigations showed that charcoal had considerably larger pores with some pores being around 45-60 µm. The pore size was also unaffected by the carbonization temperature. Charcoal from the different wood types was high in some elements (Si, Ca, Mg and K) but low in other elements (S, V and Ni) as compared to petrol coke. Analyses of the pilot anodes showed that the anodes with charcoal had lower density, poor mechanical strength, and higher CO₂ reactivity. The latter was attributed to the high K and low S content. Furthermore, it was observed that the open charcoal pores did not contribute to coal tar pitch impregnation during mixing. Based on the results from their tests, it was not recommended to use charcoal in anode production for the aluminium industry.

Huang et al. [23] employed optical and scanning electron microscopy to study the morphology and microstructure of charcoal samples made from leafy trees and softwood trees. The structure of charcoal was then compared to shot coke and petroleum coke. Results from their analysis showed that the porosities of the shot coke and petroleum coke samples were lower than those of bio-coke. They further observed some similarities in microstructures between that of the bio-coke and the petroleum coke, as both materials showed corrugated lamellae structure in contrast to the short coke that had a distorted lamellae structure. They assumed that the similarities between bio-coke and petroleum coke could provide an opportunity to use bio-coke for anode production. The large porosity of the bio-cokes was also suggested to grant access to pitch penetration during mixing, which is not supported by the work of Monsen et al. [1].

To explore further, Huang et al. [4] investigated the possibility of using bio-coke as part of the recipes in making the carbon anode for aluminium electrolysis. Bio-coke samples were made from raw wood chips that had been calcined at different temperatures and heating rates. Calcined petroleum coke was used as the reference coke material. Anode samples were manufactured using calcined petroleum coke, coal tar pitch and fine fractions of the bio-coke. The content of the bio-coke was kept at 1 %, 3 % and 5 %. The bio-cokes, as well as the anodes produced, were all characterized using relevant techniques. The outcome of the investigations showed that slow heating rate and higher calcination temperatures improved the real densities of the bio-coke samples. Anodes made from the usual petroleum coke and coal tar pitch combination mixed with a 3 % bio-coke showed promising results.

Hussein et al. [24] investigated the combined effect of heat treatment and acid washing on the properties and reactivity of charcoal using characterization techniques like helium density measurements, surface area analysis, XRD, and thermogravimetric analysis (TGA). The charcoal samples analysed were commercially made maple wood charcoal that had been washed with different concentrations of HCl before heat treating them to temperatures of about 1300 °C. Calcined petroleum coke was used as a reference for the analysis. Anodes made from coal tar pitch, petroleum coke and the pre-treated charcoal added as fines were also characterized using the techniques mentioned above. Results from their investigations showed improvements in the carbon structure of charcoal due to the elimination of structural defects and imperfections that occurs during the heat treatments. Furthermore, a reduction in the surface area of the charcoal was seen during the heat treatment, and this was explained as resulting from the micropore coalescence due to continuous growth of graphene sheets that occurs at elevated temperatures. CO₂ and air reactivity tests on the heat-treated charcoal samples showed improvements with increasing temperature of calcination. When comparing the CO2 and air reactivity performance of the heat-treated charcoal to

the calcined petroleum coke, it was found that the fossil based coke samples were superior. The poor performance of charcoal with respect to CO₂ and air reactivity was also attributed to the high contents of reaction catalysts like Ca, Na and Fe, but the low content of S is assumed to have a positive effect on CO₂ reactivity. Their observation revealed that heat treating the charcoal samples before the acid leaching led to poor performance with respect to the CO₂ and air reactivity. However, modifying the test method by introducing acid leaching before heat treatment led to better results, since most of the reaction catalysts were washed away during the acid leaching. It was also seen that the highest acid concentration gave the best removal of impurities, which also resulted in better CO2 and air reactivity test results. Pilot anodes made by substituting 5-10 % of the fine fraction of the petroleum coke with fine charcoal particles gave results comparable with the anodes made purely from the petroleum coke with no charcoal substitutes. Considering the results from their investigations, they recommended the possibility of substituting some of the petroleum coke with pretreated charcoal for anode production in the aluminium industry.

As a continuation of their previous work, Hussein et al. [25], investigated the properties of adding charcoal as part of the recipe together with calcined petroleum coke and coal tar pitch for carbon anodes to be used in the aluminium industry. For this investigation, the charcoal was pretreated by acid leaching with HCl before calcination at 1300 °C. Two sets of anodes with the pretreated charcoal added as a fine fraction was made, the overall content of the charcoal for the two anodes was kept at 5 % and 10 %, respectively. A reference anode with no added charcoal was also made. The team also investigated the effect of pitch content on anode properties using the anode sample with substituted with 10 % charcoal. Both the green and baked anodes of the three sets of anode samples were characterized by techniques including green and baked anode apparent density, specific electrical resistivity, and compressive strength. Results from the characterization methods showed decreasing performance with increasing content of charcoal on all the parameters studied. The lower green and baked anode apparent densities for the anode samples with charcoal in the recipe was attributed to the low bulk density of charcoal as compared to petroleum coke in addition to the high surface area relative to the calcined coke. The high surface area of charcoal was argued to affect the amount of pitch required for optimum coverage of the fine particles thereby affecting the viscosity of the binder matrix and consequently the compaction behaviour. The baked anode samples with charcoal in the recipe were observed to show poorer electrical and mechanical properties relative to the anodes with only calcined coke. Optimizing the pitch coverage by increasing the ratio of pitch to coke for the anode samples with 10 % total charcoal content resulted in anodes with higher green and baked densities, as well as electrical and mechanical properties comparable to that of the anodes with only calcined petroleum coke.

Sommerseth et al. [3] investigated the use of charcoal in anode production. The charcoal was made from larch and spruce wood and was calcined to 800 °C, and in some instances to 1200 and 1400 °C. It was then washed with sulfuric acid (H₂SO₄) before usage. Sulfuric acid was used as a washing medium to provide a source for sulfur, which is assumed to be positive for CO₂ reactivity. Different combinations of anode samples were made using charcoal (only as fines) and calcined petroleum coke as aggregates and a green binder and coal tar pitch as the binder. Two sets of reference anodes with one set made up of calcined petroleum coke and coal tar pitch and the other made of calcined petroleum coke and a green binder were also made. Techniques such as high resolution inductive coupled plasma mass spectrometry (ICP-MS), micro Xray computed tomography (µCT), Raman spectroscopy, BET and scanning electron microscopy (SEM) were used to characterize the charcoal. The different sets of anodes were also characterized according to the green and baked anode apparent density, specific electrical resistivity, CO2 reactivity and electrochemical consumption. Results from their studies showed that acid washing reduces the content of most elements, especially for the charcoal samples calcined at higher temperatures. Using H₂SO₄ increased the S content, as was expected. Charcoal samples from the two wood types were all shown by BET to have larger surface areas and pore volumes than the calcined petroleum coke. The surface area and pore volumes of the charcoal samples from the larch wood were also observed to decrease with increasing calcination temperatures. SEM images showed that crushing the charcoal to fines resulted in breaking the pore structures. The CO2 reactivity was observed to be lower for anode samples where the constituent charcoal had undergone higher heat treatment temperatures and washed in highly concentrated sulfuric acid. The reduction in CO₂ reactivity was attributed to the presence of sulfur introduced during the acidwashing. Increased heat treatment of the charcoal showed some improvement in the density; however, the density was still lower, and the specific electrical resistance higher relative to the calcined petroleum coke and coal tar pitch anode samples. They also observed better performance for anodes containing charcoal from larch relative to the ones from spruce. Finally, anodes made with the green binder showed higher CO₂ reactivity and electrochemical consumption as compared to those made with coal tar pitch.

Availability and Sustainability

It is argued that the sustainable use of bio based carbon materials contributes positively to reducing greenhouse gas emissions, specifically due to the CO₂ neutrality of biocarbon materials [5]. For the metallurgical and aluminium industry, the most realistic source of biomaterial right now is the forest. The wood, woodchips, etc. can be processed to provide the bio-coke and bio-pitch required to produce the bio based carbon material such as the anode. Analysis of the outlook of employing bio based materials in the metal producing industry was made by a group of experts in the area of biomaterials for the Norwegian process industry [26]. Data gathered from their analysis showed that the current forest reserves will not be enough to satisfy the needs of the process industry currently employing biomaterials such as wood chips etc. in a sustainable way. It is projected that the process industry currently using biomaterials, such as Elkem, will need up to 14-20 million m³ of biomaterials from the Norwegian forests up to 2050, however, the projections show that this need will create a deficit gap in excess of 5.5 million m³. Thus, it was suggested in the report to consider sustainable methods for the aluminium industry other than employing biomaterials. Actions such as carbon capture and storage/usage as well as the use of renewable energy sources were amongst the recommendations made.

Conclusions

The literature search has shown that there is a potential for biocarbon in the form of bio-pitch and bio-coke in the aluminium industry, thereby helping to reduce the fossil carbon footprint. However, there exist several challenges that need to be solved before successful implementation. Moreover, the availability of biomaterials that can be readily processed to provide bio-coke and bio-pitch such as wood, etc. are limited due to high demand from other industries. Thus, the aluminium industry needs to intensify research not only on biomaterials from the forest but from other sources. Finally, it is imperative for the industry to look into other strategies such as carbon capture and storage, inert anodes (for locations with renewable energy sources), as well as reducing their energy and carbon consumption by optimising their production processes.

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