Sustainable Metal Production – Use of Biocarbon and the Concern of Dusting

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Abstract. The silicon and ferroalloy industries in Norway have traditionally relied on fossil carbon products as reductants for their respective process. Efforts to reduce the fossil CO₂-emissions by introducing biocarbon has already begun, and targets of 25 to 40 % biocarbon use by 2030 have been set by various producers in Norway. An understanding of the effects of the physical properties of the carbon on the process must be obtained so that the transition can take place with minimal process interruptions.

It is well documented that charcoal is more friable than traditional fossil carbons, particularly during transportation and handling. Major issues related the fines generation are concerning material loss, effect of furnace performance, personal health and safety concerns by inhalation of particles, and possibility of dust explosions. The strength of unreacted material, the cold strength, can give good information about the dusting potential of a material, however many methods exist for these evaluations. In this work, an overview of the raised issues concerning dusting, and methods to evaluate cold strength in relation to dusting, are included, as is some relevant comparisons between charcoals and traditional carbon sources with respect to tumbling strength.

Keywords: Dusting, Biocarbon, Ferroalloys, CO2 emissions.

1 Introduction

The silicon and ferroalloy industries all use carbon materials when producing metal through carbothermic reduction processes in Submerged Arc Furnaces (SAFs). Historically, this carbon has come from fossil-based sources (coal, metallurgical coke, petroleum coke), except for some biocarbon used in ferrosilicon and silicon production. Approximate values of direct CO₂ emission from the processes are 0.9-1.3 kg CO₂/kg Mn-alloy and 5 kg CO₂/kg Si [1]. Replacing the traditional fossil carbons with biocarbons is thus desirable from an environmental point of view as these have a lower CO₂ footprint. Targets of 25 to 40 % biocarbon by 2030 have been set by various Si and ferroalloy producers within Norway [2, 3]. Good reviews looking into replacing fossil carbon with bio-based materials in metallurgical industries can be found in [4, 5].

It is well agreed upon that charcoal is more friable than fossil carbons [6], and the generation of fine particles result in several challenges for the industries to handle. The

carbon dust is mainly generated during transport, handling, and storage, as demonstrated in Brazil for the iron industry [7]. The total amount and the dust generated in different steps depends on the type of raw material (type of tree), process parameters during biocarbon production, and transport distance, which again may vary significantly when evaluating Norwegian, or other, metallurgical industries. The dust represents a direct material loss and besides the effect of dust in the furnace, obvious user problems concerning health and safety is of great importance if biocarbon is to be introduced to the processes.

In this work, the potential issues of dusting is described in more detail, and possible mitigation methods suggested. Furthermore, methods to evaluate the dusting, related to cold strength, are described and connected to the practical issues of evaluating new carbon material suitable for metallurgical processes. Finally, some experimental results evaluating traditional carbon materials and biocarbon with respect to dusting, using a tumble strength test is included.

2 Dusting Issues

2.1 Material Loss

Since the mechanical strength of traditional biocarbon products, like charcoal, is low, they generate a lot of fines during transport and handling. Hence, the potential for losses of carbon before the material reach the furnace is significant. In the breakdown from the iron-making industry in Brazil [7], fines could account for 25 % of the total produced biocarbon from the kiln to the iron blast furnace. Most of this, 86 %, was generated during loading and transport, storage, and screening (~21 % of the total carbon). Ideally, the fines should not be introduced into the furnace, and should be separated from what is introduced to the furnace. Some fines will also be lost during the transport and handling directly, as the very fine particles may easily become airborne.

Several mitigation possibilities to avoid the loss of carbon material though dust formation have been suggested. Most strategies aim to increase the strength of the material, thus making them more like the fossil carbon materials. This may be done by changing the production parameters during the biocarbon production directly (e.g., heating rate, temperature, pressure, gas atmosphere). Densification through briquetting and pelletizing may significantly reduce the losses caused by dust formation during transport and handling [4,5] by producing a less friable carbon material or by utilizing the unavoidable fines. Producing a hybrid coal-biomass blend [8] may also prove fruitful.

2.2 Furnace Performance

An understanding of the chemical, physical, electrical, and mechanical properties of biocarbon is important for understanding how to add this material to the SAF in order to produce metals. Carbon reductants are added with the metal ores from the top of the

furnace, gradually heated as they descend in the furnace. Liquid metal alloys are produced and tapped at the bottom, while gases ascend through the charge before being released mainly as CO and CO_2 off-gas. A stable furnace operation depends on an even gas flow through the bed, which requires good charge permeability. High mechanical strength is needed to ensure that the carbon bed does not collapse under the load, while high durability is wanted to minimize the amount of fines while handling and feeding the carbon into the furnace.

Fines are not suitable for furnace operation. Typically, the ferroalloy industry requires a particle size range of 5-40 mm. For instance, fossil fuel reductants with a size of 5-20 mm are used for silicomanganese alloy industries [9]. This size is required to ensure sufficient gas permeability in the charge, as smaller fines can reduce the permeability. However, considering that biocarbon have high reactivity, preferential consumption of smaller biocarbon fines (due to their high surface area) may result in some stabilization. Further issues may be related to fines being carried to the top of the furnace through the charge, and accumulating at the top or ending up in the gas cleaning system. This will lower the content of fixed carbon in the charge mixture which may disrupt the carbon balance of the furnace.

2.3 Personal Health and Safety

Dust in the smelters can have negative health consequences for the people who work there [10, 11]. The health and safety-efforts typically focus on dust control around the furnaces, essentially ignoring the raw material storage and handling. Little data exists on this problem with today's carbon materials, but the fines fraction from transport, storage and handling will increase when more charcoal is introduced. Instances where biocarbon has been used in metal production are known to result in layers of carbon dust covering every surface. This indicates how the charcoal is much more prone to dust formation by mechanical abrasion than coal and coke. It also shows how the carbon dust is easily dispersed into air and thus becomes distributed over large areas in the smelter. Thus, workers may be exposed to small biocarbon particles by inhalation and though skin contact. Proper safety measures are therefore required to mitigate the risks; however, little is known about the toxicity and exposure dangers related specifically to biocarbon.

Coal dust inhalation is known to potentially lead to the development of respiratory problems for coal miners. The risks are directly related to exposure levels, and similar problems may be identified for biocarbon in the future. The current recommendations for maximum coal dust exposure are 1 mg/m³ for a time weighted average of up to a 10-hour day [12], but such constant exposure may not be as relevant for the metallurgical industries.

The extent and selection of particles which ends up where in the body depend on various parameters, for example the particle size, aerodynamic conditions, hydration, solubility, and deposition efficiency. Many are caught in the upper airways and is mainly irritating; they may be expelled by sneezing, blowing the nose, and coughing. However, the very small particles may pass the thorax and enter the lungs, pass the

bronchi and enter the alveolar region from which some particles may be transferred into the bloodstream and/or affect the blood vessels themselves [13].

2.4 Dust Explosions

Besides the three elements needed for any fire (fuel, oxygen and ignition source), a dust explosion needs two additional elements: dispersion in air with right concentration, and confinement of the dust cloud (without the last one a flash fire may occur). The finer the particles are, the higher the surface energy and thus, the higher the risk of explosion. This definition holds true for any type of dust, while carbonaceous materials are also combustible fuels. Biocarbon is also known to self-heat and self-combust, making an actual ignition source unnecessary under certain conditions.

Under the above definition, dust explosions or flash fires already constitute a wellknown risk factor in the metallurgical plants. Biocarbon may introduce a higher risk of dust explosions both in and around the furnaces and related to storage, as they are more fragile. Activities that generate more dust, or disturb old dust, may result in the air dispersion needed to result in explosions. An explosion may disturb other dust in the surrounding area, creating again the conditions needed for another explosion, resulting in secondary and/or chain explosions that may be more violent than the initial blast.

Two of the parameters to be evaluated for any material to say if there is a risk of dust explosions are the critical dust concentration, as the minimum explosive concentration (MEC), and the ignitibility through the minimal ignition energy (MIE). These depend on particle size, size distribution, moisture content, particle shape, and, in the case of MIE, temperature. A summary of these parameters can be found elsewhere, e.g., in [14]. However, the current standards to evaluate MEC and MIE use standard conditions that may be less relevant for biocarbon in relation to furnace operation, especially due to the self-heating risks, high temperatures around the furnaces, and possible difference in atmosphere. No data regarding charcoal is found under standard conditions, while for coal the MIE has been shown to vary with its content of volatile components. Ranges between 30-100 mJ was confirmed for a coal with high volatiles, but higher values in the 1-10 J for a coal low in volatiles [15].

3 Evaluating Dusting Potential of a Carbon Material

The generation mechanism for dust and fines at room or low temperatures (such as transport, handling and storage) is mechanical/physical in nature. Therefore, the amount of dust and fines generated is strongly dependent on the mechanical strength of the material. High strength means low amounts of dust and fines, and vice versa. Mechanical strength can be investigated with multiple methods such as tumble/abrasion, drop and compression tests. The compression test is not suitable for estimating the dusting directly, but the cold strength measured by this method may indirectly be an indication of the possible fines generation. The other two tests may be used for dusting evaluation as they are directly related to how the material fractionates when the material is physically handled.

3.1 Cold Strength Methods

Tumble abrasion strength is the main method used to estimate the mechanical strength as it attempts to replicate the mechanical degradation that occurs when the material is transported and charged into the furnace. For this method a sample with a known particle size is placed in a steel drum and tumbled for a set time and speed. After tumbling the particle size is measured and the percentage of fines formed is used to estimate the mechanical strength. By including sufficiently small particle size in the distribution, the problematic fines and dust may be identified.

Another common test to determine the strength of untreated materials is the drop test. This is a simple test where the carbon material with a certain size fraction is dropped from a specified height onto a hard surface one or more times. No specific standards exist for this test, and the results depend on drop height, surface type and who is carrying out the test. The size fraction after dropping is measured. The strength is reported as either the size fraction over or under a certain set point. Depending on which number is reported, the amount of fines formed during handling can be estimated or the size fraction can be estimated.

In the case of the tumble abrasion test, the results are often reported as the tumble index (percentage over a certain size) and the abrasion index (percentage smaller than a certain size) after sieving after the test. ISO 3271 (Iron ores for blast furnace and direct reduction feedstocks — Determination of the tumble and abrasion indices [16]) defines these as wt% >6.3 mm and wt% <0.5 mm respectively, and a certain process or type of material may require set indices or changes in the limits. Similar evaluation may be done regarding the drop test.

Evaluations of the thermal abrasion strength, using the same type of tumbling test after a material have been partly reacted in a $CO:CO_2$ atmosphere, has been done in [17]. In this work, only fines below 3.33 mm after the reactivity test was evaluated, and while this may be relevant for fines and furnace perspective, it does not differentiate with the fraction that might more easily be airborne, or how the material may behave when unreacted. The results showed only minor differences in the thermal stability for the biocarbons tested (from eucalyptus wood and preserved wood) compared to the metallurgical cokes, however the initial size of the eucalyptus biocarbon was smaller than the other types of samples.

Currently, it may be difficult to define what size fractions might be relevant to investigate in relation to biocarbon dust and fines. The more traditionally considered fines from a furnace perspective has been reported in the 3-6 mm range, while smaller sizes of the particles are commonly evaluated with respect to optical or aerodynamic properties. The aerodynamic behaviour depends on the particle size, shape, and effective density. The term particular matter (PM) may be used to denote dust and fines, collectively. The term dust is used for airborne PM and/or PM which has been airborne at some point and then has settled on a surface.

3.2 Assessment of Procedures to Evaluate Biocarbon Dusting

As sieves are used to evaluate the PM dimensions in the tumble abrasion test and drop test, the connection to the actual aerodynamic properties remain unknown. Biocarbons are known to fragment into thin, possibly large flakes, which may easily be airborne even with a large diameter. Using the 0.5 mm size as a lower limit in the tumble abrasion test, as defined by the ISO standard [16] might be a very good indicator as it will likely include the sizes that are likely to cause the different issues described previously in this paper.

Use of biocarbon may result in adjustments of the physical properties of the carbon reduction materials needed for the furnace operation. Some of the current tests with defined parameters and procedures may need to be changed, and restrictions on what to use, dependent on the results, may need to be re-evaluated. For the use of biocarbon, certain mitigation strategies like pre-calcination (to get rid of volatiles, which may result in a less ignitable material [15]), or having a somewhat wet material (to increase the weight and make the possible dust formed less likely to disperse and spread) may be included in the tests.

For biocarbon it will also be necessary to change the limits due to the likely shapes of the new materials as well, as biocarbon from woodchips may be long and narrow, as such the start material will in large amounts go through e.g., a sieve of 6.3 mm. Including and reporting more fractions may also be relevant to best evaluate fines and dust, e.g., a fraction around 3 mm (like in [17]) or the commonly mentioned 5 mm [9], together with 0.5 mm may be a way to evaluate a material.

4 Experimental Evaluation of Dusting on Carbon Materials

Tumble abrasion strength was evaluated for several carbon materials in a lab setting using a Hanover drum. The carbon material was placed in the steel drum measuring 30 cm in diameter that contained 4 raisers spaced 90 degrees apart. The sample was tumbled for a total of 30 minutes at 40 rpm. This lab test is traditionally run with materials that start with size above 6.7 mm, with 50-100 g sample size. However, as the amount of some biocarbon material was limited (produced in lab settings), most tests were run with ca. 20 g. After the test, the material was sieved in six different fractions (+6.7 mm, +4.75 mm, +3.35 mm, +1.25 mm, +0.5 mm, and -0.5 mm, the smallest sieve was only included in some of the measurements).

4.1 Reference Materials

Traditional metallurgical coke (MC) and industrial charcoal (CC) are used as reference materials. As the lab test is designed for larger sample sizes, some initial tests were done with different sample sizes to evaluate if this parameter would have an effect. No large effect was observed on charcoal when using 50, 25 and 20 g sample size, or on metallurgical coke using 50 and 20 g, however the smallest sample size did appear to have a bit higher dusting for both materials. The main results are presented in Fig. 1, with only the smallest sample size included the 0.5 mm sieve. It can be observed that

almost all the fraction that is below 1.25 mm is also below 0.5 mm, and the numbers when only 1.25 mm is included should also be quite representative for the dust <0.5 mm in these instances.

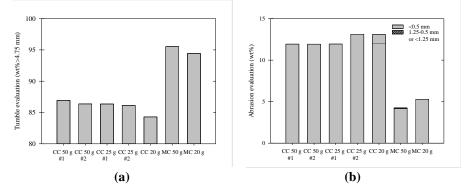


Fig. 1. The results after the tumble abrasion strength test of an industrial charcoal (CC) and a metallurgical coke (MC), evaluating different samples sized. (a) Tumble evaluation, defined here as >4.75 mm, and (b) the abrasion evaluation, in this case <1.25 mm and/or 0.5 mm.

The results confirm what is already known, the charcoal samples have significantly higher tendencies of generating dust than the traditional metallurgical cokes. While the charcoal has values in the 10-15 % range when evaluating the 0.5 mm fraction, the metallurgical coke is ~5 %. With respect to evaluating dusting for new materials, production parameters or pre-treatments that result in lower dust generation is favourable, however, processes and furnaces that previously did not accept materials with an abrasion index >6 wt% may need to re-evaluate their limits.

4.2 Biocarbon Produced from Woodchips and Steam Exploded Pellets

New biocarbon materials was produced in a laboratory setup by using a pyrolysis apparatus comprising of a vertical tubular fixed bed reactor, a condenser, and a gas monitoring system (more details on setup in [18], pyrolysis done in a similar way by Liang Wang, SINTEF Energy Research). The samples to be pyrolyzed were woodchips of Norwegian spruce or birch, and a type of steam exploded pellet.

It was demonstrated that the biocarbon materials produced this way had less dust generated compared to the industrial charcoal, independently of changing pyrolysis temperature, purge gas, and doing the pyrolysis with or without a lid. Biocarbons pyrolyzed at 500 °C without purge gas are presented with the reference materials in Fig. 2, showing all the fractions included after the tumbling test.

The results show that the new biocarbon materials are quite like the metallurgical coke when only evaluating the fraction <0.5 mm. However, the woodchips-based materials generated more particles in the 0.5-4.75 mm range, resulting in similar values as the charcoal when including these in the evaluation of fines and dust. Due to the shape of the start materials, anything larger than 4.75 mm may not be a result of fragmentation in the test, and should ideally be evaluated together (as in Fig. 1a). This

is the case for the steam exploded pellets, as these started with a diameter size smaller than the 6.7 mm sieve, and, as such, it appears that all the material has fragmented. The woodchip-based materials are more likely to break apart than just generate the very small dust, while the steam exploded pellet did not as easily break apart this way.

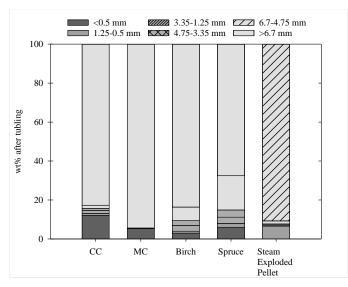


Fig. 2. The fractions after the tumble abrasion strength test of an industrial charcoal (CC), metallurgical coke (MC), and biocarbons produced at pyrolysis temperature of 500 °C using birch woodchips, spruce woodchips and steam exploded pellets.

Compared to the industrial charcoal, the lab-process produced materials with small dust generation closer to the more ideal carbon materials, but improvements can be made concerning the way the material hold together (more directly related to strength) making less of the fines that may make issues in the furnace. The steam exploded pellet showed the overall best behaviour, with retaining most of its original size (4.75-6.7 mm diameter) and generated the least amount of dust. The pelletizing process might be a good way to improve the strength and dust generation compared to other biocarbons.

5 Mitigation Strategies and Knowledge Needs

Strategies towards producing biocarbons with similar properties more similar to the fossil carbons aims to increase the strength of the material. As dust generation is related to the physical properties, products with higher strength will as such limit the issues described. Production of denser biocarbons through change in pyrolysis parameters, briquetting, pelletizing, or produce hybrid materials are considered promising, but using these types of materials may still result in more dust being generated compared to current materials. As such, other mitigation strategies to reduce the risks related to dust may still be considered.

Mitigation strategies that may reduce the issues related to health and safety in the furnace is related to keeping the dust levels on surfaces and in the air as low as possible. This may be done by design, by minimizing the amount of flat, horizontal surfaces, and have surfaces with smooth instead of rough finishes. Other goes more towards cleaning procedures, e.g., by use of approved vacuum cleaners instead of brooms and sweepers to collect the dust at regular intervals.

To choose the best mitigation strategies more knowledge is needed regarding biocarbon related to the use in metallurgical industry. More knowledge on how biocarbon dust may be distributed in air and settle in the room when is physically handled is needed. This, and knowing what effect biocarbon dust may have on the human body, may help establish exposure limits for workers. More understanding on how biocarbons may self-ignite, and the parameters related to dust explosions when evaluating the conditions at the furnace like temperature and atmosphere, is also needed. Finally, as the mechanical, chemical, physical, and electrical properties of biocarbons may be significantly different from traditional materials, the effect and tolerance of fines in the furnace may be very different from fines from fossil fuels, and knowledge of this specifically is needed to best understand how to introduce biocarbon in metallurgical processes.

6 Conclusions

All current knowledge regarding biocarbon materials and dust generation indicates that this may be problematic when introducing this new material to obtain more sustainable metal production processes. Large amount of material may be lost in transport and handling, dust can create health and safety hazards and affect the furnace operation. Biocarbon dust has a tendency to form small particles that is easily airborne. However, many of the different issues identified can be solved by the same mitigation strategy, mainly producing a stronger, more dense biocarbon material.

The tumble abrasion strength test used on biocarbons produced in lab scale from woodchips showed some improvement on the dusting characteristics compared to industrial charcoal. While the industrial charcoal had wt% <0.5 mm value between 11-13 %, the produced biocarbons had values in the 3-7 % range depending on the production parameters. This is in the same range as the metallurgical coke investigated, which was around 5 %, but the biocarbon materials from woodchips broke more easily apart during the test producing fines which may be problematic in the furnace. The pyrolyzed steam exploded pellets investigated in this work had the overall best performance of the biocarbons produced in the lab.

Some documentation regarding the dusting problems related to transport and handling of biocarbon exists, however, more understanding on how the dust will affect the furnace operations are still needed. Although the tumble abrasion test might be useful to evaluate dusting, it is also a need to evaluate under what conditions this test is best run, and what limits the different processes may need, when considering biocarbon. Acknowledgements. This research was funded by Research Council of Norway grants 294679 (BioCarbUp), 336309 (BioCarbUpgrade), and 280968 (Reduced CO2).

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