UTILIZATION OF BIOMASS IN IRONMAKING

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Abstract

Utilization of biomass as a carbon neutral is an attractive for ironmaking, so many different ways of its usage should be tried to mitigate CO₂ emissions. Wooden biomass content from 1 to 5% was used in laboratory coking furnaces as a possible renewable source of carbon instead of high volatile coal. Sawdust, crushed corn, bark and charcoal were evaluated in laboratory sinter pot device as a possible replacement of ordinary fine coke in sinter mixture. Total fuel amount was changed from 10 to 40% in individual charges. Sintering time was shortened; productivity grew up, amount of returned sinter decreased. Replacement of fine coke by biomass is advantageous while quality parameters of produced sinter were not significantly deteriorated.

Key words: biomass, carbon dioxide, coke, sinter

1. BIOMASS POTENTIAL FOR IRONMAKING

Greenhouse gases (GHG), especially carbon dioxide (CO₂), methane (CH₄) and human activity leads to increases emissions and subsequently causes global warming. Carbon footprints are defined as sum of GHG emission caused by organization, event, product or person [1]. Steel sector is responsible for max.10% of global GHG emissions if indirect emissions are taken into account. The most common way to reduce the carbon footprint is to reduce, reuse and recycling. Therefore biomass is one of promising sources for metallurgy, too. Sintered ore produced about 0.2 tonnes of CO₂ per tonne of product. Coking produced 0.5-0.3 tonnes of CO₂ per tonne of product [2]. The steel industry in Brazil where are large deposits of high quality iron ore and present an interesting feature, which is the existence of a charcoal based pig iron production. There are 85 companies, which operate more than 160 mini blast furnaces (MBF) using renewable green energy instead of fossil fuels (coke/coal dust). Charcoal fines are injected into coke based Blast Furnace (BF) tuyere, charcoal is used as a part of burden, as well as “charcoal pig iron” into EAF and BOF’s. For this type of charcoal utilization it is needed to perform additional studies concerning the phenomena involving the ashes and unburned char in the raceway, necessity for innovations in the design of tuyeres, effect of volatile matter on combustion efficiency [3]. MBS basically produces export oriented merchant pig iron [4]. The charcoal based MBS presents some peculiarities like usual inner volume lower than 350m³, usage of small fractions of lump hematite type ores and char coal as reductant. The installed capacity of the independent producers is about 15 million tons of pig iron. The MBS produced 5.8 million tons in 2010 year, world crisis hit hard this iron sector and now it is slowly recovering. The excellent tropical climate, with high rainfall and daily sunlight ensures Brazil the greatest world competitiveness of planed eucalyptus forests. It takes 2.5m³ of charcoal consumption for one of ton pig iron [5]. Carbon in integrated iron and steel production is necessary in the reduction of magnetite or hematite type iron ores. Reduction process is well described in [6,7,8] First, hematite (Fe₂O₃) is reduced by carbon monoxide (CO) to magnetite (Fe₃O₄ or Fe₃O₄,FeO). Magnetite is than reduced by carbon monoxide to wüstite (FeO or Fe₁₋ₓO). Finally wüstite is reduced by carbon monoxide to metallic iron (Fe). In each step CO₂ is also a reductant product. The energy in the blast furnace process comes from the partial coke combustion or coal fuel injected at tuyere. These produced carbon monoxide 2C(s) +O₂ (g) = 2CO (g) + energy. Decreasing the energy intensity of the process is an approach, which could decrease carbon footprint of the process. Alternative is to use renewable and carbon neutral fuels like biomass. Co-firing is simply the blending of dissimlar fuels,
with one being the dominant (coal, coke) and the other being supplement. There is wide variation in properties for the operator. Important is chemical composition, ash, halogen content, reactivity, kinetic of volatile evolution [9].

1.1 Biomass Properties

Biomass is considered as renewable because of the fast cycle of 5 -10 years, this type of cycle however can be achieved in tropical forest. CO₂ is regenerated to C by photosynthesis. Plants, algae and some bacteria and photosynthesis when CO₂ is absorbed from the atmosphere, and in the presence of sunlight and water, they produce glucose (C₆H₁₂O₆), which is a simple sugar. The sugar or carbohydrate is later consumed during respiration. The simplest method to convert biomass into energy is combustion. Combustion of cellulose (C₆H₁₀O₅) is typical for wood. CO₂ and H₂O are the products at complete combustion, and CO and H₂ are the products at incomplete combustion. The off gas contains devolatilized matter from biomass. At higher temperatures the volatiles or char react with oxygen to produce CO₂ and CO. Gasification process takes place above 590°C when energy from combustion is used to drive endothermic reactions that produce CO, CO₂, CH₄ and H₂. Gasification is a multicomponent system with both endo/exo reactions [10]. Pyrolysis is drying of biomass heated above an ambient temperature in an oxygen deficient atmosphere. Temperature of biomass pyrolysis influence contain of inorganic materials, unconverted organics, carbon residues in the char. Torrefaction is a thermal treatment of biomass at low temperature (200-300°C) in an oxygen free atmosphere. Biomass and coal have fundamentally different fuel properties. For instance, biomass is a more volatile fuel and has higher oxygen content than coal. In general, biomass contains less sulfur than coal, which translates into lower sulfur emissions as higher blending ratios of biomass are used. Wood fuels generally contain very little ash (1% or less); consequently, increasing the ratio of wood in biomass/coal blends can reduce the amount of ash that needs to be disposed. A negative aspect of biomass (especially some grasses and straws) is that it can contain more reactive potassium and chlorine than coal. Higher fuel chlorine contents can lead to greater high temperature corrosion in devices.

1.2 History of Biomass in Ironmaking

Biomass has to be pretreated before its utilization in ironmaking process, replacing coke and natural gas as a fuel in blast furnace and replacing coke as a fuel in sintering and pelletizing [11]. Utilization of biomass in converters as a replacement of coke for providing extra heat to process if needed would be good regarding content of sulphur. Char coals in blast furnace (200m³) were known in the past in Sweden (Domnarvfet), Rusia (Serovky zavod Ural) and Canada. 1 ton of char coal generates 200-400m³ of distilling gas and 7-8% of distilling products (tar). Reducing ability of char coal is higher than coke; direct reduction at char starts at 750°C. Sulphur content in char is very low. Porous char is burning faster; optimal temperature of wind was about 250°C, off gas contains more methanol (1.5%) and hydrogen (7-8%). The same quantity of char has 3-5.5 times greater volume than coke has. Smelting intensity char furnace was 1.5-1.75 times higher [12]. Carbonized biomass manifest similar characteristic to foundry coke in its composition. Biocoke from selected woody residues and shells possesses even better properties: lower ash, higher carbon content and heating value. The best produced biocoke resulted from coconut shells [13].

2. EXPERIMENTS WITH BIOMASS

Optimum biomass usage as a fine coke replacement in coal blend and sinter mixture has been studied for reducing carbon dioxide emission. Biomass was selected based on easy availability and/or replacement of
different seasonal sources without additional costs for biomass treatment. Biomass usage in the steel industry features bulk handling and the use of existing infrastructure or creating a new one. Though various studies have been conducted on woody biomass recycling, basic experimental data is still insufficient. The low density and difficult gathering of woody biomass have limited its recycling. Optimization of carbonization conditions of biomass studies showed that the weight of biomass decrease remarkably at about 300°C, which is the temperature level of cellulose decomposition in biomass. The biomass weight during carbonization noticeably decreases. At 35°C the decomposition of lignin starts and during lignin decomposition, H₂O, CO₂ and CH₄ gases are generated [14]. Crushability, dustiness, combustion and shrinkage of biomass are the challenges for operational application.

2.1 Biomass in Coal Mixture for Coke Production
Replacing the small portion 1-5% of the coal blend without significantly affecting the mechanical strength of coke was the idea for starting the series of laboratory tests. As a source of biomass were used: wooden oak tree pellets (caloric value 17.6MJ/kg), grinded wooden oak tree pellets below 3mm, RDF (refuse derived fuel) pellets (caloric value 11MJ/kg), charcoal (caloric value 25MJ/kg), and textile fiber (caloric value 32MJ/kg). The laboratory coking furnace Sole Heated Oven (SHO) ASTM D2014-97 with chamber width 280mm, length 610mm and depth 280mm (sample volume 13kg) with applied force to top 15.2kPa monitored expansion/contraction during 8 hours of heating. Movable Wall Oven (MWO) with chamber width 450mm, sample volume 300kg, coking time 18 hours, coal blend bulk density 790kg/m³. Coal blend (83% under 3mm grain size) was mixed with each biomass and tested in both SHO and MWO furnaces. The carbonizing was carried out in laboratory coking furnaces at 1250°C with heating rate of approx. 8.5°C/min. High volatile coal was replaced from 1-5% in coal blend. Obtained results were compared with base case trial without biomass addition. This set of 12 tests shows that usage of biomass in coal blend is technically possible. Biomass addition significantly changed the coal blend properties like coal blend contraction, fluidity, and dilatation, swelling index, bulk density and sulphur content. 5% of biomass addition deteriorates the coke quality significantly. 1% biomass addition deteriorates the coke quality acceptably. CSR/CRI is more sensitive to biomass addition as coke cold strength test. Textile fibers from tyre addition decrease bulk density, CSR and productivity. Questions for the next research are to determine suitable grain size for coal blend using addition of biomass, increase of bulk density of coal blend, find the mechanism of coke structure forming when using biomass [15].

2.2 Biomass in Sinter Production
Sintering is a thermal method agglomeration, in which materials are heated to the temperature at which they are softened and partially melt, which causes the grains packing to fuse. Sintering product is a polycrystalline material, whose grains are mutually bonded. Chemical transformation takes place during sintering. The initial sintering stage takes place without the participation of liquid phase; at temperature rising (100°C) sintering is accelerated due to silicate alloys that originated. Sintering of fine iron ores is related to phase transformation; initial phases differ from final ones. This is accompanied with changes in bonds between elements of these phases in the phase structure and packing. Sintering is a heterogeneous process during which the boundaries between the phases originate, translocate and disappear [16, 17]. Replacing part of coke by char put into structure more volatile matters.

2.3 Methodology for Biomass Usage in Sintering
A laboratory sinter pot device with the volume of 250kg and suction area of 0.25m² was used for carrying out a series of 25 experiments. The height of the sinter mixture layer simulating operating conditions at U. S. Steel Košice was 400mm. The equipment allowed changing the under-pressure up to the value of 10kPa. Biomass was added into the currently used sinter charge consisting of sinter ores, iron concentrate, limestone, and dolomite, some portion of recycled materials, fine coke and biomass as replacement for part
of fine coke. Crushed bark of fir and spruce tree wood, sawdust of oak and beech trees, crushed corn cobs and crushed charcoal were used as biomass sources. All types of biomass were crushed before use in order to obtain the same grain size as was the grain size of fine coke. Charcoal handling was difficult, it was necessary to wet it, given the high dustiness. 3% of total fuel was used in the sinter mixture total and it was gradually substituted with four types of biomass in the volume of 10, 20, 30 and 40%. Standard sintering was applied as the reference test, using only fine coke as a fuel. Measurements of particulate matters and combustion products composition were carried out during sintering processes. The purpose was to find out: (1) whether it is possible to substitute fine coke with biomass, (2) which biomass is optimal as substitute for fuel, (3) what will be the quality of produced sinter, including its (4) structure and (5) phase composition change. X-ray phase analysis was used to evaluate the phase composition of individual sinter fractions (+40; +25; +16; +10; +5mm) after physical testing. Structural changes were evaluated from polished samples using optical microscope and from fracture surfaces areas using scanning electron microscope. The same sintering conditions were ensured during sintering tests and charges were made with a constant fuel value. Evaluations were made according to ISO8263 1992 “Method for presentation of the results of sintering tests” to be able to compare our results with other testing equipments. It results from interdependencies plotted in Fig. 1 that after gradual addition of any biomass (within the experiment range) the apparent density of charges decreased for all charges. This in turn had an influence on sintering speed increase as well as on increase of productivity. Yield of sinter made even with 40% addition of charcoal did not decrease [20].

![Fig. 1 Bulk density, sintering time, and yield trends during laboratory sintering tests [20]](image)

Produced sinter quality changed differently with application of different biomass types. Tumbler index (TI) did not decrease up to 20% of used biomass, in case of charcoal TI did not change significantly even at 40%. Abrasion index (AI) did not decrease up to 20%, beyond this limit it decreased significantly for all biomass types. Return sinter amount of up to 20% was also acceptable; it changed under the value 20% for selected laboratory sintering conditions. Produced sinter reducibility at charcoal showed the slightest change in reducibility decrease. 10% addition of each biomass decreased only slightly the reduction properties of produced sinter. Laboratory experiment measurement results showed that charcoal was the most suitable substitute for coke dust with the least influence on produced sinter quality. Other biomass types can also be used, but they should be applied with different optimal biomass amount. In case of charcoal it was up to 20% of substitution for coke dust, for other biomass materials it was up to 10%. An interesting benefit was achieved in terms of reduced CO₂ and the results of experiments were considered to be promising [21]. Laboratory tests showed possible 2.29kg CO₂ reduction per 250kg sinter charge.
2.4 Sinter Structure Change with Biomass

Representative samples of “biomass” sinter from each grain size fractions were examined microscopically and using x-ray diffraction technique. The structure of standard sinters, especially when containing high flux additions and many different materials is very complex. Sinter is generally composed of four main phases: iron oxides (from 40 to 70vol%), ferrites (from 20 to 50vol%) most of which are complex silico-ferrite of calcium and aluminum (SCFA), glasses (up to 10vol%) and dicalcium silicate (up to 10vol%). Sinters have the potential to be quite variable in their composition. Due to different origins of the iron-ore-bearing components different chemical, mineralogical and thermal properties the sinter melts forms in different temperature intervals [18,19]. Scanning electron microscope showed the specific mechanism of biomass volatile matters components behavior and influence on the sinter structure. "Biomass" sinter had the same basicity 2, the same value of C total and has been prepared at the same sintering conditions. Fuel in the form of biomass contains more volatile matters and formed ash partly differs from coke ash. This was manifested in the structure of sinters by increased porosity and cracking. NaCl and KCl were observed in vicinity of pores in the form of complex compound SFCA. The main factors that determined the mineralogical composition and metallurgical properties of sinter was the volume and melt composition in the solid-fuel combustion zone, the rate of cooling of the sinter and the oxidation potential of the gas phase (CO₂/CO) or FeO content. FeO content in sinter decreased at a higher percentage of used biomass. In all cases the matrix of the sinter was magnetite and hematite associated with a small amount of calcium. The individual grains of hematite became recrystallized and affected the sinter strength. Sinters are inhomogeneous and contain many combinations of minerals. Flux and fuel distribution form a non uniform temperature field in the bed of the sinter pot and cause different oxidation-reduction conditions. All the studied sinter samples of different grain size studied contained the following mineral phases: magnetite Fe₃O₄, SFCA, silicate phase including dicalcium silicate Ca₂SiO₄, lamite, quartz, a small amount of Fe₂O₃ and NaCl were observed along the edges of the open pores. In all cases the matrix of the sinter with biomass contained Ca₂Fe₂₂O₃₃ associated with magnetite, hematite, wüstite and lamite, and minor phases of dicalcium silicate were calcium ferrites Ca₄Fe₁₅O₂₅, CaFe₉O₁₇ and CaFe₉Al₆O₂₀ and some small amount of NaCl [22,23]. Higher amount of volatile matter and high reactivity which came from biomass caused a large crack formation in sinter, impairing the mechanical properties of the sinter. 20% biomass addition did not show itself in structure by big differences even if it concerns individual grain size fractions. Averages of measured values were summarized, type and slightly varying content of individual phases was basically the same. Amorphous ratio of SiO₂ represents about 5%.

3. CONCLUSION

Biomass residues show a potential for the substitution of fossil fuels in both Coke and Ironmaking processes. High coke price and CO₂ emissions saving make biocoke more attractive. 1% addition of biomass in coal blend deteriorates the coke quality reasonably. Substituting 10% of fine coke with biomass did not significantly change the combustion characteristic of the sintering process or the sinter quality. The results suggest that it is feasible to substitute 10% of fine coke with biomass in the iron sintering process. It was concluded that the best results from tested biomass were obtained by charcoal addition, however seasonally it is possible to use other biomass sources too.

ACKNOWLEDGMENTS

The author is grateful to Ing.Rudolf Želinský, Ing. Peter Vlašić, Ing. Jan Tomáš and Pavol Výrostko for providing sinter pot tests with the biomass for the study. The author would also like to thank RNDr. Martin Černík, PhD. of U. S. Steel Kosice Research & Development for his contributions to the interpretation of the phase results presented in this paper.
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