# Bio mass for $CO_2$ neutral steel production

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## ABSTRACT

A process to increase the efficiency of bio mass as energy source by direct use of wood chips instead of coke in steel production is presented. Full utilisation of the bio mass constituents and excellent process control is enabled by utilisation of microwave heating for ignition of the reduction reaction and simultaneous pyrolysis of the bio mass.

The process is applicable for pig iron production as well as for iron sponge production. The paper presents a comparison of both process variants, with respect to energy consumption, product quality and integration into existing technology.

The process is run in a dual zone fixed bed reactor, with a bottom zone containing wood chips and an upper zone filled with iron ore concentrate. In the first zone the hematite is selectively absorbing 2.45 GHz microwave radiation and heated up to the desired temperature with a heating rate of >100K/min. The wood chips undergo a flash pyrolysis and react in multiple steps mainly to gaseous products, e.g., CO and $H_2$, which are immediately consumed by the reduction reaction. At the end of reduction an atmospheric plasma is ignited due to the presence of the microwave field. This enables removal of excess carbon in case of iron sponge or slag formation for purification of iron melt. The process yields, depending upon the conditions, iron sponge or raw steel for direct use in electrical arc furnaces.

***Keywords:*** Bio-mass, steel, microwave, $CO_2$ reduction

## 1 INTRODUCTION

The basic oxygen furnace (BOF) accounts for roughly two thirds of steel production and the electric arc furnace for the remaining third [1]. In 2005 the world wide crude steel production by the BOF process was in a range of 700 Mt with resulting $CO_2$ emissions of about 900 Mt (1.3 t $CO_2$ per ton crude steel [2]). Although the steel production is a mature technology, a huge potential for $CO_2$ emission reduction is predicted to exist from disruptive technologies. The goal of the European steel industry for the post-Kyoto period is to cut the $CO_2$ emissions by 50% [3].

Surprisingly, up to now renewable energy sources play a minor role in the concepts of $CO_2$ reduction. The only renewable energy source used in technical scale is charcoal, for example in small blast furnaces in Brazil [4].

Existing technology relays on large capacity furnaces, usually 10.000 t/day. On such a scale a low density bio mass residue, like waste wood, can not be applied. However, for de-centralised production facilities with much lower furnace capacity bio mass could become an interesting reducing agent, especially in regions with high bio mass production, high low quality coal resources or high economic benefits from $CO_2$-reduction. Additional benefit could be gained from combined processes, where the hydrogen and CO obtained from bio mass is utilised together with coal qualities not useful for coke production.

## 2 EXPERIMENTAL

For the lab scale investigations beech chips as bio mass and an iron ore concentrate with high hematite content and low slag foming mineral phases have been chosen ($Fe_{tot}$: 68%, $Fe_2O_3$: 97%, $SiO_2$: 1.5%, CaO: 0.08%, traces of P and S). To quantify the reaction behaviour of the materials, thermo gravimetric (TG) and Differential Scanning Calorimetry (DSC) measurements have been performed under Argon atmosphere. The evolved gases have been investigated by FTIR and mass spectroscopy up to 1050°C.

For the lab scale reduction experiments a dual zone fixed bed reactor has been used (see figure 1), with a bottom zone containing the wood chips (beech) and an upper zone with the iron ore concentrate (hematite).

The setup was placed into a 2000W, 2.45 GHz microwave cavity with an alumina fibreboard insulation. The temperature was measured by an optical pyrometer, the evolved gases were analysed on-line by an infrared spectrometer.

In the first stage of the process the hematite is selectively heated within 2 - 5 minutes to a temperature level of about 1000°C by absorption and dissipation of the 2.45 GHz frequency microwave radiation.

The dielectric loss of the hematite (ε”= 4.8) is more than 10 times higher than the loss of the beech chips (ε” = 0.4 with 10% humidity). Accordingly, the wood chips are mainly heated indirectly by heat radiation and by convection from the hematite. The wood chips undergo a flash pyrolysis and react in multiple steps mainly to gaseous products, which penetrate the hematite bed.

Within the hematite bed the CO and $H_2$ gas mixture evolved from the wood chips is heated up immediately to the temperature of the solid iron oxide and instataneously consumed for reducton of the ore to the metal. As soon as the melting point of the eutectic $Fe/Fe_3C$ is reached (1147°C), the melt flows into the remaining solid bed of pyrolysed bio mass residue. At the end of reduction the atmosphere is rich in CO from gasification of the biomass, and due to the high temperature and low dielectric strength of the atmosphere the microwave field density is high enough to ignite plasma above the melt. The atmospheric microwave plasma contributes significantly heating of the melt. Exposure to air at the end of the reaction allows the removal of excess carbon content as well as impurities like e.g. phosphorous or sulphur.

The obtained metal cast or sponge (depending on the reduction temperature) was analysed by XRD, optical microscopy and REM/EDX.

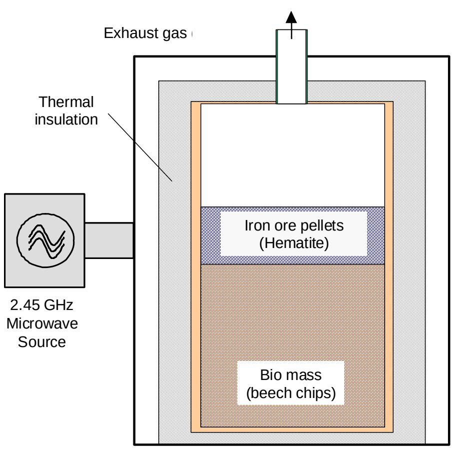


Figure 1: Lab scale set up for batch-wise production of steel from hematite ($Fe_2O_3$) and wood chips

## 3 RESULTS

The results of the TG and DSC measurements of the wood chips, the iron ore and the mixture of both are shown in figure 2. In each material an endothermic peak between 80 und 100°C accompanied by mass reduction is caused by moisture release. The endothermic decomposition of the bio mass components like cellulose, hemicellulose and lignin occurs between 280°C to 350°C, with significant weight loss. At 1050°C a charcoal und mineral salt residue of about 20wt% remains. For the iron ore no weight loss is seen until 300°C, followed by an exothermic conversion into magnetite and wustite, interrupted by an endothermal decomposition into wustite and 2% weight loss, corresponding to a peak at 750°C. The thermal behaviour of a mixture of 20% wood chips with 80% of iron ore is dominated by wood pyrolysis up to 400°C, followed by hematite and magnetite reduction reactions, first exothermal, than endothermal at almost 200°C lower temperature as compared to the thermal decomposition of hematite in Ar atmosphere.

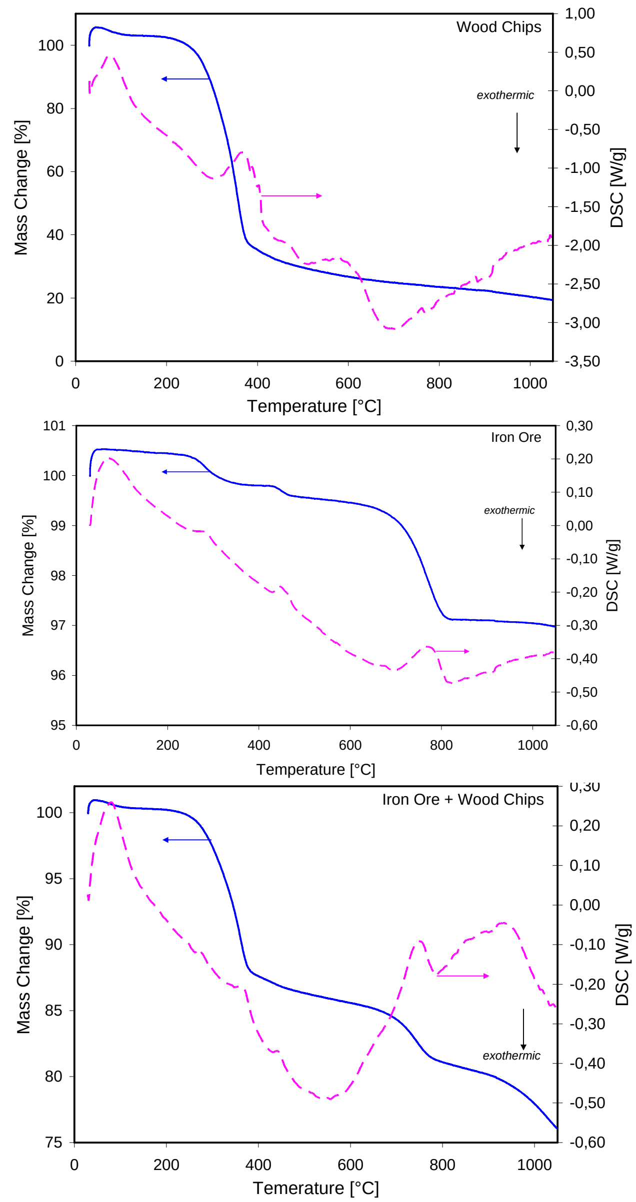


Figure 2: TG and DSC measurement of Iron Ore, wood chips and a 20 wt.% wood + 80% iron ore mixture

Therefore contribution of $H_2$ to the reduction process is assumed, followed by CO-reduction at T>800°C. The exothermal reduction of wustite is finished at 1000°C. The sequence of reactions matches well the CO-reduction of hematite [5], as shown below.

$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$

$Fe_3O_4 + H_2 \rightarrow 3FeO + H_2O$

$FeO + H_2 \rightarrow Fe + H_2O$



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$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \qquad \Delta H^\circ = -52.9 \text{ J/g mole}$$
$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \qquad \Delta H^\circ = 36.3 \text{ J/g mole}$$
$$FeO + CO \rightarrow Fe + CO_2 \qquad \Delta H^\circ = -17.3 \text{ J/g mole}$$

A typical heating profile of the microwave assisted reduction process according to the setup in figure 1 and the resulting gas emission is shown in figure 3. During the whole heating cycle the microwave power was held on a constant power level of 1000 W. Immediately after turning on the microwave power, $SO_2$, CO, $NO_x$ emission can be detected. After about 4 min the first pyrolysis step is finished and the $SO_2$- and $NO_x$-values are falling back to the ground level.

As soon as the reduction is almost complete, CO enrichment of the atmosphere occurs and plasma is ignited. The gas plasma consists of ions and radicals from the remaining gaseous species of the pyrolysis, but also of $NO_x$ from plasma assisted reaction of oxygen and nitrogen. The increasing level of $NO_x$ is an indicator for plasma ignition. The high reactivity of the plasma enables an efficient reduction of residual wustite (FeO). When the carbon residue from the bio mass, which establishes the Bouduoard-Equlibrium, is completely consumed, the CO level in the exhaust gas decreases and the microwave power is turned off. Immediately after turning off the microwave the $NO_x$ level goes down to zero.

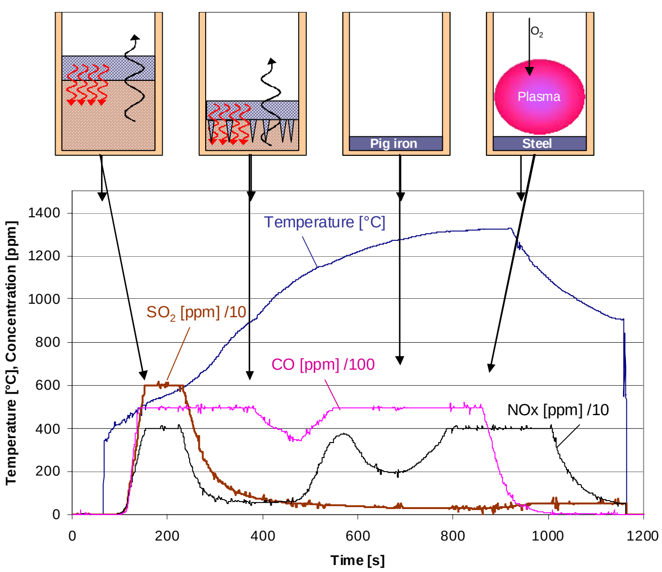


Figure 3: Heating profile and gas emission during microwave reduction of iron ore with wood chips at a constant MW-power level of 1000W (*a 2 min delay of the measured gas concentrations compared to the temperature curve is caused by the piping length to the detector; the plateau values are resulting from the measurement range of the IR-Device*).

The slag forming constituents react to a melt during the plasma assisted heating step, according to:

$$Fe_{[+C,Si,Ca,Mg]} \xrightarrow{O_2 / Plasma} Fe_{[+C]} + CO_2\uparrow + \underbrace{SiO_2 + MgO + CaO}_{\text{Slag}}$$

In case of eutectic melt formation the slag can be found as a thin layer on top of the melt In figure 4 the phase analysis of the iron ore and the obtained cast iron is shown.

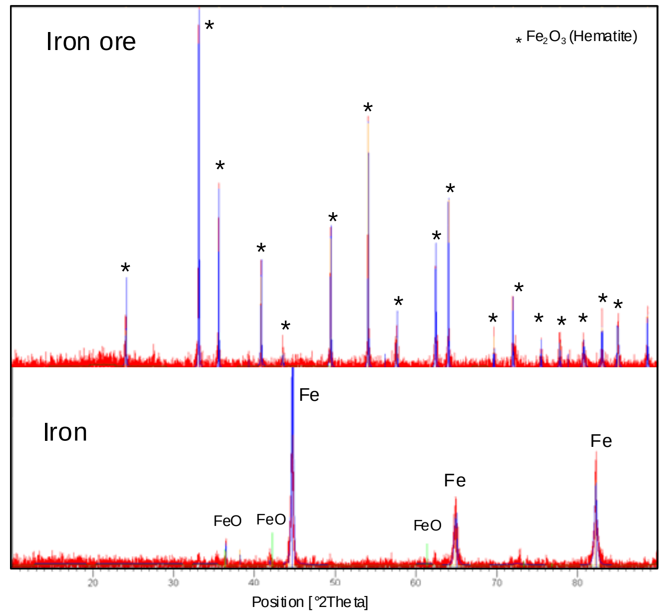


Figure 4: XRD-Phase analysis of the iron ore and the resulting steel after reduction with bio-mass

The ore is hematite, while the product consists of iron with low content of oxygen. The carbon content has been investigated by optical microscopy (see figure 5).

At the top of the bulk metal a mixed ferrite/perlite microstructure with the typical eutectoid lamellae structure is present. From this microstructure a C content 0.4 % can be estimated. In the middle of the casting a pure ferrite microstructure (C content < 0.1%) dominates.

The process enables also direct reduction instead of melt reduction. Lowering the processing temperature to 700°C – 1000°C is possible, yielding a iron sponge. Such an energy efficient process is an interesting alternative especially for hematite ores like the material used in the study with only a small amount of slag building impurities.

The microstructure and elemental composition of the iron sponge obtained from the same iron ore and bio mass as previously described was investigated by SEM and EDX. In figure 6 a cross section of the obtained iron sponge is shown. The bright areas show the cut and the grey areas the uncut grains of the sponge.

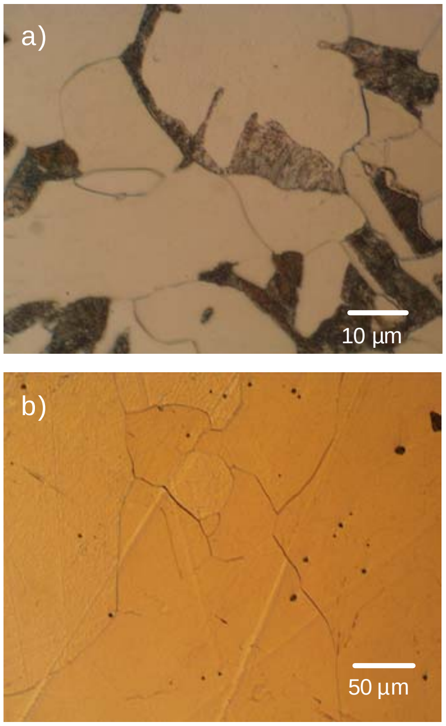


Figure 5 Microstructure of the produced steel cast
a) ferrite / perlite at the top of the steel block
b) ferrite in the middle of the steel block

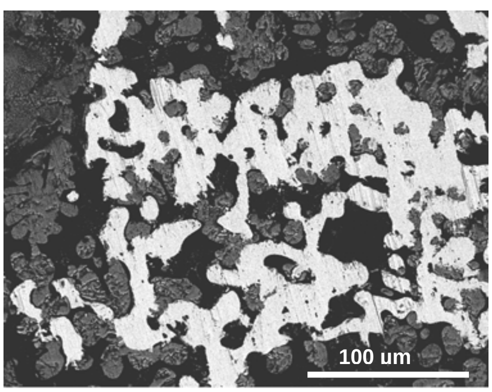


Figure 6: SEM-picture of a fine grained iron sponge obtained by direct reduction with bio mass

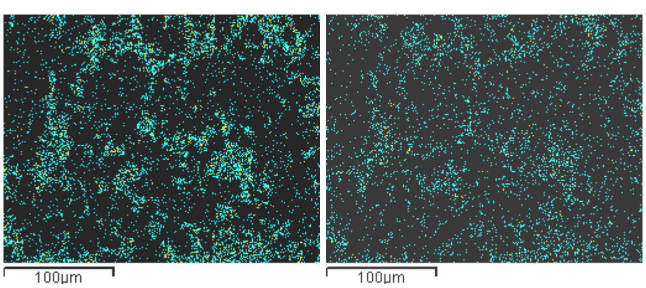


Figure 7: EDX analysis of the Ca (left) and Si (right) distribution of the section shown in figure 6

The impurities like Calcia and Silica are located mainly on the surface of the iron sponge and in the pores (see EDX analysis figure 7). This segregation of impurities indicates, that localised melting occurs possibly by the plasma immersing into the pores and causing local overheating .

## 4 CONCLUSION

The use of microwave energy enables a fast and efficient volume heating of the iron ore bed to temperatures necessary for the reduction of hematite. As reducing agents $H_2$ and CO obtained from flash pyrolysis of the bio mass were identified.
The efficiency of pyrolysis gas utilisation for the reduction process is significantly enhanced by application of microwave selective heating within a dual zone reactor.

With a calorific value of about 19 MJ/Kg (for beech chips [6]), bio mass is an efficient reductive material for steel production. The energetic efficiency of the process can be further increased by a low temperature direct reduction process resulting in a metal sponge instead of cast iron.

In a microwave assisted process the gaseous pyrolysis products can be easily ionised to generate atmospheric plasma. Because of the high reactivity of the iron oxides and radicals (especially hydrogen radicals) the reduction temperature can be further decreased and oxygen as well as carbon removal is almost complete, therefore low carbon steel is obtained. The plasma also facilitates volatile impurity removal in case of S and P, and slag formation for the mineral constituents.

Such a low temperature reduction enables not only an energy efficient process but also new reactor and material concepts. It has therefore the potential for a disruptive technology.

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