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Charcoal from agricultural residues as alternative reducing agent in metal recycling

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ABSTRACT

Typical carbonization units have the target to produce a charcoal which is in nearly all cases used as energy carrier for the production of heat in different forms. These often very old and not efficient processes are in most cases operated at temperatures between 350 and 500 °C and generate a charcoal with only medium quality. To realize an application of charcoals as CO_2-neutral reducing agent in metallurgical processes special high quality charcoals are needed, which meet metallurgical requirements - fixed carbon content of more than 85%, low ash amount and low content of volatiles. Therefore carbonization processes at higher temperature are required. The performed carbonization experiments with agricultural residues at temperatures up to 1000 °C show the possibility of the production of a charcoal which meets the requirements of various metallurgical processes and can act in these industry sector as reducing agent and substitute the so far used fossil coals and cokes. This was realized with some first reduction tests of heavy metal containing residues where charcoals showed a better performance than petroleum coke typically used in such reduction processes. The charcoal application in metal production and recycling processes as substitute of fossil carbon carriers leads to an enormous potential of saved fossil based CO_2-emissions because of the high energy and reducing agent demands in these industry sector. So the metal industry has the opportunity to fulfill environmental regulations and restrictions to reduce their CO_2-footprint and guarantee the supply of metals in Central Europe in future.

1. Introduction

At times of global warming and climate changes effective methods for an integrative environmental protection also from the industry are getting more and more important. Therefore it is becoming fundamental for the future to reduce the emissions of greenhouse gases. This fact is also publicized from the environmental legislation, wherefrom tighter reglementations occur. An example for that is the Kyoto protocol, which stipulates a worldwide reduction of the emitted greenhouse gases of 5% in the years 2008–2012 referring to the greenhouse gas emissions from 1990. These ambitious targets especially in the European Union (Austria minus 13% and Germany minus 27%) are only reachable with totally new ideas and concepts in the energy sector as well as in the producing industry. Especially the usage respectively application of biomass as CO_2-neutral reducing agent should be mentioned, which can offer the needed amounts for a technical implementation [1,2].

From literature hardly any direct use of biomass as reducing agent is reported. Some examples are the utilization of sun flower husk and residues from wood industry (e.g.

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wood chips or saw dust). Hereby only some experiments were carried out first of all in laboratory scale and their results not transferred to semi pilot or industrial scale yet. The main problem is the very fast reaction of fresh biomass and therefore a relatively low overall yield [3–6].

The use of carbonized biomass is a partly established way of using biomass in metallurgy but first of all in developing countries where mini blast furnaces are operated to produce pig iron in a small scale. In blast furnaces the main problems of a coke substitution by charcoal are the missing strength and the too high reactivity, which makes a replacement only possible in comparable small facilities which are today not the typical way of processing iron ores. These problems do not occur in such a way in the nonferrous metal industry and therefore the target was the production of charcoals which can be used in these kinds of processes. The requirements for charcoals as chemical reductants in metal processing and recycling are a fixed carbon content of more than 85% – better 90% – and an amount of volatiles lower than 10%. For that reason, higher carbonization temperatures up to 1000 °C and the absence of air are necessary, wherefore existing carbonization reactors have to be adapted or new ones have to be developed. Also low heating rates are required to lower the tar amount and to increase the charcoal output. The target is to find the most suitable material and the best process parameters for the production of a charcoal, which could be used as alternative reducing agent in a metallurgical process without major modifications of the process itself.

2. State-of-the-art carbonization techniques

Carbonization, a special form of a pyrolysis process, is one option of a thermal conversion technique for biomass to upgrade the raw material biomass into a higher valuable product. In case of carbonization this product is charcoal, which represents a CO_2-neutral and concentrated form of carbon carrier.

Typical industrial carbonization reactors work at temperatures between 400 and 500 °C, maximal 600 °C, and are often very simple and inefficient processes concerning their charcoal yield and the usage of by-products, like pyrolysis gas [7,8]. One reason for the low temperatures is the fact that in most cases air or other oxygen containing gases are used for the direct heating of the feedstock, and otherwise too much carbon would be lost due to reduction respectively burning of the charcoal inside the reactor. Typical representatives of these processes are the Degussa-retort, the Lambiotte-process, the Calusco tunnel retort and some kiln methods often used in developing countries [7–9]. A couple of new developments at this sector go in the direction of indirect heating of the process at higher temperatures. Some examples for those often continuous processes are screw or rotary furnaces in different forms from diverse companies, which at the moment mostly do not exceed the lab-scale or semi-scale status [10–13]. But with such processes the production of a higher grade charcoal for utilization more than for barbeque seems possible.

3. Investigated materials

Table 1 gives an overview of the chemical analysis of seven investigated feedstock materials. The basis of the selection of these materials was the fact that normal woody biomasses are very cost extensive and often unavailable, and lower grade as well as contaminated biomasses are not suitable for the production of high grade charcoals. So different wastes and residues from the agriculture were chosen, which are at the moment often burned or deposited for disposal in large amounts. As a result this kind of materials is available at moderate prices and sufficient amount.

For the carbonization tests the materials olive stones, cork oak cuttings, olive tree cuttings, pruning, grapevines, fruit tree cuttings and grape marc were crushed and screened to a uniform grain size of 3 mm length and 1 mm width in order to achieve comparable results. Because of the high moisture content of 46.53% of the grape marc in the condition as-delivered, this feedstock was additionally pre-dried to prevent mold and rot.

4. Carbonization tests

4.1. *Test equipment and parameters*

The carbonization tests with the seven different materials were done at 400, 550, 700, 850 and 1000 °C respectively at the absence of air. Therefore an in-house developed muffle furnace was used, which is shown as part of the whole experimental equipment in Fig. 1. This furnace was heated indirectly with electrical power and a very low fixed heating rate of 5 K/min. In addition, the muffle inside the furnace, which contains the biomass, is gas-proof and purged by

Table 1 – Chemical analysis results of the biomass samples.

Biomass Samples	Volatiles	Fixed	Ash	Water	Carbon	Hydrogen
Olive Stones	70.73	15.78	0.87	12.61	44.60	6.65
Cork oak cuttings	74.62	15.61	1.70	8.06	44.46	6.38
Olive tree cuttings	71.84	17.18	2.26	8.72	44.31	6.34
Pruning	70.55	18.30	2.49	8.66	45.31	6.14
Grapevines	71.55	16.90	3.03	8.52	44.69	6.21
Fruit tree cuttings	74.69	15.59	2.67	7.05	45.17	6.29
Grape marc (dried)	69.06	23.45	6.78	0.71	51.81	6.13