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How to Produce Green Coke?

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Abstract—According to the Financial Times the steel industry emissions accounted for 7-9% of total GHG emissions worldwide in 2019. The main share is directly related to the use of fossil coke and coal as fuels and reducing agents. About four solutions can be adopted to address such issue: direct reduction with hydrogen or syngas, electric arc furnaces, carbon capture and storage and use of biofuels (so-called “biocarbon”). These solutions can also be integrated. We propose applying innovative methods to produce biocarbon by pelletizing biocarbon with pyrolysis oil and reheating it at high temperatures to obtain materials with sufficient hardness, reduced porosity and reduced reactivity. The upgrade takes biocarbon closer to the requirements usually applied to metallurgical coke. We present also the results of technical and economic analysis plus environmental analysis on the expected final use of biocarbon in steel industry.

Keywords—coke, biocarbon, pellet, pyrolysis, hardness, durability

I. INTRODUCTION

In recent years with increasing price of carbon credits in the ETS market and growing trends towards coal phase out [1], also the most important multinational companies in e.g. the steel sector are switching to a greener steel production. As examples, Arcelor Mittal has proposed its TORERO Plant [2,3]; while ThyssenKrupp has developed a torrefaction plant for black pellet or biocarbon production [4]. The Technical Research Centre of Finland (VTT) has produced an interesting report in 2019 [5] in which a roadmap for the decarbonization of the steel industry in Europe and Finland is presented. The possible evolution of the technology is reported in Fig. 1. As can be seen, green coke or biocarbon is included as an “A-technology”, representing options which might be tested on a large scale and utilized commercially in the upcoming years. “B-technologies” can be considered instead, i.e. the use of hydrogen and electrolytic reduction. Roadmaps towards the development of low-CO_2 steel production technologies have also been proposed in [6-8].

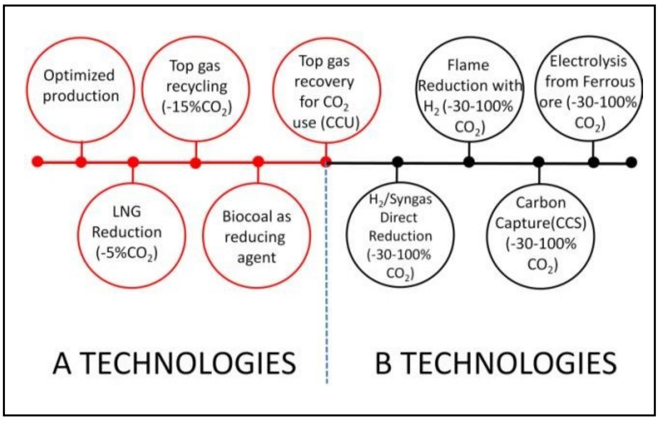

Fig. 1. Green Steel production roadmap [5]

Consequently the objective of this paper is to give an overview of the initiatives developed through the collaboration of SINTEF Norway, University of Perugia (Italy), University of Agder (Norway), University of Tuscia (Italy), University of Aalborg (Denmark), Technical University of Denmark and Huazhong University of Science and Technology (China). The tests were initiated at the University of Perugia in collaboration with SINTEF (see Fig. 2) [9-12] and then joined with the experimental campaigns and methods developed at University of Agder [13,14] and

Huazhong University of Science and Technology (HUST) [15,16]. Particular aspects in pelletizing modeling were analyzed by Aalborg University and Technical University of Denmark [17-18]. The present paper presents the results of technical optimization of pyrolysis oil content, pressure and temperature during the pelletization of a mixture of biocarbon and pyrolysis oil. The developed process is based on three steps: biomass is pyrolysed, the produced biocarbon is pelletized with the pyrolysis oil as binder and the produced pellets are then reheated. The optimization of the process was carried out based on three responses: mechanical strength, thermal strength and durability of produced pellets. In addition, an environmental feasibility analysis was performed together with estimating cost of production of biocarbon.

Fig. 2. Biocarbon pellet produced at the University of Perugia

II. TECHNICAL OPTIMIZATION OF BIOCARBON PELLET PRODUCTION

A. *Design of Experiment (DoE)*

After producing biocarbon and pyrolysis oil at a bench scale pyrolyzer at the University of Perugia the produced samples were sent to the University of Agder to perform pelletization tests. The single pellet test bench allowed to produce pellet at controlled pressure and temperature. The produced pellets were then analyzed in a pellet hardness tester (Amandus Kahl, Germany) and in an ISO tumbler 1000+ (Bioenergy Institute, Vienna, Austria), designed according to ISO 17831-1. The durability and the strength of produced biocarbon pellets before and after reheating were measured accordingly. The objective of the tests was to optimize and develop the biocarbon pellet production process to reduce biocarbon porosity and increase its strength. For this reason it was chosen to pelletize the biocarbon with pyrolysis oil as binder, allowing the oil to penetrate inside the porous biocarbon structure. The obtained pellet was reheated to increase its strength and reduce the porosity due to the polymerization of the pyrolysis oils directly inside the pores of the biocarbon. Design of Experiment (DoE) was performed through Response Surface Methodology (RSM) with Box-Behnken experimental Design (BBD). Three factors were considered (oil content, temperature and pressure) and the influence on the three responses (mechanical strength, thermal strength and durability) was evaluated. Thermal strength is indicated as the strength after the pellet reheating. In total 15 pelletization tests were performed.

B. *Main results*

The mechanical/compressive strength, thermal strength and durability of the optimized pellet are given in Tab. 1.

TABLE I. FINAL RESULTS OF BIOCARBON PELLET PRODUCTION OPTIMIZATION [14-16]

Response	***Value***
Compressive strength (MPa)	0.42 - 3
Thermal strength (MPa)	1.1- 5
Mechanical durability (%)	83.20

Due to its positive effect, the reheating treatment might be integrated in the system after pelletization. If carried out at the same temperatures as the pyrolysis process, it might directly be executed inside the same reactor setup without an excessive increase of cost. Consequently, it becomes relevant to fully understand the mechanisms which enhance the improvements in mechanical quality. The comparison of microstructure and morphology between the final reheated pellet and the raw material is shown in the scanning electron microscope (SEM) images displayed in Fig. 3, where the decreased porosity can easily be seen.

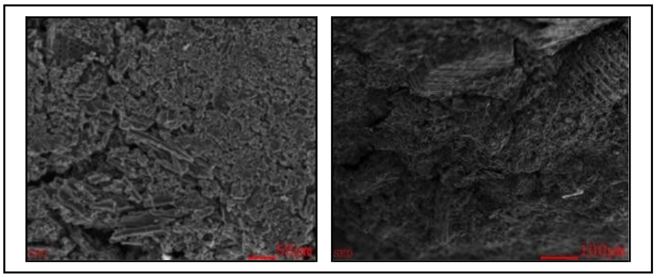

Fig. 3. Biocarbon (left) and reheated biocarbon pellet (right) [14]

III. ENVIRONMENTAL ANALYSIS

Based on the results of the optimization analysis, previous experience on coal densification [21] and from pyrolysis plants at the University of Perugia [22,23], a plant layout for the production of biocarbon pellet was developed.

A. *Biocarbon production plant layout and mass and energy balances*

The layout of the plant is proposed in Fig. 4.

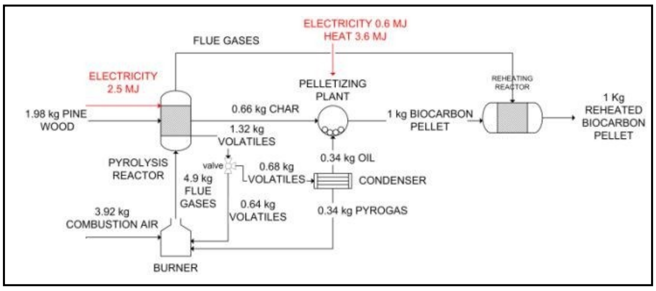

Fig. 4. Biocarbon production process layout, based on pyrolysis – pelletization - reheating [24]

To design the mass and energy balances of the reactor the following assumptions have been made:

- the yields of pyrolysis products are distributed in the following way: 1/3 char, 1/3 biooil, 1/3 pyrolysis gas;
- in the volatiles burner an air to fuel ratio of about 4 is considered, as reported also in [25];
- the electricity and heat consumption of the pelletizing plant is based on what is reported in [26].

To simulate the impact of the plant the following two processes were considered:

- "Heat, central or small-scale, natural gas {GLO} |market group for | Alloc Rec, U"; taken from Ecoinvent 3.3 database;
- "Electricity, medium voltage {NO} | market for | Alloc Rec, U"; taken from the Ecoinvent 3.3 database.

The choice of the electricity generating process took into consideration a Norwegian scenario.

B. Carbon footprint of biocarbon pellet

The carbon footprint of 1 kg of biocarbon pellet is shown in Fig. 5.

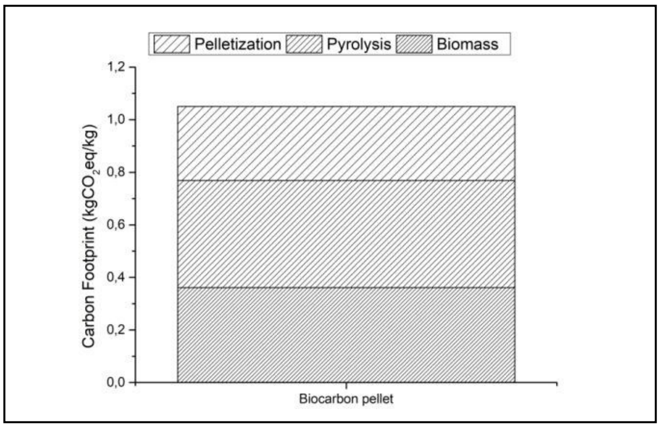

Fig. 5. Biocarbon Pellet Carbon Footprint [24]

It can be seen that the total carbon footprint is about 1 $kgCO_2eq/kg$ of biocarbon pellet. The impact is almost equally distributed between three processes: biomass collection, transport and chipping, pyrolysis and pelletization. The total carbon footprint of biocarbon pellet is comparable with that of charcoal, reported in the database Ecoinvent 3.5, and indicated with the de nomination "Charcoal {GLO} |market for| Cut-off, S". This has an impact of 1.43 $kgCO_2eq/kg$, so the biocarbon pellet produced with an integrated process has a slightly lower impact than charcoal produced with conventional reactors.

C. Carbon footprint of coke

Many studies have taken into consideration the impact of coke production, which varies depending on the technology and on the country also. Each country has in fact a different Energy mix, which can influence coke production. In this case the project "Coke {GLO} |market for| Cut-off, U" was chosen, which belongs to the Ecoinvent 3.5 database. The system boundaries are reported in Fig. 6, as taken from [27]. The lifecycle of coke starts from coal mining, which is followed by transport and thermal distillation (which is the main process used in coke production, also called coking).

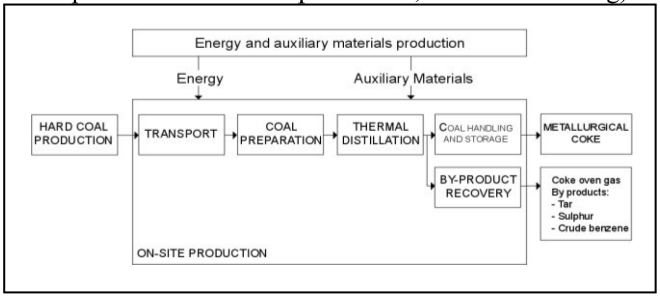

Fig. 6. Coke production system boundaries [27]

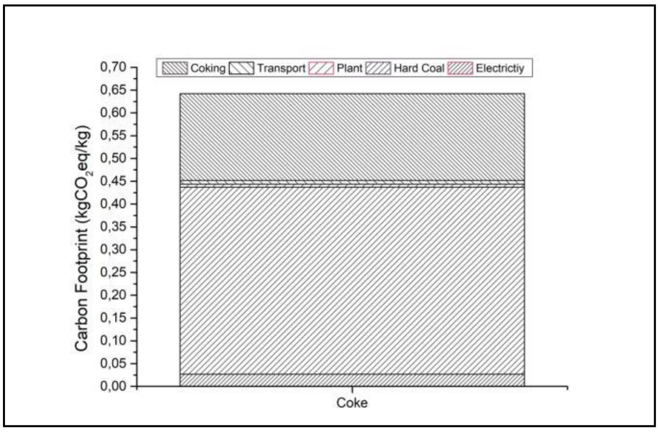

Fig. 7. Coke carbon footprint

Coke production impact is reported in Fig. 7. We can see that the impact of coke is generally lower than that of biocarbon pellet. So we can infer from this that the production of biocarbon pellet is linked with some environmental burden, it is the use phase which is convenient for the biocarbon pellet because it is not associated with GHG emissions, contrary to the use phase of coke.

The most impacting coke production phases are linked to hard coal extraction, coking and the use of electricity during the process.

D. Carbon footprint of conventional pig iron and steel

If we consider the steel sector, we can assume that about 200 kg of coke is needed to produce one ton of steel.

The system boundaries typical of steel production are reported in Fig. 8. These are taken from the draft Product Category Rule "BASIC IRON OR STEEL PRODUCTS & SPECIAL STEELS, EXCEPT CONSTRUCTION STEEL PRODUCTS", Draft, DATE 2019-10-08. This can be downloaded directly from the Environdec Website (https://www.environdec.com/), where Environdec (also known as International EPD® System) is a global program for environmental declarations based on ISO 14025 and EN 15804. An EPD on steel production has been for example already been published by Outokumpu Oy, the biggest steel producer in Europe and certified by another program operator (from Germany, Institut Bauen und Umwelt e.V.).

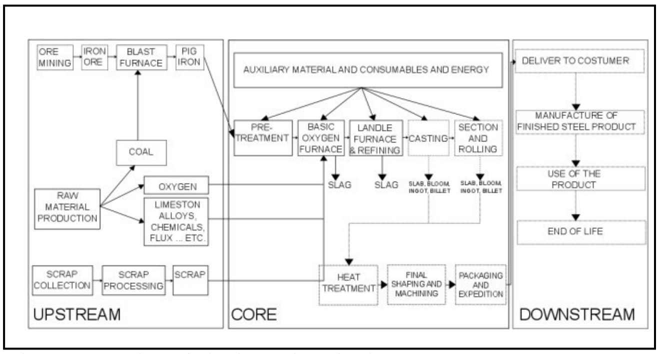

Fig. 8. System boundaries in steel production [28]

To analyze the processes reported in Fig. 8 the following dataset was considered from Ecoinvent 3.5: "Steel, low-alloyed {RoW} |steel production, converter, low-alloyed| Cut-off, U". This process takes into consideration the production of unalloyed steel using ferrochromium, ferronickel, molybdenite, liquid oxygen, pig iron and ferromanganese. Pig iron is produced in the blast furnace from iron pellet and sinter iron, using coke. Coke is the reductant used to produce both sinter and pig iron. Also some small quantities of coal are used in pig iron production. In Fig. 8 the process indicated with dotted lines are not included in this study because we chose to focus our attention on the raw material, further operations will be the same for both conventional steel and steel produced with biocarbon pellet, the latter indicated with the name "green steel".

The impact of pig iron production is shown in Fig. 9.

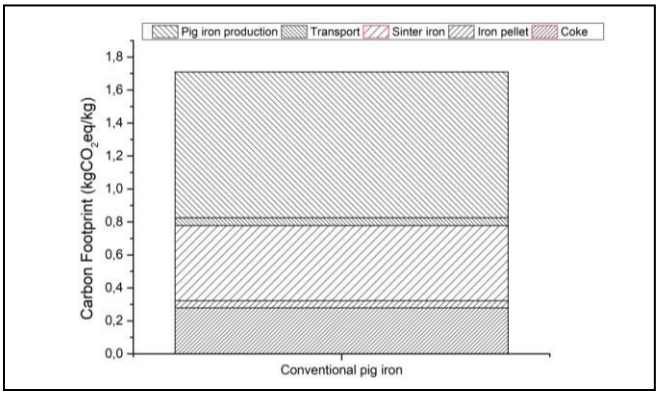

Fig. 9. Conventional pig iron carbon footprint

We see from Fig. 9 how the most impacting processes are: coke production, sinter iron production and pig iron production. Where the process "pig iron production" comprises the emissions of coke combustion to reduce iron.

Fig. 10 shows the carbon footprint of conventional unalloyed steel, produced using conventional pig iron.

We see that, if the carbon footprint of pig iron is about 1.71 $kgCO_2eq/kg$ of material, that of conventional steel is about 2.31 $kgCO_2eq/kg$ of material.

The main contributions to conventional unalloyed steel carbon footprint are ferronickel production, which accounts for about 18% of the total impact, and obviously pig iron production, which accounts for 67% of the total impact.

The emissions released by the steel production process are quite low and currently equal to 4% of the total carbon footprint. Liquid oxygen production and ferrochromium production account respectively for 3.6% and 3.02% of the total impact.

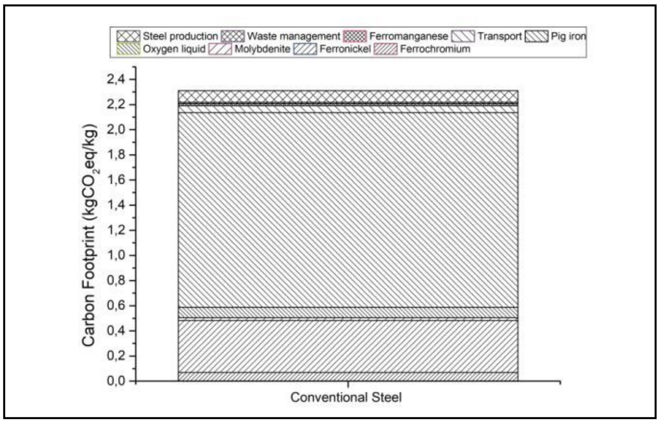

Fig. 10. Conventional steel carbon footprint

E. Carbon footprint of "green" pig iron and steel

When the biocarbon pellet is used to substitute the coke used for pig and sinter iron production, substituting also a small part of the hard coal, this can decrease the carbon footprint of pig iron and so also that of steel. We speak in this case of "green" pig iron and "green" steel.

The carbon footprint of green pig iron is shown in Fig. 11.

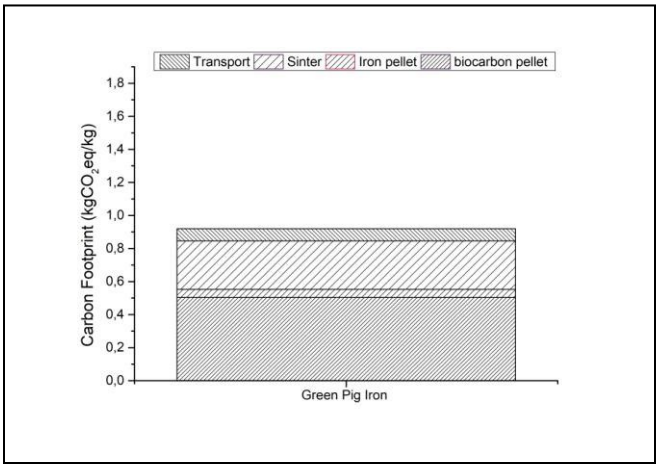

Fig. 11. Carbon footprint of green pig iron

We see from Fig. 11 that the carbon footprint of green pig iron is about 0.92 $kgCO_2eq/kg$ of pig iron. The main impacts on green pig iron production are the following:

- biocarbon pellet production accounts for 55% of the total impact;
- sinter production accounts for 32% of the total impact;
- iron pellet production accounts for 5% of the total impact;
- transport accounts for 8% of the total impact.

In this case the use of biocarbon pellet can reduce the carbon footprint of pig iron with 46%. In Fig. 12 the carbon footprint of green steel is shown.

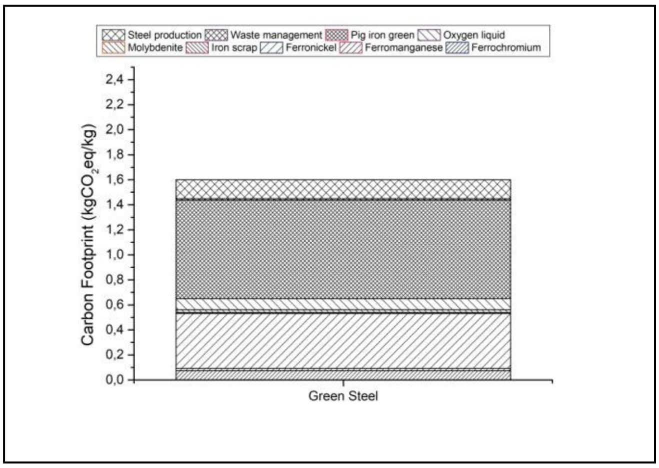

Fig. 12. Carbon footprint of green steel

From Fig. 12 it can be seen that the impact of unalloyed green steel is due to:

- green pig iron, which accounts for 49% of the total impact;
- ferronickel, which accounts for 27% of the total impact;
- ferrochromium, which accounts for 5% of the total impact;
- liquid oxygen, which accounts for 5% of the total impact;
- steel production (which includes also steel production emissions), which accounts for 9% of the total impact on the carbon footprint;
- ferromanganese, iron scrap, molybdenite and waste management, which account for the remaining.

The total impact of green steel is about 1.6 kgCO$_2$eq/kg of steel which is 31% lower than that of conventional steel.

IV. DISCUSSION

Based on what has been reported and calculated in this work the use of biocarbon pellet in the steel industry can provide a significant environmental advantage. The economic feasibility will depend on many factors, among them: the cost of the feedstock, logistics costs, costs of transformation and investments costs for the pyrolysis plant. A positive role can be played by the price of carbon credits which can bring some further income to increase the feasibility of the project. As reported in [5], if the biocarbon pellet is produced from bark at a pulp mill site and transported to a steel plant which is 275 km far from the pulp mill a total cost of production of 252 €/t of biocarbon can be obtained. This is one of the lowest that can be obtained. The feasibility of the project depends on the price of the Emission trading EUA and the price of coke. With a price of the EUA equal to 25 €/tCO$_2$ it is difficult to reach economic feasibility unless the price of coke is higher than 200 €/t. This price of coke is very difficult to achieve in the global market. So, some economic aspects still have to be optimized focusing mainly on technology and raw materials cost reduction. The quality of the material has also to be further developed focusing on approaching the same properties as for coke. It can be expected that the produced biocarbon pellet will be analyzed according to all the typical norms used to characterize coke, such as the ISO 18894:2018, in which the methods to calculate coke reactivity index and coke strength after reaction are reported.

V. CONCLUSIONS

Through the collaboration of SINTEF with University of Perugia, University of Agder, Tuscia University, University of Aalborg, Technical University of Denmark and Huazhong University of Science and Technology new methods have been developed to produce and characterize biocarbon pellet and promising characteristics of the final product have been achieved, in terms of hardness and durability. The process has still to be optimized from an economic point of view. Besides this, detailed methods for the characterization of the final biocarbon have to be developed, to ensure that its characteristics are really correspondent to those of coke.

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