Production and application of sustainable metallurgical biochar pellets

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Preface

“Charcoal-burning is a pleasant job. There is undoubtedly something intoxicating about it, and it is known that charcoal burners see things in a different light from other people; they are given to poetry and taradiddle, and wood-demons come and keep them company. Charcoal is a beautiful thing to turn out, when your kiln is burnt and opened up, and the contents spread on the ground. Smooth as silk, matter defecated, freed of weight and made imperishable, the dark experienced little mummy of the wood. The mise-en-scène of the art of charcoal-burning is in itself as lovely as possible.”

Karen Blixen, Out of Africa

Acknowledgments

A PhD is mainly the dedicate work of a single. However, the quality of the outcome is strictly affected by the interaction with other people. This precious contribution is manifested in several ways, more or less evident but equally important. I want hereby to acknowledge whomever, for a reason or another, supported me. The following list may look long, but it is surely not exhaustive. Please apologize me for that, I would really have liked to thank you all!

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Abstract

The effective decarbonization of our society must be boosted through the promotion of efficient alternatives to fossil fuels. This transition should take place gradually, involving a broad range of actors and technologies. The challenge is often merely perceived as the so-called green switch in producing electricity and heat. However, certain industrial branches are dependent on fossil fuels for their physio-chemical characteristics and less as fuel. For instance, the metallurgical industry (e.g. steel, silicon and manganese production) traditionally requires fossil coal and coke (thermally treated coal) as reducing agent in the reactions required to purify the metal ores. Unless going through a dramatic change in the technological process, the carbon neutrality of these systems must be reached finding a similar but renewable material. In this regard, biochar, a coal-like product of a thermal conversion of woody biomass, has been targeted as promising solution. Unfortunately, there are several barriers, which obstructs the utilization. Among them, the market price and the mechanical weakness are worth to be mentioned. In the following thesis, a method to improve the mechanical properties of biochar was developed and investigated. The method is based on the combination of pyrolysis with a consequent densification, with recovery of pyrolysis oil as binder and a further heat treatment. Besides, the economy of the process was addressed. This was done by trying to minimize the cost through a smart recovery of the byproducts and wastes. Whenever possible, the developed system was designed according to the Norwegian scenario, considering local feedstock and application. Throughout the thesis, the novel method was deeply investigated and optimized both in terms of quality of the final product and feasibility of the process. Some post-production related issues, which may limit the industrial diffusion, were pointed out and a solution was attempted. Finally, the sustainability of the process was studied. The results provided useful information about the suggested process and the related key-parameters. The novel knowledge may be used to produce fossil fuels-competitive and sustainable biochar materials and, hence, foster the renewable transition in the metallurgical industry.

List of papers

A. Riva, Lorenzo; Surup, Gerrit Ralf; Buø, Therese Videm; Nielsen, Henrik Kofoed (2019). *A study of densified biochar as carbon source in the silicon and ferrosilicon production.* Published in Energy.

B. Riva, Lorenzo; Nielsen, Henrik Kofoed; Skreiberg, Øyvind; Wang, Liang; Bartocci, Pietro; Barbanera, Marco; Bidini, Gianni; Fantozzi, Francesco (2019). *Analysis of optimal temperature, pressure and binder quantity for the production of biocarbon pellet to be used as a substitute for coke.* Published in Applied Energy.

C. Riva, Lorenzo; Wang, Liang; Ravenni, Giulia; Bartocci, Pietro; Buø, Therese Videm; Skreiberg, Øyvind; Fantozzi, Francesco; Nielsen, Henrik Kofoed (2020). *Considerations on factors affecting biochar densification behavior based on a multiparameter model.* Under second review step in Energy.

D. Riva, Lorenzo; Cardarelli, Alessandro; Andersen, Geir Johan; Buø, Therese Videm; Barbanera, Marco; Bartocci, Pietro; Fantozzi, Francesco; Nielsen, Henrik Kofoed (2020). *On the self-heating behavior of upgraded biochar pellets blended with pyrolysis oil: effects of process parameters.* Published in Fuel.

E. Bartocci, Pietro; Riva, Lorenzo; Nielsen, Henrik Kofoed; Yang, Qing; Yang, Haiping; Skreiberg, Øyvind; Wang, Liang; Sorbini, Giulio; Gul, Eid; Barbanera, Marco; Fantozzi, Francesco (2020). *How to produce green coke?* Accepted to Applied Energy Symposium: MIT A+B. Cambridge, USA. Postponed to 12-14 August 2020.

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Chapter 1

Introduction

1.1 Motivation

The climate change emergency urges a critical and effective counteraction. It is nowadays clear that the solution requires a mixture of options, with a short as well as long term perspective, at different degrees of complexity. Among the possible alternatives, the technological ones have been often addressed as a tool to tackle the environmental issue in typically engineering-oriented sectors. Industry, which is challenged to contribute thoroughly due to the considerable emission share, may be considered as a proper example. An industrial perspective must cope with both the product quality and the economics of the processes, a factor which often limits the diffusion of a sustainable transition. When it comes to metal production, all the considerations arisen are relevant. It is worth mention that metal industry constitutes a significant share in the global, as well as, Norwegian annual overall emissions. Often, this type of industry depends on a high consumption of fossil fuels, required both to provide heat and to enhance the chemical reactions to purify the metal ores. This type of reaction is referred as reduction: the carbon included in fossil fuels reacts with the oxygen in the metal ores, producing pure metal and carbon dioxide.

Despite the heat source may be alternate with a renewable one (e.g. by clean electricity, biomass combustion), the reducing action conventionally depends on Carbon. A solution has been indicated in biochar, a biomass product similar to fossil coal. Unfortunately, this material presents several drawbacks, which make it not competitive when compared to the fossil counterpart. The production cost and the mechanical weakness are among the most critical. In the light of what is mentioned, the scope of this research is to investigate the coupling of pyrolysis with densification, as method to enable the competitiveness of biochar. Hopefully, the observations which are drawn after the results, may represent a contribute towards a more sustainable transition.

1.2 Objective and research questions

The research object of the present thesis is mainly to develop a process, which consider the production and application of sustainable metallurgical biochar pellets. A conceptual layout of this process is presented in Figure 1.1.

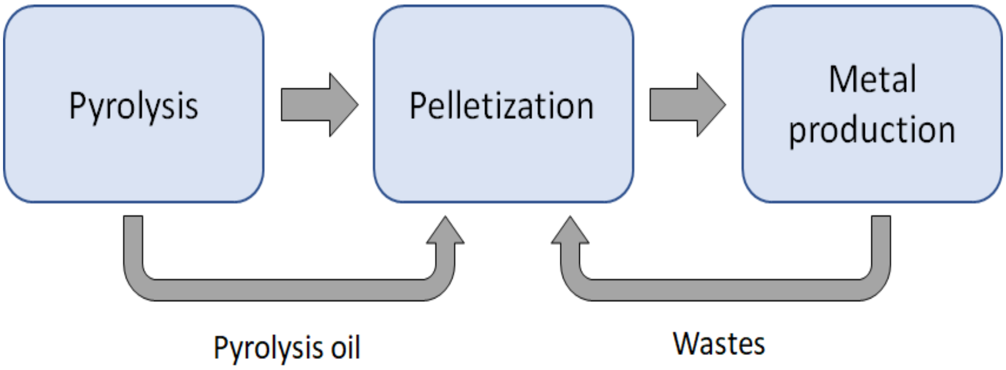


Figure 1.1: Conceptualized scheme of the proposed process, which is the main focus of the present thesis work.

The investigated process is mainly split in three main steps: pyrolysis, pelletization and metal production (application). The process has been implemented considering different criteria. Firstly, the aim is to produce a renewable carbonaceous material which may positively be applied in the reduction of metal ores. In particular, the silicon and ferrosilicon production as well as steel manufacturing have been selected as target application. As explained later on in more details, the coupling of pyrolysis and pelletization provides a competitive mechanically strong biochar characterized by high fixed carbon. This combination has therefore been deeply investigated, with the goal to understand how to achieve a competitive material in comparison to the fossil reducing agents, which are commonly used in this application. Besides, the inclusion of pre-treatment as well as post-treatment has been evaluated. However, in comparison to untreated biochar, the densified option is expected to bring about a considerable increase of cost. The process must therefore be optimized to limit the economic loss.

During the thesis, several alternatives have been considered. Normally, densification of biochar requires binders (or additives). As shown in Figure 1.1, pyrolysis oil, which is a by-product of pyrolysis, has been utilized as binder, with the aim to simultaneously improve the quality of the pellets and abate the costs by the promotion of circular economics concepts. A large part of this thesis work promotes the benefit of a method, which includes a blending of biochar with pyrolysis oil and a consequent new pyrolysis of the obtained pellets. The potential of exploiting wastes from the metal production as additive (see Figure 1.1) has also been investigated. This option is expected to provide further improvement in terms of reduction of costs, quality of the final carbonaceous material as well as environmental benefits (less dispatched wastes). Despite not largely discussed in this thesis work, the recovery of metal production wastes into the pelletization of biochar has been considered in the proposed overall process, to highlight its possible advantages. The main concept behind the realization of this suggested overall system is to provide a renewable reducing agent, which may drop the emissions in the metal production. As consequence, the sustainability of the process has been taken into account, when defining the characteristics of each step.

In the overall, the main research question, which constitutes the thread along this thesis is:

How can the production and application of sustainable metallurgical biochar pellets be optimized?

Moreover, the research sub-questions that have been answered are:

a) Is biochar pelletization suitable for metallurgical applications?

b) How is biochar pelletization affected by the main single step parameters?

c) How does biochar pelletization interact with variation of the main parameters?

d) Are biochar pellets stable and safe while stored and handled?

e) Is this process really more sustainable than fossil carbon consumption?

1.3 Thesis structure

The thesis's structure is framed upon the research questions, in a way to give a logical order to the treated topics, as well as to make the reading fluid. The structure is planned as follows:

- A brief introduction on motivations, research questions and structure of the thesis is provided in **Chapter 1**.
- In **Chapter 2**, the information necessary to thoroughly understand the developed process are provided. In detail, it is clarified why the metallurgical industry is facing an environmental issue and which solutions might address it. The chapter continues introducing biochar, as promising solution in the metallurgical sector, and densification, as a method to upgrade this material. Finally, the Norwegian scenario is briefly presented.

- Once the process is explained and discussed, the material and methods, which have been used throughout the experimental works, are presented in **Chapter 3**.

- **Chapter 4** introduces briefly the readers to the research papers, which are included in the thesis work and that are presented in the Appendices. Figure 1.2 is a visual representation of the papers in relation to the main investigated process. In Paper A, the elaboration of a process which may optimize the production of biochar pellets for the metallurgical industry are analyzed. Once the potential is demonstrated, the optimization of the biochar pellets quality, in a metallurgical perspective, is carried out in Paper B. After having researched on the quality of the pellets, the attention moves towards the evaluation of the pelletization process and the effects of the main parameters on its feasibility (Paper C). Afterwards, some important post-production issues are discussed in Paper D. Finally, in Paper E, the environmental assessment of the process is carried out.

- After the summary of the contributions, the main findings are gathered in **Chapter 5** and a discussion of them is developed.

- The conclusions, challenges and perspectives which can be drawn from this thesis are then presented in **Chapter 6**.

- The thesis concludes with the bibliography and the appendices.

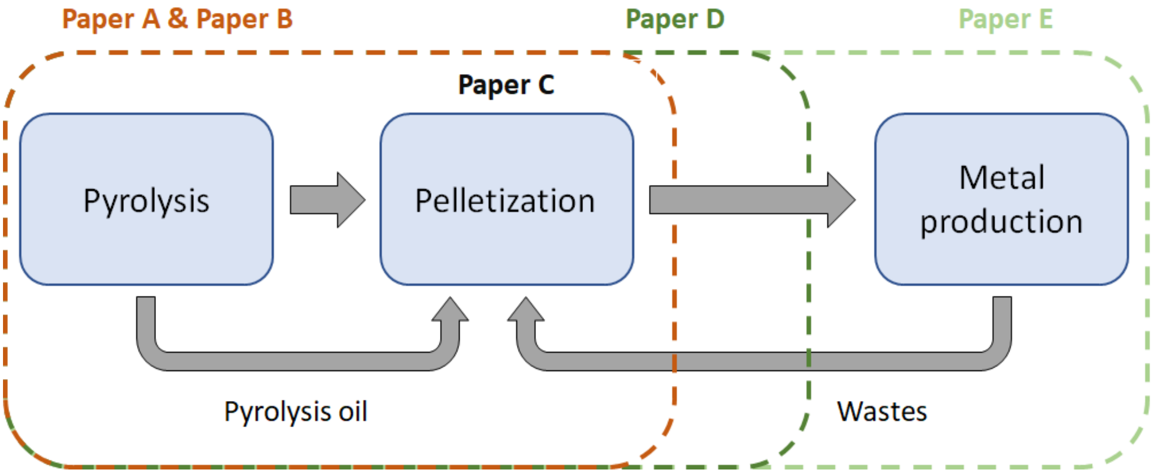


Figure 1.2: Visual representation of the research papers in relation to the main investigated process.

Chapter 2

Overview of the biochar use in the metallurgical sector

2.1 Climate change and the industry role

It is nowadays scientifically accepted that the Earth is facing an environmental threat, due to human activities. In particular, the anthropogenic greenhouse gases (GHG) emissions have been pointed as cause of an exceptional increase of global temperature [1]. This issue is commonly referred to as climate change. According to an Intergovernmental Panel for the Climate Change (IPCC) report, between the 20 and 40 percent of the global human population live in regions that have already experienced warming of more than 1.5°C above pre-industrial in at least one season [2]. It has been demonstrated a strict relation between this trend and the increase of the frequencies of natural disasters around the world [3]. Figure 2.1 can be used as an example of the association between human activities (measured as gross domestic product, GDP), global emissions and natural disasters.

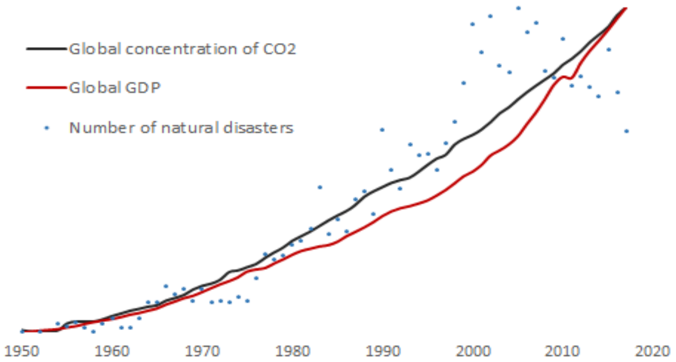


Figure 2.1: Normalized data of the number of global disasters per year, global concentration of CO_2 and global GDP. Data are elaborated after [4].

The climate change issue has been of international concern since decades. In 1992, United Nations Framework Convention on Climate Change (UNFCCC) was adopted as the first international environmental treaty to address the problem [5]. However, it was only in 2015 that a remarkable diplomatic result was obtained. During the 2015 United Nations Climate Change Conference in Paris (known as COP 21), 174 countries, representing the 55% of the global GHG emissions, agreed upon the necessity of actively reduce climate change. Each state submitted a package of pledges, named intended nationally determined contributions (INDC). For example, the members of the European Union intend to reduce domestic GHG emissions of at least 40% by 2030 compared to 1990 level [6]. A list of INDC for each country is obtainable in [7].

The modalities to achieve the targets proposed in the INDC are not stabilized *a priori*. It is however appropriate to evaluate the implementation of strategies, which may rely on the involvement of a broad spectrum of multi-field actions. In particular, the reduction of GHG emissions in the main economic sectors should be prioritized. According to the International Energy Agency (IEA), the production of electricity and heat sector has the greatest share of emissions [8]. To a certain extent, the exploitation of renewable energy is considered to be the main driver to reduce emissions and its capacity is expected to expand by 50% between 2019 and 2024 [9]. However, other categories are also characterized by a relevant negative environmental impact. As shown in Figure 2.2, the direct global emissions related to the industry are the 21% of the overall.

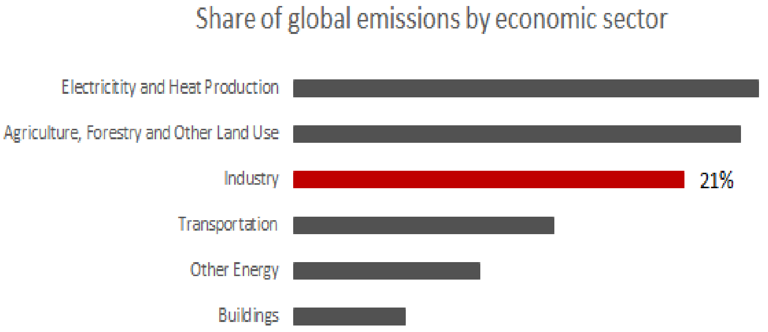


Figure 2.2: Share of global emissions by economic sector based on emissions in 2010. Data are elaborated after [10].

Differently to the electricity and heat production sector, industrial emissions are associated to complex processes, which often necessitate fossil fuels both to perform efficiently and to be market competitive. A sustainable transition is therefore more complicated to enhance, if compared to the energy sector. Due to these different trends, it has been forecast that in Europe, industry might represent the greatest economic source of emissions by 2050 [11]. A successful fight against climate change must therefore include a comprehensive evaluation of novel methods and strategies to reduce the environmental impact of the industry.

2.2 Metal production and environmental concern

Among the branches which constitute the industrial sector, metal production has a relevant role. This sub-sector includes all the facilities that deal with the production of ferrous and nonferrous metals, including primary aluminum, ferroalloy (e.g. ferrosilicon and silicon), iron and steel, lead, magnesium, zinc and nickel [12]. The metallurgical industry accounted in 2014 for the 46% of the total manufacturing value and the 11% of the GDP in the European Union [13]. According to IEA, this sector is also forecast to expand in the next years, mainly driven by the increased iron and steel production in China [14]. Therefore, despite a continuous reduction in the metallurgical energy intensity, emissions are expected to grow [14]. This information becomes even more critical when associated to the emissions of that sector. In 2018, for example, the emissions from iron and steel production were circa the 8% of the global total anthropogenic emissions [15].

The source of the emissions can be either direct or indirect. Indirect refers to the emissions related to the production of electricity required in the metallurgical process. Whereas the term direct refers to the fossil fuels directly used into the production operations. Of the total emissions from the iron and steel production, direct emissions accounted for about the 70% in 2018 [16]. A similar trend can be observed in other metallurgical branches, e.g. silicon and ferrosilicon. It is thus crucial to clarify how and why fossil fuels are used to produce metals. The routes characterizing the production of steel and silicon can be taken as example. A simplified version of these routes, which emphasizes the steps where fossil fuels are exploited, is shown in Figure 2.3.

The main process happening in steel manufacturing is the carbothermic reduction of sintered iron ores inside a blast furnace (BF) [17]. The ores are charged into the BF and get reduced by the Carbon contained into the metallurgical coke bed. This material is produced by heating coal in absence of Oxygen. Compared to untreated coal, it is stronger (to avoid the bed crushing at the bottom of the furnace) and more reactant (due to higher Carbon content and porosity) [18]. The products of the reaction are: molten pig iron, a slag containing the impurities from the ores and carbon monoxide, which becomes carbon dioxide once it reacts with the hot air (blast) present inside the furnace and used to maintain high temperatures. The molten pig iron is then processed in a oxygen converter, where the remaining Carbon impurities are expelled by further oxidation to produce crude steel. Scraps can also be utilized as raw material. In this case, an electric arc furnace (EAF) is preferred.

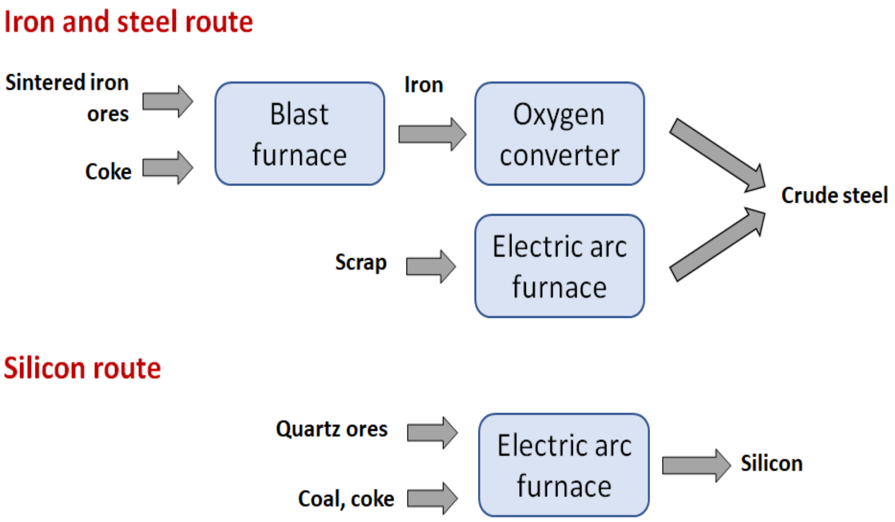


Figure 2.3: Simplified metallurgical routes for: iron and steel, consisting in a direct line (blast furnace plus oxygen converter) plus recovery of scraps through an electric arc furnace, and silicon, consisting in a single reduction in an electric arc furnace.

Differently from the BF, the heat in the EAF is mainly provided by an electric arc generated by the molten bath and three electrodes, powered by a three-phase electrical supply [19]. In an EAF, the emissions are indirect (despite sometimes electrodes are made of graphite) and are attributed to the type of source used in the power plants. According to [20], a ton of crude steel is associated to up to about 2 ton of CO_2 for BF and around 1 ton of CO_2 for EAF. However, mainly due to the type of raw material, BF is mostly used. Concerning the silicon route, EAF is instead more common, especially as submerged arc electric furnace (SAEF) [21]. Differently to a conventional EAF, the electrodes are submerged through the charge, while gas fills the cavity, which surrounds them in the lower part. The produced silicon will be located under the cavity. Moreover, Carbon, in the form of coal and coke (and sometimes woodchips or charcoal), is charged into the furnace to enhance the carbothermic reduction. The Carbon source can also be addressed as reducing agent. Therefore, emissions in silicon (and ferrosilicon) production are both direct and indirect. In a scenario where the electricity is entirely from renewable, emissions are between 3.5 and 4.7 ton of CO_2 every ton of pure metal produced [22]. Otherwise, the values can increase. For instance, considering the European electricity mix, the emissions in 1998 were about 9.5 ton of CO_2 every ton of pure metal produced [23].

With the aim to reduce the environmental footprint of these metallurgical processes, several options are possible. To a certain extent, it is straightforward to expect a reduction of indirect emissions by the increase of the renewable energy penetration in the electricity mix. However, this possibility does not depend on the direct intervention of the metallurgical sector. Instead, several options can be directly attempted *in loco*. Generally, for the metallurgical processes, which include a carbothermic reduction, several solutions have been investigated [23, 24], and they include:

- The upgrading of the process, to increase the efficiency and therefore limit the energy intensity [25, 26].
- Electro-winning, which relies on electrolysis to reduce the ores [27–29].
- Recovery of energy or by-products, which may be used in other carbon intensive systems [30, 31].
- Substitution of the solid fossil fuels with methane, which is expected to pollute less, or hydrogen, which may be theoretically considered as Carbon neutral [32–35].
- The increase in the Carbon mix, which is charged into the furnace of biomass or biochar [36–38].

Among the mentioned alternatives, the introduction of biochar in metallurgical applications has been deeply examined and it is considered promising [39]. This thesis focuses on the exploitation of this material, as way to reduce the metallurgical emissions. According to the United Nations, biochar is considered as renewable [2]. Its nature and characteristics are clarified in the next section.

2.3 Biochar as reducing agent: benefits and challenges

Biochar can also be addressed as biocarbon, charcoal and biocoal, according to the traditional applications in which it has been used. Recently, the term biochar has risen in popularity and it is mostly used among the terms. It was therefore decided to utilize only this definition throughout this thesis. Biochar is a product obtainable from biomass mainly by a thermal treatment called pyrolysis. In this process, dry biomass is heated up and decomposed under inert conditions. Due to its physio-chemical similarities to coal, biochar may be a promising alternative to fossil fuels, e.g. as energy source in heat and power plants [40–42]. However, it may be also exploited in different other sectors, e.g. as enhancer to improve soil quality [43–45], and as filter in water treatments [46, 47]. Comprehensive reviews on biochar and further potential applications are available in [48–52].

Biochar can also be obtained by other thermal treatments than pyrolysis. Torrefaction (referred sometimes as mild pyrolysis) is a similar process, which is perfromed at slighlty lower temperatures, in the range of 200 - 300°C [53]. The main product is a biochar, which is characterized, in contents, by low fixed carbon and high volatile combustible gases. Generally, it is therefore not used as coal substitute in metal production. Recently, hydrothermal carbonization (HTC) has also been implemented to optimize the production of biochar from wet biomass, usually not processed in pyrolysis [54, 55]. Gasification has also been considered as possible producing method, despite the low yields [56]. Nevertheless, pyrolysis is the industrial most common way to convert biomass into biochar. By this treatment, pyrolysis oil and pyrolysis gas are the other two main products. However, when biochar is the main product, pyrolysis is called carbonization or slow pyrolysis. The attribution of “slow” comes from the values of heating rates, in the range 1-5°C/min [49]. According to [50], heating rate has a considerable effect on the final char yields: low heating rate must be preferred to foster high char yield. In another type of pyrolysis, addressed as “fast”, heating rates are higher and the pyrolysis oil yield is optimized [57].

The carbonizing temperature has also a relevant impact on the the process. High temperatures reduce the biochar yield and the mechanical strength of the biochar but increase simultaneously the content of fixed carbon. Besides, peak temperature has a strong influence on the pore structure, surface area, reactivity and adsorption properties of the biochar [58]. Most common reactors work at atmospheric pressure, with temperatures between 300 and 600°C. Nevertheless, it was experimented carbonization at elevated pressure, demonstrating a positive influence on the char yield and fixed carbon content [59]. Pyrolysis process handles mainly solid biomass. Wood is the most common type of biomass used for industrial application. In general, the content of lignin, holocellulose and extractives in the biomass has a great influence on the process. Biomass species with high lignin contents, as wood, offer higher biochar yields [60].

Biochar can be analyzed and characterized by several properties. Some of them are useful to assess its potential in metallurgical applications. Fixed carbon is an important parameter that quantifies the Carbon-like nature of a material. As previously explained, pyrolysis temperature and heating rates strongly affect the fixed carbon. It was observed that this value can be competitive in biochar, especially if processes at high temperature [61]. In a metallurgical process, a key property is the reactivity of carbon. A good reducing agent is fundamental in smelting processes of oxides. Despite the reactivity should be tested considering the metal involved, CO_2 reactivity test has been accepted as industrial standard for coal and coke, due to its easy replicability possibility. For instance, it was demonstrated that the thermogravimetric analysis (TGA) can be used as good and accurate reactivity test [62]. Compared to coke, biochar has usually more coarse surfaces and many pores. These characteristics makes biochar a more reactive reducing agent [38].

The thermal compressive strength expresses the value of the burden that the furnace bed must bear without fracking. Differently to common compressive strength, the thermal one is usually measured after having heated up the material at high temperatures. Compared to fossil Carbon sources, biochar is mechanically weak: common values of strength vary between 1-8 MPa, while for coke they are between 13-16 MPa [63]. Even though slow heating rate can ensure improvements in strength, other parameters seem not to have significant influence [64]. This issue is generally related to a mechanical weakness of biochar, which is also associated to mass losses during the handling, transportation and storage phases [65]. The electric resistance of biochar instead is much higher than fossil reducing agents. This is a desirable characteristic for limiting energy consumptions in the electric arc furnace [58]. Biochar is also characterized by a lower Sulfur content than coal [66].

In the light of these observations it has been demonstrated that biochar can substitute entirely fossil reducing agents in the production of ferrosilicon and silicon metal [64], while it could partially reduce the coke share in the production of manganese alloys [63]. The theoretical total substitution in the steel manufacturing was instead assessed in [67], demonstrating the associated relevant environmental benefits. However, according to [39], the biggest barrier slowing the transition is the biochar production cost. It was estimated to be between 233 and 513 €/ton. Coal costs range between 15 and 110 €/ton and coke is slightly more expensive (see [68]). As expressed in [69], labor work, transportation costs, and energy costs are substantial for renewable carbon sources. To successfully achieve a transition from fossil to renewable materials in the metallurgical industry is therefore important to act aiming at improving some not yet competitive properties while abating the producing costs.

2.4 Pelletization of biochar

Densification through pelletization may be a way to overcome the low mechanical properties of biochar [65]. According to [70], pelletization has a positive impact on a material, by improving density, compressive strength and mechanical durability. Higher values of density are related to lower storage and transportation volumes, and therefore lower costs. Mechanical durability describes the tendency of a material to maintain integrity during handling and transportation [71]. Compressive strength is instead useful to simulate the weight top pellets have on the lower pellets during their storage, handling and application [72]. These properties are hence useful to estimate the improvement of the quality of a material after pelletization. During this treatment, the material is compressed at high pressures, which enhance a plastic agglomeration of particles [73]. The bonding mechanism is complex. However, as explained in [74], the dominating binding forces are mechanical interlocking, van der Waals forces, hydrogen bonds and other chemical bonds.

Several materials can be successfully pelletized without the inclusion of any external binder (or additive). For instance, wood is easily pelletizable, due to the presence of natural binders (e.g. lignin), which creates solid bridges [75]. Differently, biochar requires a considerable amount of additives, a factor which makes its industrial pelletization more complex [76]. As demonstration, Figure 2.4 shows that biochar pellets need around 30% of water to be stable. It may be reasonably assumed that it would hence be more convenient to pelletize the raw material before processing a pyrolysis. This solution would imply lower costs, since no additional binders are required. However, in comparison to this route, it was observed that the pelletization of biochar results in higher mechanical strength [77].

Figure 2.4: Biochar pellets made with a water content of, from left to right, 10, 20, 30 and 40% (total feedstock weight).

The choice is therefore strictly dependent on the type of application the biochar might be used for. For instance, in the case of a metallurgical use, higher mechanical properties might be more appealing and, as consequence, the pelletization of biochar might be preferred. Regardless of the employment, this option has been extensively investigated. The effect of the pelletizing pressure (range 32–224 MPa), water content (range 20-40%) and pyrolysis temperature (range 250-650°C), was investigated in [78]. The strongest pellets were obtained at 128 MPa, with 35% of water content and the highest pyrolysis temperature [78], highlighting the relevant effects of the latter. This relation was observed also in [79]. The necessity of adding a considerable amount of water was instead showed in [80], where the highest mechanical durability was achieved with an addition of water of 30% (total weight). Many different binders were investigated in other studies: water, lignin, starch, sawdust, calcium hydroxide, sodium hydroxide, calcium cloride, calcium oxide, fruit's peel [72,81–83]. In these works, pelletization of biochar was mainly assessed by varying binder content, particle size and pelletizing pressure.

The potential benefit of applying a second heat treatment on pellets was studied in [84], where densified biochar was carbonized, showing high fixed carbon content and improved compressive strength. The present thesis mainly focuses on the inclusion of pyrolysis oil as binder. In regards, limited research is available in Literature. In [85–87], pyrolysis oil was used as binder in the co-densification of biochar and raw biomass, demonstrating a relation with improved mechanical properties. Similar results were obtained in [88], where a blend of pyrolysis oil and biochar in ratio 1.1:1 was pelletized, as well as in [89], where the ratio was 0.42:1. The introduction of biochar pellets in the metallurgical process has been considered [61,65,82,90]. It has been demonstrated that by the reducing porosity, pelletization reduces the reactivity of biochar, despite the values are still high when compared to those of fossil fuels [65, 90]. Instead, the impact of binders on the reactivity is not clear. In [65], it was observed that the inclusion of additives may bring to different outcomes.

2.5 The Norwegian perspective

The research, which is presented in this thesis, was partially focused on the potential implementation of the proposed process in Norway. It is therefore convenient to present a brief overview of the introduced issue in relation to the Norwegian scenario. In the wake of what accorded among the European Union states, Norway is committed to a target of an at least 40% reduction of GHG by 2030 compared to 1990 levels [91]. However, as highlighted in Figure 2.5, despite an initial reduction trend in the early Nineties, the overall emissions started increasing slightly from 1994. The presented data were obtained from Norwegian Statistics [92]. In the recent years, efforts have been made to reverse the phenomenon. However, the result has been relatively weak and, compared to the 1990 level, the overall emission in 2018 were about 1% higher. The more immediate causes can be directly inferred by observing Figure 2.5. The remarkable drop of emissions in the "Industry and mining" sector has been shadowed by the increase in the "Oil and gas extraction" and "Road transportation" ones. It is therefore clear that drastic actions must be taken in regards to the last mentioned categories. Nonetheless, the impact of the industrial branch is still relevant, as it is second only to "Oil and gas extraction". If Norway wants to meet the targets declared in the INDC, it must implement strategies to further cap the emissions of this sector as well.

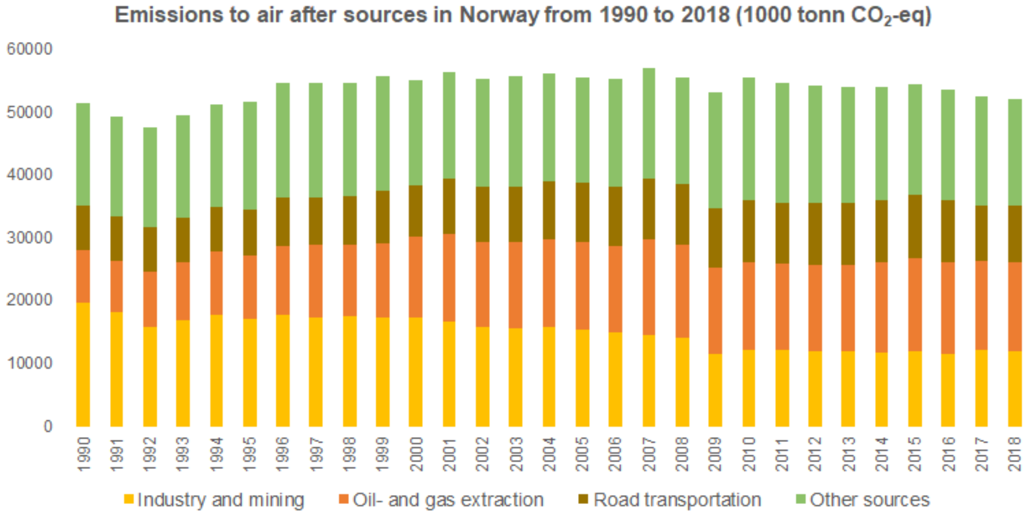


Figure 2.5: Emissions to air after sources in Norway from 1990 to 2018. Data elaborated after [92].

When the emissions share in the industrial sector are examined, it can be observed that between 2008 and 2018, the metal production contribution floated around 34% [92]. This datum implies two conclusions: (a) the metallurgical industry is a large emitter in Norway, (b) new actions must be implemented to enhance a sectorial reduction of emissions. According to [19], the main metal products processed in Norway are: aluminum, ferrosilicon and silicon metals, other ferroalloys and steel. Fossil materials are largely utilized in the related metallurgical process either as heat and Carbon source or as conductors in the electrodes. The application of biochar in the Norwegian metallurgical industry is therefore relevant. This possibility has been extensively investigated [61, 63, 64, 93–96]. In limited quantity, biochar has already been introduced (mixed often with woodchips) or considered in the process reducing mixture in several metallurgical factories around the country [97–100]. However, for the reasons which were explained through the previous sub-chapters, the renewable transition of the smelting process is not straightforward.

The opportunity is also appealing when the issue is examined from the biochar production side. Norway's surface is largely covered by forests. Following [101], approximately 8.2 millions hectares occupy about the 25% of the land area, distributed heterogeneously as shown in Figure 2.6.

Figure 2.6: Forest total area in Norway (in millions of hectares) in the interval 2014-2018. Colors are limited by the area of each Norwegian county. Data elaborated after [101].

Traditionally, this country has relied on this source for the pulp and paper industry [102]. However, already in 2006, the adoption of the know-how as well as the involvement of this type of industry into the implementation of bioenergy production in Norway was suggested [103]. According to [104], more than the 50% of the available biomass from forest is not exploited yet. Recently, studies on the feasibility of the production of biochar from Norwegian forests have thrived [105–109]. Moreover, despite still not at a large scale, Norway has experienced the upcoming of several actors, which aim to increase the national production of biochar. The related economic and environmental benefits attracted a broad group of stakeholders, which created a national biochar network (*Norsk biokullnettverk*) in 2018 [110]. Since both demand and supply are inside the border of the country, the entire chain might be developed nationally. This opportunity might enable circular economy strategies, which might hopefully bring to a reduction of production cost for biochar as well as improve the sustainability of the process. In regards to the environmental impact of biochar production in Norway, no clear information are easily obtainable. However, the effects on the environment of an increase in exploitation of forests for bioenergy was discussed in [111]. Finally, looking at Figure 2.6, it can be observed that the areas which are mostly covered by forests are in the inner part of Norway. Generally instead, the metallurgical factories are disseminated in the coastal fraction, since both the access of ships and the cooling facilities are eased. In a rough territory as the Norwegian one is, this could particularly lead to a severe increase of transportation costs. For this reason, it would be extremely important to minimize the mass losses while the biochar is delivered, so to minimize the economic loss. Densification of biochar may be a good solution to tackle this issue.

Throughout this overview chapter, the background behind the choice of investigating the application of biochar pellets, as a solution to address the environmental impact of the metallurgical industry, has been clarified. Besides, the Norwegian scenario has been introduced, to justify why, in this research, some choices have been taken, considering in addition the implementation of the proposed system in Norway. The research work, presented and discussed in the following chapters, should hence become clearer.

Chapter 3

Materials and Methods

3.1 Materials

Throughout the realization of the research work presented in this thesis, several materials were analyzed and applied. Some of the feedstock, which was not included in the published papers, is only briefly mentioned. Instead, the material, which was actually used more extensively, is described more in detail. This Materials section covers exclusively the material directly obtained by some suppliers. The biochar and pyrolysis oil, which were produced in house are described later in the next section. Generally, the untreated materials were from: a local forest in the whereabouts of the University of Agder (Grimstad, Norway), industrial providers in and outside Norway.

3.1.1 Woody feedstock

Norway spruce (*Picea abies*) as well as Scots Pine (*Pinus sylvestris*) wood chips were produced from a tree in a local forest, in Grimstad, Norway. The harvested tree was chipped and immediately dried. The chips were dried at 60°C for 24 hours and stored in an airtight box at ambient temperature. In Paper B, pine wood was obtained from an Italian furniture manufacturer.

3.1.2 Charcoal and biochar pellets

Through several deliveries carried out at different periods, charcoal was provided by Elkem ASA (Norway). The material was supplied in bags and stored "as received". According to the use, it was either applied without further treatments or milled with a 2 mm sieve hammer *millpx-mfc 90 d* (Polymix, Germany) and stored at ambient temperature in airtight boxes. Some types of biochar pellets were also obtained by the same industrial provider.

3.1.3 Pyrolysis oil and additional binders

Pyrolysis oil was generally produced in-house, with the exception of the oil used in Paper A, which was obtained from Btg-Btl (The Netherlands). Btg-btl oil is from fast pyrolysis of pinewood. Moreover, LignoBond DD from Borregaard (Norway) was used as lignosulphonate additive. This binder is produced from spruce.

3.1.4 Supplementary materials

Other materials were preliminary used. Microsilica and *radiclon* dust (silicon production waste) were provided by Elkem ASA. The same company supplied fossil coal, coke as well as petcoke. Silicon carbide (SiC) and quartz (SiO_2) were obtained from Fiven Norge AS. Carbofex OY (Finland) contributed by delivering charcoal and slow pyrolysis oil from spruce wood.

3.2 Pyrolysis and second heat treatment

Biochar and pyrolysis oil were produced through several methods in lab. The heat treatment the pellets underwent was similar in methodology. Therefore, this section lists the options that were considered and applied for both treatments.

3.2.1 Muffle furnace

Sometimes, the aim was to only produce a limited quantity of biochar. In these cases, the following method was preferred. For each experiment, about 80 g of biomass were weighted in a 700 ml alsint (Al_2O_3) crucible, which was covered with an alsint lid. Inert atmosphere was created by purging nitrogen. The crucible was then placed inside a hot muffle furnace *LT40/11/P330* (Nabertherm, Germany), which was previously heated up to the set temperature, with a heating rate of 10°C/min. The pyrolysis temperature was then kept constant by the furnace controls for 60 min, without a direct measurement of the crucible temperature. When the experiment was over, the sample was placed in a desiccator, where it was cooled down to room temperature. Finally, it was stored in an air-tight box. A similar procedure was adopted as second heat treatment in Paper B. In this case, each pellet was introduced into a quartz glass crucible covered by a quartz glass lid.

3.2.2 Slow pyrolysis reactor

In Paper C and Paper D, both biochar and pyrolysis oil were produced in-house with a modified *SQ 11 top loader furnace* (Kittec, Germany). A schematic drawing of the reactor is shown in Figure 3.1. About 100 g of wood chips were evenly distributed in a SiC retort, which was placed inside the furnace. The thickness of the retort was 2 mm, while its height and inner diameter were respectively 150 and 75 mm. Before proceeding with the pyrolysis, nitrogen was purged with a flow of 40 ml/min for 15 minutes, to generate inert atmosphere in the reactor. A thermo-computer *TC 505* (Bentrup, Germany) was used to control the heating program of the furnace, which consisted in heating up at 10°C/min up to the final pyrolysis temperature, while the original nitrogen flow was kept constant. The condensable gases (together with water) from the two condensers were collected in a quartz glass bottle, located between two condenser units. The non-condensable products were expelled through a chimney, after passing the second condensation unit. Both condensation units had a set temperature of 4°C. After one hour at constant pyrolysis temperature, the reactor was cooled down to ambient temperature. The solid product was immediately milled in a hammer mill *px-mfc 90 d* (Polymix, Germany), with a 2 mm sieve, and afterwards stored at ambient temperature in airtight boxes. The collected pyrolysis oil was poured in glass containers and stored at 4°C. A similar procedure was also applied as second heat treatment in Paper D.

3.2.3 Batch pyrolysis plant in Paper B

In Paper B, a batch pyrolysis plant was used to produce both biochar and pyrolysis oil from pine wood, which was previously seived with a 10 mm sieve cutting mill *Model SM 2000* (Retsch, Germany). This reactor was developed and set up at the Department of Engineering at the University of Perugia, Italy. The layout of the plant is presented in Figure 3.2.

About 800 g of pine wood were placed within the reactor. Inside both the reactor and the condenser unit, inert atmosphere was created by purging nitrogen, with a flow of 3 l/min. The biomass sample was then heated with a constant heating rate of about 4°C/min up to the final pyrolysis temperature. This temperature was maintained for about 30 minutes. The system was monitored using a program made in *LabVIEWTM* (National Instruments, Austin, Texas), connected through a Compact Field Point system to a P.I.D. (Proportional- Integrative-Derivative) controller. During the experiment, non condensable gases were expelled through the hood. The condensable gases, instead, were collected in the condenser unit. Once the heating was finalized, the reactor was cooled down for about 4-6 hours and the solid and liquid products where extracted.

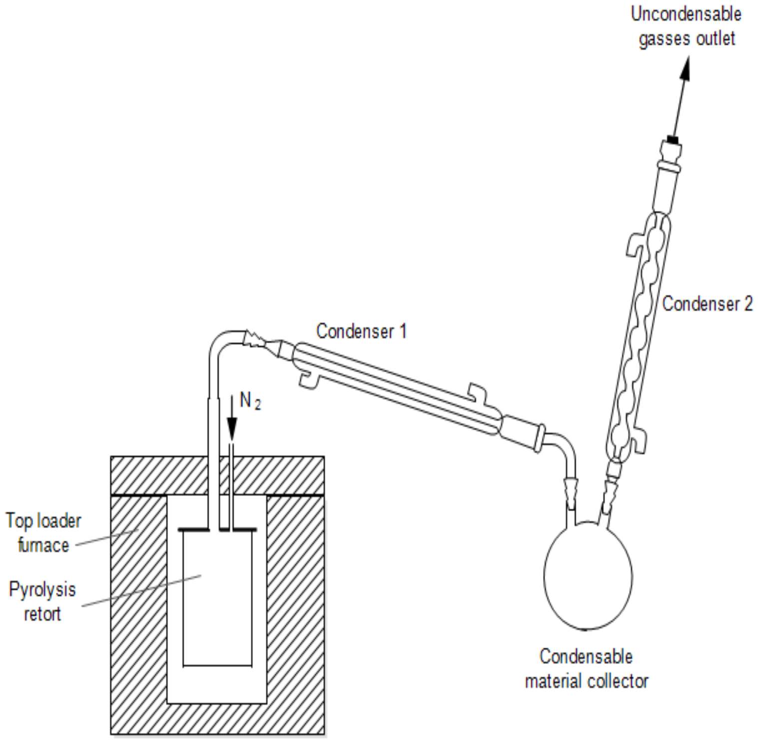


Figure 3.1: Schematic drawing of the slow pyrolysis reactor in house. The inner retort diameter is 75 mm and the flow rate is 40 ml/min.

3.2.4 High temperature furnace

In Paper A, the second heat treatment was carried out in a high temperature reduction furnace *LHTG 200-300/20-1G* (Carbolite Gero, Germany). The samples were loaded into 70 ml alumina crucibles placed inside a graphite retort. Inert atmosphere was created and maintained with argon. At the constant heating rate of 10 °C/min, the pyrolysis temperature was reached and kept for one hour. Before extraction, the furnace was cooled down to room temperature. The samples were stored in air-tight boxes. The gasses were not collected and they were expelled through a chimney.

3.3 Biochar pellets production

Throughout several experimental campaigns, different pelletization methods were utilized. The pellets analyzed in the papers were produced by the hot compact pellet press. However, important observations and assumptions come from preliminary studies conducted with a manual screw pellet press. These two methods are therefore presented. Moreover, the section includes the description of the multi-paramater model, which was applied to biochar pelletization.

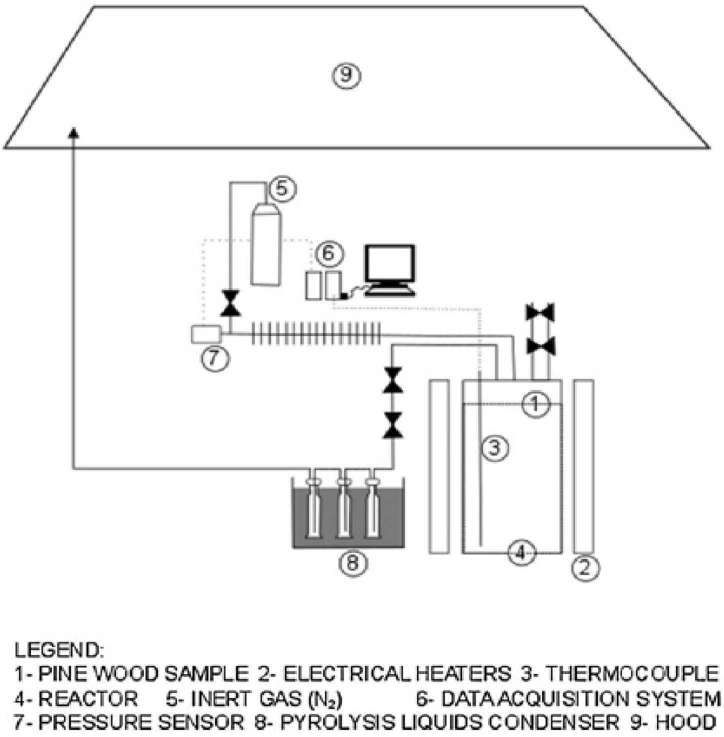


Figure 3.2: Layout of the batch pyrolysis plant at the University of Perugia, Italy (from Paper B). The inner diameter is 20 cm and the flow rate is 3 l/min.

3.3.1 Hot compact single pellet press

The layout of the hot compact single pellet press *EQ- HP-6T* (MTI, USA) is presented in Figure 3.3. The steel die (top pressing rod, sleeve, bottom pressing rod) is placed between two steel rods. Two available die-sets with different dimensions are available: one with an inner diameter of 6.250 mm, another with an inner diameter of 12 mm. The movement of the upper rod is limited by a stopper, which is fixed by a handweel. The lower rod is instead moved upwards by a hydraulic piston. Between the lower rod and the piston, a load cell *CPX1000* (Dini Argeo, Italy) is connected to a multifunction weight indicator DFWLB (Dini Argeo, Italy). The die and the rods are housed inside a split furnace with a temperature controller. Before pelletizaton, the furnace is activated and the components are heated up to the selected operational pelletizing temperature. Around 3 hours are necessary to guarantee an homogeneous distribution of temperature among the pelletization components. Once the machine is ready, the pelletization blend is prepared. The materials (biochar, binders, water, etc.) are mixed, magnetic stirred and homogenized in a beaker for approximately 15 minutes. Before loading the die, the amount of mixture per die filling is carefully weighted. According to the applied pressure and the desired final pellet length, the amount of loaded mass may change. While filling it, the die is outside the furnace. This operation was preliminary observed not to affect the temperature of the die, as the heat capacity of the die and biomass are very small compared to the total weight of the press. Once the die is loaded, it is newly placed inside the furnace. By using a pressure incrementer rod, the hydraulic piston is moved upwards, until reaching the selected final pressure, which is kept for 10 s. Afterwards, the pressure is released, the die is extracted from the furnace and the pellet is ejected. The die is then placed inside the furnace until next pellet is prepared. The pellet is cooled down to ambient temperature and stored in air-tight containers.

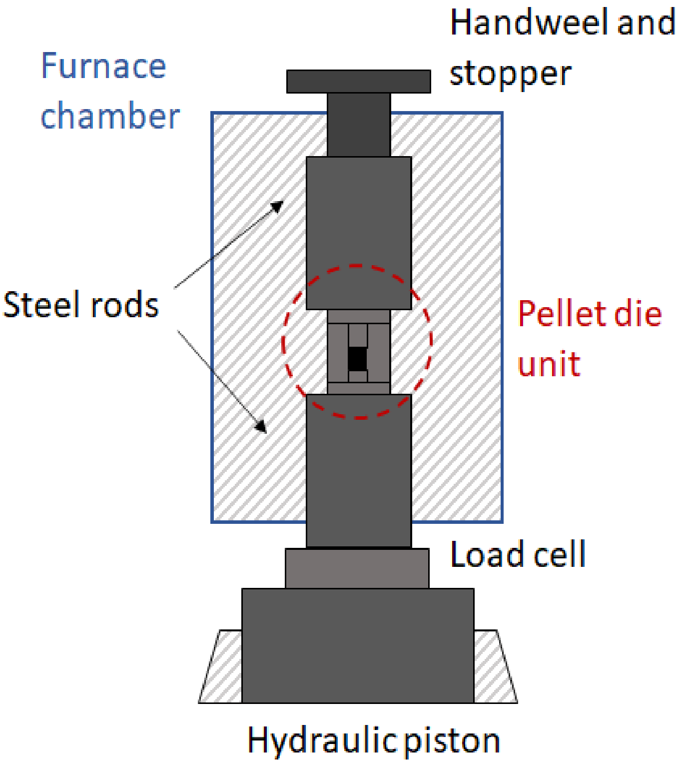


Figure 3.3: Layout of the hot compact pellet press. The main components are indicated. The pellet die unit includes a top pressing rod, a sleeve and a bottom pressing rod.

3.3.2 Manual screw pellet press

A single pellet press (Fistreem International Ltd, UK) was used for preliminary studies. The operation is similar to that of the hot compact hot pellet press. However, pressure and temperature cannot be controlled. As shown in Figure 3.4, the die unit is placed on the base of the pellet press. The upper pressing rod is then moved downwards by a screw piston coupled to a handweel.

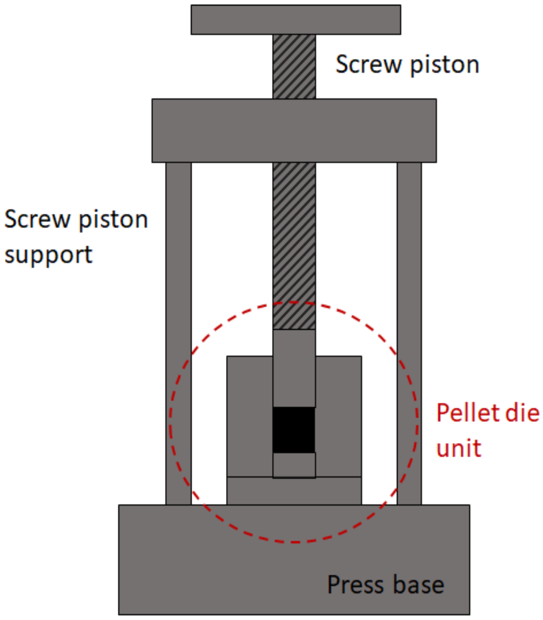


Figure 3.4: Layout of the single screw pellet press used for preliminary tests or screening. The screw piston is supported by a steel frame and a steel base acts as backstop.

3.3.3 Multiparameter model

A multiparameter model, firstly developed in [112] and then valiated in [113], was applied for the study of densification of biochar. This model permits to predict pelletization at industrial scale, by few experiments performed with a single pellet press. In comparison to the lab-scale, an industrial pellet press is generally characterized by a simultaneous production of longer pellets, due to the presence of a die matrix and rollers. However, the model focuses on the analysis of a single die, where the biomass is pressed in the way shown in Figure 3.5.

In particular, the exiting pressure (P_x), which is the longitudinal pressure the pellet experiences when ejected through the die, is computed in relation to the compression ratio c, which is defined as:

$$c = \frac{x}{2r} \qquad [-] \qquad (3.1)$$

where x and r are respectively the length and the radius of one of the dies in the die matrix of a pellet press. The main theoretical assumption behind the model is that, once the biomass is compressed in one direction, it tends to expand in the two other perpendicular directions. Under the further assumption of orthotropicity, which considers the biomass fibers perpendicularly oriented to the longitudial direction of the channel, the consequent expansion in the directions perpendicular to P_x can be described through the

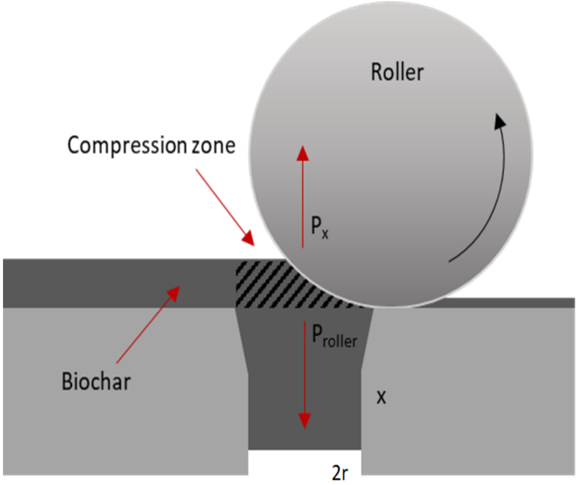


Figure 3.5: Once entered the compression zone, the biomass is pressed by the roller into a die of length x and radius r. The system die-pellet experiences a pelletizing pressure P_x, which takes into account the pressure of the roller and the friction.

Poisson's ratio (v), linked to the Poisson effect [112]. Under this consideration, the Poisson's ratio is expressed as v_{lr}, since the stress is applied longitudinally and the transverse deformation is radial [113]. Once the pre-stressing term P_{N0}, incorporating inelasticity, and the sliding friction coefficient (μ) are also included, the relation between P_x and c is represented as [112]:

$$P_x(c) = \frac{P_{N0}}{v_{lr}} e^{\mu v_{lr} c - 1} \qquad \text{[MPa]} \qquad (3.2)$$

As mentioned, the structure of Eq. 3.2 is relatively simple. However, it includes parameters, whose values may be complex to measure. In the case of biochar, they may be also hardly obtainable in the existing Literature. To overcome such issue, a new version of the model was suggested in [114]. Two new parameters (U and J) are introduced and defined as:

$$U = \mu P_{N0} \qquad \text{[(MPa)}^2 \text{ s]} \qquad (3.3)$$

$$J = \mu v_{lr} \qquad \text{[MPa s]} \qquad (3.4)$$

If Eq. 3.3 and Eq. 3.4 are inserted into Eq. 3.2, a new equation is obtained [114]:

$$P_x(c) = \frac{U}{J} e^{4Jc-1} \qquad \text{[MPa]} \qquad (3.5)$$

In comparison to Eq. 3.2, Eq. 3.5 presents a lower number of parameters, which must determined. In addition, the introduced parameters can be measured in a simpler way. Before proceeding to the description of the method, it is important to clarify how x and P_x are measured experimentally. Figure 3.6 is shown as support. Before starting with the model experimental phase, at least 20 g of pelletizing material is prepared. The hot compact single pellet press, previously described in 3.3.1 is utilized. Firstly, the die (diameter 6.25 mm) is loaded with the material (phase a) and pressed at 100 MPa (phase b). If the mass exceeds 0.15 g, the material is added in sequential layers that are pressed consequentially at the same applied pressure [114]. When a sufficient amount of mass to make a required pellet length has been loaded and pressed, the bottom pressing rod is removed and the pellet is ejected, while P_x is measured (phase c). The length of the pellet is then measured by Vernier caliper with a precision of 0.01 m and c is determined. For each compression ratio, at least three samples are tested. By preliminary studies, it was observed that to obtain the same compression ratio, it is sufficient to load equal mass. The average value and the standard deviation of the pelletizing pressure of three tests are then computed and used to elaborate the model.

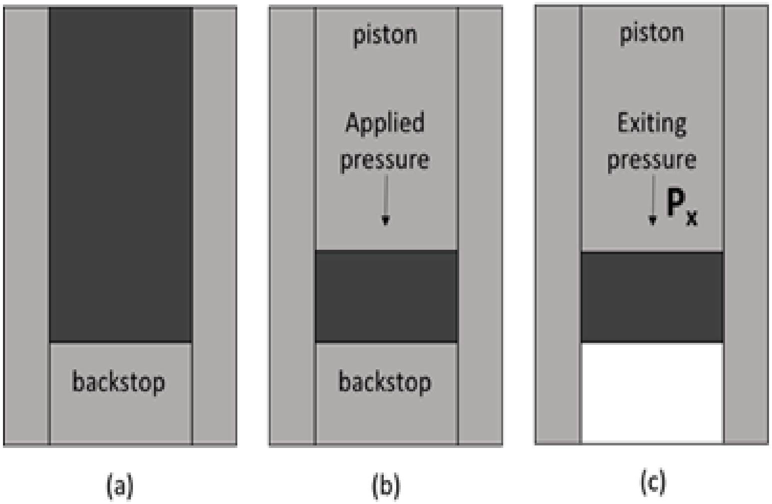


Figure 3.6: Multiparameter model lab-scale experiment. In phase (a), the backstop is included, and biochar is inserted into the die. In phase (b), the piston compresses the biochar mixture up to a defined pelletizing pressure. In phase (c), the backstop is excluded, and the pressure P_x necessary to eject the pellet is measured.

As the method to measure the exiting pressure has been clarified, the application of the model can be discussed. Aim of the model is to build a pelletizing curve, where P_x is expressed as function of c. An example is offered in Figure 3.7. For c $\ll$ 1, Eq. 3.5 can be reduced to:

$$P_x(c) = 4Uc \qquad \text{[MPa]} \quad (3.6)$$

Exploiting Eq. 3.6, the coefficient U can therefore be derived experimentally by the linear fit of the values of the exiting pressure obtained at three different c (lower than 0.75). Despite close to 1, the upper limit of 0.75 is satisfactory, since it was observed in preliminary tests that linearity is still ensured. The diagram point (0, 0) is also included in the linear fit. Taking Figure 3.7 as example, the coefficient U is extrapolated by dividing the coefficient of the linear curve by 4. The coefficient J can now be computed, by applying Eq. 3.5. Further pellets are produced at compression ratio between 1 and 3.

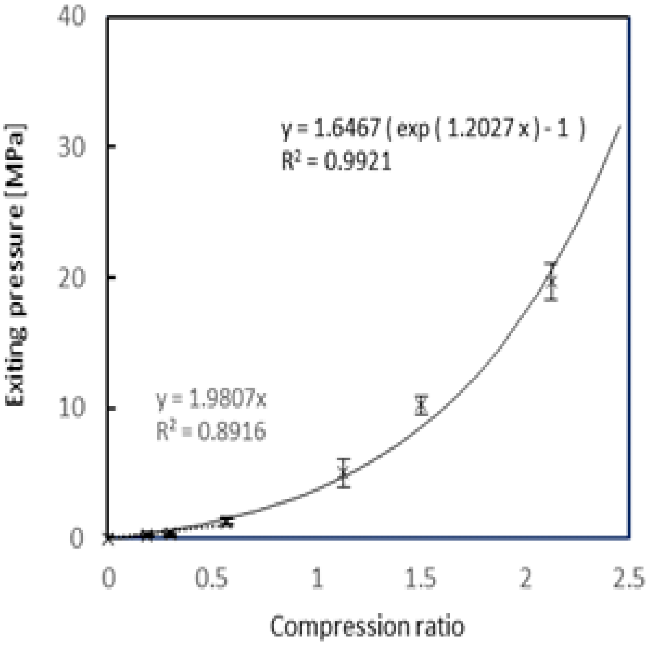


Figure 3.7: Example of pellet curve, built with the multi-parameters model.

The coefficient J can hence be extrapolated by non-linear interpolation (see Figure 3.7). Finally, the pelletizing curve is completed and it can be used to evaluate the pressure response at the higher compression ratios, conventionally used in the industry (ca. 7-8). The assumptions, which the model is based on, imply considerations that are noteworthy to mention. For instance, the model is based on the assumption that the Poisson's ratio is constant with the variation of compression ratios. As noted in [114], this is only valid at sufficiently small compression ratios. Moreover, due to the exponential trend, the extrapolation of industrial related compression ratios may be associated to a certain degree of uncertainty. Nevertheless, the suitability of the model by a single pellet press was previously demonstrated for the pelletization of both wood [114] and torrefied wood [115].

3.4 Characterization

3.4.1 Ultimate analysis

C-H-N ultimate analysis was carried out at different laboratories. In Paper A and Paper D, a *2400 Series II CHNS/O Elemental Analyzer* (PerkinElmer, USA) was used in house, according to the standard EN ISO 16948:2015. The analysis in Paper B were performed with a *CHN elemental analyzer* (LECO Truspec CHN), applying the standard UNI 15104:2011. Instead, in Paper C, an *EuroEA* (Eurovector, Italy) with *TCD* detector was used (EN ISO 16948:2015). Generally, oxygen was computed by difference of the other elements, while sulphur content was assumed negligible because. Each analysis was repeated three times.

3.4.2 Proximate analysis

Proximate analysis was carried out in a muffle furnace *LT 40/11/P330* (Nabertherm, Germany) according to EN standard procedures. The applied standards were EN 15148, EN 14774-2 and EN 14775, respectively for volatile matter, moisture content and ash content of biomass. For the biochar in Paper B, proximate analysis was performed using a thermogravimetric analyzer *TGA-701* (Leco, Italy). Same standards were applied.

3.4.3 Calorific value

In Paper B, the calorimetric analysis was realized with an *isoperibolic calorimeter AC-350* (LECO, Italy). The higher heating value (HHV) of the biochar utilized in Paper D was measured in a *C 6000* (IKA calorimeter, Germany) isoperibolic bomb calorimeter. The standard EN 14918:2009 was followed. Both cases, the analysis was performed in triplets.

3.4.4 Surface area and porosity

In Paper C, the surface area and porosity of the produced biochar were measured. The test was conducted with nitrogen adsorption at 77 K (NovaTouch, Quantachrome, USA). Initially, samples were degassed at 150 °C and 30 torr for 10 hours. The Brunauer-Emmett-Teller (BET) model was then used to calculate the surface area. Quenched Solid Density Functional Theory (QSDFT) was instead used to evaluate pore volume. This was done through the calculation model for slits and cylindrical pores on the adsorption branch.

3.4.5 Particle size distribution

In this work the particle size distribution of biochar produced at various pyrolysis temperatures, from different feedstocks, was analyzed. A laser diffraction particle size analyzer *Mastersizer 3000* (Malvern, UK) was applied. By default, the analyzer tracks the particle distribution five times per experiment. The final particle distribution was computed as average.

3.4.6 Scanning electron microscope

The morphology and the microstructure of a material can be examined by a scanning electron microscopy (SEM). This type of analysis was performed for several woody biomasses, biochars and biochar pellets. In particular, three different microscopes were utilized. In Paper A and Paper B a *JSM-6499 Scanning Microscope* (JEOL, Japan) was used. A scanning electron microscopy/energy dispersive X-ray Spectroscopy (SEM/EDS) *SU-70* (Hitachi, Japan) was operated in Paper D . Both microscopes are available at the University of Agder. In Paper C, instead, the materials were tested at Sintef (Trondheim) with a *Ultra 55 limited edition* (Zeiss, Germany).

3.5 Pellets testing

The following section covers the methods, which were specifically considered for analyzing some key-properties of the produced pellets. Usually, measurements were taken at least 24 hours after the pelletization, in order to guarantee a proper relaxation and stabilization of the densified material. These tests were performed in triplets. The average was considered as final value, if the standard deviation did not show relevant alteration. In that case, further tests were carried out.

3.5.1 Particle density

Particle density (ρ) was computed as:

$$\rho = \frac{m}{\pi r^2 l} \qquad [\mathrm{kg/m^3}] \qquad (3.7)$$

where m is the mass of the single pellet, r is the radius of the pellet, and l is its length. Mass was determined on a balance with a readability of 0.1 mg, while radius and length by a Vernier caliper with a precision of 0.01 mm.

3.5.2 Mechanical durability

The mechanical durability (*MD*) of pellets was measured in an *ISO tumbler 1000+* (Bioenergy Institute, Austria). The machine set-up follows the ISO 17831-1. A charge of pellets (m_i) is inserted in a steel box, which spins 500 times for 10 min. The material inside the box is then extracted. Before measuring the final mass (m_f), the material is filtered in a standardized round hole 3.15mm sieve, to expel fines. Mechanical durability (MD) can hence be computed as:

$$MD = 100 * \frac{m_f}{m_i} \qquad [\%] \qquad (3.8)$$

3.5.3 Shrinkage

In Paper A, the shrinkage of the pellets that underwent re-heating was evaluated. This property may give useful information about the thermal behavior of pellets. Assuming a negligible change of diameter, shrinkage (s) was hence computed as:

$$s = \frac{l - l_f}{l} \qquad [\text{-}] \qquad (3.9)$$

where l and l_f are the lengths in mm pellet have respectively before and after the second heat treatment. The lengths were measured by a Vernier caliper (precision 0.01 mm).

3.5.4 Tensile compressive strength

Tensile (sometimes addressed as radial) compressive strength (*TS*) is the crushing force applied perpendicularly to the cylindrical axis direction of a material. A visualization of the test is presented in Figure 3.8. For pellets, *TS* can be computed as:

$$TS = \frac{F}{\pi r l} \qquad [\text{Pa}] \qquad (3.10)$$

where F is the strength in Newton, necessary to break the pellet, while r and l are respectively radius and length of the pellet. Tensile strength was measured by a *hardness tester* (Amandus Kahl, Germany). During the test a pellet is compressed by a tip connected to a spring, which is moved through a piston connected to a motor. Once the pellet is broken, the machine stops. It is possible to read on the spring grid the value of the equivalent breaking mass (m_s). The precision is 1 kg. With radius and length of the pellet expressed in mm, it is then possible to convert Eq. 3.10 to:

$$TS = \frac{m_s g}{\pi r l} \qquad [\text{Pa}] \qquad (3.11)$$

Where g is the gravitational acceleration. The measurements were carried in triplets. When the value of the measured equivalent breaking mass was lower than 1 kg, TS was considered to be zero.

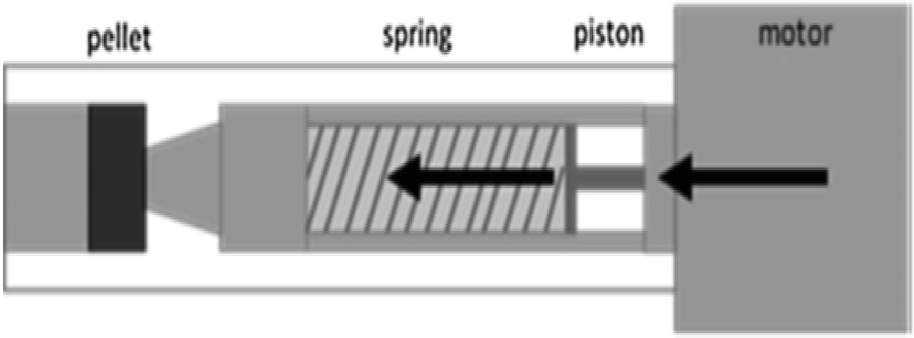


Figure 3.8: Pellet hardness tester for tensile strength.

3.5.5 Self-heating oven test

The assessment of the self-heating risk of biochar pellets was performed following the procedures described in *the classification of the Division 4.2*, suggested by the International Maritime Organization (IMO, United Nations) [116]. This classification, which is presented in Figure 3.9, categorizes solid substances according to their inclination to ignite spontaneously. According to the risk, the substances are assigned to a specific group related to the maximum allowed shipping volume. The aim of the research presented in Paper D was to clarify what makes biochar pellets fall or not into this classification. For such reason, only the first step of the classification test was considered. As shown in Figure 3.9, if a new substance does not fail this step, it is not classified as a self-heating substance of Division 4.2.

According to the procedures indicated in [116], a 100 mm stainless-steel sample cube was filled up with the tested substance. The cube faces have a mesh opening of 0.05 mm. The sample cube was then housed in a slightly larger stainless-steel box, with a mesh opening of 0.60 mm. It was then placed into a modified *SQ 11 top loader furnace* (Kittec, Germany). The temperature was regulated with a thermo-computer *TC 505* (Bentrup, Germany), which was controlled with an application designed on the software *LabVIEW 2019* (National Instrument, USA). Four Chromel-Alumel thermocouples (type k) were used to measure (with a sampling frequency of 1 Hz) the temperatures of the furnace and of the sample. Thermocouples were paired to provide redundancy, as suggested in [117].

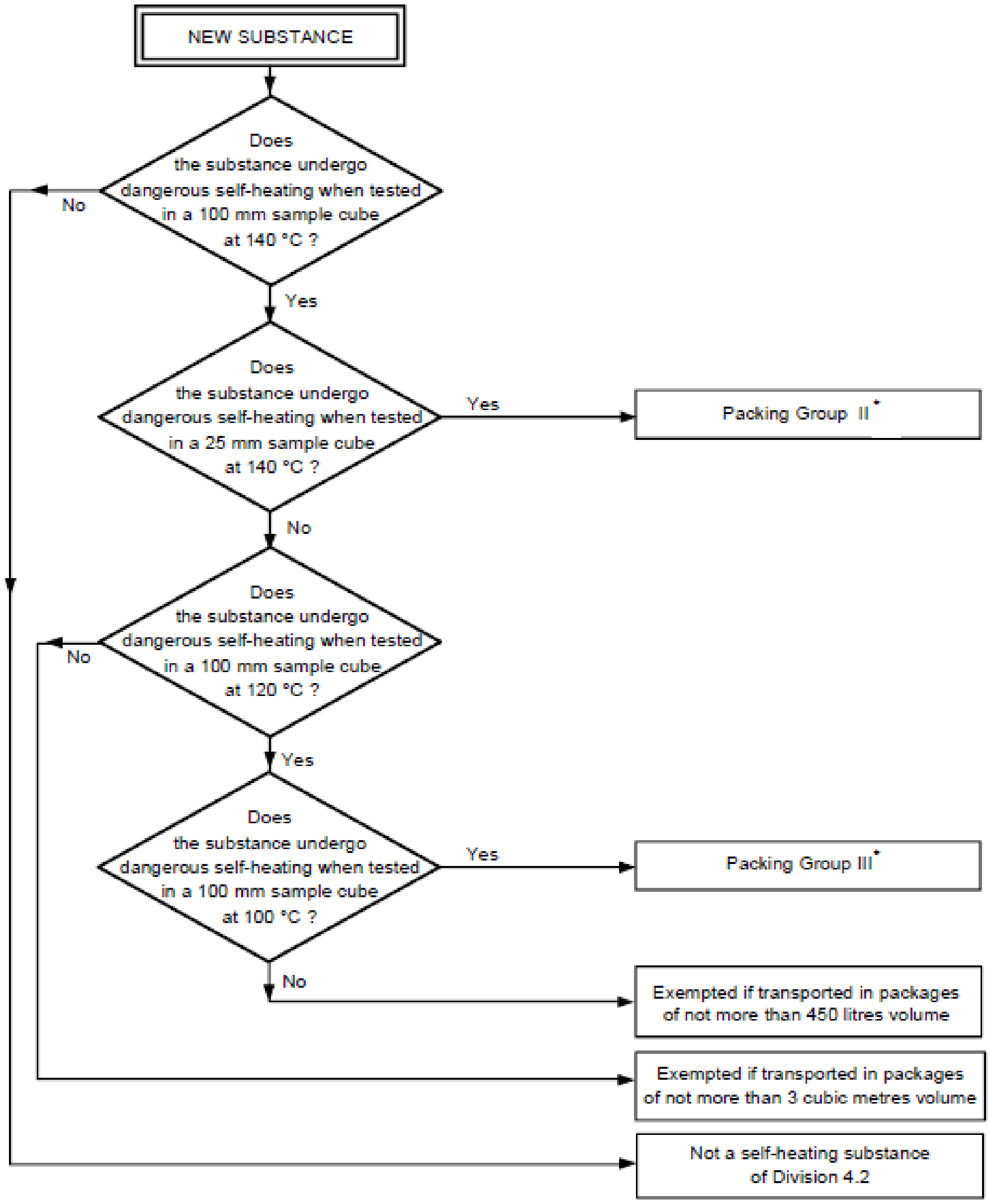


Figure 3.9: Classification of self-heating substances of IMO Division 4.2 [116].

The layout of the oven is presented in Figure 3.10 Air was forced in by an opening placed at one side of the furnace. The furnace was set up to a temperature of 140 °C which was maintained constant for 24 hours. The substance in the sample cube experiences self-heating if its temperature gets 60 °higher than the temperature of the furnace. Hence, by following Figure 3.9, if the sample temperature was registered as higher than 200 °C within 24 hours, the test was interrupted, and the substance was classified as susceptible to self-heating. Otherwise, the substance was not classified as self-heating inclined material.

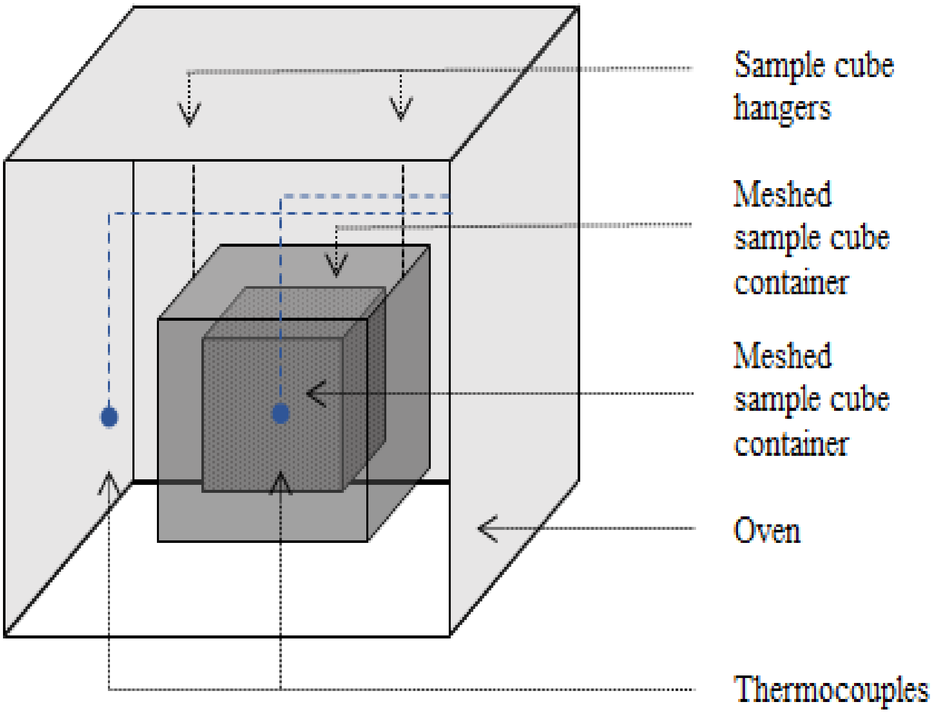


Figure 3.10: Layout of the oven set-up. The substance is placed in a meshed sample cube container housed inside a slightly bigger box with a coarser mesh. The temperature is measured at the center of the sample and inside the furnace by two sets of thermocouples.

3.5.6 Thermogravimetric and differential scanning calorimetry analysis

A *aTGA/DSC 1 Star system* (Mettler Toledo, USA) was used to perform thermogravimetric analysis (TGA) as well as differential scanning calorimetry (DSC) of selected materials. Besides, differential TGA was computed on *Excel*. More in detail, this analysis was utilized to assess: CO_2 reactivity test, oxidation, pyrolysis. In the first case, samples were placed in a 70 μl Al_2O_3 crucible and they were heated in a pure CO_2 atmosphere with a constant heating rate of 10°C/min up to 1100°C. A volume flow of 100 ml/min of pure CO_2 was used.For oxidation, the samples were placed in a 100 μl Al_2O_3 crucible. They were then heated up to 900°C at a constant heating rate of 10°C/min, with a constant dry air volume flow of 50 ml/min. In this case, the temperature of initial combustion (T_{ic}) and the temperature of maximum weight loss rate (T_{mwl}) were also computed. These measurements are usually good indicators in describing the performances of the combustion of a substance [118]. The T_{ic} is considered as the temperature at which the dry weight loss rate is 1%/min, while the T_{mwl} as the temperature characterized by the highest weight loss rate. For pyrolysis, the same method applied for oxidation was followed, but argon was applied to generate an inert atmosphere. For different analyses, the dimension of the crucible as well as the flow rate of the carrier gas were selected carefully according to preliminary tests and were based on existing literature.

3.6 Statistical method

The complexity of the interconnections characterizing the relationship between the main parameters and properties of the production of upgraded biochar pellets was analyzed by statistical experiments. In particular, Response Surface Methodology (RSM) coupled with Box-Behnken experimental design (BBD) was applied. BBD is a multi-factorial and multi-level design. In this research, it was utilized with three factors and three levels. Three responses were considered. BBD consists of a replicated center point and a set of points lying at the midpoint of each edge of the multidimensional cube defined by the levels, as shown in Figure 3.11.

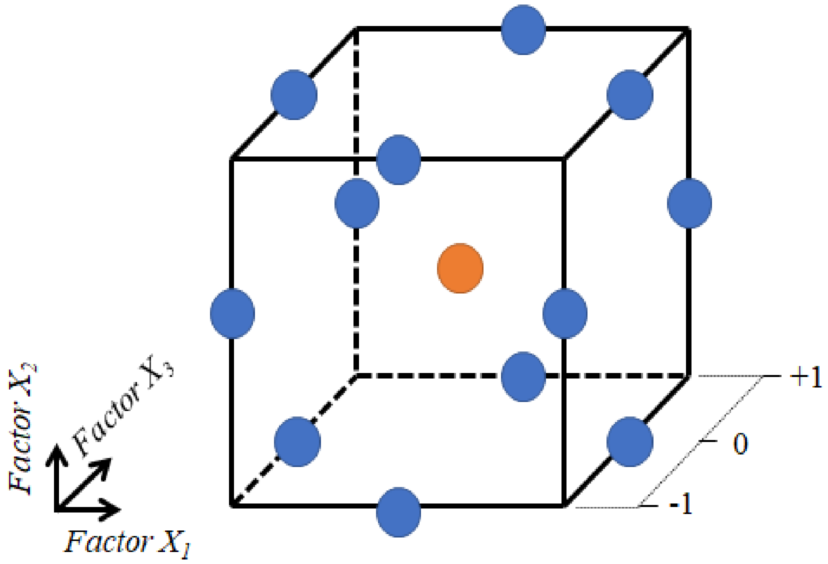


Figure 3.11: Box-Behnken experimental design with three factors and three levels.

In the experiment, three independent variables are chosen as factors, while three properties are chosen as responses. The indipendent variables are prescribed into three levels, coded +1, 0 and -1, corresponding to the minimum level, medium level, and maximum level. These levels are generally chosen according to preliminary tests. 15 runs (combinations of independent variables) are then selected randomly by the Minitab 17.1.0 software (Minitab Ltd., Coventry, UK) to minimize the bias. The center point is triplicated, in order to estimate the pure error. The value of the responses for the selected runs are experimentally obtained. Independent variables and experimental responses are hence analyzed in the software. A polynomial quadratic equation is used to fit their relationship, as follows:

$$Y_i = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j + \epsilon \tag{3.12}$$

where Y_i is the experimental response (for one of the three properties) related to each factor level combination, β_0 is the intercept coefficient, β_i, β_{ii}, and β_{ij} are the regression coefficients computed from the observed experimental values of Y. X_i and X_j are the coded levels of independent variables and ϵ is the error of the model. Analysis of variance (ANOVA) and regression analysis were hence carried out. In particular, a Fisher's F-test at 95% confidence level was performed to investigate the statistical significance of the regression coefficients. The coefficient of determination (R^2), the adjusted coefficient of determination (R^2_{adj}), and the lack of fit test were analyzed to evaluate the adequacy of the quadratic models. RSM was associated to the Derringer's desirability function. This tool is useful, when the aim is to optimized simultaneously the responses, correlated to the factors. Each response (Y_i) is converted into a dimensionless function, known as the individual desirability function (d_i) This new function ranges from 0 to 1. According to the degree of optimization of the response Y_i, 0 and 1 are respectively the least and the most desirable cases. By this conditions, d_i is expressed as:

$$d_i = \begin{cases} 0, & Y_i \leq L_i \\ [Y_i - L_i]/[U_i - L_i]^w, & L_i < Y_i \leq L_i \\ 1, & Y_i > U_i \end{cases} \tag{3.13}$$

where L_i, U_i denote the lowest and highest values of Y_i. Instead, w is denoted as the shape function for desirability, which is assumed as 1 in case of linear dependence. Once the individual desirability functions are computed, they are aggregated into a composite desirability function (D). This new function represents the geometric mean of all transformed responses. Similarly to d_i, D is a dimensionless function whose values range from 0 to 1, and it is built such way that: (a) when all the responses are on-target (d_i=1 for every response), D is equal to 1; (b) if at least one response is outside the specification limits, D is equal to zero. The expression of the composite desirability function is therefore:

$$D = \prod_{i=1}^{n} d_i^{\frac{v_i}{\sum v_i}} \tag{3.14}$$

where n is the number of responses and v_i is the weight used to evaluate the scale of desirability for each response. For the purposes of the research developed in this thesis, v_i was equal to 1, so to weight equally all the responses. Eq. 3.14 can therefore be simplified as:

$$D = [d_1 * d_2 * d_3]^{\frac{1}{3}} \tag{3.15}$$

3.7 Life Cycle Assessment (LCA)

The Life Cycle Assessment (LCA) of an hypothetical but possible application of biochar pellets as subsitute of coke for steel production was performed to show the sustainable impact of the potential shift. The analysis was taken at the University of Perugia. The software *OpenLCA* (Green Delta, Germany) was used. The LCA took into account three main processes: biochar pellets production, coke production, steel manufacturing. The biochar pellets production plant in the study case was developed over the considerations and results from Paper A, Paper B and Paper C. The layout is shown in Figure 3.12.

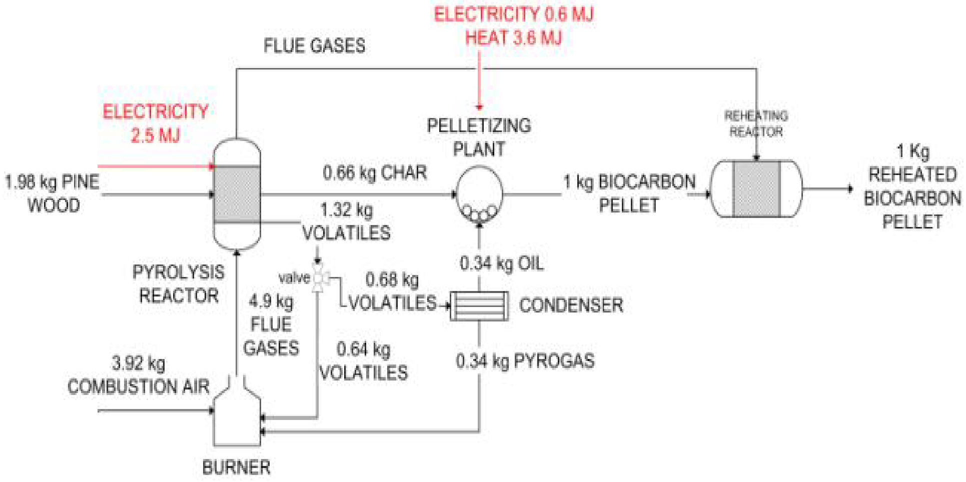


Figure 3.12: Designed biochar pellets production plant in the LCA steel production study case.

Further assumptions were necessary. In particular:

- biochar, pyrolysis oil and pyrolysis gas yields were equally assumed to be one third of the initial mass each;
- the air to fuel ratio in the volatiles burner is fixed at the value of 4, as reported in [119];
- the energy balance of pelletization was based on the work available in [120];
- the European scenario was considered. Therefore, electricity and heating follows the European data-sets, which were taken from *Ecoinvent 3.3* (Ecoinvent, Switzerland) [121].

Carbon footprint of coke was assessed using as data-set the project *"Coke GLO —market for— Cut-off, U"*, available in the *Ecoinvent 3.5* (Ecoinvent, Switzerland) database [122]. The system boundaries typical of steel production were taken from the related draft Product Category Rule (PCR), obtainable on the Environdec website [123]. Environdec is a global program for environmental declarations based on ISO 14025 and EN 15804. The data-set, necessary to analyze the processes was taken instead from the database *Ecoinvent 3.5* and it is named: *"Steel, low-alloyed RoW —steel production, converter, low-alloyed— Cut-off, U"* [122]. It was assumed that about 200 kg of coke are needed to produce one ton of steel.

Chapter 4

Main contributions

This chapter presents the main contributions that distinguish this thesis work. They can be classified into four clear topics, which are built upon the results obtained from the experiments performed in several either published or submitted papers. These research articles are briefly presented, emphasizing their relevance in regards to the related topic. The order, which the themes are presented with, follows a logical thread which has been developed with the aim to ease the comprehension of the overall research process. Moreover, the elements necessary to follow up the Discussion chapter (see Chapter 5) are provided. The complete version of the papers is available in the Appendices.

4.1 The effects of densification of biochar for metallurgical applications

The first phase of the research investigated the feasibility of applying biochar pellets in the metallurgical industry as reducing agent. In particular, several solutions were analyzed and compared to coal and coke by the evaluation of mechanical properties and CO_2 reactivity. In Paper A, it was found out that biochar pellets are generally more reactant than the conventional fossil fuels used in the metallurgical process, and the mechanical properties can be improved by adopting considerably high temperature in pyrolysis, including pyrolysis oil as binder and newly heating the pellets. Throughout the present thesis, this type of pellets is sometimes referred to as “upgraded”. Such observations were further developed in Paper B, where the pyrolysis oil content as well as pelletization temperature and pressure were optimized to obtain a strong and reactive renewable carbon source.

4.1.1 Paper A

This work was focused on investigating a process to upgrade biochar and make it more competitive towards coal and coke in metallurgical application. The graphical abstract of this paper is presented in Figure 4.1.

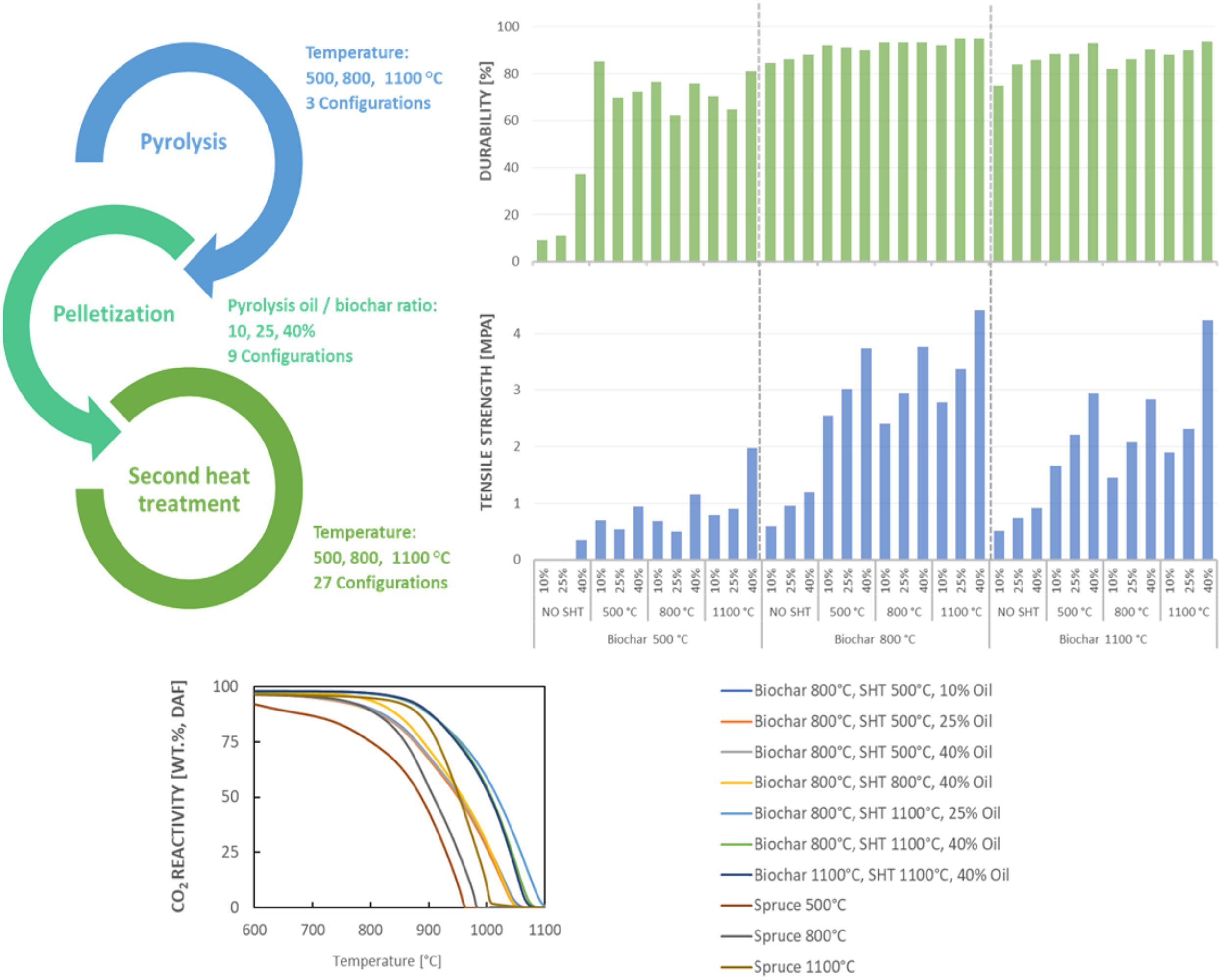


Figure 4.1: Graphical abstract based on Paper A. The conceptual process is shown on the left. While on the right, the experimental results of durability, tensile strength and CO_2 reactivity of the produced biochar pellets are highlighted.

Biochar was firstly produced from Norway spruce at different pyrolysis temperatures: 500, 800 and 1100 °C. It was then pelletized blended with 10, 25 and 40% (total blend weight) of pyrolysis oil. Lignosulphonate was also added as binder with a mass ratio 10:1 between blend and binder. The inclusion of this additive was justified by the necessity to minimize the risk of crumbling. A second heat treatment (SHT) was finally considered. It was carried out at the same temperatures of the previous pyrolysis process. The intention was to both evaluate the thermal interaction between biochar and pyrolysis oil and to imitate the thermal stability of the pellets when used in a smelting furnace. Density, tensile strength and mechanical durability were analyzed before and after the second heat treatment, as properties related to the quality of pellets. The shrinkage under SHT was measured.

The CO_2 reactivity was investigated under non-steady conditions. Analyzing the density of the pellets before SHT, it was observed that the pellet quality is strongly affected by the pyrolysis temperature, showing a relevant difference in properties between 500 and 800 °C. Instead, between 800 and 1100 °C, no clear differences were observed in this phase. Moreover, the inclusion of lignosulphonate and pyrolysis oil was beneficial for the mechanical properties of the pellets. By the second heat treatment, the quality of the pellets was improved, with an unavoidable reduction of density due to partial volatization of the binders and of the uncarbonized lignin present in the biochar. In particular, starting from biochar produced at 800 °C, it was possible by SHT to obtain pellets with a durability value higher than 90% and a tensile strength greater than 3.5 MPa (even more than 4 MPa for one specific case). By statistical analysis, no clear correlation between density, durability and tensile strength were observable. The CO_2 reactivity test showed that densification has a negative impact. However, once compared to coal and coke, pellets still showed a high reactivity. The results permitted to clarify in which extent pyrolysis oil positively interacts with the biochar structure, if thermally treated. By choosing carefully the process parameters, a strong and reactive biochar can be obtained and it may substitute coal and coke in the metallurgical production.

4.1.2 Paper B

Following the results obtained in Paper A, the research continued with the aim of further understand how to adjust the developed process, i.e. pyrolysis, pelletization and second heat treatment (SHT), so to improve and optimize the quality of the biochar pellets. This further work is described in Paper B and a visual representation of that is shown in Figure 4.2. In Paper A, it was inferred that the treatments temperature strongly affect the quality of the pellets and high temperatures are suggested. By further observations in preliminary experiments, it was inferred that the pyrolysis temperature of 600°C may represent a reasonable trade-off between pellets quality and process costs. It was therefore decided to design a potential up-scaled system, fixing the pyrolysis and SHT temperatures at 600°C.

The suggested process is visible in Figure 4.2. Once the treatments temperatures were kept fixed, a certain degree of freedom for the other parameters was viable. In details, the effect of pyrolysis oil content, pelletizing temperature and pelletizing pressure on the final quality of biochar pellets was analyzed. These factors are expected to interact in a complex way. The application of a statistical method to better understand the pelletizing behavior was therefore appropriate. Response surface methodology (RSM) with a Box-Behnken experimental design (BBD) was utilized to evaluate the impact of the parameters over the pellets quality, which was expressed in terms of mechanical durability, tensile strength and thermal strength. In this case, thermal strength was the tensile strength after the second heat treatment. It was decided to consider both values of strength, before and after SHT, to have a clearer insight of the respective impact of the parameters over the pelletization and SHT phases.

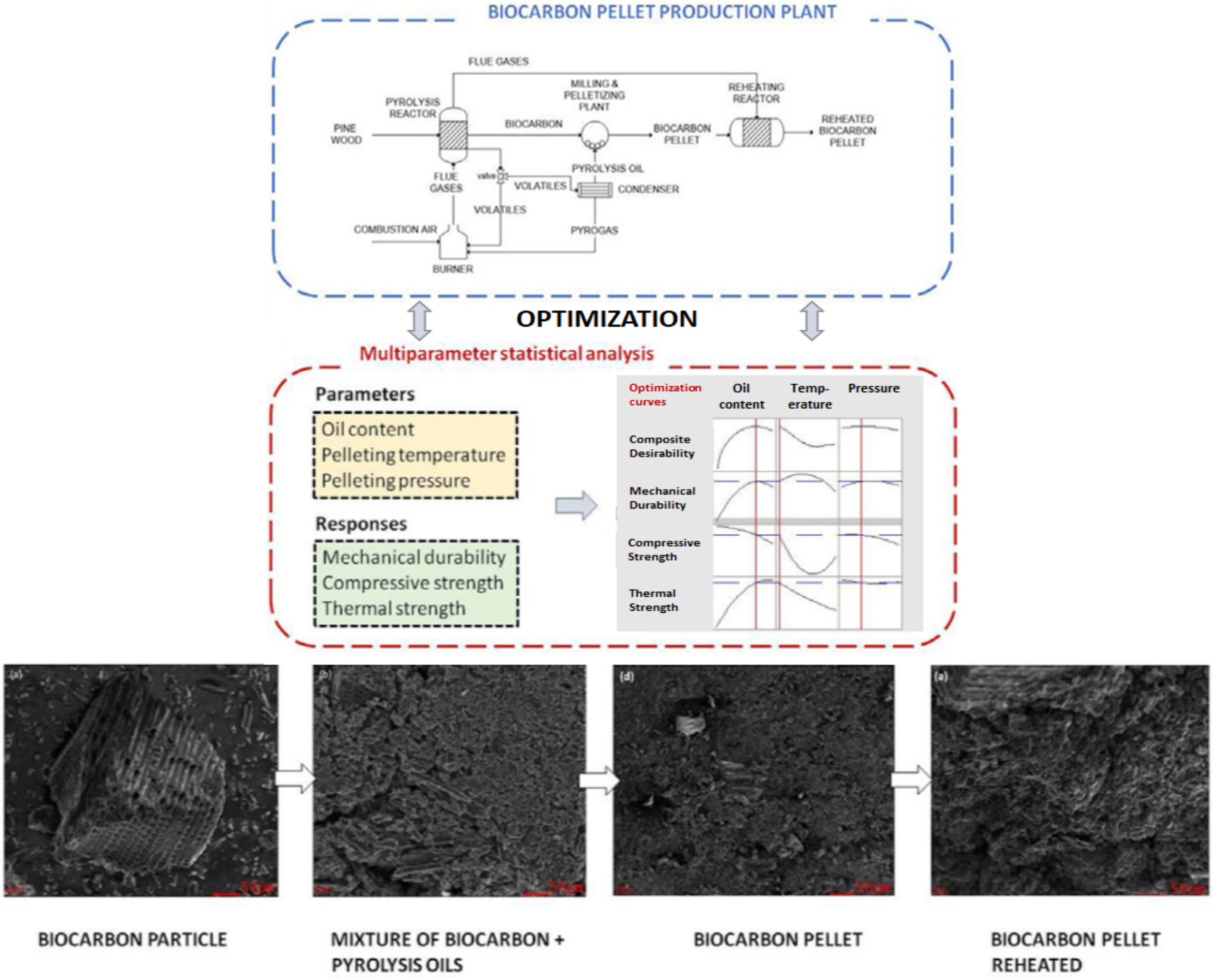


Figure 4.2: Graphical abstract from Paper B. On the upper left part, the proposed biochar pellets production process is shown. A summary of the highlights of the multiparameter statistical analysis is presented on the upper right part. The step-by-step changes into the biochar structure are displayed on the lower part.

The responses showed that pelletization was mainly affected by oil content and pelletizing temperature. Pelletizing pressure, instead, had a minor influence. Afterwards, considering the same parameters and targeted factors, the pelletization process was optimized using Derringer's desired function methodology. The optimization analysis returned a temperature equal to 60 °C, a pressure equal to 116.7 MPa, and an oil content concentration in the blend of 33.9 wt%. By the introduction of these parameters into the designed process it was possible to achieve a considerably high quality biochar pellet, characterized by a high fixed carbon content and appreciable mechanical properties.

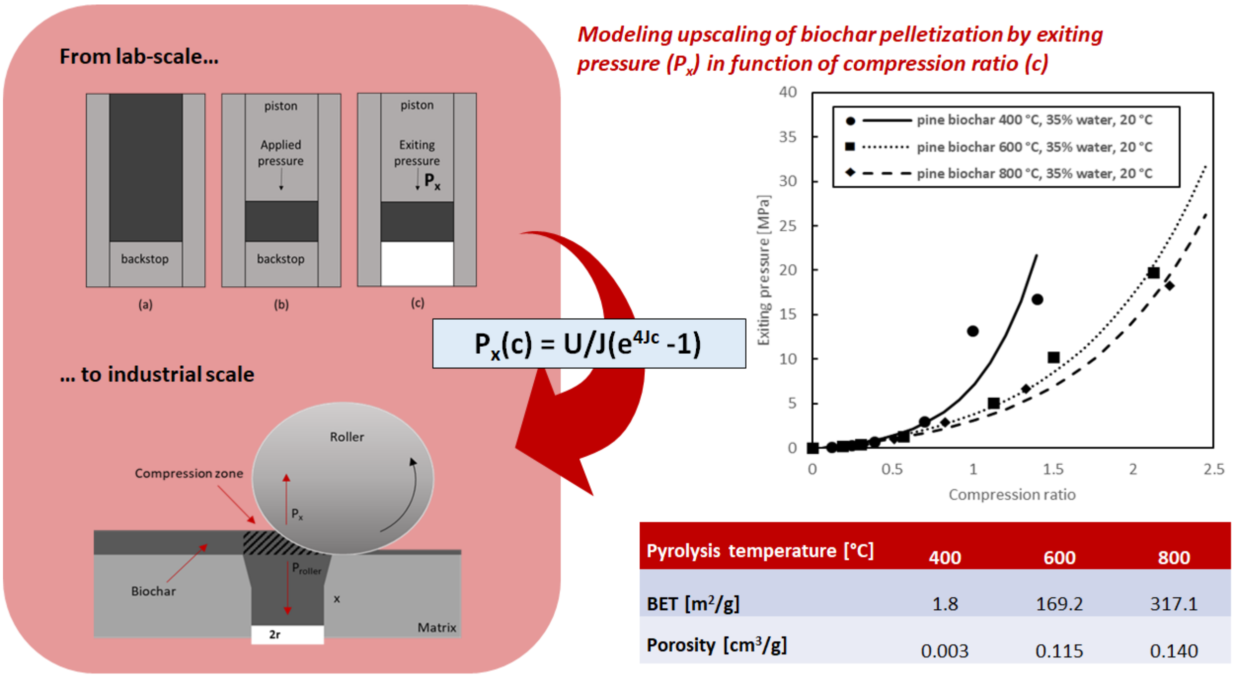
4.2 Considerations over the biochar pelletization process

As the quality of metallurgical biochar pellets was assessed, further research questions related to the up-scaling of the process had to be addressed. The pyrolysis of woody biomass has already been extensively studied by other researchers. Instead, the knowledge on pelletization of biochar is not as developed. Furthermore, at the time of the research, the existing literature about the up-scaling of the pelletization of biochar was rare. To evaluate the effective potential of the industrial production of biochar pellets, it was therefore necessary to dig further into the pelletization process. In this case, the main objective was not the quality of the produced pellets, but the feasibility of the biochar pelletization operation. In these regards, key considerations are presented in Paper C.

4.2.1 Paper C

This work is based on the application, for different configurations of biochar pellets, of a multiparameter model which relates the compression ratio (length over diameter) of the pellet to the pressure the die experiences while ejecting the pellet. This pressure plays a critical role in the process, as related to the performance and life time of the pellets machine. The model is built on experimental tests performed with a lab-scale single pellet press and permits to estimate the exiting pressure experienced at industrial scale with high compression ratios. These values are often difficult to obtain with a single pellet press. However, they are frequent in pelletization at industrial scale. As consequence, this method enables estimating how the forces along the matrix dies are affected by the key pelletization parameters, in a time and cost-effective way. A graphical representation of this paper is presented in Figure 4.3.

The interaction between ejecting pressure and compression ratio was evaluated by varying pyrolysis temperature, added water content and pelletization temperature. The ranges of these parameters were carefully selected to reflect industrially plausible values. In accordance with the experimental test results, the multiparameter model calculations showed that biochar produced at high pyrolysis temperatures is easier to pelletize. Vice versa, the pelletization of biochar at low pyrolysis temperature may be complex, if not unfeasible, due to the relevant high required pressure.



Pyrolysis temperature [°C]	400	600	800
BET [m²/g]	1.8	169.2	317.1
Porosity [cm³/g]	0.003	0.115	0.140

Figure 4.3: Graphical abstract based on Paper C. On the left, pelletization lab- and industrial scale are illustrated. On the right, the effects of the pyrolysis temperature on both the pelletizing pressure and the morphological structure of biochar are presented. At the center, the equation that relates compression ratio to pelletizing pressure and which was used in the multiparameter model is highlighted.

It was inferred that the biochar porosity and external surface, which increase at higher pyrolysis temperature, may be pointed as main factors behind such peculiar behavior. In a lower degree, the addition of water as binder was beneficial, as it was related to lower exiting pressures. Instead, no evident conclusions could be drawn by the analysis of the pelletizing temperatures: it was not possible to distinguish any clear trend. Furthermore, the inclusion of pyrolysis oil as binder was considered. The pelletization of biochar with water was compared to that of biochar with pyrolysis oil, at a fixed binder ratio. It was observed that the latter was characterized by lower exiting pressure. The multiparameter model was also applied to investigate the different behavior of pelletization, when wood does not undergo any thermal treatment and when a mild pyrolysis or a torrefaction are processed. Pelletization of untreated wood shows evidently lower exiting pressure, while when the wood was torrefied, pressures were slightly higher than when it was pyrolyzed. Additionally, density and compressive strength of the produced pellets were examined, as key mechanical properties. It was observed, to a certain extent, that these properties were positively affected by high pyrolysis temperature and inclusion of water. This final result is an important evidence, which may suggest that there is a general relation between the feasibility of the process (as lower pelletizing pressure at fixed compression ratio) and mechanical quality of the pellet.

4.3 Post-production related issues: the self-heating case

The evaluation of an engineering process is generally complex and many critical factors must be carefully considered. In the previous research works presented in this thesis, the focus was on analyzing and optimizing the main process parameters, since the efforts were on designing a system which may efficiently supply upgraded biochar pellets to the metallurgical industry. There are however many other details which might compromise the positive outcome and should therefore not be neglected. In this case, the attention was on critical post-production issues, which may hinder the industrial diffusion of the biochar pellets. In particular, it was observed that biochar pellets, when pyrolysis oil is added as binder, might experience self-heating. This phenomenon, which may lead sometimes to a spontaneous ignition of the mass, is associated to restrictions on the allowed transferable volumes, used to deliver ship and store a substance. In Paper D, the issue was thoughtfully investigated. The hope was to get an insight of the mechanisms controlling the self-heating behavior of biochar pellets, so to possibly adjust the production parameters to avoid it. The solution may boost further the competitiveness of this material.

4.3.1 Paper D

The main goal of this work was to investigate the self-heating behavior of the "upgraded" biochar pellets. In particular, the relation between this tendency and the main production parameters was deeply analyzed. The aim was to find out a strategy to avoid the classification of the produced biochar pellets as self-heating substance. However, this inclination is generally analyzed by the methodologies previously described in Chapter 3. These methods require tests that are time-consuming and necessitate a considerable amount of material, which could be hardly available at the early product development stages. As consequence, the test might act as barrier to examine various potential solutions. Beside researching how to reduce the risk, it was also studied how to possibly supplement the standard oven test (SOT) with a fast and cost-effective thermogravimetric analysis (TGA). A conceptual drawing of the paper is presented in Figure 4.4.

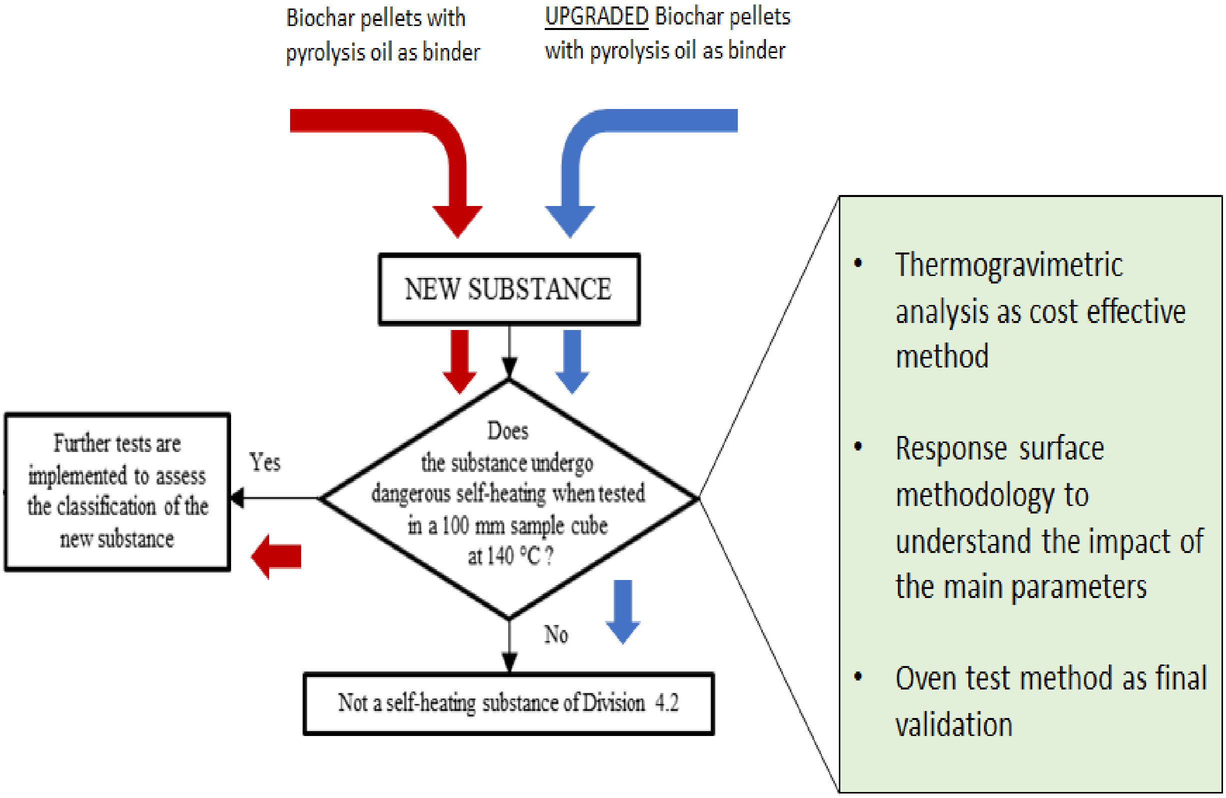


Figure 4.4: Graphical abstract based on Paper D. The normal self-heating test process is shown on the left and highlights the two divergent results of untreated and upgraded biochar pellets. In the pop-up box, the main steps carried out in this work are mentioned.

Firstly, biochar pellets, known to be prone to self-ignite, were compared through both SOT and TGA, with another similar biochar material, which instead do not show this tendency. The pellets were made of biochar and pyrolysis oil obtained from softwood. The temperature of pyrolysis and second heat treatment was between 400 and 600 °C. The TGA outcome was examined in function of the SOT result: the oxidation reactions were analyzed accordingly. Relevant kinetic factors were then selected and their relation to the main production parameters were investigated. Due to the complexity of the reaction, the analysis of the interaction between kinetic factors and production parameters was done by using Response Surface Methodology (RSM). Pyrolysis temperature, oil content and second heat treatment temperature (SHT) were selected as independent variables, and their ranges were carefully chosen so to be similar to the initial tested pellets. Initial ignition temperature, maximum mass loss rate temperature and activation energy were picked as responses.

According to the statistical analysis, the temperature of the two treatments plays a critical role in determining the risk of self-heating. Fundamentally, for instance, when pellets were produced at the lowest tested pyrolysis temperature (450 °C), the responses manifested a clear inclination to ignite. Moreover, an increase in pyrolysis oil content was associated to a higher predisposition to self-ignite. On the other hand, it was discovered that the self-heating risk may be drastically reduced by upgrading the pellets at high temperatures (i.e. SHT). The optimization of the responses, carried through a desirability function, showed that it is recommended to limit the pyrolysis oil content and perform the heat treatment at high temperatures. To a certain extent, the result is in agreement to what observed in the previous works presented in this thesis. Eventually, once the parameters were optimized to provide the desired outcome in TGA, the SOT was performed as validation both of the results and of the relation between the two different tests. Following the observations drawn by the statistical analysis, the pellets, which did not pass the initial SOT, underwent a SHT at 600°C. After the treatment, the pellets passed positively the SOT, proving the reliability of the TGA results. In particular, it was shown that a post-treatment by heating of pellets prone to self-ignition can considerably attenuate the risk, making the pellets not classifiable as self-heating substance.

4.4 Assessment of the sustainability of the production and application of metallurgical biochar pellets

Last step of this thesis was to evaluate the actual improvement in sustainability that the introduction of biochar pellets would bring about in the metallurgical industry. It is indeed reasonable to assume that the biochar carbon footprint of a metallurgical process may considerably drop, in comparison to the business as usual scenario. However, the production and application of biochar pellets would still imply the requirement of systems that nowadays rely on the direct or the indirect consumption of fossil fuels. A Life Cycle Assessment (LCA) analysis for a generic study case was therefore assessed, in comparison to fossil coke. In this case, the targeted metallurgical application was the steel manufacturing, as it is generally present in many European countries and it is relatively easy to obtain related data (at least compared to the production of other metals). The findings of this work are presented in Paper E.

4.4.1 Paper E

As often mentioned throughout this thesis, the upgraded biochar pellets can be used in metallurgical applications as a substitute of fossil coal. However, in comparison to untreated biochar, pellets are mechanically strong enough to be considered as renewable alternative to coke. This opportunity may be promising in coke-dependent processes, such as steel manufacturing and manganese alloys production. The possibility of adjusting the mechanical properties and the reactivity of pellets, by varying the binder content as well as process parameters offers the use of this material in a broad range of smelting processes, characterized by the reduction of metal ores. It is reasonable to expect convergent scenarios in different applications. Therefore it could also be acceptable to assume that the analysis of one specific metal production chain may provide useful information for other realities. As consequence, the environmental analysis related to the substitution in the steel production of coke with upgraded biochar pellets may be considered as a hint to assess the sustainability in the metallugical industry. It is however suggested (and welcomed) to evaluate case by case the environmental impact of this transition. In this case, Life Cycle Assessment (LCA) was applied.

The study case addressed in Paper E is presented in Figure 4.5. This work compares two different routes: a “conventional”, where coke is utilized as the main reducing agent and a “green” route, with upgraded biochar pellets used as carbon source. The two paths differ, as shown in Figure 4.5, only in the way the two reducing agents are produced. They continue through the same stages: the production of pig iron and, consequently, of steel. The overall process was evaluated within the European scenario. For instance, the electricity generating process was chosen accordingly. Further considerations about the LCA settings and inventories were previously anticipated and described in Chapter 3.

By the LCA, it was found out that the production of biochar pellets is more pollutant than that of coke. The specific carbon footprint of the latter was about 0.65 kgCO_2eq/kg, while that of the former was slightly higher than 1 kgCO_2eq/kg, equally distributed among biomass handling, pyrolysis and pelletization. However, the historically optimized production of coke was compared to a process in an early development stage. It is therefore expected that the carbon footprint of the biochar pellets production might reduce considerably, once the process is optimized. Moreover, this result emphasizes the importance to assess sustainability critically: the environmental benefit of biochar pellets (and biochar in general) relies on the beneficial impact in the application. This is evident when the effects of the different routes on the pig iron and steel production are analyzed. According to the analysis, the production of pig iron is the step which impacts the most environmentally.

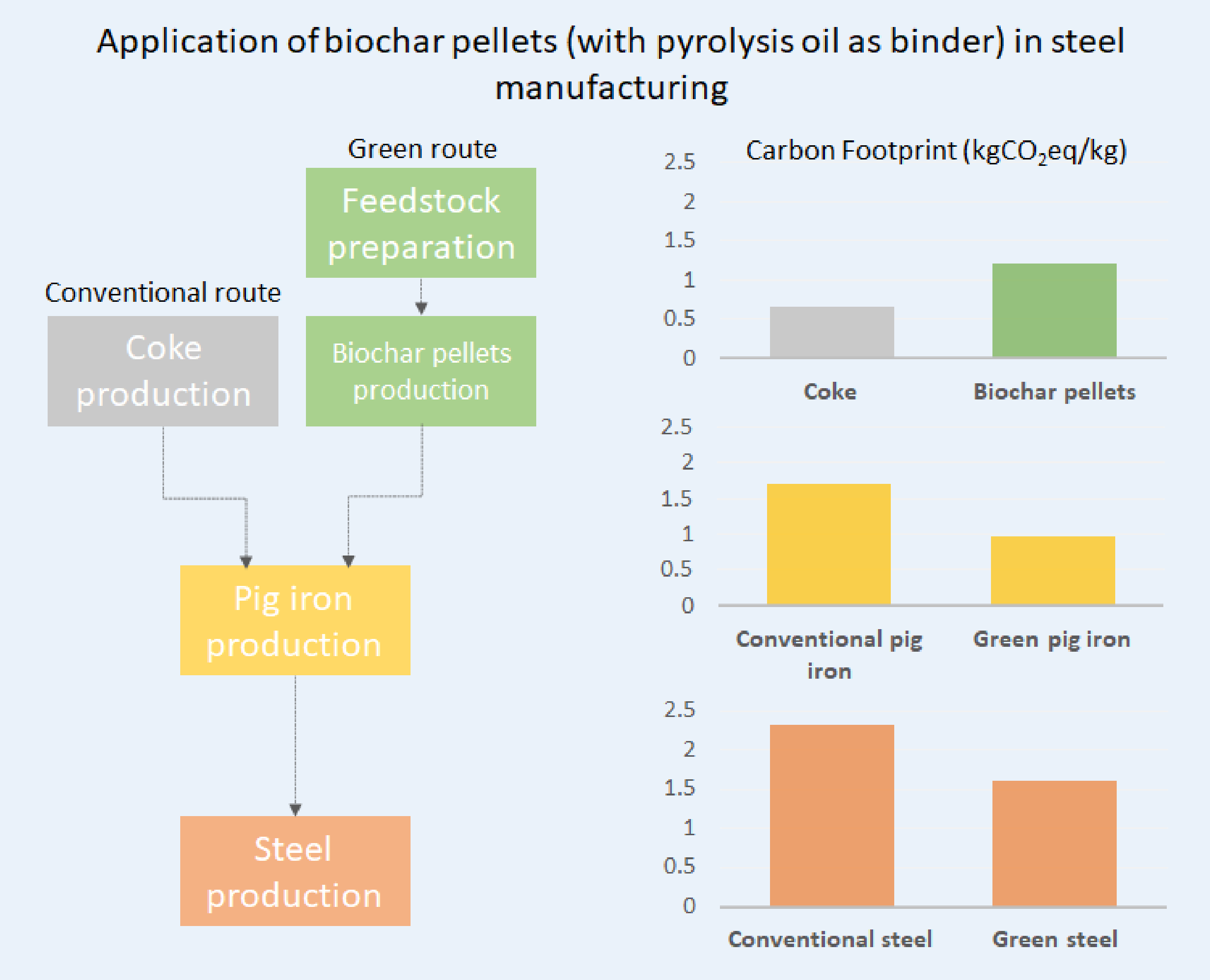


Figure 4.5: Graphical abstract based on Paper E. The two routes that have been analyzed are schematized on the left, while the comparison of the computed step-by-step carbon footprint is shown on the right. Values are per kilos of respective material.

This is mainly due the direct emissions, related to the reduction of fossil reducing agents. By definition, this contribution is considered as neutral when biochar is used. Therefore, even though biochar pellets are apparently more polluting to produce, the substitution of coke brings about a reduction of 31% in the overall specific carbon footprint of steel. Despite the considerable environmental benefits, it was also computed that biochar pellets might cost considerably more than coke. In an economic-driven industry such is the metallurgical one, it is hence fundamental to insist towards the economic optimization of the production process. It is optimistically legit to expect in the near future the introduction of stronger environmental policies, which might overcome the economic gap.

Chapter 5

Discussion over the thesis findings

The scope of this thesis was to investigate the feasibility of upgraded biochar pellets with pyrolysis oil as a reducing agent in the production of metals. The research articles presented in the present thesis cover several sub-topics, which address the main objective from different perspectives. However, the focus was mainly on the impact that some process parameters might have in affecting the metallurgical quality of this renewable Carbon source. Accordingly, it is possible to develop a discussion over the findings which were obtained in this research work. As summary, Table 5.1 provides a list of the properties that were used to assess the metallurgical feasibility in relation to the factors which were examined. More in details, the investigated parameters were: pyrolysis temperature, pyrolysis oil (and water) content, second heat treatment temperature, pelletizing pressure and pelletizing temperature. While the addressed responses were: fixed carbon, mechanical durability, compressive strength, density, reactivity, exiting pressure, self-heating, sustainable impact. The effects of the mentioned parameters on the responses are further inquired in the following sections. The iron and steel manufacturing as well as silicon and ferrosilicon production are considered as main potential final application.

Table 5.1: Effects of the main parameters on the investigated properties. The abbreviation SHT stands for second heat treatment. The symbol "+" means the properties benefits from an increase of the related parameter. While the symbol "-" means the contrary. When no sign is included, it means that the relation is either not clear or negligible.

Parameter	**Fixed Carbon**	**Mechanical durability**	**Compressive strength**	**Density**	**Reactivity**	**Exiting pressure**	**Self-heating**	**Sustainable impact**
Pyrolysis temperature	+	+	+	+	-	+	+	+
Pyrolysis oil (and water) content	-	+	+	+		+	-	+
SHT temperature	+	+	+	-	-		+	+
Pelletizing pressure		+	+	+	-		-	-
Pelletizing temperature		+	-	-				-

5.1 Pyrolysis temperature effects

The variation of the pyrolysis temperature, which was selected to produce the pelletized biochar, was observed affecting several properties. The most documented aspect in Literature is a higher degree of carbonization, with an increase of pyrolysis temperature [49]. In the present research work, this phenomenon led to higher fixed carbon content inside the biochar pellets, which were produced at higher temperatures. Moreover, it was noticed that the exiting pressure, associated to the operations of an industrial pellets machine, rapidly increases at fixed compression ratio when the pyrolysis temperature passes from 600 to 400°C. Visual differences in the outcome of pelletization of biochar produced at those temperatures can be appreciated in Figure 5.1. Relatively low values for pyrolysis temperature reduce the values of the mechanical properties.

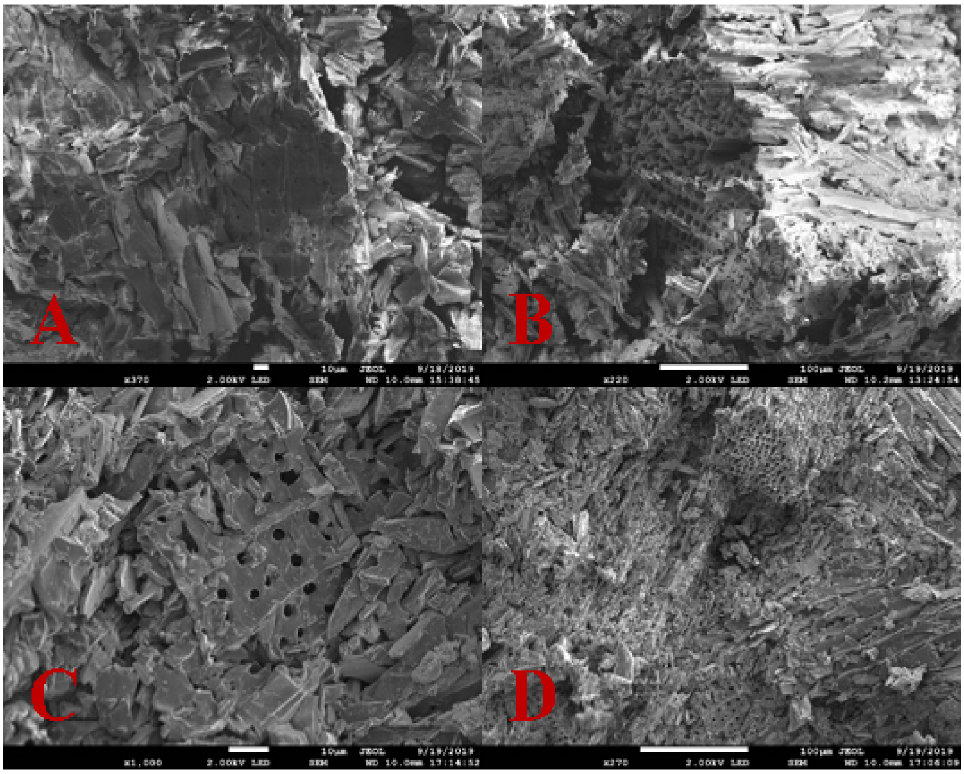


Figure 5.1: Scanning electron microscope (SEM) photos for: biochar produced at 450 °C, blended with 30% (A) and 20% (B) of pyrolysis oil; biochar produced at 600 °C, blended with 30% of pyrolysis oil (C-D) (from Paper D).

Besides, it was observed that the threshold temperature, between good and bad quality biochar pellets, was around 500°C. A similar behavior is reported in [78]. In regards, several causes were pointed out. As explained in [124], higher degrees of carbonization result in a more brittle structure, which can easily be milled in a homogeneous distribution of the particle size. As effect, a mixed particle size blend is generally easier to densify, as finer particles act as binders for the larger [70]. When the particle size distribution of biochar produced at different pyrolysis temperatures was analyzed, e.g. in Paper C, this behavior was confirmed. More homogeneous distributions were observed when the pyrolysis temperature was at least 600 °C. Besides, the capacity of a liquid binder (e.g. water, pyrolysis oil) to penetrate the structure of a material is related to its hydrophobicity. It was inferred that this property is associated to the presence of the aliphatic group on the surface of biochar, if pyrolyzed at temperature lower than 600°C [125]. When higher temperatures are used, biochar loses this group and becomes hydrophilic [126]. As consequence, the blend is more homogeneous and the binding mechanism can be successfully enhanced in the pelletization phase. Furthermore, the quality of a blend strictly depends on the porosity of the solid substance [126]. In [61], it was observed that the majority of the pores in a carbonized woody structure are inherited macropores, which do not depend on the heat treatment. However, it was also demonstrated that higher pyrolysis temperatures are associated to the formation of micropores, with an overall increase of porosity [127]. In the present research work, it was observed a considerable increase in porosity with an increase of pyrolysis temperature. Due to the consequent higher degree of densification, an increase of this property was also demonstrated to reduce the inclination to self-ignite of pelletized material, as also observed in [128].

Similar effects were observed during the CO_2 reactivity test, since higher pyrolysis temperatures led to delayed reactions, as shown in [61]. In terms of carbon footprint, it was inferred that, in an integrated system such as the one proposed in Paper B and Paper E, it is possible to achieve high pyrolysis temperatures, without relevant environmental drawbacks. In the light of what just discussed, it can be stated that pyrolysis temperature is a fundamental parameter to take into consideration while pelletizing, due to the relevant structural effects on the morphology of the biochar.

5.2 Pyrolysis oil content effects

Pyrolysis oil is usually characterized both by a considerable water content and, as liquid, by a lower fixed carbon content, if compared to biochar. In Paper B, for example, biochar and pyrolysis oil had a fixed carbon content respectively equal to 88.23% and 2.73% wb. While in Paper C, it was demonstrated that, in the pelletization phase, pyrolysis oil acts similarly to water. It is therefore acceptable to assume that an increase of the binder content reduces the value of the fixed carbon content of the produced pellets. Nevertheless, as its density is higher than that of biochar, the addition of pyrolysis oil increases the pellets density up to certain values, which are close to what observable for untreated spruce pellets [71]. In the present thesis works, the relevant water content inside slow pyrolysis oil (up to 87.2% wb) had positive effects on the exiting pressure. The binding mechanism are eased by the bridges established through water molecules [129]. As consequence, the pelletization process becomes smoother and, at fixed compression ratios, the exiting pressure gets reduced. However, it was also observed that an excessive content of pyrolysis oil (or water) has negative effects on both compressive strength and mechanical durability. It was demonstrated that these values can be maximized with a pyrolysis oil content between 30 and 35% of the total weight, as also observed in [78]. Pyrolysis oil happens to be a promising binder to upgrade the mechanical quality of biochar pellets.

Interestingly, as pyrolysis oil can be addressed as a by-product of slow pyrolysis, its environmental impact could be assumed as negligible, if the carbon footprint is solely allocated on biochar. With regards to the reactivity of the pellets, no significant observations were drawn. However, the addition of pyrolysis oil was demonstrated to be one of the main factors related to higher risks of self-heating. By penetrating the pores, the binder limits the possibility to quickly dissipate the generated heat. In the statisical analysis related to self-heating risk, the minimization of the oil content was associated to a reduced inclination to ignite. To a certain extent, this behavior happened to be the most critical issue of using pyrolysis oil as binder with biochar pellets.

5.3 Second heat treatment effects

It was observed that, when pyrolysis oil is used as binder in biochar pellets, a second heat treatment (SHT), which resembles pyrolysis, may further upgrade the quality of the pellets. Figure 5.2 shows fragments of biochar pellets which underwent a SHT and include pyrolysis oil. This figure can be used to further explain the reason behind the benefit of re-heating the pellets by a pyrolysis.

By this further pyrolysis, both the biochar parts that did not previously get carbonized and the added pyrolysis oil react around the biochar structure. A fraction of them got expelled as volatiles, while another fraction was converted into char. The result is visible in Figure 5.2. Due to volatization, the biochar pores, which were obstructed by the pyrolysis oil, are newly opened (and other micropores are formed). While the carbonized part of the binder sediments on the biochar structure, binding with it. The effects of this process are several. The fixed carbon content (FC) increases. As example, it was noticed that starting with biochar produced at 600°C (FC equal to 88.23% db), after pelletization, FC went down to 83.70% db (due to the inclusion of pyrolysis oil), but it reached 87.79%

db after a SHT carried out at the same temperature of pyrolysis. Moreover, mechanical durability and compressive strength improved considerably, with outstanding benefits for the latter. On the other hand, due to the mass loss related to volatization, a SHT is associated to a decrease of density.

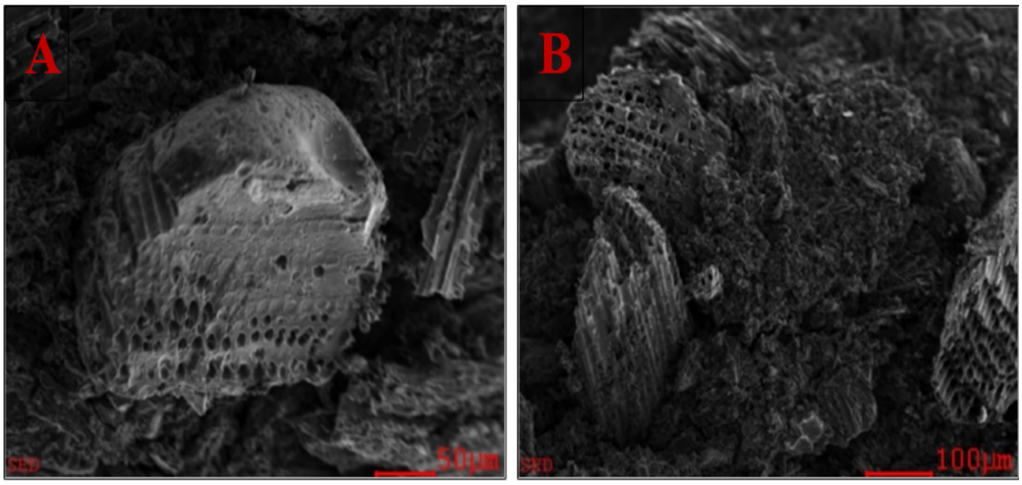


Figure 5.2: SEM photos of sections of pellets of pyrolysis oil (33.9% wb) and biochar after a second heat treatment at 600°C. Voltage and magnification: (A) 7kV x140, (B) 7kV x250 (from Paper B).

Due to the pores opening, it was observed that the risk of self-heating drops considerably. For instance, the industrial pellets investigated in Paper D, could avoid the classification as self-heating substance, if treated with a SHT at 600°C. Instead, considering the CO_2 reactivity, the effects of a SHT are strictly similar to what previously discussed on pyrolysis, i.e. the higher the process temperature, the more delayed the reaction. SHT is expected to generate additional GHG emissions. The issue can partially be tackled if the system is designed accordingly, as the one proposed in this thesis. However, it was observed that by SHT, biochar pellets approach the typical values for mechanical properties and fixed carbon content, which generally resembles those of the coke used in the metallurgical industry. Such characteristic, together with the mentioned SHT-related improvements, may make these pellets a promising substitute for both coal and coke, increasing their potential as a environmental friendly reducing agent in the production of metals. In the overall, the coupling of the addition of pyrolysis oil as binder and SHT may be expected to bring about a relevant reduction of GHG emissions and hence be addressed as sustainable.

5.4 Pelletizing pressure effects

It is known that pelletizing pressure is a fundamental parameter to consider if a proper pelletization wants to be achieved. Due to the pelletization mechanism, it is often possible to identify a threshold value of pelletizing pressure, which above that, it is not possible to further take benefits from the plastic deformation of a material and deformations becomes purely elastic [70]. This is because all the possible binding forces have been exploited and no further are available [74]. In the present work, this phenomenon was also observed to be valid for biochar pellets. After a certain pelletizing pressure, for instance, the value of the density of the pellets does not change much, as visible in Figure 5.3. It can be noticed that, according to the pyrolysis temperature which was used, density tends to oscillate around a stable value, once the pressure overtakes about 100 MPa. As a further proof, a similar pattern was observed when the exiting pressure was analyzed: it increases rapidly at low pressure and it begins fluctuating around a stable point when a certain value of pressure is reached.

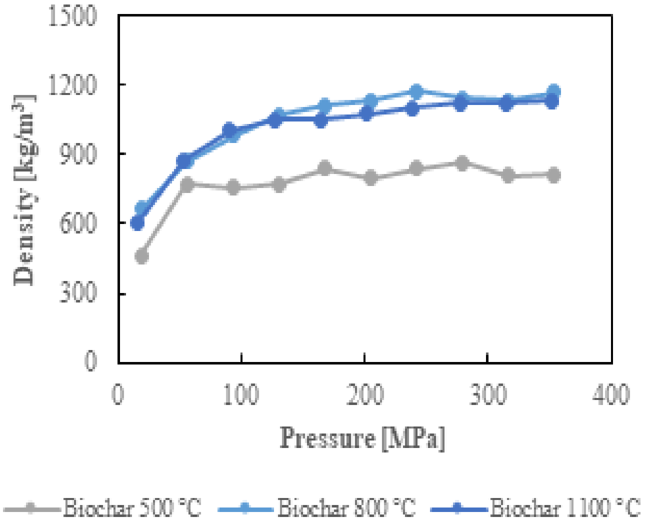


Figure 5.3: Variation of the density of the single pellets containing biochar, produced with the pyrolysis temperatures of 500, 800 and 1100 °C, when pelletizing pressure is increased.

Moreover, when mechanical durability and compressive strength were evaluated, a maximum was obtained at around 116 MPa. This value is in the range of what also discovered in [72]. It was assumed that this behavior derives from the recalcitrant nature of biochar, which imposes a limit in the densification of particles [78]. With respect to reactivity and self-heating risk, no related studies were attempted in the present work. It is nevertheless reasonable to expect a negative impact due to a reduction of porosity consequent pelletization. Furthermore, as this process is powered by electricity, its carbon footprint strictly depends on the sources exploited to produce it. In the European scenario, this component was computed to be considerable in the overall specific emissions for the production of biochar pellets. In [130], it was found out that electricity accounts for the 93% of the pelletization emissions. This result could therefore drastically change if the pelletization plant was located in a nearly total renewable electricity producer country such as Norway.

5.5 Pelletizing temperature effects

In pelletization Literature, pelletizing temperature is generally associated to the benefit it has on the densification of wood. It was indeed observed that the lignin intrinsically included in wood can act as a sort of natural binder when temperatures exceed 50°C [131]. However, limited Literature is available regarding the effects this parameter has on the pelletization of biochar. In the present work, it was observed that densification of biochar should be performed at about 60°C. Pellets produced at high temperatures (around 100 °C) were characterized by lower density, while exiting pressure and compressive strength did not change much. However, it was observed that the compressive strength of pellets produced at high temperatures and upgraded with a SHT was significantly lower. This behavior may indicate a synonym of bad pelletization, since it means the pyrolysis oil did not succesfully bound with the biochar structure.

It might also be inferred that biochar is not particularly affected by the pelletizing temperature and, therefore, the optimization of this parameter might be strongly connected to the type of binder which is utilized. For instance, in Paper A, lignosulphonate was added while pelletizing a blend of biochar and pyrolysis oil at the pelletizing temperature of 90°C. The mechanical properties of the produced pellets after SHT were remarkable. The issue, however, becomes more problematic when the industrial scale is assessed. For this type of machinery, the temperature is hardly controllable as it comes from the friction between the die matrix, the biomass and the roller [132]. The problem might be overcome by the design of an integrated system which are able to recover the produced heat. This solution might also improve the environmental footprint of pelletization. However, the investigation of this possibility was out of the scope of this work.

Chapter 6

Conclusions

6.1 Remarkable outcomes

The scope of this thesis was the study of the production and application of sustainable metallurgical biochar pellets. As explained, the idea of coupling pyrolysis of biomass to pelletization is based on the necessity to provide a material with appreciable mechanical properties. The proposed process was, therefore, suggested by taking into consideration three main aspects:

- Biochar pellets must be produced in an efficient way.
- Once obtained, their properties must satisfy the requirement desired by the metallurgical industry.
- The process must reduce the carbon footprint of the metal production.

The research sub-questions were posed accordingly. Answers were drawn through the work discussed in this thesis and presented in the appended papers. As main conclusion, it was demonstrated that the pelletization (as well as densification) of biochar might provide a superior material, which could be successfully applied in the metallurgical industry. Thanks to the upgraded mechanical properties, the utilization of biochar pellets is expected to reduce the handling and managing costs, by a decrease of mass losses, as well as to improve its usage into the furnace.

The first step in the research work was to experiment how to obtain high quality biochar pellets, suitable for the reduction of metals. Spruce, as example of softwood largely available in Northern Europe, was used as feedstock. It was discovered that the pyrolysis temperature affects the feasibility of the pelletization step. When pyrolyzed at high temperatures (greater than 500 °C), biochar was easier to pelletize and its durability and tensile strength were higher. The upgrading of biochar, to be more industrially competitive, was mainly achieved by the inclusion of pyrolysis oil as binder in the pelletization phase. It was demonstrated that, by undergoing a second heat treatment (SHT), these pellets became significantly stronger, due to the carbonization of the oil into the carbonaceous structure. It was inferred that the porosity of biochar and its slight hydrophilic inclination are the major factors affecting a proper realization of pellets. It was also demonstrated that densified biochar is still highly reactant and is therefore suitable as a reducing agent in the metals production.

Due to the promising results, the process consisting in pyrolysis, pelletization with pyrolysis oil and SHT was optimized. Pyrolysis and SHT temperatures were maintained fixed at 600 °C. A statistical analysis based on the Response Surface Methodology (RSM) coupled with a Derringer's desirability function was applied. The studied parameters were oil content, pelletizing temperature and pelletizing pressure. It was found out that the best outcome in terms of mechanical properties was achievable with an oil content of about 33%, a pelletizing temperature of 60 °C, and a pelletizing pressure of 116 MPa.

The up-scaling of the process was also considered. Because of the lack of information regarding the feasibility of the pelletization of biochar with pyrolysis oil, this step was analyzed in more detail with the application of a multi-parameters model. This method was useful to understand the performance of a pellets machine in an industrial scenario. The model return variable is the exiting pressure that the die experiences while the pellet is ejected. Since related to the operation and life of the machine, this parameter is very important to evaluate the feasibility of a pelletization process. Furthermore, densification of biochar was studied by varying pelletizing temperature, binder content and pyrolysis temperature. It was found out that pelletizing temperature does not have a significant correlation to the exiting pressure, while an increase of liquid binder affects it positively, by reducing it. In accordance to the outcomes of the other presented works, it was demonstrated that pyrolysis temperature has a strong influence on pelletization and biochar produced below 500 °C is characterized by considerable higher pressures than that produced at higher temperatures. It was observed that, as previously assumed, when pyrolyzed at higher temperatures, the porosity and external surface of biochar increases. Therefore, the binder has a major possibility of successfully penetrating the solid structure enabling the binding mechanism.

Upgraded biochar pellets with pyrolysis oil were associated to the inclination of self-heating. The behavior was deeply investigated by the novel coupling of standarized and thermogravimetric tests, which were analyzed by RSM. It was found out that densification and the inclusion of pyrolysis oil affect considerably the predisposition towards self-ignition of biochar. However, it was possible to reduce the risk by using biochar obtained through pyrolysis at high temperatures. Moreover, it was also discovered that the SHT can be beneficial, since it carbonizes the pyrolysis oil and opens the pores. As conclusion, it was therefore remarked the importance of taking a SHT, both as upgrader and to reduce self-heating risk.

Finally, by LCA, the sustainability of the process in an European scenario finalized to the production of steel was assessed. It was drawn that the carbon footprint associated to the manufacturing of biochar pellets is higher than that of coke. However, it was recognized that the biochar pellets production is still at an early developing stage and there is, therefore, a good margin of optimization, which may bring to considerable lower emissions, compared to the initial suggested system. However, when the application phase was included, the outcome changed, demonstrating that the use of biochar pellets instead of coke would reduce the carbon footprint of about 31%. The economical gap between the fossil fuel and the proposed renewable material was also addressed, estimating a difference of 200 €/ton.

6.2 Challenges and limitations

For obvious reasons, the attention in section 6.1 was mainly to highlight and discuss the most relevant results, which were obtained during the work described in this thesis. However, it is equally necessary to take a bit of time to address the main challenges and limitations this research faced. It is hope of the author that such obstacles may be investigated and overcome through the contributions of further research. Here, it follows a brief list:

- Economic costs. Throughout the thesis, it was often stressed the criticality represented in the simultaneous optimization of the quality of the product and minimization of the costs. If densified biochar needs to be realistically competitive, the cost must be abated. In this work, the issue was addressed by implementing materials recovery strategies as well as optimizing the design of the process. However, as demonstrated in Paper E, this would not be sufficient to guarantee acceptable market prices.

- High treatments temperature. It was observed that both the quality and the performance of the biochar pellets are strongly related to the application of high temperatures in pyrolysis and second heat treatment processes. Beside the straightforward increase of costs with higher temperatures, limitations might come also from technological obstacles. It is hence more convenient and feasible to keep the treatments at lower and more manageable temperatures.

- Pyrolysis oil characterization as binder. Despite the thermal behavior of the biochar-oil structure was deeply analyzed, it is still not totally clear how the physio-chemical characteristic of the pyrolysis oil may affect the binding mechanism. A better understanding of the binding mechanism may provide considerable benefits in regards to other steps of the process, e.g. the choice of the treatments temperatures. Moreover, the use of pyrolysis oil in industry may be challenging due to sticky glue like action of the oil if cold.

- Inclusion of binders. For evident time constrains, pyrolysis oil aside, it was given space only to lignosulphonate as additional binder. A selection of other additives might have provided relevant information.

- Lab-scale dependence. In a multi-step process, characterized by several parameters that interact to each other, the up-scaled outcomes might differ considerably to the lab ones. During this work, the up-scaling was only partially considered by modeling.

- Statistical significance. The considerable time necessary for the pelletization of biochar by a single pellet press, as well as the low amount of available material (pyrolysis as bottle-neck), hindered the production of a relevant amount of pellets. The number of pellets produced for each configuration in each work was always enough to guarantee both the repeatability and the significance of the statistics. However, a more exhaustive set of experiments would have surely led to more precise results.

- Woody feedstock. In Chapter 2, it was justified why this research was mainly focused on the exploitation of softwood trees, in particular, spruce and pine. However, by preliminary studies, biochar from hardwood (e.g. oak, birch and beech) happened to response positively to pelletization. A deeper investigation on the use of this type of wood might have provided useful information.

- Sustainability. The environmental impact of the process was briefly assessed. The aim was to emphasize the reduction in terms of emissions, in comparison to the fossil fuels conventionally used in the metallurgical sector. However, due to the complexity of the system, more updated and extended inventories in LCA should be considered. Moreover, the impact of the feedstock harvesting and management has been slightly addressed, despite its crucial role to guarantee the sustainability of the process.

6.3 Perspectives

In the light of the limitations and challenges, which may act as barriers to the production and application of upgraded biochar pellets, a continuation of the related research is highly suggested. In general, the present work introduced and emphasized the possibility to obtain biochar with superior mechanical qualities by a specific multi-steps process. There are still many sub-research questions to address.

- The choice of the parameters as well as a proper configuration might be further investigated by an integrated model optimization. Such analysis might be enriched by additional experiments including various types of biomass, binders and mixtures. The aim would be to find "the best recipe". Once an exhaustive database is built, it will be easier to assess the techno-economic assessment of the process, so to work actively towards the minimization of the costs.

- Exhaustive research on the application of pyrolysis oil as binder is highly suggested. It is indeed relevant to pursue the characterization of this material in relation to pelletization. This study should be coupled to a further investigation on the hygroscopic properties of biochar, as well as its inclination to blend with binders. The aim would be to obtain a richer insight on the binding mechanism between biochar and pyrolysis oil. Once this behavior is clearer, it will become easier to further upgrade the mechanical properties of the pellets, reaching outstanding values.

- The metallurgical application should be analyzed by *ad hoc* experiments, according to the type of metal produced. For instance, it would be interesting to perform SiO reactivity tests, to gather more information around the performance of biochar pellets in the silicon and ferrosilicon production. Moreover, the process should consider the inclusion of wastes and material from the metallurgical step. The fines from the commercial charcoal, which is currently used, could be used this way. Pellets of biochar, pyrolysis oil and silicon-derivated wastes are worthy to be studied, as a method to increase the efficiency in the electric arc furnaces. Similar considerations might be drawn for the steel production.

- Once the processes and parameters affecting the overall system are clearer, time should be spent to evaluate potential post-production issues. For example, the biochar pellets self-heating risk plot should be further improved and upgraded so to facilitate the selection of the process parameters. Moreover, further efforts should be made to conform the pellet product to the market requirements and standards.

- Upgraded biochar pellets might be utilized in other application, e.g. co-firing, agricultural purposes, animal feeding, etc. The implementation of experiments to investigate the different usages is highly encouraged.

- Due to the industrial relevance, further works are suggested to aim at a greater cohesion between university and interested industrial partners. Such cluster might achieve more complete results, if the agricultural and forest management sectors, related to the acquisition of the feedstock, would be taken into account, aside metallurgical companies. When the Norwegian scenario is considered, it is worth to mention that the production of upgraded biochar pellets would relay on the creation of a new market branch, covering a broad technological chain. Therefore, it would be highly interesting to enrich this engineering-related study by a cooperation with other research fields, e.g. social impact, economical perspectives and environmental policies.
- Multi-field studies might turn to be beneficial for a deeper and critical assessment of the environmental impact of the production and application of the biochar pellets. In this regard, the system might be transformed or adjusted to minimize the carbon footprint. Hence, techno-economic analysis might be coupled trying to find a balance between economic feasibility and sustainable impact.

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Paper A

A study of densified biochar as carbon source in the silicon and ferrosilicon production by Riva, Lorenzo; Surup, Gerrit Ralf; Buø, Therese Videm; Nielsen, Henrik Kofoed. Published in Energy (2019).

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A study of densified biochar as carbon source in the silicon and ferrosilicon production

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ABSTRACT

Biochar pellets were investigated as renewable reducing agents in substitution of coal and coke in the silicon and ferrosilicon production, where a high reactivity, good mechanical properties and low feedstock costs are appreciated. The usage of pyrolysis oil as binder was investigated as way to improve the quality of the pellets. Norway spruce biochar produced at 500, 800 and 1100 °C, was pelletized blended with pyrolysis oil and lignosulphonate. A second heat treatment was carried out at the same temperatures to evaluate the interaction between biochar and pyrolysis oil and to imitate the thermal stability of the pellets when used in a furnace. Density, tensile strength and mechanical durability were analyzed before and after the second heat treatment. The CO_2 reactivity was investigated under non-steady conditions. It was observed that the pellet quality is affected by the pyrolysis temperature, showing a relevant difference in properties between 500 °C and 800 °C. The combination of lignosulphonate and pyrolysis oil improved considerably the density and mechanical durability of the pellets. By the second heat treatment, the quality of the pellets was bettered significantly. Densification seems to reduce CO_2 reactivity; however, pellets showed a still high reactivity.

1. Introduction

By the Paris Agreement in 2015, Norway pledged to cap the emissions at 40% of the level in 1990 by 2030 [1]. In a country, where the electricity and heat production are already almost entirely covered by renewable sources, the challenge may turn to be relatively complex. Other sectors than energy production must be targeted. The metallurgical sector, for example, represents almost the 8% of the Norwegian emissions [2]. This industrial branch relies largely on electricity and fossil fuels, mainly coal and its derivatives, namely coke. In particular, Norway is one of the world's biggest producers of silicon and ferrosilicon products. These materials are produced in electric arc furnaces from the raw materials quartz and carbon reducing materials. The main reduction material is fossil coal. Coke and biocarbon materials like biochar and wood chips are also used. Despite the electric power provided is almost entirely renewable, the total specific CO_2 emissions for the silicon and ferrosilicon industry in Norway have been therefore estimated to be between 3.5 and 4.7 tons for every ton of material produced [3]. Biochar, a coal-like material obtained by slow pyrolysis of biomass, can be used as a renewable reducing agent and may partly or fully replace fossil agents [4]. Pyrolysis is a thermal process consisting in heating in absence of oxygen to a specific temperature at a defined heating rate. During the process, an initial phase is characterized by the production of char and condensable gases and it is followed by a second step which involves complex chain reactions, that break down the condensable gases into the final products: non-condensable gases, pyrolysis oil and biochar [5]. The process has been largely investigated and an extended study is presented in [6]. Pyrolysis is defined slow when it has relatively long residence time, low heating rate and the main product is biochar. When processed and managed in a sustainable way, the usage of this carbonaceous material can be considered as carbon-neutral. Its usage has been researched in many other applications such as soil remediation, carbon sequestration, co-firing and catalyst support [7–9]. However, biochar presents several issues in the smelting process of metal ores. Therefore, biochar

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Abbreviations: daf, dry ash free basis; db, dry basis; DTG, derivative thermogravimetry; SEM, scanning electrode microscope; SHT, second heat treatment; TGA, thermogravimetric analysis; TS, tensile strength; wb, wet basis.

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represents generally only a limited amount of the carbonaceous materials mix used in the furnace [10]. Typical values of the main parameters affecting the usage in a furnace and the comparison to metallurgical coke are provided in [11]. Main issues come from low bulk density, low carbon and energy density and from high transportation and storage costs [12]. Another major obstacle is its low mechanical strength, as reported in [13]. These obstacles are mainly reflected into considerable mass losses throughout the handling and transportation steps and in instabilities during the operation of the furnace. Densification of biochar has therefore been targeted as possible partial solution to address such challenges [14]. A densification like pelletization results generally into an increase of both mechanical strength, mechanical durability and density compared to untreated biomass [15]. These parameters are hence useful to understand in which degree the aforementioned issues are tackled. Mechanical durability describes the tendency of a material to maintain integrity during handling and transportation and it is usually computed as ratio between the initial mass and the final mass of the wood pellets after having been shacked in a tumbler. Following the ISO 17831-1 for wood pellets, a minimum sample mass of 500 g is required [16]. When pellets are produced in lab scale, this precondition may be complicated to satisfy. However, according to [17], the test of a single pellet replicates the standardized test with a good extent of accuracy (especially for durability values higher than 90%), with a tendency to slightly underestimate the value. For such reason, the results from the single pellet tumbler test can be used in prediction of the real test. Moreover, it has been noticed that pellets show a good correlation between mechanical durability and density [18]. Another characteristic property of pellets is the mechanical strength, which is useful to simulate the weight top pellets have on the lower pellets during their storage, handling and application [19]. According to the procedure, strength can be measured as either tensile or compressive. Tensile strength is measured by a compression perpendicular to the cylinder axis direction of the pellets, while in the compressive strength, the force is parallel. It is worth to mention that tensile strength is generally lower than compressive strength [14].

Unlike wood pellets, the densification of biochar requires a considerable amount of additives to be stable, which makes the process challenging when applied at large scale [20]. It is common practice to use a considerable amount of water, to add binders as lignin or starch, and eventually to strengthen the pellets by the introduction of hardeners. For example, in [21], biochar was pelletized blended with lignin and hardened with $Ca(OH)_2$, NaOH, $CaCl_2$ and CaO. Calcium compounds have proved to increase the mechanical properties and stability [21]. Lignin has been tested in [12], where it has been compared to starch, $Ca(OH)_2$ and Na(OH). Starch has also been used in [14] with palm kernel shell biochar to make pellets as solid fuel. In [22] instead, at the optimum pelletization pressure of 128 MPa and with 35% of water content, pellets exhibited superior quality when biochar was produced at 550–650 °C, rather than lower pyrolysis temperatures. The importance of water in the pelletization process was observed in [23], where only biochar pellets with at least 30% of water content had satisfying mechanical durability values. In Wu et al., the densified biochar underwent a heat treatment to carbonize or dissolve undesired substances of the binders [24].

Most of the mentioned research, deals with the densification of biochar produced at low temperatures. However, biochar produced at high temperatures is known to have higher fixed carbon and higher mechanical properties, characteristics that might be appealing in the metallurgical sector.

In order to minimize transportation costs, in addition to densification, the exploitation of biomass resources nearby the final user is interesting. Hence in this work, Norway spruce (*Picea abies*) has been considered, due to its large availability and relatively low cost in Norway [25,26]. By the knowledge of the authors, studies about the densification of spruce biochar are rare. Nevertheless, an example of the usage of spruce sawdust as feedstock to produce biochar pellets has been provided in [21], where the importance of using binders to guarantee stability has been confirmed.

The co-products of the biochar production may be recovered and recirculated into the feedstock treatment chain with economic benefits. Use of pyrolysis oil as an additive will increase the mass yield of biochar and at the same time, this additive may improve the quality of the pellets. According to [27], pyrolysis oil has a positive influence on the mechanical durability and hydrophobicity of torrefied (mild pyrolysis) wood pellets when used as additive. In [28], pyrolysis oil improved considerably the compressive strength of torrefied pellets. Pyrolysis oil has also been used as binder for biochar pellets with positive results in [29–31], where it was demonstrated that it works efficiently guaranteeing stronger and more dense pellets.

The application of biochar pellets in the metallurgical industry has been already contemplated by several researchers, despite focusing on the steel production [12,32]. In the smelting processes, the rate at which the carbonaceous material reduces the metal ores is expressed as reactivity. In the silicon and ferrosilicon production, the SiO reactivity is considered. Compared to fossil fuel, biochar has higher reactivity [10]. However, how binders and densification affect this property is not definitely clear and more research needs to be done. Recently an approach of an answer has been provided in [13], where the CO_2 gasification of densified biochar has been tested by thermogravimetric analysis (TGA). A CO_2 reactivity test by TGA can be a more replicable and cheap way, compared to a conventional SiO reactivity test, to understand if a material is a good reactant in the silicon and ferrosilicon production process [33,34]. Densification is also claimed to slightly decrease the reactivity rate mainly because of reduction of porosity, while the introduction of binder can impact differently [13]. Moreover, as suggested in [35], the higher the pyrolysis temperature, the slower the reaction.

It is noteworthy to mention that both how biochar undergoes pelletization and how pyrolysis temperature affects the pelletization process have not extensively questioned. Different studies however enlightened the interaction between biochar and water, which is a behavior that could provide an insight of the binding mechanism in the densification process. As explained in [36] for conventional biochar and confirmed for higher pyrolysis temperatures in [37], biochar happens to lose hydrophobicity with increasing pyrolysis temperatures. Main causes are probably the higher porosity of the material and the disappearance of the phenolic groups on the surface [37]. It has also been noticed that the porosity increase at higher pyrolysis temperature [38].Therefore, the binding mechanism between water and biochar might be not enabled when biochar is produced at low temperatures. The increase of porosity and the loss of the hydrophobic property at higher temperatures instead could lead to better densified products.

How the bonded structure reacts at high temperatures is also relevant when the metallurgical application is taken into account. According to [39], lignin main degradation, for example, occurs at 400 °C and it continues by the production of non-condensable gases and polycyclic aromatic groups at higher temperatures. Instead, as reported in [40], in the pyrolysis process oil yield has generally a maximum at approximately 500 °C and decreases at higher temperatures in favor of the gas yield. Pyrolysis oil, lignin and water are therefore expected to get expelled by devolatization and evaporation while the pellets are heated. However, if oil is well bonded with the carbonaceous structure of the biochar, high temperatures might enhance further carbonization of the mixture, leading to a mechanically more stable and promising product for smelting.

For such reason, more research should be carried out to understand both the biochar pelletization mechanism and the application of biochar pellets in smelters. As consequence, the objectives of this study were:

- to examine the application of pellets made of biochar and pyrolysis oil in the silicon and ferrosilicon production;
- to highlight the influence of high pyrolysis temperatures and pyrolysis oil on the densification process;
- to understand the thermal behavior of the pellets.

In particular, this work was intended to investigate the interaction under high temperatures between biochar and pyrolysis oil, and to achieve an insight of a possible application in electric arc furnaces in the silicon and ferrosilicon production. The aim is to observe how each suggested added process may affect the final application. Since costs are expected to increase due to a higher complexity, the intention is to understand if the improvements might make the proposed option cost-effective by giving a more desirable renewable carbon source.

2. Materials and methods

A visual summary of the experiments with wood chips as a feedstock is presented in Fig. 1.

2.1. Feedstock and binders

Norway spruce (*Picea abies*) wood chips were produced from a tree in a local forest, in Grimstad, Norway. Immediately after felling and chipping, wood chips were dried at 60 °C and stored in an airtight box at ambient temperature. Pyrolysis oil from Btg-btl (The Netherlands) was used as binder. As declared by the producer, it has been obtained by the fast pyrolysis of pinewood [41]. Despite produced by different processes, the oils from slow and fast pyrolysis are similar in terms of coke residue formation. Due to this similarity, which is shown in S1 in the supplementary material, their behavior is therefore not expected to differ significantly when applied as binder. Since broadly available, the latter was preferred for the realization of this work. LignoBond DD from Borregaard (Norway) was also used as lignosulphonate additive. This additive is normally a commercial binder based on a co-product from 2nd generation fuels. The chemical analysis of the feedstock is shown in Table 1.

2.2. Pyrolysis

Biochar was produced at three different pyrolysis temperatures: 500, 800 and 1100 °C. The pyrolysis of the sample was carried out in a muffle furnace *LT40/11/P330* (Nabertherm, Germany). Prior to the pyrolysis, the muffle furnace was heated to the set temperature. For each temperature, 80 g of spruce woodchips was weighted in a 700 mL alsint crucible covered with an alsint lid. The sample was purged in a nitrogen atmosphere, placed in the center of the hot muffle, and kept at the desired temperature for 60 min after being heated at 10 K/min. After the pyrolysis was completed, the sample was removed from the muffle furnace, placed in a desiccator and cooled to room temperature. The obtained biochar was milled in a hammer mill *px-mfc 90 d* (Polymix, Germany), sieved to a particle size less 2 mm and stored at ambient temperature in airtight boxes. The particle size distribution of the produced biochar was analyzed by a laser diffraction particle size analyzer *Mastersizer 3000* (Malvern, UK). Results are presented in Fig. 2. No minimum size

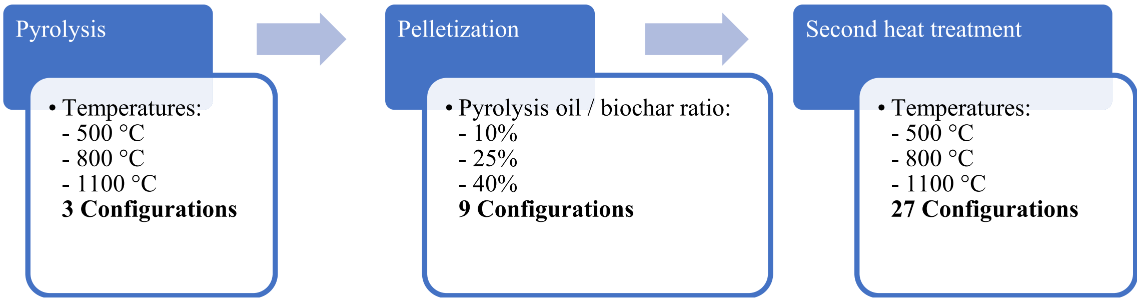

Fig. 1. Sample preparation layout. Biochar is produced at three different pyrolysis temperatures: 500 °C, 800 °C and 1100 °C. Each pyrolysis product is then pelletized adding three different pyrolysis oil contents by weight: 10%, 25%, 40%. Eventually the 9 cases are heated once more at 500 °C, 800 °C and 1100 °C. In the overall, 27 different configurations have been tested.

Table 1
Proximate analysis and ultimate analysis of untreated spruce, biochar from spruce produced at 500 °C, 800 °C, 1100 °C, lignin and pyrolysis oil. Values for the proximate analysis are reported in percentage in wet basis (%wb) and percentage in dry basis (%db). In the ultimate analysis, values are given in percentage in dry ash free basis (%daf). Analyses of the pyrolysis oil have been taken from [41].

Material	Spruce	Biochar 500 °C	Biochar 800 °C	Biochar 1100 °C	Ligno-sulphonate	Pyrolysis Oil
Proximate analysis						
Moisture [%wb]	8.6	2.3	1.9	3.2	6.5	24.5
Volatile [%db]	80.6	17.5	8.5	6.8	59.9	-
Ash [%db]	0.8	2.0	2.0	2.2	21.2	-
Fixed carbon [%db]	18.6	80.5	89.5	91.0	18.9	-
Ultimate analysis						
C [%daf]	53.2	82.8	85.7	91.0	40.0	46
H [%daf]	6.1	2.9	1	0.5	4.9	7
N [%daf]	0.1	0.6	0.6	0.6	<0.01	<0.01
O [%daf]	40.6	13.7	12.7	7.9	55.2	47

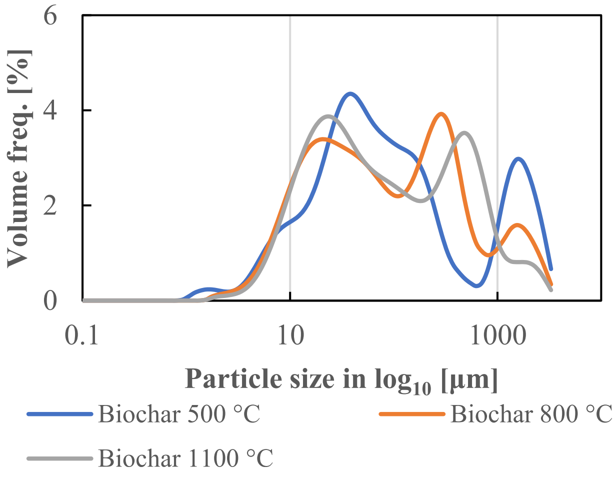

Fig. 2. Particle size distribution for the biochar produced with the pyrolysis temperatures of 500 °C, 800 °C, 1100 °C after milling and sieving to a diameter less than 2 mm.

requirements were taken into account, in order to use finer particles as intrinsic binder to cover the void between larger particles.

2.3. Pelletization

Three different mass ratios between pyrolysis oil and biochar were considered: 10%, 25%, 40%. The selection of such wide range was motivated by the intention of capturing a possible optimum ratio and to fully understand how pyrolysis oil affects the pellets properties. For each composition, at least 2 g of biochar blended with pyrolysis oil was prepared. Then, lignosulphonate was added, with a mass ratio 10:1 between the blend and the binder. Finally, the water content was adjusted to 35% of the total weight by addition of water. The blend was homogenized in a beaker by a magnetic stirrer for about 10 min. The investigated compositions are stated in Table 2. The pellets were pressed by a compact hot pellet press (MLI, USA). The inner diameter of the die was 6.250 mm. The die was fulfilled with 0.15 g of mixture. Following [22], the pelletizing pressure was set to 128 MPa. According to some preliminary pressure tests, presented in S2 in the supplementary material, density does not have a relevant increase after 128 MPa. This value was therefore considered acceptable. Pressure was fixed manually by a hydraulic piston and kept fixed for 10 s before pressure release and extraction of the pellet. Pelleting time was chosen accordingly to [42], once ensured by preliminary observations as sufficient to achieve stability. Pelletization was carried out at 90 °C, to simulate an industrial pelleting process. Before pelletization, the die and other moving parts were heated up to maintain 90 °C during the entire process. At least twelve pellets were produced for each configuration. Pellets were then stored and cooled down in airtight boxes at ambient temperature.

2.4. Second heat treatment

A second heat treatment following the same procedure and temperatures as the pyrolysis step was used to observe and analyze the thermal interaction between biochar and binders and subsequently the influence on the final pellet quality. For each temperature, three pellets were heated up for 60 min. The treated pellets were then stored in air-tight boxes at ambient temperature.

2.5. Characterization of biochar pellets

Analysis. A *2400 Series II CHNS/O Elemental Analyzer* (PerkinElmer, USA) was used for the CHN ultimate analysis. Oxygen was computed by difference of the other elements. Sulphur content was assumed negligible because, despite present in low amount in the lignosulphonate, it was estimated to be less than 0.5% of the pellets total weight. Proximate analysis was carried out in the muffle furnace *LT 40/11/P330* (Nabertherm, Germany) according to ISO standard procedures. To measure the volatile matters, EN 15148 was applied. Scanning electron microscope (SEM) images of the samples were obtained by *JSM-6499 Scanning Microscope* (JEOL, Japan).

Density. Particle density was computed indirectly as $\rho = m/\pi r^2 l$, where m is the mass of the single pellet, r is the radius of the pellet while l is its length. Mass was determined on a balance with a readability of 0.1 mg, while radius and length by a Vernier caliper with a precision of 0.01 mm. Measurements were taken at least 24 h after the pelletization. The mechanical durability was carried out on single pellets and each configuration was carried out as a triplet.

Mechanical durability. The mechanical durability of a single pellet was measured by an *ISO tumbler 1000+* (Bioenergy, Austria) parametrized following the ISO 17831-1. In the test the pellet spins inside a steel box which rotates 500 times within 10 min. Mechanical durability is then the ratio between the weighted pellet mass after and before the treatment. Pellets were tested before and after the second heat treatment.

Tensile strength. Pellets were tested by a *pellet hardness tester* (Amandus Kahl, Germany). The machine measures the tensile strength in kilograms by an equivalence between the elastic compression of a spring that moves a piston against the pellet side and the force equivalent mass. Tensile strength (TS) is applied perpendicularly to the cylindrical axis direction. Following the procedure in [43], the correspondent value in MPa was computed by the equation $TS = m_s g/\pi r l$, where m_s is the force equivalent mass and g is the gravitational acceleration. When the pellets were fragile, the value of the strength was too small to be tracked by the tester. In this case, it was therefore set to zero.

Shrinkage. The shrinkage of the pellets after the second heat

Table 2
Composition of the configuration blends tested (weight percentage wet basis).

Configuration number	Pyrolysis Temperature [°C]	Biochar [%]	Pyrolysis Oil [%]	Ligno-sulphonate [%]	Water added [%]
1	500	55.8	6.2	6.2	31.8
2	500	48.0	16.0	6.4	29.5
3	500	39.7	26.5	6.6	27.2
4	800	55.7	6.2	6.2	32.0
5	800	47.9	16.0	6.4	29.8
6	800	39.6	26.4	6.6	27.3
7	1100	56.3	6.3	6.3	31.2
8	1100	48.4	16.1	6.4	29.1
9	1100	39.9	26.6	6.7	26.8

treatments was also taken into consideration. This value can provide further information about the response of the pellets when heated at high temperatures. It was computed as $s = (l\text{-}l_f)/l$, where l_f is the length of the pellets after the treatment. The length was measured by a Vernier caliper with a precision of 0.01 mm.

CO_2 reactivity. Only pellets from configurations, which resulted in acceptable mechanical properties were tested. However, the selection included different pyrolysis temperatures, oil content and second heat treatment temperatures, in order to investigate their influence on the reactivity of the pellet. The CO_2 reactivity test was conducted in a *TGA/DSC 1 Star system* (Mettler Toledo, USA). Samples were heated in a pure CO_2 atmosphere with a constant heating rate of 10 $Kmin^{-1}$ up to 1100 °C. A volume flow of 100 $ml\ min^{-1}$ of pure CO_2 was used.

3. Results and discussion

3.1. Pelletization

The density of the pellets with different oil additions is shown in Fig. 3a. As expected and observed in [31], more oil means increased density, which again normally means improved mechanical properties. Curves seem to suggest a linear correlation between the amount of oil added and the density. Biochar produced at 500 °C and 800 °C undergo pelletization in a different way, while only small distinctions appear between 800 °C and 1100 °C. Pellets with biochar produced at the lowest pyrolysis temperature have a considerably lower density in comparison to pellets with biochar produced at higher pyrolysis temperatures, which instead are characterized by values in line with previous works regarding spruce pellets [13], biochar pellets [17] and biochar pellets blended with pyrolysis oil [26]. A hint of this phenomenon was already anticipated in the samples' preparation: 500 °C mixture requires more stirring to get as homogeneous as the ones from other temperatures. This could be caused by the different hydrologic property and the higher porosity, biochar has according to the pyrolysis temperature. Biochar produced at 500 °C is hydrophobic and less porous. As consequence, the binder mechanism fundamental to enhance a good pelletization cannot work properly. Biochar produced at 800 °C and 1100 °C are not hydrophobic and have higher porosity. Hence the pelletization works more efficiently. Considering that porosity increases at higher pyrolysis temperature, the negligible difference in density between biochar produced at 800 °C and 1100 °C suggests that the hydrophilic behavior is the primary driver in the pelletization process. This assumption is further supported by the variation in mass of the mixtures measured as ratio between the initial mass used in pelletization and the single pellet mass measured after 24 h, which is presented in Fig. 3b. The mass lost is supposed to be mainly due to the evaporation of water, devolatization of pyrolysis oil and leakage of these liquids during pelletization. Biochar pyrolyzed at 500 °C has lost more mass, suggesting that the binding mechanism has not successfully enhanced.

3.2. Second heat treatment process

The biochar yield of the pellets after the second heat treatment (SHT) is presented in Fig. 4. The yield was computed as ratio of the biochar pellets weight before and after second heat treatment. The graph shows a considerable distinction in yields for the pellets that were heated at 500 °C and 800 °C, while only a slight difference is observable between 800 and 1100 °C. This difference is related to the thermal behavior of biochar, pyrolysis oil and lignin. When treated at high temperatures, a consistent part of the oil is converted to gas, while lignin experiences devolatization. These binders are therefore expected to have been expelled in considerable extent, explaining concurrently the inverse proportionality between the content of binders and the biochar yield. In addition, the biochar originally included in the pellets is further carbonized and partially ejected as gas. Moreover, pellets with biochar produced at 500 °C have lower biochar yields, regardless of the temperature of the second heat treatment. Generally, slow pyrolysis at low temperatures is incomplete. It means that the pyrolysis oil which is produced during pyrolysis is not entirely dissolved in the condensed phase and some traces are visible throughout the biochar structure. If treated at higher temperatures, biochar will therefore lose this component. Biochar produced at higher temperatures instead is not affected by this behavior. This explains why the second heat treatment for biochar produced at 800 °C and 1100 °C provided higher biochar yields. Table 3 shows the chemical analysis of the pellets which underwent second heat treatment. Despite containing pyrolysis oil and lignosulphonate, which have originally a high volatile matter content, pellets now have characteristics similar to untreated biochar: high fixed carbon, low ash and volatile matter content. The second heat treatment may therefore be useful to carbonize the binders and purify the pellets, as suggested in [24].

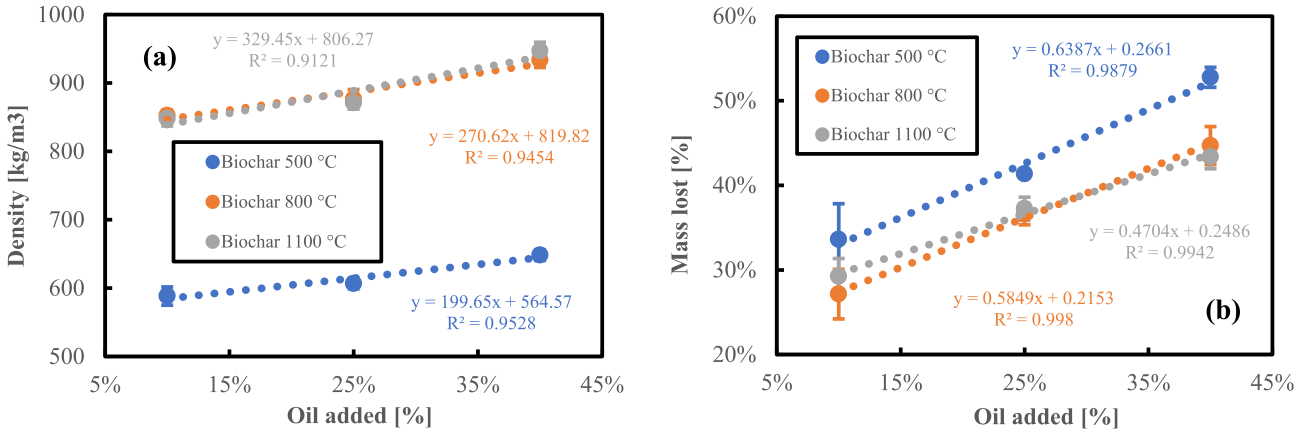

Fig. 3. Post-densification density of the pellets blended with different pyrolysis oil additions (a). Mass lost during the post-densification stabilization of the pellets with different pyrolysis oil additions (b).

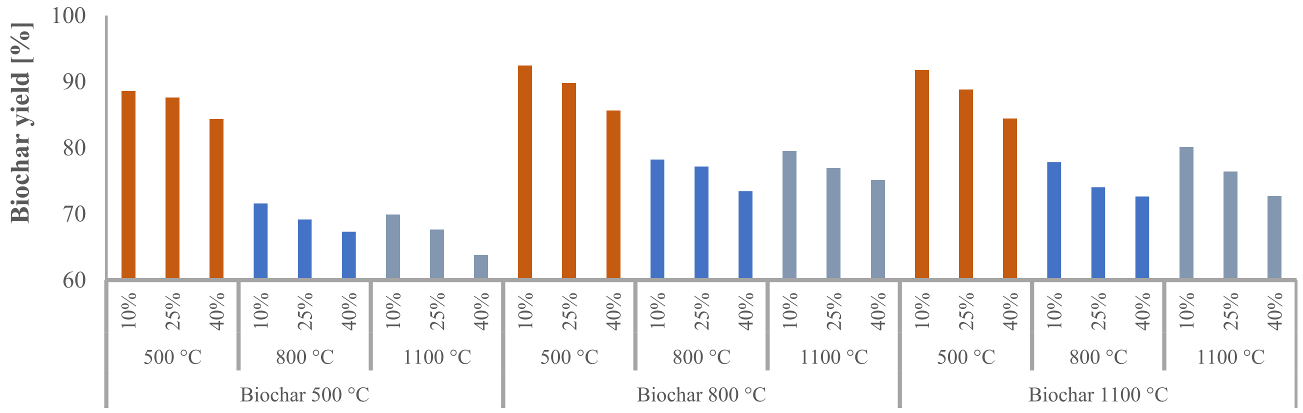

Fig. 4. Biochar yield after a second heat treatment. Data are divided first by temperature of the original pyrolysis temperature used to produce biochar, then by the temperature of the second heat treatment and finally by the percentage of pyrolysis oil added.

Table 3
Ultimate analysis and proximate analysis for all the post second heat treatment configurations. Ultimate analysis values are reported as percentages in dry ash free basis (%daf), while proximate analysis values percentages in dry basis (%db).

Pyrolysis Temperature [°C]	Second heat treatment [°C]	Pyrolysis Oil Content [%]	C [%daf]	H [%daf]	N [%daf]	O [%daf]	Fixed Content [%db]	Ash [%db]	Volatile matter [%db]
500	500								
		10	81.6	1.7	0.2	16.5	76.3	1.6	22.1
		25	84.1	4.1	0.8	11.0	77.7	2.8	19.5
		40	84.1	4.1	0.2	11.7	76.9	2.6	20.6
	800								
		10	90.7	2.4	0.8	6.1	88.3	3.0	8.6
		25	88.3	1.4	0.4	9.9	81.2	0.1	18.7
		40	89.6	1.1	0.6	8.8	88.6	1.0	10.5
	1100								
		10	90.9	0.1	0.8	8.1	88.3	0.1	11.6
		25	93.1	0.6	0.8	5.4	87.8	6.9	5.3
		40	93.0	0.1	1.1	5.8	89.2	4.0	6.8
800	500								
		10	91.1	0.2	1.9	6.8	83.2	2.9	13.9
		25	89.8	0.8	0.0	9.4	87.3	3.1	9.6
		40	89.3	0.8	1.4	8.5	85.4	2.8	11.7
	800								
		10	93.4	0.9	1.7	3.9	84.2	3.5	12.3
		25	90.2	1.0	1.8	7.0	87.5	0.1	12.4
		40	91.8	0.7	1.6	6.0	82.0	0.5	17.5
	1100								
		10	95.0	0.3	0.2	4.6	90.2	3.7	6.1
		25	95.9	2.6	1.1	0.4	89.8	1.2	9.1
		40	93.5	0.1	0.9	5.5	92.2	2.0	5.8
1100	500								
		10	94.6	0.5	1.1	3.7	88.6	1.0	10.4
		25	90.1	0.3	0.7	8.9	88.7	1.8	9.5
		40	90.0	0.5	0.9	8.5	84.4	3.1	12.5
	800								
		10	96.3	0.0	0.1	3.6	90.2	3.8	6.0
		25	96.6	0.0	0.0	3.4	83.9	4.1	12.3
		40	96.3	0.0	0.0	3.7	82.1	4.4	13.6
	1100								
		10	95.5	0.0	0.0	4.5	90.3	2.2	7.5
		25	94.6	0.2	1.6	3.6	88.1	3.6	8.3
		40	97.8	0.0	0.8	1.4	87.0	3.9	9.1

3.3. *Second heat treatment influence*

The physical properties of the biochar pellets are shown in Fig. 5. As presented in Fig. 5a, the second heat treatment (SHT) reduces the density of the pellets. The higher the temperature of the treatment, the lower the density. As previously explained, during the heat treatment pellets lost part of their mass and their porosity increased. The reduction of density is more accentuated when the oil content is higher, due to a higher amount of volatiles expelled during the treatment. However, pellets appeared to be visually stable when heat is applied, suggesting that the SHT improves their mechanical properties. This can be observed by the values of both mechanical durability and tensile strength in Fig. 5b and c. Regarding the mechanical durability, Fig. 5b shows that pellets produced at 800 °C and 1100 °C present acceptable values, when compared to EN Plus certification requirements [16], enforcing the assumption that pelletization works better when biochar is produced at high pyrolysis temperatures. Mechanical durability values

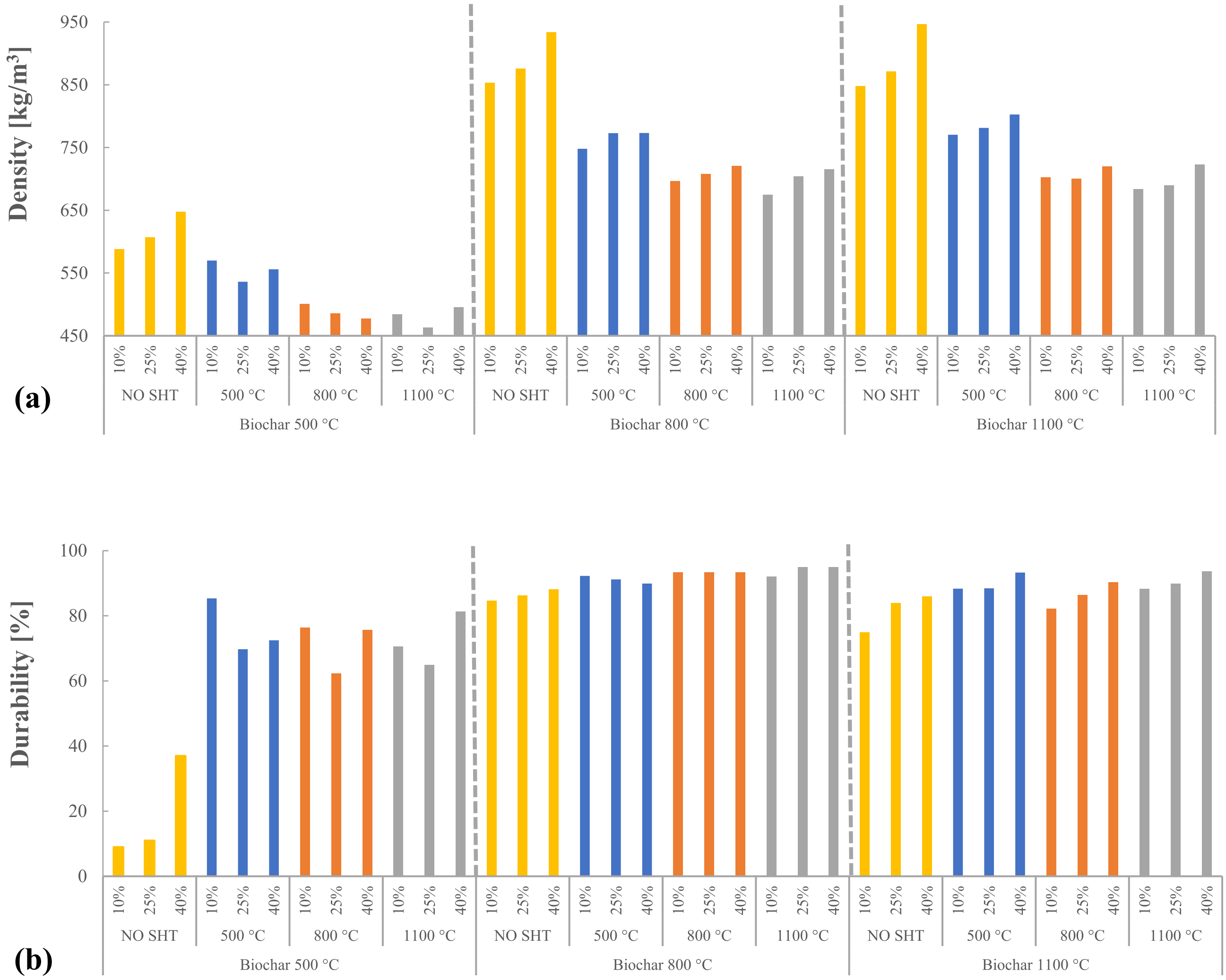

Fig. 5. Second heat treatment (SHT) and oil content influence on (a) density (b) durability (c) mechanical strength and (d) shrinkage. Data are divided first by temperature of the pyrolysis temperature used to produce biochar, then by the temperature of the second heat treatment and finally by the percentage of pyrolysis oil added. In(c) the sign (−) means the value is negative.

are generally comparable to the results obtained in [23]. Fig. 5b suggests also that the temperature of the SHT and the pyrolysis oil content affect slightly the mechanical durability.

The tensile strength values of the pellets are shown in Fig. 5c. This property is both affected by the temperature of the SHT and by the amount of pyrolysis oil added. When compared to [14,31], biochar pellets are characterized by high values for the tensile strength, especially when they undergo the SHT. It is complicated to compare pellets to untreated biochar since usually strength is measured as compressive. However, if as previously mentioned, it is assumed that tensile is generally lower than compressive strength, the biochar pellets are also strong when confronted to the normal biochar used in the metallurgical application [11].

The values of the mechanical properties indicate that the binding mechanism between biochar and pyrolysis oil is further enabled when heat is applied in a SHT. The high temperatures lead to a further carbonization of the bonded structure formed between biochar and binders during the pelletization phase.

By the values of the properties before the SHT provided in Fig. 5, it can be noticed that pelletization provided better quality pellets when biochar produced at higher pyrolysis temperatures was used. Biochar produced at 800 °C and 1100 °C is characterized by high porosity. The additives can therefore penetrate more easily into the biochar structure and chemically bind while pelletization occurs. Moreover, differently to biochar produced at 500 °C, it is not hydrophobic. Since the used binders have a high moisture content and water was also added to facilitate the pelletization, the pellets produced at high pyrolysis temperatures were hence also more stable while cooling down.

Shrinkage is presented in Fig. 5d. As suggested by the resulting biochar yield analysis, pellets with biochar produced at 500 °C are characterized by higher shrinkage. Quite interestingly, it seems like pellets with an oil content ratio of 25% have higher shrinkage. This could probably be related to the interaction between the pyrolysis oil and the porous structure of the biochar during the pelletization phase: the content may be already enough to affect the structure of the pellets but not enough to penetrate in the deepest pores optimizing the bonding mechanism. However, data are not enough clear to elaborate a more precise conclusion. Moreover, there is no correlation between the shrinkage and the biochar pellets yield.

The mechanisms affecting the final pellets can be better understood by the help of the scanning electron microscope (SEM).

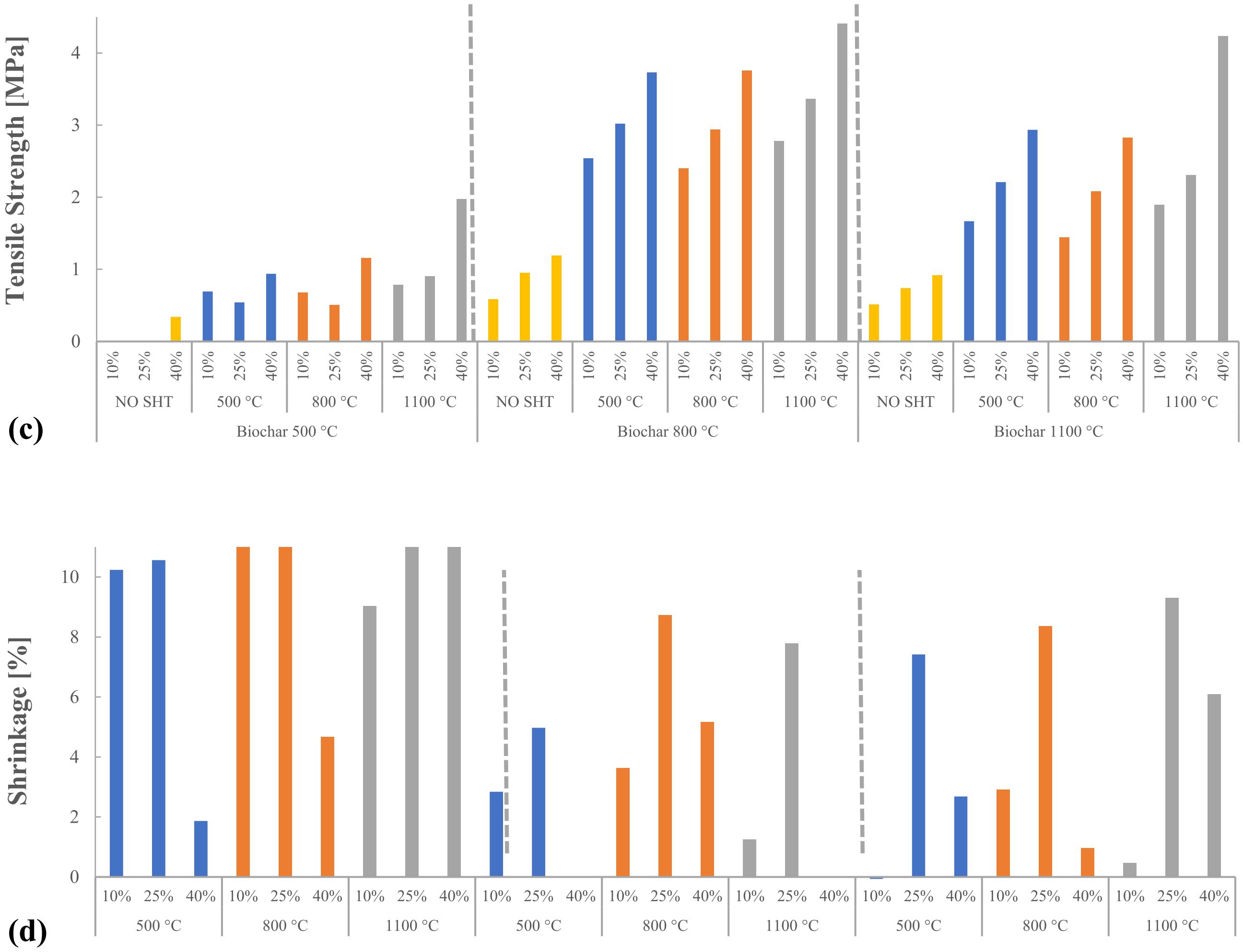

Fig. 5. (*continued*).

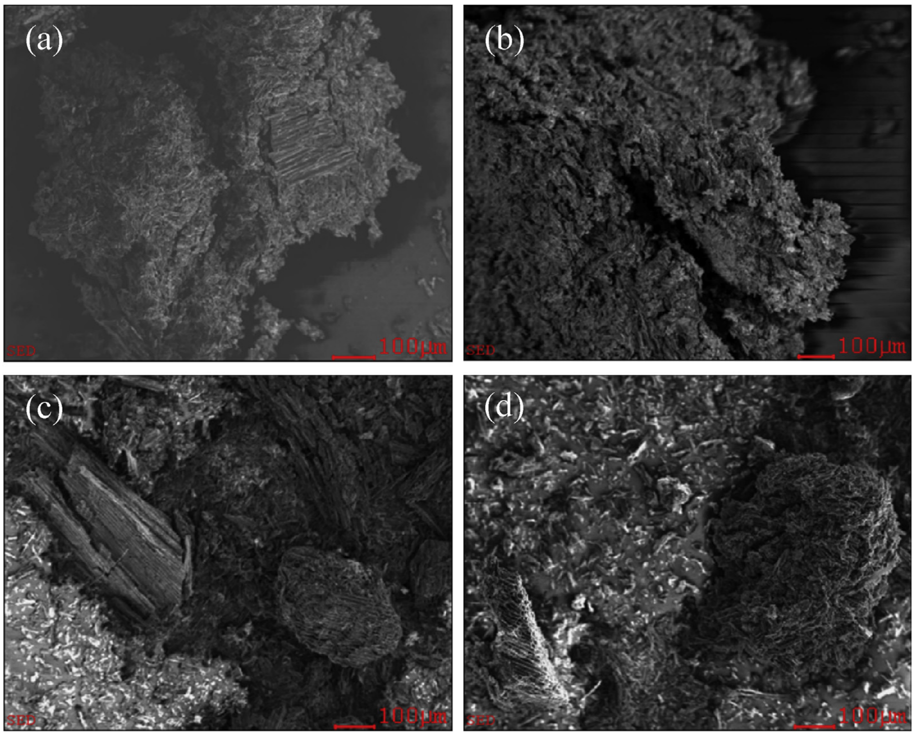

Fig. 6. SEM pictures of (a) mixture of spruce biochar produced at 500 °C, 40% oil content; (b) pellet with biochar produced at 500 °C, 40% oil content; (c) and (d) pellet with biochar produced at 500 °C and heated by a SHT at 800 °C.

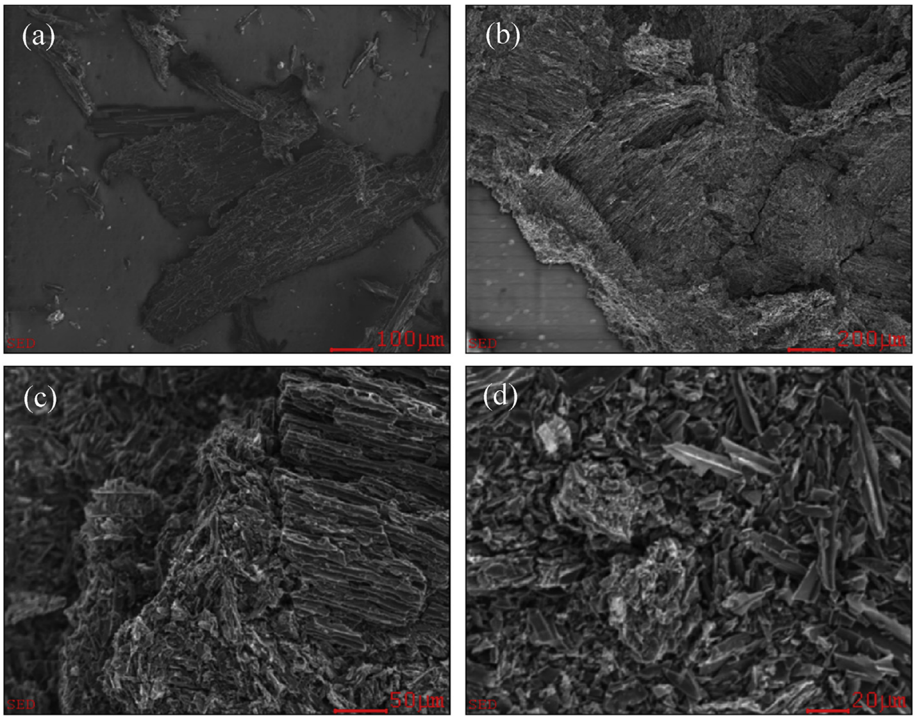

Fig. 7. SEM pictures of (a) mixture of spruce biochar produced at 800 °C, 40% oil content; (b) pellet with biochar produced at 800 °C, 40% oil content; (c) and (d) pellet with biochar produced at 800 °C and heated by a SHT at 800 °C.

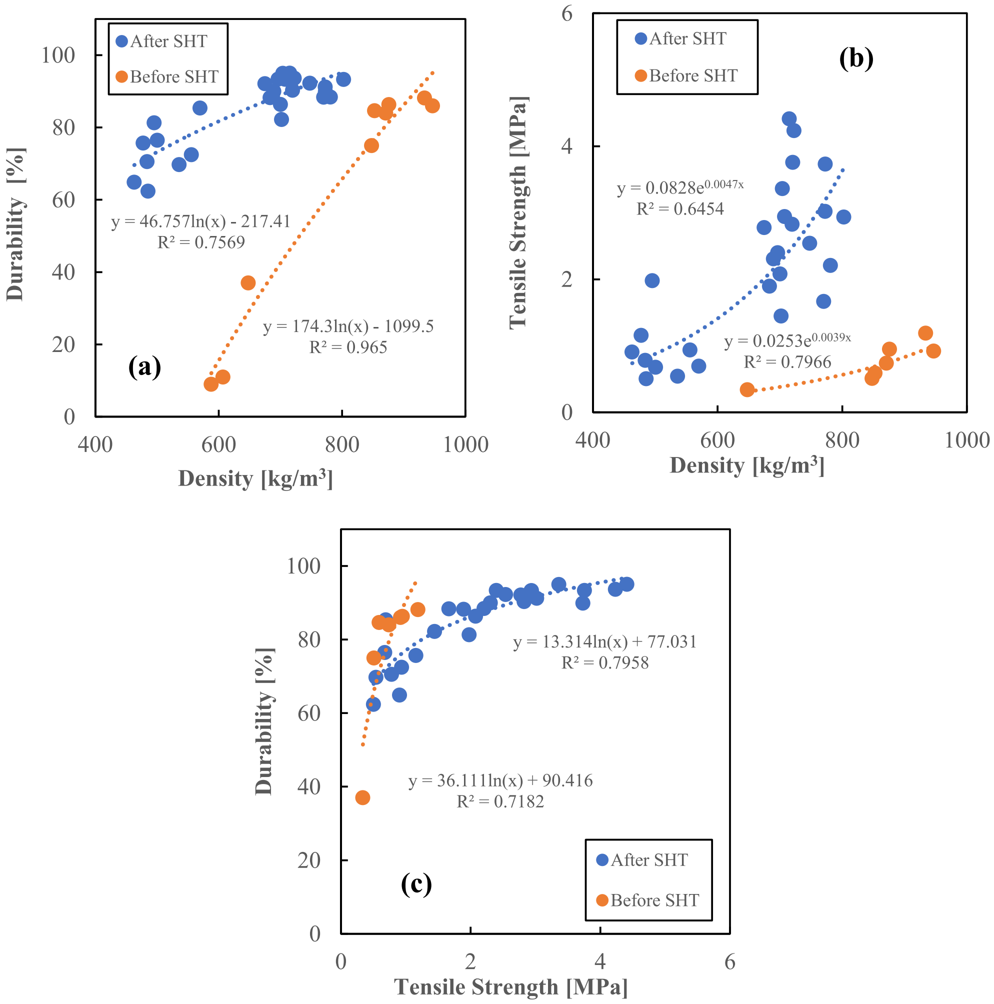

Fig. 8. Correlations of the values measured before and after second heat treatment (SHT) between (a) density and durability, (b) density and tensile strength, (c) tensile strength and durability.

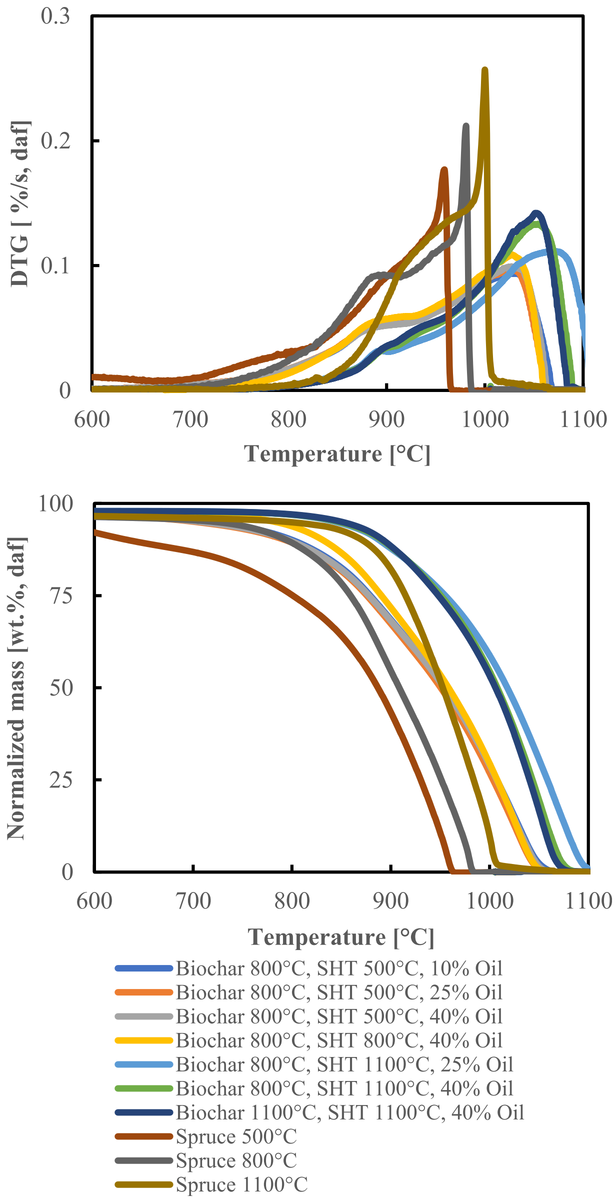

Fig. 9. CO_2 Reactivity for some of the configurations, in comparison to the behavior of untreated biochar pyrolyzed at the same temperatures. Upper graph shows the derivative thermogravimetry (DTG, wt = weight total, daf = dry ash free), wile the lower graph shows the normalized mass (wt = weight total, daf = dry ash free).

Fig. 6 visualizes the main changes occurring in each step for pellets with biochar produced at 500 °C and with an amount of oil added of 40%. As suggested by the results of the mechanical properties, pelletization of biochar does not work properly for this temperature and this can be seen by the help of Fig. 6a and b, where the mixture before and after pelletization does not show clear differences. When instead the pellet is heated newly by a second heat treatment, biochar and binders start interacting enhancing stronger agglomerating mechanism. This can be seen in Fig. 6c and d. If same analysis is carried out for pellets with biochar produced at 800 °C a difference can be already seen between Fig. 7a and Fig. 7b, which show biochar pellet before and after pelletization. In this case, the thermal interaction between biochar and binders strengthened the structure of the biochar pellets and it can be observed comparing Fig. 7c and d. To help the comprehension of the previous pictures, S3 in the supplementary material presents photos of the pyrolysis oil analyzed alone before being blended.

Throughout the SEM observations it is possible to attempt an overall explanation of the main chemical reactions enhanced by the heat treatment. Due to the higher porosity characterizing biochar produced at high temperatures, pyrolysis oil penetrates the solid structure covering the pores and heading to a homogenized mixture. Pyrolysis oil can therefore act properly as binder in the pelleting phase. Once the pellet is heated, pyrolysis oil undergoes tar-cracking: its organic part is partially carbonized, while the rest evaporates. As result, the biochar structure is further strengthened by the solidification of the bonded zones. The volatiles are expelled by exiting through the pores and thus unveiling a part of them. This phenomenon is assumed to affect the pellet shrinkage.

Fig. 8 shows the possible correlations between density, mechanical durability and tensile strength before and after the second heat treatment. The only correlation with a significantly high R^2 coefficient is between density and mechanical durability before the SHT, which is included in Fig. 8a, confirming what stated in [18]. Density and strength relation, visible in Fig. 8b, is slightly exponential and more accentuated before undergoing the second heat treatment. The interaction between strength and durability seems not to be affected by the heat process, following a general logarithmic trend shown in Fig. 8c. In general, as seen in [17], compressive strength is moderately correlated to density and mechanical durability.

3.4. CO_2 reactivity

The results of the CO_2 reactivity test are shown in Fig. 9, where the pellets are compared to untreated biochar produced at different pyrolysis temperatures. With respect to the feedstock, pellets show an expected slightly lower reactivity [13], that means they require higher temperatures to enhance the reaction. Reactivity is also affected by the maximum temperature they have been processed with. The higher the pyrolysis or second heat treatment temperature, the higher the temperature needed to fully enhance the reaction, as confirmed in [35]. Instead, the variation of oil content and the lignosulphonate do not have any considerable impact, probably since these materials became biochar-like by the carbonization which occurs during the second heat treatment. Looking at the derivative thermogravimetry (DTG) graph, it is also interesting to observe that densified pellets are characterized by a smoother reaction curve when compared to untreated biochar. This behavior could turn out to be beneficial inside the furnace, since once densified biochar would take more time to react. Therefore, instead being consumed in the very upper part of the lower temperature zone, biochar would get more distributed and the efficiency of the carbothermic reduction might increase. However, it is reasonable to

Table 4
Summary of the main improvements provided by the addition of each process.

Added process	High temperature pyrolysis	Densification	Pyrolysis oil as binder	Second heat treatment
Benefits	•Higher fixed carbon content •Lower volatiles	•Better mechanical properties •Reduction of mass losses •Fines recovery	•Pyrolysis by-product recovery •Better mechanical properties	•Significantly better mechanical properties •Higher fixed carbon content •Lower volatiles

simply assume that the densified pellets will have a very high reactivity even if the reactivity is somewhat lower than the untreated pellets.

3.5. Summary discussion

In the light of what has been discussed, the coupling of pyrolysis at high temperatures and densification of biochar with pyrolysis oil may turn to be an interesting option to foster the use of biochar in the silicon and ferrosilicon production. The addition of further processes in the conventional feedstock preparation is expected to increase the cost. However, the improvements, summarized in Table 4, may act as counterweight and make the option cost-effective. Moreover, the intensification of emissions related taxes as measure to tackle climate change is becoming a realistic option. This possibility, if contemplated, could make the solution more economically appealing.

4. Conclusions

This study was intended to investigate the use of densified biochar in the silicon and ferrosilicon production. Several pyrolysis temperatures were considered, and their influence analyzed. The experiments exhibited a clear distinction between pellets consisting of biochar produced at 500 °C and 800 °C, without showing relevant differences between the latter and higher temperatures. In particular, the biochar produced at 800 °C provided generally the most suitable pellets for smelting processes. The usage of pyrolysis oil as binder was evaluated as way to recover this pyrolysis by-product and improve the quality of the pellets. The addition of this binder contributed to increasing the density and, in certain extents, the tensile strength and the mechanical durability. Better mechanical properties are tendentially appreciable since they are related to a reduction of costs in the handling and transportation of biochar. It is also noteworthy to mention that the biochar fines, commonly generated throughout the industrial process chain and treated as waste, may be recovered as additional carbon source input of the densification step. By a subsequent second heat treatment of the pellets, it was observed that tensile strength and mechanical durability increased significantly, due to the conglomeration of the carbonized fraction of the pyrolysis oil into the biochar structure. Moreover, this treatment showed that pellets are thermally stable, behavior which might be beneficial inside the furnace. The results exhibited also an appreciable correlation between density and mechanical durability, especially before the second heat treatment. Tensile strength was instead moderately correlated to density and mechanical durability. Reactivity was mainly affected by the densification of the material and the highest temperature used during both the pyrolysis and the second heat treatment. The usage of binders instead did not show any clear influence on the reactivity. Biochar pellets are still characterized by high reactivity compared to conventional carbon sources. In the overall, the agglomeration of biochar and pyrolysis oil provides a promising material to apply in the silicon and ferrosilicon production, with respect to the original untreated feedstock. The expected increase of costs might reasonably be balanced by the discussed improvements.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.energy.2019.06.013.

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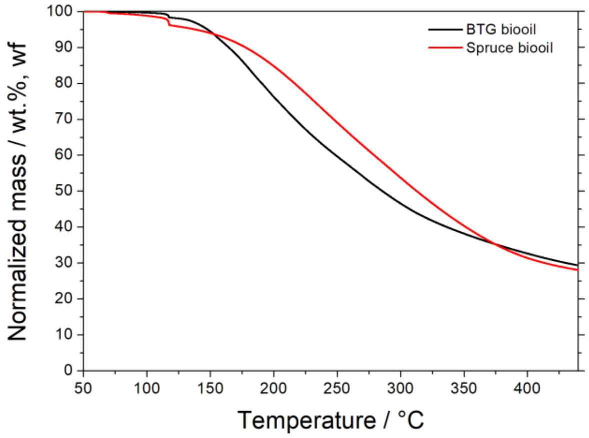
Supplementary materials

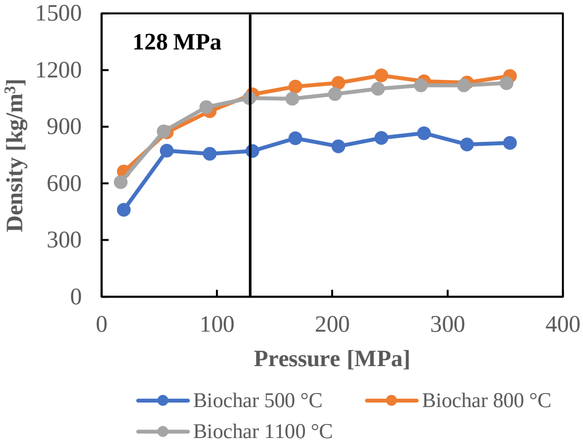
Biooil distillation curve

The distillation curves of the water free fast pyrolysis biooil (BTG oil) and spruce biooil were investigated by using a thermogravimetric instrument TGA/DSC 1 STARe System (Mettler Toledo, USA). Prior to the experiment, the water fraction of the biooil was separated by a vacuum distillation (temperature: 70 °C, pressure: 300 mbar). For each experiment, 100 µL of sample were pipetted into alumina crucible. The samples were heated at a constant heating rate of 10 K min^{-1} to 110 °C and kept at this temperature for 10 min to remove the remaining water fraction. The water free biooil sample was subsequently heated in argon (volume flow: 50 ml min^{-1}) to 450 °C at a heating rate of 5 K min^{-1}. The experiments were carried out as a double determination.

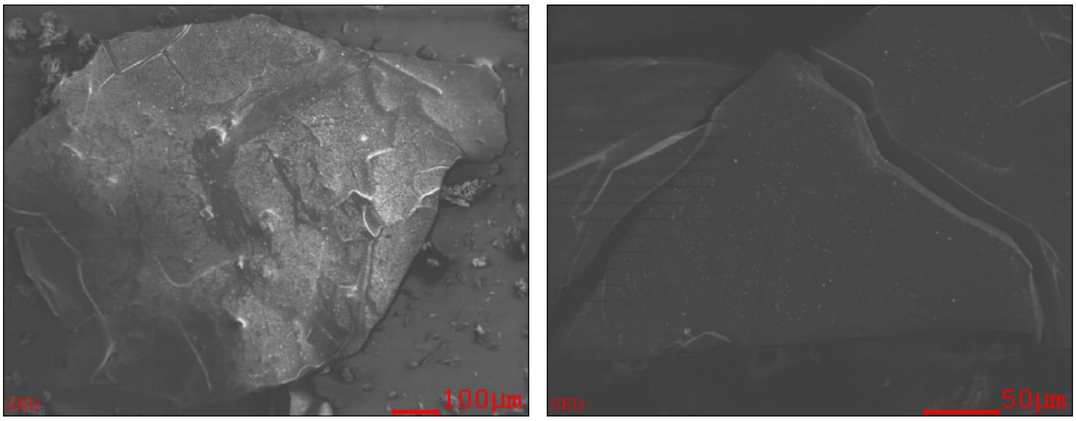


S1: Normalized mass curve of BTG biooil and spruce biooil from fast and slow pyrolysis in the temperature range between 50 and 450 °C.

S1 shows that the bio-pitch fraction of the BTG biooil sample is similar to the biooil produced under slow pyrolysis conditions. The carbon content of the spruce bio-pitch was determined to 73 wt.%, respectively 71 wt.% for the BTG biooil with similar hydrogen content of about 4%. The results indicate that the chemical composition of both biooils are similar after the secondary heat treatment.



S2. Variation of the density of the single pellets containing biochar produced with the pyrolysis temperatures of 500 °C, 800 °C, 1100 °C when pelletizing pressure is increased.



S3. SEM pictures of the pyrolysis oil at different magnitudes.

Paper B

Analysis of optimal temperature, pressure and binder quantity for the production of biocarbon pellet to be used as a substitute for coke by Riva, Lorenzo; Nielsen, Henrik Kofoed; Skreiberg, Øyvind; Wang, Liang; Bartocci, Pietro; Barbanera, Marco; Bidini, Gianni; Fantozzi, Francesco. Published in Applied Energy (2019).

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Analysis of optimal temperature, pressure and binder quantity for the production of biocarbon pellet to be used as a substitute for coke

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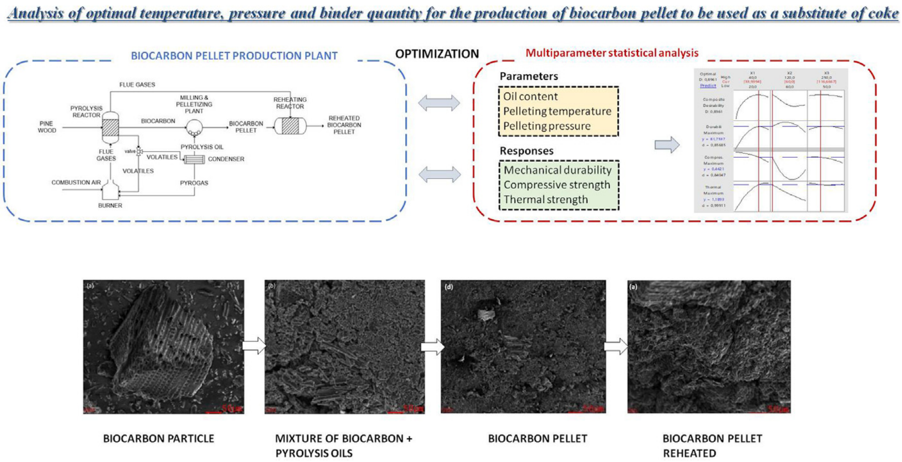
HIGHLIGHTS

- Biocarbon is pelletized using pyrolysis oil as binder and reheating after densification.
- Optimum content of pyrolysis oil is 33.9 wt%.
- Optimum pelleting pressure is 116 MPa.
- Mechanical durability of the obtained pellet is 81.7%.
- The fixed carbon content of the reheated biocarbon pellet is 87.79%.

GRAPHICAL ABSTRACT



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Biocarbon
Pine wood chips

ABSTRACT

In order to contribute to the decarbonization of the economy, efficient alternatives to coal and coke should be found not only in the power sector but also in the industrial sectors (like steel, silicon and manganese production) in which coal and coke are used as a reductant and for steel production also as a fuel. To this aim many research works have been focused on the development of a coke substitute based on woody biomass and known as "biocarbon". There are still barriers to overcome, among them: the biocarbon low density, poor mechanical strength and high reactivity. In this paper a new biocarbon production methodology is proposed, based on: pyrolysis at 600 °C, densification (using pyrolysis oil as binder), reheating of the obtained pellet. Response surface methodology with a Box-Behnken experimental design was utilized to evaluate the effects of the process conditions on the pellet's quality. Responses showed that densification was mainly affected by oil content and pelleting temperature, while pelleting pressure had a minor influence. The pelleting process has been finally optimized using Derringer's desired function methodology. Optimal pelletizing conditions are: temperature equal to 60 °C, pressure equal to 116.7 MPa, oil content concentration of 33.9 wt%. These results are relevant for

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metal production industries at a global level. The identified optimal parameters of the new biocarbon production process can contribute to replace coke with sustainable fuels and probably reduce great part of the related greenhouse gases emissions.

1. Introduction

Vegetal biomass can be used as a valid substitute for fossil fuels, reducing Greenhouse Gases (GHG) emissions and energy imports [1]. Since what's emitted during combustion is absorbed during its growth, biomass is assumed to be carbon neutral [2]. A remarkable characteristic of biomass is the possibility to be converted by various processes into a widespread category of products, that can efficiently fit systems previously designed for fossil fuels [3]. For example, biocarbon is a product similar to coke and coal and is obtained by thermally treating of the biomass in absence of oxygen [4]. This treatment (pyrolysis) is usually performed at ambient pressure at temperatures between 300 and 600 °C [5]. Besides heat and power production, biocarbon is also a sustainable alternative for the metallurgical industry, where carbonaceous materials are needed for the reduction of metal ores [6]. Its application has already been discussed widely and its potential is acknowledged. Monsen et al. [7] investigated the use of charcoal in silicomanganese production; [8] analysed the kinetics during reduction of iron ore pellets using biochar. Surup et al. [9] performed a characterization of renewable reductants and charcoal-based pellets for the use in ferroalloy industries; while [10] took into consideration the use of charcoal for manganese alloy production. Bui et al. [11] studied CO_2 gasification of charcoals in the context of metallurgical application and Wang et al. [12] analysed CO_2 reactivity of woody biomass biocarbons. However, once compared to the conventional largely used fossil fuels, biocarbon defects in mechanical properties: it is generally characterized by lower density and compressive strength [13]. The transition towards renewable materials is therefore challenged, since these properties affect the metallurgical process both technically and economically. By increasing the density and improving the mechanical properties, densification through pelletization may be a way to overcome the aforementioned issues [14]. The benefits of pelletization are generally associated to improvements in terms of energy density, compressive strength and mechanical durability [15]. The outcome of the pelletizing process is strictly affected by the characteristics of the raw material such as particle size, chemical composition, moisture content and by operating conditions such as temperature, pressure, residence time. In [16], pellets were produced at ambient temperature at 6 MPa for 30 s and the addition of water was associated to an improvement in terms of hardening and durability. Also in [17] biocarbon pellets showed durability higher than 80% only when water was 30% of the total weight. Similar results were obtained in [18], where stronger pellets were produced with higher pelletizing pressure while a mixed particle size was suggested. The effect of the pelletizing pressure within the range 32–224 MPa and water content from 20% to 40% was investigated in [19], and the combination of 128 MPa and 35 wt% water provided the strongest pellets. Binders are generally necessary to guarantee desirable properties of biocarbon pellets [20]. Bio-oil, which is a by-product of pyrolysis, may be used as binder in order to both improve the energy recovery of the process and to improve the characteristics of the biocarbon pellets. Moreover, its organic nature makes this binder environmental friendly [21]. In [22], the introduction of bio-oil as binder improved the mechanical properties and the energy density of biocarbon pellets. Co-densification of biocarbon and bio-oil was also investigated in [23,24], where the capability of pyrolysis oil to form stronger interlocking of particles was assumed to enhance physical stability. The potential of using bio-oil as binder to improve the energy recovery and reduce waste was also discussed in [25]. The introduction of bio-oil for metallurgical biocarbon pellets was treated in [26], where the binder proved to give positive effects. The implication of a potential application in the metallurgical industry can be investigated by analyzing the thermal strength. Thermal strength is a property which describes how a material reacts mechanically at high temperatures and it is generally useful in metallurgical applications to predict the behavior in the upper part of the furnace [10]. Once the material has undergone a thermal treatment, its mechanical properties are tested. To date, limited literature has analyzed the influence of pyrolysis oil when used as binders on the thermal strength of the obtained biocarbon pellet. However, it was previously demonstrated that the mechanical properties of biocarbon pellets blended with pyrolysis oil improved significantly when the pellets were thermally treated at high temperatures, due to a further carbonization (and polymerization) of the biocarbon-oil structure [26]. A second pyrolysis (or reheating step) of the biocarbon pellets with bio-oil may therefore be included within the production chain, to offer higher quality and more stable pellets. Nonetheless, due to the broad set of parameters affecting the quality of the pellets, the optimization of the overall process is not straightforward. A study on the optimization of biocarbon pellets production is provided in [17]. How parameters affect each other is however not straightforward and easily interpretable [27,28]. As suggested in [29], statistical methods should be utilized when the effects of process parameters are not easily distinguishable. In this work it has been decided to adopt the Response Surface Methodology (RSM) [30]. This method aims at achieving the best system performance by describing the overall process through a mathematical model [31]. When the evaluation depends on several responses, a desirability function is implemented to successfully optimize the final solution by the co-optimization of all coexistent functions [32,33]. In the study of [34] multivariate statistics is applied to poplar wood densification. Ferreira et al. [35] apply the Box-Behnken design to the optimization of analytical methods. Dritsa et al. use multivariate statistics to optimize polluting substances degradation by fungi [36]. However, biocarbon and raw wood differ in chemical and physical composition and therefore the available results should not be lightheartedly used for pyrolyzed biomass.

By the knowledge of the authors, it is difficult to find any research involving the use of the desirability function as approach to optimize the pelletizing parameters and the content of binder. It was therefore the intention of this work to find the optimal conditions to successfully densify biocarbon, obtained by pyrolysis of pine. At the same time, the effect of using bio-oil as binder was investigated. The target parameters to be maximized through the response surface analysis are: compressive strength, mechanical durability and thermal strength. Since we wanted to improve the mechanical properties of biocarbon (once pelletized), compressive strength and mechanical durability were analyzed because they are the most commonly used tests for the characterization of wood pellet quality. Thermal strength was then also selected to be evaluated: the impact of the second reheating treatment can give an idea of the behavior of the pellets once introduced in the reduction furnace. Optimization was carried out by pelletizing at different combinations of temperature, pelletizing pressure and bio-oil content and examining the results by RSM.

2. Materials and methods

2.1. Biocarbon and pyrolysis oil production

The pine wood sample (see Fig. 1) was taken from an Italian company producing furniture. The pine wood was cut to thin slices and then milled, using a cutting mill *Model SM 2000* (Retsch, Germany). The diameter of the sieve was 10 mm.

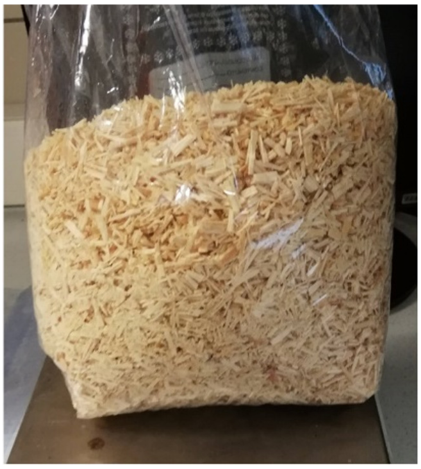


Fig. 1. Milled pine sample.

Once milled, the sample was analyzed. Each analysis was repeated three times. Proximate analysis was performed using a thermogravimetric analyzer (*LECO TGA-701*). Thermogravimetric analysis was performed also with a heating rate of 10 °C/min and a final temperature of 900 °C (using *Netzsch TGA 209 F1 Libra*). Ultimate analysis was done using a CHN elemental analyzer (*LECO Truspec CHN*); calorimetric analysis was realized with an isoperibolic calorimeter (*LECO AC-350*). The analysis was performed according to the norms shown in Table 1.

The results of the characterization of milled pine wood are shown in Table 2.

After the characterization, the sample was inserted into the reactor. The batch pyrolysis plant, presented in Fig. 2, is made of the following components: reactor (4), furnace (2), inert gas storage and piping (5), pressure and temperature sensors (3,7), control system (6), gas outlet pipes and filter valves. The system is controlled using a program made in LabVIEW^{TM} (National Instruments, Austin, Texas). The software is connected through a Compact Field Point system to a P.I.D. (Proportional-Integrative-Derivative) controller, which practically regulates the current flow to the electrical heaters to reach the setpoint temperature inside the reactor. The reactor was realized at the Department of Engineering, University of Perugia (Italy), to provide useful data for pyrolysis plant simulations and to provide mass and energy balances data for the IPRP (Integrated Pyrolysis Regenerated Plant) pilot.

The experimental tests were performed based on the following steps:

1. charging the reactor with about 800 g of pine wood;
2. the reactor and the condenser (4,8) are flushed with nitrogen (3 l/min) to have an inert atmosphere;
3. the reactor is heated with a constant heating rate (about 4 °C/min). During the heating process the non condensable gases exit through the hood and condensable gases are collected in the condenser;
4. once the final pyrolysis temperature is reached (i.e. 600 °C), this is maintained for 30 min;
5. when the reaction is finished the reactor is cooled down for about 4–6 h;
6. the reactor is opened to extract the solid products.

Table 2
Characterization of the pine wood feedstock.

Parameter	Value
Moisture [%wb]	8.21 ± 0.3
Volatiles [%db]	81.18 ± 1.8
Ash [%db]	0.70 ± 0.05
Fixed Carbon [%db]	18.12 ± 1.3
C [%db]	52.10 ± 2.1
H [%db]	6.01 ± 0.9
N [%db]	0.07 ± 0.01
O [%db]	42.82 ± 1.5
HHVdb [MJ/kg]	18.40 ± 0.22

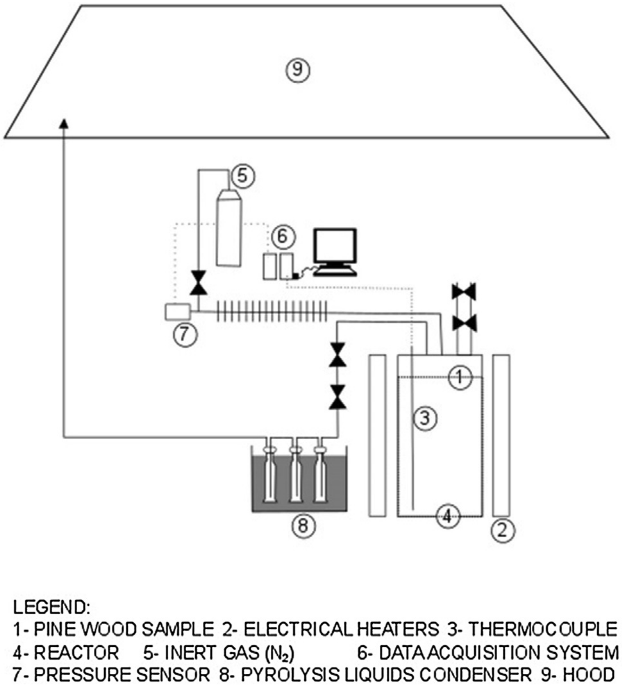


Fig. 2. Experimental setup for pyrolysis tests at the University of Perugia, Italy.

Char and pyrolysis oils HHVs were measured using a calorimeter, while the HHV of pyrolysis non-condensable gases was calculated based on their composition.

2.2. Pelletization tests

Before undergoing pelletization, biocarbon was milled in a hammer mill *px-mfc 90 d* (Polymix, Germany), sieved to a particle size less than 2 mm and stored at ambient temperature in airtight boxes. The particle size distribution of the milled biocarbon was analyzed by a laser diffraction particle size analyzer *Mastersizer 3000* (Malvern, UK). The

Table 1
Norms followed for the analysis of the pine wood sample.

Standard	Analytical procedure	Type of analysis	Instrument
UNI 14774-2:2010	Solid Biofuels – Determination of Moisture Content – Oven Dry Method –Part2: Total Moisture – Simplified Method	PROXIMATE ANALYSIS	LECO TGA 701
UNI 14775:2010	Solid Biofuels – Determination of Ash Content		
UNI 15148:2009	Determination of the Content of Volatile Matter		
UNI 15104:2011	Solid Biofuels. Determination of Total Content of Carbon, Hydrogen and Nitrogen. Instrumental Methods	ULTIMATE ANALYSIS	LECO Truspec CHN
UNI 14918:2009	Solid Biofuels – Determination of Calorific Value	CALORIMETRY	LECO AC-350

result is presented in Fig. 3. For each composition, at least 5 g of mixture of biocarbon and pyrolysis oil was prepared. The blend was homogenized in a beaker by a magnetic stirrer for about 10 min. The pellets were pressed by a compact hot pellet press (MTI, USA). The inner diameter of the die was 6.25 mm. The die was filled with 0.5 g of mixture. Pressure was set manually to the desired value by a hydraulic piston and kept fixed for 10 s before pressure release and extraction of the pellet. Pelletizing pressure was measured by a load cell *CPX1000* (Dini Argeo, Italy) connected to a multifunction weight indicator *DFWLB* (Dini Argeo, Italy). Before pelletization, the die and other moving parts were heated up to the operating temperature. After the process, pellets were stored and cooled down in airtight boxes at ambient temperature.

2.3. Mechanical durability

The mechanical durability of pellets was measured in an *ISO tumbler 1000+* (Bioenergy Institute, Vienna, Austria), designed according to the ISO 17831-1. The durability test is performed by inserting a charge of pellets inside a steel box which spins 500 times in 10 min. After the test, the material inside the box was filtered in a round hole 3.15 mm sieve to expel fines. Mechanical durability (MD) was computed as:

$$\mathrm{MD} = 100 * \mathrm{m_f}/\mathrm{m_i} \tag{1}$$

where m_i is the mass of the pellets before the tumbler test and m_f is the mass of the pellets after the test and after filtration.

2.4. Compressive strength

Pellets were tested by a pellet hardness tester (Amandus Kahl, Germany). The machine measures the strength in kilograms by an equivalence between the elastic compression of a spring that moves a piston against the pellet side and the force equivalent mass. Strength (S) is applied perpendicularly to the cylindrical axis direction. Following the procedure in [34], the correspondent value (expressed in MPa) was computed by the equation:

$$\mathrm{S} = \mathrm{m_s g}/\pi \mathrm{rl} \tag{2}$$

where m_s is the force equivalent mass, g is the gravitational acceleration, r and l respectively are the radius and length of the pellet. A visualization of the method is offered in Fig. 4.

2.5. Thermal strength

To measure the thermal strength, at least one pellet for each configuration was heated in a muffle furnace *LT40/11/P330* (Nabertherm, Germany) at 600 °C. The furnace was first stabilized to the desired temperature. The sample was then inserted into a quartz glass crucible covered by a quartz glass lid and placed at the center of the hot muffle. It was heated for 60 min. Once the process was terminated, the hot pellets were stored in a desiccator and cooled down at room temperature. The compressive strength of the heated pellets was then measured after 24 h, following the method previously explained.

2.6. Optimum analyses and verification

Once estimated the optimum through RSM, samples were produced according to the identified parameters and analyzed at the University of Agder in Norway. Proximate analysis was performed following the procedure described in EN 14775 (by a standard ash test at 550 °C) for the ash content and EN 15148 for the volatile matters. The elemental analysis was carried out with a *2400 Series II CHNS/O Elemental Analyzer* (PerkinElmer, USA), following EN 15104:2011. Oxygen was calculated by difference. Sulphur was assumed negligible. Analyses were done both before and after the heat treatment performed to test the thermal strength. Each analysis was repeated three times. Mechanical durability, compressive strength and thermal strength of the optimized pellets were measured by the aforementioned methods. Images of the untreated biocarbon, the mixture of biocarbon and pyrolysis oils (at the optimum ratio) and of the optimized pellets before and after heat treatment were obtained by *JSM-6499 Scanning Microscope* (JEOL, Japan).

2.7. Design of experiments

The Response Surface Methodology (RSM) with Box-Behnken experimental Design (BBD) was applied to optimize biocarbon pellet production and to analyze the correlation between responses and factors. BBD is a three factors and three levels design, consisting of a replicated center point and a set of points lying at the midpoint of each edge of the multidimensional cube that defines the space of interest. BBD was employed because it has been demonstrated that this kind of design provides slightly and significantly higher efficiency than the central composite design and the three-level full factorial design, respectively [35].

The relationship between the variables and the responses was correlated with a polynomial quadratic equation that was fitted as follows:

$$\mathrm{Y} = \beta_0 + \sum \beta_i \mathrm{X_i} + \sum \beta_{ii} \mathrm{X_i^2} + \sum \beta_{ij} \mathrm{X_i X_j} + \varepsilon \tag{3}$$

where Y is the measured response related to each factor level combination, β_0 is the intercept coefficient, β_i, β_{ii}, and β_{ij} are the regression coefficients computed from the observed experimental values of Y, X_i and X_j are the coded levels of independent variables and ε is the error of the model.

In this study, the percentage of pyrolysis oil (X1), the pelletizing temperature (X2), and the pelletizing pressure (X3) were assumed as the independent variables and the compressive strength (Y1), the thermal strength (Y2) and the mechanical durability (Y3) of the produced pellets were designed as the responses. Each independent variable was prescribed into three levels, coded +1, 0 and −1, corresponding to the minimum level, medium level, and maximum level. The low, medium, and high levels of each process factor were assumed based on results obtained from preliminary tests. The independent variables and their coded values are shown in Table 3.

According to the BBD model 15 runs were carried out, with triplicate center points, in order to estimate the pure error. The 15 runs were selected randomly by the Minitab 17.1.0 software (Minitab Ltd., Coventry, UK) to minimize the bias and are shown in Table 4, together with the observed responses.

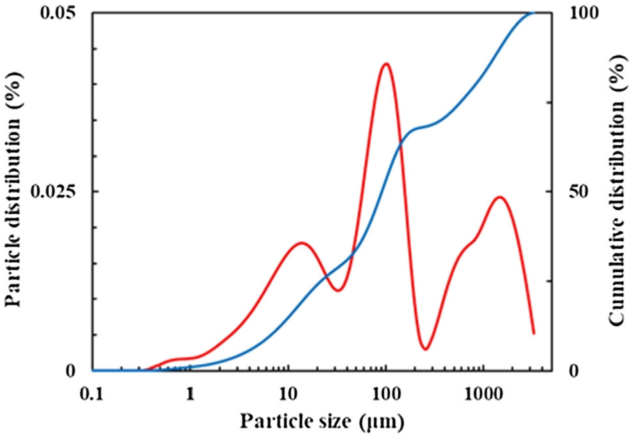


Fig. 3. Particle distribution of biocarbon after milling with a cutting mill and sieving with a 2 mm sieve.

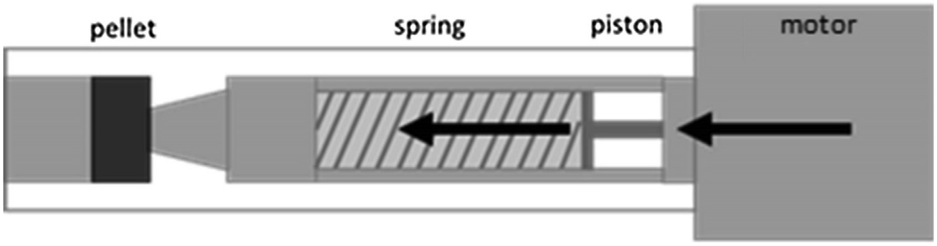


Fig. 4. Pellet hardness tester set-up layout, University of Agder, Norway.

Table 3
Investigated factors used in the experimental design and their levels (coded and uncoded).

Independent factors	Levels		
	−1	0	+1
Pyrolysis oil content, X_1 (%)	10	20	30
Temperature, X_2 (°C)	90	130	170
Pressure, X_3 (MPa)	50	150	250

2.8. Statistical analysis

Analysis of variance (ANOVA) and regression analysis were carried out with Minitab 17.1.0 software (UK), in order to investigate the statistical significance of the regression coefficients by performing the Fisher‘s F-test at 95% confidence level. In particular, P-values ≤ 0.05 demonstrate that the model terms are significant and closer to the actual experimental outcomes while higher values could be due to noise in the data.

The adequacy of the quadratic models was evaluated based on the coefficient of determination (R^2), the adjusted coefficient of determination (R^2-adj), and the lack of fit test. In particular, the accuracy of the experimental data is measured by R^2 while the R^2-adj values determine the deviation of data predicted from the models. High differences between R^2 and R^2-adj values are due to the non-significant model terms.

Furthermore, the lack of fit test is carried out by comparing the variability of the actual model residuals to the variability between observations at replicate settings of the factors [36]. A model is statistically significant at the 95% confidence level if the p value of the lack of fit test is higher than 0.05. Quadratic models were also used for the construction of three-dimensional (3D) contour plots and for evaluating the interactive effect of each factor.

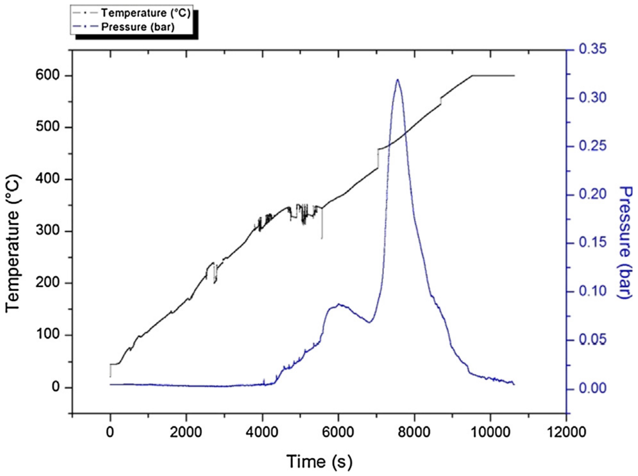


Fig. 5. Trend of temperature and gauge pressure inside the pyrolysis batch reactor versus time.

3. Results

3.1. Pyrolysis tests results

The pyrolysis test lasted for about 3 h. The trend of temperature and gauge pressure inside the reactor during the pyrolysis tests are provided in Fig. 5. Between approximately 300 and 450 °C the pressure rapidly peaks. The behavior is related to the formation in the reactor of gases produced by biomass degradation, which, according to [37], occurs within that temperature range. When the decomposition is concluded, the reactor can stabilize to ambient pressure again. The temperature gradient is not linear because of heat losses from the reactor insulated walls.

The pictures of the biocarbon and of the pyrolysis oil obtained from

Table 4
Box-Behnken design and experimental results for each response.

Run Order	X_1 (%)	X_2 (°C)	X_3 (MPa)	Compressive Strength, (Y1)		Thermal Strength at 600 °C (Y2)		Mechanical Durability (Y3)	
				Actual (MPa)	Predicted (MPa)	Actual (MPa)	Predicted (MPa)	Actual (%)	Predicted (%)
1	40	90	50	0.22	0.21	1.01	0.99	82.68	79.73
2	30	90	150	0.24	0.25	0.90	0.89	90.18	92.51
3	30	120	250	0.34	0.33	0.81	0.82	33.40	33.04
4	20	90	50	0.22	0.22	0.45	0.48	19.07	18.81
5	30	60	250	0.41	0.41	1.11	1.11	74.91	72.05
6	20	120	150	0.27	0.27	0.44	0.42	13.89	11.29
7	30	120	50	0.29	0.29	0.79	0.79	60.03	62.89
8	30	90	150	0.26	0.25	0.89	0.89	93.46	92.51
9	30	90	150	0.25	0.25	0.88	0.89	93.89	92.51
10	40	60	150	0.39	0.39	1.19	1.22	66.96	69.56
11	40	120	150	0.33	0.34	0.70	0.72	29.34	29.44
12	40	90	250	0.20	0.20	0.99	0.96	48.13	48.39
13	20	90	250	0.19	0.20	0.50	0.52	27.67	30.62
14	30	60	50	0.45	0.46	1.14	1.13	61.37	61.73
15	20	60	150	0.49	0.48	0.57	0.55	9.11	9.02

the pyrolysis of pine wood are reported in Fig. 6.

The characterization of pyrolysis oil and biocarbon was performed according to the same methodology used in the characterization of the feedstock (i.e. pine wood). The yields of the pyrolysis products are the following: 28 wt% biocarbon, 26 wt% pyrolysis oil, 46 wt% pyrolysis gas. The characterization of pyrolysis oil and biocarbon is reported in Table 5. Non-condensable gases were the product with the highest mass yield, while pyrolysis oil and biocarbon were produced in similar quantities. The results are similar to those provided by other pyrolysis studies available in literature [37]. Biocarbon is characterized by a high fixed carbon content, low moisture content and high heating value, while pyrolysis oil presents a high content of moisture and volatiles, with a lower heating value. Both products have a modest ash content. The values are comparable to those reported in literature for pine pyrolysis products (e.g. [38,39]).

The biocarbon structure and its change with the introduction of pyrolysis oil as binder was analyzed by Scanning Electron Microscope and it is shown in Fig. 7. Biocarbon is distinguished by a characteristic highly porous structure, as reported by Kizito et al. for wood and rice husks biochar [40], García-Jaramillo et al. [41] for biochar obtained from different feedstock and used as a sorbent and by Eggleston et al. [42] for biochar obtained from by-products of the sugar industry. The pattern can be seen in Fig. 7a. When the pyrolysis oil is added, it penetrates easily the pores distributed around the surface. The appearance becomes homogenous and the porosity decreases drastically, as shown in Fig. 7b and confirmed in [26]. After the collection of biocarbon and oils from the pyrolysis test, oils were used as binder to obtain an improved pellet with lower porosity and higher density, compared to the initial biocarbon. The performed tests are based on a new strategy to overcome biocarbon technical problems when it is used for metallurgical or industrial applications. In fact Ruksathamcharoen et al. [43] demonstrated that an optimization of the pelletizing temperature is needed; temperature is one of the parameters that influence pellet mechanical properties [44] and combustion behavior [45], together with pressure and the type of binder. Sawdust can be used as a binder [46], but also lignin and other materials [20]. Also the water content has a great influence on the final pellet quality. So the variables to optimize are several.

Table 5
Characterization of biocarbon and pyrolysis oil.

Parameter	Biocarbon	Pyrolysis oil
Moisture [%wb]	0.86 ± 0.03	87.2 ± 2.5
Volatiles [%db]	7.55 ± 0.9	96.85 ± 2.0
Ash [%db]	4.22 ± 0.8	0.43 ± 0.2
Fixed Carbon [%db]	88.23 ± 2.1	2.73 ± 0.5
C [%db]	90.2 ± 1.8	56.21 ± 1.3
H [%db]	1.3 ± 0.2	6.30 ± 0.85
N [%db]	0.11 ± 0.01	0.15 ± 0.04
O [%db]	8.39 ± 1.5	37.34 ± 01.1
HHVdb [MJ/kg]	32.41 ± 0.31	25.30 ± 0.25

3.2. Pelletization test/regression models and ANOVA analysis

The results of the pelletization tests, based on three replicates, together with the predicted values from the BBD model are shown in Table 4. In summary, the response values for Y_1, Y_2, and Y_3 ranged from 0.19 to 0.49, 0.44 to 1.19, 9.11% to 93.89%, respectively. By applying multiple regression analysis, a relationship between the responses and the variables was obtained and expressed by the following second-order polynomial quadratic equations, in terms of coded factors:

$$Y1 = 1.967 + 0.00075X1 - 0.03575X2 - 0.000200X3 - 0.000225X1 * X1 + 0.000158X2 * X2 - 0.000002X3 * X3 + 0.000133X1 * X2 + 0.000002X1 * X3 + 0.000008X2 * X3 \quad (4)$$

$$Y2 = -1.583 + 0.1708X1 - 0.00292X2 - 0.001100X3 - 0.001950X1 * X1 + 0.000033X2 * X2 + 0.000004X3 * X3 - 0.000300X1 * X2 - 0.000018X1 * X3 + 0.000004X2 * X3 \quad (5)$$

$$Y3 = -707.2 + 29.48\,X1 + 6.211X2 + 0.8839X3 - 0.3786X1 * X1 - 0.02758X2 * X2 - 0.001026X3 * X3 - 0.03533X1 * X2 - 0.01079X1 * X3 - 0.003348X2 * X3 \quad (6)$$

Statistical analysis of variance (ANOVA) of the main effects and the interactions for responses of compressive strength, thermal strength, and mechanical durability, together with the test of statistical significance for the quadratic models are reported in Table 6.

Results in Table 6 show that the F-values are equal to 53.79, 115.89, and 124.37 for compressive strength, thermal strength, and mechanical durability, respectively. This indicates that the regression quadratic models are significant ($P < 0.05$). Moreover, the suitability of BBD was demonstrated by the high values of R^2, obtained for all responses ($R^2 = 0.9898$, 0.99952, and 0.9956 for Y_1, $Y_{2,}$ and Y_3, respectively). However, since the quadratic models include additional terms, due to the three level independent variables, the adjusted coefficient of determination (R^2 adj) is more useful to check the level of fit, being less sensitive to the degrees of freedom [47]. All R^2 adj values were higher than 0.95 and very close to the R^2 values, demonstrating the accuracy of the obtained models and the correspondence with the responses. The adequacy of the quadratic models was also confirmed by the lack-of-fit test. P-values of the lack of fit were equal to 0.226, 0.072 and 0.213 for Y_1, $Y_{2,}$ and Y_3, respectively, indicating a non-significant shortage of the

Fig. 6. Pine wood biocarbon (left); Pine wood pyrolysis oil (right) produced at University of Perugia, Italy.

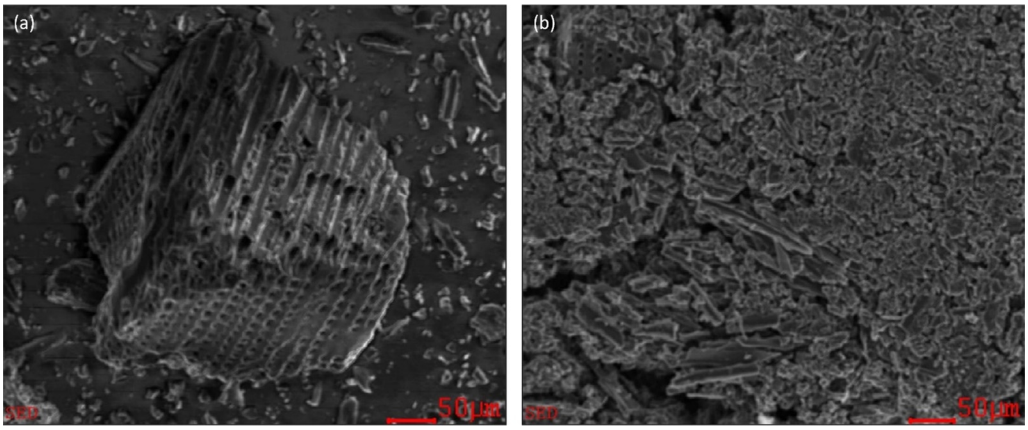


Fig. 7. SEM photos of: (a) a biocarbon particle (15 kV, magnification 200 ×) and (b) section of a mixture of pyrolysis oil and biocarbon with biooil concentration equal to 33.4 wt% (15 kV, magnification 250 ×).

Table 6
ANOVA of response surface quadratic models applied to biocarbon pellet production.

Source	DF	F-value	Prob > F
Compressive strength			
Model	9	53.79	< 0.0001
X_1	1	0.44	0.536
X_2	1	127.50	< 0.0001
X_3	1	0.78	0.416
X_1^2	1	7.33	0.042
X_2^2	1	294.03	< 0.0001
X_3^2	1	5.79	0.061
X_1X_2	1	25.10	0.004
X_1X_3	1	0.10	0.767
X_2X_3	1	7.94	0.037
Lack of fit (LOF)	14	3.58	0.226
$R^2 = 0.9898$, $R^2_{adj} = 0.9714$			
Thermal strength			
Model	9	115.89	< 0.0001
X_1	1	564.38	< 0.0001
X_2	1	244.38	< 0.0001
X_3	1	0.06	0.815
X_1^2	1	170.18	< 0.0001
X_2^2	1	4.03	0.101
X_3^2	1	8.08	0.036
X_1X_2	1	39.27	0.002
X_1X_3	1	1.48	0.277
X_2X_3	1	0.76	0.424
Lack of fit (LOF)	14	13.08	0.072
$R^2 = 0.9952$, $R^2_{adj} = 0.99866$			
Mechanical durability			
Model	9	124.37	< 0.0001
X_1	1	276.73	< 0.0001
X_2	1	64.02	< 0.0001
X_3	1	17.03	0.009
X_1^2	1	473.18	< 0.0001
X_2^2	1	203.37	< 0.0001
X_3^2	1	34.75	0.002
X_1X_2	1	40.18	0.001
X_1X_3	1	41.61	0.001
X_2X_3	1	36.06	0.002
Lack of fit (LOF)	14	3.86	0.213
$R^2 = 0.9956$, $R^2_{adj} = 0.9875$			

mathematical models in the prediction of experimental data. Various diagnostic tests, such as predicted versus actual values and normal probability plots of the residuals further verified the adequacy of the models. First of all, the good correlation between the experimental values and the values predicted by the statistical models, showed the fitting ability of the proposed models (Fig. 8).

Secondly, Fig. 9 shows the normal probability plots of the residuals. It can be noted that points are closely widespread around a straight line. It can thus be concluded that data were normally distributed and the variation of the predicted from the actual values was randomly distributed [48].

3.3. Effect of independent variables on the pelletization process

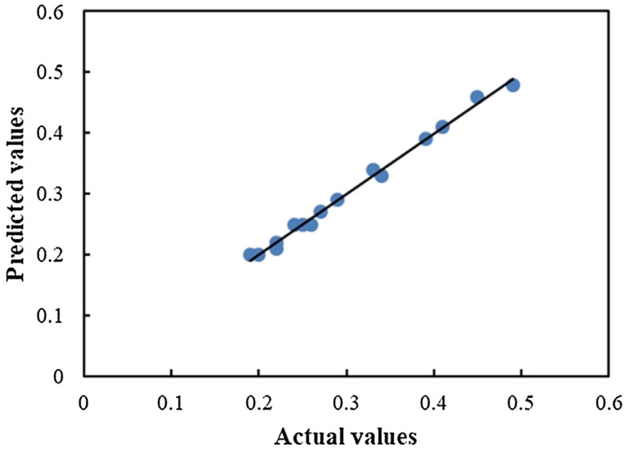
Three-dimensional (3D) surface plots were used to represent the predicted model equations and the influence of the independent variables on the compressive strength, thermal strength, and mechanical durability. The response surface plots show the influence of two factors on the pelletization process while the third is kept at its medium level. The response surface plots showing the influence of process parameters on compressive strength, thermal strength, and mechanical durability are shown in Fig. 10, Fig. 11, and Fig. 12, respectively.

3.3.1. Effect on compressive strength

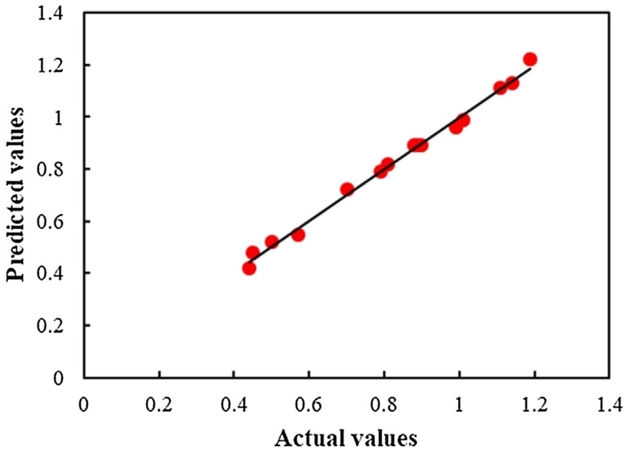
Fig. 10 shows the effects of pyrolysis oil content (X1), temperature (X2), and pressure (X3) on the compressive strength.

According to the F-values and P-values shown in Table 6, it can be noted that the pelletization temperature has the most significant effect on compressive strength, in both linear and quadratic manner. The strong influence of pelletizing temperature on compressive strength has already been documented by [15,45]. On the other hand, the compressive strength is not significantly affected ($p > 0.05$) by the linear term of the pyrolysis oil content and the pelletization pressure. Among the interaction terms, pyrolysis oil content-temperature and temperature-pressure have a quite statistically significant effect on the compressive strength. In addition, among the quadratic terms, pyrolysis oil content (X12) shows also a significant effect on the response and its negative coefficient in Eq. (4) indicates that it inversely affects the specific surface area. Fig. 10a shows the effect of temperature (X2), pressure (X3), and their reciprocal interaction on compressive strength, when pyrolysis oil content (X1) was fixed at 30%. The result revealed that the increase of the pelletization temperature from 60 to 96 °C at first decreased the compressive strength, while a further increase caused an increase of the response. As discussed in [15], temperature influence is strictly related to the biomass which undergoes pelletization. Since studies on densification of biocarbon in relation to the pelletizing temperature are hardly obtainable, it has not been possible to compare the obtained results with existing literature. The negative peak is expected to be associated to the evaporation of the water included into the pyrolysis oil, while the following increase might be caused by the beginning of thermal interactions between the solid fraction of the binder and the biocarbon structure. From Fig. 10b, c, it was confirmed that pyrolysis oil content and pelletization pressure had a small influence on the compressive strength; however, when the pelletization

(a) Compressive strength [MPa]



(b) Thermal strength [MPa]



(c) Mechanical Durability [%]

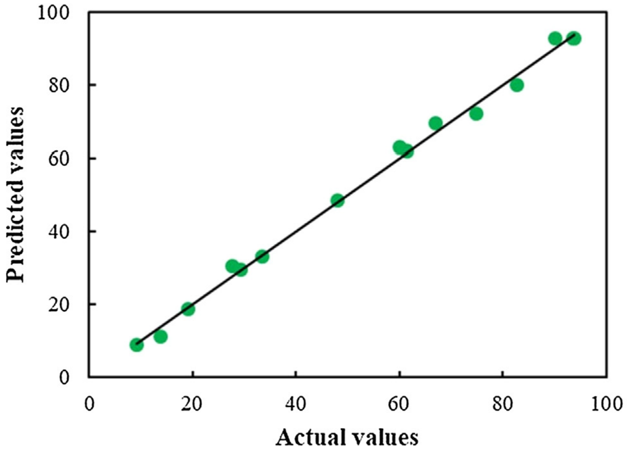


Fig. 8. Relationship between predicted and actual values of (a) compressive strength, (b) thermal strength, (c) mechanical durability.

temperature was fixed at 90 °C, a region where the compressive strength is maximum can be defined: X1: 27.6–30.5%, X3: 121–152 MPa. These ranges are similar to those reported in [14,18,19]. During the pelletizing experiments, it was noticed that elevated amounts of pyrolysis oil caused liquid dispersion. An excessive content of binder could oversaturate the porous structure of biocarbon and partially disable the bounding mechanism. As consequence compressive strength is affected negatively. As proposed in [19], the peak of pelletizing pressure could instead be justified by the recalcitrant nature of biocarbon, which imposes a limit in the densification of the particles.

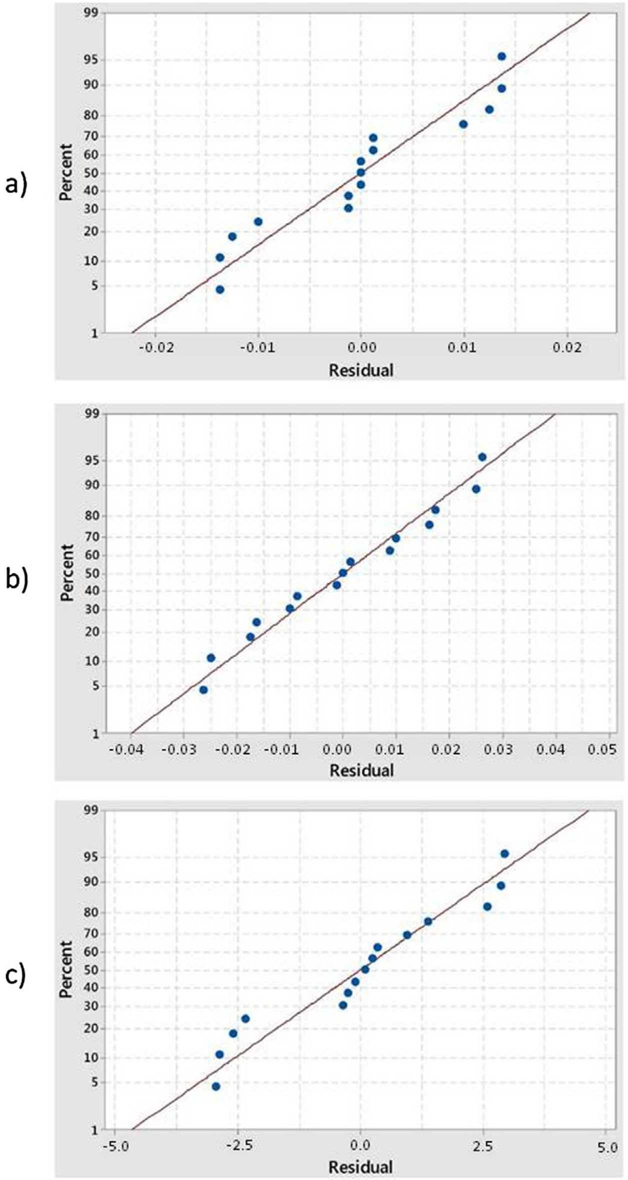


Fig. 9. Normal probability plots of residuals of (a) compressive strength, (b) thermal strength, (c) mechanical durability.

3.3.2. Effect on thermal strength

According to the P-values in Table 6, the effects of pyrolysis oil content, pelletization temperature and the interactions effects of X1*X1, X3*X3, and X1*X2 are statistically significant for the thermal strength. From the F-values in the ANOVA table, it can be noted that the pyrolysis oil content had a greater effect on the thermal strength. The strong influence of pyrolysis oil on thermal strength was observed also in [9,26]. From Eq. (5), it can be inferred that the positive coefficients of factors X1 and X1*X2 indicate a favorable effect on the thermal strength, while the negative coefficients of factors X2, X2*X2, and X3*X3 indicate an unfavorable effect on that. The interactive effect of pyrolysis oil content, pelletization temperature and pelletization pressure on the thermal strength are given in Fig. 11.

The response decreased with the increase of the pelletization temperature. While evaluating the response obtained by changing the pyrolysis oil content, it was noted that for any fixed value of X2 and X3, the thermal strength increased with the increasing of pyrolysis oil content up to a value of about 36% and then it dropped. Maximum

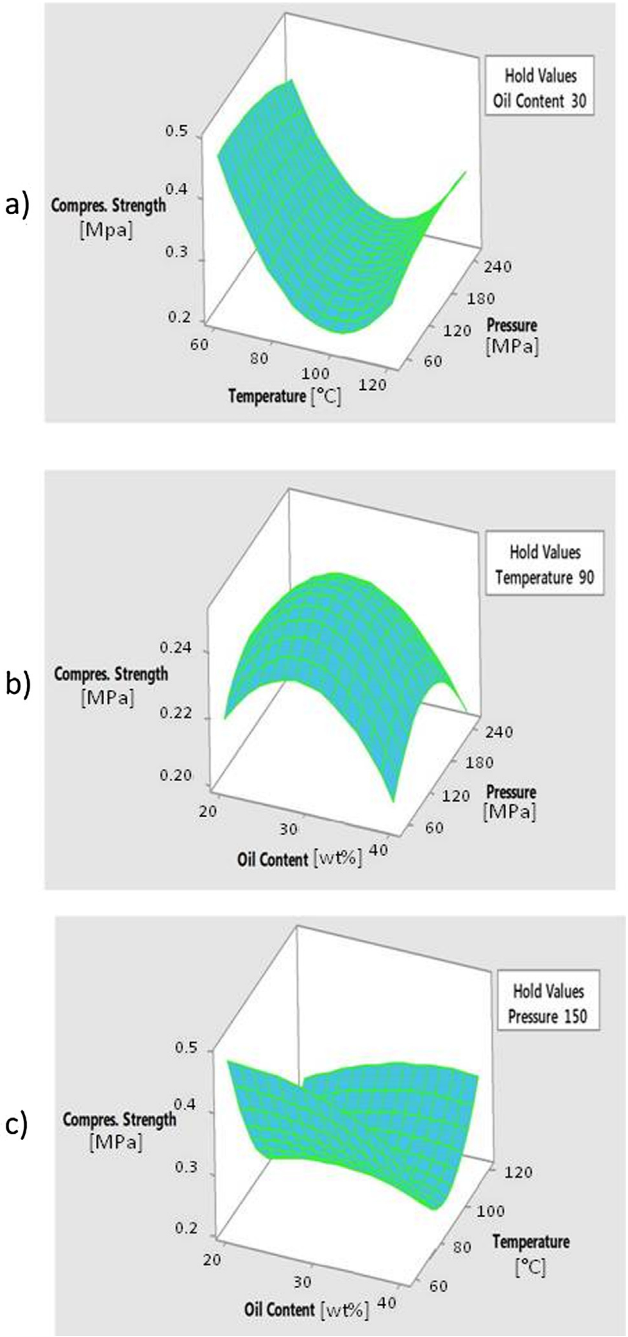


Fig. 10. 3D response surface plots of compressive strength showing the effect of process variables at: (a) fixed oil content, (b) fixed pelletizing temperature, (c) fixed pelletizing pressure.

thermal strength (1.28 MPa) was observed when temperature and pressure assumed the lowest values, 60 °C and 50 MPa, respectively. Limited literature about pelletizing temperature and pressure effects on thermal strength is available and any attempt of comparison is therefore challenging. While Fig. 11a shows a weak contribution of the pelletizing pressure, Fig. 11b exhibits a negative impact of temperature on thermal strength. The effect may be justified by the devolatilization of the binder, which is more important when pellettizing temperature increases. As a consequence, once undergoing the heat treatment, at constant added pyrolysis oil content and pressure, pellets have less binder available inside to react and this increases thermal interactions within the biocarbon.

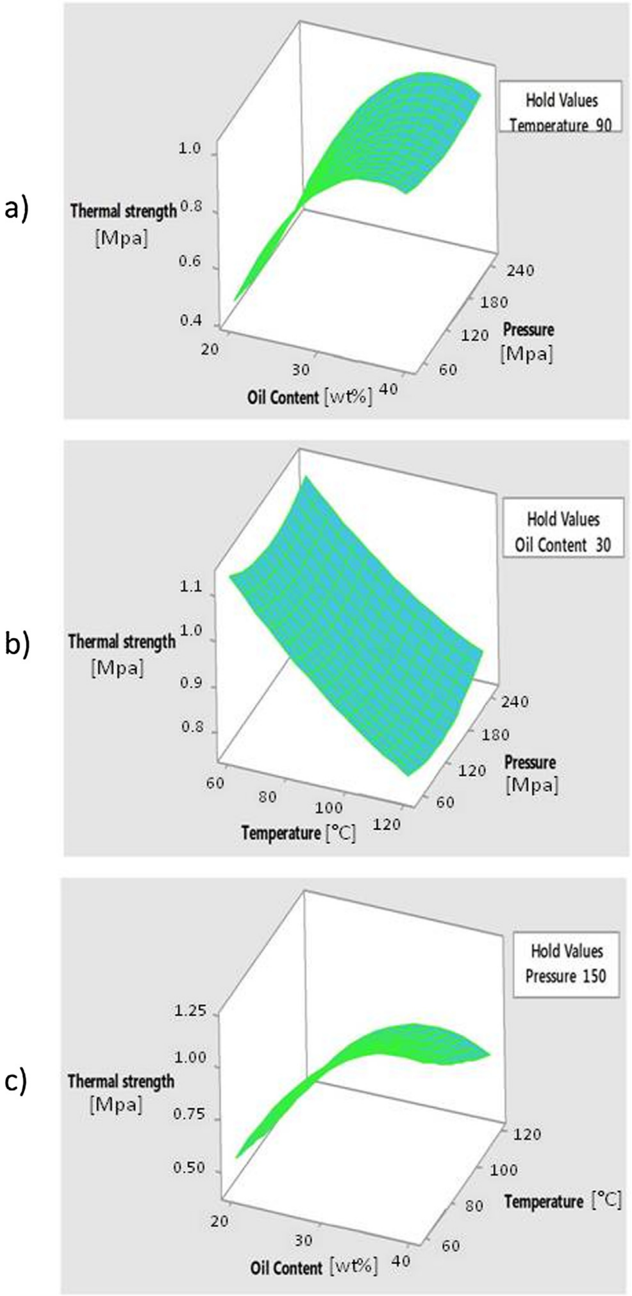


Fig. 11. 3D response surface plots of thermal strength showing the effect of process variables at: (a) fixed pelletizing temperature, (b) fixed oil content, (c) fixed pelletizing pressure.

3.3.3. *Effect on mechanical durability*

In the mechanical durability model, all factors are significant terms because the value of p is < 0.05. Therefore, the pyrolysis oil content (X1), the pelletization temperature (X2) and the pelletization pressure (X3) show a significant influence on the response on mechanical durability. Pyrolysis oil content has the highest influence on the model with a coefficient value of 29.48, compared to the pelletization temperature and pressure, which have coefficient values of 6.211 and 0.8839, respectively. All these factors have positive influence toward the model. Significant interactions between factors have been detected by the model, indicating that there are mutual effects and interactions between these factors.

The interaction of X1X2 with mechanical durability, as shown in Fig. 12a, can be explained as follows: at constant pelletization pressure

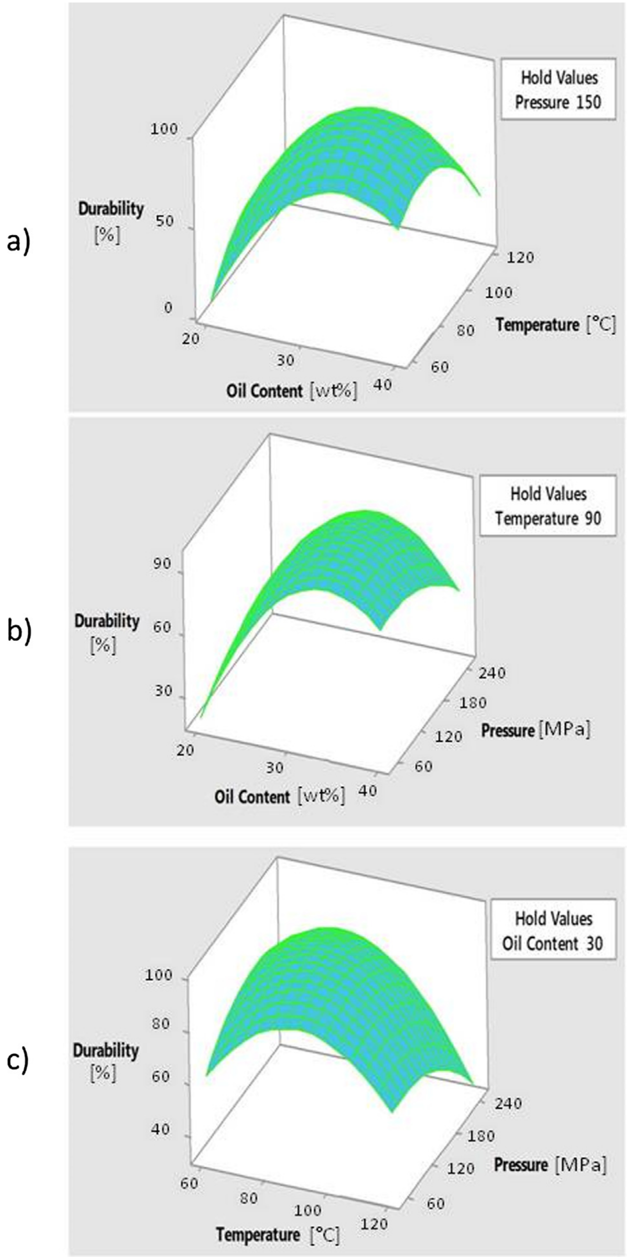


Fig. 12. 3D response surface plots of mechanical durability showing the effect of process variables at: (a) fixed pelletizing pressure, (b) fixed pelletizing temperature, (c) fixed oil content.

(150 MPa), for pyrolysis oil content (*X1*) of 20% and at a temperature (*X2*) of 60 °C, a mechanical durability of 9.01% was obtained, but with an increase in the pyrolysis oil content to 34.0% with the same pelletizing temperature, the mechanical durability increased to 83.20%. An increase in pelletization temperature to 82.4 °C with same pyrolysis oil content increased the mechanical durability to 96.20% while, decreasing the pyrolysis oil content to 32.9%, the highest mechanical durability response was obtained (about 96.61%). Similarly, the interaction of *X1X3* with response is shown in Fig. 12b. As reported in [49,50], pelletizing temperature affects significantly mechanical durability and its influence depends closely on the type of biomass. The thermal behavior of the material, which affects the compressive strength, impacts probably also the mechanical durability, to a certain extent. However, the different trends of compressive strength and mechanical durability confirm the absence of a significant correlation between the two properties, as stated in [28]. For a pyrolysis oil content (*X1*) of 20% and pelletization pressure (X2) of 50 MPa a mechanical durability of 18.81% was achieved at a constant temperature of 90 °C. An increase in pyrolysis oil content to 30% at constant pressure increased the mechanical durability to 87.13% and with a further increase of pyrolysis oil content to 33.1% and of pressure to 110.6 MPa, also the mechanical durability increased to 96.65%. Likewise, Fig. 12c represents the interaction of parameters X2X3 with the response, at constant pyrolysis oil content of 30%, for temperature of 120 °C and pressure of 250 MPa. A mechanical durability of 33.04% was obtained.

With a temperature of 85.5 °C and a pressure of 132.8 MPa the maximum value for mechanical durability was obtained (i.e. 93.65%). According to these results, it can be concluded that among all the interactions (X1X2, X2X3, X1X3), pyrolysis oil content and pelletization temperature are the ones which mainly influences the mechanical durability. Similar trends were observed in [17,51] and are justified by the same assumptions made for compressive strength.

3.4. Optimization of responses using the desirability function approach

In the production of biocarbon pellets, relatively high compressive strength, thermal strength and mechanical durability are desired since high values of abrasive resistance and hardness improve the competitiveness of pellet in the commercial market, affecting the efficiency of storage and feeding processes. Nevertheless, the optimization of all responses under the same operative conditions is difficult because their regions of interest are different. Multi-response optimization was therefore applied, in order to evaluate the conditions on the independent factors that lead simultaneously to the optimal values of the response variables. In this regard, the Derringer's desirability function-based approach [52] was employed to solve the multiple response optimization problem. The approach is to transform each response (Y_i) into a dimensionless function, known as the individual desirability function (d_i), ranging from 0 to 1 (from the lowest to the highest desirability) [53]. If the response Y_i is at its target the most desirable case is obtained ($d_i = 1$), otherwise, $d_i = 0$ (the least desirable case). If a response is to be maximized, its individual desirability function is defined as:

$$di = \begin{cases} 0, \text{ if } Y_i \leqslant L_i \\ [(Y_i - L_i)/(U_i - L_i)]^w, \text{ if } L_i < Y_i \leqslant U_i \\ 1, \text{ if } Y_i > U_i \end{cases}$$

where L_i, U_i denote the lowest and highest values of Y_i and w is the shape function for desirability. In this study, a linear dependence (w = 1) was assumed.

Then, these functions are aggregated into a composite desirability function (D) that is a geometric mean of all transformed responses:

$$D = [d_1^{v1} * d_2^{v2} * \cdots * d_n^{vn}]^{1/n},\ 0 \leq v_i \leq 1(i = 1, 2, \cdots n),\ \sum_{i=1}^{n} v_i = 1 \quad (7)$$

where d_i is the individual response desirability of the response Y_i, n is the number of responses and v_i is the weight used to evaluate the scale of desirability (in this case all weights were assumed equal to 1, giving the same importance to each response). D values range from 0 to 1 and the aim is to maximize D, which is equal to one when all responses are on-target and, equal to zero, when at least one response is outside of the specification limits.

In this work, the purpose of the optimization is to achieve maximum compressive strength, thermal strength and mechanical durability alongside the best conditions of variables. The optimization calculations were carried out by the Minitab 17 software and the results of predicting optimal conditions are reported in Fig. 13.

The optimal operating conditions for the maximum responses based on Derringer's desirability function approach are found to be pyrolysis oil content of 33.9%, pelletization temperature of 60 °C, and pelletization pressure of 116.7 MPa. Under these conditions, the predicted

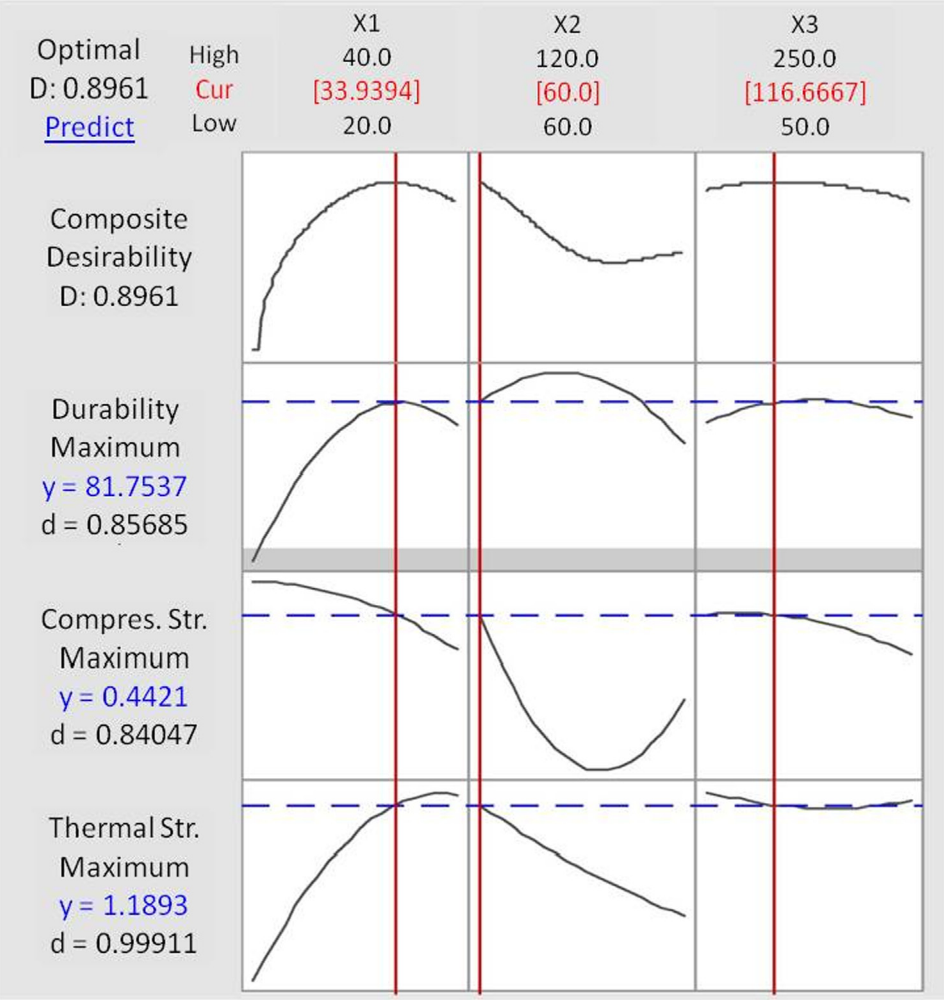


Fig. 13. Plots for simultaneous optimization of operating variables (i.e. temperature, pressure and pyrolysis oil content).

compressive strength, thermal strength, and mechanical durability are found to be 0.44 MPa, 1.19 MPa, and 81.75%, respectively. The composite desirability value was close to 1 (0.8961) which demonstrated that good results were achieved for all responses, even if, by analyzing the individual desirability functions, it can be noted that these conditions are more effective at maximizing the thermal strength (d = 0.999) than the other two responses.

Then, new tests of pelletization with the predicted levels of the independent variables were carried out to analyze the validity of the optimization procedure. Table 7 demonstrates that the observed values were mostly close to the predicted values and within acceptable predicted error ranges.

The density of the optimized pellet was 1068 kg/m^3.

3.5. Thermal treatment effect

As observable in Table 7, pellets produced under the optimum conditions increased significantly in strength, when undergoing a heat treatment. The value increased approximately 170%. The behavior was generally noticed for all the experimental configurations and confirmed by the model. Similar trend was observed and reported in [26]. Due to the great benefit it provides, a second heat 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 without an excessive increase of cost. Consequently, it becomes relevant to fully understand the mechanisms which enhance the improvements in mechanical quality. Pellets before and after heat treatment were therefore analyzed. The characterization of the two samples is presented in Table 8. The relatively high moisture content of the untreated pellets drops when they are heated, due to the evaporation of water and the typical hydrophobicity of biocarbon. Part of the volatiles contained into the pyrolysis oil are converted into fixed carbon. Ash changes slightly. When compared to the biocarbon produced during pyrolysis, after the new heat treatment the composition of the pellets is similar to the untreated biocarbon (Table 5), especially in terms of fixed carbon content. Quite interestingly, the addition of

Table 7
The measured and the predicted values of the responses under the optimum conditions.

Response	Predicted value	Experimental value	Deviation (%)
Compressive strength (MPa)	0.44	0.42 ± 0.02	−5.26%
Thermal strength (MPa)	1.19	1.07 ± 0.05	−11.50%
Mechanical durability (%)	81.75	83.20 ± 1.20	1.76%

Table 8
Ultimate and proximate analysis of the sample produced at optimum conditions at the University of Agder (Norway) in comparison to the original biocarbon produced at the University of Perugia (Italy).

Parameter	Optimum	Optimum heated at 600 °C	Original biocarbon
Moisture [%wb]	15.87 ± 0.88	2.41 ± 0.39	0.86 ± 0.03
Volatiles [%db]	15.36 ± 0.01	11.83 ± 2.99	7.55 ± 0.9
Ash [%db]	0.94 ± 0.02	0.38 ± 0.05	4.22 ± 0.8
Fixed Carbon [%db]	83.70 ± 0.88	87.79 ± 0.5	88.23 ± 2.1
C [%db]	87.91 ± 0.18	90.75 ± 1.67	90.2 ± 1.8
H [%db]	2.84 ± 0.08	1.64 ± 0.03	1.3 ± 0.2
N [%db]	0.57 ± 0.10	0.20 ± 0.19	0.11 ± 0.01
O [%db]	8.68 ± 1.5	7.41 ± 1.72	8.39 ± 1.5

pyrolysis oil contributed to transpose part of the amount of ash into the volatile contents. The heat treatment of biocarbon pellets happened to be a good option to restore the initial composition of the untreated biocarbon and the addition of oil an opportunity to modify it partially. An insight on the mechanism behind the strengthening of the pellets can be provided by the help of SEM photos. Sections of the biocarbon pellets before heat treatment are shown in Fig. 14. Pyrolysis oil particles can be easily spotted due to the lighter color, compared to biocarbon. Particles of pyrolysis oil, which act as binder among bigger biocarbon areas, are distinguishable in Fig. 14a–c. In Fig. 14a, a pyrolysis oil particle bonds two biocarbon regions divided by a fracture line. The bonding mechanism is also appreciable in Fig. 14b, c, where a stretched pyrolysis oil particle acts as binder. Fractures aside, the pellets structure is homogenous, and it is mainly characterized by biocarbon macro-areas blended with some pyrolysis oil particles, as visible in Fig. 14d. As previously observed in Fig. 7b, where the mixture of biocarbon and pyrolysis oil before pelletization was shown, the typical biocarbon porous structure has disappeared, substituted by a compacted and homogenous mixture [24]. As result, compared to untreated biocarbon pellets, treated biocarbon pellet are expected to have better mechanical properties, as reported in [9,13].

Sections of pellets after the heat treatment are shown in Fig. 15. Part of the pyrolysis oil got volatized, leaving the porous biocarbon structure. The other part got carbonized, permanently occluding part of the pores. As result, the pellets are expected not to present any more single oil particles, but a unique “partially porous” structure of bounded particles. The phenomenon is particularly appreciable in Fig. 15c where a single biocarbon particle is partially divided in two parts, one of which is highly porous. The improvement in mechanical properties can therefore be related to the strengthened char structure due to carbonization of particles of pyrolysis oil which were previously bonded to biocarbon. Similar results were obtained and observed in [26].

4. Discussion

4.1. Comparison of biocarbon pellet strength with that of coke

As reported in [54] strength is a key parameter for coke. It influences deeply its performance in industrial applications. Three types of strength can be identified: cold strength, load bearing strength (on the top of the furnace) and thermal or hot strength (in lower regions inside the furnace). If we look at standardized methods for the measuring of compressive strength, according to a report of the European Commission on coke quality and its prediction [55] the compressive strength should be measured through a diametral compression method which is comparable to the one adopted in this study. From literature (see Table 9) we can see that the compressive strength of coke can reach even 23 MPa [54] but for example for European cokes we can have also values of 4.42–6.61 MPa [55].

If we compare those values with literature tests we see that [20] obtained values of compressive strength comprised between 0.65 and 3.82 MPa, these were obtained with a biomass (rice husk) which is quite different from the one used in this study (pine wood); the higher ash content of rice husk and especially the high silicon content could

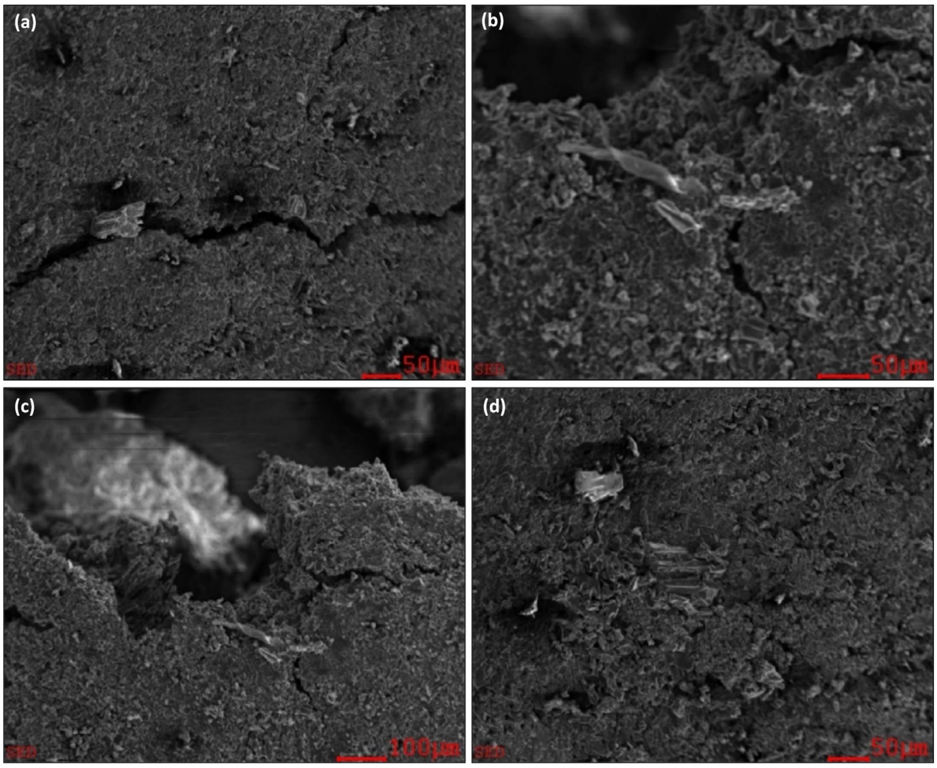


Fig. 14. SEM photos of sections of pellets of pyrolysis oil and biocarbon with mass ratio 33.9%. Voltage and magnification: (a) 15 kV 239×, (b) 15 kV 230×, (c) 7 kV 180×, (d) 15 kV 250×.

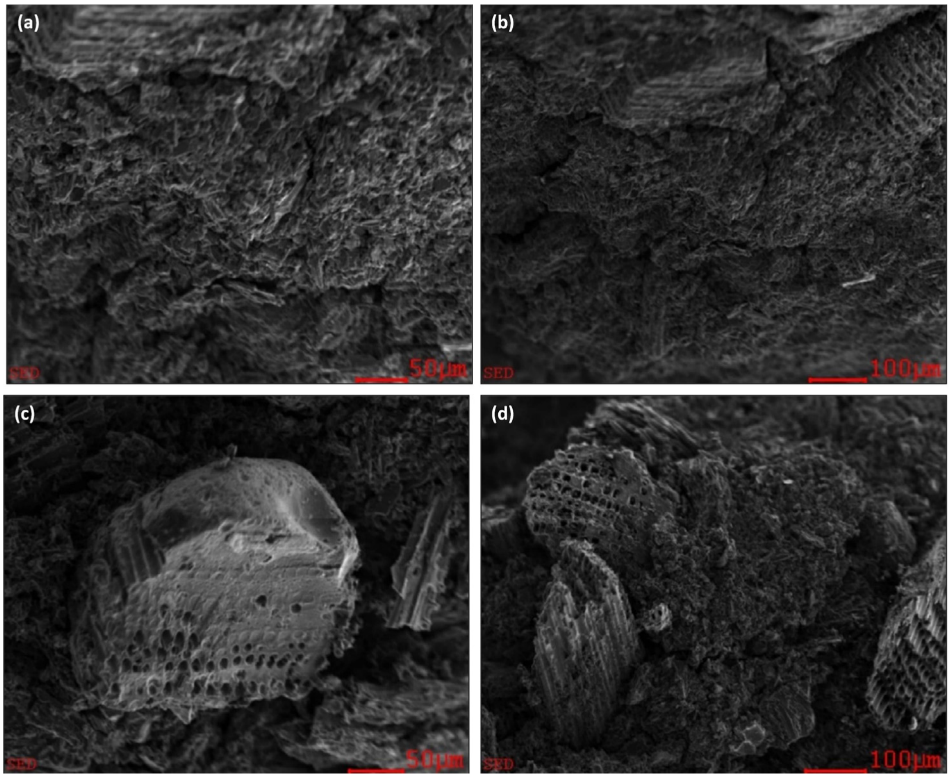


Fig. 15. SEM photos of sections of pellets of pyrolysis oil and biocarbon with mass ratio 33.9% after a second heat treatment. Voltage and magnification: (a) 7 kV 270×, (b) 7 kV 140×, (c) 7 kV 140×, (d) 7 kV 250×.

Table 9
Comparison of biocarbon pellet strength with that of coke.

Fuel type	Compressive Strength (MPa)	Source
Biocarbon		
Biocarbon pellet cold compressive strength	0.44	This study
Biocarbon pellet thermal compressive strength	1.19	This study
Biocarbon pellet from rice (raw)	0.65	[20]
Biocarbon pellet from rice (using lignin as binder)	3.82	[20]
Biocarbon pellet from rice (using lignin plus CaOH)	5.55	[20]
Biocarbon pellet from rice (using lignin plus NaOH)	> 10	[20]
Biocarbon pellet from Norway spruce	about 0.1–4	[26]
Coke		
Coke	4–23	[54,55]
Coke ashes	0.86–6	[56]
Lignite briquettes	about 0.5–9	[57]
FormCoke process	55–28	[58]
BIOMASS		
Eucalyptus Pellet	7.7	[59]
MixedWood Pellet	7.9	[59]
Miscanthus Pellet	6.6	[59]
Sunflower Pellet	5.8	[59]
Microwave Pellet	5.5	[59]
Steam Exploded Pellet	16.7	[59]

increase the compressive strength of the final pellet. It is interesting to note that the value of 3.82 MPa of strength has been obtained using lignin as a binder. Lignin results to be the most convenient binder for biocarbon pelletization but it has a cost, contrary to pyrolysis oils. Optimal lignin concentration has been found to be comprised between 10 and 15 wt%; while optimal water content was found to be about 20 wt% [20]. Even higher compressive strengths can be obtained by mixing lignin with CaOH and NaOH, nevertheless these additives would influence the chemical performance of the obtained fuel, once it is used in the furnaces. In the study of [26] the researchers achieved a quite low compressive strength with biocarbon produced at low temperatures while with biocarbon produced at higher temperatures the compressive strength increased to a maximum of about 4 MPa.

4.2. The importance of the fixed carbon content in the biocarbon pellet

Being a reducing agent biocarbon needs to have high fixed carbon content. The value obtained in this study is compared with others available in literature as shown in Table 10.

As we can see from Table 10, the biocarbon pellet produced in this study has a high fixed carbon content, comparable with the one of coke. As we know the carbon content is proportional to pyrolysis temperature [19], the higher the pyrolysis temperature, the higher the fixed carbon content. Rice husk pellet, which had an interesting compressive strength has low fixed carbon content, given that the ash content in rice husk is considerably higher than that of pine wood. Pine wood and wood in general appears to be an interesting material for producing biocarbon also for this reason. We see from Table 10 that biocarbon

Table 10
Comparison of biocarbon fixed carbon content with that of coke.

Fuel type	Fixed carbon content (wt%)	Source
Biocarbon		
Biocarbon pellet	83.70 ± 0.88	This study
Biocarbon pellet reheated	87.79 ± 0.5	This study
Biocarbon pellet from rice	59.52	[20]
Biocarbon pellet from Norway spruce	76.3–90.3	[26]
Coke		
Petroleum coke	88.26	[60]
BIOMASS		
Pine wood	10.97	[61]

pellet produced from pine wood has about 8 times the fixed carbon content of raw pine wood pellet (equal to 10.97 wt%). This means that raw biomass has a fixed carbon content which makes it not convenient to use it as a reductant.

4.3. Biocarbon production plant layout

Taking into consideration the results of this study and also the FormCoke process description reported in [58] we proposed an improved methodology for biocarbon pellet production based on heat integration at the pyrolysis plant level, combined with reheating of the final pelletized biocarbon. As it can be seen from Fig. 16, first the slow pyrolysis of pinewood is performed at 600 °C, in order to obtain a biocarbon which has already a high fixed carbon content. Volatiles are partly condensed to obtain the required pyrolysis oils to be used as a binder in pelletization, the remaining quantity of volatiles is burned together with syngas to provide the heat necessary to maintain the pyrolysis process. If more heat is needed this can be provided also using electrical heating. The condensed oils can be oxygenated before mixing, to increase oxygen content and also partially distilled to reduce water content. It is recognized that oxygen-containing functional groups have a significant influence on the compressive briquette strength due to the ability of forming more hydrogen bonds [57].

The biocarbon produced from pyrolysis should be milled to very fine particles. This is because the compressive strength is also influenced by porosity. The finer the particles dimension is, the lower will the porosity of the obtained pellet become. After milling the biocarbon particles are mixed with pyrolysis oils and subsequently pelletized at the optimal conditions which have been found in this study. The obtained pellet has to finally be reheated. The advantages of the proposed methodology are the following:

- the use of pyrolysis oil as a binder provides both: the water required for the pelletization process and the increase in oxygenated compounds in the pelletized mixture;
- it is recognized that oxygen-containing functional groups have a significant influence on the compressive pellet strength due to the ability of forming more hydrogen bonds [57];
- the reheating causes an increase in fixed carbon content;
- during reheating we can have a decrease in porosity, due to the polymerization of part of the oils in the macropores of the biocarbon pellet;
- the use of pyrolysis oil as a binder, instead of lignin and starch, can lower the operative costs of biocarbon pellet production.

Further research efforts have to be focused on increasing the biocarbon pellet strength, as well as improving milling of the particles and pretreatment of the used pyrolysis oil.

5. Conclusions

This work was carried out to analyze the coupling between pyrolysis of wood and pelletization of the obtained biocarbon, using recovered pyrolysis oil as binder. The target application was the metallurgic industry. Pyrolysis yields showed that enough pyrolysis oil is produced to ensure its availability as binder. Pelletization results demonstrated that pyrolysis oil eases the production of biocarbon pellets. Moreover, it was observed that by a heat treatment the pellets became stronger, due to the carbonization of pyrolysis oil into the already existing biocarbon structure. A multivariate statistical method was used to optimize the process and hence the quality of the pellet. A Box-Behnken response surface design was tested, and the considered process conditions were the variation of oil content, the pelletizing temperature and the pelletizing pressure. Response surface models of mechanical durability, compressive strength and thermal strength were computed. The regression models returned high R^2, showing good affinity to the experimental data. According to the Derringer's desired function methodology, optimum conditions for the pellets production were computed at 33.9% of oil content, 60 °C as pelletizing temperature and 116 MPa as pelletizing pressure. The predicted values resulted in a mechanical durability of 81.7%, a compressive strength of 0.44 MPa and a thermal strength of 1.18 MPa. The values obtained experimentally at the optimized conditions were similar. The statistical method helped also in understanding the mutual influence of the process parameters. The responses were only slightly affected by the pelletizing pressure, showing a higher variation by change of temperature and a more evident dependence on oil content.

Taking into consideration the results of this study we propose an improved methodology for biocarbon pellet production based on heat integration at the pyrolysis plant level, combined with reheating of the final pelletized biocarbon. The complete methodology consists of the following steps: pyrolysis at 600 °C, densification (using pyrolysis oil as binder), reheating of the obtained pellet. The advantages of the proposed methodology are the following: the use of pyrolysis oil as a binder provides both: the water required for the pelletization process and the increase in oxygenated compounds in the pelletized mixture; it is recognized that oxygen-containing functional groups have a significant influence on the compressive pellet strength due to the ability of forming more hydrogen bonds; the reheating causes an increase in fixed carbon content; during reheating we can have a decrease in porosity, due to the polymerization of part of the oils in the macropores of the biocarbon pellet; the use of pyrolysis oil as a binder, instead of lignin and starch, can lower the operative costs of biocarbon pellet production.

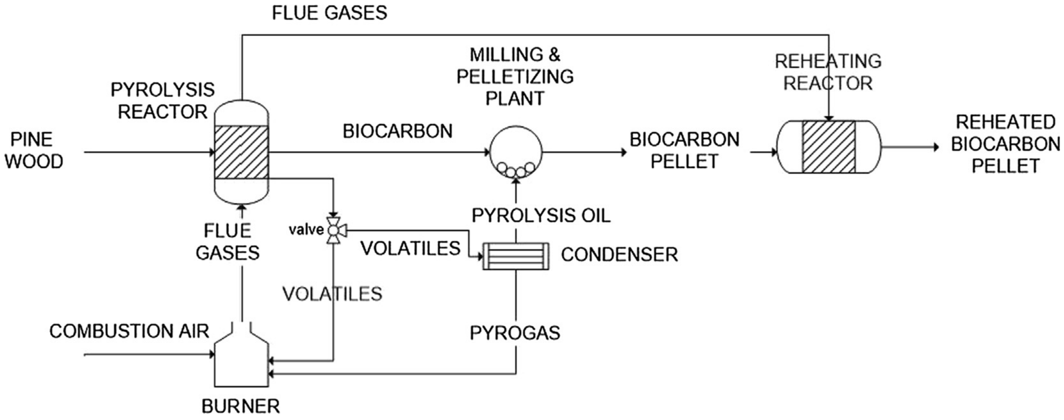


Fig. 16. Biocarbon pellet production plant layout.

Acknowledgments

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Paper C

Considerations on factors affecting biochar densification behavior based on a multiparameter model by Riva, Lorenzo; Wang, Liang; Ravenni, Giulia; Bartocci, Pietro; Buø, Therese Videm; Skreiberg, Øyvind; Fantozzi, Francesco; Nielsen, Henrik Kofoed. Under second review step in Energy (2020).

Considerations on factors affecting biochar densification behavior based on a multiparameter model

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Declarations of interest: none

Abbreviations[1]

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[1] **Abbreviations:**

BET - Brunauer-Emmett-Teller
D - density
db – dry basis
IPCC – Intergovernmental Panel on Climate Change
PB – pine biochar
QSDFT - Quenched Solid Density Functional Theory
SEM – scanning electron microscope
TP – torrefied pine
TCD – thermal conductivity detector
TS – tensile strength
UP – untreated pine
wb – wet basis

Abstract

Biochar is a promising sustainable solution to foster the carbon neutrality of current fossil carbon-based industrial processes. Pelletization can improve the mechanical and physiochemical characteristics of biochar, including reducing mass and carbon losses during transportation, handling and utilization. In this work, a multiparameter model, coupled to a single pellet press unit, was applied to predict the biochar pelletizing behavior in an upscaled pellet mill. It enabled estimating how the forces along the matrix dies are affected by the key pelletization parameters, in a time and cost-effective way. The studied parameters were pyrolysis temperature, added water content and pelletization temperature, which were varied to reflect industrially plausible values. In accordance with the experimental test results, the multiparameter model calculations showed that biochar produced at high pyrolysis temperatures is easier to pelletize. Addition of water improved pelletization behaviors of the studied biochar, while pelletization temperature did not give evident effects. Furthermore, the inclusion of pyrolysis oil as binder was considered and its effect on the pelletization process investigated. Additionally, density and compressive strength of the produced pellets were examined, as key mechanical properties significantly affecting logistic and utilization of biochar pellets. Correlations between these mechanical properties and key pelletization parameters were evaluated.

Keywords: densification, pelletization, modeling, pyrolysis, pyrolysis oil, biochar.

1 Introduction

With the necessity of abandoning the consumption of fossil fuels, biomass has been targeted as possible substitute. In particular, biochar produced from biomass is very versatile and can be used for many applications. Biochar is a promising alternative of fossil fuels to be used as energy source in heat and power plants [1]–[4] and reducing agent in metallurgical applications [5]–[7]. Biochar can also be used as enhancer to improve soil quality [8]–[10] and as filter in water treatments [11], [12], Recently, The Intergovernmental Panel on Climate Change (IPCC) included this material as a carbon neutral option to tackle climate change, recognizing the possibility to contribute as carbon negative source as well [13]. A more comprehensive lists of different uses has been provided in [14]–[16].

Among several challenges that are related to the utilization of biochar, the low mechanical strength of biochar, which may lead to considerable mass losses (and therefore increases of costs) in the handling and transportation steps, can be improved by densification [17]. Densification of biochar has recently been previously attempted and studied in a few works [17]–[23]. However, the focuses were on the effects of binders on the mechanical properties, combustion properties and co-densification of biochar with untreated biomass or coal. Only few studies focused on the biochar pelletization process and the properties of pelletized biochar. Some of them, for instance, investigated the effects of the pyrolysis temperature on the biochar densification behaviors [18], [20], [21]. With the aim to perform biochar pelletization at industrial scale, it is necessary to question the feasibility of the process and to quantify the factors affecting the densification of biochar. One important step in that direction might be done by establishing, developing and validating a versatile model that can predict and evaluate densification behaviors of specific biochar and effects of varies factors. Utilization of such a model could make it easy to predict and screen feasibility to pelletize of different biochar and binder mixture in an industrial process. Experiment works in combination with pellet production models have been done to gain a deeper understandings of biomass pelletization and the effects of controlling parameters. In particular, in 2006, Holm et al. used a laboratory scale single pellet press to simulate the densification of biomass in industrial-scale pelletizers [24]. A multiparameter model describing the forces built up along the dies of the pellet mill matrix was consequently developed and validated [24]. The main quality of this model is that it provides a wide set of information of the pelleting behavior of the studied biomasses upon changes in key parameters (e.g. pelleting temperature or water content) by performing a limited number of lab tests. The model was used and validated for evaluating densification of different woody biomasses [25] and further improved and simplified by the same research group [26]. The main assumption of this model is that the densification of the biomass to pellets is possible due to the combination of the roller pressure and the back pressure that is generated by the friction between the material and the walls of the channels [26]. A schematic drawing of the pellet densification process is presented in Fig. 1. This representation mainly focuses on the forces acting along the channel, which can be related to the energy consumed in the pelleting phase and to the stress borne by the channel itself [24]. The pelleting pressure P_x, is the parameter directly associated to the forces acting along the die and therefore it is critical to assess the feasibility of a pelletization process. In the model, P_x is computed in relation to the dimensions of the pellets so to ease any upscaling evaluation. The model however was validated and applied only with woody biomass. In 2017, Arnavat et al. demonstrated that it could be successfully used for assessing pelletization of torrefied wood [27]. However, as observed in [28], [29], despite produced by similar treatments, torrefied wood and biochar differ in a considerable extent. It is indeed not obvious to expect biochar to have the same pelleting behavior of torrefied wood. It becomes hence interesting to further study the possibility of using the model for pelletization of biochar and to assess the effects of the biochar pelletization behaviors under different conditions. The application of this model and the results assessment can be a quick and efficient measure which can provide necessary information for the design and operation of industrial scale biochar pelletization, with a reduction of potential time, operational costs, numbers of trial tests and materials needed.

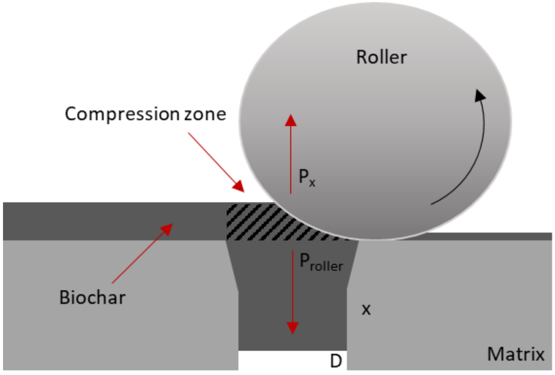

Fig. 1. Pelleting process principle with rotating roller and fixed matrix. D and x are respectively the diameter and the length of the die. P_{roller} is the pressure generated by the roller on the pelletized biomass, while P_x is the pelleting pressure.

In the present work, pine wood was used as feedstock for biochar production under different pyrolysis temperatures. The multiparameter model was applied to evaluated effects of three parameters, including pyrolysis temperature, added water content and pelletizing pressure, on pelletization behaviors of pine wood biochar. The model was first applied for a base case at fixed pyrolysis temperature, water content and pelleting temperature. Secondly, keeping the other two parameters constant, one parameter mentioned above was varied and effects of it on the biochar pelleting process studied. The model was also applied for studying pelletization of biochar using pyrolysis oil as binder. In our previous work, using pyrolysis oil as binder has been investigated and proved as a promising measured to improve the quality of biochar pellets [21] . Particularly, in the scheme proposed in Fig. 2, the utilization of pyrolysis oil as binder can enhance the use of a pyrolysis by-product and optimize the whole biochar value chain with benefit to increase the quality of biochar pellets.

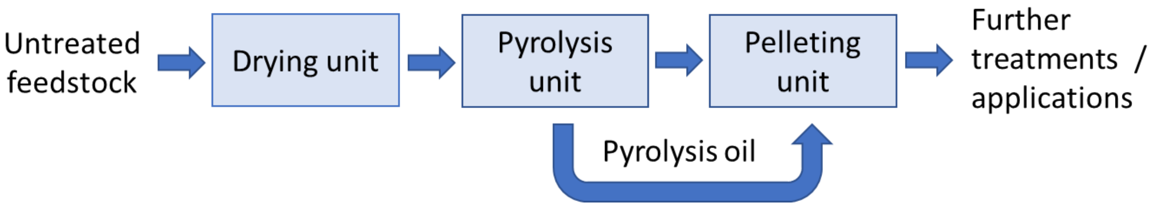

Fig. 2. Conceptual scheme of an integrated pyrolysis-pelletization process, with recovered pyrolysis oil as binder.

Further research on pyrolysis oil as binder can be found in [16], [18], [26]. Densification of biochar was compared to wood and torrefied wood pelleting, since the model was previously validated and applied for these materials [26], [27]. Moreover, they have been already studied and discussed (see [30]–[32]) and a comparison might contribute to enrich the discussion by further observations. Further relationships between the model and the mechanical properties of the pellets were investigated by measuring density and compressive strength.

2 Material and methods

2.1 Feedstock and biochar production

A Scots Pine (*Pinus Sylvestris*) tree was harvested from a local forest located in Grimstad, Norway. The harvested tree was shredded into chips that were dried at 60 °C for 24 hours and stored in an airtight box at ambient temperature. Biochar was produced from the chips at three different pyrolysis temperatures: 400, 600 and 800 °C. A layout of the pyrolysis process is illustrated in Fig. 3. Approximately 100 g of biomass was placed inside the furnace, evenly spread in a Silicon carbide retort. The reactor was purged with a flow of 40 ml/min of N_2 to generate inert atmosphere in the reactor. The feedstock was then heated up at a selected rate of 10 °C/min to a desired temperature and kept at that temperature for 1 hour. During one experiment, volatiles and gases leaving the reactor were cooled down by two serially connected heat exchangers. The condensable volatiles were collected in a glass bottle. For current work, incondensable gases were not analyzed and were directly expelled through ventilation. At the end of the process, the heating of the furnace was turned off and the produced biochar was cooled down in nitrogen atmosphere to avoid oxidation of the material. After cooled down to room temperature, the biochar was milled in a hammer mill *px-mfc 90 d* (Polymix, Germany) with a 2 mm sieve. The ground biochar produced under different conditions was stored at ambient temperature in airtight boxes. The particle size distribution of the produced biochar was analyzed by a laser diffraction particle size analyzer *Mastersizer 3000* (Malvern, UK). Following the considerations already mentioned in [20], no further size screening was carried out and pelletization was done with a mixed particle size biochar mixture. The condensates collected from the biochar production experiments were stored in airtight containers at 4 °C, without any further treatment.

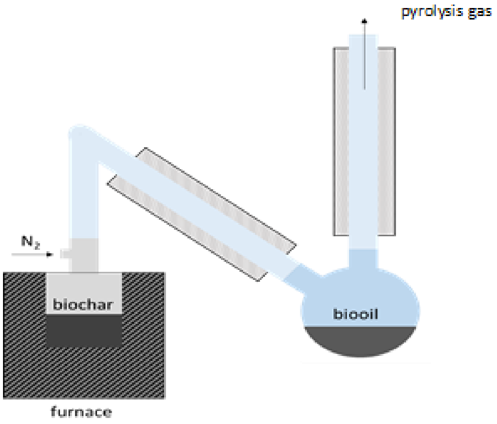

Fig. 3. Layout of the pyrolysis unit with an electrical external heated pyrolysis retort, cooling jackets and collection of pyrolysis oil.

2.2 Model theory

The main assumption of this model is that, once the biomass is compressed in one direction, it tends to expand in the two other perpendicular directions. It is therefore possible to relate the pelletizing pressure (P_x), which is equal the pressure the material experiences to exit the die (it will also be referred as exiting pressure), to the Poisson effect by the Poisson's ratio (v). This ratio v describes the expansion in directions perpendicular to the direction of compression and under the assumption of orthotropicity, i.e. the biomass fibers are perpendicularly oriented to the longitudinal direction of the channel [27]. The other parameters included in the model are: the pre-stressing term (P_{N0}), incorporating inelasticity, the sliding friction coefficient (μ) and the compression ratio (c). The compression ratio is:

$$c = x/2r \qquad \text{Eq.1}$$

where x is the length of the channel and r its radius. By the model presented in [24], it is then possible to gather all the parameters into the equation for P_x as function of c:

$$P_x(c) = P_{N0}/v_{lr}(e^{\mu v_{lr} c} - 1) \qquad \text{Eq.2}$$

In the Poisson's ratio v_{lr}, the subscript l denotes the direction of the applied stress (longitudinal) while r denotes the direction of the transverse deformation [25]. Despite its relative simplicity, Eq. 2 has several parameters that need to be derived experimentally, making the model complicated to fit to various biomass whose properties are unknown. In [26], a new version of Eq. 2 was suggested. It was shown that it is indeed possible to recombine the parameters μ, v and P_{N0} into two new terms: U and J. These new parameters can be estimated by a limited number of experiments, and following [26], are expressed as:

$$U = \mu P_{N0} \qquad \text{Eq.3}$$

$J = \mu v_{lr}$ Eq.4

Inserting Eq. 3 and Eq. 4 into Eq. 2, a simplified version is obtained:

$P_x(c) = U/J(e^{4Jc} -1)$ Eq.5

This new equation, as shown in [24], for c<<1 can be reduced to:

$P_x(c) = 4Uc$ Eq.6

In Eq. 6, U can therefore be derived experimentally by measuring the exiting pressure (with the method shown in Fig. 4) for pellets made with very low c, by linear fit. Once U is known, it can be used in Eq. 5 to obtain J. New measurements must be performed at higher c and J can then be extrapolated by non-linear interpolation. It is thus possible with relatively few experiments to obtain all the needed parameters of Eq. 5, and the equation can finally be used. As stated in [26], the procedure relies on the assumption that the Poisson's ratios are constant with the variation of compression ratios and it is therefore only valid under the assumption that the measurements are made at sufficiently small compression ratios. Moreover, a certain degree of uncertainty is related to the extrapolation of compression ratios that better fit the industrial cases (c = 7-8) [27]. However, the model has been demonstrated to work successfully for wood and torrefied wood [26], [27]. The benefits of this model are relevant since:

- the possibility of building up the curve with a limited number of experiments and material makes it time and material saving;
- limiting the curve parameters to U and J, it becomes easier to understand how external parameters such as pelleting temperature, water content and variations in pelleting material impact on the $P_x(c)$ vs. c curve.

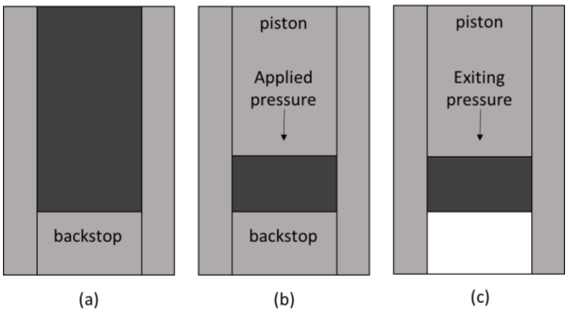

Fig. 4. Lab-scale experiment divided in phases. In phase (a), the backstop is included, and biochar is inserted into to die. In phase (b), the piston compresses the biochar up to a defined pressure. In phase (c), the backstop is excluded, and the pressure necessary to eject the pellet is measured.

2.3 Biochar pelletization

For each tested composition, at least 20 g of a biochar and water mixture was prepared at different ratios. The blend was homogenized in a beaker by a magnetic stirrer for about 10 minutes. The biochar with and without mixing of water or binder were pressed by a hot single pellet press (MTI, USA). The inner diameter of the die was 6.25 mm. For press test, the exiting pressure was measured at three different compression ratios below 0.75, so to extrapolate U in the linear region. The diagram point (0, 0) was also included. For each compression ratio, at least three biochar pellets with same water addition ratio were produced. The average value and the standard deviation of the exiting pressure of these three tests were computed. Once U was obtained, it was used to compute J, by fitting the new values of pressure measured at higher compression ratios. The initial applied pressure was 100 MPa. This value was chosen because the exiting pressure tends to oscillate around a constant value when the applied pressure was higher than 100 MPa, as can be seen in Fig. 5.

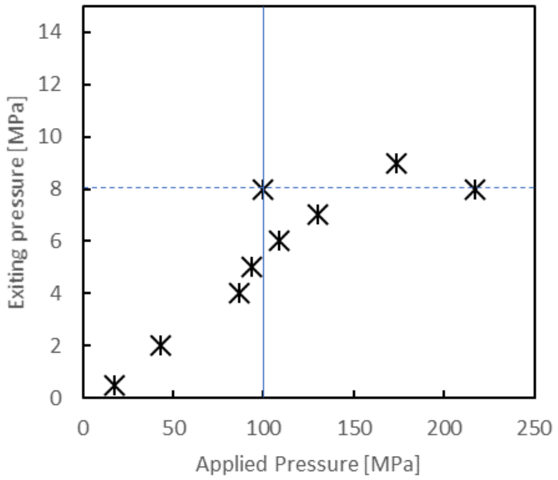

Fig. 5. Measured exiting pressure as function of tested applied pressure for pellets made at 20 °C with biochar produced at 600 °C and a mixing of 35 wt% water. The continuous blue line marks the applied pressure at 100 MPa, while the dotted blue line marks the exiting pressure related to that applied pressure.

Before pelletization, the die and other moving parts of the single pellet press were heated up to the operating temperature, which was then maintained during the pelletization process. Pressure was set manually to the desired value with a hydraulic piston and kept for 10 s before pressure release and extraction of the pellet. The exiting pressure was measured by a load cell *CPX1000* (Dini Argeo, Italy) connected to a multifunction weight indicator *DFWLB* (Dini Argeo, Italy). Biochar pellets were made by sequential layers pressed at the same pressure when the material was exceeding 0.15 g, according to [26].

After the process, the pellets were cooled down and stored in airtight boxes at ambient temperature. The list of the configurations that have been tested in this work is presented in Table 1.

Table 1. List of the configurations that have been tested. Number 1 is referred to also as “base case”.

Number	Pyrolysis temperature [°C]	Pelleting temperature [°C]	Water content [wb%]
1	600	20	35
2	600	20	25
3	600	20	45
4	600	60	35
5	600	90	35
6	600	120	35
7	400	20	35
8	800	20	35

2.4 Compressive strength test

The compressive strength of the produced biochar pellets were tested by a pellet hardness tester (Amandus Kahl, Germany). Strength was applied perpendicularly to the cylindrical axis direction. The measured value for compressive strength is normally and here referred to as a tensile strength (TS). Following the procedure in [33], the tensile strength was computed by the equation:

$$TS = m_s g / \pi r l \qquad \text{Eq.7}$$

where m_s is the force equivalent mass which the pellet hardness tester measures for the obtained strength, g is the gravitational acceleration, r and l respectively are the radius and length of the pellets.

2.5 Pellet density test

The particle density of the biochar pellets was computed indirectly as $\rho = m / \pi r2l$, where m was the mass. Mass was determined on a balance with a readability of 0.1 mg, while radius and length were measured with a Vernier caliper with a precision of 0.01 mm. All density and strength measurements were taken at least 24 hours after the pelletization. As shown in Fig. 6, density and compressive strength tend to stabilize when the compression ratio is higher than circa 0.85, for pellets with biochar produced at different pyrolysis temperatures and water as binder (35% of total weight). For both compressive strength and density measurements, at least six samples characterized by a compression ratio higher than 0.85 were selected, to avoid the uncertainty region.

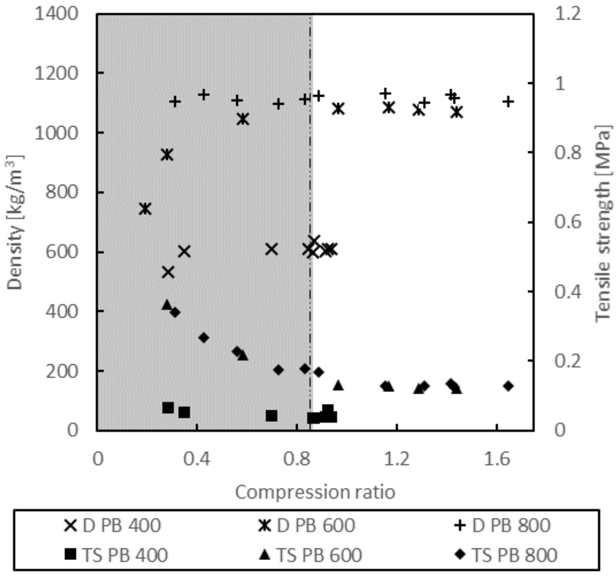

Fig. 6. Density (D) and tensile strength (TS) measured at different compression ratio for pellets of pine biochar (PB) produced at 400, 600 and 800 °C (reported in the legend as 400, 600 and 800) and a water content of 35%. The white region of the area, starting after c=0.85, highlights the stable zone.

2.6 Characterization of pellets and biochar

An *EuroEA* (Eurovector, Italy) with TCD detector was used for the C-H-N ultimate analysis. Oxygen was computed by difference of the other elements. The proximate analysis of the produced biochar was conducted through the procedures described in standards EN 15148, EN 14774-2 and EN 14775, which were applied respectively for volatile matter, moisture content and ash content. Surface area and porosity of the produced biochar were measured with N_2 adsorption at 77 K (*NovaTouch*, Quantachrome, USA). The Brunauer-Emmett-Teller (BET) model was used to calculate the surface area. Pore volume was evaluated with Quenched Solid Density Functional Theory (QSDFT) using the calculation model for slits and cylindrical pores on the adsorption branch. Before each measurement of surface area and porosity, samples were degassed at 150 °C for 10 hours. Morphology and microstructure of selected biochar pellet samples were examined by a scanning electron microscopy (Zeiss Ultra 55 limited edition). One biochar pellet was fixed on a sample tap and the outmost surface was scanned.

3 Results and discussions

3.1 Determination of the parameters

The model was first applied with biochar produced at 600 °C, mixed with pure water (35% of total weight) and pelletized at 20 °C. In this work, this configuration is also referred to as “base case”. The pelleting curve that was obtained is presented in Fig. 7. The first four dots (including the diagram point (0, 0)) were used to obtain U by linear fitting. The fitting line is plotted and its equation and R^2 presented right above the curve. Using the value of U and adding three other dots at higher compression ratios, it was possible to complete the curve by non-linear fitting. The pelleting curve equation is displayed in Fig. 7. For this configuration U was 0.49 and J was 0.30. The high value of regression coefficient R^2 shows that the model fits well the values from the samples. Small standard deviations show a good repeatability. Generally, the curve shows a similar trend compared to what was observed in [26], [27]. The model can therefore successfully be applied for biochar pellets.

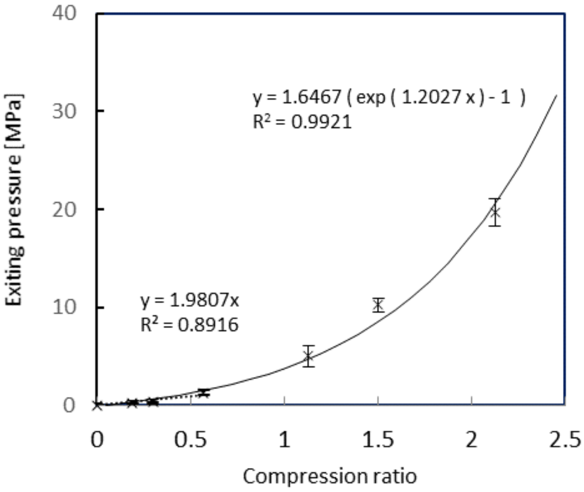

Fig. 7. Experimental data and data fittings to determine the U and J for pellets with biochar produced at 600 °C, pelletized at 25 °C of and with a water content of 35% in the pelletized mixture. The experimental data, displayed with a cross, are the average of the measurements carried at each compression ratio, while the error bars indicate the standard deviations. The dotted line represents the linear region, while the continuous line is the non-linear fitting.

3.2 Influence of water as binder

The pelleting curves and the coefficient values for biochar pellets produced with different water contents are presented in Fig. 8 and Fig. 9, respectively. Despite a similar trend in the linear region with compression ratio in the range of 0-1, the curves start deviating more evidently towards the fully exponential zone. that, at fixed compression ratio, a higher water content is tendentially related to a lower exiting pressure. It can be observed that both U and J tend to decrease with increasing water content. However, the degree of uncertainty makes it difficult to attempt any more precise correlation between these coefficients and the water content.

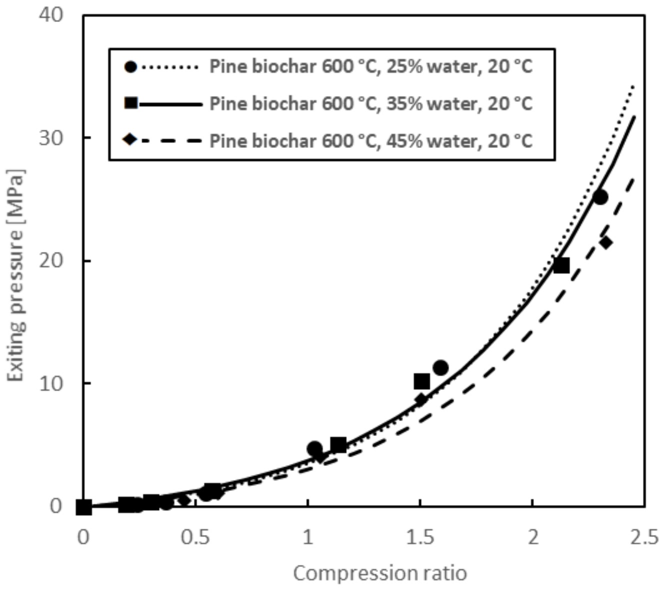

Fig. 8. Exiting pressure curves for biochar produced at 600 °C and pelletized at 20 °C with different water contents. For each configuration, the legend shows a marker and a line. The markers display the experimental data, while the three line represents the modeled curve values.

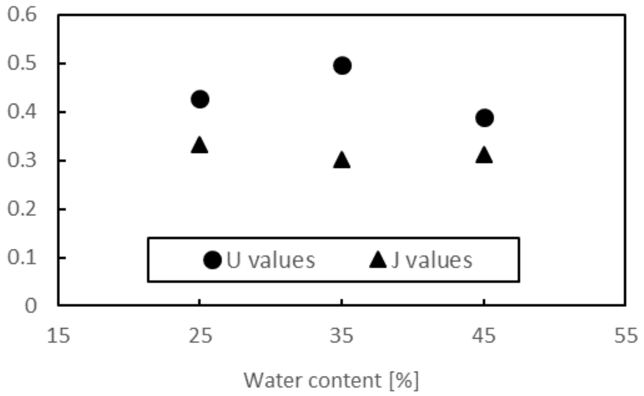

Fig. 9. Values of U and J for biochar produced at 600 °C and pelletized at 20 °C with different water contents.

The beneficial effect of water on reducing exiting pressure of a biomass single pellet press has been reported in [34] and [35]. As stated in [35], pelletization of biomass is generally strongly affected by addition of water. Densification consists of the mechanical interlocking of fibers either by adhesion forces between large particles or chemical bonds and van der Waals's forces for small particles [36]. Water molecules can optimize the binding of particles by establishing bridges that connect the biomass particles when direct interactions among them do not exist [37]. As result of this, the use of water as binder is beneficial both as quality enhancer to improve the strength of pellets and as lubricant to smooth the process for pelletizing biomass particles. Considering the definitions of U and J in Eq. 3 and Eq. 4, it becomes plausible to assume that water acts on the three coefficients μ, P_{N0} and v_{lr}. It could therefore be inferred that the pelleting process would benefit from a further increase in the water content to a certain extent. Instead, as observed in [31], an excess of water in the densification might cause particle-to-particle lubrication, a phenomenon where the center of the pellet extrudes faster than the exterior and it is related to an increase of mechanical fragility. However, biochar densification requires a considerable amount of water (or liquid binder, similar to water), since the solid bridges between particles are not enough to enhance plastic deformation. Without water or liquid binder, it would therefore become challenging to track the exiting pressure since the ejected material would still be in powder form. Therefore, the optimum content of binder to enhance a proper pelletization is expected to be within the range investigated in the present work. It also agrees with the results reported in [21].

3.3 Influence of pelleting temperature

Biochar produced at 600 °C was pelletized with a water content of 35% at different pelleting temperatures and the respective curves were derived. The results are shown in Fig. 10. The curves obtained with a pelleting temperature of 20 and 120 °C returned slightly higher exiting pressures in comparison with those obtained at 60 and 90 °C. The biochar produced at 600 °C has stable properties and is therefore not expected to change in the temperature range that was selected for these pelletization tests. The considerable amount of water as binder could instead affect the pelletization process in relation to the pelleting temperature, especially as the die temperature approaches 100 °C. However, no evident observations in this regard arise from the pelleting curves in Fig. 10. A possible reason might be the selected compression time, which was relatively short, in combination with the good homogeneity of the biochar-water mixture. Longer compression times might be useful to catch possible more evident differences between the pelleting curves.

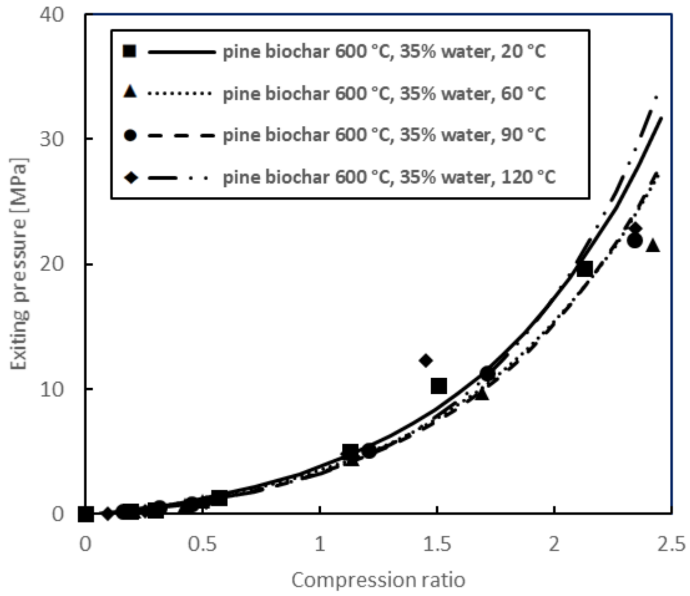

Fig. 10. Exiting pressure curves for biochar produced at 600 °C and pelletized at several temperatures with a water content of 35%. For each configuration, the legend shows a marker and a line. The markers display the experimental data, while the three line represents the modeled curve values.

Further observations can be drawn when the coefficients U and J are analyzed, as shown in Fig. 11. In [26], [27] it was observed a decreasing trend for the coefficient U values, while J was roughly constant, i.e. not influenced by the pelleting temperature. Similar trends are confirmed for the pelletization of biochar when varying pelleting temperature. The linear correlation of U presents a R^2 of 0.94, while it is easily visible that J oscillates around 0.30, with a maximum variation of 13%.

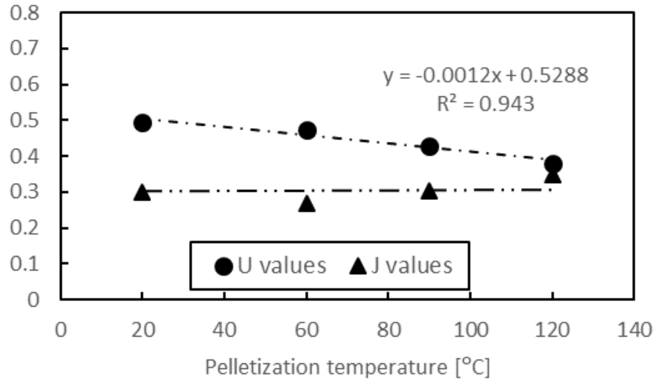

Fig. 11. Values of U and J for biochar produced at 600 °C and pelletized at increasing temperatures with a water content of 35%.

Such behavior makes it difficult to clearly define the dependence of pelleting temperature on the coefficients μ, P_{N0} and v_{lr}, because they mutually affect the coefficients of the model. However, it is possible to simplify the model by assuming that U is linear and dependent on the temperature and that J is constant [26]. In this case, the average of the J values previously obtained and presented in Fig. 11 was selected as constant. With these assumptions, further attempts were made to analyze the effects of the pelleting temperature. The new pelletization exiting pressure curves are presented in Fig. 12. With the exception of some data points in the curves at 20 and 120 °C, the curves seem to fit successfully the experimental results. From the new simplified curves, it can be seen that the exiting pressure at fixed compression ratio decreases upon increasing the pelleting temperature. This agrees with what was observed in [20] and [21], where the cause was attributed to the plastic deformation of lignin due to temperatures above the glass temperature. However, by a certain extent, the content of lignin in the feedstock might be quite low and, hence, not enough to deform and behave as plastic and act as a binder. For such circumstances, water might be a principal driver which affects the pelletization process. At high pelletization temperatures, the water might evaporate and be present between the pellet and the die, acting as lubricating layer which reduces the friction. The possibility of computing U by linear interpolation and setting J constant can nevertheless be assumed to provide acceptable accurate results to briefly evaluate the pelleting conditions by varying the process temperature, simplifying the operational analysis. Further investigations are needed to obtain better understanding of the effect of the temperature on the pelletization of biochar when using water as binder.

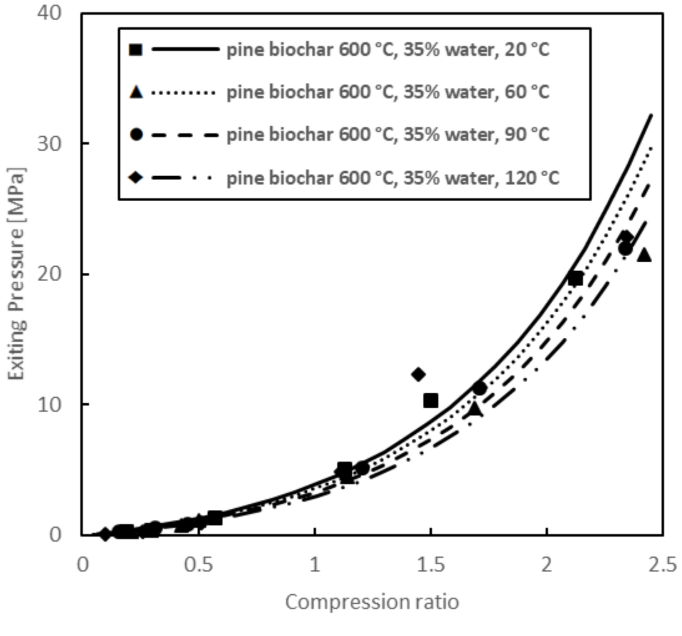

Fig. 12. Exiting pressure curves for biochar produced at 600 °C and pelletized at several temperatures with a water content of 35%, assuming U function of the pelleting temperature and J constant (0.30). For each configuration, the legend shows a marker and a line. The markers display the experimental data, while the three line represents the modeled curve values.

3.4 Influence of biochar production temperature

When the pelleting curves of biochar produced at different pyrolysis temperatures are compared, two clear trends are distinguishable. The curves are presented in Fig. 13 and the coefficients in Fig. 14. Compared to those pyrolyzed at 600 and 800 °C, biochar produced at 400 °C is characterized by a short linear region and a rapid exponential region, suggesting that the material might face practical challenges if compressed at industrial compression ratios (ca. 7-8). On the other hand, pelletization of biochar produced at 800 °C seems to perform better, and the exiting pressures are lower than the base case. When the coefficients U and J are analyzed in Fig. 13, it can be noticed that J reduces dramatically between 400 and 600 °C, while no evident trends are observable for U. It is hence not possible to reveal the reason for this behavior by only analyzing the coefficients. The benefit of pyrolyzing at higher temperatures are reported in similar works, where the focus was on the effects on mechanical properties of biochar pellets [18], [20]. Therefore, it appears interesting to look further into this effect.

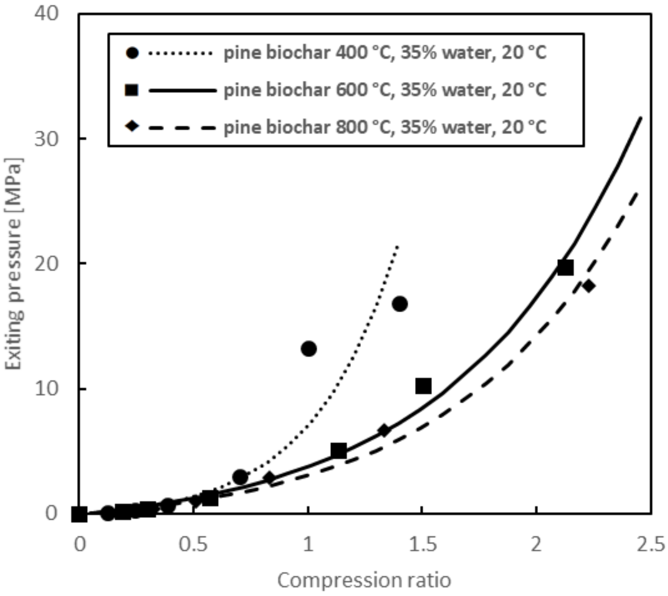

Fig. 13. Exiting pressure curves for biochar produced at different pyrolysis temperatures and pelletized at 20 °C with a water content of 35%. For each configuration, the legend shows a marker and a line. The markers display the experimental data, while the three line represents the modeled curve values.

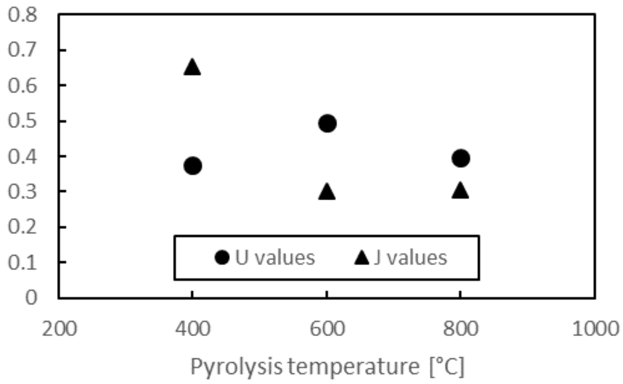

Fig. 14. Values of U and J for biochar produced at different pyrolysis temperatures and pelletized at 20 °C with a water content of 35%.

As explained in [38], higher pyrolysis temperatures result in a biochar structure with much less fibers but more brittle structure. For a specific grinding time, a larger fraction of small particles can therefore be obtained from the biochar sample produced at a higher pyrolysis temperature. The particle size distributions for biochar produced at 600 and 800 °C, as presented in Fig. 15, are similar and characterized by a wider range with a considerable peak at smaller particle sizes. In comparison, biochar produced at 400 °C has a narrower particle size distribution, and a significant fraction of the particles has larger particle sizes in the range of 50-100 μm. Due to the presence of smaller particles and wider particle size distribution, biochar pyrolyzed at higher temperature is expected to perform better in pelletization.

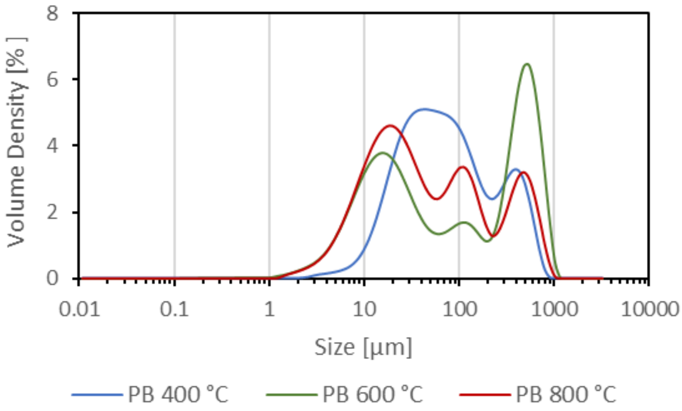

Fig. 15. Particle size distribution for pine biochar (PB) produced at 400, 600 and 800 °C.

Table 2. Ultimate analysis, proximate analysis, BET and porosity of biochar produced at 400, 600 and 800 °C. The acronym db and wb stand for dry and wet basis. Standard deviations of proximate analysis results are included in parenthesis.

Pyrolysis temperature [°C]	400	600	800
Ultimate analysis			
C [% db]	74.1	85	94.3
H [% db]	4.4	2.6	1.3
N [% db]	-	-	-
O [% db]	21.5	12.4	4.4
Proximate analysis			
Fixed Carbon [% wb]	63.7 (±1.2)	85.2 (±0.5)	93.2 (±0.4)
Volatile matters [% wb]	34.2 (±0.6)	13.0 (±0.1)	4.3 (±0.3)
Ash [% wb]	1.3 (±0.1)	1.5 (±0.1)	1.5 (±0.1)
Moisture content [% wb]	0.8 (±1.0)	0.3 (±0.3)	1.0 (±0.3)
BET [m^2/g]	1.8	169.2	317.1
Porosity [cm^3/g]	0.003	0.115	0.140

The biochar particles with different sizes have also a different capacity to adsorb and capture water. Therefore, as water is added as binder, the particles with different sizes play different roles and affect the pelletization process. According to [39], porosity and hydrophobicity are the main biochar characteristics influencing the water uptake capacity of biochar. Pores can be divided in different classes according to their size. In biochar, they are mainly macropores (0.1-1000 μm) inherited by the woody structure and are not much affected by the pyrolysis process [40]. However, it was demonstrated that porosity increases considerably at higher pyrolysis temperatures due to the formation of micropores (0.0001-0.001 μm) [41], in agreement with the specific surface area and porosity analysis of the tested biochar shown in Table 2. Both surface areas and porosity are lowest for the biochar produced at 400 °C, while the biochars produced at 600 and 800 °C have significantly higher surface areas and porosity. A similar increase of surface area and porosity of biochar produced at higher temperatures are reported in [41], [42]. The phenomenon is expected to be associated to the further devolatilization and carbonization of biomass which occur at elevated pyrolysis temperatures [43]. This is confirmed by the considerably lower amount of oxygen in the ultimate analysis and volatile matter in the proximate analysis (Table 2) for the samples produced at high temperatures. On the other hand, hydrophobicity is heavily related to presence of the functional aliphatic group on the surface of the carbonaceous structure [44]. It has been stated that biochar pyrolyzed at temperatures higher than 600 °C generally lose this group [45]. Therefore, the surface of biochar produced at high temperatures will be more hydrophilic and more porous. Water can then be expected to penetrate more easily into the solid structure and the binding of particles will be enhanced. In conclusions, there is an important evidence that pyrolysis temperature affects the performance of biochar in the pelleting phase both by producing biochar characterized by a wider particle size distribution and by modifying the structural capacity of the material to uptake water.

3.5 Influence of pyrolysis oil as binder

Pelletization of biochar with pyrolysis oil as binder were also studied and the pelleting curve is presented in Fig. 16. The oil produced during pyrolysis and then stored was used. 35% of pyrolysis oil was mixed with biochar produced at 600 °C for producing pellets, which was compared to the base case, as the 35% of water content was added with the same biochar. As shown in Fig. 16, no significant difference is visible between the curves obtained from tests using the two binders; however, pyrolysis oil returns somewhat lower values of exiting pressure. The pyrolysis oil used in the current work has a high water content (85.1 ± 1.4 wb%) and also contains a certain fraction of non-water compounds. According to [46], pyrolysis oil, produced at temperature between 600 and 900 °C, is characterized by high carbon content, but also a considerable oxygen content. In particular, at circa 600 °C, the main compounds are (in order of decreasing quantity): 1-hydroxy-2-butanone, hydroxyacetone, methanol and acetic acid [47]. How and in what extent these non-water compounds affect the pelletization and the pellets quality is however not clear. Considering the outstanding features associated to the use of pyrolysis oil as binder (see [20], for instance), it could be relevant to investigate which of these compounds has a major role in the enhancement of the binding mechanism, or what is the role of the carbon and oxygen content. In this way, the qualities of this binder could be further developed and upgraded. However, such research was beyond the scope of this work.

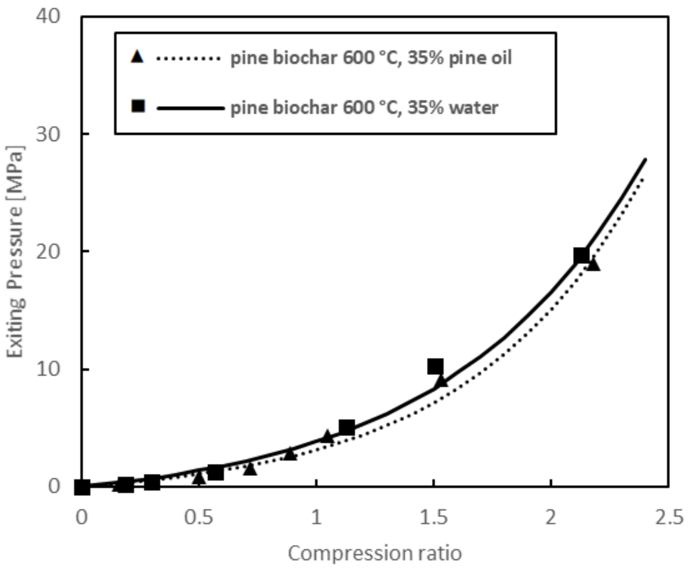

Fig. 16. Comparison between pelleting pressure curves of biochar produced at 600 °C and densified at 20 °C with either 35% of water content or of pyrolysis oil of total feedstock weight. For each configuration, the legend shows a marker and a line. The markers display the experimental data, while the three line represents the modeled curve values.

Fig. 17, instead, shows representative SEM images of the morphology and microstructure of pellets from pine biochar produced at 800 °C with addition of 35% water (referred to as PB 800) and pine biochar produced at 600 °C with addition of 35% of pyrolysis oil (referred to as PB 600-O). These two configurations were compared because of their similar morphology. The comparison might therefore be helpful in identifying differences between the water and pyrolysis oil as binder. Both biochar pellets display compact and dense structure. Compared to PB 600-O, the PB 800 pellet has more smoothed surface. However, a few cracks highlighted by white arrows can be seen in Fig. 17 (a), which were not observed from the PB 600-O pellet in Fig. 17 (d). Presence of these cracks indicates more susceptible breakage of PB 800 during durability tests and further handling, transportation and storage. Fig. 17 (c) and (f) show images of areas highlighted respectively in Fig. 17 (b) and (e), with the same high magnification. Fig. 17 (c) shows that the biochar particles have rather smaller sizes, in comparison to the PB 600-O biochar pellet displayed in Fig. 17 (f). This is in line with particle size distribution analysis results shown in Fig. 15, where biochar produced at 600 °C has a larger fraction of particles with size in the range of 500-1000 μm.

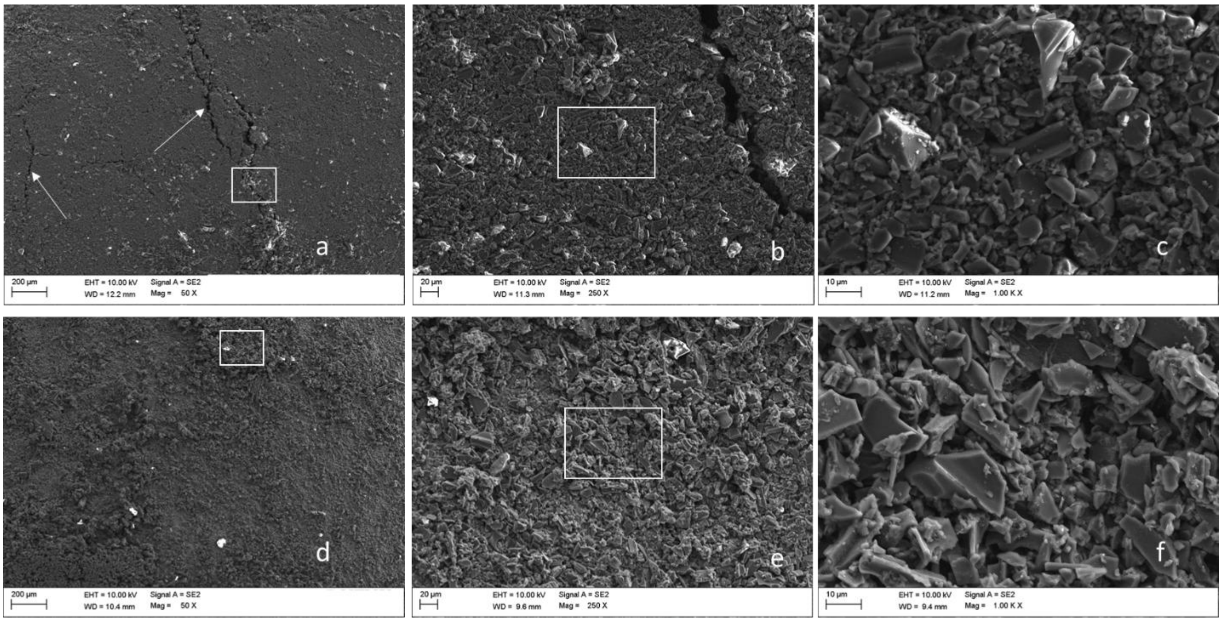

Fig. 17. SEM images of pine biochar produced at 800 °C ((a), (b) and (c)) with addition of 35% water and pine biochar produced at 600 °C with addition of 35% bio-oil ((d), (e) and (f)).

3.6 *Comparison with untreated wood and torrefied wood*

The base case of this work was compared to pelleting curves of two different pine-based pellets: untreated wood (with a water content of 10%) and torrefied wood with a heating rate of 2 °C/min up to 275 °C for 2 hours in nitrogen atmosphere (with a water content of 5%), processed and pelletized according to the methods used for the base case. The results are presented in Fig. 18. At high compression ratios, untreated pine was characterized by the lowest exiting pressures. The values were coherent with what was previously presented in [48]. When the exiting pressures in relation to the compression ratios are compared to several other feedstocks pelletized in [24] and [25], pine pellets return similar values, confirming that untreated softwood has favorable properties for the pelletization. Due to similarities, it is worthy to compare the torrefied and pyrolyzed pine wood in terms of pelletization. Compared to torrefied wood, lower exiting pressures were obtained during pelletization of biochar produced at 600 °C. It is important to mention that the torrefaction settings were chosen as representative, without any concern about an optimal pelletization outcome. Moreover, as mentioned in [51], pelletization of torrefied wood requires higher temperatures to overcome the glass temperature of the lignin and enhance its binding properties. The pelleting curve obtained in this paper is comparable with published results [27] [34]. At low compression ratios, torrefied pellets have higher exiting pressure values, indicating that the coefficient U is higher, as well. Therefore, according to Eq. 3, the torrefied material might be characterized by higher sliding friction coefficient and pre-stressing pressure. As mentioned in [26], these terms are complex to compute and hardly obtainable in literature. However, it is possible to attempt an explanation focusing on the different degrees of carbonization and thermal degradation generated by pyrolysis and torrefaction. While hemicellulose mainly degrades in temperature ranges between 250 and 300 °C, followed by extensive cellulose degradation at slightly higher temperatures (275-350 °C [52]), lignin degradation occurs in a much wider temperature range, up to above 600°C [53]. Hence, torrefied wood at 270 °C contains still a relevant amount of hemicellulose and most of the cellulose [38], which will play a considerable positive role during the pelletization process. In contrast, the three main components in biomass are almost completely degraded after the pyrolysis treatment and following carbonization [54]. In addition, biochar from the pyrolysis treatment has graphene-like sheets structure, causing an increase of the elasticity of the material [55]. This behavior might therefore be associated to a decrease of the prestressing term, impacting on the coefficient U. This could explain the different trend in the linear region for torrefied and pyrolyzed pellets.

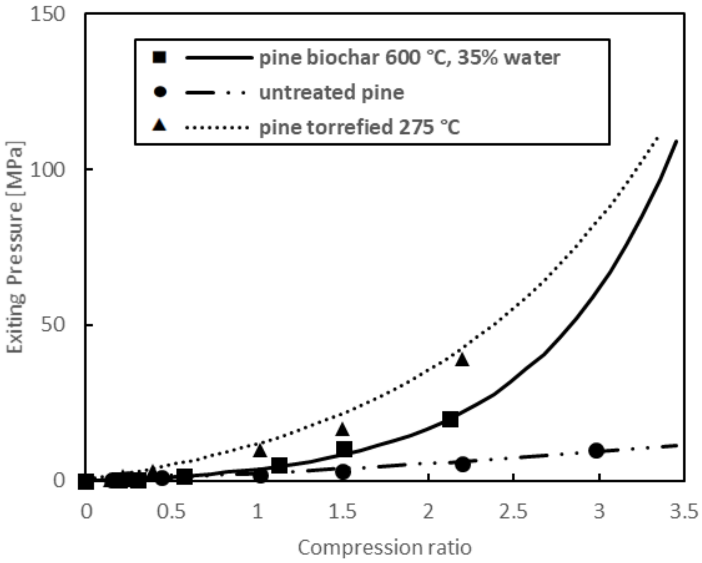

Fig. 18. Comparison between pelleting pressure curves of biochar produced at 600 °C and densified at 20 °C with a 35% water content, untreated pine woodchips pellets (water content 10%), woodchips torrefied at 275 °C (water content 5%) densified at 20 °C. For each configuration, the legend shows a marker and a line. The markers display the experimental data, while the three line represents the modeled curve values.

3.7 *Influence on mechanical properties*

For each configuration tested in this work, the density and the compressive strength of the pellets were measured. The results are presented in Fig. 19 and Fig. 20. In Fig. 19 the density values are compared. The pellets from biochar produced at 800 °C had the highest density, followed by the ones from biochar produced at 600 °C and at 400 °C. The effect of the pyrolysis temperature on the density appears to align with the analysis of pelleting curves: the lower the values of exiting pressure at fixed compression ratio, the higher the density of the produced biochar pellet. The results indicate that a smooth pelleting process yielding dense pellets is feasible and also easier to manage and work with. This is however not enough to justify a general strong correlation between pelleting pressure and density, since untreated wood pellets presented contrasting results. It could therefore be inferred that the properties of the pelletized material can also considerably affect the characteristics of pellets, to a higher extent than the pelleting process. However, in this case, it is noteworthy to mention that the wood pellets were characterized by lower density values than what are generally observed, since the pelleting temperature was not high enough to enhance the lignin binding mechanism [56]. Quite interestingly, when varying the water content, the maximum density of biochar pellets was observed at the value of 35%, while it was slightly lower with 45% of water content. Since the water is denser than biochar, an increase of binder content might easily be related to an increase of density. The results suggest that above a certain threshold the porous structure of biochar cannot absorb all the water and gets over-saturated. Density was negatively affected by an increase in pelleting temperature. The increase of temperature enhances water evaporation during the process, and give negative effects on densification of biochar. Indeed, at higher pelleting temperatures, the density value is similar to the one observed for pellets with 25 % of water content, demonstrating that a relevant amount of water was lost. When pyrolysis oil was used as binder, the density of biochar pellet was lower and characterized by a considerably high uncertainty. Pyrolysis oil is tendentially unstable and a relevant amount was presumably volatized in the pellets cooling phase, with a consequent decrease in density.

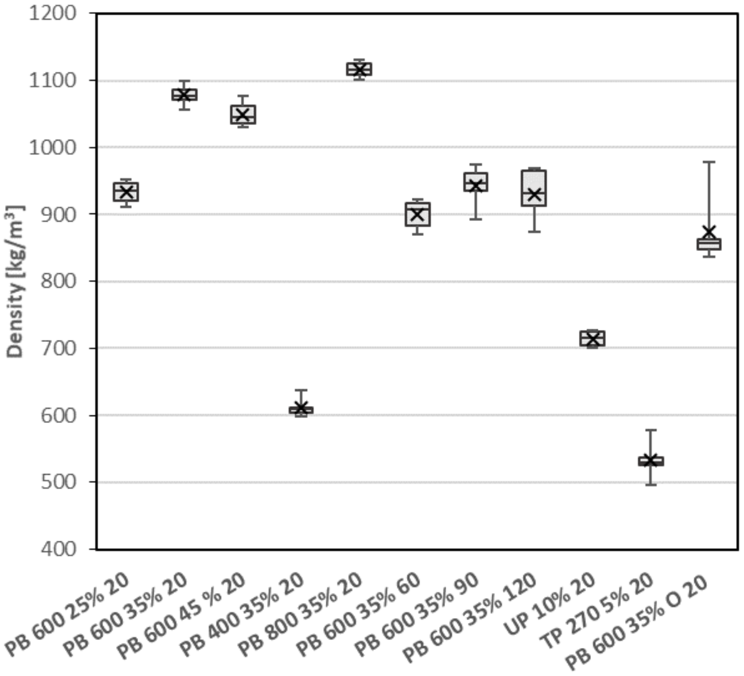

Fig. 19. Particle density of pellets studied and compared in this work. In the name code PB refers to pine biochar, UP to untreated pine, TP to torrefied pine. The first number following the type of treatment is the pyrolysis temperature in °C, then the percentage of water is signed and finally the pelleting temperature in °C. In the last label O stands for Oil, meaning the binder was pyrolysis oil.

Fig. 20 reports the value of the tensile compressive strength of produced biochar pellets. The positive effect of an increase of pyrolysis temperature was confirmed, suggesting a possible correlation between density and strength, too. In this case, pellets with biochar produced at 600 and 800 °C have similar strength values. This result, combined with the analysis of the modelled curves and density values, suggests that it is not necessary to carry out pyrolysis at excessively high temperatures to obtain a sufficient mechanical pellet quality and contain the energy consumption in the pelleting process. Compressive strength seems to benefit of an increased water content. This result, combined with the water content effects on density presented in Fig.19, confirms that generally low moisture content is associated to mechanical weakness of biochar pellets, while too high moisture content affects negatively density [37]. Nevertheless, as explained in [57] for biomass in general, and verified in [20] and [21] for biochar, an excessive moisture content might lead to incompressibility and hence mechanically weaker pellets. This behavior is strictly close to what is observed for density, confirming that the binding mechanism between biochar and water are partially compromised. These results show that, as a rule of thumb, the trend in the modelled pelleting curves can already give important information about the mechanical properties of the pellets. However, no statistically significant correlations could be derived. Differently to density, strength is higher when water is substituted with pyrolysis oil. Despite the water volatilization affecting the density of the pellets, the composition of the pyrolysis oil provides a stronger binding mechanism, making it a promising binder.

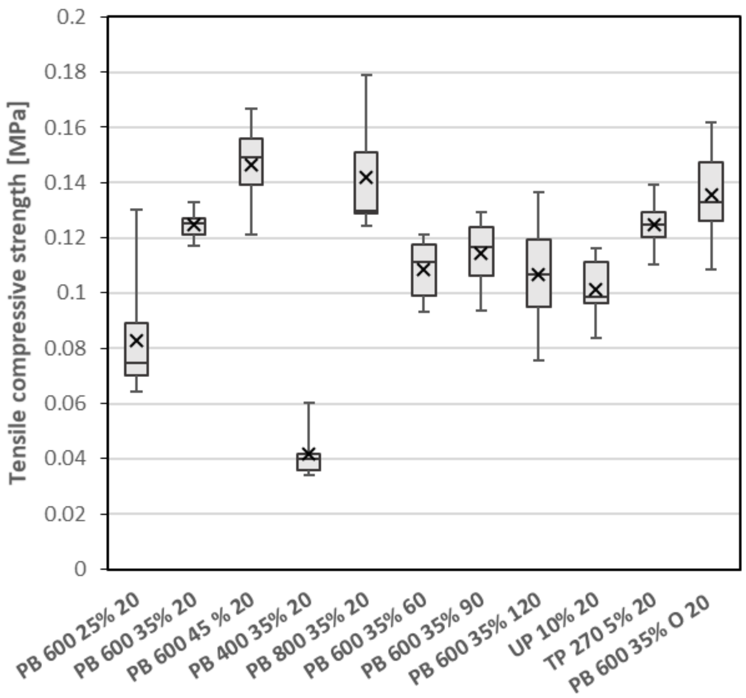

Fig. 20. Tensile compressive strength of pellets studied and compared in this work. In the name code PB refers to pine biochar, UP to untreated pine, TP to torrefied pine. The first number following the type of treatment is the pyrolysis temperature in Celsius degrees, then the percentage of water is signed and finally the pelleting temperature in degrees Celsius. In the last label O stands for Oil, meaning the binder was pyrolysis oil.

4 Conclusions

This work intended to enlighten on the mechanism underneath the pelleting process of pyrolyzed biomass by the help of a multiparameter model previously implemented and used to analyze pelletization of wood and torrefied wood. The preliminary evaluation of upscaled scenarios based on this lab scale analysis might help to facilitate the industrial feasibility of biochar densification process, which recently has turned to be promising for cofiring and metallurgical applications. The multiparameter model was firstly applied to a case base (pine pyrolyzed at 600 °C mixed with 35% of water and pelletized at 20 °C) and the feasibility of fitting the pelleting pressure as function of the compression ratio was verified. Afterwards, starting from pine, pelleting curves modeling the variation of the exiting pressure in relation to the compression ratio of the pellets were built, with variation of water content (between 25 and 45%), pelleting temperature (between 20 and 120 °C), and pyrolysis temperature (between 400 and 800 °C). For biochar pellets produced under each configuration, density and tensile compressive strength were measured to analyze the mechanical quality of the pellets. It was hence found out that:

- Pelletization of biochar requires lower exiting pressures at increasing water contents. Compressive strength benefits also of higher water contents, while the density gets reduced at high water content.
- The pelleting temperature did not particularly affect the exiting pellet pressure, while both density and compressive strength are tendentially higher at lower pelleting temperatures. It is therefore acceptable to state that during pelletization, effects of other parameters should be considered more carefully than the pelleting temperature. Among the different cases, the pelleting curves at different pelleting temperatures were the only ones characterized by a linear trend for the coefficient U. When computing J by assuming linearity of J, the curves were still close to the empirical data, suggesting that this parameter is hence the easiest to model.
- The model for different pyrolysis temperatures returned the curves most deviating from each other. In particular, a considerable influence on pelleting pressure was observed between biochar produced at 400 and 600 °C. Especially for biochar produced at 400 °C, the outcome showed that pelletization of such material would be challenging. On the other hand, no relevant differences were noticed between 600 and 800 °C. The same trend was observed for density and compressive strength. Such result seems to suggest that, for densification, it is necessary to pyrolyze at relatively high temperatures, but without the need to go to elevated temperatures.

Water was compared with pyrolysis oil to evaluate its performance as binder in the pelleting phase. The same percentage 35% wt water and pyrolysis oil was considered and tested as binder, respectively. The comparison between pellet exiting pressures for water and pyrolysis oil as binder did not provide relevant differences. Moreover, when the mechanical properties were measured, it was observed that a reduction in density is balanced by an increase in compressive strength.

Finally, the base case was compared to the pelleting curves of untreated pine and torrefied pine. Tests were carried out to understand both the feasibility of biochar pelletization in relation to more established pelleting technology and in what extent they differ. Wood pellets proved to be easier to pelletize, however, biochar pellets showed exiting pressure values lower than for torrefied pellets.

Results from the current work contribute to foster the research on biochar densification, offering an exhaustive insight useful to comprehend some basic phenomena which might occur in the pelleting process and easing further and more detailed studies.

Acknowledgments

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Paper D

On the self-heating behavior of upgraded biochar pellets blended with pyrolysis oil: effects of process parameters by Riva, Lorenzo; Cardarelli, Alessandro; Andersen, Geir Johan; Buø, Therese Videm; Barbanera, Marco; Bartocci, Pietro; Fantozzi, Francesco; Nielsen, Henrik Kofoed. Published in Fuel (2020).

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Full Length Article

On the self-heating behavior of upgraded biochar pellets blended with pyrolysis oil: Effects of process parameters

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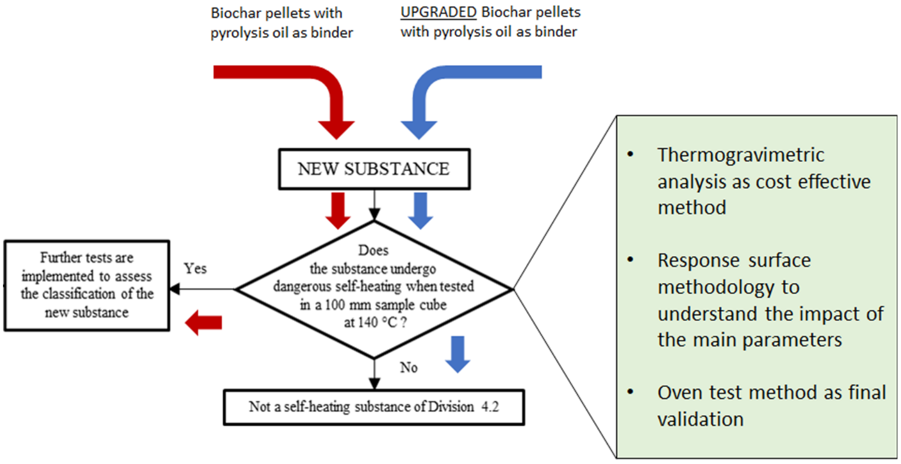
GRAPHICAL ABSTRACT



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ABSTRACT

Biochar obtained from biomass pyrolysis is a promising carbon neutral material which can be used in substitution of fossil coal and coke in metallurgical applications. Biochar's mechanical properties improve significantly without compromising reactivity, when upgraded by densification with pyrolysis oil and reheated. However, upgraded biochar pellets use in the industry is limited due to the risks associated with self-heating. This issue must be seriously considered for further industrial production of upgraded biochar pellets. Self-heating oven tests are generally time-consuming and limit the possibility of testing various potential solutions. The aim of this work was both to investigate the self-heating behavior of densified biochar and to possibly substitute the standard oven test with a fast and cost-effective thermogravimetric analysis. This was done by using Response Surface Methodology, where pyrolysis temperature, oil content and treatment temperature were selected as independent variables. By statistical analysis it was possible to understand that self-heating risk can be drastically reduced by upgrading the pellets at high temperatures (i.e. re-heating). In addition, through the analysis of the initial combustion temperature, the maximum weight loss rate and the activation energy

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(considered as responses of the model), it was possible to understand how to predict the results of the self-heating oven tests through thermogravimetric analysis.

1. Introduction

Greenhouse Gases (GHG) should be reduced implementing not a single but many possible sustainable solutions [1]. Due its carbonaceous nature, biochar might efficiently be applied in industries which are typically dependent on fossil coal and coke [2]. A specific sector, where biochar has been largely considered as a promising solution, is the metallurgical industry [3–8]. Unfortunately, the metallurgical application of biochar is limited by the uncompetitive price (in comparison to coal and coke) and insufficient mechanical characteristics [9]. The latter issue results in challenges both in handling, transportation, storage with a consequent increase of costs, due to mass losses [10]. There are problems also in the smelting furnace, where strong and stable materials are appreciated [8]. A solution has been suggested and investigated in [11], where biochar was densified using pyrolysis oil as binder and the produced pellets were newly pyrolyzed (re-heated). The process improved considerably density, mechanical durability and compressive strength of the biochar, without compromising fixed carbon content and reactivity, which are fundamental properties requested by the industry [12]. The same solution was further developed at an industrial scale in [13]. Recently, the industrial production of thermally treated biochar pellets with pyrolysis oil has been further investigated. However, it is still not very clear how densification and addition of pyrolysis oil may increase the risk of self-heating, which is the tendency of certain porous fuels to undergo spontaneous exothermic reactions, in absence of any external ignition, at relatively low temperatures and in an oxidative atmosphere [14]. When the heat generated cannot be entirely dispersed, the temperature increases, potentially leading to ignition [15,16]. Since the heat generation is related to the volume, while the heat losses to the surface, the risk increases when the material is stored in large piles, limiting the possibility to transport and store large volumes [17]. A test method evaluating self-heating risk is already available, and it is based on the combustion theory and empirical observations [18,19]. The method is based on heating the sample in an isothermal oven test, where volumes, temperatures and test times are fixed. Using this test it is possible to scale up the results to larger volumes and understand if a material can be stored and shipped safely [20]. This methodology can be followed by applying either the standard test EN 15,188 or the UN IMO test N.4 [21]. This kind of test has been used for several biomasses [20,22,23]. It was also applied to biochar in [15,21]. In particular, it was observed in [15], that the pyrolysis temperature has a strong impact on the self-heating behavior of biochar and, when the biomass is pyrolyzed at 450 °C, the resulting biochar has a relatively high risk of igniting. The standard oven tests, however, necessitate of a considerable amount of material and their completion requires generally 24 h. Other faster methods have been hence studied and applied [15]. For its simplicity and low demand in term of material and time, thermal analysis has been deeply studied as a feasible alternative to study self-heating of biomass [24–27]. This method focuses on assessing the self-heating behavior of a material by analyzing the kinetics involved in the oxidation reaction. However, it is not very clear how to associate the results to a volume, and therefore to a real risk in storage and shipping [15]. A deeper study on the thermal analysis results might therefore help in understanding how to make correspond the results of this test to those obtained with the oven. As a consequence of this, thermal analysis has been used as a reliable screening test before performing the more exhaustive oven test. In the present work, a new approach is tested to enlighten the relations between the oven test and thermal gravimetric analysis. Initially, the self-heating behavior of biochar pellets with pyrolysis oil as binder are tested by both UN test and thermogravimetric analysis (TGA). By the comparison of results, an experimental campaign is carried out using a thermogravimetric analyzer. To evaluate the complex phenomena affecting the combustion trends of the tested configurations, it has been previously decided to use Response Surface Methodology (RSM) [28]. As suggested in [29], RSM may be useful when the effects of process parameters are not easily distinguishable. This method aims to achieve the best system performance by describing the overall process through a mathematical model [30,31]. In the present work, this statistical model is used in a novel way to evaluate how to produce the biochar/oil pellets to limit the self-heating risk. The aim is to provide further knowledge about how to process biochar pellets blended with pyrolysis oils, in order to avoid self-ignition in the storing and shipping phase. By the knowledge of the authors, no works on this topic are available in literature. Moreover, a new approach to couple thermal analysis and oven test to analyze self-heating is proposed. This solution might facilitate the self-heating assessment of treated biochar pellets with a reduction of costs, easing their potential industrial production and application.

2. Material and methods

2.1. Feedstock and biochar production

Approximately 5 kg of industrially produced biochar pellets of metallurgical quality were acquired. They were made of softwood pyrolyzed at a temperature between 400 and 600 °C. Before pelletization, the biochar was blended with an industry type pyrolysis oil with a ratio between 20 and 60% of oil. The pellets were then further pyrolyzed in a second heat treatment at the same range of temperatures used in the first pyrolysis. Their average length was about 1.2 cm, as well as the average diameter. Throughout the work, these pellets are named as IBP1. Other biochar pellets were produced in-house, carefully choosing the feedstock and parameters so to have a product with characteristics similar to the provided pellets. A Norway spruce (*Picea abies*) tree was harvested from a local forest in Grimstad, Norway. The tree was felled and chipped. The wood chips were dried at 60 °C for 24 h and then stored in an air-tight tank at ambient temperature. The biochar was generated by the chips in a slow pyrolysis reactor. A modified *SQ 11* top loader furnace (Kittec, Germany) was used for the pyrolysis and a thermo-computer *TC 505* (Bentrup, Germany) was used to control the heating program of the furnace. A Silicon carbide retort was evenly filled up with approximately 100 g of chips and placed inside the furnace. It was then purged with a 40 ml/min nitrogen flow for 15 min before heating, to generate inert atmosphere in the reactor. The feedstock was heated up with a heating rate of 10 °C/min up to the desired temperature. Generally, the pyrolysis temperature used in this work were 450, 600 and 750 °C. The final temperature was kept for 1 h. During the experiment, the nitrogen flow was kept constant. At the end of the session, the feedstock was cooled down to ambient temperature and milled in a hammer mill *px-mfc 90 d* (Polymix, Germany), with a 2 mm sieve. The biochar powders were stored at ambient temperature in airtight boxes. A two stages condensation unit (with set temperature equal to 4 °C) was used to cool down the volatiles and gases leaving the reactor. The non-condensable products were expelled through a chimney. The condensable gases were collected in a quartz glass bottle, cooled down to ambient temperature and stored in air-tight containers at 4 °C, without any further treatment. The second heat treatment was performed at the same range of temperatures used for the pyrolysis and following the same method. Throughout the work, IBP1 treated at 600 °C is referred as IBPT.

2.2. Production of upgraded biochar pellets with pyrolysis oil as binder

Biochar pellets were obtained by using a compact hot single pellet press *EQ- HP-6T* (MTI, USA). Before pelletization, milled biochar was blended with pyrolysis oil at different ratios. For each configuration, the pyrolysis oil produced during the same pyrolysis process which produced the biochar was considered, so to simulate a realistic process chain. As explained in the supplementary information S1, the thermal degradation of pyrolysis oil is not particularly affected by the pyrolysis temperature. The oils produced at different temperatures can therefore be assumed to behave similarly. The blend was mixed, stirred and homogenized in a beaker for approximately 15 min. The pellets die had an inner diameter of 6.25 mm. The amount of mixture fed into the die of the pellet press was carefully regulated for each configuration so to have a maximum pellet length of 4.50 mm. The pelletizing pressure was set by a hydraulic piston to 128 MPa and kept for 10 s before releasing it [32]. Pressure was regulated by a load cell *CPX1000* (Dini Argeo, Italy) connected to a multifunction weight indicator *DFWLB* (Dini Argeo, Italy). The machine components were previously heated up to the operational pelleting temperature of 90 °C. After the extraction, pellets were cooled down to ambient temperature and stored in air-tight containers.

2.3. Biochar characterization

Proximate analysis was carried out following the standards EN 14774-2 for the moisture content, EN 15148 for the volatile matter and EN 14775 for the ash content. A *2400 Series II* CHNS/O Elemental Analyzer (PerkinElmer, USA) was used for the C–H–N ultimate analysis. Oxygen was computed by difference with the other elements. Sulphur content was assumed negligible. The higher heating value (HHV) of the biochar was measured in a *C 6000* (IKA calorimeter, Germany) bomb calorimeter. The characterization of the materials which were pelletized is shown in Table 1. A laser diffraction particle size analyzer *Mastersizer 3000* (Malvern, UK) was used to analyze the particle size distribution of the biochar before pelletization. The resulting distributions are presented in Fig. 1. All measurements were conducted in triplicate. The morphology and microstructure of selected materials were examined by a scanning electron microscopy/energy dispersive X-ray Spectroscopy (SEM/EDS) *SU-70* (Hitachi, Japan).

2.4. Thermogravimetric analysis

The thermal decomposition was performed by using the thermogravimetric instrument *TGA/DSC 1 SRTARe System* (Mettler Toledo, USA). The pellet was loaded into a 100 ml Al_2O_3 crucible. It was then heated up to 900 °C at a constant heating rate of 10 °C/min, with a constant dry air volume flow of 50 ml/min. The temperature of initial combustion (T_{ic}) and the temperature of maximum weight loss rate (T_{mwl}) were directly computed by analyzing the results. The T_{ic} was considered as the temperature at which the dry weight loss is 1%/min, while the T_{mwl} as the temperature characterized by the highest weight loss rate, as shown in the example presented in Fig. 2. Some pellets were also treated following the same methodology but substituting the air bottle with argon. The related observations are available in the Supplementary material S2. The activation energy of the reaction was extrapolated by plotting the variation of the specific reaction rate versus the sample temperature, in the range of temperatures where the reaction occurs, under the assumptions and methodology presented in [33].

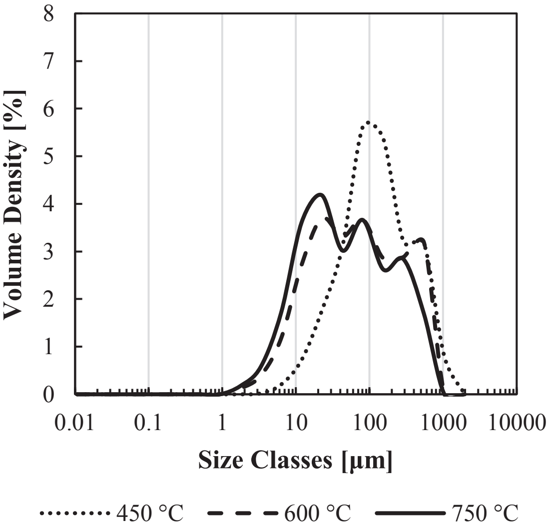

Fig. 1. Laser particle size distribution for the biochar produced, before pelletization.

2.5. Statistical model and desirability function

In order to analyze the possible correlations between the biochar pellets production factors and the effects on the self-heating risk behavior, Response Surface Methodology (RSM) with Box-Behnken experimental Design (BBD) was applied. Compared to other common experimental designs, BBD provides generally slightly and significantly higher efficiency [34], and therefore it was selected for this work. BBD

Table 1
Proximate analysis, ultimate analysis and high heating value (HHV), with related norms and machine, for the untreated spruce wood and for the spruce biochar produced in house at 450, 600 and 750 °C.

Material	Spruce					
Pyrolysis temperature [°C]	untreated	450	600	750	Standard	Instrument
Proximate analysis						LT40/11/P330 (Nabertherm, Germany)
Moisture [%wb]	8.6 ± 0.4	3.2 ± 0.7	5.0 ± 0.6	7.5 ± 0.6	EN 14774–2	
Volatile matter [%db]	80.6 ± 0.3	32.1 ± 0.5	14.6 ± 0.5	9.4 ± 0.3	EN 15148	
Fixed Carbon [%db]	18.6 ± 0.7	62.6 ± 0.7	78.1 ± 0.1	80.7 ± 0.6		
Ash [%db]	0.8 ± 0.3	2.0 ± 0.3	2.3 ± 0.3	2.4 ± 0.2	EN 14775	
Ultimate analysis					EN 16948	2400 Series II CHNS/O Elemental Analyzer (PerkinElmer, USA)
C [%daf]	53.2 ± 0.3	77.8 ± 0.6	89.0 ± 0.5	92.7 ± 0.5		
H [%daf]	6.1 ± 0.2	2.3 ± 0.4	3.1 ± 0.4	2.1 ± 0.3		
N [%daf]	0.1 ± 0.2	3.9 ± 0.2	2.7 ± 0.4	1.7 ± 0.2		
O [%daf]	40.6 ± 0.4	15.8 ± 0.5	5.1 ± 0.2	3.4 ± 0.5		
HHV [MJ/kg, db]	n.a.	29.1 ± 0.3	32.0 ± 0.4	31.9 ± 0.1	EN 14918	Mastersizer 3000 (Malvern, UK)

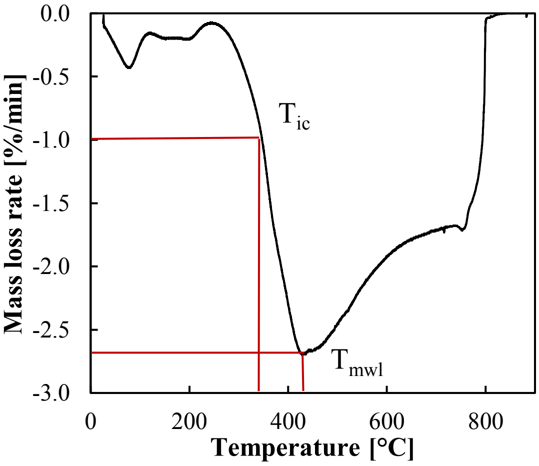

Fig. 2. Differential thermogravimetric (DTG) curve for biochar produced by pyrolysis at 450 °C. The temperature of initial combustion and maximum weight loss are reported.

is a three factors and three levels design, consisting of a replicated center point and a set of points lying at the midpoint of each edge of the multidimensional cube that defines the space of interest. A polynomial quadratic equation was applied to investigate the relationship between the variables and the responses. The independent variables and the associated coded levels that were used in the present work, are presented in Table 2. The pyrolysis temperature (X_1), the pyrolysis oil content (X_2), and the second heat treatment temperature (X_3) were assumed as the independent variables. Each independent variable was prescribed into three levels, coded −1, 0 and +1, corresponding to the minimum level, medium level, and maximum level. Each process factor level was carefully selected based on preliminary tests. For the analyzed biochar pellets, the responses were the initial combustion temperature (Y_1), the maximum weight loss temperature (Y_2) and the activation energy (Y_3).

The statistical model was implemented by *Minitab 17.1.0 software* (Minitab Ltd., Coventry, UK). To minimize the bias, 15 runs were selected randomly by the software. They were then carried out, with triplicate center points, in order to estimate the pure error. The combinations of independent variables for each run, together with the observed responses, are shown in Table 3. Analysis of variance (ANOVA) and regression analysis were carried out in order to investigate the statistical significance of the regression coefficients. This was done by performing the Fisher‘s F-test at 95% confidence level, following the method described in [29]. To better understand how self-heating risks could be minimized, multi-response optimization was applied. The multiple response problem was addressed by using the Derringer's desirability function based approach [35]. The method is described in a more exhaustive way in [13].

2.6. Self-heating substances classification test

A specific experiment was designed to test the self-heating behavior of the pellets, according to the classification of the Division 4.2, suggested by the International Maritime Organization (IMO, United Nations) [36]. The test aims at classifying substances in packing groups, which are related to the admissible shipping volumes. In the present work, only the first step was tested, because as shown in Fig. 3, if a new substance passes this step, it is not classified as a self-heating substance of Division 4.2. A stainless-steel cubic basket of 100 mm side with a mesh opening of 0.05 mm was used. The basket sample was housed in a slightly larger cubic container with a mesh opening of 0.60 mm and placed into a modified *SQ 11 top loader furnace* (Kittec, Germany). Air was forced in by an opening placed at one side of the furnace. The furnace was set up to a temperature of 140 °C which was maintained constant for 24 h. A thermo-computer *TC 505* (Bentrup, Germany) controlled with an application designed on the software LabVIEW 2019 (National Instrument, USA) was used to regulate the temperatures inside the furnace. The temperatures were measured by four Chromel-Alumel thermocouples (type k). Despite the test requires respectively only one thermocouple, an additional one was used to provide redundancy. The data were collected with a frequency of 1 Hz. If the difference between the temperature of the sample and the temperature of the furnace was exceeding 60 °C (i.e. sample temperature equal to 200 °C), the test was interrupted and considered as not passed. If the threshold temperature difference was not reached within 24 h, the test was considered as passed.

3. Results and discussion

3.1. Standard test and TGA for industrial biochar pellet

The industrially produced pellets IBP1 were tested with the IMO test. As previously mentioned, these pellets were known not to pass the test. As comparison, another biochar material, which previously passed the test was analyzed. This material was named IBP2 and was provided by the same supplier, which currently uses as Carbon source in a metallurgical application. IBP2 is not pelletized and does not include pyrolysis oil, but it was produced at similar treatment temperatures, in comparison to IBP1. Fig. 4 shows the two different trends for the IMO test performed on IBP1 and IBP2. The results confirmed the initial expectations. The two materials were also compared through a TGA test. Fig. 5 reports the respective normalized mass loss rates per minute. For both materials, a first peak is tracked at around 100 °C, showing water evaporation (water is included into the pyrolysis oil). Secondly, the oxidation phase is distinguished by an evident single peak. Combustion ends with the burn-out of the biochars. Generally the trends are similar to what is observed at the same range of temperatures in [15,37]. According to [38], the characteristic single peak associated to the combustion of biochar is related to the high content of fixed carbon, which makes the material react fast. This behavior is different from the conventional combustion of biomasses, where different peaks are observable and they are linked to the combustion of hemicellulose, cellulose and lignin [20].

For both IBP1 and IBP2, T_{ic}, T_{mwl} and E_a were computed. The two materials present divergent trends: IPB1 is characterized by high E_a and low T_{ic} and T_{mwl}, while IPB2 has high combustion temperatures and low activation energy. The obtained parameters are listed in Table 4.

Low T_{ic} and T_{mwl} are generally associated to a higher predisposition to self-ignition [39]. These value are close to what observed in [38]. For both materials, the activation energy is low, when compared to other tested chars [40,41]. However, in these works, biochar was produced at considerably higher pyrolysis temperatures. Instead, the activation energy values are similar to what observed in [42], where the pyrolysis temperatures were lower. Moreover, by reducing the porosity and reactive surface of the material, the activation energy should generally improve through pelletization [43]. Nevertheless, as observed in [44,45], the computed activation energies of densified biomass might still be very low. Besides, in [46], it was observed that densification

Table 2
Investigated parameters used in the experimental design and their levels (coded and uncoded).

Independent variables	Symbols	Coded levels		
		−1	0	1
Pyrolysis temperature [°C]	X1	450	600	750
Pyrolysis oil content [%]	X2	20	30	40
Second heat treatment temperature[°C]	X3	450	600	750

Table 3
Box-Behnken design and experimental results for each response.

Run order	X_1 [°C]	X_2 [%]	X_3 [°C]	T_{ic} [Y_1]		T_{mwl} [Y_2]		E_a [Y_3]	
				Actual [°C]	Predicted [°C]	Actual [°C]	Predicted [°C]	Actual [kJ/mol]	Predicted [kJ/mol]
1	450	30	450	307.17	309.26	375.50	378.72	21.52	22.16
2	450	20	600	341.50	339.75	402.50	399.07	44.96	45.55
3	450	40	600	336.50	334.74	405.67	403.96	54.38	52.83
4	450	30	750	368.67	368.48	425.33	428.22	37.25	37.22
5	600	20	450	351.33	349.83	420.67	421.43	67.02	65.46
6	600	40	450	346.50	345.23	421.83	420.98	48.19	48.80
7	600	30	600	361.50	357.48	431.00	429.91	70.74	71.17
8	600	30	600	356.50	357.48	428.00	429.91	71.04	71.17
9	600	30	600	355.83	357.48	430.00	429.91	72.20	71.17
10	600	20	750	385.00	385.37	456.67	458.03	67.41	66.47
11	600	40	750	391.17	391.77	468.33	468.08	59.04	60.27
12	750	30	450	379.33	378.61	449.00	446.58	37.16	36.85
13	750	20	600	384.17	385.00	457.17	459.37	68.93	70.13
14	750	40	600	391.00	391.82	460.17	464.08	40.92	39.99
15	750	30	750	404.50	401.47	483.50	480.78	35.25	34.27

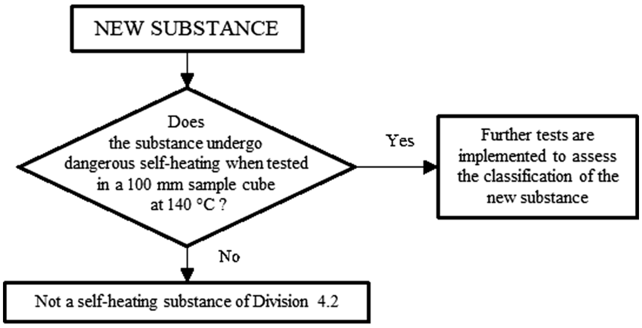

Fig. 3. First step of the classification of self-heating substances of Division 4.2, according to IMO (UN) [38], modified.

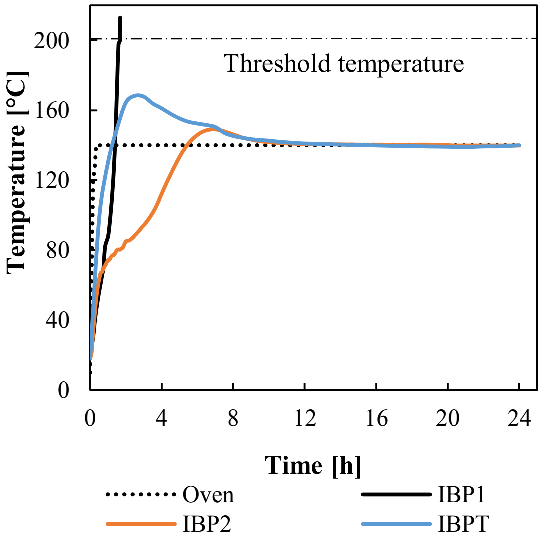

Fig. 4. Comparison between IBP1, IBP2 and IBPT in the UN-IMO self-heating test with 10 cm side cube.

tendentially decreases the T_{ic} and T_{mwl} of a material, in an extent strictly affected by the type and content of binder. According to the combustion curves presented in Fig. 5, there are instead not evident specific trends that may be directly associated to pyrolysis oil. Also in [45], the addition of coal tar as binder did not affect particularly the characteristics of the combustion. It should be considered that pyrolysis oil included in IBP1 underwent a further pyrolysis at mild temperatures. Hence, that pyrolysis oil partially volatized and only the carbonized fractions, which resembles char, is therefore present [32]. From the combination of the standardized test and the TGA test, it could hence be inferred that the densification with addition of pyrolysis oil, which brings to a reduction of porosity and surface area during the pelletization phase [13], is the major factor affecting the self-heating behavior of the analyzed pellets. The ratio between volume and external surface increases, resulting in a lower release of the generated heat.

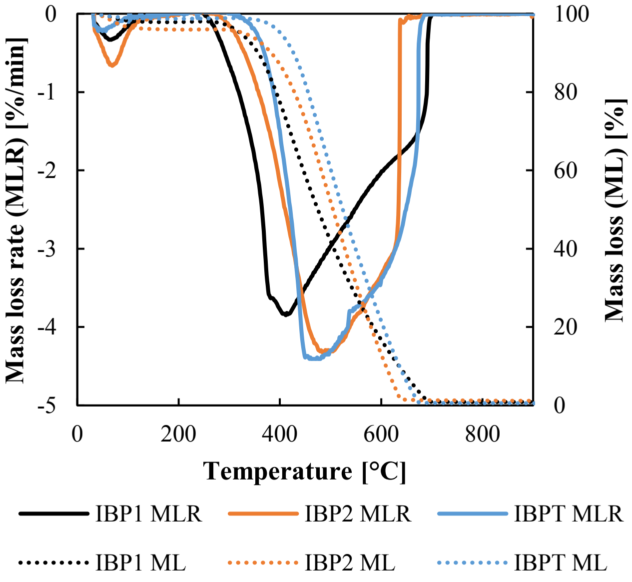

Fig. 5. Comparison in TGA between IBP1, IBP2 and IBPT.

Table 4
Temperature of initial combustion (T_{ic}), maximum weight loss temperature (T_{mwl}) and activation energy (E_a) for the materials IBP1, IBP2 and IBPT.

Material	T_{ic} [°C]	T_{mwl} [°C]	E_a [kJ/mol]
IBP1	308.6 ± 1.2	383.6 ± 3.6	59.6 ± 2.6
IBP2	348.7 ± 1.5	481.5 ± 2.7	38.2 ± 2.2
IBPT	367.3 ± 2.0	459.4 ± 4.3	44.1 ± 1.8

3.2. Box–Behnken statistical analysis

The self-heating behavior was then further investigated by the statistical analysis of the produced biochar pellets. In order to evaluate the effects of pyrolysis temperature (X_1), pyrolysis oil content (X_2), and second heat treatment temperature (X_3) on initial combustion temperature (Y_1), maximum weight loss temperature (Y_2), and activation energy (Y_3), the experimental data shown in Table 3 were subjected to regression analysis. The final predicted process models were obtained as:

$$Y_1 = 246.6 + 0.3069X_1 - 4.92X_2 - 0.0001X_3 + 0.000039X_1X_1 + 0.0447X_2X_2 + 0.000271X_3X_3 + 0.001972X_1X_2 - 0.000404X_1X_3 + 0.001833X_2X_3 \quad (1)$$

$$Y_2 = 293.2 + 0.486X_1 - 3.87X_2 - 0.189X_3 - 0.000152X_1X_1 + 0.0513X_2X_2 + 0.000315X_3X_3 - 0.00003X_1X_2 - 0.000170X_1X_3 + 0.00175X_2X_3$$

$$Y_3 = -665.4 + 1.5687X_1 - 0.451X_2 + 0.8973X_3 - 0.001037X_1X_1 + 0.04294X_2X_2 - 0.000676X_3X_3 - 0.006238X_1X_2 - 0.000196X_1X_3 + 0.001743X_2X_3 \quad (3)$$

The adequacy of the models was analyzed through ANOVA analysis and the results are presented in Table 5. The calculated F-values of 120.83, 84.14, and 166.32 for Y_1, Y_2, and Y_3, respectively demonstrated that the models were highly significant ($p \leq 0.001$) because there is only a 0.01% chance that these large F-values can occur due to noise. The values of R^2 were 0.9954. 0.9934, 0.9967 for Y_1, Y_2, and Y_3, showing that only 0.0046%, 0.0066%, and 0.0033% of the total variations were not explained by the regression models. Furthermore, the values of R^2_{adj} (0.9872, 0.9816, 0.9907) were very high and close to the values of R^2, confirming that the regression models were highly significant. The acceptability of the quadratic models was also confirmed by the lack of fit (LOF) test which is a measure of the failure of a model to predict data in the experimental domain at which points are not included in the regression. A p-value higher than 0.05 means that LOF is insignificant due to relative pure error. Thus, the lack of fit p-values (0.593, 0.594 and 0.139 for each response) confirms that the models can be effectively employed for the prediction.

3.3. Effect of independent variables on the responses

According to the F-values and p-values shown in Table 5, it can be noted that for the initial combustion temperature X_1, X_3, X_2^2, X_3^2, X_1X_3 are significant model terms because their p-values were higher than 0.05. The positive sign in the model equation indicates synergistic effects and the negative sign means antagonistic effects on the response. Therefore, from Eq. (1) pyrolysis temperature has a positive effect on the initial combustion temperature, while oil content and second heat treatment have a negative effect. However, the positive sign of quadratic effect of second heat treatment temperature (X_3X_3) indicates that initial combustion temperature decreases up to a certain threshold with increasing SHT temperature after which it increases. From the F-values, it can be noted that the pyrolysis temperature had a greater effect on the initial combustion temperature. To investigate the interactive effect of two factors on initial combustion temperature, contour plots were drawn maintaining the third factor at constant level equal to its middle value (i.e. X_1: 600 °C, X_2: 30%, X_3: 600 °C). Fig. 6 shows clearly that the initial combustion temperature increased with increase in pyrolysis and second heat temperatures while the oil content has little influence on this response. In particular, it can be noted that the effect of the oil content is different inside its range of variation because T_{in} has a minimum when the oil content is equal to 30%. However, as a result of the interactive effects, the maximum value of the response (404.5 °C) was obtained when all three independent variables were at their maximum values.

A similar trend was obtained for the maximum weight loss temperature, for which Eq. (2) shows that linear pyrolysis temperature, linear second heat treatment temperature, and quadratic pyrolysis temperature terms had statistically significant effects on the response. Eq. (2) is depicted as two-dimensional contour plots in Fig. 7. The highest values of initial combustion temperature were reached at the high levels of pyrolysis temperature and second heat treatment temperature. Oil content seems to show a quadratic behavior where the T_{mwl} reaches a minimum at approximately 30%. However, an important result from the ANOVA analysis is that the percentage of pyrolysis oil had no significant linear, quadratic and interactive effects on the maximum weight loss temperature.

As regards the activation energy, all linear, quadratic, and interaction terms were significant. In detail, having the highest *F*-value and regression coefficient, the pyrolysis temperature affected most significantly the activation energy. The oil content, and the second heat treatment temperature also significantly influenced activation energy, even though their influence was lower than that of the pyrolysis temperature. Furthermore, the negative coefficients of the quadratic terms $X_1{}^2$ and $X_2{}^2$ denoted that there is a possible point of inflexion after which the independent variables have a negative or positive effect on the activation energy. As shown in Fig. 8, E_a increased with an increase in pyrolysis temperature and second heat treatment temperature both from nearly 450 to 600 °C; nevertheless, beyond 600 °C, activation energy decreased with increasing both temperatures. Fig. 8 shows also that in order to achieve maximum activation energy the oil content should be less than about 33%. Generally, it comes out that responses tend to get maximized when the temperatures of pyrolysis and second heat treatment are high, and the oil content is low.

Table 5
ANOVA of response surface quadratic models.

Source	DF	F-value	Prob > F
Initial combustion temperature			
Model	9	120.83	< 0.0001
X_1	1	618.08	< 0.0001
X_2	1	0.15	0.717
X_3	1	399.77	< 0.0001
X_1^2	1	0.34	0.586
X_2^2	1	8.65	0.032
X_3^2	1	16.09	0.010
X_1X_2	1	4.11	0.098
X_1X_3	1	38.77	0.002
X_2X_3	1	3.55	0.118
Lack of fit	3	0.81	0.593
$R^2 = 0.9954$. $R^2_{adj} = 0.9872$			
Maximum weight loss temperature			
Model	9	84,14	< 0.0001
X_1	1	490,56	< 0.0001
X_2	1	3,05	0,141
X_3	1	235,40	< 0.0001
X_1^2	1	2,92	0,148
X_2^2	1	6,56	0,051
X_3^2	1	12,53	0,017
X_1X_2	1	0,00	0,984
X_1X_3	1	3,98	0,103
X_2X_3	1	1,86	0,093
Lack of fit	3	9,89	0.594
$R^2 = 0.9934$. $R^2_{adj} = 0.9816$			
Activation energy			
Model	9	166,32	< 0.0001
X_1	1	29,22	0,003
X_2	1	105,09	< 0.0001
X_3	1	31,55	0,002
X_1^2	1	805,82	< 0.0001
X_2^2	1	27,31	0,003
X_3^2	1	342,64	< 0.0001
X_1X_2	1	140,50	< 0.0001
X_1X_3	1	31,21	0,003
X_2X_3	1	10,97	0,021
Lack of fit	3	6,35	0,139
$R^2 = 0.9967$. $R^2_{adj} = 0.9907$			

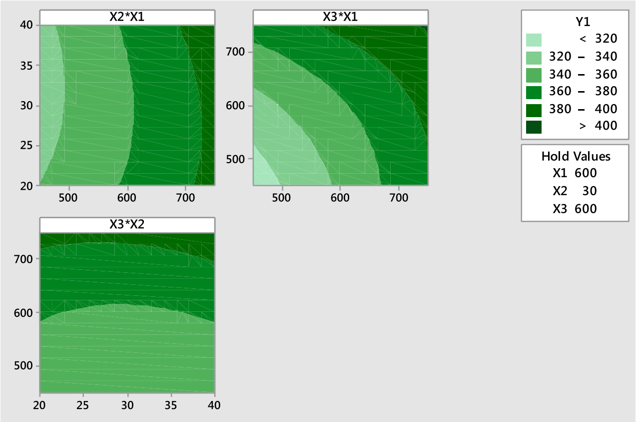

Fig. 6. Contour plots of the initial combustion temperature.

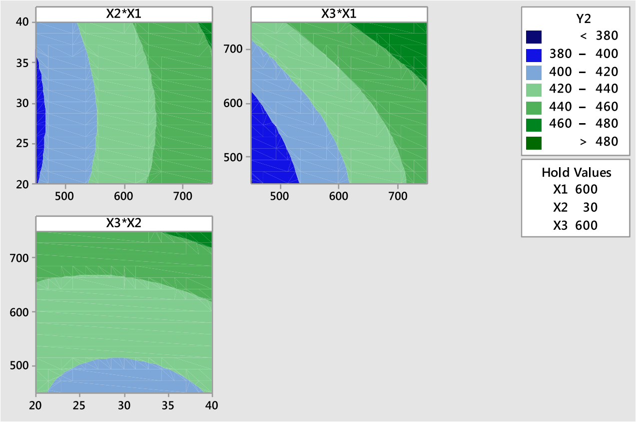

Fig. 7. Contour plots of the maximum weight loss temperature.

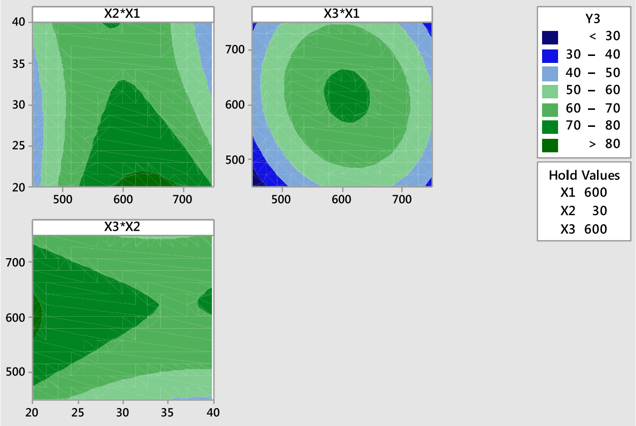

Fig. 8. Contour plots of the activation energy.

3.4. Optimization of responses using the desirability function approach

In the production of biochar pellets, high initial combustion temperature, high maximum mass loss rate temperature and high activation energy are desired in order to decrease the self-heating risk. However, the optimization of all responses under the same operative conditions is difficult, because their intervals of variation are different. For this reason, the multi-response optimization for T_{in}, T_{mwl}, and E_a was carried out by desirability function approach. Composite desirability evaluates how the settings optimize a set of responses overall [29]. In this study, the same weight for all responses and an importance parameter equal to 1 were assumed. As it can be noted from the Supplementary material Fig. S3, the composite desirability (D) of the optimization was 0.8751, that was quite close to the ideal value of 1, which denotes that the chosen optimum settings were in favor of all responses. In particular, the maximum T_{in}, T_{mwl}, and E_a were found to be 390.2 °C, 467.2 °C, and 68.4 kJ/mol, respectively at an optimal parametric combination of pyrolysis temperature = 698.5 °C, oil content = 20%, and second heat treatment temperature = 716.7 °C.

3.5. Discussion over the effects of the independent variables

As support to the statistical analysis, further analyses were taken to consolidate the arisen considerations. Fig. 9 shows the effect of the pyrolysis temperature on the structure of pellets. The differences at different magnitude between pellets produced with biochar at 450 °C (Fig. 9.A-B) and 600 °C (Fig. 9.C-D) are shown. The formers are less compacted, and the particles are tendentially bigger and less porous, as previously shown in Fig. 1. Porous sections are more visible for the biochar produced at 600 °C. Pellets with biochar produced at 450 °C are less compact and less porous and have higher propensity to ignite. The result suggests porosity has a major impact in determining the self-heating behavior, compared to densification, as commented in [47]. Fig. 10 shows instead the impact of using pyrolysis oil as binder. When the binder is included, the reaction starts at lower temperatures and proceeds at a slower pace, without manifesting a rapid oxidation. Pyrolysis oil covers the pores, limiting the transfer of heat. Therefore, the material will be heated up and get ignited faster. The oxidation then will proceed slower since less surface is available. As confirmation, when the specific exothermic energy was computed, both curves have similar results (ca. 10 kJ/kg). Once the pellets are newly treated with re-heating, the porosity increases and the ratio between volume and external surfaces decreases, with direct benefit in terms of higher heat losses. This is clearly shown in Fig. 11. Pellets with biochar produced at 450 °C present a more compact and porous structure, when treated at 600 °C (Fig. 11.A), in comparison to Fig. 9.B. Fig. 11.B-D show instead that a fraction of the pyrolysis oil got volatized and parts of it are carbonized in the newly open porous surface.

3.6. Analysis of the treated industrial pellets

According to the results obtained by the statistical analysis, the industrial pellets IBP1 were further treated by a second heat treatment at 600 °C (IBPT). The idea was to intervene on the pellets, to possibly increase the responses. IBPT was then further analyzed by TGA. The normalized mass loss rate per minute is shown in Fig. 5, in comparison to IBP1 and IBP2. Once treated, IBPT differ from IBP1, approaching the trend observed with IBP2. Both T_{ic} and T_{mw} increased up to 367.3 ± 2.0 °C and 459.4 ± 4.3 °C, respectively. Instead, the activation energy E_a decreased to 44.1 ± 1.8 kJ/mol. These values are compared to what obtained with IBP1 and IBP2 in Table 4. Despite that the statistical results showed a correlation between the increase of E_a and the increase of second heat treatment temperature, IBPT is characterized by a lower activation energy than IBP1. However, if the contour plot in Fig. 8, showing the effect on the activation energy of the binder and the second heat treatment, is considered, it can be noticed that easily distinguishable patterns are not present. It is therefore complex to predict the behavior outside the selected range of binder content. The oils used in IBP1 were produced by an optimized industrial process, and they might therefore present a lower water content compared to the lab-produced pyrolysis oils. At fixed weight, the former ones might have a higher organic compounds content. The actual oil content in IBPT could therefore lay outside the selected range, and above 40%. As observed in [13], oil as binder tends to provide negative effects on pellet quality when the content is too high. This result implies that the influence of pyrolysis oil on the activation energy represents an interesting topic for further works. However, if IBPT is compared to IBP2, which is considered no self-heating risk material, values of T_{ic}

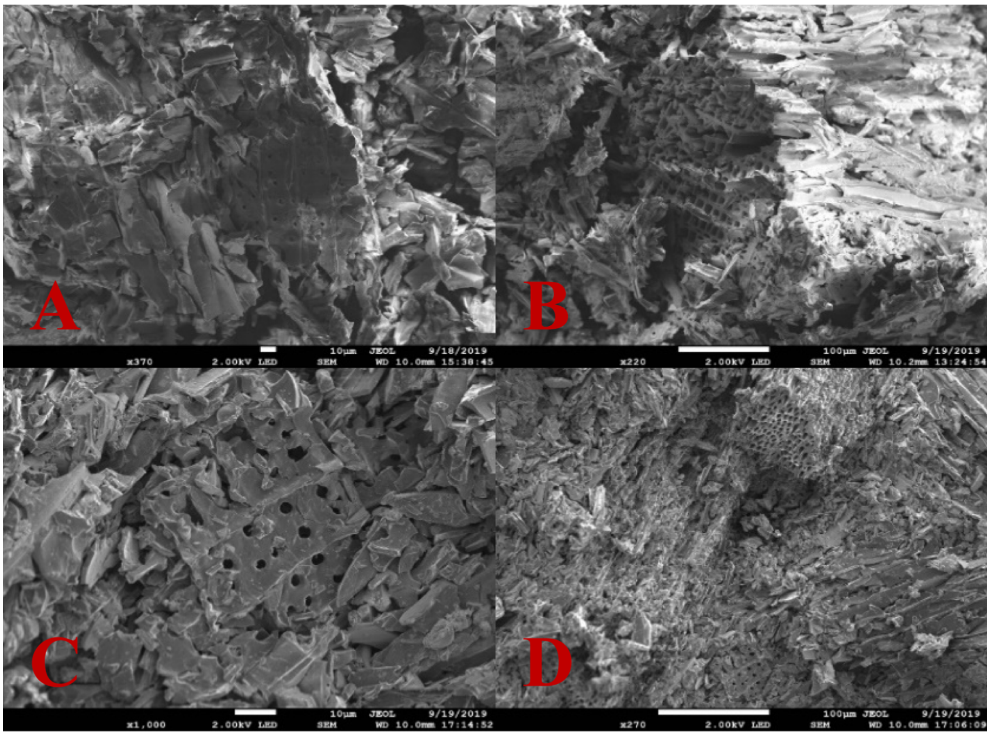

Fig. 9. Scanning electron microscope (SEM) photos for: biochar produced at 450 °C, blended with 30% (A) and 20% (B) of pyrolysis oil; biochar produced at 600 °C, blended with 30% of pyrolysis oil (C-D).

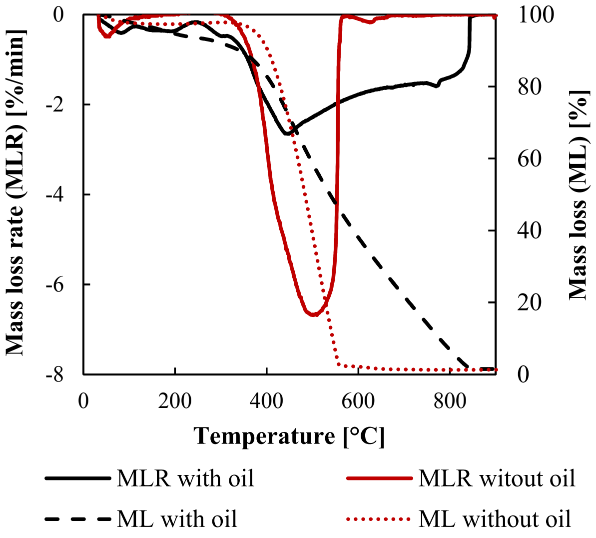

Fig. 10. Comparison in TGA between pellet with biochar produced at 600 °C, with and without pyrolysis oil as binder (30%).

differ of +5.1%, values of T_{mwl} differ of −4.9% and values of E_a differ of −13.6%. This suggests a low predisposition for self-heating. As previously observed, when pyrolysis oil is used as binder, a further pyrolysis treatment enables the partial volatilization of it, with a consequent increase of porosity and surface area. The material can hence dissipate heat faster, delaying the oxidation process and the risk of self-heating. IBPT was also tested by IMO procedure. The result is presented in Fig. 4. After the treatment, the material can successfully pass the test and it is not classified as self-heated material. Such result leads to some important considerations. When pyrolysis oil is used as binder, a second heat treatment at high temperatures is highly recommended, since the self-heating risk drastically drops. Considering that the coupling of oil and treatment was also observed to be associated to a strong improvements in mechanical properties [13,32], this result offers a further confirmation of the utility of processing a second heat treatment for this kind of biochar pellets. The direct cost related to the inclusion of a further heat treatment, might be balanced by evident benefits both in the application and in the transportation and storage of biochar pellets. Moreover, according to the results, T_{ic} and T_{mwl} may be key factors associated to self-heating behavior, while the relation to activation energy is less clear. The results legitimate the TGA as a useful screening test before performing the standardized tests for biochar, with a consequent reduction in research and development (R&D) costs. This possibility was hinted in [15], but not clearly showed.

3.7. E_a vs. T_{mwl} graph for self-heating risk evaluation

A graph, including the values of E_a and T_{mwl} for all the configurations analyzed in this work, was built and it is presented in Fig. 12. This graph was used upon the idea of simplifying what has been discussed so far and defining an easily usable and interpretable criterium to assess the self-heating risk of biochar pellets. In [27], a similar diagram was presented and different categories of risk were listed, according to values obtained from several types of coal and biomass. These materials are characterized by lower values of E_a and T_{mwl} than those analyzed in the present work. According to [27], the self-heating risk decreases at higher T_{mwl}. The graph must therefore be adjusted accordingly. This was done, for example, in [25], where new areas or risk were suggested. Similar considerations were used in [48]. None of these works studied either biochar or densified materials. Hence, according to the assumptions which were drawn in the mentioned literature, a new risk graph was built up. The aim is to adjust the diagram to make it suitable to assess the self-heating behavior of biochar pellets. The graph in Fig. 12 locates materials in different areas of risk, considering their values of E_a and T_{mwl}. The areas or risk are divided in: very high, high, low, very low; according to the tendency pellets had to self-ignite in the oven test. In particular:

- the very high risk and high risk areas are traced considering the

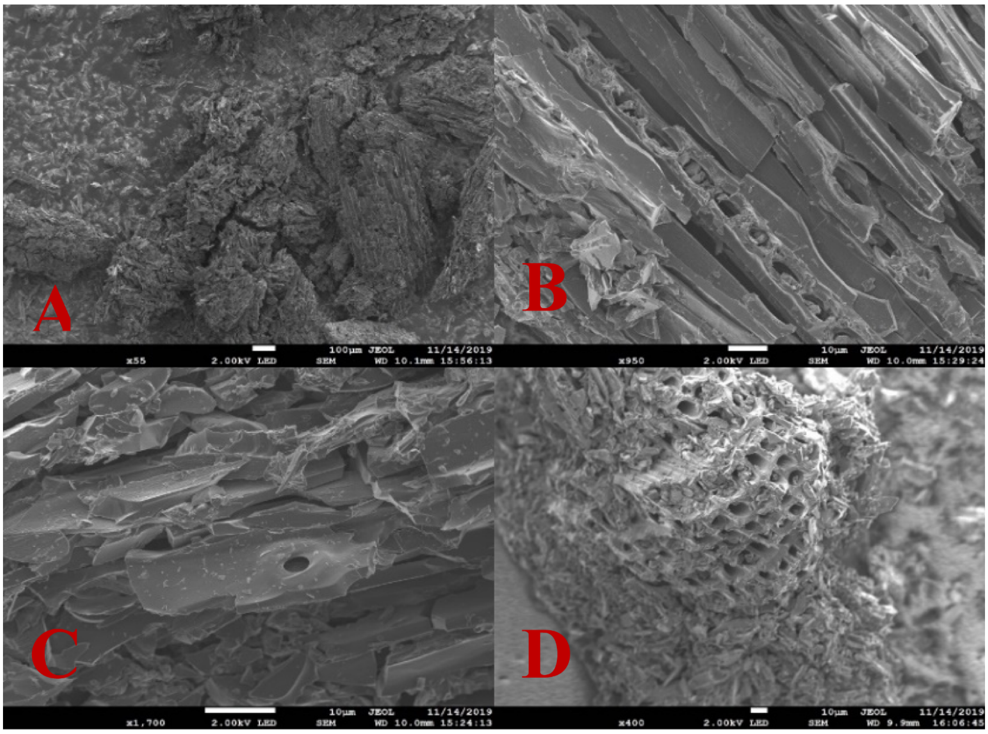

Fig. 11. Scanning electron microscope (SEM) photos for: biochar produced at 450 °C, blended with 30% of pyrolysis oil, treated at 600C (A); biochar produced at 600 °C, blended with 30% of pyrolysis oil, treated at 600 °C (B-C); biochar produced at 750 °C, blended with 30% of pyrolysis oil, treated at 750 °C (D).

values of E_a and T_{mwl} of two selected materials. The high risk area is limited by the values obtained from the TGA of IBP1. The very high risk region was instead built according to the tests carried out with a further provided material labelled as IBP3. This material was industrially produced in the same way of IBP1 by the same provider, with the addition of a further curing treatment. From preliminary studies, IPB3 provided the highest tendency to ignite.

- The low and very low risk areas are marked considering exclusively the T_{mwl}, because its effect on self-heating behavior is considered predominant over E_a. The low risk and the very low risk areas are limited by IBP2 and IBPT, respectively.
- Between the high risk and the low risk areas, the findings were not enough to predict successfully the oven test response. This zone is therefore considered as an uncertainty area, where TGA cannot detect precisely the outcome of the oven test.

IBP1, IBP2, IBP3 and IBPBT were used as benchmark since their inclination to self-heating was assessed by standardized tests. Moreover, as they are currently produced industrially, they might provide relevant information, once other materials are analyzed. According to Fig. 12, some considerations can be extracted. Pellets including biochar produced at 450 °C must undergo a second heat treatment at least at 600 °C to move outside the high risk area. At the same time, even if treated at 600 °C, the pellets with biochar produced

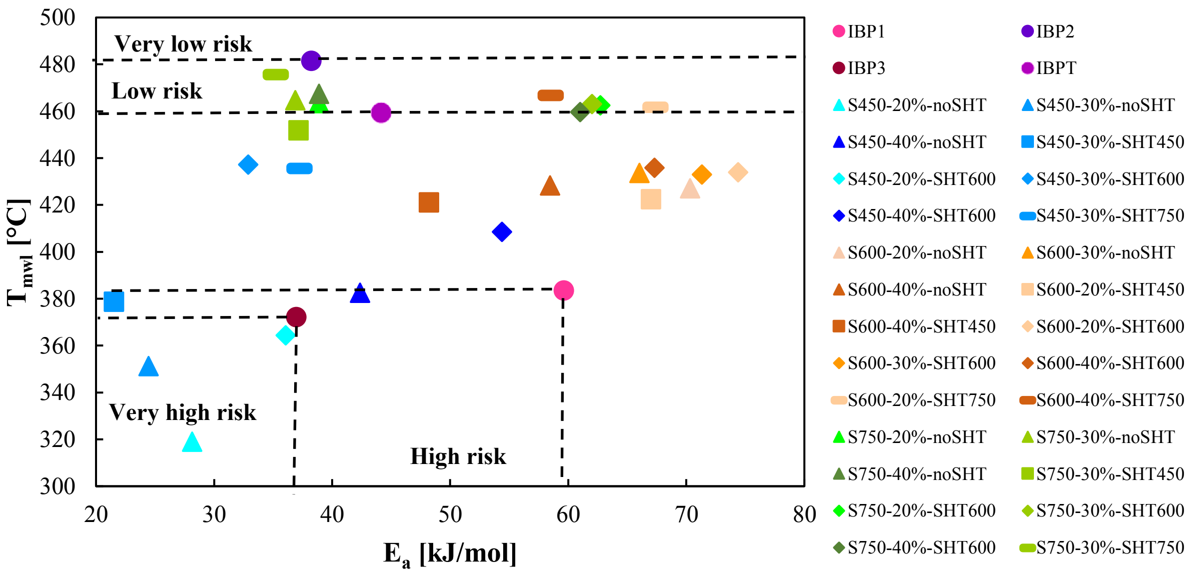

Fig. 12. Activation energy (E_a) vs Maximum weight loss temperature (T_{mwl}) graph, associated to suggested risk areas based upon all the configurations analyzed throughout this work.

at 450 °C and with 20% of pyrolysis oil as binder have high self-heating risk. It is possible that the oil content was not enough to affect significantly the structure of the pellets. The porosity of the re-heated biochar pellets is therefore yet similar to the untreated biochar. When biochar was produced at 600 or 750 °C, the risk is tendentially lower. In this case, it can be observed that all the combinations, having at least either pyrolysis or second heat treatment carried at 750 °C, are placed in the nearby of the suggested low risk line. These results confirm the importance of processing the heating treatments at high temperatures, so to limit the tendency of pellets to self-ignite. The effect of pyrolysis oil as binder varies according to the initial pyrolysis temperature. For high pyrolysis temperatures, an increase of oil content leads to a decrease of activation energy, without having an observable impact on the maximum weight loss temperature. When the pyrolysis temperature is 450 °C, the effect of the oil content is less clear and should be addressed in further works. These results may be useful to adjust the process parameters of pellets production, according to their possible place in the graph.

4. Conclusions

The statistical analysis permitted to identify the main variables, which affect the self-heating behavior of upgraded biochar pellets blended with pyrolysis oil. It was found out that it is possible to intervene on the self-heating behavior of biochar pellets by choosing carefully the temperatures in pyrolysis and in the second heat treatment. Upgraded biochar pellets present a lower self-heating risk, if one of the heat treatments is processed at least at 600 °C. The findings were then further validated by a standardize self-heating test. It was observed that pellets, which previously did not pass the test, could successfully pass it, once re-heated at 600 °C. The result legitimates the analysis and observations obtained by the thermogravimetric experiments, as a valid and useful feedback to understand how a material may reacts in the standardized test. In this peculiar case, the TGA tests helped in rapidly finding a solution about an existing problem experienced at an industrial scale. This work is therefore intended to show two novel and important findings:

- biochar pellets blended with pyrolysis oil have been previously demonstrated to offer good quality in terms of mechanical properties. However, the use of pyrolysis oil as binder it is associated to an increase of risk of self-ignition. In the present work, it was observed that the self-ignition behavior of biochar pellets blended with pyrolysis oil is strongly affected by the pyrolysis temperature and it is possible to decrease the risk of self-ignition by newly thermally treating the pellets with a further pyrolysis at high temperatures.
- TGA can provide important information about the self-heating behavior of biochar pellets, and in general of a material. This option is strictly related to a reduction of costs in terms of time and material, enabling the possibility of testing a more extended set of configurations both at a research and industrial scale.

Moreover, a risk tendency graph was built upon the obtained results. This graph is not intended to be exhaustive and complete but can potentially support further developments on industrial use of biochar pellets.

CRediT authorship contribution statement

Lorenzo Riva: Conceptualization, Methodology, Software, Validation, Investigation, Data curation, Writing - original draft. **Alessandro Cardarelli:** Validation, Investigation, Software, Data curation, Writing - original draft. **Geir Johan Andersen:** Conceptualization, Resources, Methodology. **Therese Videm Buø:** Conceptualization, Resources, Methodology. **Marco Barbanera:** Visualization, Software, Formal analysis, Writing - original draft. **Pietro Bartocci:** Data curation, Supervision, Writing - review & editing. **Francesco Fantozzi:** Supervision, Resources. **Henrik Kofoed Nielsen:** Supervision, Resources, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2020.118395.

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Supplementary Material

S1. In Fig. S1, the normalized mass loss and the normalized mass loss rate per minute for pyrolysis oil produced at 450, 600 and 750 °C are shown. The cruves were obtained following the method described in the manuscript. In Fig. S1(a), it is possible to observe that the oxidation of the oils seems not to be affected particularly by the pyrolysis temperature. When the curves are compared, pyrolysis oil produced at 750 °C starts oxidizing at a slightly lower temperature, while the pyrolysis oil produced at 450 °C burns off at a bit lower temperature. Similar observations can be drawn by observing Fig. S1(b). The only noteworthy behavior is associated to the pyrolysis oil produced at 450 °C, since it reaches the temperature of maximum weight loss at higher rates. This trend explains why the oxidation of this oil concludes faster. However, it is easily observable that both the temperature of initial combustion and the temperature of maximum weight loss are hardly distinguishable between the curves. It is therefore reasonable to assume that the pyrolysis oil is not significantly affected by the pyrolysis temperature, when the combustion behavior is analyzed by thermal analysis.

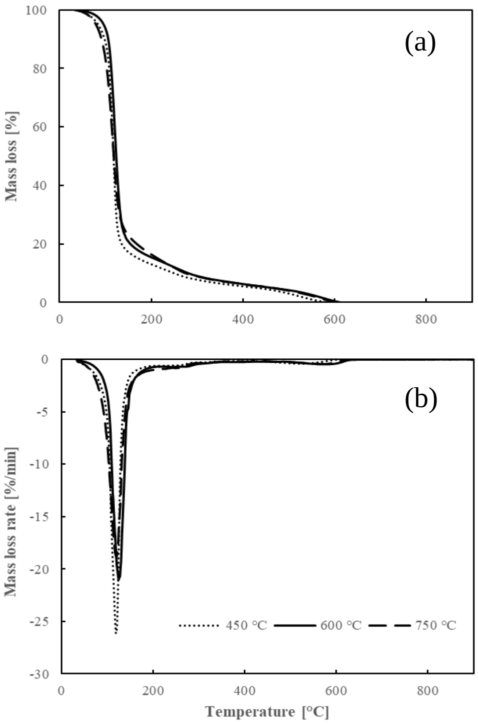

Fig. S1. Thermal analysis of pyrolysis oil produced at 450, 600 and 750 °C, with normalized mass loss in (a) and normalized mass loss rate in (b).

S2. Fig.S2 shows the normalized mass loss and the normalized mass loss rate per minute for the combustion and pyrolysis of pellets with biochar produced 750 °C and 30% of pyrolysis oil as binder. The methods are described in the manuscript. Observing Fig. S2(a), combustion and pyrolysis are simlarly characterized by an initial phase concluding at ca. 250 °C. In this phase, the main reactions occuring are evaporation of the water included in the pyrolysis oil and volatization of organic matter. At higher temperatures, the oxidation starts and the curves clearly differ. This behavior is confirmed by the mass loss rate per minute trends shown in Fig. S2(b). After a common initial phase, the oxidation reaction starts leading to a rapid increase of the rate, while the pyrolysis curve is mainly flat, with the excpetion of an increase of rate after 600 °C, due to a further carbonization of the biochar. By Fig. S2, it is therefore possible to state that what observed while combusting is not related to pyrolysis.

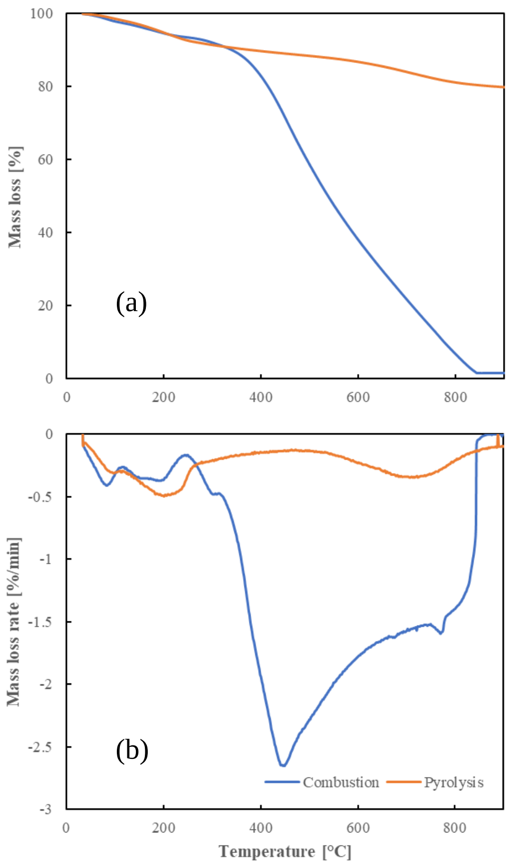

Fig. S2. Thermal analysis for combustion (blue) and pyrolysis (orange) of with biochar produced 750 °C and 30% of pyrolysis oil, , with normalized mass loss in (a) and normalized mass loss rate in (b).

S3. Supplementary material for the optimization test is presented in Fig. S3. The desirability functions for each response as function of each variables are shown, as well as their indexes. Fig. S3 shows also the composite desirability functions and the optimum values for the indipendent variables.

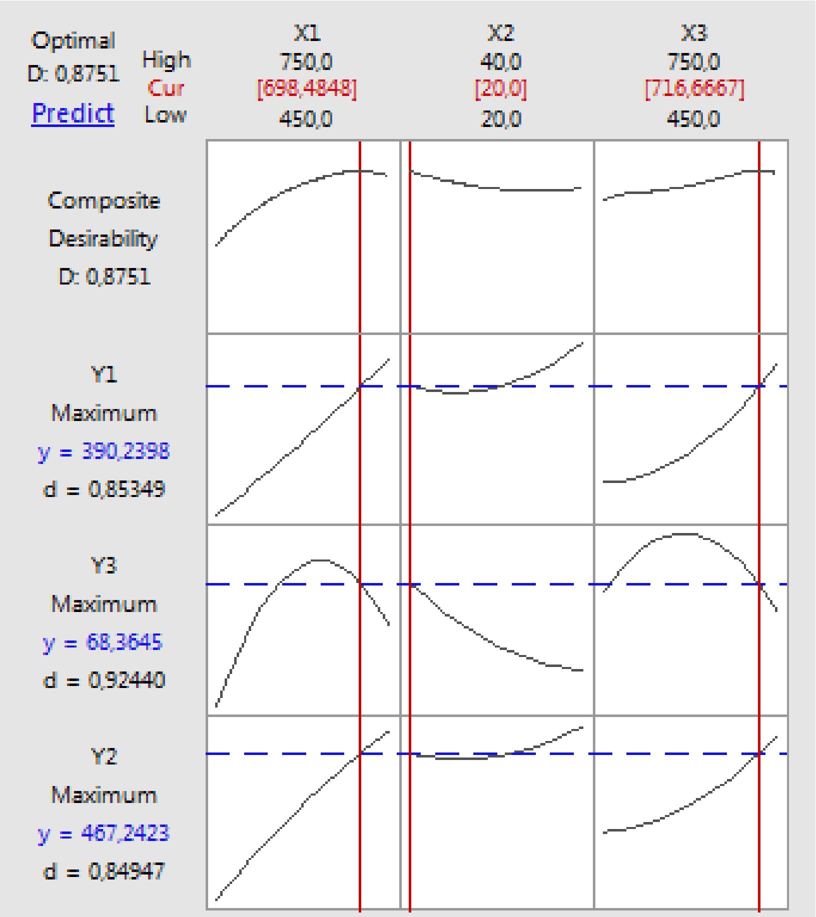

Fig. S3. Optimization plots of pyrolysis temperature, pyrolysis oil content, second heat treatment temperature**.**

Paper E

How to produce green coke? by Bartocci, Pietro; Riva, Lorenzo; Nielsen, Henrik Kofoed; Yang, Qing; Yang, Haiping; Skreiberg, Øyvind; Wang, Liang; Sorbini, Giulio; Gul, Eid; Barbanera, Marco; Fantozzi, Francesco. Accepted to Applied Energy Symposium: MIT A+B. Cambridge, USA. Postponed to 12-14 August 2020 (2020).

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].

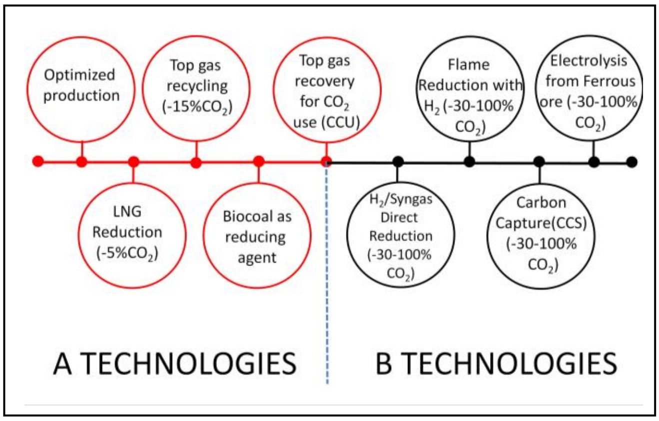

Fig. 1. Green Steel production roadmap [5]

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.

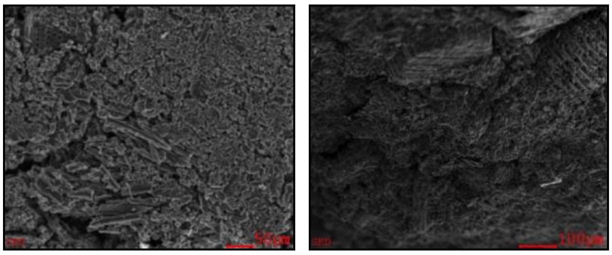

Fig. 3. Biocarbon (left) and reheated biocarbon pellet (right) [14]

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.

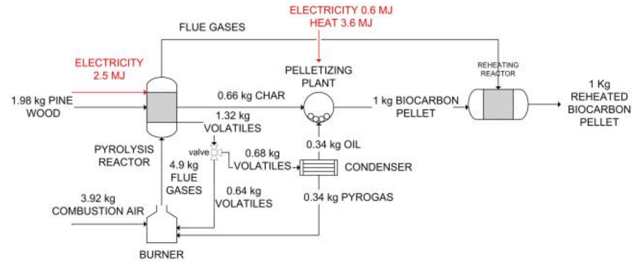

Fig. 4. Biocarbon production process layout, based on pyrolysis – pelletization - reheating [24]

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 mix, AC, consumption mix, at consumer, 1 kV – 60 kV EU-27 S”; taken from the Ecoinvent 3.3 database.

The choice of the electricity has been done assuming that the results can be generalized to an average European scenario.

B. *Carbon footprint of biocarbon pellet*

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

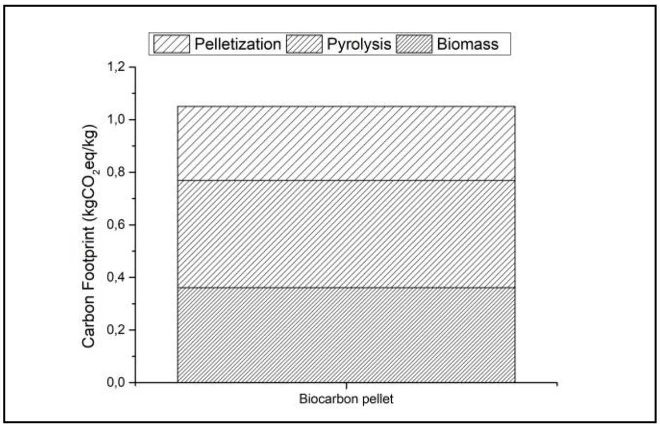

Fig. 5. Biocarbon Pellet Carbon Footprint (comprehensive of reheating) [24]

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).

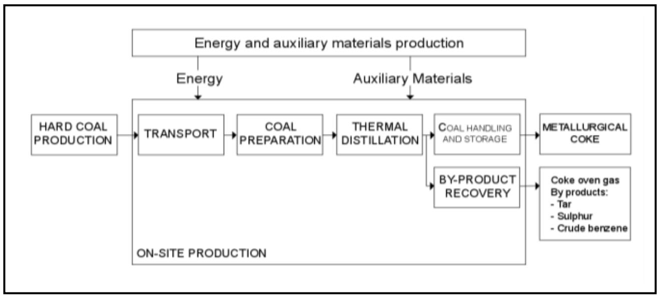

Fig. 6. Coke production system boundaries [27]

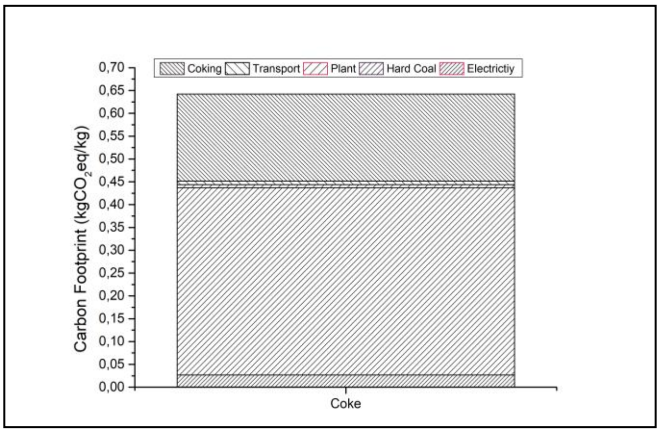

Fig. 7. Coke carbon footprint

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.).

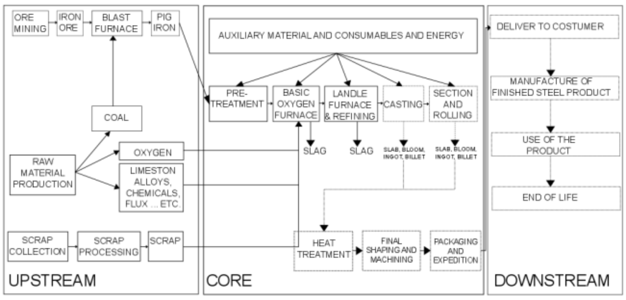

Fig. 8. System boundaries in steel production [28]

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.

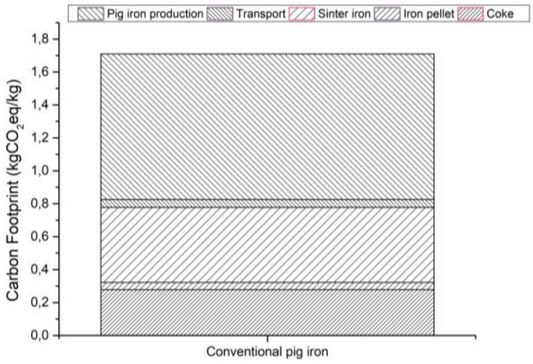

Fig. 9. Conventional pig iron carbon footprint

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.

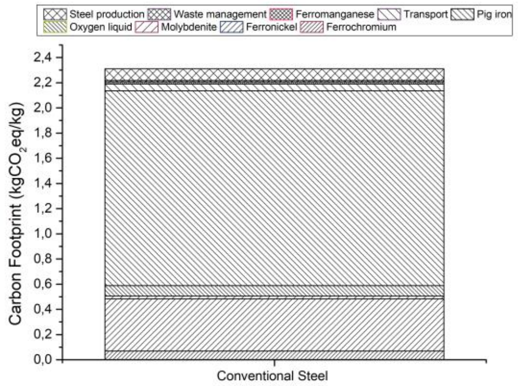

Fig. 10. Conventional steel carbon footprint

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.

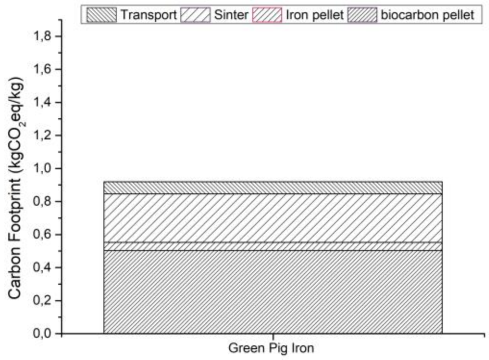

Fig. 11. Carbon footprint of green pig iron

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.

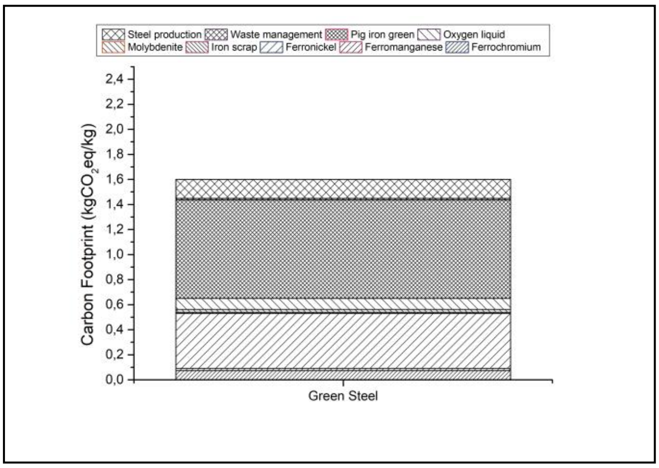

Fig. 12. Carbon footprint of green steel

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.

Acknowledgment

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List of contributions

Conferences

- Biochar for metallurgical applications. *Nordic biochar network conference.* Stockholm, 16-17 October 2019
- Validation and application of a multiparameter model for the densification of biochar. *Biochar II: Production, characterization and applications.* Cetraro (Italy), 15-20 September 2019
- LCA analysis of biocarbon pellet production to substitute coke. *International Conference on Energy, Ecology and Environment (ICEEE 2019).* Stavanger, 23-26 July 2019
- Biochar Pelletization for Metallurgical Applications. *26th European Biomass Conference and Exhibition.* Copenhagen, 14-17 May 2018

Workshops

- Biochar pellets for the silicon production. *Si-day.* Trondheim, 6 February 2019
- Biochar research at the University of Agder. *Bio-carbon workshop.* Trondheim, 1 April 2019

Other presentations

- Biokull pellets. *Skogsbasert biodrivstoff og biokull produksjon i Agder.* Grimstad 20 April 2018