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.

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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

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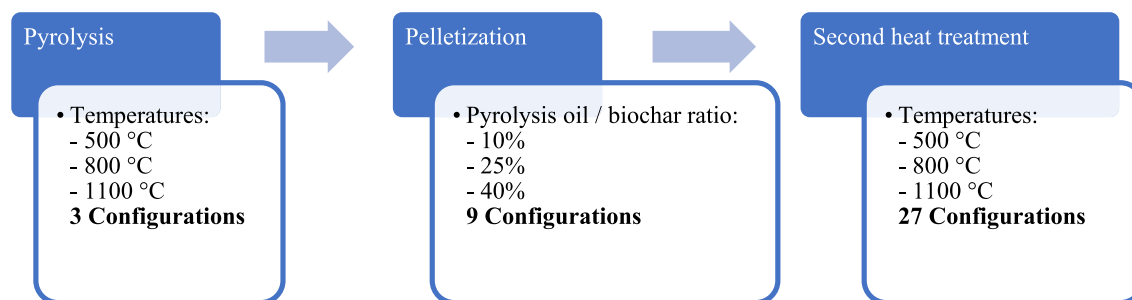
Fig. 1. Sample preparation layout. Biochar is produced at three different pyrolysis temperatures: 500 °C, 800 °C and 1100 °C. Each pyrolysis product is then pelletized adding three different pyrolysis oil contents by weight: 10%, 25%, 40%. Eventually the 9 cases are heated once more at 500 °C, 800 °C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

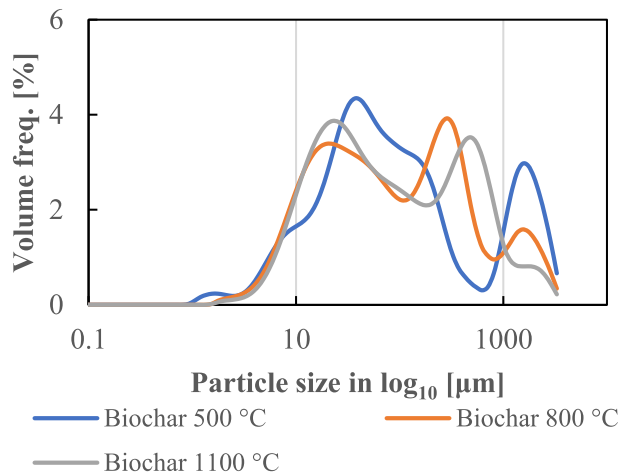| Material	Spruce	Biochar 500 °C	Biochar 800 °C	Biochar 1100 °C	Ligno-sulphonate	Pyrolysis Oil
Proximate analysis						
Moisture [%wb]	8.6	2.3	1.9	3.2	6.5	24.5
Volatile [%db]	80.6	17.5	8.5	6.8	59.9	-
Ash [%db]	0.8	2.0	2.0	2.2	21.2	-
Fixed carbon [%db]	18.6	80.5	89.5	91.0	18.9	-
Ultimate analysis						
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 $s = (l-l_f)/l$, 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.

CO₂ 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].
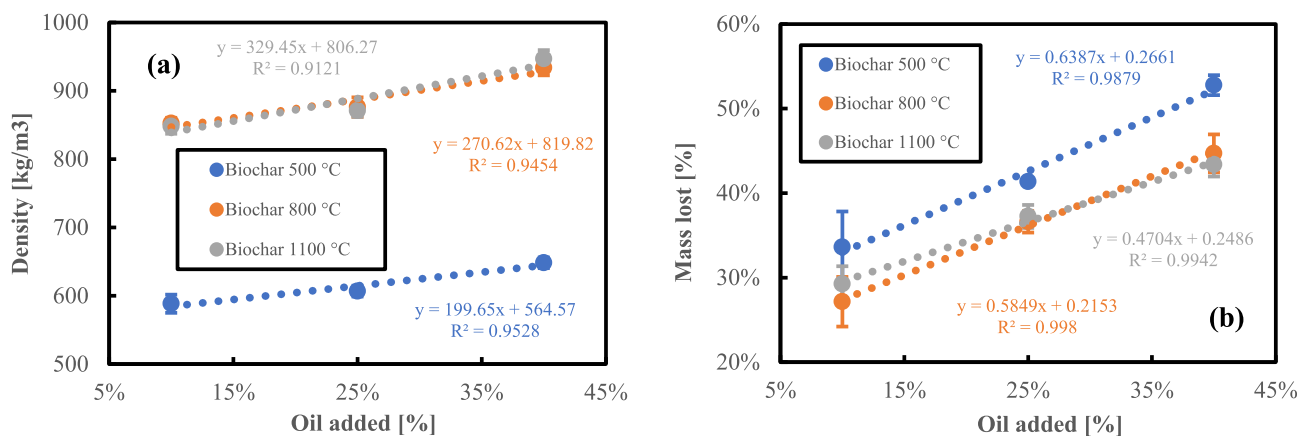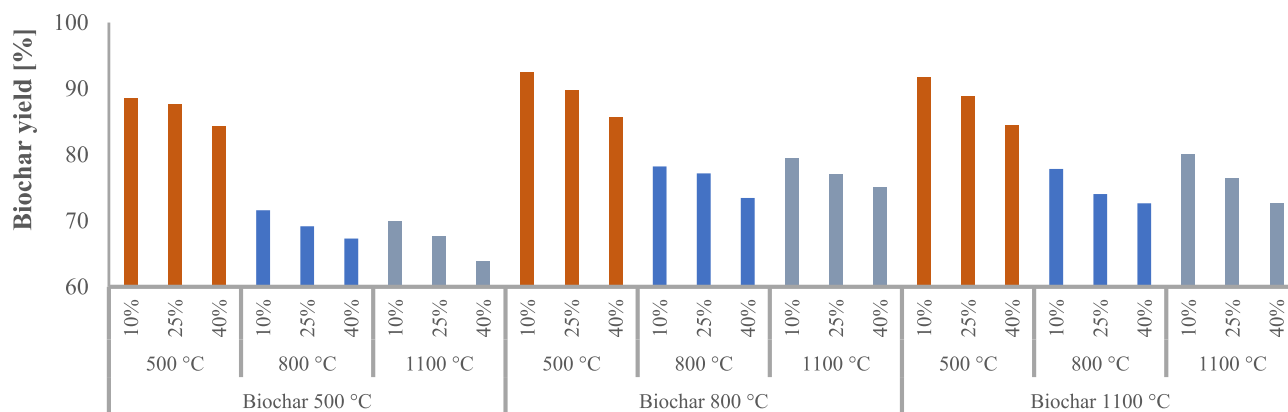

Fig. 3. Post-densification density of the pellets blended with different pyrolysis oil additions (a). Mass lost during the post-densification stabilization of the pellets with different pyrolysis oil additions (b).

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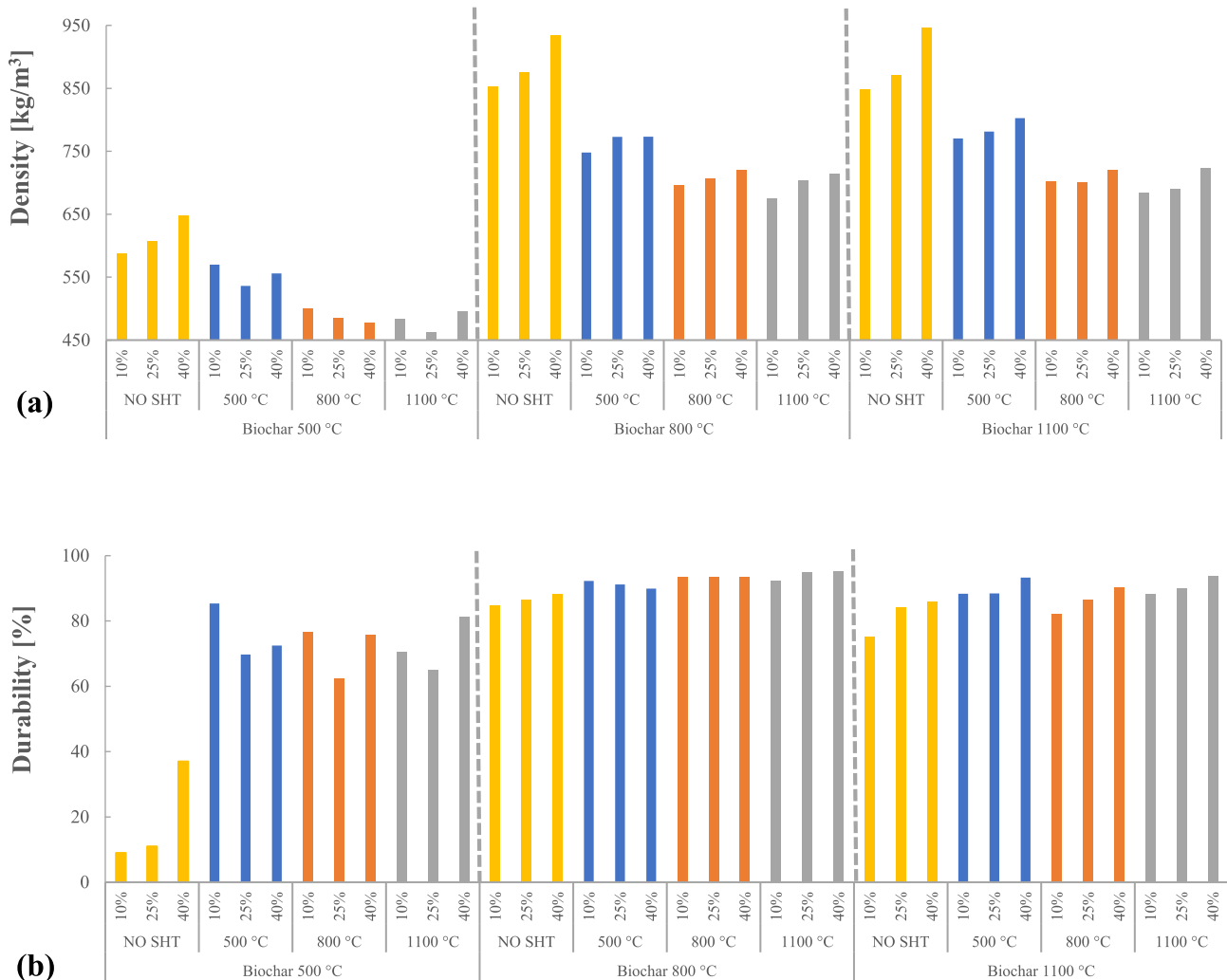
Fig. 5. Second heat treatment (SHT) and oil content influence on (a) density (b) durability (c) mechanical strength and (d) shrinkage. Data are divided first by temperature of the pyrolysis temperature used to produce biochar, then by the temperature of the second heat treatment and finally by the percentage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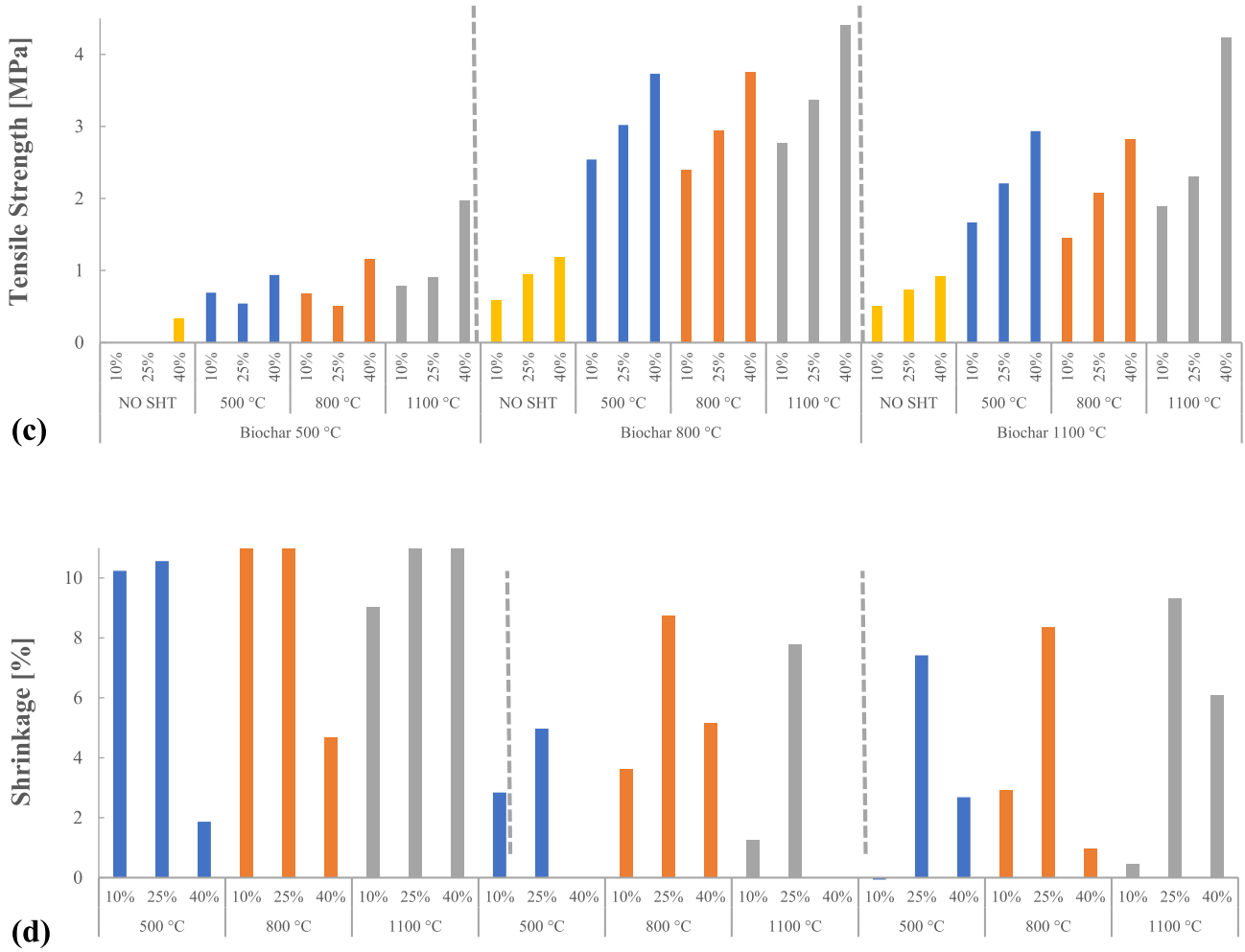
(c)

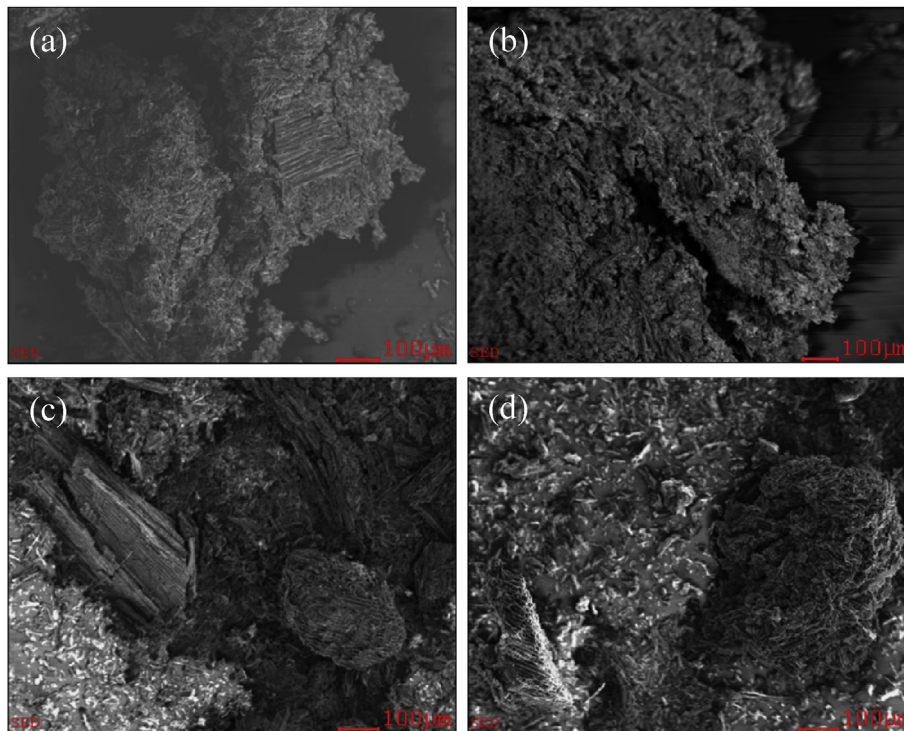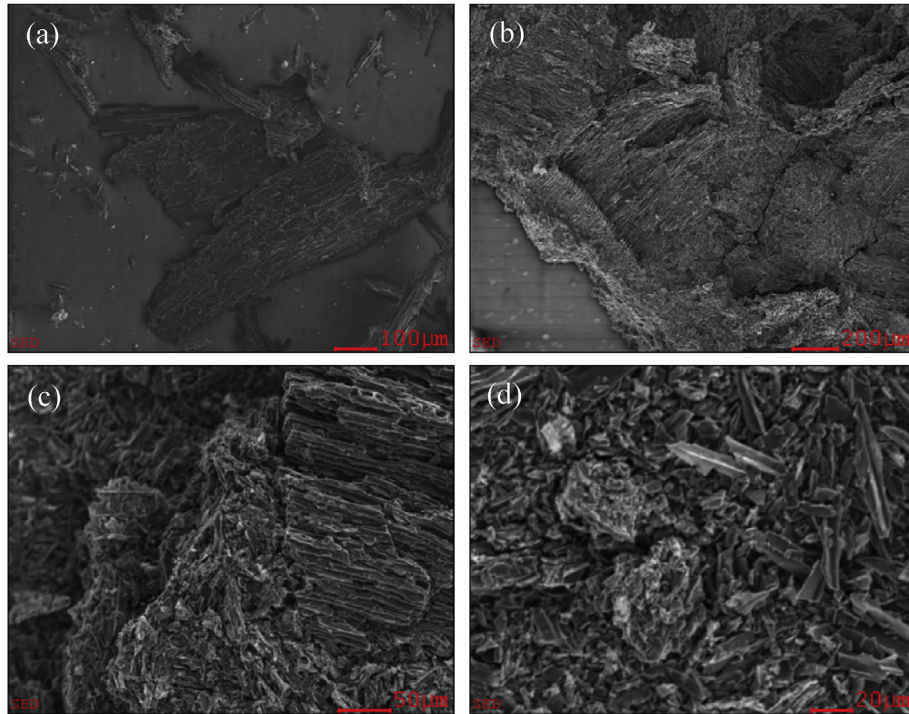**(d)**

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.
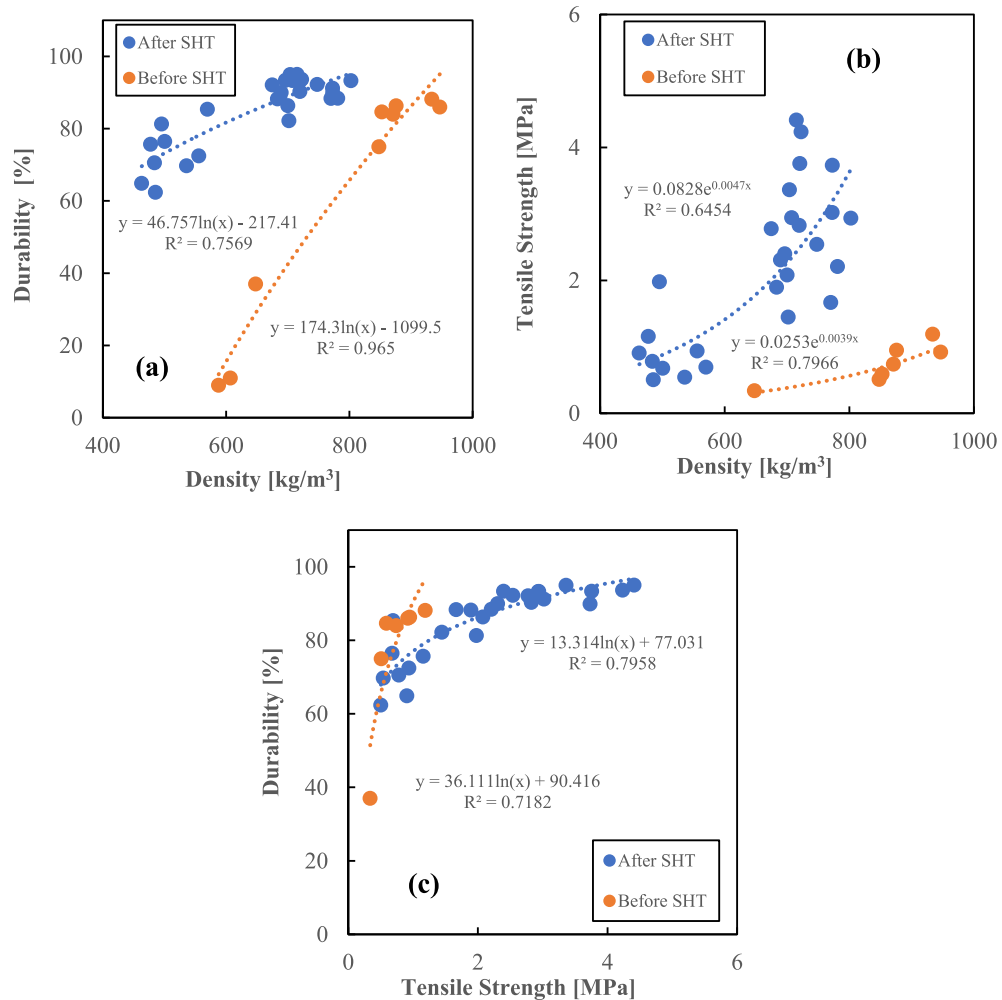
Fig. 8. Correlations of the values measured before and after second heat treatment (SHT) between (a) density and durability, (b) density and tensile strength, (c) tensile strength and durability.
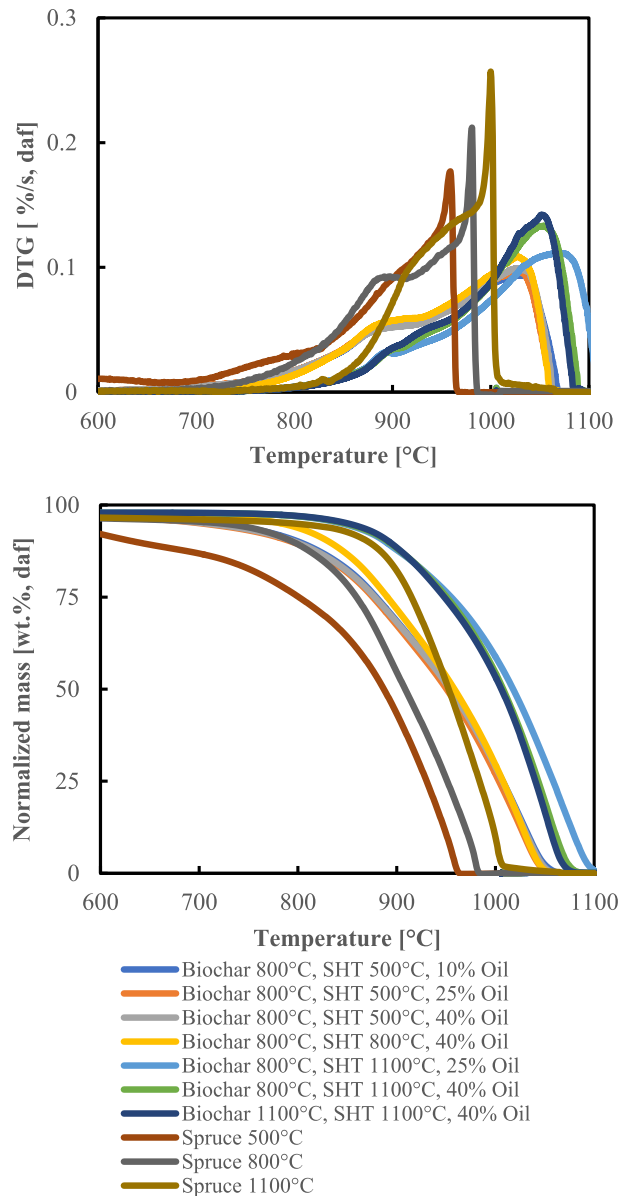
Fig. 9. CO$_2$ Reactivity for some of the configurations, in comparison to the behavior of untreated biochar pyrolyzed at the same temperatures. Upper graph shows the derivative thermogravimetry (DTG, wt = weight total, daf = dry ash free), wile the lower graph shows the normalized mass (wt = weight 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.

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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