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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

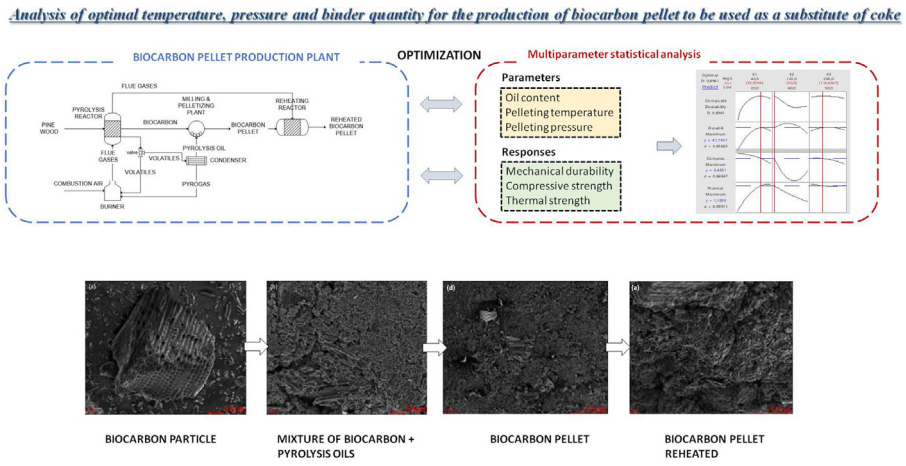
Lorenzo Riva[a,*], Henrik Kofoed Nielsen[a], Øyvind Skreiberg[b], Liang Wang[b], Pietro Bartocci[c,**], Marco Barbanera[d], Gianni Bidini[c], Francesco Fantozzi[c]

[a] Department of Engineering Sciences, University of Agder, Postboks 509, 4898 Grimstad, Norway
[b] SINTEF Energy Research, Postboks 4761 Torgarden, Trondheim, Norway
[c] Department of Engineering, University of Perugia, Via G. Duranti 67, 06125 Perugia, Italy
[d] Department of Economics, Engineering, Society and Business Organization, University of Tuscia, 01100 Viterbo, Italy

## 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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## 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

* Corresponding author.
** Corresponding author.
*E-mail addresses:* lorenzo.riva@uia.no (L. Riva), bartocci@crbnet.it (P. Bartocci).

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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.

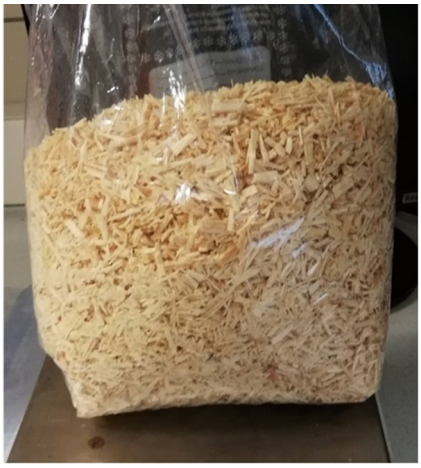

**Fig. 1.** Milled pine sample.

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™ (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 |

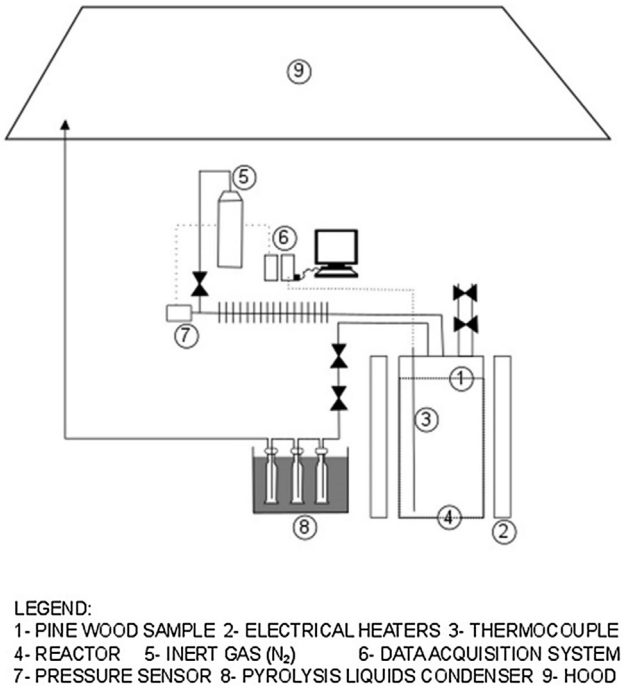


**Fig. 2.** Experimental setup for pyrolysis tests at the University of Perugia, Italy.

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:

$$MD = 100 * m_f/m_i \quad (1)$$

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:

$$S = m_s g/\pi r l \quad (2)$$

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:

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j + \varepsilon \quad (3)$$

where Y is the measured response related to each factor level combination, $\beta_0$ is the intercept coefficient, $\beta_i$, $\beta_{ii}$, and $\beta_{ij}$ 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 $\varepsilon$ 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.

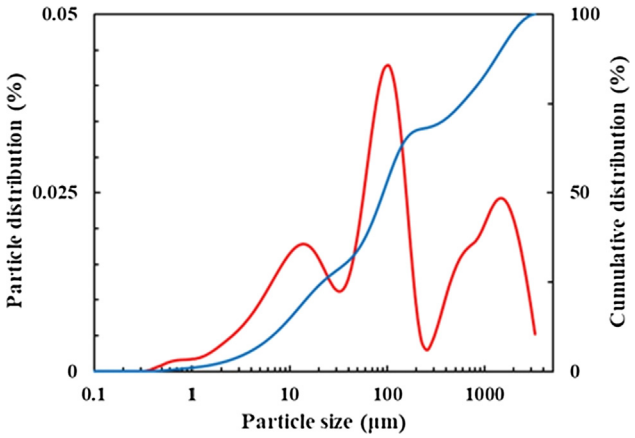


**Fig. 3.** Particle distribution of biocarbon after milling with a cutting mill and sieving with a 2 mm sieve.

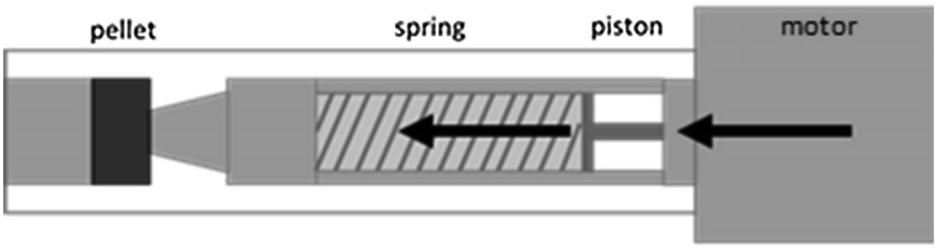


**Fig. 4.** Pellet hardness tester set-up layout, University of Agder, Norway.

**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.

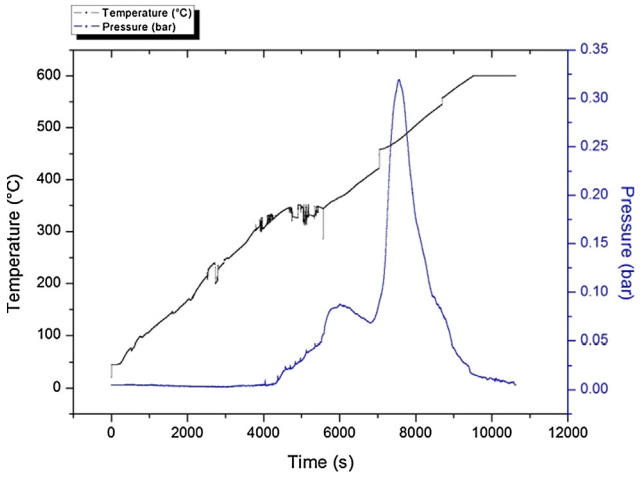


**Fig. 5.** Trend of temperature and gauge pressure inside the pyrolysis batch reactor versus time.

## 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.

### 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:

**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 |

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

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

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

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.

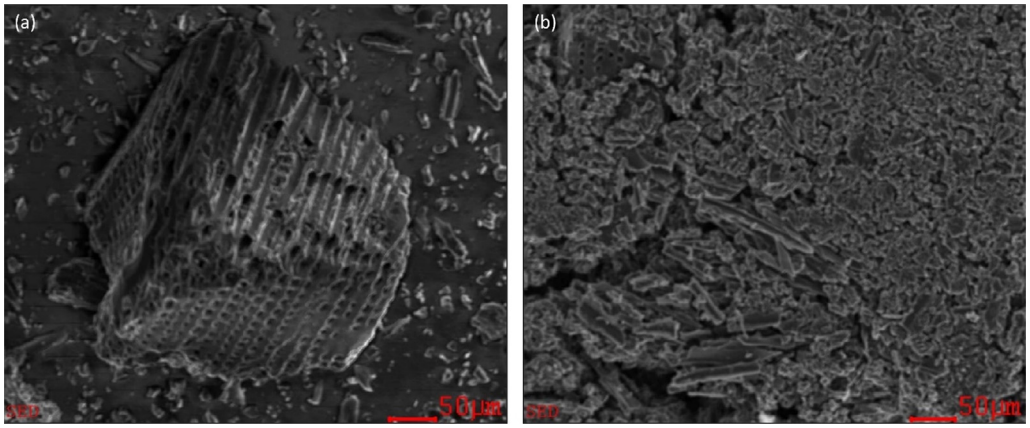


**Fig. 7.** SEM photos of: (a) a biocarbon particle (15 kV, magnification 200×) and (b) section of a mixture of pyrolysis oil and biocarbon with biooil concentration equal to 33.4 wt% (15 kV, magnification 250×).

**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

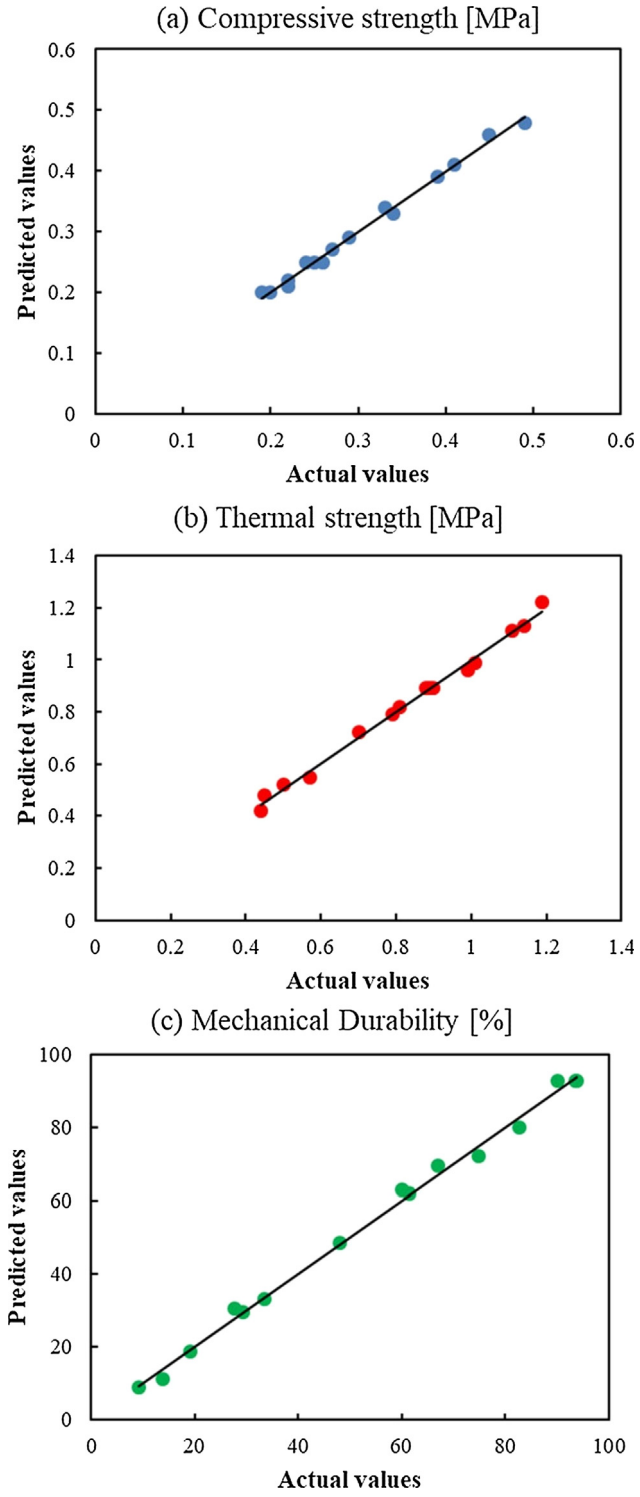


**Fig. 8.** Relationship between predicted and actual values of (a) compressive strength, (b) thermal strength, (c) mechanical durability.

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

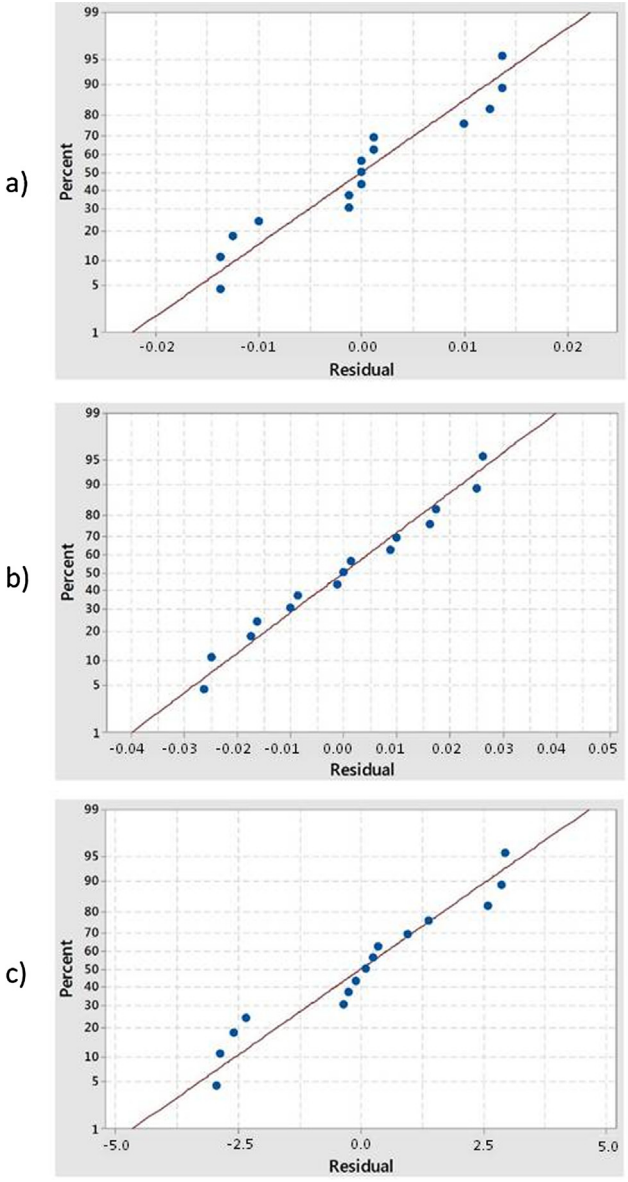


**Fig. 9.** Normal probability plots of residuals of (a) compressive strength, (b) thermal strength, (c) mechanical durability.

biocarbon, which imposes a limit in the densification of the particles.

### 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

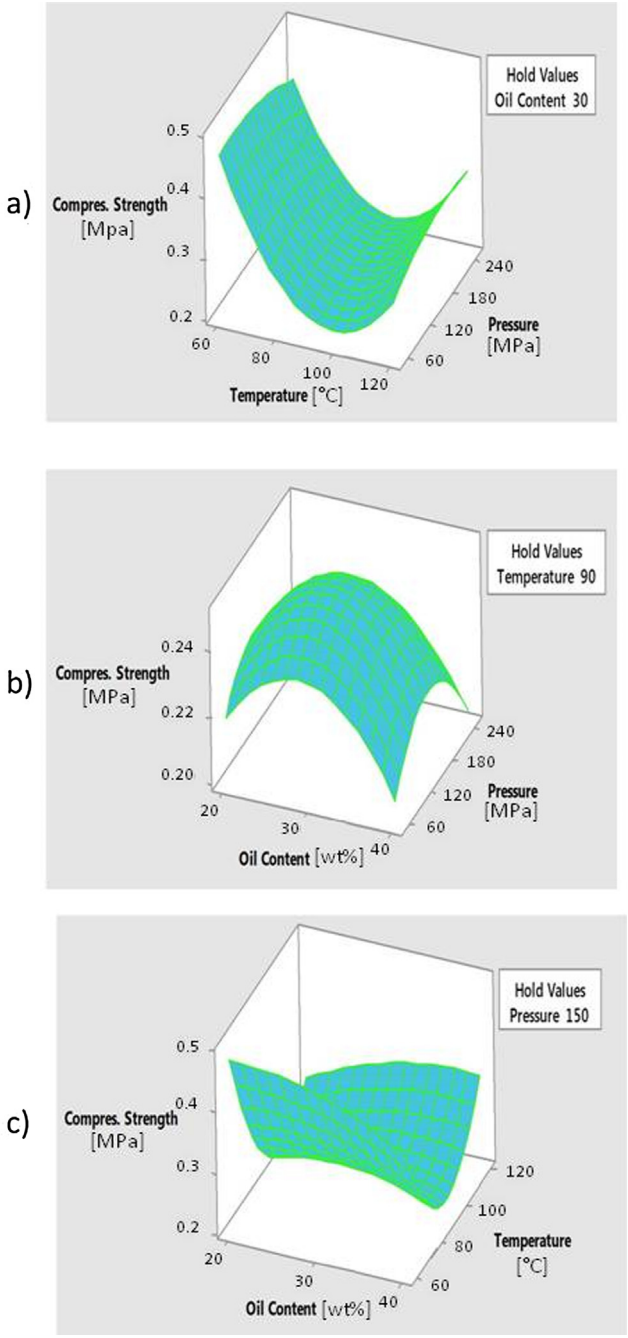


**Fig. 10.** 3D response surface plots of compressive strength showing the effect of process variables at: (a) fixed oil content, (b) fixed pelletizing temperature, (c) fixed pelletizing pressure.

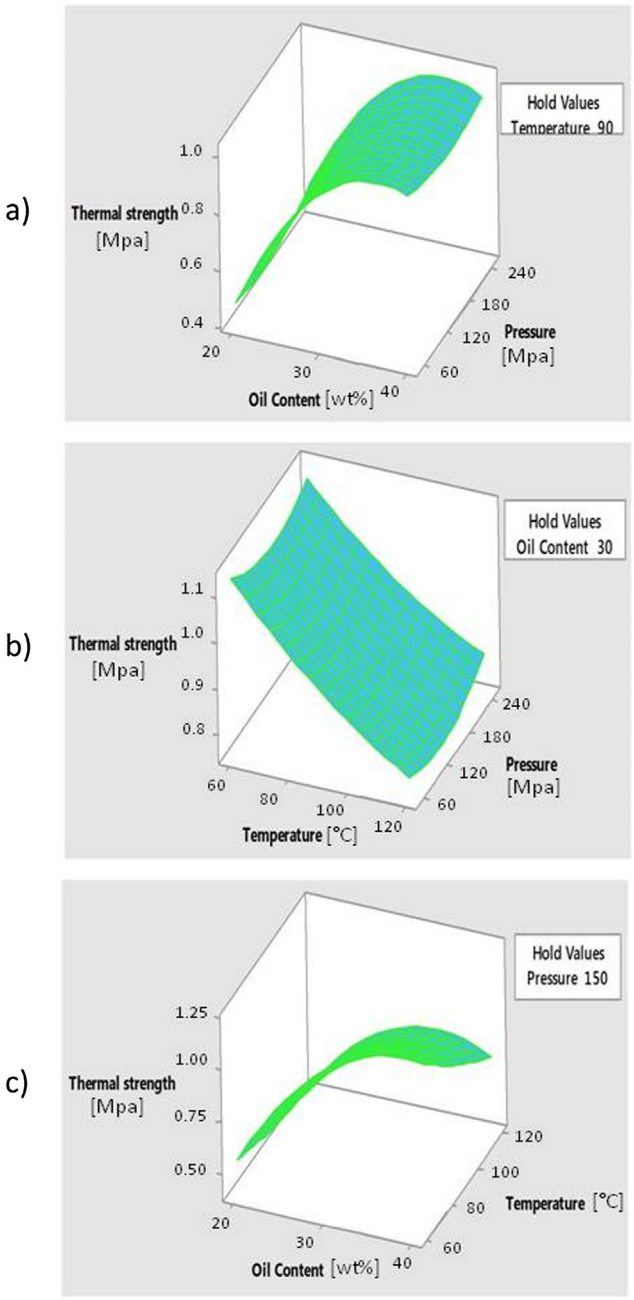


**Fig. 11.** 3D response surface plots of thermal strength showing the effect of process variables at: (a) fixed pelletizing temperature, (b) fixed oil content, (c) fixed pelletizing pressure.

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.

### 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

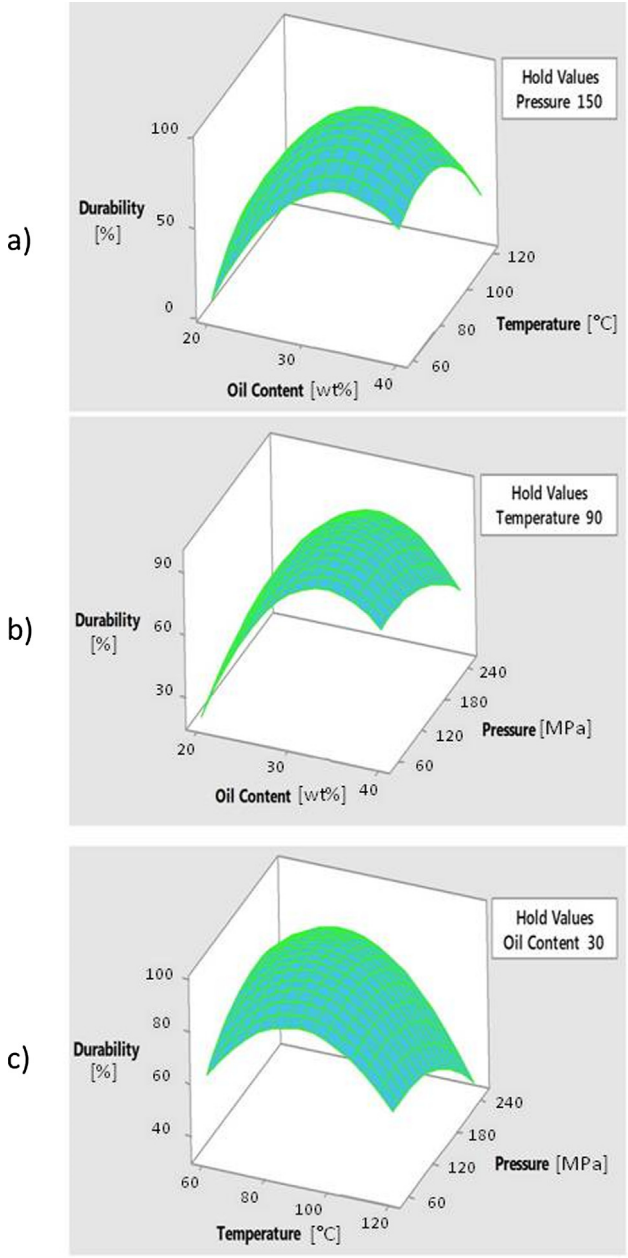


**Fig. 12.** 3D response surface plots of mechanical durability showing the effect of process variables at: (a) fixed pelletizing pressure, (b) fixed pelletizing temperature, (c) fixed oil content.

(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

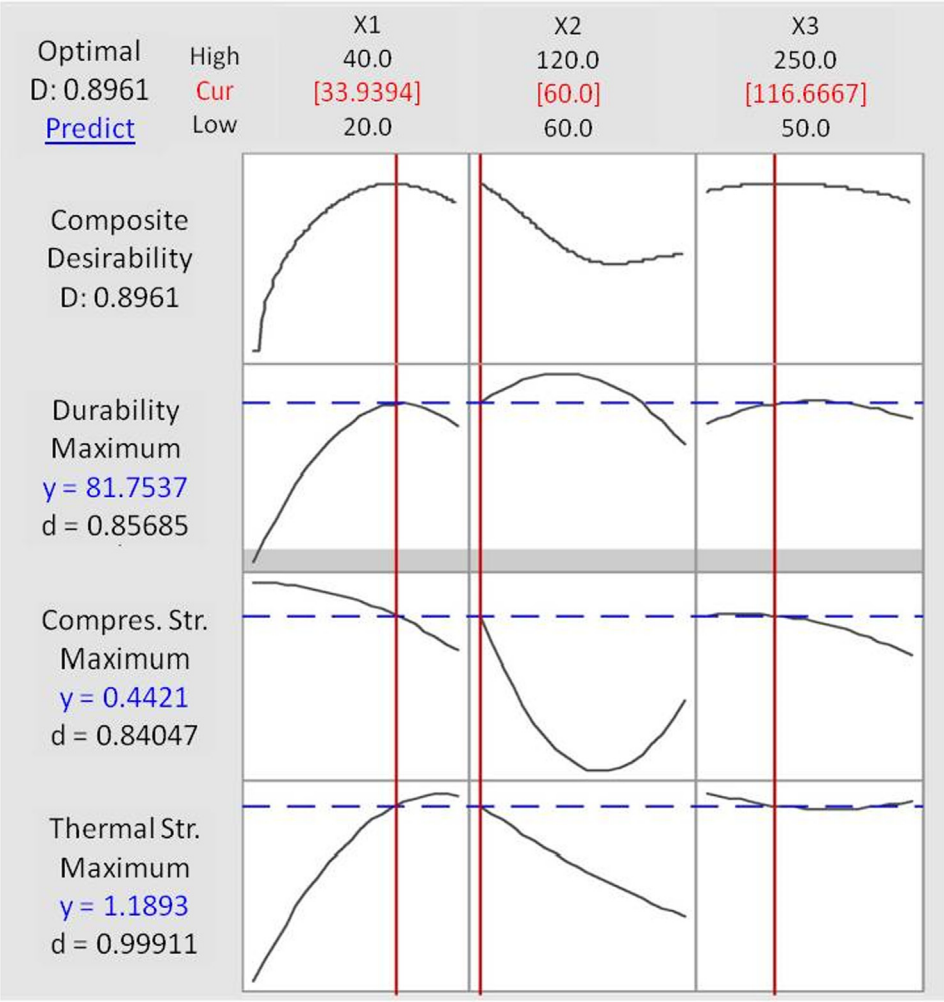


**Fig. 13.** Plots for simultaneous optimization of operating variables (i.e. temperature, pressure and pyrolysis oil content).

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

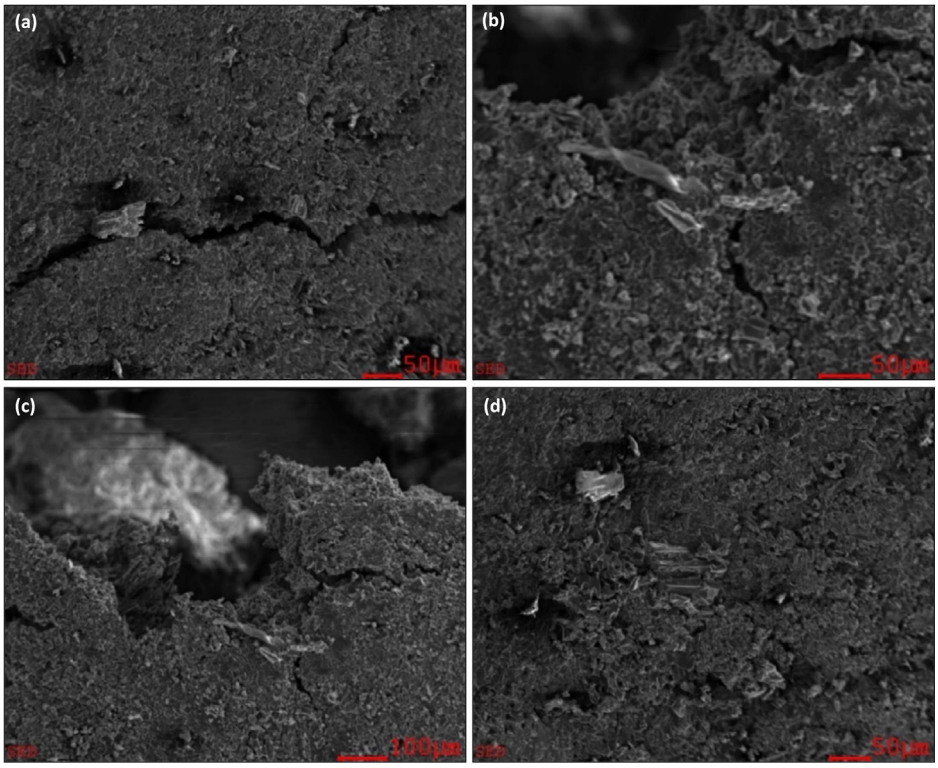


**Fig. 14.** SEM photos of sections of pellets of pyrolysis oil and biocarbon with mass ratio 33.9%. Voltage and magnification: (a) 15 kV 239×, (b) 15 kV 230×, (c) 7 kV 180×, (d) 15 kV 250×.

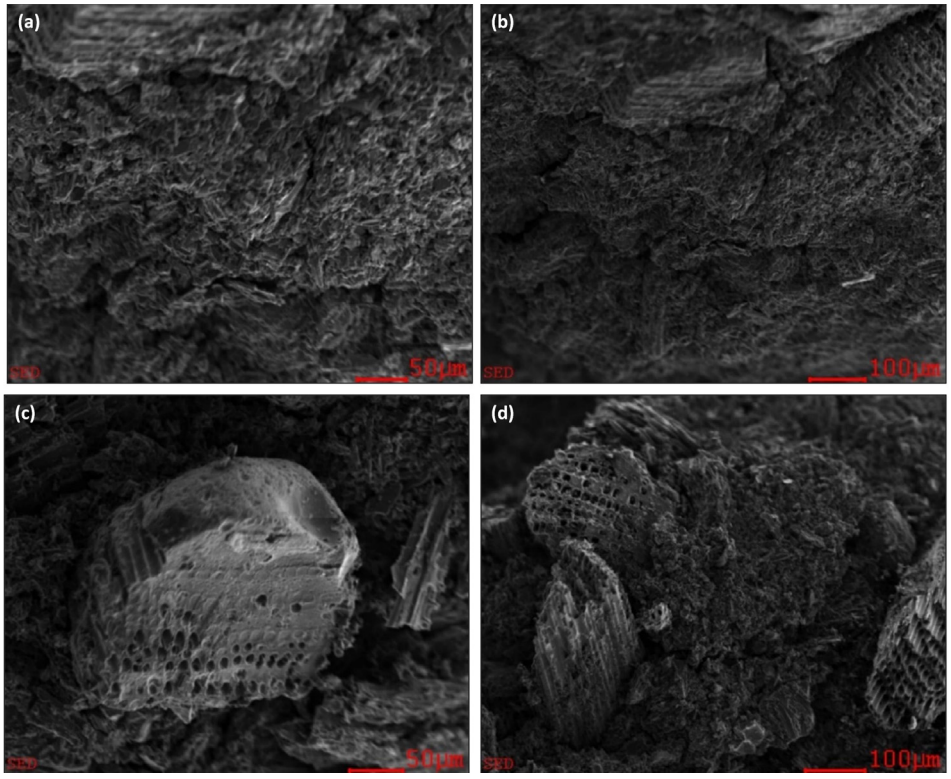


**Fig. 15.** SEM photos of sections of pellets of pyrolysis oil and biocarbon with mass ratio 33.9% after a second heat treatment. Voltage and magnification: (a) 7 kV 270×, (b) 7 kV 140×, (c) 7 kV 140×, (d) 7 kV 250×.

**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.

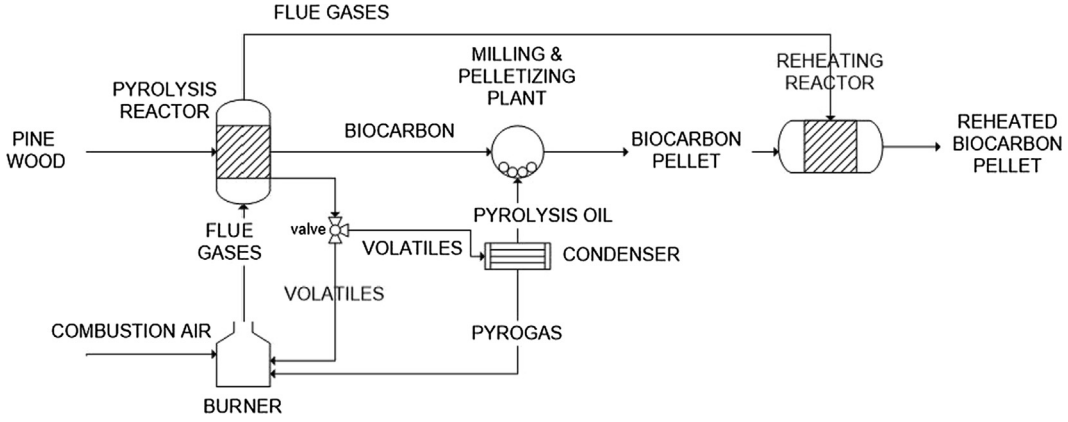


**Fig. 16.** Biocarbon pellet production plant layout.

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