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Process Intensification: Activated Carbon Production from Biochar Produced by Gasification

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Abstract
The recent increase in the number of policies to protect the environment has led to a rise in the worldwide demand for activated carbon, which is the most extensively utilized adsorbent in numerous industries and has a high probability to be used in energy and agriculture sectors as electrodes in supercapacitors and for fertilizer production. This paper is about the production of activated biochar from oak woodchips char generated by an updraft fixed bed gasifier reactor. Following this, by using steam as activating agents and thermal energy from produced syngas, the resulting highly microporous carbonaceous bio-material has been subjected to physical activation at 750 °C. The properties of activated biochar include adsorption/desorption of N2 in order to identify the physical adsorption and surface area measurement, thermogravimetric analysis (TGA), Fourier Transform Infrared Spectrophotometer (FT-IR), X-Ray Diffractometer (XRD), and scanning electron microscopy (SEM). The biochar surface area, generated as a result of the gasification process, showed substantial improvement after steam activation. Also, significant discrepancies were obtained from the surface volume and areas of biochar by-products from the gasifier and activated biochar obtained by steam activation after the gasification treatment [Total pore volume 0.022 cm3 g−1 and 0.231 cm3 g−1, BET surface area 21.35 and 458.28 m2 g−1, respectively]. Besides, the two samples yielded noteworthy differences in their performances. As a consequence, the kinetics of steam gasification is quicker and more efficient for the conversion of the biochar to activated carbon. The pore sizes of the carbon produced by steam activation were distributed over a wide spectrum of values, and both micro and mesoporous structures were developed.
1. Introduction

1.1. Activated Carbon

The adsorption of air and water contaminants on the activated carbon surface is frequently used in air and water treatment systems. Conventional biological treatment processes are efficient in removing biodegradable organics. These processes, however, have limited ability to remove lignins, humic substances, pesticides and residual organic compounds of colour and odour-producing organics. The performance of activated carbon in removing such organic compounds has been proven. Activated carbon filters used for water treatment in homes are usually made of either powdered activated carbon (PAC) or granular activated carbon (GAC). The powdered activated carbon is made of powdered carbon with a particle size of <0.18 mm and its diameter in the range of between 0.25 and 1.15 mm. It is generally used in batch type of reactors and is subsequently filtered off. It is used in the treatment of liquids and cleaning of the flue gases. Granular activated carbon is produced from 0.2-5 mm particle size irregular carbon. For liquid and gas phase substances, it is applied on adsorption columns [1-3].

1.2. Biochar

The increase in production and providing its energy demand, which has emerged in the last century with the increasing population, is becoming vastly important. The environmental impacts caused by the increase in production draw attention and higher consumption create problems for our limited natural sources. The necessity of treatment for the prevention of soil, air and water pollution is among the topics that are especially emphasized at international conferences by the scientist and experts. It is necessary for humanity to take joint decisions to increase the sensitivity of countries on environmental issues and to take and implement the necessary legal measures [4].

Biochar is a by-product with high carbon content produced through the conversion of biomass into synthesis gas (syngas) by the advance thermal gasification method using partial oxidation. Intensified gasification of biomass process through partial oxidation is a recently developed, environmentally clean and renewable energy technology [5]. As a result of the gasification of the biomass, the biochar, which has high carbon content, is produced as a by-product. Biochar obtained as a by-product from gasification of woody biomass mainly
contains Carbon (85% w/w), Nitrogen, Hydrogen, Phosphorus, Calcium, Magnesium and Iron. Production of activated carbon from biochar by-product is possible. To convert biochar into activated carbon, it is necessary to remove the specific contaminants to complete and dimension the activation.

Biomass is a renewable energy source but can cause environmental issues when it is not properly utilised. Therefore, it needs to be dealt with the correct technology as compared to other renewable energy sources. Since biomass thermal utilisation is carbon neutral, it does not cause global warming hence climate change, and due to its amount, it has high energy potential. Thermochemical methods are generally used to obtain energy from biomass. Known thermochemical methods are combustion, pyrolysis, and gasification. The gasification process has several advantages over other thermal processes: the ability to dissolve at lower reactor volumes, the formation of low amounts of contaminants, and the more efficient utilisation of the produced synthetic gas (syngas). Compared to pyrolysis, it has the advantages of working autothermically without the need for external energy. Compared to other processes, gasification of woody biomass is stated to be one of the most suitable options for optimizing the conversion efficiency of the fuel’s chemical energy [6-7]. The stoichiometric reaction of woody biomass with partial oxygen results in flammable product gases and thus gasification. The basic equation of the gasification of biomass is as follows:

\[
\text{Biomass} + \text{partial oxidation (1/2 O}_2\text{)} \gg \text{H}_2, \text{CO, CO}_2, \text{CH}_4, \text{C}_x\text{H}_y + \text{Biochar}
\]  

Various types of reactors are available for gasification. To not digress from the subject, the kinetics of gasification reaction was not elaborated. Fixed-bed biomass gasification reactors are used for synthesis gas generation and biochar production. Fixed bed gasification reactors efficiently convert biomass to synthesis gas and are the type of reactor suitable for the production of biochar as a by-product of high carbon content (85-90% w/w carbon) [8-9].

The biomass fed into the gasification system passes through four sections in the reactor and is converted into product gas (synthesis gas) and biochar as a by-product. The biomass passes through the drying, pyrolysis, reduction and oxidation zones in the reactor and is converted into biochar at elevated temperatures (800-1100 °C). The amount of biochar produced depends on the biomass type and the operational conditions. 10% to 20% of the biomass fed to the reactor is produced as biochar [10-12].
Recently, researchers have begun to be interested in biochar produced as a by-product from biomass by thermal conversion pathways (>700 °C), such as pyrolysis, thermal carbonization, flash carbonization and gasification [13]. Many studies have suggested that biochar can be used in CO₂ adsorption, soil remediation, and air pollution removal [14-16]. Additionally, the use of the synthesis gas produced by thermochemical conversion of biomass causing environmental problems as a renewable energy source provides an advantage while the efficiency potential of biochar produced as a by-product will make these systems very attractive [17].

1.3. Steam Activation

Physical activation improves the surface pores of biochar and affects the chemical properties of the surface (such as surface functional groups, hydrophobicity and polarity). The physical activation methods used for biochar are generally steam and gas activation. The steam activation of the biochar is usually carried out after the thermal carbonization of the biomass. The surface porosity of biochar increases after pyrolysis. Also, with steam activation, the activated biochar will gain higher porosity. The chemical formulas 2 and 3 are as follows [18]:

\[
\begin{align*}
C + H_2O & \rightarrow CO + H_2; \quad \Delta H = 117 \text{ kJ/mol} \\
CO + H_2O & \rightarrow CO_2 + H_2; \quad \Delta H = 41 \text{ kJ/mol}
\end{align*}
\]

With the H₂O (steam) and carbon reaction during the activation process, three outcomes emerge: 1- removal of the volatile and tar from the surface, 2- formation of new micropores, and 3- expansion of existing pores [19-20].

Studies on steam activation have shown that biochar’s surface area and micropores increase. For example, the surface area of biochar (136-793 m² g⁻¹) obtained by rapid pyrolysis (800 °C, 45 min) was increased as a result of the steam activation. All these measurements were performed with BET isotherm [21]. In another study, biochar (700 °C) from tea residue biomass was activated by steam and its surface area was obtained as 576.1 m² g⁻¹, pore volume as 0.109 cm³ g⁻¹, and pore diameter as 1.998 nm (before activation, the surface area was 342.2 m² g⁻¹, pore volume 0.022 cm³ g⁻¹ and pore diameter 1.756 nm) [22]. The steam activated biochar formed at 700 °C indicated the highest absorption capacity (37.7 mg g⁻¹) at
pH 3. With a 55% growth in absorption ability compared to non-activated biochar produced at the same conditions. Consequently, activation with steam has a potential to enhance the adsorption capability of biochar. At 700 °C produced biochar derived from plant-based biomass detected relatively low surface areas (9.27 m² g⁻¹). Due to the formation of tar during the thermal decomposition, the pores in the biochar are blocked [23]. Steam activated biochar derived from bamboo waste had a larger surface area compared to non-activated bamboo biochar. Optimum conditions for activation are detected at 850 °C and 120 min activation time. Under these conditions, BET surface area of activated biochar 1210 m² g⁻¹ and total pore volume of 0.542 cm³ g⁻¹ was obtained. This study showed that bamboo waste could be used to arrange new micropores to activated biochar through steam activation [24]. In a research, activation of the rice husk biochar has been carried out at 800 °C by using steam. The micro and meso porous structured biochar were produced, 1365 m² g⁻¹ surface area was obtained at the end of 15 min [25]. A paper presents a study into the effect of different activation conditions and adsorption characteristics of biochar evaluated from tyre rubber waste. Steam was used as an oxidising agent and total micropore volumes and BET surface areas increased to 0.554 cm³ g⁻¹ and 1070 m² g⁻¹, respectively. Consequently, steam was observed to generate a narrower extensive micro porosity [26]. An experimental test represents the production of activated biochar from barley straw using steam activation method. Activation has been conducted due to maximise the micropore volumes and BET surface area of the biochar. Optimal conditions for steam activation were obtained a hold time of 1 h at 700 °C. The micropore volume and surface area of activated biochar were 0.2304 cm³ g⁻¹ and 552 m² g⁻¹, respectively [27]. A study investigates, activated biochar were produced from date stone wastes by steam activation. The effect of activation hold time on surface textural structure properties of raw date stone and biochar produced were studied. Results indicate the presence of cellulose and hemicellulose in the raw material, and the predominance of carbon content. The highest microporous volume is 0.716 cm³ g⁻¹ and specific surface area is 635 m² g⁻¹, are obtained through biochar activated under steam at 700°C for 6h [28]. Study was conducted to investigate the effect of sulfur in activated biochar production prepared from apricot stones by steam activation process. The activation temperature and time tested were in the ranges of 650–850 °C for 1–4 h. The experimental results revealed that surface area of biochar is 1092 m² g⁻¹ was obtained from apricot stone at activation conditions of 800°C for 4
The experimental results indicated that commercial production of porous activated biochar from apricot stones is reasonable [29].

In a study, the significance of the nature and composition of the biomass was demonstrated in the process performed by the steam activation of three different biomass including wheat straw, coconut shell, and willow [30]. For these three biomass substances, activated carbons with specific surface areas of respectively 246 m² g⁻¹, 626 m² g⁻¹, and 840 m² g⁻¹ were produced. Although physical activation using steam significantly increases surface area and porosity, there is a disadvantage of using steam activation. This is the loss of aromaticity and polarity in steam activated carbons compared to the genuine biochar [31]. However, using a combination of CO₂ and steam activation has been reported to produce activated carbons with better surface area and pore structure compared to using only CO₂ or steam for activation. In the study, activated carbon was produced from biochar obtained from olive kernel biomass using CO₂, steam and a combination of CO₂/steam. A combined CO₂/steam activation under similar experimental conditions has been reported to produce a higher surface area (1187 m² g⁻¹) compared to the specific surface area obtained by using only CO₂ (572 m² g⁻¹) or steam (1074 m² g⁻¹) [32]. From the aforementioned studies, it can be concluded that the reaction of steam with carbon occurs in a shorter period compared to the reaction of CO₂ with carbon. While generally micro pores activated carbons are produced by using CO₂ in physical activation, meso and macro pores are formed in the structure during activation with steam [33]. The reason for the difference in pores is attributed to the conversion of developed micro pores into wide meso/macro pores and the faster reaction of the fixed carbon in the biomass structure of the steam. Also, it is possible to produce more pores using steam as it can penetrate the inner surface of the fixed carbon. On the other hand, CO₂ stagnates in its reaction with the fixed carbon and therefore more homogeneous micro pores are added to the structure due to activation by using CO₂. Determining the specified exposure time of the biomass at high temperatures with the activation agent is a critical decision to achieve high surface properties. The significance of biochar steam activation time was emphasized in some studies. It has been determined that there is a decrease in the surface pores of biochar exposed to long activation time [34].

Chemical and physical processes are needed to increase the utilisation value of biochar. Several processes are required such as separation of biochar into suitable granule size,
obtaining carbon black, activation of pores by chemical processes, and the sizing of activated carbon. The failure to use biochar, produced as a by-product of biomass gasification, as an efficient product, constitutes a disadvantage in all respects considering the spread of such technologies. As a result of the studies conducted, it is observed that biochar, produced as a by-product by gasification of woody biomass, is only used as a soil conditioner in small amounts. However, it is generally burned inefficiently in the combustion boilers. To this end, this study investigates the conversion of biochar, which is currently produced as a by-product by gasification of woody biomass, into activated carbon, which is a widely used valuable product. Several studies have emphasized that surface area and pore volume increase with the conversion of biomass at high temperatures by thermal methods [35]. Thus, it is envisaged in the present study that the process of converting the biochar to be obtained by gasification at high temperatures (800-1000 °C) into activated carbon by specific activation methods may have many advantages. The need for extra energy from external sources such as utilisation of fossil fuels to reach these temperatures in conventional carbon conversion systems causes high operational costs. Considering all this, it is expected that high quality activated carbons to be obtained from biochar will be available in the market at low costs.

2. Experimental

2.1. Materials and Methods

In this experimental study, oak woodchip was gasified in an updraft gasifier. By-product biochar was activated in the activation unit integrated into the gasification system. The proximate and ultimate analyses of the oak woodchips were conducted, and the results are presented in the result and discussion section. Proximate and elemental analyses were performed to determine the usability of biochar produced after the gasification of biomass for the production of activated biochar. Proximate analyses of moisture (ASTM D 7582-12), ash (ASTM E 1755-01), fixed carbon (ASTM D 3172-13) and volatile matter (ASTM D 7582-12) were made according to certain standard methods. The Lower heating value was determined by using ASTM D 5863-13 standard method. The amounts of C, H, N, and S were determined in the element analyser and the amount of oxygen was determined by using the standard of ASTM D 3176-09.
Using a Thermal Analyzer, the thermogravimetric carbonization analysis of oak woodchips was performed. Approximately 10 mg samples with an average particle size of 0.25 mm were heated at 10 °C min\(^{-1}\) from room temperature to 800 °C under nitrogen flow. Throughout the measurements, the nitrogen flow was kept constant at 10 cm\(^3\) min\(^{-1}\).

Activation of the biochar that was produced in the gasification system in the GTU Gasification Laboratory was performed. For the preparation of the biochar and activated biochar, the oak woodchips were first carbonized by gasification at 800-1000 °C for 1-2 hours. Then, the resultant biochar produced as a by-product from the gasifier was activated by steam at three different temperatures (700 °C, 750 °C and 850 °C) utilising thermal heat generated from syngas burner and different activation times conducted (30, 60, and 90 min). The amount of 5.5 kg by-product biochar sample was used in each run. During the final process, the reactor was cooled under inert injection of nitrogen gas and then the activated carbon was removed from the reactor and weighted in order to determine the burn-off undergone in the reaction.

For steam activation, a stainless-steel vertical reactor illustrated in Figure 1 was used and integrated to the system to heat the biochar samples of each 5.5 kg. Throughout the experiment, the exact heating rate and steam flow rate (\(\sim 20 °C \text{ min}^{-1}\), 1.3 kg min\(^{-1}\), respectively) were applied. Referring to Equation 2, the optimal stoichiometric steam amount was determined and calculated for the system.

Figure 1. Schematic diagram of the experimental biochar activation setup with gasifier: (1) Main biomass feeding hopper; (2) Updraft gasifier; (3) Biochar by-product; (4) Syngas exit.
pipe; (5) Syngas burner; (6) Air; (7) Thermal heater; (8) Exhaust waste heat; (9) Pressure regulator; (10) Steam generator; (11) Jacket heater and insulation; (12) Biochar activation reactor; (13) Nitrogen inert gas; (14) Stack gas; (15) Gas clean-up; (16) Stack

2.2. The characterization of the biochar and activated biochar

The characterization of the biochar and activated biochar was determined at 77 K by means of an automatic adsorption instrument to identify the textural properties of the produced biochar and activated biochar. Before the gas adsorption measurements, the samples were degassed at 300 °C under vacuum for 5 h. The N$_2$ adsorption isotherm was achieved over a relative pressure, $P/P_0$, ranging from roughly $10^{-6}$ to 1. The Brunauer–Emmett–Teller (BET) and t-plot methods were employed to determine the surface area, micropore surface area, and pore volume of the biochar and activated biochar, respectively. Relative pressures in the 0.01-0.15 range were applied to evaluate the BET surface areas. The total pore volumes ($V_t$, cm$^3$ g$^{-1}$) were considered to be the liquid volumes of N$_2$ at high relative pressure near unity (~0.99).

Scanning electron microscopy (SEM) analysis was performed to investigate the surface, textural, porosity, and structural properties of activated biochar produced under different conditions. SEM analysis were taken by enlarging x500 size to observe changes in surface morphological structure before and after activation.

To examine the crystal structure, XRD profiles of each sample were obtained at room temperature, using a Cu Kα X-ray source, under 40 kV and 30 mA analysis conditions. Diffraction data were taken on a scale ranging from 2θ = 0-90°.

In order to qualitatively determine surface functional groups, FT-IR spectra were obtained at room temperature, with the support of diamond orbital attenuated total reflection (ATR) accessory, by scanning 128 times in the range of 500-4000 cm$^{-1}$ band at 4 cm$^{-1}$ separation sensitivity. Samples were placed directly on the diamond crystal and were analysed by applying pressure to allow it to fully interact with the diamond crystal.

3. Results and Discussion

As shown in Figure 2, activation of biochar produced from the gasification system at Gebze Technical University (GTU) Gasification Experimental Rig (Figure 3) has been completed. The
biochar obtained by the gasification of the oak type woodchips biomass (Figure 4) in the gasification system at GTU was treated with the physical partial activation method integrated to the gasification system. There are different wood-based sources for biochar production. Highest carbon content is provided from oak wood chip feedstock. Therefore, in the present study, biochar produced from oak woodchip feedstock were used for the production of activated carbon materials. Table 1 summarizes the composition of oak woodchip feedstock. In addition, the proximate and elemental analysis of the oak woodchip is given in Table 2 & 3 respectively, and Figure 5 represents the TGA tracings for oak woodchips.

Figure 2. (-1-) Oak woodchips, (-2a-) gasification by-product Biochar, (-2b-) Activated Biochar with steam activation

Figure 3. Gasification System in Gebze Technical University
Figure 4. Oak woodchips gasification by-products (Biochar)

Table 1. Analysis results of oak woodchip feedstock

<table>
<thead>
<tr>
<th>ANALYSIS</th>
<th>unit</th>
<th>ANALYSIS RESULTS</th>
<th>METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Original based</td>
<td>In air dry based</td>
</tr>
<tr>
<td>Moisture</td>
<td>% wt.</td>
<td>45.01</td>
<td>2.95</td>
</tr>
<tr>
<td>Ash</td>
<td>% wt.</td>
<td>0.22</td>
<td>0.4</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>% wt.</td>
<td>44.92</td>
<td>79.27</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>% wt.</td>
<td>9.85</td>
<td>17.39</td>
</tr>
<tr>
<td>Total Sulfur</td>
<td>% wt.</td>
<td>0.06</td>
<td>0.1</td>
</tr>
<tr>
<td>Sulfur in Ash</td>
<td>% wt.</td>
<td>1.38</td>
<td>-</td>
</tr>
<tr>
<td>Lower Heating Value</td>
<td>cal/g</td>
<td>2330</td>
<td>4533</td>
</tr>
<tr>
<td>Higher Heating Value</td>
<td>cal/g</td>
<td>2749</td>
<td>4852</td>
</tr>
</tbody>
</table>

According to the proximate and elemental analysis data given in Table 1 and Table 2, it is understood that oak wood chip has a good potential and represents ideal feedstock to produce suitable biochar via gasification due its high carbon content and higher heating values. In addition, it appears to be an excellent source of feedstock for the gasification process due to its low ash content.
**Table 2. The results of elemental analysis of oak woodchip feedstock**

<table>
<thead>
<tr>
<th>ANALYSIS</th>
<th>Unit</th>
<th>Oak Woodchip</th>
<th>METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (Carbon)</td>
<td>% wt.</td>
<td>52.38</td>
<td>ASTM D 5373-13</td>
</tr>
<tr>
<td>H (Hydrogen)</td>
<td>% wt.</td>
<td>6.57</td>
<td>ASTM D 5373-14</td>
</tr>
<tr>
<td>N (Nitrogen)</td>
<td>% wt.</td>
<td>0.27</td>
<td>ASTM D 5373-15</td>
</tr>
<tr>
<td>S (Sulfur)</td>
<td>% wt.</td>
<td>0.1</td>
<td>ASTM D 4239-13</td>
</tr>
<tr>
<td>Ash</td>
<td>% wt.</td>
<td>0.41</td>
<td>ASTM E 1755-01</td>
</tr>
<tr>
<td>O (Oxygen)</td>
<td>% wt.</td>
<td>40.27</td>
<td>ASTM D 3176-09</td>
</tr>
</tbody>
</table>

**Table 3. Halogen and ash analysis results of oak woodchip feedstock**

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Unit</th>
<th>Oak Woodchip</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>%</td>
<td>&lt;0.05</td>
<td>Ion Chromatography</td>
</tr>
<tr>
<td>Chlorine</td>
<td>%</td>
<td>&lt;0.02</td>
<td>ISO 587</td>
</tr>
<tr>
<td>Bulk Density</td>
<td>kg/m³</td>
<td>367.8</td>
<td>EN 787-11</td>
</tr>
<tr>
<td>SiO₂</td>
<td>%</td>
<td>14.5</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>%</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>%</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>%</td>
<td>37.3</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>%</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td>%</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>%</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>%</td>
<td>19.3</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>%</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>%</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

According to the halogen and ash analysis given in Table 3, the mineral and metal content in the oak woodchip feedstock caused the formation of the cratered shape biochar, which also acted as a natural catalyst during the gasification reactions, thereby providing the desired or better syngas yield.
Figure 5 shows the results from Thermo-Gravimetric Analyses (TGA) carried out on oak woodchips samples. The thermal degradation of oak woodchips takes place in three stages. The first stage, which occurs at temperatures ranging between 30 °C and 100 °C, involves the loss of moisture content in the wood with approximately the weight loss of 10 wt.%. The second stage with nearly 20 wt.% weight loss was occurred whilst temperature rising from 150 °C to 250 °C. This step is related to the release of volatiles resulting from the degradation of hemicellulose. In the third stage occurring at 300–550 °C is characterized by the decomposition of cellulose and lignin. The maximum rate occurred at the third section almost with the weight loss of around 45 wt.%. Nevertheless, no significant weight loss is observed above 650 °C, indicating that a temperature of level or above could be preferred for preparation of the activated biochar. The total of weight loss recorded was approximately 85%.

Biochar extraction was obtained after uniform ligneous biomass gasification. Since it has high fixed carbon content and is suitable for active carbon production, feedstock has been determined as an oak woodchip. The supplied biomass was utilised directly in gasification without any prior treatment. The optimum temperatures determined in this gasification tests were in the range of 800-1000 °C, while the air/fuel ratio was determined as 1.6 and the gasification system operations were carried out accordingly. The applied gasification conditions are shown in the mass and energy diagram given in Figure 6. The energy value of
the feedstock was calculated as 20 MJ/kg on a dry basis. Additionally, about 80 kg/h of ambient air was used for the gasification agent. According to the conditions in this operational tests, 5.5 kg of biochar is obtained per hour from 50 kg/h fuel supply to the gasifier. In addition, total 850 MJ syngas gas thermal energy determined in the mass energy balance which was utilised as an energy source for the activation unit that was integrated into the system in order to apply process intensification. These tests were a fine example of the intensification since two processes namely gasification and activation retrofitted to each other to preserve and to use heat in the process as compared to conventional activation.

![Mass and energy balance for gasifier during the production of biochar](image)

**Figure 6.** Mass and energy balance for gasifier during the production of biochar

One critical aspect in the assessment of the potential for activated biochar production from oak woodchip by using the updraft gasifier is the energy and mass balance of the process. The mass and energy equilibrium on the reactor provide a quantitative measure of the efficiency for conversion of feedstock to produced gas and biochar using this particular type of gasifier. Mass and energy balances for a specific type of feedstock will vary from one type of gasifier to another as the thermodynamic equilibria and reaction kinetics of the three head reactions in gasification vary depending on the gasifier operating conditions.
The mass balance analysis on the gasifier requires an evaluation of the inputs to and outputs from the gasifier. From the calculations, achieving 100% closure is not easy to obtain and the results illustrate the complications of acquiring this data. However, the mass balance closure for initial run was found to be average 85% which represents a reasonable figure for the initial proof of concept assessment of oak woodchip gasification study trials. Mass and energy balance diagram for initial run is given in Figure 6.

Considering the data in mass and energy balance, the reactor was operated, and syngas and biochar production were obtained at high rates close to theoretical calculations. During operations, approximately 5.5 kg of biochar were obtained per hour, and this produced biochar were transferred to the biochar activation unit shown in Figure 1. Also, syngas produced by gasification was burned to a specially designed syngas burner and thermal heat obtained is transferred through the thermal heater to the biochar activation unit. During the experimental study, 9 different activation operations were performed under different temperature (700 °C, 750 °C and 850 °C) and each with a different residence time (30, 60, and 90 min). Due to the reactor design, a heating rate of approximately 20 °C min⁻¹ was conducted in all studies, which is a favourable condition for activating biochar. At the same time, the steam flow rate was applied as 1.3 kg min⁻¹ in accordance with this heating rate and reactor design.

Approximately, gasifier by-product of 5.5 kg of biochar were transferred to the activation reactor. The first experiment was carried out at 700 °C for 30 minutes residence time. Then same procedure applied at 60 minutes and 90 minutes residence time at 700 °C, after which the samples were cooled with nitrogen gas. Subsequently, experiments were carried out at 750 °C and 850 °C under the same conditions. For calculating burn-off values of the samples formed after activation were extracted from the biochar obtained by weight from the first value and were determined as a percentage. Effects of activation time and temperature on burn off of activated biochar are given in Figure 7. In addition, BET surface area and total pore volume analyses were performed in each sample obtained and given in Figure 8 and Figure 9.
According to Figure 7, during the activation of the biochar with steam method, there is a mass loss between 40 and 70 percent. It is evident from the figure that the biochar regularly loses mass due to an increase in the activation temperature and residence time. It is clearly seen from the data that the highest mass loss is observed at 850 °C when activation period reaches to 90 minutes. The possible reason for that is some carbon element in the biochar structure reacts with H₂O at high temperatures and forms CO and H₂ gas (synthesis gas). In this thermochemical process, carbon leaves the structure and causes mass loss but creates more pores in the structure.
Figure 8. Progress of BET surface area and total pore volume with burn off of activated biochar

Figure 9. Effect of activation time and temperature on BET surface area of activated biochar
Physical adsorption and surface area measurement (BET) were performed. According to BET surface area and total pore volume analysis shown in Figure 8 and Figure 9, it is clearly seen that temperature and residence times have a significant effect on the formation of surface morphology of biochar. As it can be understood from these figures, it is inferred that the most appropriate one of the temperature and residence time intervals applied for activation for oak biochar in 60 minutes at 750 °C.

The resultant biochar produced from the gasification as a by-product was compared with partially activated biochar utilising steam in Table 4. It was determined that the volume and area of the surface pores of the steam treated biochar increased significantly (Total pore volume 0.022 cm$^3$ g$^{-1}$ and 0.231 cm$^3$ g$^{-1}$, BET surface area 21.35 and 458.28 m$^2$ g$^{-1}$, respectively). It was compared with the commercial activated carbon used in water filters produced from coconut shell and physical adsorption and surface area measurement was presented in detail (0.326 cm$^3$/g – 648.96 m$^2$/g).

BET surface area analyses were carried out from biochar and by activating the biochar obtained as a result of gasification in the steam activation unit shown in the Figure 1 at the specified temperatures. According to the results obtained, it is given in the Table 4 and the most suitable temperature for activation was found at 750 °C. Since the 1-hour residence time activated biochar at 750 °C is the highest result (458.28 m$^2$ g$^{-1}$), other analyses such as FTIR, XRD and SEM of the selected activated biochar obtained were conducted. Also, these results were compared with the biochar produced from gasifier without any activation.

<table>
<thead>
<tr>
<th>BET results(m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biochar</td>
</tr>
<tr>
<td>Activated Biochar (750 °C, 60 min)</td>
</tr>
</tbody>
</table>

Finally, during steam activation process, the porosity increased apparently when the temperature rose to about 750 °C. On the other hand, the micrographs obtained from the biochar and activated biochar showed no discrepancies in terms of morphological properties. As both samples yielded different porosity values, this result can be said to be coherent with the physisorption results obtained from surface analyses.
The discussion section, first of all, deals with the properties of the carbonization process. The produced activated biochar was found to yield an increase in the surface area (from 21.35 to 458.28 m$^2$ g$^{-1}$) and total volume (from 0.022 cm$^3$ g$^{-1}$ to 0.231 cm$^3$ g$^{-1}$) as a result of the transition from limited air to steam in the gasification system. Generally, the rise in the temperature of the gasification process causes a higher discharge of volatile matter. This, in turn, leads to an increase in the original porous structure that will be further developed during the activation phase. On the other hand, high temperature in the gasification process results in the softening and sintering of the high molecular weight volatiles, which leads to the depolymerization and shrinkage of the particles. This also causes a reduction in the micropore surface area and volume. Nevertheless, a temperature below 700 °C in the gasification phase impedes the complete devolatilization of the low molecular weight volatiles, and as a result, prevents the initial porosity from being further developed.

An increase in the temperature from 800 to 1000 °C leads to a decrease in the yield efficiency of biochar from gasified oak woodchips. This is caused by the oak woodchips being partially decomposed in gaseous products. Therefore, the ideal gasification and activation temperatures are 750 °C, which was used to activate the samples in the following.

The ratio of the mass of activated biochar to the mass of the raw material is calculated to determine the yield of activated biochar. The oak biochar activated at 750 °C were examined to evaluate the effects of the activation temperature and the hold time on the yield of activated biochar. The sample that underwent activation with steam at pre-determined activation temperatures and constant hold time (1 h), different hold times, and constant activation temperature (750 °C) produced the results.

An activation temperature of 750 °C at constant hold time caused a change in the yield of activated biochar. This is linked to the elimination of volatile matter arising from the decomposition of main oak wood chips compounds, i.e., cellulose (a long glucose polymer without branches) and hemicellulose (composed of a variety of branched saccharides). Due to the decomposition of all cellulose and hemicellulose, the yield becomes stable at a temperature of above 700 °C. As a result, lignin, the third component of oak woodchips that is more challenging to decompose, remains. In fact, lignin is known to decompose slowly at a temperature ranging from room temperature to 900 °C [38]. Yet, the decomposition of cellulose and hemicellulose generates a porosity in oak wood chips that enables more efficient diffusion of oxygen to the particles. Hence, an increase is obtained in the kinetic reaction of...
lignin with oxygen. According to these results, the more cellulose and hemicellulose the raw material contains, the faster the decomposition of lignin takes place. The decomposition of the biomass actually occurs in two steps during activation: the decomposition of the cellulose and hemicellulose takes place first. This first step leads to an increase in the porosity of the activated biochar, and, as a result, the oxidizing agent can easily diffuse into the particles. Secondly, the lignin reacts with the oxidizing agent.

The endothermic reaction of carbon with water to produce carbon dioxide and hydrogen is thermodynamically more desired and is quicker at 750 °C. Longer hold time generates an increase in the amount of discharged volatile matter.

Surface energies of oak biochar produced after gasification were measured by a scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) analysis was performed at Gebze Technical University (GTU) Laboratories (Figure 10 and Table 5). Surface pores were clearly seen in SEM analyses and images were found to be consistent. In addition, biochar produced after oak gasification process has a carbon content of about 80-85% and decided that it can be used for activated carbon production as a raw material. These findings are confirmed by energy-dispersive X-ray spectrometry measured at different areas of the sample since Si, O, K, Ca, and Mg were observed on the surface (see the spectrum in Table 5), which mainly contributed to the formation of low melting point eutectics.
Figure 10. SEM analysis of biochar (a,b,c) and activated biochar (d,e,f)

<table>
<thead>
<tr>
<th>Material</th>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Error %</th>
<th>Net Int.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Biochar (750 °C, 60 min.)</td>
<td>C</td>
<td>84.28</td>
<td>87.72</td>
<td>0</td>
<td>11607.58</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>15.72</td>
<td>12.28</td>
<td>0.01</td>
<td>827.78</td>
</tr>
<tr>
<td>Biochar without any activation</td>
<td>C</td>
<td>79.66</td>
<td>84.32</td>
<td>0</td>
<td>30208.26</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>19.14</td>
<td>15.21</td>
<td>0</td>
<td>3085.12</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>0.22</td>
<td>0.12</td>
<td>0.02</td>
<td>221.97</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>0.17</td>
<td>0.08</td>
<td>0.02</td>
<td>183.87</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>0.13</td>
<td>0.06</td>
<td>0.02</td>
<td>153.36</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>0.36</td>
<td>0.12</td>
<td>0.03</td>
<td>225.72</td>
</tr>
<tr>
<td></td>
<td>Ca</td>
<td>0.32</td>
<td>0.1</td>
<td>0.03</td>
<td>166.7</td>
</tr>
</tbody>
</table>
**Table 5.** Energy Dispersive Spectroscopy (EDS) analysis of oak woodchips biochar and activated biochar

XRD is an analysis method to prove whether the structure is crystalline. This method, which is widely used in the synthesis of activated carbon, helps us to see whether there is a crystal in the structure. Although activated carbons are generally amorphous structures, crystals can be found in the activated carbon structure depending on the synthesis methods.

Considering the XRD results showed in Figure 11 of the synthesized activated biochar, it is seen that there is no crystalline phase in the structure and the structure is completely amorphous. In addition, it was understandable that no peak was seen in the previous studies since the synthesis conditions were considered to be quite amorphous. It is seen that all activated carbon samples have 3 different amorphous phases. A horizontal basic line can be seen in the diffractogram of biochar and activated biochar, which indicates that a significant proportion of the matter is amorphous. It can be inferred from the XDR pattern of the biochar that the gasification process had a significant impact. Owing to the decomposition of cellulose and hemicellulose during the thermal treatment, the diffraction peaks achieved at $2\theta = 16.3$ and $20.60$ disappear. Subsequent to the pyrolysis, only two broad diffraction peaks at around $23.58^\circ$ and $43^\circ$ remain, which could be related to the presence of carbon and graphite [39].

![Figure 11. Activated Biochar and Biochar XRD analyses](image-url)
Surface functional groups of the biochar at high temperature (750 °C) with steam were measured. Surface functional groups (FT-IR) of the biochar were also analysed in the laboratories at GTU. Considering the formation of surface functional groups of the biochar, these analyses revealed that gasification is a correct method in the production of activated carbon. As seen in Figure 12, as expected for activated carbon, C-H stretching vibration was observed at 2973 cm\(^{-1}\), C=O, and C=N at \(\sim1591\) cm\(^{-1}\), and C-O stretching at \(\sim1045\) cm\(^{-1}\). Also, stretching was found in the alcohols, phenols and/or ether, ester groups. As in the case of commercial activated carbon, the strong band is seen at about 799 cm\(^{-1}\) that is described as COOH vibrations in carboxylic groups; biochar and partially activated biochar were also observed.

![Figure 12. Surface Functional Group Analysis of biochar, activated biochar and commercial activated carbon (FTIR)](image)

### 4. Conclusion

This paper investigated the production possibility of activated carbon from biochar generated as by-product from gasification of oak woodchips by means of the physical activation method
with an activating agent, pure steam. According to the SEM examination of raw biochar obtained from oak woodchips and activated biochar, the gasification process led to a gradual increase in the porosity, and the steam process caused further activation. Carbons with increased porosity and surface area are produced by the steam activation of biochar from oak woodchips. The sub-stoichiometric air gasification resulted in a maximum BET surface area and micropore volume of 21.35 m²/g and 0.022 cm³/g, respectively. On the other hand, steam activation of biochar further resulted in a maximum BET surface area and micropore volume of 458.28 m²/g and 0.231 cm³/g, respectively. Hence, steam activation yielded a more than ten-fold increase in this study. Also, oxygen functional groups (carboxylates, lactones, and phenols) on the surface led to a high degree of aromaticity in the activated biochar.

One of the major contributions of this study for the state-of-the-art is that the production of activated carbon will not require external thermal energy for the activation anymore, which causes a considerable increase in the cost of the production. Process is intensified by eliminating thermal activation step and biochar produced as a by-product as a result of gasification has a high carbon content, highly porous structure and it is a semi-activated substance. Previous studies have also shown that specific processes can be employed for the conversion of biochar into activated carbon. Furthermore, less costly and more sustainable production of activated carbon can be obtained by using by-product biochar produced from biomass gasification systems.

To sum up, if prepared under optimal settings, the activated biochar produced from oak woodchips can have a large surface area and microporous volume. These highly porous carbon substances produced with low production costs can be effectively used to control environmental pollution through, for example, adsorption of gaseous pollutants and heavy metals.

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**References**


