Print ISSN : 0972-8813
e-ISSN : 2582-2780

[Vol. 22(3) September-December 2024]

Pantnagar Journal of Research

(Formerly International Journal of Basic and Applied Agricultural Research ISSN : 2349-8765)

G.B. Pant University of Agriculture & Technology, Pantnagar

PANTNAGAR JOURNAL OF RESEARCH

Vol. 22(3) September-December 2024

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Analyzing the role of biomass properties in determining activated biochar yield

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ABSTRACT: This study investigates the impact of four biomass materials—pine cone, paddy straw, coconut shell and pine needle on the yield and quality of activated biochar. Biomass was characterized for composition, proximate and ultimate properties. The chemical activation process was performed using phosphoric acid (H_3PO_4) under varying conditions of activation time (20, 40 and 60 minutes), temperature (400°C, 450°C and 500°C) and impregnation ratio (1: 1.25, 1: 1.5 and 1: 1.75). Results showed that coconut shell produced the highest biochar yield, ranging from 65.23% to 48.77%, followed by pine needle (47.39%–57.81%) and pine cone (52.75%–45.23%). Paddy straw exhibited the lowest yield, from 39.6% to 33.72%. Biomass with higher carbon content and lignin, such as coconut shell, produced higher biochar yields, while materials with lower lignin, like pine cone and paddy straw, had lower yields. Longer activation times and higher temperatures reduced biochar yield by promoting volatile production. Surface area and porosity analysis indicated that coconut shell and pine needle biochar had the highest surface areas, beneficial for adsorption. The study demonstrates that phosphoric acid activation is an effective, cost-efficient method for producing biochar with desirable properties for environmental applications like water treatment, soil amendment and air purification.

Key words: Activated biochar, biochar, chemical activation, pyrolysis

Biomass is organic material from wastes, forest residues, woody energy crops, microalgae and animal waste that is a renewable energy source. It is carbon-based material made up of organic molecules that contain hydrogen, oxygen, nitrogen and other atoms. Biomass can be burned directly to produce heat or electricity or converted to liquid and gaseous fuels like ethanol or biodiesel. Plants absorb carbon dioxide (CO_2) from the atmosphere to construct biomass, using energy from the sun. The world produces an estimated 146 billion metric tons of biomass annually, mostly from wild plant growth (Balat and Ayar, 2005). India produces about 990 million metric tons of agricultural biomass annually. Biomass provides 32% of all the primary energy use in the country at present. Some of this generated biomass is utilized for combustion as fiber, packaging material, fuel, paper and pulp. However, a major part of these gets decomposed or burnt in an uncontrolled manner which causes environmental pollution (Koul *et al.*, 2022). So, to minimize this causes the biomass is converted into different use full forms by different conversion processes. Thermochemical conversion, Pyrolysis, Liquefaction, Torrefaction, Combustion, Transesterification, Catalytic upgradation and Biorefineries etc. these are some conversion processes to convert the biomass into energy and other products. Out of this thermochemical conversion process use heat to convert biomass into sustainable fuels. It's faster than biochemical conversion and takes place at higher temperatures (Wang and Wu, 2023). Thermochemical conversion process includes pyrolysis, Torrefaction and Hydrothermal liquefaction. In pyrolysis process bio-oil, bio char, syngas and tar were formed. An emerging term for carbonaceous materials was biochar that refer to carbon sequestration, soil remediation and sustainable fuels. Biochar is defined as charcoal and carbon-rich material produced by partial oxidation (pyrolysis at $\leq$ 700 °C in the absence or limited supply of oxygen) of carbonaceous organic sources such as wood and plants (Bhattacharya *et al.*, 2024). By converting biomass waste into biochar, the carbon that would otherwise be released into the atmosphere through decomposition is sequestered, contributing to carbon mitigation efforts. In recent years, significant attention has been given to optimizing pyrolysis conditions to enhance biochar yield and quality.

However, research is still limited in understanding how the design and structural characteristics of biochar influence its physicochemical properties and their corresponding applications. There is a need for further exploration into the relationship between biochar's molecular structure and its performance in various applications, such as soil enhancement, carbon sequestration and waste remediation.

The aim of this study is to analyse the impact of four common and abundantly available biomass materials: pine cone, paddy straw, coconut shell and pine needle on the yield and quality of activated biochar. The objectives of this study are to examine the physical and chemical properties of each biomass material and their influence on the pyrolysis process, to determine the relationship between material properties and the yield of activated biochar, to evaluate the potential applications of the activated biochar in soil amendment, water treatment, air purification and other uses and to assess the role of these biomass sources in contributing to waste management and environmental sustainability.

MATERIALS AND METHODS

The raw material of experiment was collected from various places. Pine cone (Pinus-roxburgii) and pine needle biomass were collected from pine forests located in Nainital, Uttarakhand, India. Paddy Straw from Crop Research Center, G. B Pant University of Agriculture and Technology, Uttarakhand, India and coconut shell from local market at Pantnagar. In

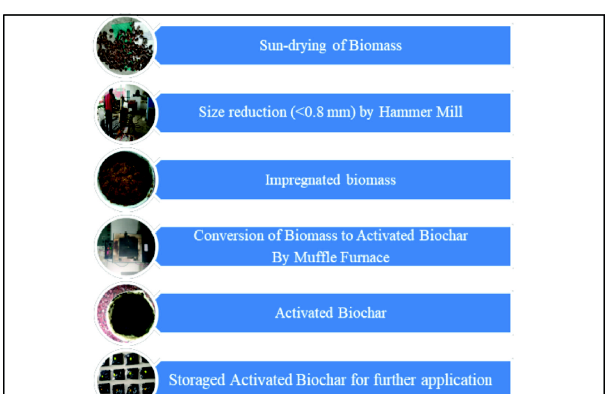

Fig. 1: Chemical activation process

proximate analysis moisture content, volatile matter, fixed carbon content and ash content of above biomass was determined as per ASTM D 3173, ASTM D 3175-02 and ASTM D 3174, respectively. The extractive, lignin, cellulose and hemicellulose content in biomass precursors significantly influence the thermal degradation process and the resulting end products. The composition of these components in biomass was determined using the method proposed by Yang *et al.* (2006). Ultimate analysis was done using CHNO Analyzer and Calorific value was determined using bomb calorimeter present in departmental laboratory.

Biochar is a charcoal-like substance obtained through the thermochemical conversion process of pyrolysis, which involves thermal decomposition in the absence of oxygen at temperatures ranging from 400°C to 600°C and under atmospheric pressure. Efficient utilization of biomass is its conversion to activated biochar with either of the two methods, physical and chemical activation. The process of chemical activation constitutes of impregnation and activation process with use of acid and base as activation agent and shown in Fig.1. The chemical activation process was adopted for the research due to the fact that it is conducted at lower temperature, results in relatively higher yield, higher surface area, narrow range of well-developed surface area and performed in a single step (Ghritalahre *et al.*, 2023). For the activation firstly sun-dried biomass was reduced to <0.8 mm size using hammer mill present at departmental workshop. After reduction 50-gram dried sample was impregnated in acid at specific level as mention in Table 1 for 24 hours at room temperature. Acid used in this study was phosphoric acid (H_3PO_4). Phosphoric acid activation of lignocellulosic materials has become an increasingly used technique for the large-scale production of activated carbons because of environmental advantages and several other benefits such as facility of recovery (only washing with water) as compared to $ZnCl_2$ activation, low energy cost and high char yield over the physical activation. Phosphoric acid plays important role in the acid-catalysed conversion of lignocellulosic materials into a highly porous activated carbon as stated by Khalili *et al.* (2015).

Impregnated biomass sample was then put in muffle furnace for the activation at specific temperature and time. In this experiment effect of various parameters viz. activation time, activation temperature and impregnation ratio of activating agent on yield of activated biochar was determined by considering different levels of these parameters as shown in Table 1. All treatments were conducted using a combination of one activation time (20, 40 and 60 minutes), one activation temperature (400°C, 450°C and 500°C) and one impregnation ratio (1: 1.25, 1: 1.5 and 1: 1.75). A total of 27 combinations were formed, labelled from T1 to T27. Activated biochar was washed with distil water several times till it shows pH 7 or neutral. This process was done to wash excess acid present in pores. This washed biochar was dried in oven and stored in seal pack bags for further characterisation.

RESULTS AND DISCUSSION

The analysis of pine cone, paddy straw, coconut shell and pine needle biomass were conducted according to the protocol discussed and the obtained data of composition, proximate and ultimate analysis was shown in Table 2.

From Fig. 2 it is observed that extractive was maximum (16.86 %) in pine needle and minimum (5.45 %) in pine cone biomass. Cellulose was maximum (41.2 %) in pine cone and minimum (15.13 %) in coconut shell. Hemicellulose was maximum (31.8 %) in coconut shell and minimum (23.2 %) in pine cone and lignin was maximum (44.7 %) in coconut shell and minimum (28.85 %) in paddy straw.

Table 1: Process parameters used in the preparation of activated biochar

Biomass	Pine Cone, Pine needle, Paddy straw and Coconut shell
Activation time, minutes	20, 40, 60
Activation temperature, °C	400, 450, 500
Impregnation ratio	1: 1.25, 1: 1.5, 1: 1.75

Extractives in biomass includes non-structural components such as oils, resins and waxes. They volatilize at lower temperature during the pyrolysis process and reduces the overall char yield by contributing more to the formation of gases and tar during pyrolysis. Cellulose and Hemicellulose these polysaccharides are major contributors to char formation. During pyrolysis, cellulose contributes to the formation of biochar, but its decomposition also releases a significant amount of volatile gases. The higher the cellulose content, the lower the biochar yield, as more material is converted into gases rather than solid char as stated by Mandlekar *et al.* (2018). Hemicellulose decomposes at a lower temperature range compared to cellulose. It also contributes to volatile products during pyrolysis, leading to a lower yield of biochar but it can also

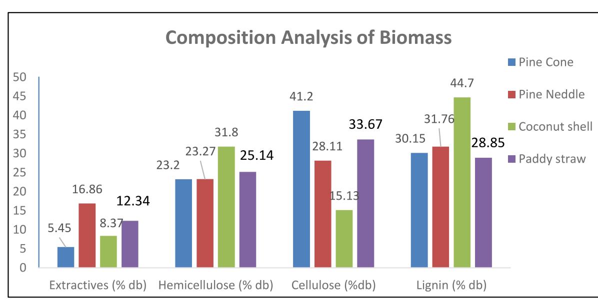

Fig. 2: Comparison between composition analysis of biomass

Table 2: Composition, proximate and ultimate analysis of biomasses

Composition Analysis:	Pine Cone	Pine Needle	Coconut shell	Paddy straw	Ultimate Analysis:				
Extractives (% db)	5.45	16.86	8.37	12.34	C (% db)	46.14	45.6	54.55	36.07
					H (% db)	7.8	4.8	5.75	5.2
Cellulose (% db)	41.2	28.11	15.13	33.67	N (% db)	0.5	0.8	0.86	0.64
Hemicellulose (% db)	23.2	23.27	31.8	25.14	O (% db)	45.56	46.4	37.64	34.54
Lignin (% db)	30.15	31.76	44.7	28.85	HHV (MJ /kg)	18.96	27.31	29.51	13.12
Proximate Analysis:									
Volatiles (% db)	77.58	74.2	68.8	64.27	Fixed carbon (% db)	16.28	15.6	20.6	12.79
Ash content (% db)	0.98	2.4	1.2	11.25	Moisture content (% wb)	5.16	7.8	9.4	11.69

impact the porosity and surface area of the resulting biochar, which are important for activation. Lignin was complex aromatic polymer that decomposes over a wide temperature range and it is more resistant to thermal degradation than cellulose and hemicellulose. A higher lignin content generally results in a higher yield of biochar because more of the biomass is converted into solid char (Kopp Alves *et al.*, 2024). Lignin contributes to the stability and carbon content of the biochar, making it a crucial component for producing high-quality activated biochar. Lignin is known for its high char-forming potential. The degradation of lignin is temperature-dependent, with higher temperatures leading to increased char formation.

In proximate analysis of biomass volatile matter, ash content and moisture content were determined. From the Fig.3 it is observed that volatile matter is more in pine cone than all other biomass. Ash content is maximum in paddy straw. Fixed carbon content is calculated by subtracting volatile matter, ash content and moisture content from 100. Moisture content in biomass affects at initial stages of pyrolysis. High moisture content requires additional energy to evaporate the water, which can reduce the efficiency of the pyrolysis process and lower the yield of biochar. Excess moisture can lead to incomplete carbonization, resulting in a biochar with lower fixed carbon content and possibly higher volatile content (Adeniyi *et al.*, 2024). To maximize biochar yield, biomass is typically dried to reduce moisture content before pyrolysis process.

Volatile matter consists of compounds that vaporize during the heating process, such as gases and tars. Biomass with high volatile matter content tends to produce less biochar, as more of the material is lost as gases and liquids during pyrolysis. The release of volatile matter results in lower solid residue, reducing the overall yield of biochar. However, controlling the pyrolysis conditions can influence the retention of certain volatiles, impacting the surface area and porosity of the final biochar as suggested by Tomczyk *et al.* (2020). Ash content refers to the inorganic mineral residue left after the complete combustion of the biomass. High ash content in biomass typically leads to a lower yield of activated biochar, as it indicates a higher presence of non-combustible material that does not contribute to the formation of biochar. Ash can also affect the quality of the biochar by influencing its pH, mineral content and potential catalytic properties during activation. The fixed carbon content also contributes to the structural integrity, adsorption capacity and overall stability of the activated biochar, making it a crucial factor in determining both yield and quality. The ultimate analysis measures the percentage of carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) on a dry basis (% db), which indicates the elemental composition of the biomass. The Fig.4 presents the ultimate analysis and higher heating value (HHV) of four different biomass materials: pine cone, pine needle, coconut shell and paddy straw. These parameter gives chemical composition and energy potential of each biomass type, which are important for applications like biochar production and bioenergy.

(Tripathi *et al.*, 2016) reported that biomass with a high carbon content generally produces a higher yield of biochar because carbon is the primary

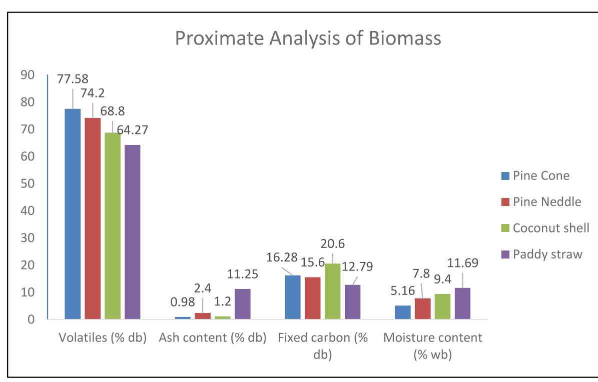

Fig. 3: Comparison between proximate analysis of biomass

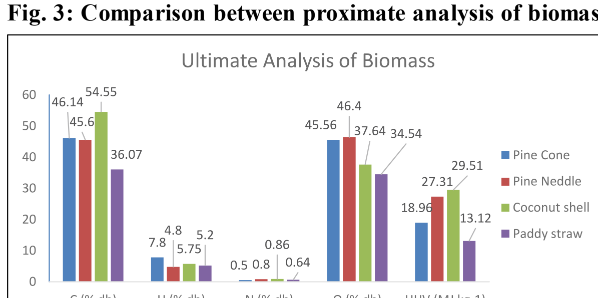

Fig. 4: Comparison between ultimate analysis of biomass

component that remains as solid residue after pyrolysis. The higher the initial carbon content, the more material is available to form the solid char. Hydrogen content in biomass is associated with the volatile components that are released during pyrolysis. High hydrogen content results in the production of more gases and liquids (such as water and hydrocarbons), which decreases the solid yield of biochar. Hydrogen in the biomass tends to form volatile compounds, which are lost during pyrolysis, thereby reducing the final biochar yield. Nitrogen content in biomass is usually found in proteins and other nitrogenous compounds. During pyrolysis, nitrogen is mostly released as volatile gases like ammonia (NH_3) or nitrogen oxides (NO_x). While nitrogen has a lesser direct impact on the yield of biochar, it is important for applications in soil amendment or adsorption processes. Excessive nitrogen may also lead to the formation of toxic by-products during pyrolysis. Oxygen content in biomass is associated with the presence of functional groups like hydroxyls, carboxyl's and carbonyls. High oxygen content typically leads to lower biochar yield, as oxygen-rich components tend to decompose into volatile compounds (such as CO, CO_2 and water) during pyrolysis. Biomass with high oxygen content often results in more gas and liquid by-products, reducing the amount of solid char produced. The higher oxygen content can influence the chemical reactivity and surface chemistry of the resulting biochar.

From fig. 4 it is observed that coconut shell has maximum carbon content (54.55%) than other

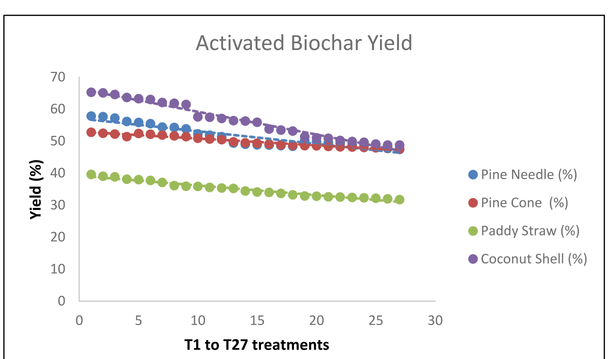

Fig. 5: Comparison between yield of activated biochar

biomass resulting in higher calorific value (HHV-29.51MJ/kg). Similarly, paddy straw contains minimum carbon content (36.07%) and resulting in lower calorific value (HHV-13.12 MJ/kg) when compare to other biomasses used in this study.

Fig.5 represents the yield of activated biochar derived from four types of biomasses—pine cone, pine needle, paddy straw and coconut shell—across 27 different treatments. The treatments vary based on three parameters: activation time, activation temperature and impregnation ratio as shown in Table. 1.

Longer activation times generally result in more extensive pyrolysis, leading to greater decomposition of the biomass and potentially lower biochar yield as more material is converted to gases and liquids. This might be because longer activation times can result in increased pore development and loss of carbon during the activation process. Higher temperatures tend to increase the thermal degradation of biomass, reducing the yield of solid biochar while increasing the formation of volatiles. Higher temperatures can enhance pore development and carbon activation, but excessive temperatures can lead to char degradation and reduced yield (Sun *et al.,* 2017). The impregnation ratio refers to the amount of chemical activator relative to the biomass. A higher ratio can enhance the activation process, potentially increasing surface area and porosity but decreasing the yield as more biomass is consumed. The coconut shell yields the highest biochar across all treatments, maintaining a range from about 65.23 % to 48.77 %. Despite the variations in time, temperature and impregnation ratio, coconut shell's high carbon content and lower oxygen content help to retain a significant amount of solid biochar even at more aggressive activation conditions. Pine needle yield start at 47.39 - 57.81 % and gradually decrease, similar to coconut shell but consistently lower. As the activation time increases or temperature rises, the yield drops slightly, indicating that the pine needle is more sensitive to these conditions than coconut shell. Pine cone biochar yields are generally lower, starting at 52.75 % and following a similar downward trend with more aggressive treatments. Like the pine needle, the pine cone shows a decrease in yield with higher temperatures and longer activation times. The higher hydrogen content in pine cones likely contributes to more volatile production, reducing the yield. Paddy straw has the lowest yield across all treatments, starting from 39.6 % and decreasing further with harsher activation conditions. The low carbon content and higher ash content in paddy straw contribute to its lower yield, especially under higher temperatures and longer activation times, which further decompose the biomass.

Across all biomass types, increasing activation time, temperature or impregnation ratio tends to reduce biochar yield. This is consistent with the expectation that harsher conditions drive more complete conversion of biomass into gases and liquids, leaving less solid char. Coconut shell maintaining higher yields even under the most severe treatments, likely due to its higher carbon content and structural stability. Phosphoric acid activation offers several environmental benefits, such as waste reduction by converting biomass into valuable products like biochar and activated carbon, which also contribute to carbon sequestration and climate change mitigation. However, the process can have environmental drawbacks, including the potential hazards of handling and disposing of phosphoric acid, which can contaminate soil and water if not properly managed. Additionally, the energy-intensive nature of the activation process, often relying on fossil fuels, may offset some sustainability gains unless renewable energy is used. In terms of cost-effectiveness, phosphoric acid is relatively inexpensive and the high-quality products produced justify the added expense, especially in large-scale operations where costs decrease. However, small-scale operations may face higher costs for both materials and energy and careful management is needed to ensure the process remains environmentally and financially sustainable.

CONCLUSION

In this study it is concluded that biomass with high carbon content can produce high-yield and high-energy biochar. Choosing biomass with a high lignin content and low extractive content can maximize char yield. In pyrolysis process bio-oil, bio char, syngas and tar were formed. The chemical activation process provides greater effect than physical treatment by resulting in relatively higher yield, higher surface area, narrow range of well-developed surface area and performed in a single step. Use of phosphoric acid as activating agent benefited such as low energy cost and higher char yield over the physical activation. Other parameters, such as temperature, heating rate and residence time can affect adsorption capacity. The obtained activated carbon could be used for environmental pollution issues, such as water treatment, pollutant removal and CO_2 capture etc. and even as a component in cosmetics and personal care products. The limitations of this study include the incompatibility of phosphoric acid with certain feedstocks, as well as challenges related to its recovery and reusability. Future research should focus on exploring the properties of activated biochar produced using various activating agents and evaluate their performance across a wider range of feedstocks to enhance the versatility and sustainability of the activation process.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support for this work from Chhatrapati Shahu Maharaj Research, Training and Human Development Institute (SARTHI), Pune, Govt. of Maharashtra.

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Received: August 31, 2024
Accepted: December 12, 2024