

Biochar Activation: A Sustainable Carbon Production from Biomass

Abstract

Biochar, derived from biomass pyrolysis, enhances soil fertility, water retention, and mitigates climate change. The global biochar market is projected to reach USD 3.82 billion by 2027. Activation processes, including chemical methods like sulfuric acid modification, enhance biochar's versatility. Modified biochar effectively retains sulfa methazine, improves soil pH, and demonstrates potential in soil enhancement, wastewater treatment, and heavy metal removal. The study explored 18 pyrolysis combinations, revealing physically and chemically activated cotton stalk bio-char characteristics, such as ash content, volatile matter, fixed carbon, and yields of bio-char, bio-oil, and pyro-gas. At 500°C, biochar fixed carbon was nearly three times higher than raw biomass, enhancing its efficacy.

Key words: Activation, Bio-char, Cotton stalk, Slow pyrolysis, Proximate analysis, Pyrolyzer.

Introduction

The sun, a luminous ball of gas, is Earth's primary energy source, radiating light and heat through nuclear fusion. This process converts hydrogen to helium, releasing vast amounts of energy that sustain life, drive weather patterns, and support all living organisms. Photosynthesis, powered by the sun's radiant energy, plays a pivotal role. It converts sunlight into chemical energy, producing glucose and releasing oxygen. This process forms the foundation of the food chain, maintaining a delicate balance in the ecosystem and regulating oxygen levels.

Photosynthesis not only powers plant growth but also influences the ecosystem through biomass production. Biomass encompasses living organisms and organic matter, serving as a renewable energy source for heat, electricity, and biofuels. Common sources include wood, agricultural residues, and organic waste. Biomass production, crucial for the carbon cycle, reduces greenhouse gases and mitigates climate change. Leveraging biomass potential offers a promising alternative to fossil fuels.

Biochar, derived from biomass pyrolysis, finds versatile usage, especially in agriculture. It enhances soil fertility, water retention, and carbon sequestration, aiding in climate change mitigation. In India, the vast agricultural sector generates significant biomass resources, actively promoted for energy needs. The global biochar market, projected to reach USD 3.82 billion by 2027, highlights its growing significance. Biochar, a by-product of biomass pyrolysis, aligns with India's pursuit of greener and sustainable energy solutions. Biochar, derived from agricultural crop residues through thermo chemical processes, aids in effective crop waste management. Its growing significance stems from distinctive features like high organic carbon content, stability, ample surface area, and cation exchange capacity. Its addition does not change the thermodynamic equilibrium of the reaction but do have an effect on reaction rate and product formation (Patra *et al.*, 2021).

Activated biochar, a refined form, garners attention in waste utilization. This review compiles insights from over 150 recent publications, offering a comprehensive overview of its preparation, characterization, and analytical techniques. Physicochemical attributes of activated biochar vary with feedstock, pyrolysis conditions, and activation method, pivotal for tailored environmental applications (Panwar & Pawar, 2020).

Physical activation or high-temperature steam purging creates pores in biochar, enhancing its properties. Gas purging elevates surface area and pore volume, with steam activation less effective compared to chemical and impregnation methods. Sulphuric and oxalic acid-modified biochar proves ideal for soil amendment. Alkaline activation boosts surface area and oxygen-containing groups, while metal oxide-modified biochar exhibits superior functionalities for contaminant sorption in water treatment. In summary, activated biochar holds vast environmental potential, especially in remediation efforts (Panwar & Pawar, 2020).

Activated biochar, derived through pyrolysis, undergoes processes like physical or chemical activation to enhance its properties. These activation methods increase its adsorption capacity and effectiveness. Physical activation involves high temperatures and gases, creating pores and increasing surface area. Chemical activation includes impregnation with activating agents, leading to a porous structure.

Biochar activation gains global attention for its applications in environmental and agricultural sectors, offering improved nutrient-holding capabilities.

The activation process aims to enhance the surface area, pore volume, pore diameter, and porosity of activated biochar or carbon. Physical and chemical activation are the two primary methods for modifying the physical properties and shapes of the resulting product.

For instance, acid-modified reed biochar showed increased surface area, while starch rice food waste-derived biochar exhibited a maximum BET surface area of 1547 m²/g with phosphoric acid modification. This strategy enhances thermal stability and introduces surface acidity through oxygen-phosphorus surface groups (Cao *et al.*, 2018).

Physical activation of biochar involves subjecting biochar to high temperatures in the presence of a gas, typically steam or carbon dioxide, to create pores and increase its surface area. This process, known as activation, enhances biochar's adsorption capacity and makes it an effective material for various environmental applications. During physical activation, the high temperatures cause the decomposition of volatile matter and the release of gases, creating a porous structure within the biochar. The increased surface area and pore volume allow biochar to adsorb pollutants, such as heavy metals or organic compounds, from air or water. Additionally, physical activation modifies the biochar's physicochemical properties, influencing its reactivity and suitability for specific remediation or filtration purposes (Bardestani & Kaliaguine, 2018).

Chemical activation, also known as wet oxidation, involves impregnating biochar with activating agents and heating under inert conditions. Acid modification, oxidizing agent modification, alkalinity modification, and metal salt modification are steps in this process. Chemical activation, with its low process time and temperature, yields biochar with larger surface areas (3600 m²/g) and well-developed microporous structures, making it ideal for various environmental applications (Isahak *et al.* 2013).

Chemical activation is widely preferred due to its features and encompasses both one-step and two-step processes. In one-step modification, carbonization and activation occur simultaneously with the aid of a chemical agent. In the two-step process, raw material is first carbonized, followed by chemical activation. Acid

activation, a crucial chemical modification, introduces acid functional groups onto biochar, altering its physicochemical properties. Acidic agents like sulfuric and oxalic acids have proven effective for biochar modification, addressing soil improvement and amendment needs (Xu *et al.*, 2021). Chemical activation is a widely adopted process, involving one-step or two-step modifications. Acid activation, using agents like sulfuric and oxalic acids, is essential for introducing acid functional groups and eliminating metallic impurities. Acid-modified biochar influences soil characteristics, nutrient content, and pH. Acid modification improves surface area, with the type of acid, impregnation ratio, and activation temperature playing key roles (Ippolito *et al.*, 2016).

Materials and Methods

For performing activation of biochar batch type pyrolyser was developed by a college of agricultural engineering and technology, Junagadh agricultural university, Junagadh. Which shown in picture below (Makavana *et al.*, 2020).



Fig. 1 Experimental batch type pyrolyser

The pyrolyzing unit consists of a stainless-steel reactor activation chamber (4-5 mm thickness) with outer surface insulation to minimize heat loss due to radiation. The reactor is mounted on a stand for structural stability. An opening at the bottom allows removal of activated biochar. A manual stirrer, attached to the top, ensures

periodic agitation (1-2 gentle rotations every 10-15 minutes) of reactants inside the chamber (Makavana *et al.*, 2020).

Raw material is fed from a hopper, designed for seamless flow to the reactor chamber through a feed inlet pipe. The feed inlet pipe doubles as a gas flow pipe, enabling pyrolyzed gas movement to the condenser when the feed control valve is closed. A valve on the gas flow pipe regulates gas flow from the reactor to the condenser (Makavana *et al.*, 2020).

The condenser, a long concentric cylindrical chamber, has a uniformly converging bottom with a 15 cm diameter inner cylinder and a 2.5 cm gap to the outer cylinder. An electric motor circulates water between the cylinders, with an inlet at the bottom and an outlet at the top, maintaining cooling. Pyrolyzed gas enters from the top, and as it cools, suspended oil particles condense on the inner cylinder's surface. Condensed oil drains automatically from the bottom due to gravity. Cooled and condensed gas, with a higher temperature than non-condensed gas, flows through a small outlet pipe beside the large inlet pipe, directly connecting to the burner for utilization. The water for the condenser is continuously circulated from a water tank under the condensing unit. This batch-type pyrolyzer efficiently converts raw material into activated biochar while recovering valuable condensed oil (Makavana *et al.*, 2020).

In pyrolysing unit for physical activation gas inlet pipe was attach in chamber to spread purging gas in chamber and pore to all biomass material. For best result gas inlet pipe was fitted to side top of reactor unit and one Gas flow controller valve mechanism attach to the gas line for controlling gas flow rate which indicates gas flow it's range 1 litre to 10 litre per hour (Makavana *et al.*, 2020).

Cotton stalk considered as the biomass material. It was collected from the Research Farms, JAU, Junagadh and converted into shredded material with the help of shredder. The shredded stalk is used as feed stalk in the pyrolyser during the activation of biochar study.

In physical activation biomass pass through slow pyrolysis at the target temperature with a heating rate of $10^{\circ}\text{C min}^{-1}$ and a holding time of 60 min. three temperatures as 300, 400, and 500°C and three time 60, 120 and 180 minute was

using for the activation. The resultant biochar was named $C_wA_xT_yM_z$ where C indicate type of biomass, A indicate types of activation, T indicate temperature and M indicate residence or activation time (Xu *et al.*, 2021).

In physical activation carbon dioxide (CO_2) gas was used as the purging gas for better yield of activated biochar and biomass pyrolysis to the target temperatures (300, 400, and 500°C) with a heating rate of $10^\circ C \text{ min}^{-1}$. The CO_2 feeding pump feed gas flow of 10 liter per hour gas and its started 10 min before reaching the target pyrolysis temperature, and then the CO_2 was entered in the heating zone of biochar. The highest temperatures were set as 500°C. Carbon dioxide gas cylinder attach with flow controller and controller attach with pyrolyser (Xu *et al.*, 2021).

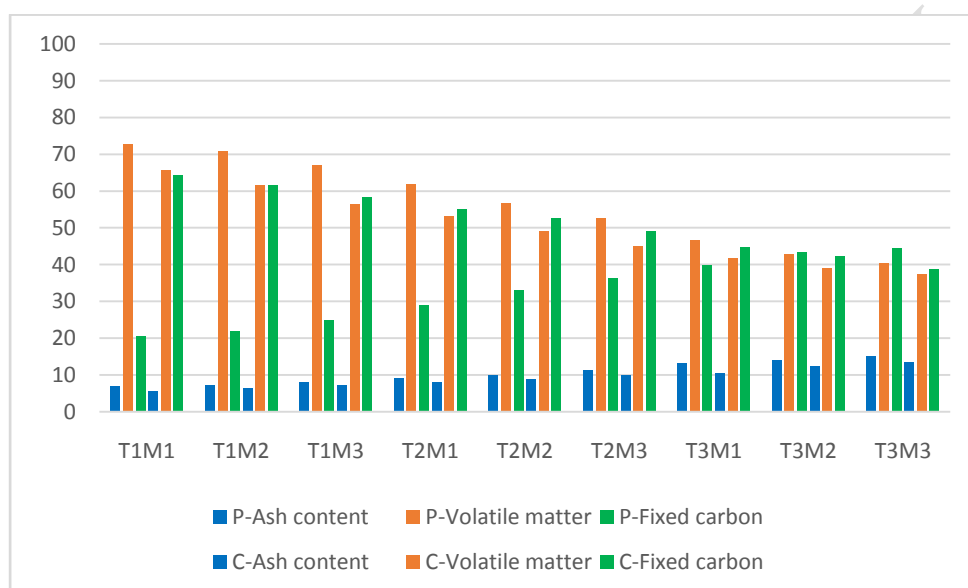
Acid activation was performed by treating the Cotton stalk with 1 M(mole) H_2SO_4 (solid-to-liquid ratio as 1 kg per 20 liter) for 24 h. The acid pre-treated stalk was filtered and dried at 60°C for 24 h before pyrolysis. 300°C, 400°C and 500°C and three time 60, 120 and 180 minute was chosen as the pyrolysis activation temperature, and heating rate same as the physical activation process ($10^\circ C \text{ min}^{-1}$ and 60 min) (Xu *et al.*, 2021).

Result and discussion

After both activations produced activated biochar taken for proximate analysis and measurement production yield of biochar which is crucial for carbon production. So in both activation we measure proximate analysis parameter like ash content, volatile matter and fixed carbon and in production yield measurement of biochar yield, bio-oil yield and pyro-gas yield.

In Physical Activation the value of cotton stalk ash content of bio-char was ranged from a minimum of 6.68 % (d.b.) at 300 °C with 60 min residence time to a maximum of 15.10 % (d.b.) at 500 °C with 180 min residence time. The value of volatile matter of cotton stalk bio-char was ranged from a minimum of 40.40 % (d.b) at 500 °C with 180 min residence time to a maximum of 72.64 % (d.b) at 300 °C with 60 min residence time. The value of fixed carbon of cotton stalk bio-char was ranged from a minimum of 20.49 % (d.b) at 300°C with 60 min residence time to a maximum of 44.49 % (d.b) at 500 °C with 180 min residence time.

In the physically activated bio-char yield of cotton stalk was ranged from a minimum of 30.40 % at 500 °C with 180 min residence time to a maximum of 50.4 % at 300 °C with 60 min residence time. The yield of cotton stalk bio-oil was ranged from a minimum of 8.6 % at 300 °C with 60 min residence time to a maximum of 22.00 % at 500 °C with 180 min residence time. The yield of cotton stalk pyro-gas was ranged from a minimum of 41 % at 300 °C with 60 min residence time to a maximum of 47.2 % at 500 °C with 180 min residence time.



*Where P = Physical activation and C = Chemical activation

Fig. 2 Graphical details about proximate analysis of activated biochar

In chemical activation the value of cotton stalk ash content of bio-char was ranged from a minimum of 5.48 % (d.b.) at 300 °C with 60 min residence time to a maximum of 13.52 % (d.b.) at 500 °C with 180 min residence time. The value of volatile matter of cotton stalk bio-char was ranged from a minimum of 37.38 % (d.b) at 500 °C with 180 min residence time to a maximum of 65.54 % (d.b) at 300 °C with 60 min residence time. The value of fixed carbon of cotton stalk bio-char was ranged from a minimum of 28.96 % (d.b) at 300°C with 60 min residence time to a maximum of 49.08 % (d.b) at 500°C with 180min residence time.

Table: 1 Proximate analysis of physically activated biochar

Sr. No.	Treatment Name	Ash content (% d.b)	Volatile matter(% d.b)	Fixed carbon(% d.b)
1	T ₁ M ₁	6.86	72.64	20.49
2	T ₁ M ₂	7.36	70.72	21.91
3	T ₁ M ₃	7.96	67.09	24.94
4	T ₂ M ₁	9.10	61.85	29.04
5	T ₂ M ₂	10.06	56.75	33.18
6	T ₂ M ₃	11.31	52.46	36.22
7	T ₃ M ₁	13.27	46.73	39.99
8	T ₃ M ₂	14.02	42.72	43.25
9	T ₃ M ₃	15.10	40.40	44.49

Table: 2 Proximate analysis of chemically activated biochar

Sr. No.	Treatment Name	Ash content (% d.b)	Volatile matter(% d.b)	Fixed carbon(% d.b)
1	T ₁ M ₁	5.48	65.54	64.38
2	T ₁ M ₂	6.28	61.43	61.68
3	T ₁ M ₃	7.28	56.34	58.37
4	T ₂ M ₁	7.94	53.05	55.21
5	T ₂ M ₂	8.81	49.05	52.61
6	T ₂ M ₃	9.81	45.06	48.98
7	T ₃ M ₁	10.51	41.57	44.82
8	T ₃ M ₂	12.42	39.10	42.41
9	T ₃ M ₃	13.52	37.38	38.74

In the chemically activated bio-char yield of chemically activated cotton stalk was ranged from a minimum of 30.90 % at 500 °C with 180 min residence time to a maximum of 53.20 % at 300 °C with 60 min residence time. The yield of chemically activated cotton stalk bio-oil was ranged from a minimum of 7.8 % at 300 °C with 60 min residence time to a maximum of 21.6 % at 500 °C with 180 min residence time. The yield of chemically activated cotton stalk pyro-gas was ranged from a 39.0 % at 300 °C with 60 min residence time to a maximum of 47.5 % at 500 °C with 180 min residence time.

The fixed carbon, volatile matter and ash content were found as 15.47, 79.16 and 5.91 % (d.b) respectively for cotton stalk. After physical activation of cotton stalk

biomass fixed carbon was increase to 44.49 % and after chemical activation it was around 49.08 % which is around three times more than the cotton stalk biomass.

Conclusions

In comparison ash content is generally lower in physically activated bio-char compared to chemically activated bio-char. Volatile matter tends to be higher in physically activated bio-char at lower temperatures and residence times. Fixed carbon content shows variations but can be higher in chemically activated bio-char at higher temperatures. Bio-char yield is comparable, but physically activated bio-char tends to have a slightly higher maximum yield. Bio-oil yield is relatively similar for both activation methods, with some variations at specific conditions. Pyro-gas yield is comparable, but physically activated bio-char may have a slightly lower minimum yield.

The choice between physical and chemical activation depends on specific application requirements. Generally, physically activated bio-char exhibits lower ash content and slightly higher bio-char yield. Chemical activation, on the other hand, may result in higher fixed carbon content. Consideration should be given to the desired properties for a particular end use, such as soil amendment or carbon sequestration, when determining the better activation method.

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