

Influence Of Process Parameters On Carbonization And Activation Of Rice Husk

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Abstract

The rice husk is waste generated from milling of paddy and creating environmental concern for its elective disposal. It is a cheap organic source for product like activated carbon. Activated Carbon (AC) is solid, carbonaceous, non-hazardous, and highly porous complex compound produced from carbonization of organic material. The demand of cheap agricultural and industrial waste for effective utilization is growing rapidly. Rice husk, due to its high cellulose and lignin content, can be used as source of activated carbon. In the present study, influence of temperature and time on carbonization of rice husk for production of activated carbon was attempted. The rice husk was carbonized at fixed temperature and time followed by activated process at different temperature and residence time. The carbon dioxide was used as activated agents during activation process. Both the parameters temperature and time found to have significant effect on recovery and surface area. However, the recovery reduced abruptly at elevated temperature. The surface area increases with increase in residence time. Under the study the optimum condition for recovery and surface area was achieved at 900°C and 60 min residence time. The recovery and surface area at optimum conditions were 19.80%, and 589.67m²/g, respectively. The activated carbon was also analyzed for its proximate composition.

Keywords: Rice Husk, Carbon, Physical Activation, Characterization.

1. INTRODUCTION

Rice husk (RH) abundantly available in India is being used as commercial fuel in brick kilns, furnaces and boilers resulting in environmental pollution. In India about 122 million tonnes of paddy production was recorded during 2020-2021[1]. This production of paddy generates around 24 million tonnes of rice husk [2]. Recently, Rice husks utilization attracted interest as organic source material for different application. RH composed of cellulose, hemicelluloses, lignin, ash and the other trace elements to the tune of 24.3%, 34.4%, 19.2%, 18.85% and 3.25%, respectively. The elemental analysis of RH resulted as Carbon 37.05%, Hydrogen 8.80%, Nitrogen 11.06%, Silicon 9.01% and Oxygen 35.03 % [3, 4]. RHs are presently used either as a heating source in India, or left it as waste. RHs can be converted into more value added material i.e. activated carbon. Activated carbon (AC) being a highly porous carbonized material has versatile industrial applications such as purification and filtration, electrode material, catalytic material and energy storage (5, 6, 7]. AC is highly porous and thermal stable material having rich surface functional groups. AC is prepared through carbonization of organic material followed by different physical or chemical activation processes. The most of commercial activated carbon is produced from petroleum precursor like bituminous coal petroleum pitch and polymers etc. However, the application of this activated carbon found to be limited. There is great interest for activated

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carbon produced from organic material. Rice husk is an agricultural waste which can be converted into activated carbon with excellent properties. A few wastes from agriculture viz almond shells, hazelnut shells, poplars, walnut, sawdust, sugarcane bagasse coconut bunch, including rice husk have been investigated to produce activated carbon [8, 9, 10, 11, 12, 13, 14]. However, the chemical method of activation was mostly investigated. The physical activated of carbon has several advantages and first preferred by end users. Physical activation is a thermal decomposition process of the carbon source material followed by the introduction of an activating agent. The process is a slow oxidation of the carbon atoms of carbonized material with activation agents at elevated temperature. The whole process of production of activated carbon from organic source influenced by different parameters viz. type of organic material, carbonization temperature, activation temperature, residence time activation agents etc. [15]. The commonly investigated activation agents are carbon di oxide and steam. Both of the activation agents found to have significantly effect on meso and micro porous carbon. The temperature and residence time are two key parameters which significantly affect the carbonization as well as activation process. The values of optimized temperature and time varies with type of bio material. Ma et al. physically produced mesoporous activated carbon from precursor of Sargassum Fusiforme under carbon di oxide environment as activation agents with high surface area (1329 m²/g) and total pore volume (1.18 cm³/g). However different temperature and time was not investigated [16].

The temperature causes the decomposition of biomaterial along with the release of volatile elements. The volatile matters leave the pores spaces inside the biomaterial with action of temperature at lower level. The increasing the temperature further, there is depolymerization and breaking of C-O and C-C bond bonds in the biomaterial. A temperature of 400° C, the carbon-carbon bonds of cellulose are reported to be breakdown, however, lignin decomposition takes place at slightly higher temperatures [17]. The addition of temperature further can enhance the speed of the carbonization reaction, but too high temperature resulted in higher ash that can close pores developed during the reaction.

Under this study, the rice husk was investigated for activated carbon under different temperature and time. The carbonization of rice husk and its physical activation was carried out in single step. The carbonization was carried out at fixed temperature. The temperature and time was investigated for activation of carbonized rice husk under carbon di oxide environment.

2. MATERIAL AND METHODS

2.1 Experimental material

The rice husk was collected from rice mill, washed in deionized water and dried for 24 h in hot air oven at 60°C. The dried rice husk was stored for all experimental study

2.2 Carbonization and activation of rice husk

The carbonization and activation of rice husk were carried out in one step in the pyrolysis reactor. The reactor consists of reactor chamber with a capacity of 500g of rice husk. The reactor was sealed for leakage of air. It was insulated with ceramic blanket to avoid heat loss. There is provision of gas flow into the reactor. The outlet was provided to escape pyrolysed vapour from the reactor. The temperature was controlled through PID controller and K type thermocouple. In the first step the rice husk was carbonized at 400°C for 45 min. The volatile vapours were allowed to escape outside the reactor to enhance the porosity. After the carbonization process, the temperature was increased to the level of activation temperature to activate the carbonized char. The nitrogen gas was forced into the reactor during increase of temperature from carbonization temperature to activation temperature. After reaching activation temperature, carbon-di-oxide as activation agents was forced in to the reactor chamber for activation.

2.3 Experimental Plan

The response surface methodology was adopted to investigate the process parameter for activation. The activation temperature (700-900 °C) and Activation time (60- 150 min) on the recovery, and surface area of activated carbons were investigated. Three factor three levels with two centre point and 10 runs in total were performed in the experiments. All the experiments are conducted in laboratory scale batch type reactor.

2.4 Characterization of rice husk activated carbon

2.4.1 Proximate analysis

Proximate analysis provides basic characterization information about biochars including moisture, volatile matter (VM), fixed carbon (FC) and ash content. Proximate analysis was carried out to obtain the values of ash content, volatile matter (VM) and fixed carbon of biochar and raw rice husk using methods described below

Moisture content

The moisture content of rice husk activated carbon was determined using hot air oven method in accordance with ASTM standard D3173 (2007). The sample of one gram of activated carbon was heated at 105 ± 5 °C in hot air oven till constant weight and moisture loss was used to calculate the moisture content in percent.

Volatile material

Volatile matter refers to the kind of element that, under particular situations, is released from a compound in the form of gases. In accordance with ASTM D3175 (2007), a known quantity of oven-dried samples was put inside the muffle furnace in crucible with a lid at 950 ± 20 °C for 7 minutes. Following sample weighting, the volatile matter can be computed as follows:

$$\text{Volatile Matter Percentage (VM), \%} = \frac{W_2 - W_3}{W_1} \times 100$$

Where,

W_3 = Weight of sample after heating at 950 ± 20 °C for 7 min in a muffle furnace.

Ash content

Ash is the fraction of the material that is still non-combustible after being heated at a high temperature. The percentage of ash content was calculated using the accepted procedure ASTM-D3174. The remaining sample was heated at 750°C for 4 hours in a muffle furnace using the ASTM-D3174 procedure. The following formula has been used to determine the sample's ash content:

$$\text{Ash Content (AC), \%} = \frac{W_3 - W_4}{W_1} \times 100$$

Where,

W_4 = Weight of sample after heating at 700 ± 50 °C for 4h in a muffle furnace.

Fixed carbon content

By subtracting the calculated amount of moisture, volatile matter, and ash content of the sample, the approximate value of fixed carbon can be estimated

$$\text{FC (\%)} = 100 - (\text{MC} + \text{VM} + \text{AC})(\%)$$

2.4.2 Carbon Recovery

The activated carbon recovery after activation process is an important parameter to characterize the biomass for production of activated carbon. The recovery depends upon temperature and residence time. The recovery is calculated using following equation.

$$\text{Carbon Recovery (CY)} = W_{rs} / W_{ac} \times 100\%$$

W_{rs} = Weight of rice straw before activation

W_{ac} = Weight of activated carbon

2.4.3 Surface area

Activated carbon is characterized with low-volume pores in different range for adsorption. The activated carbon was analysed for surface areas from N₂ adsorption at 77 K using a Micromeritics ASAP-2010 instrument (Micromeritics Instrument Corp.) and the Brunauer–Emmett–Teller equation was used to calculate the surface area. Samples need to outgassed at 110°C for 6 hours before analysis. N₂ adsorption of all samples were performed at -196 °C

2.4.4 Fourier-transform infrared (FT-IR) spectroscopy

FTIR analysis was performed to determine surface group attached to biochar. FTIR was carried out on FT-IR spectrometer (Shimadzu Corp) equipped with a bright ceramic light source, a KBr beamsplitter, and a deuterated triglycine sulfate doped with L-alanine (DLATGS) detector. The measurements of the sample were collected over the range of 4000-600 cm⁻¹. All samples were ground into powders prior to the spectral acquisition. All spectra were in Transmittance units.

3. RESULTS AND DISCUSSION

3.1 Proximate analysis

The proximate analysis was performed for all the samples of rice husk activated carbon. The results of analysis are shown in the table 1. The moisture in the rice husk activated carbon was almost vanished in all the samples. The volatile matter was released during the activation process and the release of this volatile matter generates pore inside the activated carbon. Higher the activation temperature higher was the release of volatile matter. The presence of activation agents (CO₂) during the activation process reacted homogeneously with volatile matter generated from rice husk reduces the deposition of tar formed on the carbon thereby increases the porosity. There are heterogeneous reactions between the surface of the biomass and the activation agent. These reactions tend to affects the chemical functional groups on surface of carbon during activation [17]. The effect of temperature on fixed carbon of activated carbon is shown in fig 1. The fixed carbon was increased with increase in temperature for lowest time of residence 60 min however for other time the fixed carbon decreased with temperature. This indicates that the oxidation of carbon atom of activated carbon took place at elevated temperature thereby generation of pore inside the carbon in presence of activation agents.

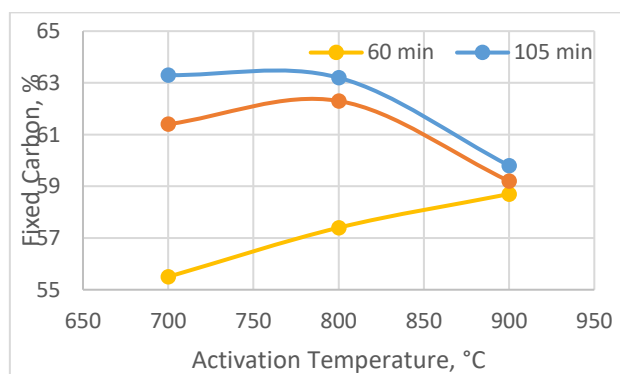


Fig.1 The effect of temperature on fixed carbon of activated carbon.

3.2 Carbon recovery and surface area

The influence of temperature and residence time on the carbon recovery and surface area during the pyrolysis of biomass can be evaluated from Table 2. Higher the activation temperature with higher activation time recovery found to be very less. Both activation temperature and time found to be highly significant for production of activation carbon. With

increase in activation time at this temperature the recovery found to reduce significantly. It indicates that carbon di oxide devolatize the char mostly at temperature between 800-900 °C. Further increase in activation time gasification reaction may take place which reduces the recovery significantly. The weight loss was caused due to dehydrocyclization and aromatization of alkanes, accompanied by the release of hydrogen at elevated temperatures [19]. Therefore, the recovery was found to be low at higher temperature however at this temperature the surface area was found to be more. Hence for better surface area the carbonized material was activated at temperature range between 700 to 900°C.

3.3 Fourier-transform infrared (FT-IR) spectroscopy

FT-IR spectroscopy is a tool to observe the shift change of chemical composition. The aliphatic loss process is represented by the band of FT-IR with aliphatic C–H stretching (2950–2850 cm^{-1}) and aromatic carbon appeared with C–H stretching (750–900 and 3050–3000 cm^{-1}). The charring process modifies the functional group, and but thus aliphatic C groups decrease aromatic C increases. The FTIR spectrum of rice husk and its biochar is presented in fig 2. Important peaks in the Rice husk are O-H stretch, aliphatic stretch, aromatic C-H stretch, C=O stretch and aromatic rings. In biochar, O-H stretch and C=H stretch almost disappear and aliphatic shifted to aromatic stretch indicating that more stable carbon in the biochar.

4. CONCLUSION

The rice husk was carbonized and activated under carbon di oxide environment in a single step at different activation temperatures and residence times in a batch type reactor. The maximum recovery to the tune of 20% could be achieved with a surface area of around 600 m^2/g . The increasing the temperature further reduced the recovery without enhancing the surface area significantly. The temperature found to have more significant effect than the residence time. The FTIR spectrum indicates the presence of surface groups on the biochar. Hence the optimum condition is required to prepare the activated carbon from rice husk.

Table 1 - The proximate analysis of activation carbon at different activation temperature and time

No	Temperature, °C	Activation time, min	Proximate analysis		
			MC	VM	Ash
1	700	60	5.24	10.56	28.69
2	700	105	4.55	8.25	24.56
3	700	150	3.66	8.46	26.43
4	800	60	3.86	7.85	32.21
5	800	105	3.68	6.22	28.45
6	800	150	3.35	7.73	26.88
7	900	60	4.12	5.82	32.64
8	900	105	3.24	4.59	32.45
9	900	150	2.87	4.35	33.15

Table 2 - The Effect of temperature and residence time on recovery and surface area

No	Temperature, °C	Activation time, min	Recovery, %	Surface area (m^2/g)
1	700	60	25	233.45

2	700	105	23	388.25
3	700	150	21	428.71
4	800	60	23	281.23
5	800	105	20	495.65
6	800	150	19	409.95
7	900	60	20	561.28
8	900	105	10	864.58
9	900	150	7	835.00

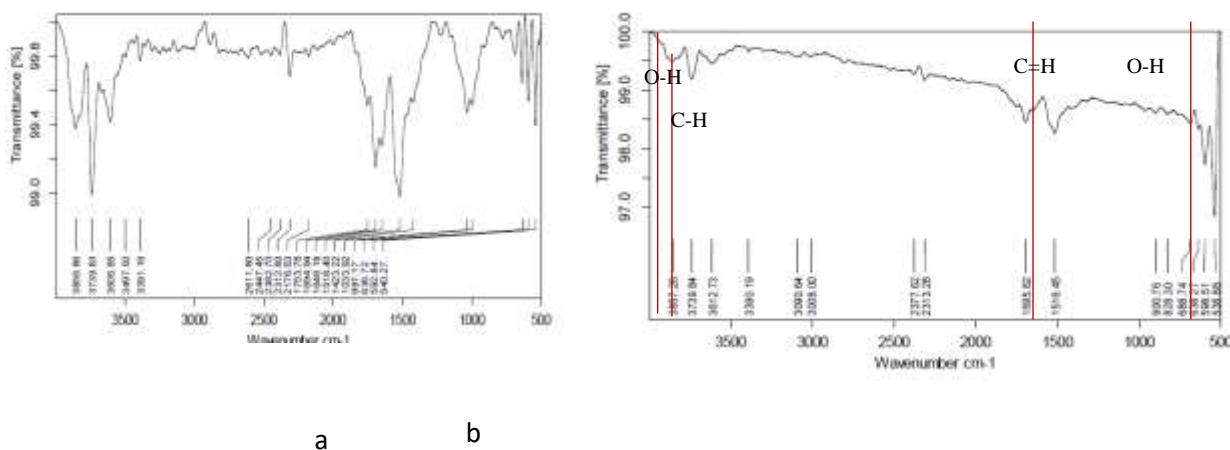


Fig 2 : FTIR of rice husk (a) and rice husk biochar (b)

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