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Productivity Analysis Of Biochar Prepared From Different Raw Materials

[1]Jigesh Mehta,[2]Nirali Tharwala,[3]Dhara Rojivadiya

[1,2,3] Asssistant Professor

[1]Department of Chemical Engineering,

[1]Shroff S R Rotary Insitute of Chemical Technology, Ankleshwar,India

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***Abstract*— Bio-Char, a black solid is an intermediate solid residue formed in the pyrolysis or gasification of most biomass with many potential applications. High bio char production is achieved at low temperature and low heating rate process. Bio char can be prepared from various bio mass which is normally solid waste in agriculture crop. The properties of bio char is heavily depends on biomass feedstock, gasifier design and operating condition. This work reports the biochar production from biomass material like corn stover and groundnut shells using specially designed gasifier. Solid yield is reported and also characterization of bio char is done. Proximate and Ultimate analysis of bio char is reported. Adsorption characterietics are studied by using oxalic acid and also Freundlich isotherm are plotted. Finally, results shows that the bio char is a good adsorbent also.**

***IndexTerms*— Bio-char, Adsorption, Gasifier, Pyrolysis**

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1. Introduction

Biomass is an important renewable source contributing to the world's economy, sustainability and energy security. In developing countries, the use of biomass is of high interest as these countries have economy largely based on agriculture and forestry. As fossil fuel is depleting, there is an urgent need to exploit any type of biomass as renewable source by converting them to various transportable forms of green fuels. Technologies to transform biomass into bio energy vary from normal combustion to thermal processes requiring higher temperature and pressure such as pyrolysis and gasification [1].

Pyrolysis is a thermal decomposition process that occurs at moderate temperature in which the biomass is rapidly heated in the absence of oxygen or air to produce a mixture of condensable liquids (biomass), gases and bio-char. Pyrolysis can convert biomass from a variety of sources including agricultural and forestry residues- into liquid, solid and gaseous forms. The properties of the bio-char obtained after biomass pyrolysis has a direct influence on subsequent bio-char oxidation step, since the amount and type of pores determine the gas accessibility to the active surface sites. Properties of bio-char are decisively affected, not only by properties of parent material, but also by operating conditions used, mainly the heating rate, the maximum temperature experienced and the resistance time at this temperature. This is due to the fact that these variables, together with biomass properties, influence the amount and nature of volatiles produced during pyrolysis, as well as their rate of release.

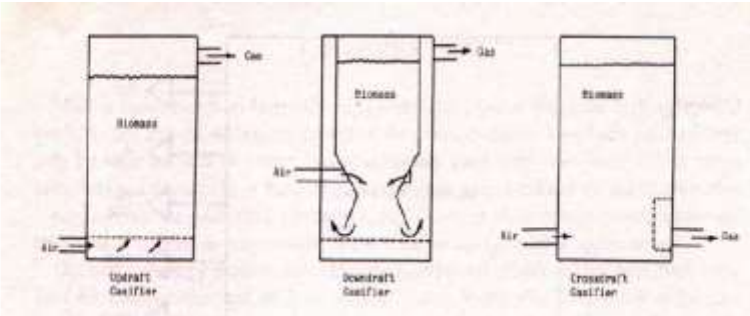
Slow pyrolysis is a conventional pyrolysis process whereby the heating rate is kept slow (approximately 0.1-1 °C/s). This slow heating rate leads to higher char yield than the liquid and gaseous products. Fast pyrolysis uses much faster heating rates (about 10-200°C) and is considered as a better process than slow pyrolysis for producing liquid or gases. In fast pyrolysis the liquid product yield is higher since the fast heating rates allow the conversion of thermally instable biomass compounds to a liquid product before they form undesired coke. Flash pyrolysis is an improved version of fast pyrolysis, whereby the heating rates are very high >1000°C/s, with reaction time of few to several seconds [3].

1.2 Gasification

Biomass gasification means incomplete combustion leads to production of combustible gases consisting of Carbon monoxide (CO), Hydrogen (H_2) and traces of Methane (CH_4). This mixture is called producer gas [3]. Since there is an interaction of air or oxygen and biomass in the gasifier, they are classified according to the way air or oxygen is introduced in it. There are three types of gasifiers: Downdraft, Updraft and Cross draft as shown in fig. 1 and various reaction zones in gasification are shown in fig.2

1.3 Biochar and its applications:

Carbonization is the conversion of an organic substance into carbon. In the partial or total absence of oxygen the thermal decomposition of plant derived biomass (pyrolysis) can be manipulated to yield, and in addition to CO_2 and in variable ratio, combustible gases (chiefly H_2, CO, CH_4), volatile oils, tarry vapors, and a solid carbon-rich residue generically referred to as char. A characteristic of biochar is that it comprise



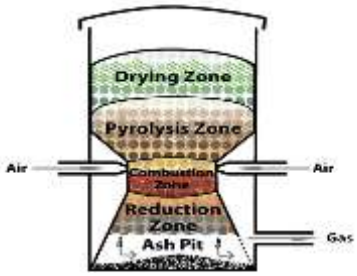


Fig.1 Types of Gasifiers[3]   Fig.2 Reaction Zone[3]

mainly stable aromatic forms of organic carbon and compared to the carbon in a pyrolysis feedstock, cannot readily be returned to the atmosphere as CO_2 even under favorable environmental and biological conditions, such as those that may prevail in the soil. Biochar is in beneficial purposes in as storage for volatile nutrients, as absorber in functional clothing, as insulation in the building industry, as energy storage in batteries, as a filter in a sewage plant, as a silage agent or as a feed supplement [8].

1.4 Adsorption isotherms:

Several models have been used in literature to describe the experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most widely used. In the present work Freundlich model is used.

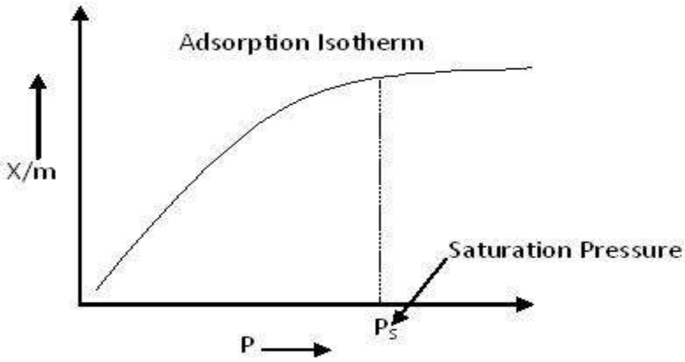


Fig.3 Freundlich Adsorption Isotherm Curve

Freundlich Adsorption Isotherm:

An adsorption isotherm is a curve relating the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. The relation between oxalic acid uptake capacity (mg/g) and residual solute remains in solution (mg/L) at equilibrium is given by

$\log(X/M) = \log K + (1/n) \log C$ . . . . . (1)

where,

Slope 1/n is the sorption intensity & intercept Log k is a measure of adsorbent capacity. The valve of k and n are calculated from the intercept and slope of the plot of log X/m versus log C respectively. Fig. 3 represents Freundlich Adsorption isotherm.

Langmuir Adsorption Isotherm :

Langmuir visualized the dynamic equilibrium between adsorbate molecules in the gas phase at a pressure P and the adsorbed entities in the surface layer, the fraction of the site covered being θ.

A plot of m/x against 1/P gives a straight line with slope and intercept equal to 1/a and K/a respectively. Langmuir isotherm shows that at low pressures of the adsorbate, the extent of adsorption is linear and at high pressure the extent of adsorption is a constant. This form of isotherm is shown in fig. 4 [16].

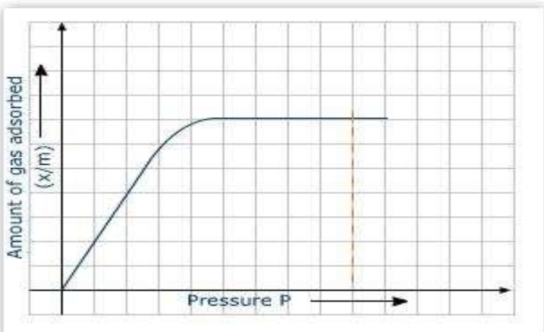


Fig.4 Langmuir adsorption isotherm curve

BET Adsorption Isotherm :

Brunauer–Emmett–Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material.

The resulting BET equation is

$$\frac{1}{v\left[\left(\frac{p_o}{p}\right)-1\right]} = \frac{c-1}{v_m c}\left(\frac{p}{p_o}\right) + \frac{1}{v_m c} \qquad \ldots\ldots (2)$$

Where

p and p_o are the equilibrium and the saturation pressure of adsorbate at the temperature of adsorption and v is the adsorbed gas quantity (for example, in volume units). v_m is the monolayer adsorbed gas quantity c is the BET constant,

$$c = exp\left(\frac{E_1 - E_L}{RT}\right) \qquad \ldots\ldots (3)$$

Where E_1 is the heat of adsorption for the first layer, and E_L is that for the second and higher layers. Equation (1) is an adsorption isotherm and can be plotted as a straight line with $1/v\,[(p_o/p) - 1]$ on the y-axis and $\emptyset = P\,/\,Po$ on the x-axis according to experimental results. The linear relationship of this equation is maintained only in the range of $0.05 < P/P_o < 0.35$

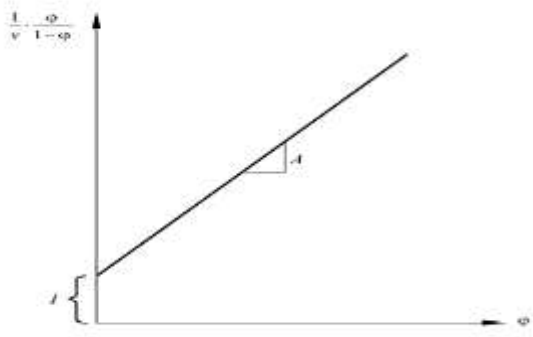


Fig.5 BET plot

The value of the slope A and the y-intercept I of the line are used to calculate the monolayer adsorbed gas quantity v_m and the BET constant C. The following equations can be used:

$$v_m = \frac{1}{A+I} \qquad \ldots\ldots (4)$$

$$c = 1 + \frac{A}{I} \qquad \ldots\ldots (5)$$

2. Materials and Methods

2.1 Feed Material :

Various biomass can be used as raw material for gasification andtwo biomass is used to produce char.

1) Groundnut Shells 2) Corn Stovers

2.2 Feed Material Analysis : Proximate and Ultimate Analysis

The proximate analysis gives moisture content, volatile content (when heated to 950^0 C), the free carbon remaining at that point, the ash (mineral) in the sample and the high heating value (HHV) based on the complete combustion of the sample to carbon dioxide and liquid water[6]. For the ultimate analysis, C, H, S, O and N are determined by chemical analysis and expressed on a moisture free basis. Ash is determined as in proximate analysis and is calculated on moisture free basis[6].

The proximate and ultimate analysis of bio mass feedstocks is shown in table 1.

Table 1: Proximate and Ultimate Analysis and Calorific Valve of biomass

Property	**Corn Stovers**	**Groundnut Shells**
Proximate Analysis	**% Dry basis**	
Moisture content	-	-
Ash content	**5.58**	**3.10**

Volatile matter	**75.17**	**68.10**
Fixed carbon	**19.25**	**28.80**
Ultimate Analysis		
Carbon	**43.65**	**49.32**
Hydrogen	**5.56**	**7.27**
Nitrogen	**0.61**	**1.16**
Sulphur	**0.01**	**0.02**
Oxygen	**43.31**	**39.15**
Total (with halides)	**93.14**	**96.92**
Calorific Value		
HHV (MJ/kg)	**17.65**	**19.85**

2.3 Preparation of Biochar

The Groundnut shell is collected from one of the oil mill from Anand and Corn stovers from the market. This raw material was cleaned and dried under sunlight for longer period of time each individual gasification run. Following is the gasifier in which gasification of feedstock is taken. The gasifier is fabricated from 1.5 mm mild steel sheet. And diameter is 600 mm and height is 600 mm. On the top conical head is used of height 450 mm. At bottom of shell perforated tray is used to separate out the biochar. It is shown in the figure (6).

Fig.6 Gasification apparatus

The details of gasification experiments are performed for bio mass are shown in table 2

Table 2 : % yield of biomass obtained after pyrolysis

Runs	Feed stacks	Mass of biomass taken, gm	Bio char Produced, Gm	% yield of biomass
Run 1	Corn Stover	350	35	10.00
Run 2	Groundnut shells	1880	140	7.44

Run 1and 2 are shown in below figure (7) and (8)

Fig.7 Biochar obtained by Corn Stover

Fig.8 Biochar obtained by Groundnut Shell

3. Results and Discussion:

3.1 Analysis of Biochar obtained by gasification of Corn Stover and Groundnut Shells:

Proximate and ultimate analysis of biochar is done at Choksi laboratories and result shown in table 3.

Table 3: Proximate & Ultimate Analysis and Calorific Value of biochar from biomass

Property	Bio char from Corn Stovers	Bio char from Groundnut Shells
Proximate Analysis	**On Dry basis**	
Moisture content	**3.62**	**3.27**
Ash content	**28.71**	**28.21**
Volatile matter	**26.41**	**8.26**
Fixed carbon	**44.88**	**63.49**
Ultimate Analysis		
Carbon	**58.83**	**54.72**
Hydrogen	**4.99**	**3.22**
Nitrogen	**1.85**	**2**
Sulphur	**-**	**-**
Oxygen	**5.62**	**11.85**
Total (with halides)	**71.29**	**71.79**
Calorific Value		
HHV (kcal/kg)	**4888.34**	**2795.88**

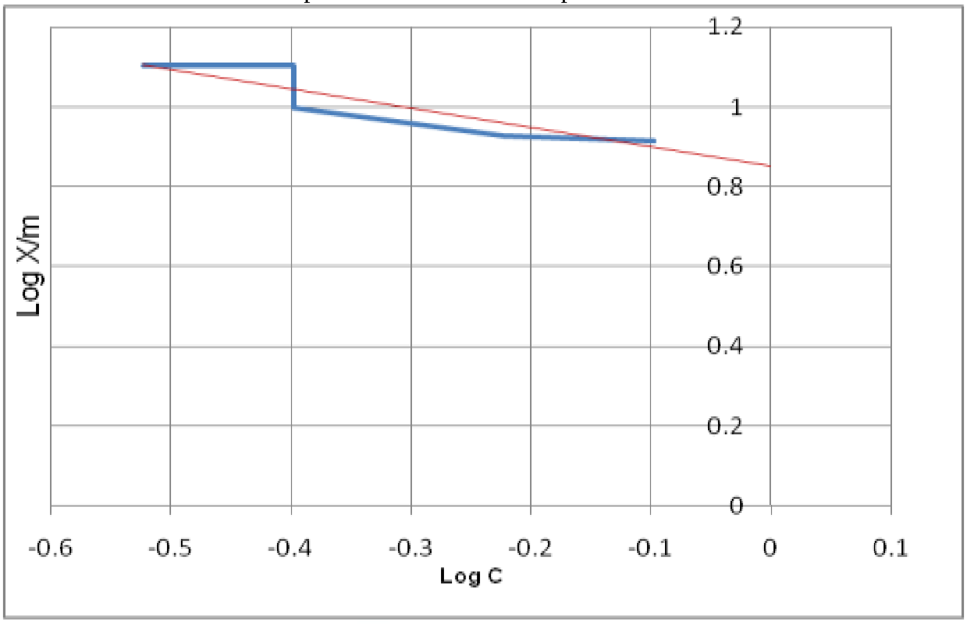
The oxygen content of biochar is quite less than the oxygen content of raw biomass. It is due to the high content of oxygen in ash that decompose during analysis [13].Our samples also contain high ash and the oxygen contains with ash may be decompose in gasification. As aspected, carbon content of biochar is high but less than pyrolysis based biochar. The carbon content of biochar from corn stoves is higher than the carbon content of biochar from groundnut shell. Hydrogen content in biochar is lower than the raw biomass due to gasification. The calorific value of the bio char is higher than the raw bio mass. It means that there enhancement of quality, if it will be used as fuel.

3.2 Adsorption characteristics of Biochar:

There are various applications of biochar. One of the application is it can be used as adsorbent. In this study adsorption of oxalic acid on biochar was tested. 500 ml of 0.5N oxalic acid solution was prepared. About 2 gm of the Bio char put into 5 different sets. Using Burette, 50, 40, 30, 20 and 10 ml of 0.5N oxalic acid are added in 0, 10, 20, 30 and 40 ml of distilled water respectively. Total volume of mixture is 50 ml. The mixtures were shaken for 1 hour and liquid of each of the bottles is filtered through a filter paper and titrated against standardized $KMnO_4$ solution until pink color appears.

Freunlich isotherm is prepared and analyzed for the bio char samples prepared from both biomass. Figure 9 is Freundlich isotherm for biochar which is prepared from corn stoves and figure 10 is the isotherm for biochar prepared form groundnut shell. In figure 9 the graph is almost straight line which says that the it it follows the adsorption pattern as per Freundlich. But in figure 10 the graph is not perfectly straight line for all concentration. But for lower concentration it follows the Freundlich isotherm.

Fig. 9 Freundlich isotherm plot for run-1
Slope = -0.48713 & Intercept = 0.85184



Material: Biochar obtained from gasification of groundnut shells

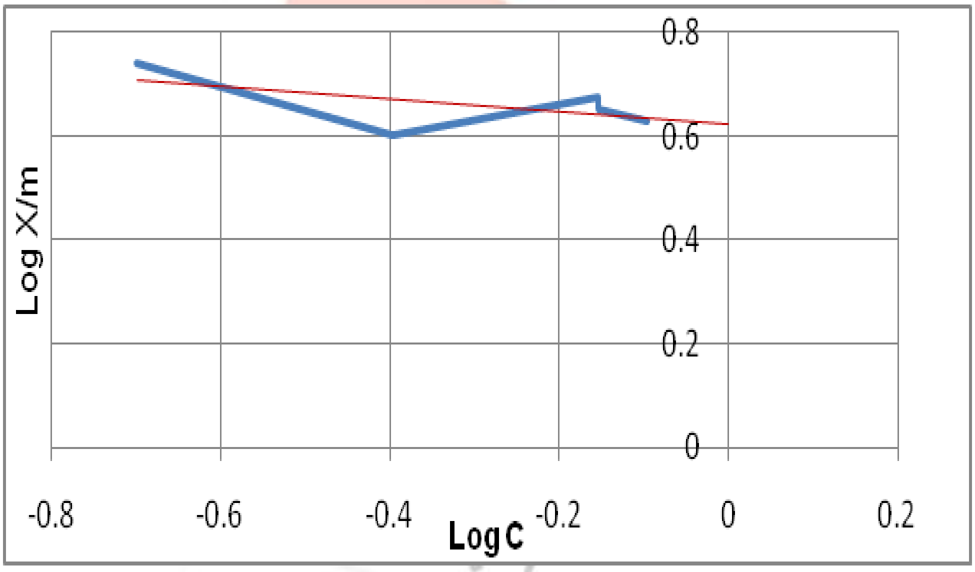


Fig.10 Freundlich isotherm plot for run-2
Slope = -0.124424009 & Intercept = 0.622726163

4. Conclusion

It was found that the bio-char product can be characterized as a carbon rich, high calorific value material. Also the biomass with lower ash content and higher percentage of Fixed Carbon Content is desirable so as to obtain more conversion. The results of oxalic acid adsorption isotherms experiment shows that biochar prepared from biomass has suitable adsorption capacity of oxalic acid and adsorption is highly dependent on adsorbent dose and contact time. The Freundlich adsorption isotherm study of oxalic acid matched best for biochar obtained from corn stovers. Thus biochar produced from different materials can act as effective adsorbent with different adsorption efficiencies.

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