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Activated Carbon from Coconut Shell using Fluidized Bed Reactor and its Simulation

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ABSTRACT

Simulation has been done on the production of chemically activated carbon from coconut shell by pyrolysis using fluidized bed reactor. The effect of process variables such as void fraction, particle size, sphericity, fluidizing velocity, fluidized bubbling bed wake, char density on the design of fluidized bed reactor leading to production and quality of activated carbon have been studied and dealt with in the present paper . The established mathematical equations describing the Fluidized Bed Reactor have been listed for its simulation. MATLAB programming has been done resorting to the real life data obtained from industries fluidized bed reactor for production of activated carbon.

KEYWORDS: *Activation, Pyrolysis, Activated carbon, Coconut shell, Fluidized bed reactor, MATLAB programming, Simulation .*

INTRODUCTION

Activated carbon is known as a unique and effective agent for purification and recovery of trace material. During the last two to three decades, treatment with active carbon has become an important unit process for separations and purifications in the food, pharmaceuticals, sugar, chemical and other processing industries. Nowadays it is used in widely varied industries like portable and industrial waste water treatment, soft drink, semiconductor, gold recovery, petrochemical, solvent recovery, domestic and waste disposal, air conditioning, fridge deodorization. Activated carbon is an amorphous form of elemental carbon and is prepared by destructive distillation of any one of a variety of carbonaceous raw materials, including wood, coal or coconut shell. It is produced by activation process which is nothing but heating the char in an atmosphere of superheated steam and removal of the tar blocking the micro fine structure of the char. The average ultimate analysis of the coconut shell pyrolysis products express C 48%, O 45.5%, H 5.8%, N 0.3%, S 0.4% which is comparable with other carbon rich bio mass like groundnut shell, walnut shell, peanut shell or almond shell. *Bulk density*, *hardness,* and *particle size distribution* are the most important physical characteristics of activated carbon for better rate of adsorption kinetics. There are mainly three forms of activated carbon –*granular* irregular shaped size ranging from 0.2 to 5 mm; *pelletized* extruded and cylindrical shaped with size range from 0.8 to 5 mm and *powdered* with size less than 0.2 mm. The activated carbon *porosity* can be measured by the extent of adsorption of iodine from a solution. By ASTM D 28 standard method test, the iodine number gives the *total surface area*of activated carbon. According to the market research firm named Roskill, the forecasting data of global activated carbon supply is about 948 KT whereas the present world demand is forecast to be 1.3 MT. In India coconut shell claims to be one prominent raw material for producing high quality activated carbon manufacture, owing to its low ash content, high carbon content, and natural pore structure with high strength and modulus property along with high lignin content. Coconut shell is an important raw material for activated carbon manufacture, especially in the southern states because of its abundant availability. Kochi-based Indo German Carbons Ltd. claims to be the largest player in the country and the third largest in the world in the production of coconut shell-activated carbon is also planning to expand capacity to 20,000-tons per annum from the present 14,000 tons per annum (18).There are around 50 producers of Activated Carbon in India, mostly in Medium and Small Scale Industries sector. Total production capacity of India is about 80 kilotons. Total domestic demand for activated carbon is about 50-kt, with the vegetables oil sector, the largest end use sector accounting for some 35-kt of demand. The supply and demand gap dictates for setting up of the activated carbon manufacturing unit leading to more reactor efficiency. The production of activated carbon from coconut shell involves two processes - *pyrolysis* and activation. In pyrolysis process for carbonization to char formation, the crushed coconut shells in the size range of 3-4 mm are retained in the pyrolysis unit for some 2hrs. at 600^0C temperature and 6 bar pressure. The Proximate analysis for coconut shell char expresses the composition like Fixed carbon 63%, Volatile matter 18.6%, Ash 14%, Moisture 4.8%, Caloric value 6220 cals/gm and characteristic in terms of BET surface area $43m^2$/gm. In Activation process after the char getting its size further reduced is preferred to be sent to the Fluidized Bed Reactor instead of the conventional one. The char is activated by steam at about 900^0C temperature and the pressure like 1.5 bar. Air is unsuitable as fluidizing medium, because it helps in combustion of carbon. Owing to lower cost, CO_2 can be used as the fluidized medium. Besides the char, bio-oil vapour, steam and incondensable gas like CO, CO_2 and H_2 as by-product are produced to form syngas. Activated carbon may be envisaged as the most probable alternative use as the fuel for boiler, the cost of produced activated carbon is roughly equal to the Lower Heating Value of activated carbon in MWh/Kg multiplied by the biomass price fixed at Rs.1750/- per MWh based on the statistical data and forecasting (24). From economic analysis it is found that in the present marketplace activated carbon produced by FBR costs approximately Rs. 250/Kg which is much lesser than the cost for conventional Reactor. Basically 8 stages of endothermic and exothermic chemical reactions take place. There are various conventional processes including the one employing most widely used Rotary Kiln for the production of activated carbon. Throughout the world particularly in developing and developed countries continuously research work is being undertaken to exploit the advantages of fluidized bed technique over the conventional techniques in various industries (1-24). Because of various advantages inter alia better gas-solid contact and high heat and mass transfer rates, superior heat distribution, significant improvement of adsorptive properties over the conventional techniques, Fluidized Bed Reactor (FBR) is recommended to be used in industry for getting the maximum energy retention and recycling the generated excess heat for producing activated carbon from coconut shell. Fast depleting the fossil fuel like coal, energy security, also the environmental concerns motivate using the fluidized bed technique for activation of non conventional fuel like coconut shell. It is reported (2,3,11,24) that the FBR has better heat transfer rates up to 1000 W/m^2K compared to the fixed bed reactor having the rate up to $100W/m^2$ K. Besides widely studied variable parameters for fluidized bed technique, bubble wake is considered as the dominating factor influencing the transport properties required for design of the FBR. The present paper deals with the simulation of the FBR and effect of various parameters like minimum fluidization velocity, void fraction, particle diameter, particle sphericity, velocity of solid driven by wake, fraction of total bed occupied by bubble not including wake using the MATLAB programming.

IMPORTANT PARAMETERS OF *FBR*

***Fluidization velocity*:** As the char density decreases with reaction time, the fluidizing velocity also decreases. The Iodine Number, i.e., mg. of iodine absorbed per gm. of carbon indicating the extent of micro pore distribution in carbon, increases with the increase of fluidizing velocity up to some critical limit like 8 times the minimum fluidizing velocity beyond which the iodine number falls as still the fluidizing velocity increases.

***Particle size*:** Iodine number increases with increase of particle size because of the lower reaction rate owing to the less macro pore on the chars. During the reaction the density of solid particle reduces up to say 20% of the original value, particle size remaining virtually almost same.

***Bed height*:** Because ofthe slugging behavior with poor gas – solid contact, as the bed height decreases, the Iodine number increases.

***Bed temperature*:** Lower activation temperature of a fluidized bed predicts the higher Iodine number. At a particular bed temperature as the reaction time increases, the Iodine number also increases. Better activation is expected to be available at relatively lower bed temperature, with no significant improvement at higher bed temperature.

***Pressure drop*:** Beyond the minimum fluidization condition as the fluidization velocity increases, the pressure drop decreases, leading to the non-homogeneous expanded bed with rising of the gas bubbles.

***Bed expansion ratio*:** At a particular fluidizing velocity the bed expansion ratio is defined as the ratio of the average fluidized bed height and the initial static height of the fixed bed.

The nature of trend of the variation of two of the above parameters namely particle diameter, minimum fluidization velocity dealt with in this present paper is comparable with the nature of curves on different systems reported elsewhere (2,3,6,7,10,19).

Multistage unit of FBR gives a more uniform residence time distribution for the char particles. It extends better heat recovery for the endothermic gasification reaction by secondary combustion of the produced carbon monoxide and hydrogen. The FBR design has to take into consideration the various fluidizing conditions in the stages concerned of the unit. The schematic diagram of a two-stage FBR for activation of coconut shell is shown in the following figure1.

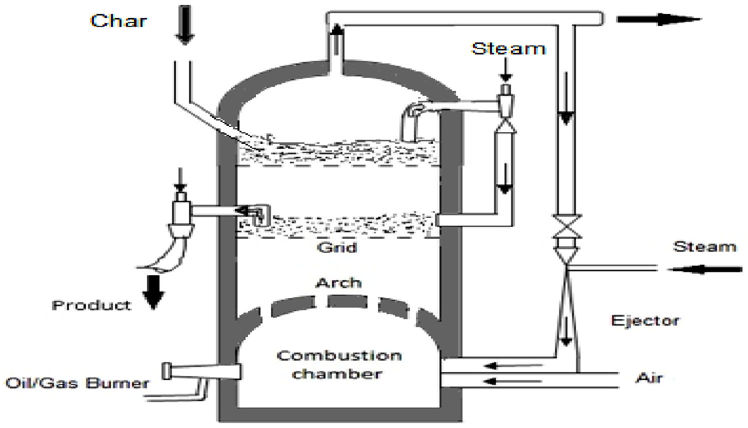

Figure1 : Two-stage FBR for activation

MATHEMATICAL EQUATIONS DESCRIBING THE *FBR*

Kunii and Levenspiel proposed the Bubbling Bed Modelhaving the bubble phase and emulsion phase in the FBR comprehensively follows the mathematical expressions (1).The fluidized bed consists of three regions namely bubble, cloud and emulsion with the wake being the part of the cloud region which is intermediate between bubble and emulsion phase.
Solid mass of the fluidized bed,

$$W_s = \rho_c A_c h_s (1 - \epsilon_s) = \rho_c A_c h (1 - \epsilon) \qquad (1)$$

where, A_c is the bed cross-sectional area, h_s is the static bed height , h is the bed height, ϵ_s is the static bed porosity, ϵ is the expanded bed porosity , and $\rho_c$is the density of the bed particles.
The pressure drop,

$$\Delta p = g(\rho_c - \rho_g)(1 - \varepsilon)h, \qquad (2)$$

whereρ_g *is* fluid density, ε is void fraction of the fluidized bed.
For the FBR, in order to calculateϵ_s, the following mathematical equation isapplicable:

$$\epsilon_s = 1 - \left(\frac{r}{6}\right). \qquad (3)$$

where, r is the particle radius.
Minimum fluidization velocity,u_{mf} can be computed from the mathematical expression

$$u_{mf} = [(\Phi D_p)^2 / 150\mu]\,[g(\rho_c - \rho_g)]\,[(\epsilon_{mf}^3 / 1 - \epsilon_{mf})], \qquad (4)$$

where, μ is gas viscosity measured as for a homogeneous fluid, quantified property inverse of fluidity, g is gravitational acceleration, $\rho_c$is char particle density, ρ_g is fluidizing gas density. This expression is valid for small char particles with Reynold's number less than 20.
For large char particles with Reynold's number higher than 1000, the equation to be applicable is, $u_{mf}^2 = (\Phi D_p / 1.75)\,(\rho_c - \rho_g)/\rho_g).g\epsilon_{mf}^3$ (5)

Spherical particle surface area, $A_S = \pi Dp^2 = \pi\left(\left[\frac{6Vp}{\pi}\right]^{1/3}\right)^2$ (6)

The sphericity, being the ratio of sphere surface (A_S) to particle surface (A_p) both at same volume, $\Phi = \frac{As}{Ap} = \frac{\pi\left(\left[\frac{6Vp}{\pi}\right]^{1/3}\right)^2}{Ap}$ (7)

The sphericity for spherical particle is 1 and for non-spherical particle, it is less than 1.
The void fraction, ϵ can be considered to be a time average value envisaging that the upper surface of the fluidized bed is considered as usually uneven and more or less oscillating.

The void fraction at minimum fluidizing condition $\epsilon_{mf}=\left(\frac{0.0711}{\Phi}\right)^{1/3}$ (8)

The mathematical equation for the bubble rise velocity can be formulated as
$u_{br} = 0.711(gd_b)^{1/2}$, (9)

where, the notation d_b is the bubble diameter measured as the diameter of sphere having the same volume as the spherical cap bubble.
The absolute rise velocity of bubble in the bubbling bed model can be manipulated by
$u_b=(u_o - u_{mf}) + 0.711(gd_b)^{1/2}$, where u_o is superficial fluid velocity. (10)

For fast moving large bubbles, gas enters lower fraction of bubble, leaving at the top of the same, subsequently is swept around and returning to the bubble itself. Surrounding the bubble this region of circulation is termed as *cloud*. The shape of the lower part of the bubble being concave results because pressure in the lower portion of the bubble is less than in the surrounding emulsion phase, leading to unstable partial collapse of bubble and the turbulent mixing. This turbulence forms the *wake*.
By material balance for solid particles crossing any horizontal plane of the FBR, considering the emulsion and wake, neglecting the cloud, the equation for downward flowing solid velocityin the emulsion is established as
$u_s(1 - \delta - \alpha\delta) = \alpha\delta u_b$, (11)
where, δ is the fraction of the bed occupied by the bubbles and α is the volume ratio of the wake to bubble. δ value has been kept below 0.5 with the indication of possible conditions of rising bubbles in the bed, however, for small slow bubbles near the bottom of the bed of FBR, $0.1<\delta<0.2$.

Hence, $u_s= \frac{\alpha\delta ub}{(1 - \delta - \alpha\delta)}$, (12)

where, u_s is mean downward velocity of solid in emulsion phase and $(1 - \delta - \alpha\delta)$ is the bed fraction of the emulsion phase including the cloud.
Computing the material balance of gas flow in the FBR, one can find the following relation:
$u_o = \delta u_b + \epsilon_{mf}\alpha\delta u_b + \epsilon_{mf}(1 - \delta - \alpha\delta)u_e$, (13)
u_e being the upward velocity of gas through the emulsion phase.

$u_e = (u_{mf}/\in_{mf}) - u_s$ (14)
The bubble fraction occupied in the bed is equated by the mathematical expression as follows:

$\delta= \frac{uo - umf}{ub - umf(1+\alpha)}$ (15)

Ignoring the wake at the condition of ub>>umf, the following simplified relation is valid for FBR :

$\delta = \frac{uo - umf}{ub}$ (16)

The frequency of bubbles passing the tip of a probe used for recording is given by
$n= u_b/h$, (17)

where, h is the height between two successive bubbles registered on the probe .

Eventually the mathematical manipulated expression for the approximate bubble diameter,
$d_b = 1.5/n(u_o - u_{mf})$ (18)

And bubble velocity,
$u_b = u_o - u_{mf} + 22.26 d_b^{1/2}$ (19)
$u_o = 1.3 u_{mf}$ for small slow bubbles near the bottom of the bed. (20)

SIMULATED RESULT

The above established 20 mathematical equations have been resorted to using the MATLAB programming. The following 6 figures comprising 20 sets of trend of variation of the 6parameters namely particle diameter, particle sphericity, minimum fluidizing velocity, void fraction, velocity of solid driven by wake, fraction of total bed occupied by bubble not including wake have been generated. At various char densities like 2.04, 1.248, 1.186, 1.049 gm/cm^3 the generated graphs (figures 2- 5) for the variation of minimum fluidizing velocity, void fraction and particle sphericity respectively with particle diameter and the variation of void fraction vs. minimum fluidization velocity have shown the same trend resulting the decrease of the minimum fluidizing velocity proportionately with decrease of the char density. At a particular char density, as the particle diameter increases, the minimum fluidizing velocity increases at lower rate initially and thereafter at a very steep rate. With the change of density of char, there shows hardly any change of variation of void fraction vs. particle diameter expectedly, similarly no significant change in the variation of void fraction vs. minimum fluidization velocity with the change of char density. The same way in case of changing the char density, the trend of the graphs of particle sphericity vs. particle diameter is exactly the same with no change of variation. The figures 6-7 have shown the variation of velocity of solid driven by wake with char particle diameter for the two cases of 10% and 20% volume of wake per bubble. As the percentage volume of wake per bubble increases, there has got no change of trend of variation of velocity of solid driven by wake with the particle diameter. However, as the particle diameter increases up to 1.4 cm, the velocity of solid driven by wake increases steadily and thereafter in case of gradual increase of particle diameter there observes steep and regular increase of the velocity of solid driven by wake in case of 20% volume of wake, but in case of reducing this volume % of wake to 10, this increase of solid driven by wake is steep and somewhat irregular in the range of 1.4 cm to 1.8 cm. The simulated results with agreement of the reported experimental data can be explained by the fact that when the bubbles disengage from the bed surface, particle entrainment occurs.

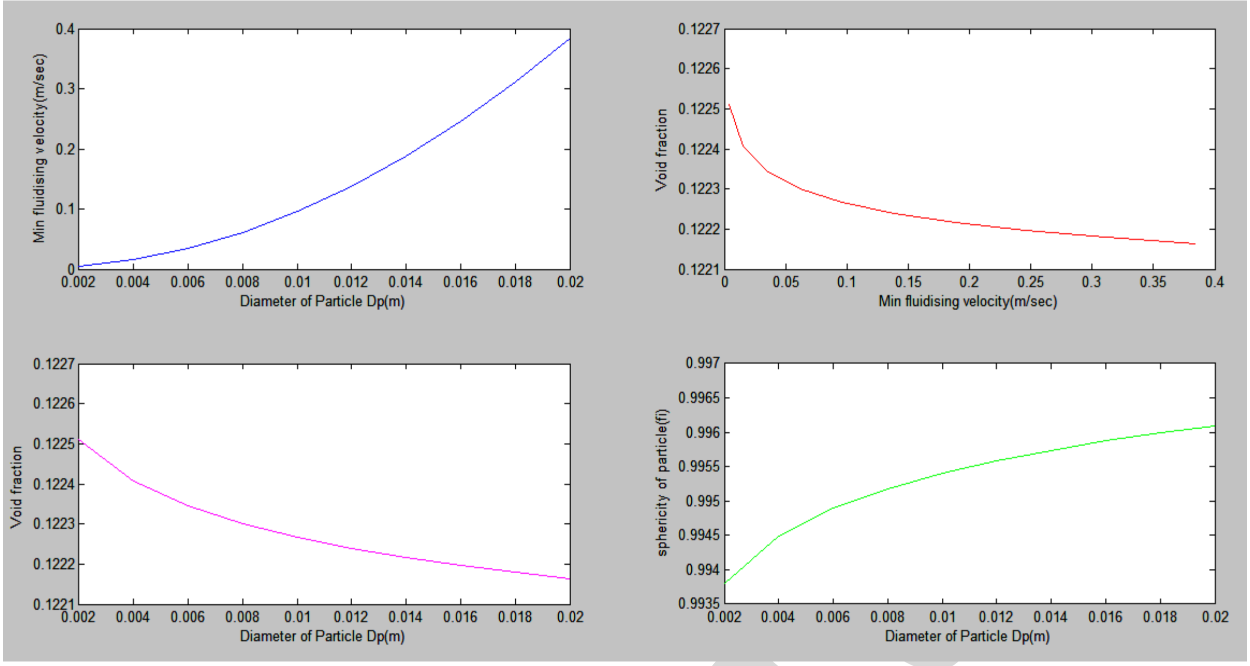

Figure 2: Char density 2.04 gm/cm^3

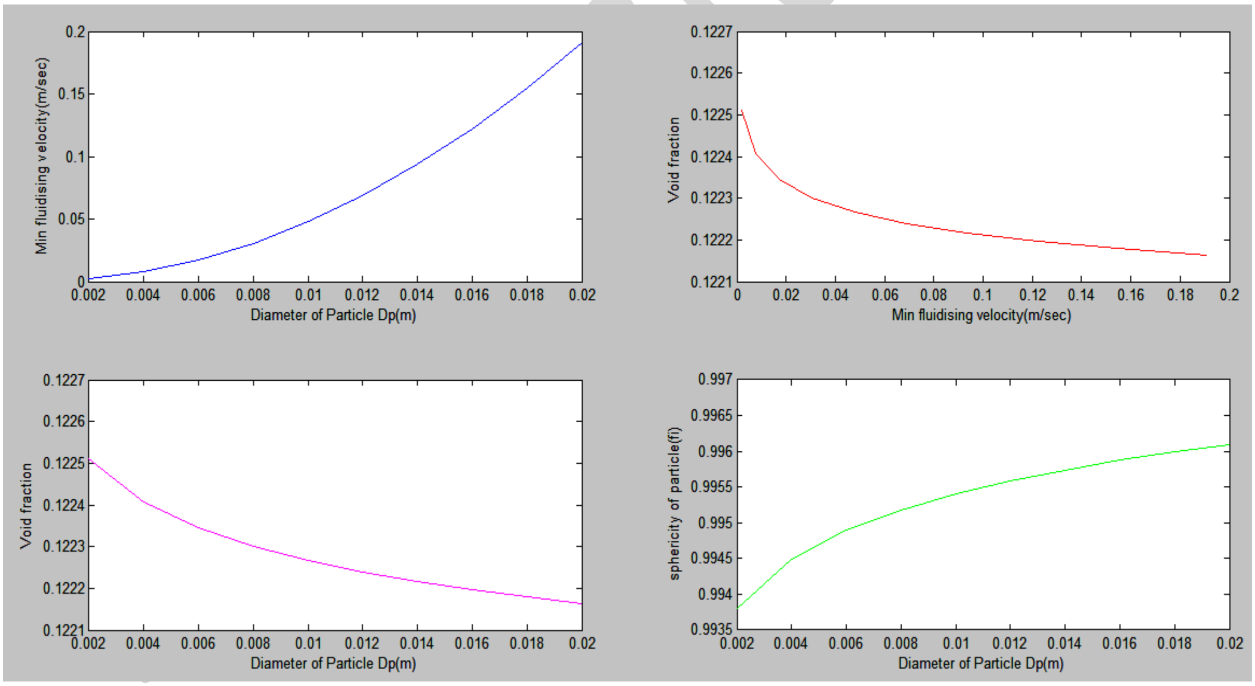

Figure 3: Char density 1.248 gm/cm^3

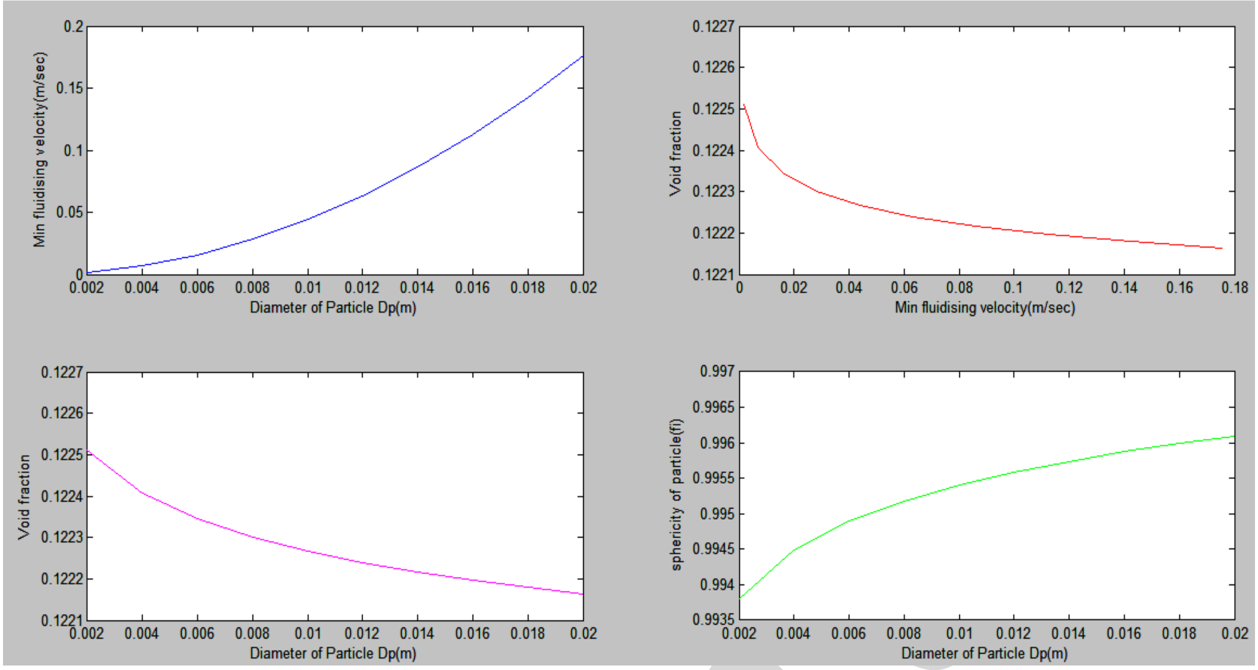

Figure 4: Char density 1.186 gm/cm^3

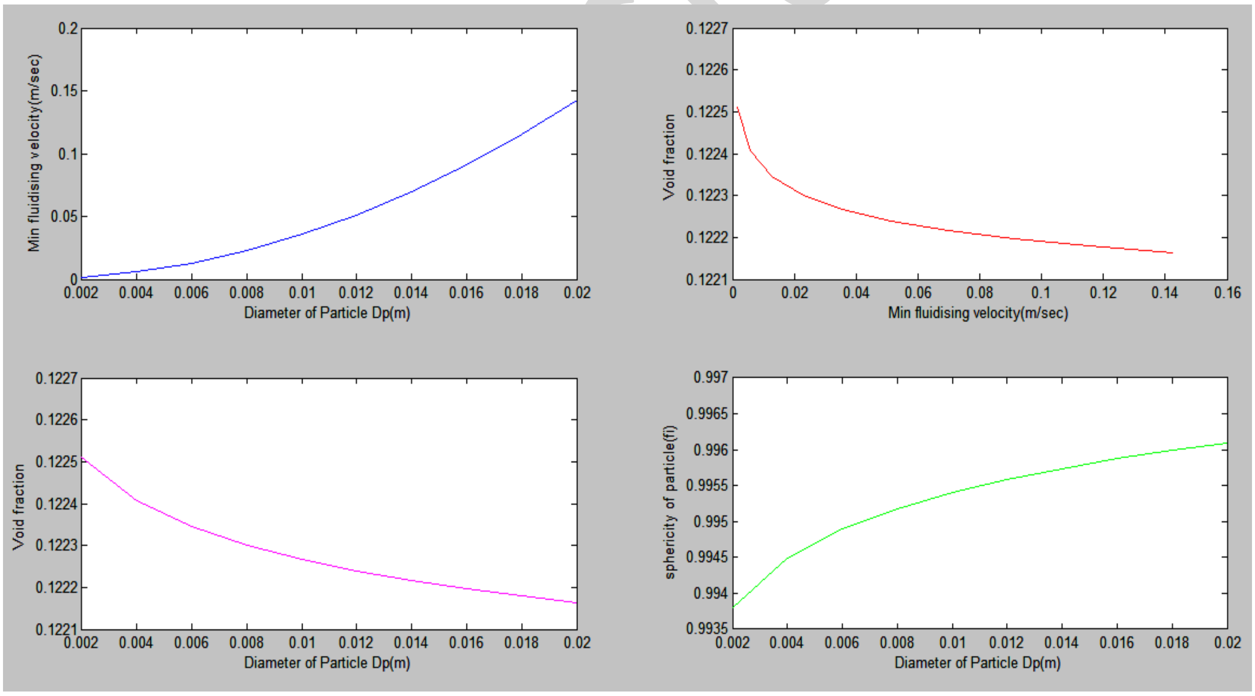

Figure 5: Char density 1.049 gm/cm^3

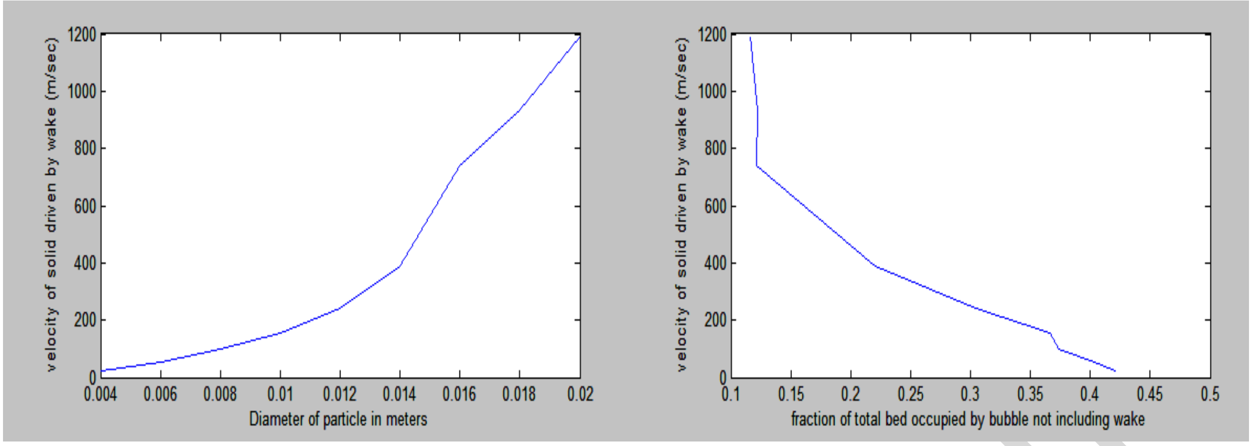

Figure 6. Variation of velocity of solid driven by wake with particle diameter and with fraction of total bed occupied by bubble not including wake, both for 10% vol. of wake per bubble.

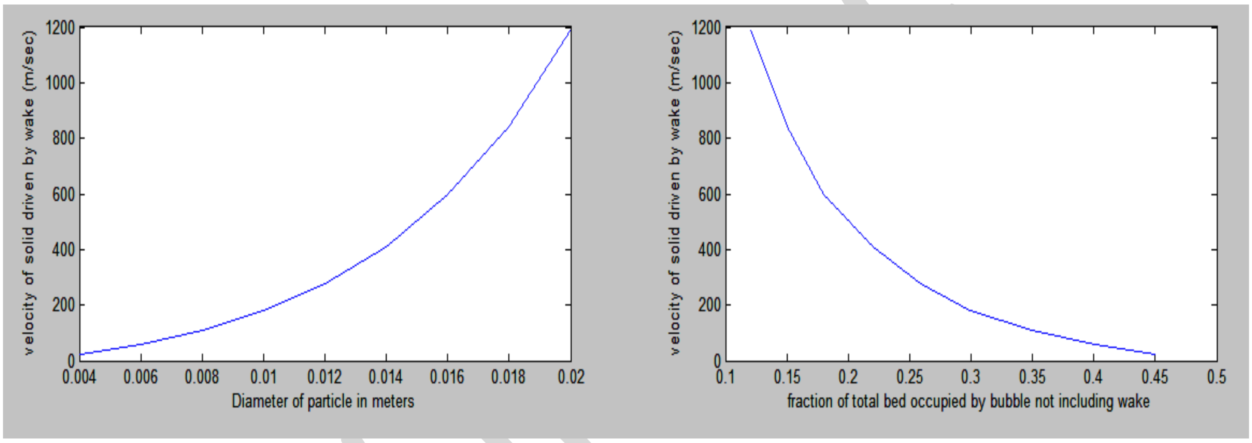

Figure 7.Variation of velocity of solid driven by wake with particle diameter and with fraction of total bed occupied by bubble not including wake, both for 20% vol. of wake per bubble.

CONCLUSION

The MATLAB generated graphs show the nature of parabolic relation between particle diameter and minimum fluidizing velocity. With the increase of the coconut shell char density, the minimum fluidizing velocity increases. The trend of the graphs predicts that with increase in minimum fluidizing velocity the void fraction decreases drastically initially up to 2 cm/sec, thereafter the rate of decrease of the void fraction is very small as the minimum fluidization velocity increases. The variation of void fraction and particle sphericity with particle diameter is opposite in nature. Withincrease in particle diameter, the velocity of solid driven by wake increases initially slowly and then steeply. The nature of incremental variation of velocity of solid driven by wake with increase of char particle diameter in the early stage as gradual slow is opposite to the velocity of solid driven by wake vs. fraction of total bed occupied by the bubble not including wake. The irregular incremental variation of the velocity of solid driven by wake as the fraction of total bed occupied by bubble not including wake increases in case of 10% volume of wake per bubble, unlike in case of 20%

leading to smooth regular variation can be explained owing to the cause of the factor of frequency of bubbles passing the tip of a probe used for recording in the FBR.The simulated data would be helpful in designing and operation of FBR for more cost effective industrial production of activated carbon.

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