International Journal of Scientific Engineering and Science
Volume 3, Issue 6, pp. 15-18, 2019. ISSN (Online): 2456-7361

Improving the Surface Areas and Pore Volumes of Bio-char Produced from Pyrolysis of Cotton Gin Trash via Steam Activation Process

Joan Hernandez-Maglinao[1], Sergio C. Capareda[1]
[1]Biological and Agricultural Engineering Department, Texas A&M University, College Station, Texas, USA 77843

***Abstract*— *Cotton gin trash (CGT) was pyrolyzed in a batch reactor and the char produced was activated with superheated steam to generate an activated carbon product. Activated carbon is a valuable adsorptive material for water and wastewater treatment systems. The main objective of the study is to compare the activated carbon produced from CGT with commercial grade activated carbon. The effect of pyrolysis temperature (600^oC, 700^oC and 800^oC), activation temperature (250^oC-600^oC) and exposure time (30, 45 and 60 minutes) on the properties of activated carbon were made. Result showed an increase in the iodine number from 200 to 427 was observed at 700^0C and 45 minutes exposure time. These data indicate that CGT may be a potential feedstock for making commercial grade powdered activated carbons that may be used for wastewater treatments.*

In this paper, we introduce the term biomass iodine number (BIN). Some biomass-based activated carbon have similar performance with commercial grade activated carbon even if the former has high inorganic components hence, lowering its iodine number. The use of BIN would make it easier to compare commercial grade activated carbon (with very low ash content) with biomass-based activated carbon (high in ash) when it comes to determining the loading rates for pollutant clean up. The optimized activated carbon produced from this study has a BIN of 642 and comparable with lower grade commercial activated carbon with iodine number of 600. If the loading rate of this biomass-based activated carbon is increased by 40%, its adsorptive properties will be equal to that of a commercial grade activated carbon with iodine number of 1000. Hence, this new terminology for biomass-based activated carbon is important for trading biomass-based activated carbon with relatively high ash contents but of equal adsorptive properties with commercial-grade materials.

***Keywords*— *Activated carbon; adsorption; biomass iodine number; cotton gin trash; pyrolysis; steam activation.*

I. INTRODUCTION

Activated carbon, a widely used adsorbent, is mainly composed of carbonaceous material with high surface area and porous structures [1]. Raw materials for its production are chosen depending on their price, purity, potential high value product, extent of activation and stability of supply [2]. Numerous studies have been devoted to the preparation of low-cost high quality carbon adsorbents for treatment and purification of water, air as well as various chemical and natural products [1] and [3]. The raw materials being used are usually carbonaceous materials like wood [4], coal [5], nut shells [6], husks [7], and most agricultural byproducts materials [1], [3], and [8].

The characteristics of activated carbon largely depend on the activation method employed: the physical and chemical method. The physical method of activation involves carbonization of raw material in inert atmosphere and activation of the char in the presence of carbon dioxide or steam. Chemical activation, on the other hand, consists of impregnation of chemicals such as $ZnCl_2$ or phosphoric acid followed by pyrolysis [3].

Cotton gin trash (CGT) is a byproduct produced from the cotton ginning process. About 227 kg (500 lbs) CGT per bale of cotton is being produced using a stripper cotton gin while 45-90 kg (100-200 lbs) CGT per bale of cotton is being generated using a picker cotton gin [9]. According to USDA statistics of 2018, approximately 4.6 million metric tons of CGT is being generated annually across the US cotton planting areas and more than a million metric tons of that comes from Texas alone.

Numerous researches have been made on the disposal of CGT and its commercial application. It is usually sold as an animal feed and compost material. The production of highly valuable product from CGT is of interest due to stricter environmental regulations and the associated disposal cost [10]. Earlier CGT gasification studies [11] were also focused on bio-char production and convert the bio-char into activated carbon.

Activated carbon was produced from cotton gin trash via pyrolysis and steam activation in this study. The iodine number was used to describe the extent of activation at different pyrolysis conditions. The aim of this work is to investigate the feasibility of preparing high quality activated carbon from CGT using mild steam activation and its compare its properties with commercially available activated carbon. Iodine number and ash analysis were conducted to introduce the concept of biomass iodine number (BIN), the adsorption capacity of the biomass-based activated carbon when ash portion was considered.

II. MATERIALS AND METHODS

2.1 Cotton Gin Trash Samples Used

The cotton gin trash samples used for the production of activated carbon were obtained from Varisco Court Gin Company (Bryan, TX). The samples were collected, air dried at room temperature and hammer milled to pass through a screen having a 6.0 mm diameter holes. The moisture content of the air dried sample was determined using ASTM method

E1756-95 [12] while the higher heating value (HHV) of the air dried sample was analyzed using the Parr Bomb Calorimeter (Model No. 6200).

2.2 Pyrolysis and Activation Process

The prepared CGT was carbonized inside a completely sealed horizontal steel tube (schedule 80 pipe) reactor. Inside the reactor was a steel tray holder containing 100 g of prepared sample. To optimize the pyrolysis condition for char production, samples were pyrolyzed at different temperature settings (600^{0}C, 700^{0}C, and 800^{0}C) for 30, 45 and 60 minutes exposure time. The horizontal tube-type furnace (Thermolyte Model No.79300) with length and inside diameter of 21.50 and 3.0 inches, respectively, was used to supply heat to the system. The horizontal reactor was also equipped with external accessories such as condenser, cold traps, and displacement tanks to collect the liquid and the non-condensable gas byproducts. After the pyrolysis process, the system was cooled below 100^{0}C before opening the reactor. The collected char was kept in a desiccator, then weighed and stored in sealed PET bags for the further activation. Figure1 shows the schematic of the pyrolysis setup used in the experiment.

The experimental set up shown in Figure 1 was also used in the steam activation process of the raw char. The steel bed used has a top plate made of fine metal screen to hold 30 g of char on the top. To produce the steam for char activation, one liter of water was placed beneath the reactor and heated at temperatures ranging from 250-600^{o}C. The horizontal reactor was maintained at ambient pressure by allowing the steam produced to vent to the atmosphere for 1 hour.

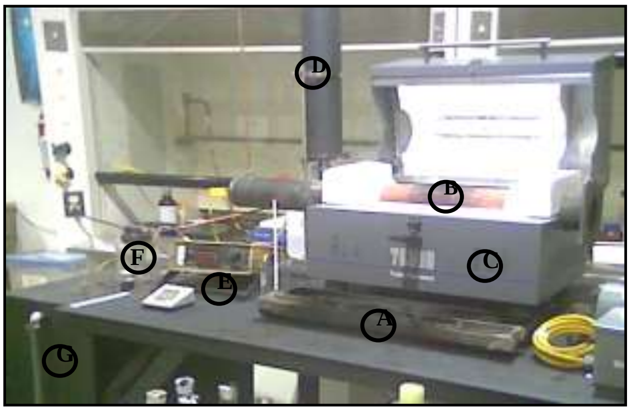

Figure 1. The pyrolysis setup used in the experiment showing the following component parts: (A) steel tray, (B) horizontal tube reactor, (C) tube furnace, (D), condenser, (E) thermocouple reader, (F) cold trap, and (G) displacement tanks.

2.3 Iodine Number Determination

The surface area and pore volume of the raw char and activated carbon prepared from CGT were characterized via the adsorption capacity towards iodine determined using standard method (ASTM D4607-94) [13].

2.4 Ash Determination and Biomass Iodine Number

The CGT activated carbon and commercially available granular activated carbon were analyzed for ash content using the Thermolyte furnace via ASTM method D2866-94 [14]. Using the ash content from the analysis, the biomass iodine number is being proposed and shown as Equation (1).

$$BIN = \frac{Iodine\ Number}{1-Ash\ Content} \qquad \text{Equation (1)}$$

This biomass iodine number can be compared with the iodine number of commercially available activated carbon. Normally commercial activated carbons have negligible ash content and this low-ash property of most commercial-grade activated carbons will not affect its iodine numbers. However, it will difficult to compare biomass-based activated carbon and commercial activated carbon simply by using the common iodine number designations. By incorporating the ash content of biomass-based activated carbon, one should be able to compare the two types of activated carbon and have meaningful loading rates calculations during adsorption processes.

III. RESULTS AND DISCUSSIONS

Pyrolysis is a carbonization process in the complete absence of oxygen or any oxidizing agent. The average moisture content of the CGT used in the pyrolysis process was 20 wt. % (dry basis). After the pyrolysis of cotton gin trash in the horizontal tube batch reactor, the effect of temperature and pyrolysis time on the char production was determined. Results are shown in Figure 2. The figure shows that the char yield has decreased as the pyrolysis temperature is increased from 600 to 800 ^{0}C. An increase in pyrolysis time from 30 to 60 minutes has no significant linear relationship on the solid production at constant pyrolysis temperature. The maximum solid yield was observed at temperature of 600^{0}C (38-40%) while the least solid production was observed at 800^{0}C (28-34%). The effect of pyrolysis temperature on the char yield is due to difference in the amount of the volatiles released during pyrolysis [6] and [15].

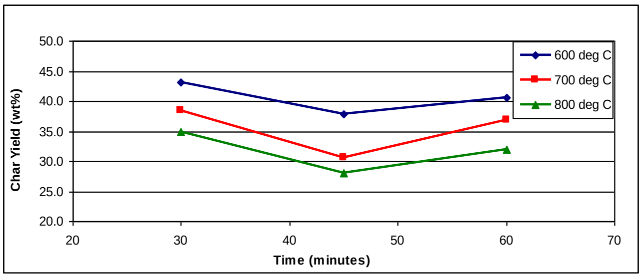

Figure 2. The char yield at different temperatures with increasing pyrolysis time.

The effect of pyrolysis temperature and time on the adsorptive property of CGT activated carbon was also investigated. The CGT char was activated by mild superheated steam for 1 hour at ambient pressure and temperature in the range between 250^{o}C-600^{o}C. The iodine number, which is defined as the mg of iodine adsorbed per g of activated carbon, was used as the measure of adsorption capacity of char and activated carbon produced. Iodine value expresses the actual adsorptive power of the adsorbent [2] and supposed to

International Journal of Scientific Engineering and Science
Volume 3, Issue 6, pp. 15-18, 2019. ISSN (Online): 2456-7361

be a better indication of pollutant adsorption. Thus it is a more practical parameter to use than the specific surface area and pore volume of the adsorbent using the most common BET analyzer.

For the iodine number determination of the raw char, results showed that as the pyrolysis time is increased from 30 to 60 minutes, the iodine number decreased from 300 to 200 at 600^{0}C. While at 700^{0}C and 800^{0}C, no significant trend of iodine value was observed. The average iodine number of the raw CGT char was measured and the average was about 200.

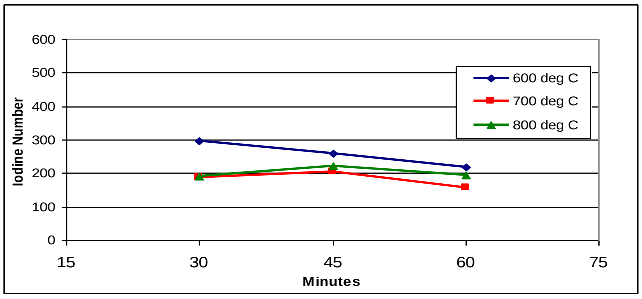

Figure 3. Iodine number of CGT char at different pyrolysis temperatures with increasing pyrolysis time.

After an hour of steam activation at atmospheric condition and temperature in the range from 250-600 ^{0}C, more porous structures were developed which resulted in an increased surface area and adsorption capacity. Figure 4 shows the results using 45 minutes of exposure time. This gave the highest iodine number for activated carbon pyrolyzed at 600^{0}C, 700^{0}C and 800^{0}C. The activation process has the optimum increase in iodine value, from 200 to 429, at 700^{0}C pyrolysis temperature.

Generally, carbonization and activation temperature have a significant effect on the formation of activated carbon porous structures [2]. Results showed that the iodine number value of CGT activated carbon increased with pyrolysis temperature from 600^{0}C to 700^{0}C while it decreased above 700^{0}C. This may be explained by the thermal degradation occurring at temperatures above 700^{0}C while incomplete carbonization at temperature below that. Thus, based on the data gathered the optimum pyrolysis temperature appears to be about 700^{0}C.

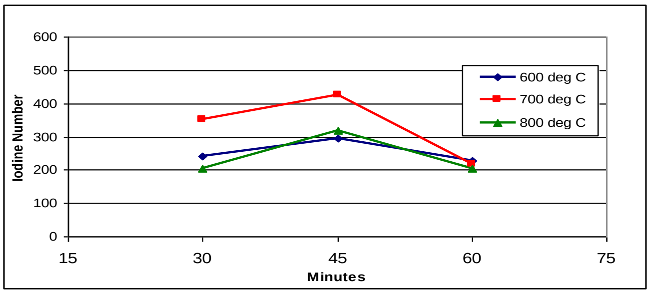

Figure 4. Iodine number of CGT activated carbon at different pyrolysis temperatures with increasing pyrolysis time.

Table 1 shows the results of the ash analysis of the activated carbon produced from cotton gin trash. The ash content is increased as the pyrolysis time and temperature are increased. Compared with the commercially available activated carbon, the biomass activated carbon has significantly large amount of ash, an average of approximately 30%. Only 2% ash was measured using the commercially available granular activated carbon. This ash difference creates a disadvantage to biomass-based activated carbon.

Ash has no adsorbing power but contributes to the total mass of activated carbon used for iodine number calculation. In the analyses previously made, only 70 to 80% of the material carbons are responsible for adsorption. It is difficult to compare CGT-based activated carbon with commercially available activated carbon due to the high ash content of CGT char. To make the comparison of adsorptive property practical, the same amount of pure carbon must be considered. Thus, the concept of biomass iodine number (BIN) was introduced (Equation 1) and the values obtained are shown in Table 1.

TABLE 1. Ash content of activated carbon and biomass iodine numbers (BIN) at different pyrolysis time and temperature.

CGT Activated Carbon Properties	30 Minutes		
Temperature -->	**600^{0}C**	**700^{0}C**	**800^{0}C**
Iodine No.	240	352	203
Ash Content	0.2257	0.2306	0.2327
BIN	310	457	265
	45 Minutes		
Temperature -->	**600^{0}C**	**700^{0}C**	**800^{0}C**
Iodine No.	294	427	318
Ash Content	0.3006	0.3352	0.3412
BIN	420	**642**	483

BIN is the amount in mg of iodine adsorbed per gram of the carbon only portion in the material. Using biomass iodine number, only the adsorptive power of the pure carbon present will be used in the iodine number calculation. Using Equation 1, the iodine number of any activated carbon prepared from biomass can be compared with the iodine number of commercially available activated carbon. For example, the 642 BIN of the CGT activated carbon prepared at 700^{0}C and 45 minutes pyrolysis is comparable with commercially available activated carbon from lignite with an iodine number of 600. Future adsorptive experiments will be made in the future to validate this claim.

Activated carbons are now manufactured into many other composite materials [16]. Recent advances showed the potential to further convert these activated carbon into graphene nano-particles [17] and [18]. More importantly, activated carbons are shown as powerful adsorbents of pharmaceuticals such as ibuprofen appearing in wastewater treatment plants [19]. The average iodine numbers of commercial carbons is around 1000 [19]. Hence, biomass-based activated carbon with a BIN of 600 will have the same adsorptive properties with low-grade commercial activated carbon having iodine number of 600.

To equal the adsorptive properties of commercial activated carbon (with iodine number of 1000), biomass-based AC with BIN of 600 will simply have to be loaded more by an additional 40% to equal the adsorptive properties of commercial activated carbons. Hence, the pricing for biomass-based activated carbon, will now become competitive with commercial grade if one will use the concept of BIN for trade.

The current price of commercial activated carbon ranged from \$1000-\$3000/metric ton and Calgon Carbon, a major worldwide AC supplier announced a 10-15% increase in price and due to diminishing supply [20]. Hence, the proposed trade valuation for biomass-based AC using BIN will provide excellent incentives to other AC sources.

IV. CONCLUSIONS

This study illustrated that cotton gin trash can be used for the production of activated carbon. This can be achieved via mild steam activation. The adsorptive ability of CGT char can be improved appreciably. The activation process that had the optimum increase in iodine value, from 200 to 429, was observed at 700^0C pyrolysis temperature and 45 minutes exposure time.

The iodine number of CGT activated carbon can be made comparable with commercially available activated carbon when ash content is considered. The use of biomass iodine number (BIN), defined as the mg of iodine adsorbed per gram of pure carbon used excluding ash, make this possible. CGT activated carbon pyrolyzed at 700^0C for 45 minutes has an iodine value of 427 that is equivalent to 642 BIN. This BIN value is comparable with commercially available activated carbon from lignite having an iodine number of 600. Hence the trade price for biomass-based AC must be made using the concept of BIN.

Excess CGT could be converted into highly valuable activated carbon and a potential source of revenue. Since CGT is abundantly produced and yet underutilized, production of activated carbon via pyrolysis and steam activation is an opportunity to compete with the existing market for activated carbon. Thermal conversion of CGT into activated carbon reduces the space for CGT disposal.

Detailed analysis of the energy and mass balance for the entire pyrolysis and steam activation process of CGT is being made to improve the process design and justify the feasibility of a large scale production. In addition, the use biomass-based activated carbon will be simulated in waste treatment to study the physical properties and pore characteristics of CGT activated carbon.

ACKNOWLEDGEMENTS

The study was made possible with the assistance, materials and/or financial support from the following entities: The Cotton Foundation, TAMU Cotton Chair, Texas A&M University AgriLife Research, and Varisco Court Gin Company.

REFERENCES

[1] Abdel-Nasser A, El-Hendawy. Surface and adsorptive properties of carbon prepared from biomass. Applied Surface Science 2005; 252: 287-295.
[2] Kim DS. Activated carbon from peach stones using phosphoric acid activation at medium temperatures. Journal of Environmental Science and Health 2004; 5:1301-1318.
[3] Budinova T, Ekinci E, Yardin F, Grimm A, Bjornbom E, Kimkova V, Goranova M. Characterization and application of activated carbon produced by H_3PO_4 and water vapor activation. Fuel Processing Technology 2006; 80:899-905.
[4] Ahmad AL, Loh MM, Aziz JA. Preparation and characterization of activated carbon from oil palm wood and its evaluation on methylene blue adsorption. Dye and Pigments 2006; 20:1-10.
[5] Luzano-Castello D, Alcaniz-Monge J, Cazorla-Amoros D, Linares-Solano A, Zhu W, Kapteijn F, Moulijn JA. Adsorption properties of carbon molecular sieve prepared from an activated carbon at pitch pyrolysis. Carbon 2005; 43:1643-1651.
[6] Lua AC, Yang T, Guo J. Effects of pyrolysis conditions on the properties of activated carbons prepared from pistachio-nut shells. J Anal. Appl. Pyrolysis 2004; 72: 279-287.
[7] Baquero MC, Giraldo L, Moreno JC, Suarez-Garcia F, Martinez-Alonzo A, Tascon JMD. Activated carbons by pyrolysis of coffee bean husks in presence of phosphoric acid. J Anal. Appl. Pyrolysis 2003; 70: 779-784.
[8] Duran-Valle CJ, Gomez-Corzo M, Pastor-Villegas J, Gomez-Seranno V. Study of cherry stone as raw material in preparation of carbonaceous adsorbents. J Anal. Appl. Pyrolysis 2005; 73: 59-67.
[9] Holt GA, G.L. Barker, R.V. Baker, and A. Brashears. Various parameters of cotton gin trash produced from the gin processing machinery. Proceedings Beltwide Cotton Conferences. San Antonio, TX, January 4-8, 2000.
[10] Jeoh T, Agblevor FA. Characterization and fermentation of steam exploded cotton gin waste. Biomass and Bioenergy 2001; 21:109-120.
[11] Capareda, S.C. 1990. Studies on Activated Carbon Produced from Thermal gasification of Biomass Wastes. Ph.D. Dissertation, Biological and Agricultural Engineering Department, Texas A&M University, College Station, TX.
[12] ASTM E1756-95. Test method for the determination of total solid in biomass. In: 2006 Annual Book of ASTM Standard. Vol. 11.06. American Society for Testing and Materials, West Conshohocken, PA.
[13] ASTM D4607. Test method for the determination of iodine number of activated carbon. In: 2006 Annual Book of ASTM Standard. Vol. 15.01. American Society for Testing and Materials, West Conshohocken, PA.
[14] ASTM D2866. Test method for total ash content of activated carbon. In: 2006 Annual Book of ASTM Standard. Vol. 15.01. American Society for Testing and Materials, West Conshohocken, PA.
[15] Chattopadhyaya G, Maconald DG, Bakhshi NN, Mohammadzadeh JSS, Dalai AK. Preparation and characterization of chars and activated carbons from Saskatchewan lignite. Fuel Processing Technology 2006; 87: 997-1006.
[16] Kelly, A., and C. Zweben. Comprehensive Composite Materials. Pergamon Press, Elsevier Science Direct, UK. 2000.
[17] Pandey, A., M. Stocker, T. Bhaskar and R. K. Sukumaran. Recent Advances in Thermochemical Conversion of Biomass. 2015. Elsevier Science Direct UK.
[18] Ronsse, F, R. W. Nachenius and W. Prins. Carbonization of Biomass. In: Recent Advances in Thermochemical Conversion of Biomass (Pandey, A., M. Stocker, T. Bhaskar and R. K. Sukumaran, EDS). 2015. Elsevier Science Direct UK. Pp 293-324.
[19] Mestre, A. S., M. Galhetas, and M. A. Andrade. Micro-pore size distribution of activated carbons: A key factor for a deeper understanding of adsorption mechanism of pharmaceuticals. The Bulletin of the Spanish Group of the Coals (40): 22-27. Zaragoza, Spain, June 2016.
[20] Calgon Carbon Corporation. Calgon Carbon Corporation Announces Global Price Increase. January 17, 2019 Press Release. Pittsburgh, Pensylvannia, USA. Available at: https://www.calgoncarbon.com/media/press-releases/2019-17-01/calgon-carbon-corporation-announces-global-price-increase/. Calgon Carbon, USA, A Kuraray Company.