Effect of Acidic Pretreatment of Carbon Precursor on the Characteristics of Carbon Obtained from a Typical Solid Waste

Salman Masoudi Soltani[1] and Sara Kazemi Yazdi[2] [+]

[1,2]Department of Chemical and Environmental Engineering, The University of Nottingham (Malaysia Campus), Broga Road, 43500 Semenyih, Selangor, Malaysia

Abstract. Cellulosic materials and cellulose derivatives have been long used in the production of various materials. These include various products such as papers, cigarette filters and sanitary pads. Cigarette filters, containing 95% cellulose acetate fibers, are responsible for one of the largest solid wastes generation today. In this work, the effect of acidic impregnation of cigarette filters, followed by a simple one-step carbonization of cigarette filters, on porous carbon characteristics is investigated. Adsorption-desorption isotherms, scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX) as well as thermal gravimetric analysis (TGA) have been employed to characterize the pyrolyzed product. It was seen that the Brunauer, Emmet, and Teller (BET) surface area considerably decreases by around 72% when acidic impregnation is applied which is in agreement with some earlier reports in the literature. This work suggests that unlike many cellulosic materials, acidic impregnation of cigarette butts could possibly fail to obtain desired porous carbon.

Keywords: Activated Carbon, Porous Carbon, Cigarette Filter, Carbonization, Acidic Treatment

1. Introduction

Today porous carbons are being used in various industrial fields. These include separation processes as adsorbents, catalysts and catalytic supports, as well as in electrical and energy storage devices. Amongst different production methods, direct pyrolysis of a carbonaceous material is the most straight forward technique in the production of activated carbon. In the past few years the use of different polymeric materials as carbonaceous precursors to synthesize carbon materials, has led to the production of activated carbons with new or improved porosity characteristics [1]. To modify synthesized carbon, acidic/basic impregnation of carbon precursors or carbon have been studied by several researchers. However, it has been sugested that acidic impregnation of cellulosic materials before carbonization could enhance carbonization yield due to water elimination from the carbon precursor by the acidic agent which can itself prevent unwanted chemical reactions at high temperatures which can result in lower carbon yield [2].

Around 766,571 metric tons of cigarette butts are being littered every year in the world [3]. This huge solid waste generated each year worldwide poses a critical issue for disposal regulations, mainly because there are countless disposal points. Along with the importance to collect and dispose of butts in a safe way, cigarette butts are known be of toxic, hazardous waste [4]. Different proposals have been made to prevent cigarette butt pollution, but none of them has been effective [3]. Cigarette filters are made of 95% non-biodegradable cellulose acetate and the balance is made from papers and rayon. The cellulose acetate tow fibers are thinner than sewing thread, white and packed tightly together to create a filter. Although they are mainly made of cellulose acetate, a plasticizer, triacetin (glycerol triacetate) is applied to bond the fibers [5]. To date, very few investigatetions have been made on recycling cigarette butts as porous carbon materials. Polars *et al*. [6] reported the synthesis of porous carbon from cigarette filters with a surface area of 262 m^2/g.

[+] Corresponding author. Tel.: +60-389248710
  E-mail address: Sara.Yazdi@nottingham.edu.my

Acidic/basic impregnation of cellulosic precursors or carbons, synthesized from a cellulosic precursor, has been reported in the literature [2, 7, 8]. However, acidic impregnation of cigarette butts before carbonization has not been reported elsewhere. Interestingly enough, the BET surface area decreased when acidic impregnation was applied to cigarette filters. Also, surface morphology completely changed compared to non-treated carbonized filters. TGA analysis also, showed no increase in carbon yield. All and all, it could be understood that acidic pretreatment of cigarette filters for the production of porous carbon could possibly fail to obtain high-yiled, high-surface-area carbons.

2. Materials and Methods

Freshly smoked cigarettes were collected, all belonging to the same cigarette manufacturer. The butts were then removed from within the cigarette paper. Then 1.9 g of filter was first impregnated with 50 ml sulfuric acid (1 M) and the mixture was placed on a shaker for 24 hours. Next, the excess sulfuric acid was drained by pressing the filter inside filter papers [2]. Impregnated filters (0.28% weight ratio of filter to impregnation solution) were placed into a ceramic furnace crucible and then inside a steel tube furnace (Carbolite Co.) without any oven drying. N_2 gas flow was supplied from a nearby nitrogen capsule which was directly connected to a flow meter and then the furnace tube. Before any run, nitrogen was allowed to pass through the furnace for a few minutes to make sure the furnace tube was free of any excess oxygen. Nitrogen flow rate was set to 100 cm^3/min in all experiments. Carbonization temperatures were set to 900 °C (for non-impregnated filters) and 500 °C (for acid-impregnated filters). Carbonization (hold) times were adjusted to 2 hours for both experiments. The heating rates was controlled at 5 °C/min. To prevent any unwanted oxidation at elevated temperatures, before taking out the sample after its pyrolysis was complete, the furnace was left closed for several hours with the same nitrogen gas flow rate. This allowed the ambient temperature to be achieved. Then the sample was taken out. To characterize the synthesized carbon, adsorption-desorption isotherms were obtained using a Micromeritics Co. surface analyzer using liquid nitrogen at 77 K as the analysis gas. Prior to the analysis the samples were degassed for 6 hours at 300 °C at a heating rate of 3 °C/min to make sure no gas molecules or other impurities were trapped inside the pores. An FE-SEM/EDX (Quanta Co.) was used to study the surface morphology and elemental analysis of the materials. Also, a METTLER TOELDO (Star System) Co. thermo gravimetric analyzer (TGA) was used to study the thermal decomposition of the smoked cigarette filters.

3. Results and Discussions

3.1. Adsorption-Desorption Experiments

Initially the typical relative pressure range of 0.05 to 0.3 was selected to calculate the BET surface area [9]. However, it was seen that the linear region for the BET equation should be limited to 0.05 to around 0.18 p/°p to validate the calculated BET area for both samples. The isotherms below clearly are a type IV isotherm which is obtained for solids containing pores in the mesopores range [9]. The most important feature of type IV isotherms is the presence of hysteresis which means the amount adsorbed is always greater at any given relative pressure along the desorption branch than along the adsorption branch [9] This feature is visibly seen in both isotherms. However in Fig. 1, the desorption branch does not meet the adsorption branch of the isotherm. Polarz, et al, also reported similar phenomenon with an open-end desorption branch. This phenomenon is known for certain carbon materials and might be due to changes in the bulk density upon nitrogen sorption or the irreversible adsorption of nitrogen. Moreover, this effect might also be connected with retarded adsorption, where the adsorbing and desorbing molecules have to overcome a certain energy barrier, which might be a consequence of the presence of narrow pores, penetration into which is difficult because of steric considerations [6]. From the BET equation, surface areas of 117.2 m^2/g and 413.2 m^2/g have been calculated for Fig. 1 and 2, respectively. Also by the application of BJH method using the adsorption branch of the isotherm, an average pore size of 2.86 nm and 3.92 nm were evaluated for Fig. 1 and 2, respectively. Meanwhile, the single point adsorption total pore volume of pores is measured to be 0.05 and 0.25cm^3/g at around p/p°=0.99 from the isotherm data for Fig. 1 and 2, respectively. It was observed that impregnation of the cigarette filters with sulfuric acid (1 M), extremely lowers the pore volume as well as average pore size. Also, BET surface area, the total micro and meso porous area decreased by around 72%.

The decrease in pore volume is attributed to the destruction of pore walls and extreme etching caused by sulfuric acid at elevated temperatures [10].
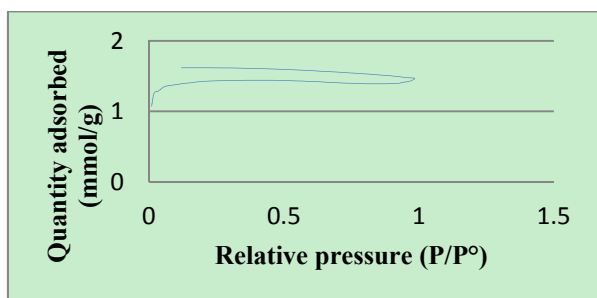

Fig. 1: Adsorption-desorption isotherm of porous carbon synthesized by carbonization of acid-impregnated cigarette filters at 500 °C and 5 °C/min for 2 hours.
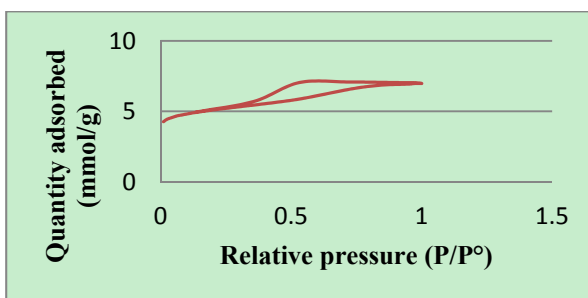
Fig.2: Adsorption-desorption isotherm (Carbonized filters at 900 °C and 5 smoked °C/min for 2 hours)

3.2.   Scanning Electron Microscopy (SEM)

The surface morphology and pore structures on the surface of the carbonized carbon samples at three different temperatures are shown in Fig. 2, 3 and 4. It is seen that by an increase in temperature, the surface mprphology also changes. Impregnated filters show a completely different morphology from that of non-impregnated sample. Although macropores are still visible on the surface in Fig. 5, but the accessibility of maso and micropores in real applications may also be hindered due to the much more limitted number of macropores on the surface. On the other hand non-treated sample boosts numerous macropores on its surface which can potentially facilitate adsorption rates.
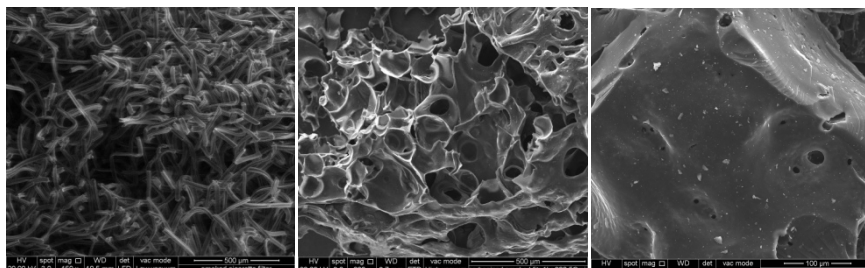

Fig. 3: Smoked cigarette filter

Fig. 4: Carbonized filter at 900 °C for 2 hr at 5 °C/min

Fig. 5: Impregnated filter carbonized at 500 °C for 2 hr at 5 °C/min

3.3.   Thermal gravimetric analysis (TGA)

Fig. 6 shows the TGA results obtained by the thermal decomposition of smoked cigarette filters in an inert atmosphere. When ramping starts, a mass loss of around 10% is seen until 280 °C is reached. This could be due to the evaporation of the water content in the used cigarette filters. The sample shows a sharp weight-loss which begins at about 280 °C and is ended at 370 °C. This weight-loss can be due to dehydration and acetic acid removal and corresponds to a mass loss of 70 % [6]. By increasing the temperature to 900 °C another weight-loss of 9% is observed. This may be due to the incomplete degree of carbonization (C_xH_y species) [6]. The final weight-loss shows a final carbon yield of around 11% which is almost in good agreement with our synthesized carbon [11]. However, the impregnated sample shows significant weight loss from very beginning. This can be due to the role of dehydrating agent that sulfuric acid plays. Most of water in the initial acid evaporates at below 100 °C and small amount of concentrated acid remains distributed among fibers. It is reported that sulfuric acid extracts water from cellulose materials at above 120 °C which then evaporates immediately and prevents unwanted reaction of water with carbon at high temperature [2].

This should lead to higher carbon yields. However, in the case of cigarette filter it appears that although possibly water elimination happens (due to fast weight loss which is in agreement with [2]), but higher carbon yield could not be reached.
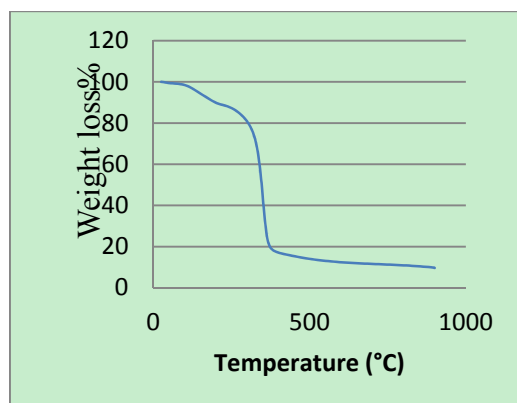

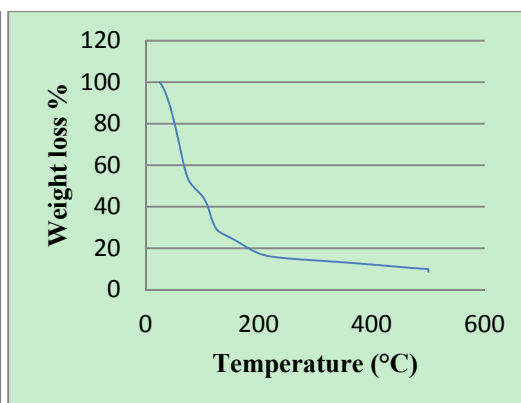Fig. 6: TGA graph of cigarette filter (at 900 °C at 5 °C/min for 2 hr)

Fig. 7: TGA graph of acid impregnated cigarette filter (500 °C, 5 °C/min, 2hr)

3.4. Energy-dispersive X-ray spectroscopy (EDX).

EDX was used to investigate the elemental composition of the carbonized impregnated cigarette filter. The EDX spectrum is shown in fig. 6. It is observed that more than 94% (by weight) of the porous matter is made of carbon. Oxygen contributes most to the remaining weight balance which is possibly found among the surface groups. the spectrum shows that almost all sulfuric acid has been either decomposed or evaporated during the process, leaving trace amount of sulfur (0.4% by weight).
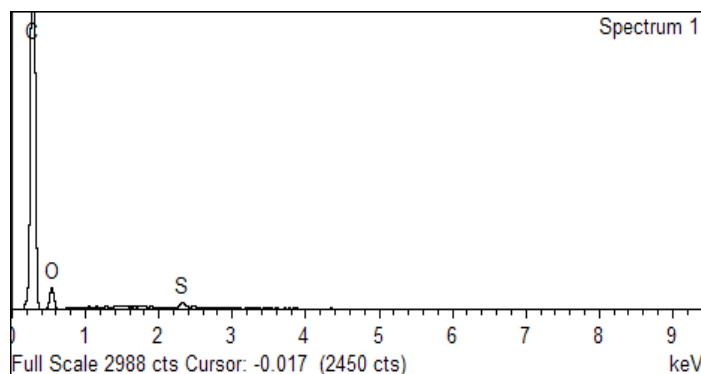

Fig. 8: EDX elemental analysis of impregnated filter after carbonization (500 °C, 5 °C/min for 2 hr)

4. Conclusions

This study shows that acidic impregnation of cigarette filter with sulfuric acid (1 M) fails to obtain higher carbon yield and improved BET surface area. The former is in contrast to acidic impregnation of cellulosic materials studied so far. However, the decreased BET surface area, suggests that possibly sulfuric acid could not be a suitable impregnating agent for cigarette filters as precursors to porous carbons.

5. Acknowledgements

6. References

[1] M.B. Vazquez-Santos, A. Castro-Muniz, A. Martinez-Alonso, J.M. Tascon. Porous texture evolution in activated carbon fibers prepared from poly (p-phenylene benzobisoxazole) by carbon dioxide activation. *Microporous and mesoporous materials.* 2008, 116*:* 622-626.

[2] D.Y. Kim, Y. Nishiyama, M. Wada, W Kuga, S. Kuga. High-yield carbonization of cellulose by sulfuric acid impregnation. *Cellulose.* 2001, 8: 29-33.

[3] E.A. Smith, T.E. Novotny. Whose butt is it? tobacco industry research about smokers and cigarette butt waste. *Tobacco journal.* 2011, 20: 2-9.

[4] R. Barnes. Regulating the disposal of cigarette butts as toxic hazardous waste. *Tobacco control*, 2011, 20: 45-48.

[5] Information on http://www.longwood.edu/cleanva/cigbuttfilters.htm

[6] S. Polarz, B. Smarsly, J.H. Schattka. Hierarchical porous carbon structures from cellulose acetate fibers. *Chem. Mater.*2002*,* 4: 2940-2945.

[7] W. Tongpoothron, M. Sriuttha, P. Homchan, S. Chanthai, C. Ruangviriyachai. Preparation of activated carbon derived from Jatropha curcas fruit shell by simple thermo-chemical activation and characterization of their physio-chemical properties, *Chemical engineering research and design.*2011, 89: 335-340

[8] R.L. Tseng. Physical and chemical properties and adsorption type of activated carbon prepared from plum kernels by NaOH activation. *Journal of hazardous materials.* 2007, 147: 1020-1027.

[9] R.C. Bansal and M. Goyal. *Activated carbon adsorption.*Taylor & Francis Group, 2005.

[10] C.Y. Yin, M.K. Aroua, W.M. Ashri, W. Daud. Review of modification of activated carbon for enhancing contaminant uptakes from aqueous solutions. *Separation and purification technology*. 2007, 52: 403-415.

[11] K. Laszlo,A. Bota, L.G. Nagy. Comparative adsorption study on carbons from polymer precursors. *Carbon.* 2000, 38: 1965-1976.