The Effect of Pyrolysis Time and Heating Rate on the Surface Area and Pore Size Properties of Porous Carbon Obtained from the Pyrolysis of a Cellulosic Waste

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Abstract. In this paper we are reporting the fabrication of porous carbon by the direct one-step carbonization of waste cigarette filters. Applying a new set of operational parameters compared to previous work, the Brunauer, Emmet, and Teller (BET) surface area could increase by about 37%. This was done by increasing the carbonization period and heating rate from 7 to 9 hours and 1 to 3 °C/min, respectively. Scanning electron microscopy (SEM) could very well demonstrate the formation of pores on the surface of synthetic carbon. However, the surface morphology of the pyrolyzed carbon was completely different when changing the synthesis parameters compared to earlier reports. To further investigate the pyrolysis process, thermal gravimetric analyses (TGA) were carefully carried out. Since cellulose acetate is a major constituent in many products, recycling such waste in order to synthesize high-surface-area porous carbons would be a promising technology in the future.

Keywords: cellulose acetate, cigarette filter, Porous carbon, pyrolysis

1. Introduction

Porous carbon materials have been prepared in different ways to produce task-specific carbonaceous materials. These synthetic rich-in-carbon matters can then be used in industrial or scientific realms. They can be utilized in separation processes as adsorbents, as catalysts and catalytic supports, and in electrical and energy storage devices. There are several methods to synthesize porous carbon amongst which direct pyrolysis of a carbonaceous material is the most straight forward approach. In recent years use of various types of polymers as precursors for carbon materials has led to activated carbons with new or improved porosity characteristics [1].

As much as 766,571 metric tons of butts wind up every year as litter worldwide [2]. The trillions of cigarette butts generated each year throughout the world pose a significant challenge for disposal regulations, primarily because there are millions of points of disposal, along with the necessity to segregate, collect and dispose of butts in a safe manner, and cigarette butts are toxic, hazardous waste [3]. Numerous proposals have been made to prevent or mitigate cigarette butt pollution, but none has been effective; cigarette butts are consistently found to be the single most collected item in beach clean-ups and litter surveys [2]. Cigarette filters are made of 95% non-biodegradable cellulose acetate (a plastic), and the balance are made from papers and rayon. The cellulose acetate tow fibers are thinner than sewing thread, white and packed tightly together to create a filter; they can look like cotton. Cigarette butts contain fibrous matter. Spreading apart the matrix reveals more than 12,000 white fibers. Microscopically they are Y shaped. Although they are mainly made of cellulose acetate, a plasticizer, triacetin (glycerol triacetate) is applied to bond the fibers [4]. To date, very few investigatetions have been made on recycling cigarette butts as porous carbon materials.

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Polarz et al. [5] reported the synthesis of porous carbon from cigarette filters with a surface area of 262 m^2/g. However, they did not study the effect of carbonization duration nor heating rate effect on the resulted porous carbon. In this work we could observe a 37% increase in BET surface area by simply elevating pyrolysis time and heating rate. Doing so, carbon yield could also reach the maximum amount of 15% which is the highest value reported by [6].

2. Materials and methods

Newly smoked cigarettes were collected all belonging to the same cigarette manufacturer. The butts were then removed and unwrapped from within the cigarette paper. They were then placed into a ceramic furnace crucible and next placed inside a steel tube furnace (Carbolite Co.). N_2 gas flow was supplied from a nearby nitrogen capsule which was directly connected to a flow meter and then the furnace tube. Prior to any experiment, nitrogen was allowed to pass through the furnace for several minutes to make sure the furnace tube was free of any oxygen. Nitrogen flow rate was set to 100 cm^3/min in all experiments. Carbonization temperature, carbonization duration and heating rate were set to 800 °C, 9 hr and 3 °C/min, respectively. Before taking out the sample after its pyrolysis was complete, the furnace was left unopened overnight with the same nitrogen gas flow rate, until it reached the ambient temperature. Then the sample was taken out to prevent any unwanted oxidation at elevated temperatures. To characterize the synthesized carbon, adsorption-desorption isotherms were obtained using a Micromeritics Co. surface analyzer using liquid nitrogen (77 K) as the analysis gas. Prior to the analysis the sample was degassed for 6 hours at 300 °C at a heating rate of 3 °C/min to make sure no gas molecules were trapped inside the pores. An FE-SEM (Quanta) was used to take surface images of the materials. Also, a METTLER TOELDO (Star System) Co. thermo gravimetric analyzer was used to study the thermal decomposition of the smoked cigarette filters. To simulate the synthesis conditions, the temperature increased at a heating rate of 3 °C/min and was kept at 800 °C for 5 hours in a nitrogen flow at 100 cm^3/min.

3. Results and Discussions

3.1. Thermal Gravimetric Analyses (TGA)

Fig 1 shows the TGA/DSC results obtained by the thermal decomposition of smoked cigarette filters in an inert atmosphere. In the initial stage of heating, a mass loss of around 10% is observed up to 280 °C. This could be due to the evaporation of the water content in the used cigarette filters. The weight loss trend from here on shows that sample's sharp weight loss starts at about 280 °C and is completed 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 800 °C another weight loss of 8% 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 12% which is in good agreement with our synthesized carbon [6].
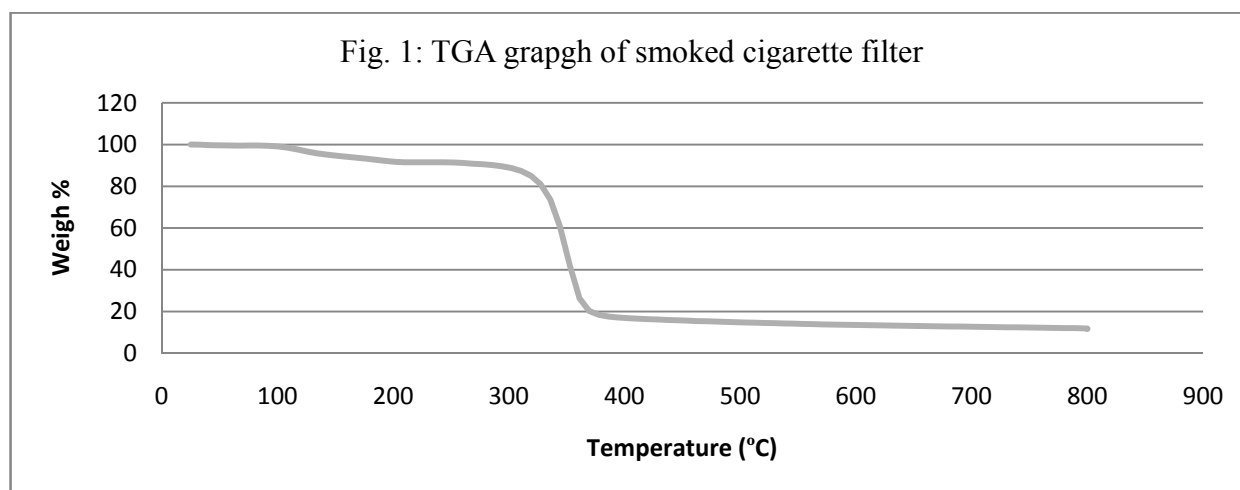

Fig. 1: TGA graph of the smoked cigarette filter (heating rate: 5 °C/min, N_2 gas flow rate: 100 ml/min)

3.2. Adsorption-Desorption Isotherms

The isotherm obtained in fig 1 is marginally classified as adsorption-desorption isotherm type IV by The International Union of Pure and Applied Chemistry (IUPAC) for porous materials [7]. This isotherm is the characteristics of a mesoporous material [8]. However, the quite broad desorption branch of the isotherm is a sign of a pore system with a distinct poly dispersity in size [5]. Polarz, et al, also reported similar isotherm with the 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 [5]. Using BET model to measure micro and meso pore surface area, a surface area of 360 m^2/g was calculated. The linear BET adsorption range was found to be between 0.05 to 0.3 P/P^0. This BET value is around 37% higher than the value reported by Polarz et al. Also the micro pore surface area calculated using t-plot method, shows that the synthesized material has 317 m^2/g microporous surface area. Also, total pore volume was calculated to be 0.184 cm3/g considering total amount of nitrogen adsorbed at P/P^0 =0.984. The higher value of micropore area compared to that of mesopores can be attributed to the increased carbonization time which leads to the shrinkage of the carbon and the collapses of mesopores carbon walls and as a consequence, the creation of smaller micropores [9]. The faster heating rate, on the other hand, might hinder full deterioration of carbon walls and mesopores at elevated carbonization time.
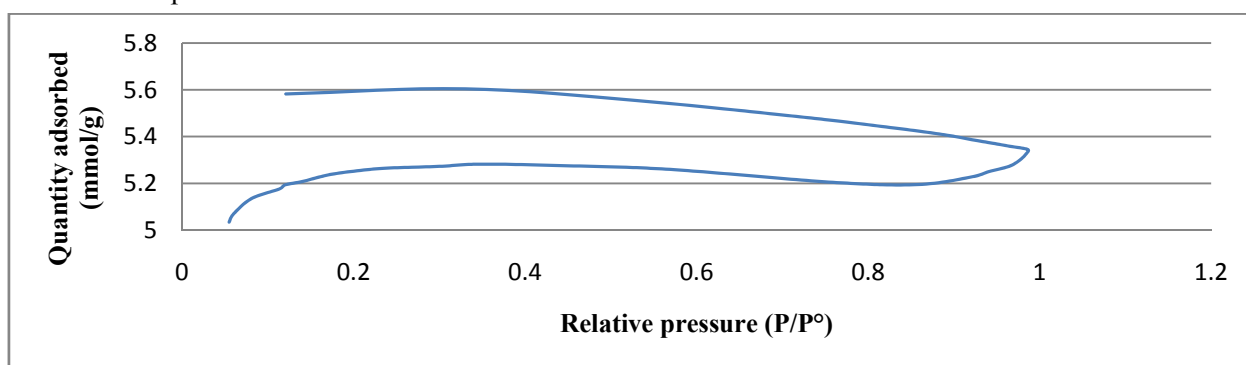
Fig. 2: Nitrogen adsorption-desorption isotherm of smoked cigarette filter at 77 K (Sample was degassed at 300 °C for 6 hours before analysis)

Meanwhile, using BJH method applied to the adsorption section of the isotherm, the average pore width is estimated to be 3 nm compared to 4 nm reported by Polarz et al. This may also be due to the increased carbonization time which alternatively may give a chance to the carbon walls to collapse and form smaller pores. Total pore volume and t-plot micropore volume are calculated to be 0.185 cm^3/g and 0.164 cm^3/g, respectively.

3.3. Scanning Electron Microscopy (SEM)

Fig. 3 and fig. 4 show the surface morphology of the smoked cigarette filters and the carbonized cigarette filters, respectively. The long cellulose acetate chains are very well illustrated in fig 1. Fig. 1 shows the lack of any porosity in the initial material. However, when carbonized at mentioned conditions, a totally different surface structure was obtained. The SEM image can successfully show the presence of macro pores and porous structure on the surface of the synthesized carbon.
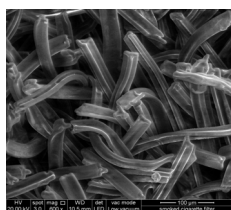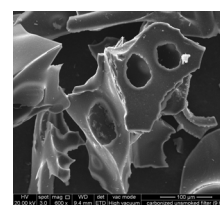
Fig. 1: Raw cigarette filter   Fig. 2: Carbonized filters at 800 ºC for 9 hr at 3 ºC/min
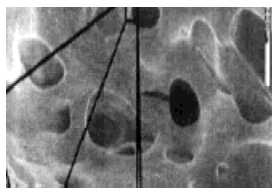
Fig. 3: Carbonized filters at 800 ºC for 7 hr at 1 ºC/min (Adopted from [5])

Fig. 3, for comparison, shows the SEM image reported by Polarz et al when cigarette filters were carbonized at 800 °C for 7 hours at a very slow heating rate of 1 °C/min. Fig 2 and fig. 3 show the different morphology resulted from two different operational conditions. It appears that the higher carbonization time results in the partial destruction of the surface pores and could possibly generate higher surface area.

4. Conclusion

The results highlight the interesting effect of carbonization time and heating rate on the BET surface area of the porous carbon synthesized from the pyrolysis of cigarette filters. The results demonstrate the potential capabilities of future studies in order to optimize the current process and yielding higher porous surface area by the pyrolysis of cigarette filters. Also, as cigarette filters mainly consist of cellulose acetate, other cellulose acetate and cellulosic waste can accordingly be nominated to be recycled via the production of porous carbons.

5. Acknowledgements

6. References

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