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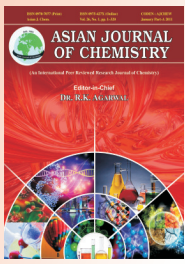

Effect of CO_2 Flow Rate on the Synthesis of Sliced Activated Carbon from Date Palm Tree Fronds (Agro Waste) by Physical Activation

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Among all the date producing countries, Saudi Arabia produced around 15 % of the total production around the world. During the pruning process of date palm trees, fronds are considered as a agro waste material. Due to the voluminous availability, the date palm fronds are considered as a starting material for activated carbon (AC) production. The BET surface areas of the activated carbons prepared at a CO_2 flow rate of 25, 50, 100, 150, 200 and 250 mL/min after 0.5 h activation time are 610,1094, 854, 877, 866 and 886 m^2/g, respectively. The activated carbon prepared at a flow rate of 50 mL/min attains larger surface area 1094 m^2/g. Effect of CO_2 flow rate on the synthesis strongly affects the BET surface area and pore volume, they both increases at a flow rate from 25 to 50 mL/min from 25 to 50 mL/min, whereas a constant behaviour were observed at a flow rate of CO_2 from 100 to 250 mL/min. Moreover by increasing the CO_2 flow rate the yield decreases linearly from 23.25 to 14.70 %.

Keywords: Sliced activated carbon, Palm tree fronds, Physical activation, Porous carbon.

INTRODUCTION

The date palm tree fronds is a waste product of date fruit during pruning which is largely grown in the Middle East Asia, North African countries and North American desert region. In these regions it is a more economically viable material for the production of activated carbon. Saudi Arabia produced 15 % of the total date production and is considered as a major date producer in the date producing countries[1]. and around 75000 tons of date palm tree waste in the form of fronds, foliar and thorns are produced during pruning of the trees[2].

Activated carbon synthesis from agro waste mainly contains lignocellulosic materials and is considered as a best material for synthesis. Different biomasses has already been reported for the synthesis of activated carbon like coconut shell[3-5] rice husk[6] and bagasse[7] date oil waste[8-11], woods[12-15] date seed[16,17]. Normally, for the preparation of activated carbon from physical activation two main steps are involved. First step is the carbonization of biomass in the inert atmosphere[18]. Second step is the activation process for the growth of BET surface area and pore volume of activated carbon. Physical activation and chemical activation are the two different methods for activation. The effect of ramp rate on the synthesis of sliced activated carbon from date palm tree fronds has already been published[19].

The objective of the present work was to study the practicability of synthesis of adequate activated carbons from date palm tree fronds by physical activation. The influence of different flow rates of CO_2 as activation medium was studied whereas other parameters such as the activation temperature, the heating ramp rate, the dwell time and the reaction vessel pressure remains constant. The sliced activated carbons was studied using various techniques such as thermogravimetric analysis (TGA), BET surface area, pore volume, pore size and Fourier transform infrared spectroscopy (FTIR).

EXPERIMENTAL

Date palm tree fronds were used as the precursor in the present study. The proximate properties of the date palm frond (precursor) are given in Table-1. Proximate analysis of date palm tree fronds was conducted as per the method given in GB/T12496.1-12496. 22(1999) and the results were expressed in terms of moisture, volatile matter, ash and fixed carbon content.

The fronds were dried at 110 °C for 8 h to reduce the moisture content, sliced with sophisticated wood cutter to a size range of 2-3 mm. Pyrolysis of the date palm tree fronds and activation of the resulting chars were both carried out in a horizontal stainless-steel tube alloy 330 reactor (UNS N08330) having ID 30 mm, OD 36 mm by Sandmeyer steel company,

TABLE-1
PROPERTIES OF THE DATE PALM TREE FRONDS

Proximate analysis (wt %)			
Moisture	Volatile	Fixed carbon	Ash
9.1	74.6	10.3	6.0

Carbolyte MTF 12/38/250 tube furnace was used during the study. During the pyrolysis process, about 4 g of sliced precursor was used in high alumina sample tray to prepare the chars. Grade 5 (99.999 %) nitrogen gas at a flow rate of 150 mL/min was passed through the reactor right from the beginning of the pyrolysis process. The furnace temperature was increased from room temperature to 850 °C at a heating rate of 10 °C/min when the temperature of 850 °C was reached the activation gas carbon dioxide was introduced at a flow rate starting from 25 to 250 mL/min for 0.5 h. After activation the furnace was cooled down to room temperature using nitrogen gas. The scheme of the process is shown below in Fig. 1.

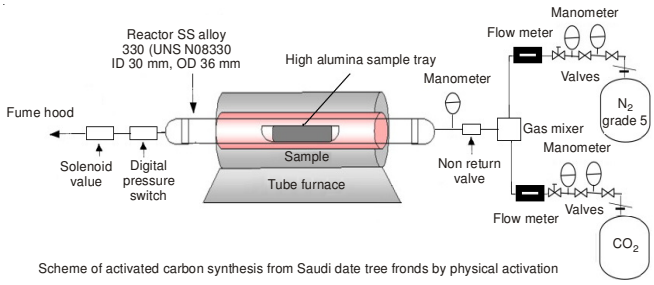

Fig. 1. Scheme of process

Remaining all the parameters like the activation temperature, the heating ramp rate, the dwell time and the reaction vessel pressure were kept constant to studied the optimum level for CO_2 for the process.

RESULTS AND DISCUSSION

Thermogravimetric analysis (TGA) of date palm tree fronds: Thermogravimetric (TG) experiments were carried out by a Mettler Toledo thermo-gravimetric analyzer (TGA/DSC1 Star System) in order to determine the pyrolysis behaviour of date palm tree fronds. The dried fronds was subjected to measure from 25-900 °C at heating rate 10 °C min^{-1} under flow of nitrogen gas maintained at 900 °C for 15 min. Fig. 2 shows the thermogravimetric curve of raw date palm tree frond by weight in a N_2 atmosphere and at a 10 °C min^{-1} heating rate. It can be seen from the Fig. 2, little weight loss observed at a temperature below 150 °C because of the moisture in the date

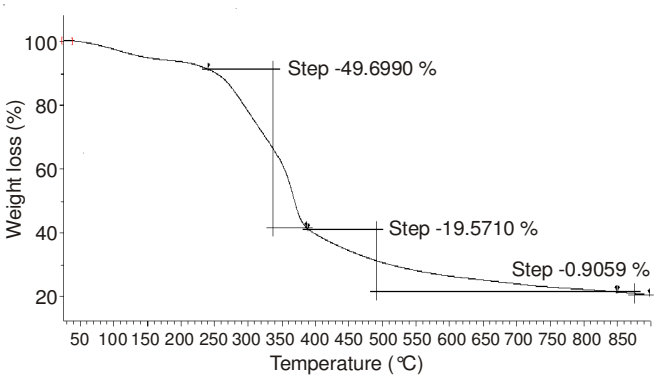

Fig. 2. Thermo gravimetric analysis of the date palm tree frond

palm tree fronds. The second stage *i.e.* 250 to 375 °C represents a significant weight loss due to the decomposition of cellulose and hemi-cellulose of the sample in to the condensable gas like (acetic acid, methanol and, wood tar) and uncondensable gas such as (CO, CO_2, CH_4, H_2, H_2O). During the third stage *i.e.* from 375-850 °C, here in the start lignin begins to decompose and lose weight total loss at this stage is around 19 %. A plateau curve at temperature over 850 °C showed the weight unchanged at this stage. This curve suggests, at 850 °C, carbon yield is 20 %. The carbon at this stage is acceptable as a precursor for producing activated carbon because a carbon with 10-15 % volatile is not too tight and can easily react with activating reagent to produce big surface and huge pore volume. So it is apparent that date palm tree frond can be a good raw material.

BET surface area, pore size and pore volume: Specific surface areas, pore size and pore volumes of the activated carbons were determined by N_2 gas adsorption at 77 K with an automated adsorption instrument (GEMINI VII, 2390 Micro-meritics). Prior to the determination, the sample (about 0.05 g) was degassed for 45 min at 150 °C under nitrogen to remove moisture and other volatiles from the sample. The surface area of activated carbon produced at various activation temperatures is shown in Table-2. The highest surface area 1094 m^2g^{-1} for activated carbon prepared at 850 °C was obtained.

Effects of CO_2 flow rate on the yield, BET surface area and pore volume of activated carbons are given in Table-2. The yield of the activated carbon decreases linearly when the CO_2 flow rate was increased from 25 to 250 mL/min,. The increased flow rate enhances the carbon-CO_2 reaction and increases the carbon burnoff, which results in a decrease in yield. Flow rates greater than 50 mL/min are overgenerous, resulting in a linear decrease in yields, Increasing the CO_2 flow rate from 50 to 250 mL/min decreases the BET surface

TABLE-2
SURFACE AREA PORE VOLUME, PORE SIZE AND YIELD OF ACTIVATED CARBON

S #	Sample name	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)	Yield (%)
1	SAC-850-10-30-25-0.25	610	0.2501	16.41	23.25
2	SAC-850-10-30-50-0.25	1094	0.4382	16.09	18.75
3	SAC-850-10-30-100-0.25	854	0.3486	16.32	16.00
4	SAC-850-10-30-150-0.25	877	0.3570	16.28	15.55
5	SAC-850-10-30-200-0.25	866	0.3602	16.63	15.05
6	SAC-850-10-30-250-0.25	886	0.3788	17.10	14.70

Note: a-b-c-d-e-f denotes sliced activated carbon-activation temperature (°C)-ramp rate (°C/min)-dwell time (min)-CO_2 flow rate (min)-reaction vessel pressure (bar).

area of the activated carbon and at 100 mL/min and above surface area is roughly the same. Increasing the CO_2 flow rate from 25 to 50 mL/min increases the BET surface area of the activated carbons This means that, at a flow rate of 25 mL/min, the carbon burnoff due to carbon-CO_2 reaction is not sufficiently high to maximize the BET surface area in the activated carbons. At 25 mL/min, it is also possible that the volatiles released from the samples might not be completely entrained in the low-velocity CO_2 flow but be deposited on the sample surface again, thereby hindering pore development. At a flow rate of 50 mL/min, the BET surface areas are of maximum values.

For CO_2 flow rates of 100 mL/min and greater, the higher flow velocities above that for 50 mL/min reduce the contact time between the CO_2 molecules and the sample surface and thereby decrease the diffusion of the molecules into the pore structures and hence reduced BET values are obtained. The results presented in Table-2 also indicate that the pore volume above 100 mL/min is generally insensitive to varying CO_2 flow rates used in these tests. So, flow rate of 50 mL/min was suitable to get the maximum surface area and pore volume compare to the other flow rates. Fig. 3 elaborates the effect of CO_2 flow rate on BET surface area and pore volume and Fig. 4 explains about the effect of CO_2 flow rate on the yield of the synthesized activated carbon.

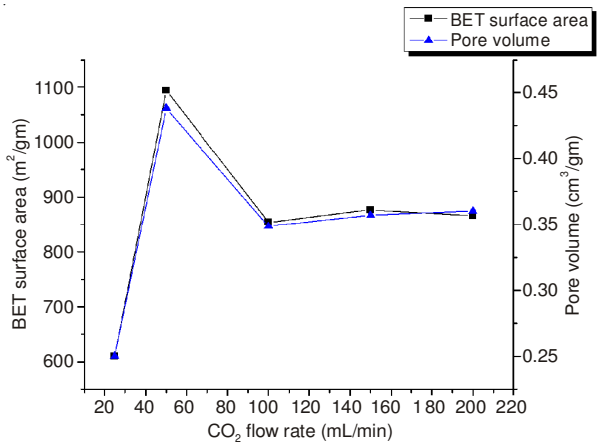

Fig. 3. Effect of CO_2 flow rate on surface area and pore volume

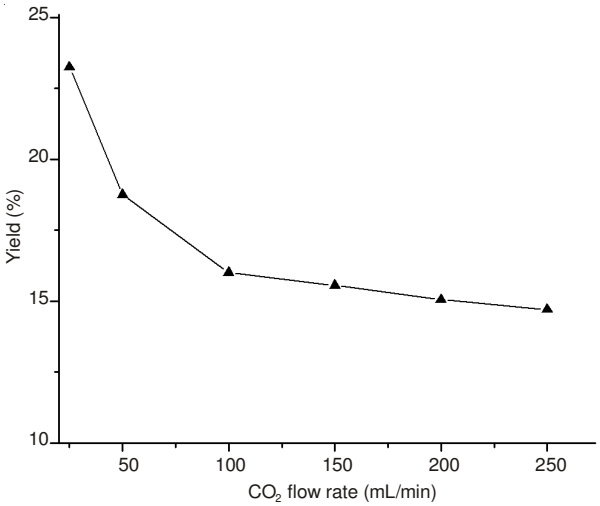

Fig. 4. Effect of CO_2 flow rate on yield of activated carbon

FTIR analysis: The FTIR spectrum of the palm tree frond is shown in Fig. 5. The band at about 3410 cm^{-1} is attributed to ν(O-H) vibrations in hydroxyl groups. The hydrogen-bonded OH groups is usually in the range of 3650-3200 cm^{-1} for alcohols and phenols. The band located at around 2918 cm^{-1} corresponds to ν(C-H) vibrations in methyl and methylene groups[20]. This band is contrary to the δ(C-H) vibrational bands for -CH_3- and -CH_2=, which are located at around 1323 and 1425 cm^{-1}. It is very useful to identify the methyl and methylene groups in a given compound[21,22]. The band appearing at 1734 cm^{-1} was attributed to the carbonyl (C=O) groups. The olefinic ν(C=C) absorptions cause the band at about 1635 cm^{-1} while the skeletal C=C vibrations in aromatic rings cause another two bands at about 1516 and 1466 cm^{-1}. The appearance of bands between 1323 and 893 cm^{-1} could be assigned to C-O stretching vibrations. Another small shoulder at 1116 cm^{-1} and a relatively intense band at about 1055 cm^{-1} could be assigned to alcohol (R-OH) groups. The C-H out-of-plane bending in benzene derivative vibrations cause the band at 893 cm^{-1}. Finally, the ν(O-H) band is located at 604 cm^{-1}. From the above analyses, the main oxygen groups present in palm tree fronds are the carbonyl groups, ethers, esters, alcohols and phenol groups.

The FTIR spectrum of the sliced activated carbon prepared at 850 °C is also shown in Fig. 5. Comparing the spectrum of the sliced activated carbon with that of the raw date palm tree frond, the ν(O-H) vibrations in hydroxyl groups still exist, corresponding to the band at about 3436 cm^{-1}. However, the C-H vibrations in methyl and methylene groups (*e.g.*, bands at 2923 and 1632 cm^{-1}) are not discernable in the sliced activated carbon, indicating that there is a decrease in aliphaticity by the heat treatment process[23]. In contrast, the aromatic C-H stretching band at 2923 cm^{-1} appears. Finally, the ν(O-H) band is located at 510 cm^{-1}. The decrease in the oxygen groups like ether and alcohol, with the heat treatment process of pyrolysis, indicates that these parts of the functional groups are thermally unstable[21].

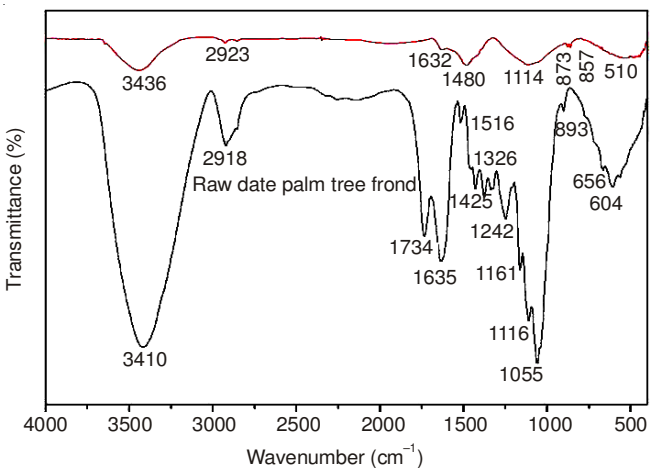

Fig. 5. FTIR of raw date palm tree frond and SAC-850-10-30-50-0.25 activated carbon at 850 °C

Conclusion

Sliced activated carbon prepared at a CO_2 flow rate of 50 mL/min has a larger surface area, pore volume and has a larger

adsorption capacity compare to other flow rates. 16.09 Å Pore size confirms that at the optimum condition of CO_2 flow rate, the synthesized sliced activated carbon is predominantly microporous.

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