Impact of reaction vessel pressure on the synthesis of sliced activated carbon from date palm tree fronds

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Abstract

The effects of the reaction vessel pressure on the BET surface area, pore volume and pore size of the synthesis of sliced activated carbons (SAC) at 850 °C starting from 0.10 to 0.40 bar were investigated. Other synthetic variables like dwell time, CO_2 flow rate and heating ramp rate were kept constant during the whole study. Methodology involves a single step procedure using the mixture of gases (N_2 and CO_2). During activation of flow rate, the both gases are kept at 150 and 50 ml/min, respectively. The BET surface areas of the SAC prepared at 0.10, 0.15, 0.20, 0.25, 0.30, 0.35 and 0.40 bar after 30 min of activation time were 666, 745, 895, 1094, 835, 658 and 625 m^2/g, respectively. Scanning electron microscopy (SEM) for surface morphology, energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM) for nano particle size were also carried out, which confirmeds the same trend.

Keywords: activated carbon, physical activation, gaseous mixture, Saudi date fronds, agro waste.

Available online at the Journal website: http://www.ache.org.rs/HI/

SCIENTIFIC PAPER

UDC 66.07:661.183.2:543.42

Hem. Ind. **69** (5) 561–565 (2015)

doi: 10.2298/HEMIND140820078S

Any type of carbonaceous material [1] can be a good precursor for the synthesis of activated carbon for instance oil-palm stones [2], palm shell [3], olive stones [4], coconut shell [5], nut shell [6], agricultural wastes [7,8], etc. Date palm tree fronds in the Kingdom of Saudi Arabia are the waste material from the date trees during pruning process [9]. This locally available waste material is ideal for the synthesis. The synthesis steps of activated carbon from physical method normally involve two stages, in the first stage it involves the carbonization of the raw material in an inert atmosphere like nitrogen and in the second stage, the activation of the carbonized products with steam and/or CO_2. During the first stage, *i.e.*, in the carbonization step, all the volatile matters are released, and the remaining solid carbon structure is generally called as char. In the second stage, *i.e.*, the activation step, the char produced in the first stage reacts with activating agents to form activated carbon (AC) with enhanced pore structure and surface properties. Nevertheless, well modified activated carbon for explicit application and having a specific surface area greater than 500 $m^2\ g^{-1}$ cannot be easily obtained by simply carbonizing the carbonaceous materials or biomass above, and due to its ready availability and stability in production, much study has been done on coal for the industrial production of activated carbon [10–13].

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Paper received: 20 August, 2014
Paper accepted: 22 October, 2014

During chemical activation, the raw material is first impregnated with certain chemicals like phosphoric acid (H_3PO_4), potassium hydroxide (KOH), calcium chloride ($CaCl_2$) and zinc chloride ($ZnCl_2$) and then carbonization was carried out in a furnace.

Regardless of the benefits provided by the chemical activation process, the chemical consumption led to the secondary pollution problem during the disposal stage. For that reason, the physical activation consists of single step carbonization followed by activation using steam or carbon dioxide (CO_2) as the activation agent is the most commonly used. Yet, since single stage CO_2 activation has received lack of scientific research and there is still limited publication data in the literature. In view of that, further research work on this area is deemed very momentous. Through recent published research [14], one step activation process on the coconut shell produces comparable results as the two step approaches. The benefits of utilizing the single step activation are due to lower operating time and the energy consumption. The effect of ramp rate and the CO_2 flow rate on the synthesis of sliced activated carbon (SAC) from date palm tree has already been published [15,16]. The objective of the present work was to study the effect of reaction vessel pressure on the synthesis of effective SAC from date palm tree fronds by physical activation.

EXPERIMENTAL

The date palm tree fronds were dried at 105 °C for 8 h to reduce the moisture content followed by the slicing of the dried fronds with sophisticated wood

cutter to a size range of 2–3 mm. 4.0 g of the sliced precursor was used for the study. Pyrolysis was carried out at a temperature of 850 °C by using Grade 5 (99.999%) nitrogen gas at a flow rate of 150 ml/min whereas the activation was done with a mixture of Grade 5 nitrogen and carbon dioxide gas at a flow rate of 150 and 50 ml/min, respectively. Carbolyte MTF 12/38/250 horizontal tube furnace was used both for pyrolysis and activation processes. The effects of the reaction vessel pressure were studied from 0.10 to 0.40 bars during the study and the prepared activated carbon was characterized by calculating BET surface area, pore size, pore volume, SEM, EDS and TEM. Digital pressure switch, solenoid valve from SMC Japan and the indigenously developed electronics facilitated the process to attain the desired pressure within a variation of ±0.02 bar. Fig. 1 shows the schematic of the process.

RESULTS AND DISCUSSION

BET surface area, pore size and pore volume

BET surface areas, pore size and pore volumes of the SAC prepared from date palm tree fronds were determined by N_2 gas adsorption at 77 K with an automated adsorption instrument (Gemini VII, 2390 Micromeritics). 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 effects of the reaction vessel pressure on the, BET surface area, pore volume and pore size of the SAC at 850 °C starting from 0.10 to 0.40 bar are shown in Table 1.

Decreasing the system pressure from 0.40 to 0.25 bar increases the evolution of volatiles from raw materials by drawing off organic vapor and uncondensable gas formed during the activation process in the reactor, resulting in pore development thus increasing in the activated carbon. However, further decreasing the system pressure to 0.10 bar, results in significant decline in the BET surface area and pore volume of the activated carbon. This can be attributed to very fast volatilization of the volatiles generated during the activation process, which may affect the formation of activated carbon and decrease the number of pore and even destroy the pore structures.

From Table 1, it can be seen that the pore surface area and the pore volume of the activated carbon exhibit identical trends. At the system pressure of 0.25 bar, the pore surface area and the pore volume have maximum values of 1094 m^2/g and 0.4382 cm^3/g, respectively. The BET surface area, the total pore volume and the average pore diameter all reach the maximum at the system pressure of 0.25 bar, but the pore surface

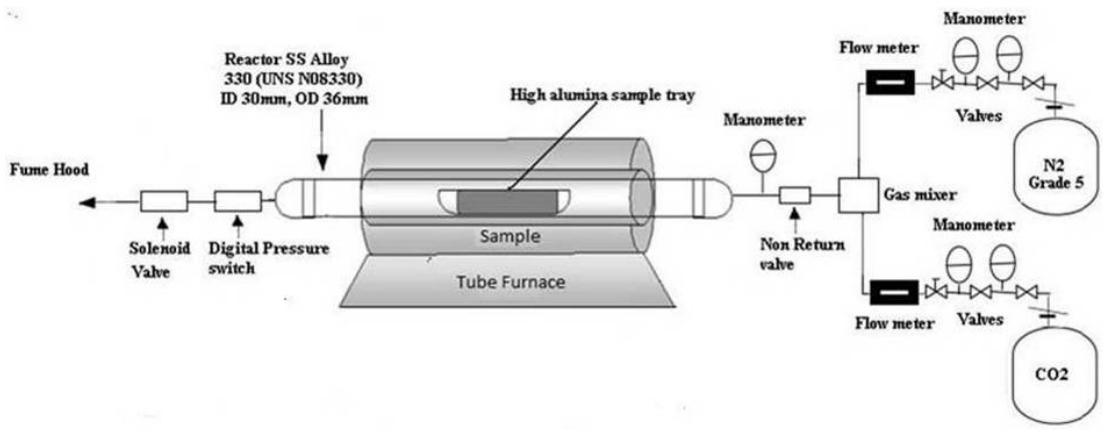

Figure 1. Schematic of process.

Table 1. Effect of reaction vessel pressure on surface area, pore volume and pore size of activated carbon; a-b-c-d-e-f denotes SAC--activation temperature (°C)-heating ramp rate (°C/min)-activation dwell time (min)-CO_2 flow rate (ml/min)-reaction vessel pressure (bar)

Sample No.	Sample name	Surface area, m^2/g	Pore volume, cm^3/g	Pore size, Å
1	SAC^a-850^b-10^c-30^d-50^e-0.40^f	666	0.2817	16.94
2	SAC^a-850^b-10^c-30^d-50^e-0.35^f	745	0.3207	17.21
3	SAC^a-850^b-10^c-30^d-50^e-0.30^f	895	0.3620	16.16
4	SAC^a-850^b-10^c-30^d-50^e-0.25^f	1094	0.4382	16.09
5	SAC^a-850^b-10^c-30^d-50^e-0.20^f	835	0.3540	16.96
6	SAC^a-850^b-10^c-30^d-50^e-0.15^f	658	0.2820	17.13
7	SAC^a-850^b-10^c-30^d-50^e-0.10^f	625	0.2697	17.24

area and pore volume are lower than those obtained at the system pressure of 0.25 bar. The result indicates that system pressure of 0.25 bar is beneficial to develop the pore structure of activated carbon during physical activation process. The effects of reaction vessel pressure on the surface area, pore volume and pore size of the activated carbons are shown in Fig. 2a and b.

SEM Analysis

SEM analysis was carried out by using Jeol JSM--6380 LA instrument. Figure 3 shows the scanning electron microscope (SEM) graphs for: a) the raw date fronds. The image clearly shows the surface is curvy due to cellulose, hemicelluloses and lignin and with less slit like fractures or cracks. Pyrolysis and activation at reaction vessel pressure of 0.25 bar produced predominantly micro porous with a little presence of mesoporosity as shown in Fig. 3b.

EDS Analysis

Table 2 shows the EDS results of date palm tree frond and SAC prepared at the optimum condition of reaction vessel pressure *i.e.*, 0.25 bar. The determined element content includes carbon (C), oxygen (O), and other elements. Among the elements, those that should be mainly focused on are the carbon and oxygen content. An activated carbon will usually have higher carbon content than the starting material. In this case, the carbon content is 57.53% for raw date fronds, whereas the carbon content increased to 77.83% after the optimized reaction vessel condition for SAC^a-850^b--10^c-30^d-50^e-0.25^f (see Table 1 for definition). This phenomenon is due to the volatilization of H and O atom from the carbon matrix during the activation process at high temperature.

Table 2: EDS results (%) of date palm tree frond and SAC^a-850^b-10^c-30^d-50^e-0.25^f (see Table 1 for definition)

No.	Sample name	Carbon	Oxygen	Others
1	Date Palm Tree Frond	57.83	39.20	2.97
2	SAC^a-850^b-10^c-30^d-50^e-0.25^f	77.83	16.16	6.01

TEM Analysis

The pore size distribution observed in the TEM images was calculated using the program Image J and plotted in graph. Figure 4a shows the tem image of SAC^a-850^b-10^c-30^d-50^e-0.25^f and Figure 4b shows the graphical illustration of the particle size distribution. The TEM results clearly indicate that the product is fairly uniform and is present in the form of nanoparticles.

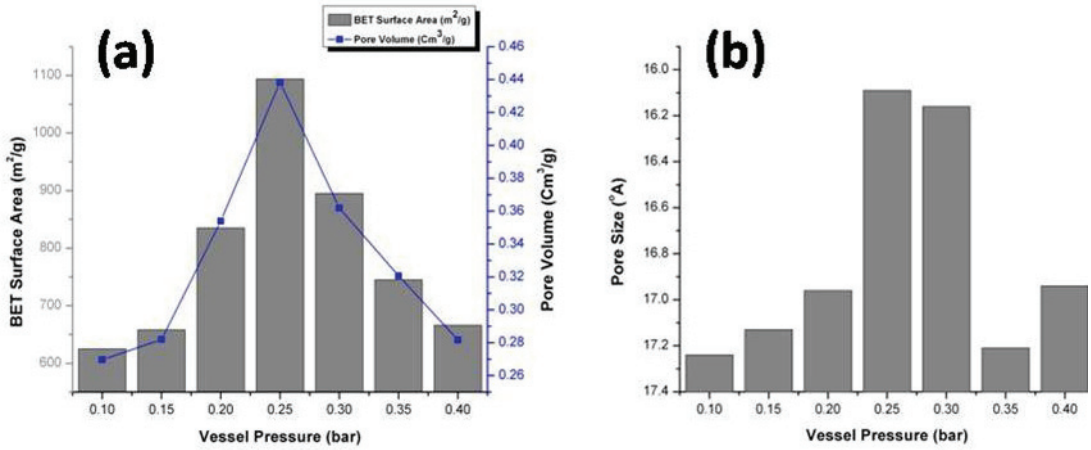

Figure 2. Effects of reaction vessel pressure on: a) surface area and pore volume and b) pore size.

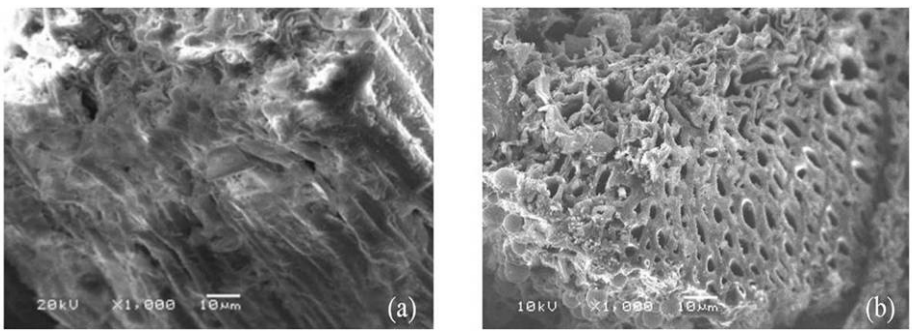

Figure 3: SEM micrographs showing the surface morphologies of: a) raw date frond and b) SAC^a-850^b-10^c-30^d-50^e-0.25^f (see Table 1 for definition).

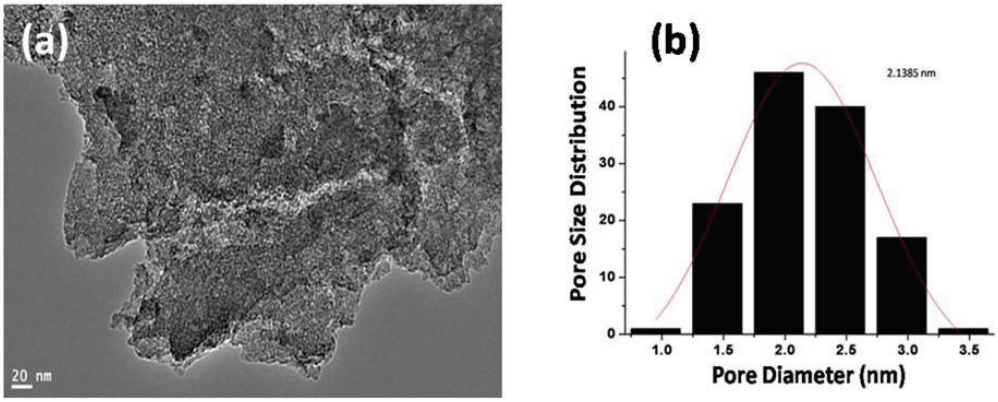

Figure 4. TEM image of: a) SAC^a-850^b-10^c-30^d-50^e-0.25^f and b) graphical illustration of the particle size distribution.

As per my knowledge there is no data available on the effect of vessel pressure on the synthesis of activated carbon from any agro waste material, the literature shows that the BET surface area of activated carbon from cherry stones, grape seeds, nut shells, pistachio-nut shells, almond shells, corn cob, oak, corn hull, corn stover, rice husk, and pecan shells reported in the review article [17] and they all have lower BET surface area and pore volume except the pistachio nut shell which also has a lower surface area, but has a bit higher pore volume as compared to the activated carbon prepared in this study.

CONCLUSION

SAC prepared from date palm tree fronds at a reaction vessel pressure varying from 0.1 to 0.4 bar. The pressure of 0.25 bar was found to be optimum, as it produced SAC with larger surface area of 1094 m^2/g and pore volume 0.4382 cm^3/g as compared to the ones obtained under other pressure conditions studied. The pore size 16.09 Å at 0.25 bar verifies that the synthesized activated carbon is predominantly micro porous. This shows that the pressure of the reaction vessel plays an important role in obtaining high surface area. Synthesized SAC can be used as effective adsorbent for NO_x/SO_x emission adsorption from electricity generation plants, purification of gases, sewage treatment and many other applications, the further studies in this direction are being carried out by the group and shall be reported later.

Acknowledgements

This Research was supported by King Saud University, Deanship of Scientific Research, College of Science Research Center.

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IZVOD

UTICAJ PRITISKA U REAKCIONOM SUDU NA SINTEZU REŽNJEVITOG AKTIVNOG UGLJA IZ LIŠĆA DRVETA URME

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(Naučni rad)

Proučavan je uticaj pritiska u reakcionom sudu na specifičnu BET površinu, zapreminu i veličinu pora režnjevitog aktivnog uglja (SAC) na 850 °C, pri primenjenim pritiscima od 0,10 do 0,40 bar. Druge promenljive, kao što su reakciono vreme, protok CO_2 i brzina zagrevanja rampe su održavane konstantnim za vreme čitavog istraživanja. Metodologija uključuje jednostepeni proces upotrebom smeše gasova (N_2 i CO_2). Za vreme aktivacije protok oba gasa je održavan na 150 (N_2) i 50 ml/min (CO_2). BET površine pripremljenog SAC pri pritiscima od 0,10; 0,15; 0,20; 0,25; 0,30; 0,35 i 0,40 bar posle perioda aktivacije od 30 min su 666, 745, 895, 1094, 835, 658 i 625 m^2/g, redom. Primenjene metode, SEM za ispitivanje morfologije površine, EDS analiza i TEM za ispitivanje veličine nano čestica, takođe, pokazuju isti trend.

Ključne reči: Aktivni ugalj • Fizička aktivacija • Gasna smeša • Lišće drveta saudijske urme • Poljoprivredni otpad