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The Study of Activated Carbon Derived from Rubberwood Sawdust (*Heavea brasiliensis*): Textural and Chemical Characterization

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ABSTRACT

This present work comprehensively addresses the effects of using dehydrating agents such as potassium hydroxide on activated carbons prepared from rubber wood sawdust (RW). A two-stage activation process method was used; with semi-carbonization stage at 200°C for 15 minutes as the first stage followed by an activation stage at 500°C for 45 minutes as the second stage. The precursor material with the impregnation agent was exposed straightaway to semi-carbonization and activation temperature unlike the specific temperature progression as reported in the literature. All experiments were conducted in a laboratory scale muffle furnace under static conditions in a self generated atmosphere covering process parameters such as impregnation ratios. We found that by using this method, the RW20% prepared with the impregnation ratio of 20% KOH had the highest Iodine Number and Methylene Blue adsorption capacity which were 72.39mg/g and 40mg/g respectively.

Keywords : *Activated carbons, two-stage activation process, physical and chemical properties*

Introduction

Activated carbons, due to their structural properties and relatively low cost are among the more important industrial carbons used for adsorption of pollutants from air and water streams. This material can be designed for adsorption of specific adsorbate, by using appropriate precursor (Anuar et al. 2003, 2004a, 2002, 2001), dehydrating agent and by optimizing the activation process conditions. Several activating agents have been reported for chemical activation process; however the most important and commonly used activating agents are zinc chloride, potassium hydroxide and alkaline metals. This agent, which has dehydrating properties, will influence the pyrolytic decomposition and retard the formation of tars during the carbonization process, increasing the carbon yield (Gergova et al. 1994). A number of activation methods have been reported in the literature using KOH as an activating agent. Chemical activation by KOH was first reported in the late 1970s by AMOCO Corporation (Marsh et al. 1982), and these carbons were commercialized by the Anderson Development Company in the 1980s (O'Grady & Wennerberg 1986). Since then, there have been many studies reporting on the activation of carbons using KOH (Otawa et al. 1997, 1993; Ahmadpour & Do 1996, 1997; Laine & Calafat 1991; Hu & Srinivasan 1999). The chemical nature of activated carbon significantly influences its adsorptive, electrochemical, catalytic, and other properties. However, few papers report on the effects on chemical preparation conditions and preparation methods on the carbon. Generally, activation methods can be classified as single-stage or two-stage activation process carried out either in inert medium or a self-generated atmosphere as shown in Table 1. Table 1 summarizes efforts by researchers to prepare activated carbons using various methods with reference to the precursors, experiment conditions and results. Table 2 summarizes efforts by researchers to prepare activated carbons using KOH as the dehydrating agent.

Table 1: Summary of earlier works by researchers to prepare activated carbons using various methods.

Researcher	Precursor	Experimental Condition	Results
Kirubakaran et al. (1991).	Coconut Shell	Two stage in N ₂ atm; A.T=400 to 600°C; A.time=2hrs.	S.A > 1000m ² /g at I.R.=1.5
Toles et al. (1998).	Macadamia shell, pecan, walnut and almond	Single and two stage; N ₂ and self-generated atm.; S.C.T.=170°C; S.C. time=30min.; A.T.=450°C; A. time=1h	S.A=1100 to 1600 m ² /g. Activation in self-generated atm gave the highest S.A.
Dastgheib & Rockstraw (2001).	Pecan Shells	Three stage activation: 1) liquid-stage activation at 160°C 2) primary activation at 160-210°C 3) secondary activation at 300-500°C for 30 min, I.R.=3	S.A=1071 m ² /g. S.A. increases until secondary A.T of 450°C and reduces when temperature increases above 450°C.
Lafi (2001).	Acorns and olive seeds	A single stage with self-generated atmosphere. A.T=400-800°C. A.time=1h	A.T=800°C produced the highest Methylene Blue no. of 130mg/g

Table 2: Summary of earlier works by researchers to prepare activated carbons using KOH impregnations.

Researchers	Precursors	Experimental conditions	Results
Diaz-Teran et al. (2003).	Esparto grass (<i>Stipa tenacis-sima</i>)	N ₂ atm.; K ₂ CO ₃ used as refer-ence; I.R.: 0.2-4.0; A.T: 400° C, 600°C, 800°C; A.time: 30min;	Highest S.A. of 1960 m ² /g obtained at 800°C. KOH activation more effective than K ₂ CO ₃ . K ₂ CO ₃ enhances mesopore formation.
Lillo-Ródenas et al. (2003).	Anthracite	N ₂ , CO ₂ , steam and atm. comb.; varying gas flow rate; NaOH and Na ₂ CO ₃ used as activating agent; I.R.: 3.0-4.0; A.T: 760°C; A.time: 1h;	Highest S.A. of 2193 m ² /g obtained at N ₂ flow of 500ml/min. NaOH not effective under CO ₂ atmosphere. Na ₂ CO ₃ not an activating agent. Reaction between NaOH and C begins at ~ 570 °C, for KOH/C at 400 °C.
Ganan et al. (2004).	Mesophase coal pitch	N ₂ atm.; 1& 2-step activation; I.R.: 1.0-6.0; A. T.: 375-900°C, 450°C, A.time:1-2 hrs. Air gasification conducted.	Highest S.A. for 1 step activation: 638 m ² /g at I.R.=3. Highest S.A. for 2 step activation: 2346 m ² /g at IR=3. Air gasification at 300 °C - no significant improvement in carbon texture.
Carvalho et al. (2003)	Cork waste	N ₂ atm.; 1&2-step activation; A.T: 300°C & 500-900°C ; A.time.: 0-16 h	Highest S.A.=1415 m ² /g. Increase of I.R. has positive effect initially but opposite situation is observed at high I.R.

S.A =surface area; S.C.T=semi-carbonization temperature; S.C. time=semi-carbonization time; A.T=activation temperature; A. time=activation time; I.R. =impregnation ratio.

Malaysia has been one of the main rubber producers and exporters in the Asian region for decades. As the demand for natural rubber started to decrease and Malaysian rubber plantations began to shift their activities towards other forms of agriculture commodities, rubber trees from these rubber plantations were utilized for many other purposes, some of which are furniture-making, construction and pulp processing. This project currently undertakes the task to utilize rubber wood sawdust as a precursor for activated carbon. The preparation of activated carbon from rubber wood sawdust is one of the ways of adding value to rubber wood and this material can easily be sourced from the furniture industry wastes. This paper explains the effect of KOH impregnation to the precursors prepared by using a two-stage activation process method in a self-generated atmosphere. Trial and error methods were used to achieve a high surface area carbon with desired pore size by optimizing the process parameters such as the activation time, activation temperature and impregnation ratio.

Experiment

Prior to the impregnation process, precursors were washed with distilled water and dried in an oven at 110°C for 24 hours. This was done to remove sand, branch fibers and dirt from contaminating the samples as explained in our previous papers (Anuar *et al.* 2003, 2004a, 2002, 2001). Impregnation process was done using KOH as the dehydrating agent. 5g, 10g, 15g, 20g and 25g of granular KOH were placed separately into 5 Erlenmeyer flask (250ml). 100ml of distilled water and 20g of precursor was added into each of the flask. The flask was then placed in orbital shaker model 721 Protech for a week. The samples were dried overnight in an oven at 110°C. A muffle furnace model Carbolite RHF 1500 was used to semi-carbonized the samples at 200°C for 15 minutes as the first stage followed by an activation stage at 500°C for 45 minutes as the second stage. The precursor material with the impregnation agent was exposed straightaway to semi-carbonization and activation temperature unlike the specific temperature progression methods as described in earlier works (Anuar *et al.* 2003, 2004a, 2002, 2001; Diaz-Teran *et al.* 2003; Lillo-Ródenas *et al.* 2003; Ganan *et al.* 2004; Carvalho *et al.* 2003). After that, the activated carbons were refluxed in an acid solution (0.1M HNO₃) to remove metals ions, tar and ash followed by distilled water (10 times) to remove the acid. The activated carbons were dried in an oven at 110°C for a week, after which, yield percentage, moisture and ash content, pH (Anon 1994), scanning electronic microscopy of the selected activated carbon were done. The scanning electronic microscopy was done using JEOL JSM 5610. Adsorption studies regarding the treatment of landfill leachate with the activated carbon, surface area and porosity studies will be presented in our next paper.

Result and Discussions

Temperature, heating period, materials, dehydrating agent and the method of carbonization and activation play an important role in determining the properties of the resulting activated carbon. Previous work in our laboratories (Anuar *et al.* 2003, 2004a, 2002, 2001) suggested that the temperature played an important role to produce optimum surface area for the carbons.

Percentage of yield, pH, moisture and ash contents

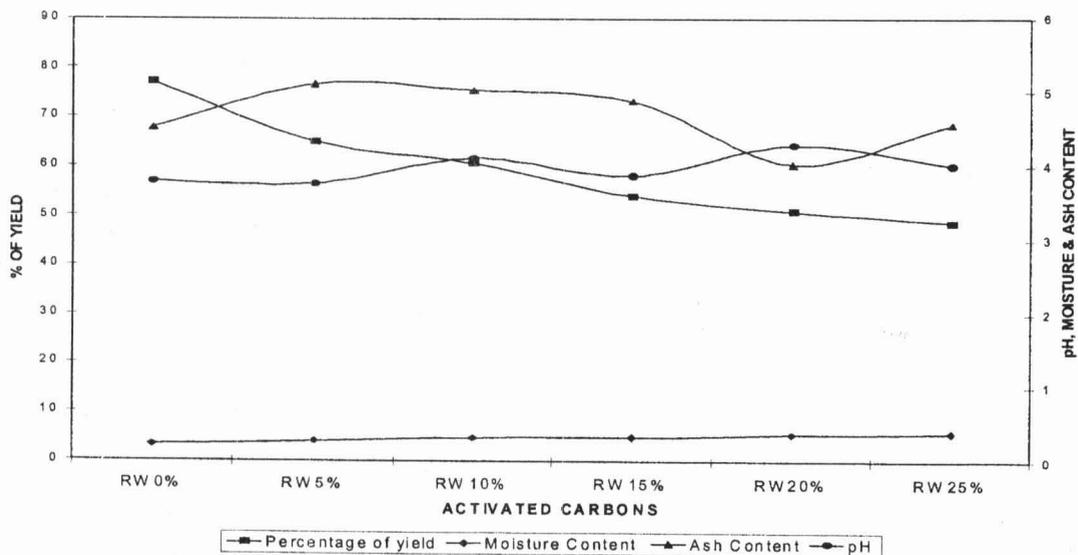


Fig. 1: The effect of KOH impregnations (wt%) on the percentage of yield, pH, moisture and ash contents of the rubber wood sawdust activated carbons.

The overall yield of the activated carbon was calculated based on the initial weight of the pre-dried precursor. Relatively high yields of the final products are expected in manufacturing commercial adsorbents. Figure 1 shows the effect of KOH impregnations (wt%) on the percentage of yield, pH, moisture and ash content of rubber wood sawdust. The percentage for yield for rubber wood sawdust was between 48-77% with RW0% giving the highest percentage of 77%. Increasing the KOH-to-precursor ratio decreased the overall yield for rubber wood sawdust activated carbons. This was because the potassium ions attached onto the carbon surface, acting as catalyst to accelerate direct

reaction between the carbon and KOH. These reactions contributed to the evolution of more volatile matter in the form of smoke and gasses (Lillo-Rodenas *et al.* 2003). Rubber wood sawdust is a typical carbonaceous biomass therefore, the following reaction occurred during KOH impregnation process:



During semi-carbonization (1st stage) will result in the following products:



Char usually contains a majority of carbon, C(~75-80%); some oxygen, O(~15-17%) and some hydrogen, H(< 3%). Tar consists of phenols, CH₃COOH, CH₃OH, (CH₃)₂CO, and other high molecular weight hydrocarbons. Gaseous components include H₂C, CO₂, CO, etc (Jankowska *et al.* 1991).

The following reaction occurred during the activation (2nd stage) process:



At activation temperature, metallic potassium intercalated with the carbon matrix, resulting in the widening and formation of new pores. Secondary reactions possibly took place as well between H₂O (eq3), C and KOH resulted in the formation of 'extra' K₂CO₃ as shown in the following equation:



Potassium carbonate (K₂CO₃) is known to produce well-developed internal porosity on the activated carbon (Anuar *et al.* 2004b).

Our observation recorded that the pH of the activated carbons was about 4. This is due to the washing process using nitric acid. Moisture and ash content for the activated carbon ranged from 3 - 6% and 4 - 5% respectively. The activated carbons showed a reducing pattern for the ash content and an increasing pattern for the moisture content as the impregnation ratio of KOH was increased. This was because higher concentration of KOH inhibits excessive burn-off, and lowering ash formation. KOH also has an affinity for adsorbing water, this accounted for the increasing pattern of the moisture content as the concentration of KOH increases in figure 1.

Physical Appearance

The activated carbons were photographed after activation, and these photographs showed an interesting physical appearance. Figure 3 shows the photographs of the untreated RW, RW0% and RW25%.

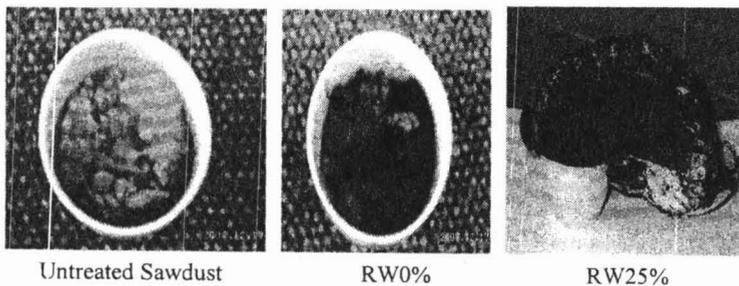
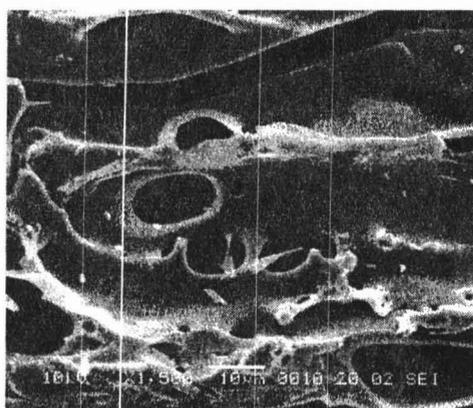


Fig. 2: Photographs of the untreated sawdust, physically activated carbon; RW0% and chemically activated carbon; RW25%.

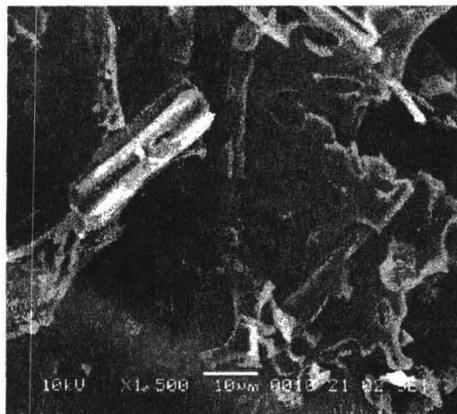
The untreated sawdust was light brownish in colour whereas the physically activated carbon, RW0%, was dark brown in colour. Chemically activated carbon, RW25%, was black in colour. The RW0% maintain the similar shape and structure as untreated sawdust but RW25% underwent remarkable physical change as shown in figure 2. The shape of the sawdust was completely lost and the RW25% took the shape of the crucible that was used as a reactor.

RW25% had a sponge-like appearance and was very brittle. It is possible that KOH deposition on the surface of the material according to eq1 during impregnation and eq4 during activation contributed to extensive gasification that produced the sponge-like appearance. Morphological studies using scanning electron microscopy also corroborated this finding.

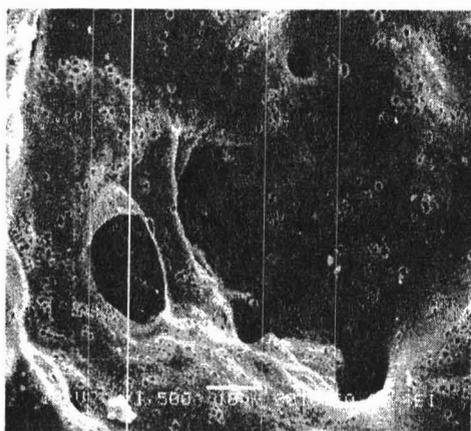
Scanning Electron Microscopy



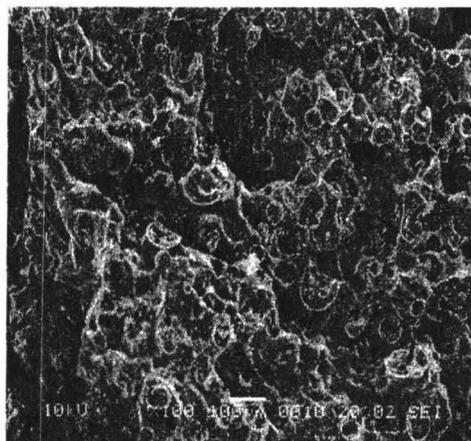
Untreated sawdust



OPS0%



RW25%



RW25%-overview

Fig. 4: The electron micrographs of untreated sawdust, RW0%, RW25% and RW25%-overview.

SEM was used to study the morphological structure on the prepared activated carbons. The surface structure of the untreated sawdust has dirt-covered, unclear and small pores. The surface structure of the physically activated carbon (RW0%) has clean and burnout pores with clear definition. The chemically impregnated activated carbon (RW25%) also showed similar traits but some of the pores were clearly enlarged with a lot of smaller pores surrounding the bigger pores. This clearly demonstrates that KOH helped to encourage pore enlargement. The pores were also elongated in shape. This is characteristically unique to KOH impregnated activated carbons. If the morphological structures are viewed as a whole (RW25%-overview), we can see that the structure is completely different as compare to RW0%. This was due to the reaction of KOH with the lignocellulosic material giving a burn-out sponge-like structure. These findings correspond with the physical appearance results of the activated carbons. Our results suggest that the chemical activator played an important part in clearing, restructuring and producing better pores. These findings are consistent with the findings of other researchers. Potassium compounds are effective catalyst for activation (Anuar et al. 2004b).

Conclusion

In conclusion, this study showed that the use of dehydrating agent and the two-step activation process in self-

generated atmosphere played a major role in shaping and transforming precursors into activated carbons. Granular KOH was used as a dehydrating agent, produced a very different activated carbon, changing not only the pore structure and morphology of the activated carbon but also giving the sponge-like physical appearance of the precursor itself. The precursor, rubber wood sawdust, was changed from its natural form to take the shape to the reactor. It is our opinion that extensive gasification coupled with activation temperature of 500°C contributed to this change.

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References

- Anuar, K., Collin, G. J., Zulkarnain, Z., Hussein, M. Z., Haron, M.J. & Abdullah, A. H. (2003). Surface area and porosity studies of activated carbons prepared from oil palm shells (*Elaeis Guineensis*) using physical and chemical activators such as CO₂, H₃PO₄, K₃PO₄ and KOH. *ASEAN J. of Sci. And Tech. for Dev.* 20(2): 149-158.
- Anuar, K., Collin, G. J., Zulkarnain, Z., Hussein, M. Z., Haron, M.J. & Abdullah, A. H. (2004a). Activated carbons prepared from oil palm shells: application for column separation of heavy metals. *Indian Chem. Soc.* 81(12): 946-949.
- Anuar, K., Collin, G. J., Faujan B.H.A., Zulkarnain, Z., Hussein, M. Z. & Abdullah, A. H. (2002). Preparation and characterization of activated carbon from Resak wood (*Vatica Hullettii*): surface area and porosity studies. *Oriental J. of Chem.* 18(1): 43-46.
- Anuar, K., Collin, G. J., Faujan B.H.A., Zulkarnain, Z., Hussein, M. Z. & Abdullah, A. H. (2001). Preparation and characterizations of activated carbon from Resak wood (*Vatica Hullettii*). *Res. J. of Chem. Environ.* 5(3): 21-24.
- Gergova, K., Petrov, N. & Eser, S. (1994). Adsorption properties and microstructure of activated carbons produced from agricultural by-products by steam pyrolysis. *Carbon.* 32: 693-702.
- Marsh, H., Crawford, T.M. & O'Grady, T.M., Wennerberg, A.N. (1982). Carbons of high surface area. A study by adsorption and high resolution electron microscopy. *Carbon.* 20: 419-426.
- O'Grady, T.M. & Wennerberg, A.N. (1986). Petroleum-Derived Carbons, High-Surface-Area Active Carbon. *ACS Symposium Series 303, American Chemical Society:* 302.
- Otawa, T., Nojima, Y. & Miyazaki, T. (1997). Development of KOH activated high surface area carbon and its application to drinking water purification. *Carbon.* 35: 1315-1319.
- Otawa, T., Tanibata, R. & Itoh, M. (1993). Production and adsorption characteristics of MAXSORB: High-surface-area active carbon. *Gas Sep. Purif.* 7: 241-245.
- Ahmadpour, A. & Do, D.D. (1996). The preparation of active carbons from coal by chemical and physical activation. *Carbon.* 34: 471-479.
- Ahmadpour, A. & Do, D.D. (1997). The preparation of activated carbon from macadamia nutshell by chemical activation. *Carbon.* 35: 1723-1732.
- Hu, Z.H. & Vansant, E.F. (1995). Chemical activation of elutrilite producing carbon-aluminosilicate composite adsorbent. *Carbon.* 33: 1293-1300.
- Laine, J. & Calafat, A. (1991). Factors affecting the preparation of activated carbons from coconut shell catalyzed by potassium. *Carbon.* 29: 949-953.
- Hu, Z.H. & Srinivasan, M.P. (1999). Preparation of high-surface-area activated carbons from coconut shell. *Micropor. Mesopor. Mater.* 27: 11-18.