Influence of Physical Mixing Ratio on Pore Development in Highly Porous Carbon Prepared From Nipa Palm Husk Using Hydrothermal Carbonization with Chemical Activation

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Abstract. In this study, porous carbon materials were prepared from nipa palm (Nypa fruiticans) husk using hydrothermal carbonization process with KOH activation through physical mixing. In order to investigate effects of factors on carbon products, hydrothermal temperature and duration were set to 180°C and 8 hours, and KOH:hydrochar activation weight ratio at 1:1, 1:2 and 1:3, respectively. Prepared carbon materials then were carbonized at 900°C for 2 hours under nitrogen atmosphere and characterized by scanning electron microscope, fourier-transform infrared spectroscopy and x-ray diffraction. According to the results, carbon material produced using physical mixing activation ratio of 1:1 shows the most significant pore development and surface chemical properties, leads to finding a promising way to prepare environmental-friendly highly porous carbon material from biomass.

1. Introduction
Thailand is an agricultural country and has variety of plant species, leads to plenty of biomass available. Agricultural residues from plantation or orcharding are usually been thrown away or let them decompose over time, which yield little or no benefits from doing so. An alternative way to utilize large number of residues is enhancing their properties or changing their structures such as using as fuel[1,2], direct fertilizers or as precursor for activated carbon[3].

Activated carbon has extraordinary porosity, mechanical and electrical properties[4]. Thus, it becomes an ideal material for adsorption[3,4,5,6], catalytic[7,8], structural and energy applications[1,2]. Activated carbon is mainly prepared from biomasses because they have organic structure with high carbon content called lignocellulosic components, consists of three vital types-cellulose, hemicellulose and lignin[9]. Pyrolysis used to be the main way to transform lignocellulosic components in biomass into char, yielding higher carbon content. However, pyrolysis method requires high energy to operate[10]. Hydrothermal carbonization process has gained in popularity as it requires less operation temperature than conventional pyrolysis. With hydrothermal carbonization method, biomass chemical decomposition can occur under controlled or self-generated pressure.[11] Water added to raw biomass helps in breaking chemical bonds in lignocellulosic components, removing excessive water and carboxyl group in biomass. Temperature and pressure promote reconstruction of organic compounds through polymerization, condensation and aromatization.[12]

Chemical activation is a method to prepare porous activated carbon. It has purposes to develop suitable porosity and surface chemical composition, leads to adsorption enhancement. Some
substances such as sodium hydroxide (NaOH), potassium hydroxide (KOH) or phosphoric acid (H₃PO₄) are widely used as an activating agent. Impregnation is a popular way as it uses activating agent solution to penetrate into biomass structure, yielding porosity development. But according to P Nowicki’s work on influences of chemical activation methods toward porosity of activated carbon prepared from pine cones shows that activated carbon prepared by physical mixing- another method of activation using solid activating agent- yields more porosity than one prepared by impregnation. However, there are not many studies about suitable physical mixing ratios towards carbon material’s structural development.

In this work, suitable physical mixing ratio was examined via mesoporous carbon powder preparation from nipa palm husk (Nypa fruiticans) using hydrothermal carbonization process along with chemical activation using KOH physical mixing. The aim on this work is to investigate the effect of physical mixing ratios of activating agent and hydrochar towards physical pore structure alternation. This research also has an object to introduce higher performance activation method to produce porous carbon materials with better porosity but use lower energy, reaction time and activation agent cost, leads to encouragement in more effective way to utilize biomasses to valuable products.

2. Materials and methods

2.1. Material
Nipa palm husks (Nypa fruiticans) are collected from local plantation source in Samut Songkhram, Thailand. Pelletized analysis-grade potassium hydroxide is obtained from Carlo Erba Reagents. Dry nipa palm husks were separated from shells, ground using blender and handheld grinder, and then sieved to obtain coarse powdered nipa palm husk (abbreviated as NPH).

2.2. Hydrothermal process
20g of NPH was loaded with 40ml of deionized water into Teflon vessel. Pack the closed vessel into stainless steel reactor and put in oven at 180°C for 8 hours under self-generated pressure. After finishing the hydrothermal process, the reactor was rapidly cooled down to halt the reaction using water. Hydrochar was removed from vessel and then was dried in oven at 90°C for 24 hours.

2.3. Activation using physical mixing
Pelletized KOH was ground and mixed with dried hydrochar with weight ratios between KOH and hydrochar as 1:1, 1:2 and 1:3, respectively. (4g of hydrochar was used. 4g, 2g and 1.33g of KOH were used.) Mixing was carried out for at least 15 minutes. Finally, the mixture was dried in oven at 90°C.

2.4. Carbonization
Dried activated mixture was loaded in a ceramic boat and inserted into horizontal tube furnace. Carbonization was done at 900°C for 2 hours, with heating rate of 10°C/min under continuous nitrogen gas atmosphere. (flow rate 100m³/min) The resulting carbon material was washed with deionized water to neutralize pH and was dried in oven at 90°C for 90 minutes so it completely dried. Prepared samples were denoted as HTC180-08-X:Y while X:Y is each physical mixing ratio.

2.5. Characterization
Morphology of prepared porous carbon were investigated using scanning electron microscope (Zeiss EVO MA10). Gold sputtering was done to enable conductive surface operation. 10kV electron acceleration voltage was used and magnification scale is 1000x. Fourier transform infrared spectroscopy technique (Perkin Elmer Spectrum Two) was used to observe surface chemical properties. Scanning wavenumber range is 4000-400cm⁻¹ in ART mode. FT-IR spectra was reported as %T.

X-ray diffraction technique (SmartLab Rigaku) was used for investigating carbon formation in prepared carbon materials. CuKα was used as an x-ray source, theta-2-theta mode was used for every measurement and scanning angle range was 20-90°.
3. Results and discussion

3.1. Morphology of prepared porous carbon from nipa palm husks

![SEM images of (a) raw nipa palm husk powder, (b) HTC180-08-1:1, (c) HTC180-08-1:2 and (d) HTC180-08-1:3.](image)

Figure 1. SEM images of (a) raw nipa palm husk powder, (b) HTC180-08-1:1, (c) HTC180-08-1:2 and (d) HTC180-08-1:3.

SEM images show the significant effect of activating agent which initiate alternations of physical structures in hydrochar prepared from nipa palm husk powder. When compares morphology image of raw nipa palm husk powder in Figure 1 (a) to the others, pore distribution increases as physical mixing ratio is higher. Pores development in HTC180-08-1:1 in Figure 1 (b) which is the highest KOH physical mixing concentration, shows larger pores with estimated size of 5-10μm, surrounded by dispersed smaller pores. Less significant pore structures can be found in HTC180-08-1:2 in Figure 1 (c), as activation concentration is lower than aforementioned sample. And in HTC-180-08-1:3 in Figure 1 (d) barely yields pore development but structures are mildly altered due to hydrothermal treatment.

3.2. Surface chemical properties of prepared porous carbon from nipa palm husks

Fourier transform infrared spectroscopy was used to observe effects of hydrothermal carbonization and chemical activation towards surface chemical behaviors and checkup for activating agent residue.
According to FT-IR spectra of prepared porous carbon materials illustrated in Figure 2, shows that hydrothermal carbonization helps in restructuring chemical components in nipa palm husk powder by getting rid of organic compounds consist of hydroxyl group at wavenumber of around 2920cm⁻¹, alkyl group at around 1440cm⁻¹ and ester/ether group at around 1050cm⁻¹. Moreover, carbonyl group at around 1700cm⁻¹ and aromatic C-H bonding at 680cm⁻¹ are raised as well. From these transmittance peaks changes from plenty of functional groups in NPH in Figure 2 (a) to carbon materials in Figure 2 (b-d), can be summed up that aromatic structures are promoted during hydrothermal carbonization with KOH physical mixing, whereas other functional groups in biomass complex structures are almost completely transformed, these affect to enhancing in carbon content of the materials.

3.3. Crystallinity of prepared porous carbon from nipa palm husks

X-ray diffraction technique was used to ensure carbon structures in prepared porous carbon materials and diffractograms are shown in Figure 3. By comparing raw NPH to carbon materials prepared at different mixing ratios. There are new diffraction peaks appeared in carbon materials. Peaks at 2-theta
of 26° and 43° indicate carbon material’s (002) and (101) planar structures, respectively. Smaller peak near 2θ of 30° shows graphitic structure.

From the diffractograms, can be clearly pointed out that hydrothermal carbonization and chemical activation also induct carbon restructure. Restructuring occurs by fragmenting organic polymers in biomass by hydrolysis and decarboxylation.[11] During hydrothermal treatment, fragmentation and reconstruction occurs simultaneously, results in increased orderly structures.[12] Moreover, orderly structures tend to be appeared at less severe conditions as in HTC180-08-1:2 and 1:3 has higher intensity at graphite peak than in 1:1.

4. Conclusions
By combining hydrothermal carbonization method with physical mixing-based chemical activation, highly porous carbon material can be prepared using less energy and activation cost. Physical mixing concentration ratio plays a crucial role in pore development both physical and chemical ways. As shown in results, porosity is significantly increased along with higher concentration. For surface chemical aspect, changing activation concentration doesn’t alter chemical properties in carbon materials. That means any concentrations can offer satisfied chemical structure transformation. Crystallinity is affected by severity of hydrothermal and activation conditions; milder conditions yields more orderly-constructed carbon structure than in severer ones. From all of these, can be clearly summed up that using a moderate temperature and balanced chemical activation factors are preferred choice to synthesize highly porous carbon materials from biomasses. And exactly, further studies on the most suitable concentrations on each type of biomasses may be required to achieve the most satisfied results.

5. References
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