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Analysis of Hydrothermal Carbonization Temperature on The Quality Standard of Activated Carbon from Rice Husk as Porous Materials

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Abstract. Rice husks were a significant component of side product agriculture in the rice milling process. It is a classic environmental problem as a source of agricultural waste. To utilize cellulose as a major component in rice husk, there has been substantial study undertaken on the preparation of activated carbon as porous materials. Studies of porous activated carbon (PAC) show the importance of the application of porous materials such as adsorbents to remove environmental pollutants. This present research aimed to inquire the effect of carbonization temperature (600, 700, 800, and 900ºC) with HCl as chemical activated solution. The PAC products were analyzed with the quality standard base on the national standard of Indonesia by number SNI 06-3730-1995. Analyzing the standard parameters of PAC were moisture content, ash content, volatile matter, fixed carbon, and the amount of iodine absorption capacity have been studied. The PAC products were characterized with FTIR and BET surface area analyzed to evaluate the porous of PAC. Returning to the initial inquiry of this investigation, it is now possible to state that carbonization temperature is at 700ºC. The higher specific surface area (504,03 cm^2/g), pore volume (0,258 nm), and micropore diameter (0,896 nm) have been analyzed by multipoint BET method. Based on quality standards analyzed, the moisture content (0,67%) and volatile matter (15,71%) to related for activated carbon from rice husk. A number of feasible future studies of activated carbon from the natural source using the same experimental setup are evident.

INTRODUCTION

Utilize of rice husk as a natural carbon source has contributed to the decline in agricultural waste. Rice husk is one of the side products of rice milling process. According to South Sulawesi BPS data, the rice production in 2021 approximately have contribute1,03 million tons of rice husk [1]. In recent years, rice husk has been renewed research in the development of a side product agricultural. Therefore, the component of rice husk that has been reported that the carbon major content source 32% cellulose, 21% hemicellulose, 22% lignin, and 15% ash. Activated carbon can be produced from rice husk because of it is the potential content [2]. To exploit the potential resource of rice husk in Indonesia, the used of activated carbon from natural and biodegradable source is important and low-cost investment for a wide range of scientific and technology process.

The concept of activated carbon and porous material are related to increase the function of the highest adsorption capacity. Studies on porous activated material such as porous silica, porous carbon, and nanoparticle represent a growing field [3], [4]. Determining the impact of porous specification on adsorption capacity is important for the study of PAC. The effect of process variable, such as temperature, surfactant template, and the timing process are a common condition which has considerable impact on properties of porous materials [5], [6].

Several a number methods have been attempted to prepare activated carbon. Previous studies have explored the physical and the chemical activation method. Activated carbon has been prepared by microwave power 350 W by physical method and direct prepare in phosphoric acid chemical solution [7]. Data from several sources have obtained the effect of the activating agents in the chemical method. Another important finding is that the activating agent varies can be depicted by the physical characteristic of activated carbon [8]. It is probable therefore that the preparation activated carbon by combined physical and chemical method. The carbonization temperature is operate 450-850°C, requires short time, well-controlled porosity, to produces of activated carbon with a high specific surface area [9], [10]. More recently, there have been a growing number of publications focusing on activated carbon from corn shell with $ZnCl_2$-HCl chemical activator agent at 850ºC. The high surface area of BET method of activated carbon sample was established 1779 m^2/g [11].

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Many natural resources have been suggested to obtain activated carbon as porous materials. Pomegranate fruit peel was to prepare activated carbon using KOH and CO_2 as activator agent. The high surface area of the carbon products are 845,96 m^2/g with preparation gasification methods. The fixed carbon content has been increased to 75,24% and volatile matter 17,6% [12]. Thus far, a number of studies have confirmed the effectiveness of waste coffee as carbon source. Some activator agents were used to compare the properties of activated carbon product, such as base and acid chemical solution[8]. Study of porous activated carbon show the important of material science. This research provides the first extensive examination of rice husk as economic natural source for porous activated carbon materials.

The aim of this research is to critically analyze the effect of carbonization temperature and compare the H_3PO_4 than HCl as chemical activator agent. The product of activated carbon (AC) was analyzed of quality standard base on the national standard of Indonesia (SNI 06-3730-1995) and characterized the spectra by FTIR spectroscopy and properties of porous materials.

METHODOLOGY OF RESEARCH

In most recent study, quality standard analysis of activated carbon as porous materials have been measured in two investigation, it is proximate analysis and characterization of functional groups and physisorption analysis. The natural resource of rice husk was got from the accumulated waste of the Maros district milling process in Indonesia. All chemical reagents to prepare activated carbon such as NaOH (natrium hydroxide, Merck) and HCl (cloride acid, Merck) were used without purification process. The other chemical reagents for preparing of analysis quality standard of activated carbon were gained from J.T Baker

Preparation of activated carbon

Rice husks were collected from rice mill in Maros district, South Sulawesi. Rice husks were washed to remove the useless component and dried with radiation of the sun to release the free water in rice husk surface. For the first step to prepare activated carbon, the dry rice husk was burned in the rotary cylinder with radiation of fire gas until the carbon black product was obtained. The next steps were the carbonization process in the furnace at the temperature variable (600, 700, 800, and 900°C). The carbonization process occurred for 4 hours in a stainless-steel vessel with anaerob condition of carbon sample. The carbon black product was crushed and sieved it with a particle size distribution of 250 μm.

To activate the carbon black was used by chemical solution as activation agent. Before the activation process, 200 mL of NaOH 10% chemical solution was added into 10 g of carbon black, then heated and stirred with together at 70°C for 60 minutes. The following step, it cooled and separated with a centrifuge tube. The sediment residue was rinsed with hot distilled water until neutral (pH = 7) then it dried in an oven at 105°C. For activation process, 10 g of carbon black free contaminant was mixed with 200 mL of activation reagent (HCl) as chemical activation method and soaked it for 24 hours at room temperature. To finish step, the activated carbon sample was washed with hot distilled water until neutral (pH 7), and dried it with oven instrument to release the wash water at 110°C until the weigh in constant condition

Analysis of quality standard

The qualitative standard analysis of activated carbon (AC) sample based on SNI 06-3730-1995, this test is widely available and has been used in many investigational studies. There are five parameters to evaluate the properties of AC sample

Adsorption capacity of iodine

Activated carbon sample has the adsorption capacity of iodine. Base on SNI 06-3730-1995, the minimum standard of adsorption capacity of I_2 is 750 mg/g. To estimate the adsorption capacity of I_2, amount 0.5 g of activated carbon was added into 25 mL of 0.1 N iodine solution. The solution was shaken for 15 minutes and filtered. 10 mL of the clear filtrate was titrated with 1 N concentration of $Na_2S_2O_3$. Adsorption capacity of iodine (mg/g) is determined by the equation 1.

$$\mathbf{I_2}\left(\frac{\mathbf{mg}}{\mathbf{g}}\right) = \frac{\left(\mathbf{10} - \frac{\mathbf{V*N}}{\mathbf{0.1}}\right)}{\mathbf{W}} \times \mathbf{12.69} \times \mathbf{5} \quad (1)$$

where are
V : Volume of sodium thiosulphate (mL)
N : Normality concentration of sodium thiosulphate
12,69 : the amount of iodine corresponds to one ml of 0.1 N sodium thiosulphate solution
W : sample weight (g)

Moisture content

The moisture content is the number of water component in the activated carbon material. To calculate the moisture content, one gram of activated carbon sample was heated at 115°C for 3 hours. For heating and cooling processing of sample was repeatedly until the find constant weight. The moisture content was calculated by equation 2

$$\mathbf{M} = \frac{\mathbf{I-D}}{\mathbf{I}}\mathbf{x\ 100\%} \quad (2)$$

where are
M : moisture content (%)
I : initial weight of sample (g)
D : constant weight of dry sample (g)

Ash content

Ash content of the material is the inorganic component non-combustion when the material was burn. The maximal standard quality of ash content for activated carbon sample base on SNI 06-3730-1995 are 2,5%. To prepare the ash content of activated carbon, the amount 2-3 gram of sample was burned at 900°C for 2 hours. The residual was represented the ash content of activated carbon sample. Ash content was calculated by equation 3.

$$\mathbf{Ash\ content} = \frac{\mathbf{A}}{\mathbf{W}}\mathbf{x\ 100\%} \quad (3)$$

where are
A : weight of ash (g)
W : weight of sample (g)

Volatile matter

The volatile matter content is the fixed organic component in material that the component will volatilize for the firing process without air at 950°C. The maximum percentage of volatile matter content of activated carbon is 15%. To quantify the volatile matter content, the sample was counted about one gram in porcelain cup. Burn on the furnace at 950°C for 5 minutes, cool in the desiccator, and scale using an analytical balance instrument. The process was repeated until the constant weight. Volatile matter content was calculated by equation 4.

$$\mathbf{V_m} = \frac{(\mathbf{W_1 - W_2})}{\mathbf{W_1}}\ \mathbf{X\ 100\%} \quad (4)$$

Where are
V_m : volatile matter (%)
W_1 : initial weight of activated carbon (g)
W_2 : weight of dried activated carbon (g)

Fixed carbon

Fixed carbon is the solid product of residual combustion after removing volatile matter and ash content. To find out the fixed carbon content is the remain composition after reduce volatile matter and ash content. The minimal standard content of fixed carbon is 65%.

$$\mathbf{FC} = \mathbf{100} - (\%\mathbf{A} + \%\mathbf{Vm}) \quad (5)$$

Where are
FC : fixed carbon (%)
A : ash content (%)
Vm : volatile matter (%)

Characterization of Activated Carbon

All of the activated carbon sample were characterized to determine the physicochemical properties. The type of 8400S Shimadzu FTIR instrument were conducted to quantify the functional group and spectra of chemical bond. Following the physisorption analysis data were decided the surface area using multipoint BET method, pore diameter, and pore volume of porous activated carbon. The parameter instrument Quanta Chrome Nova touch 4LX was used nitrogen adsorbate model and bath temperature condition at -195,8ºC.

RESULTS AND DISCUSSION

The first set of questions aimed to assess the effect of carbonization temperature for preparing the porous activated carbon from rise husk as economic natural resource. To evaluate the quality standard of AC sample, the parameters analysis base on SNI 06-3730-1995 questionnaire was used.

TABLE 1. Quality standard analysis of activated carbon

Sample		Moisture content (%)	Ash content (%)	Volatile matter (%)	Fixed carbon (%)	Adsorption capacity of iodine (mg/g)
Chemical activator	Temp variable (ºC)					
HCl	600	3,48	13,29	21,40	65,31	691,25
	700	2,53	12,40	18,55	69,05	618,88
	800	0,67	19,63	16,51	63,86	546,88
	900	0,78	29,41	15,71	54,88	468,75
SNI 06-3730-1995		max. 15	max. 10	max. 25	min. 65	min. 750

Determining the amount adsorption capacity of iodine for AC samples is one of the most common quality standards of porous materials. Investigating the adsorption capacity is a continuing concern of the iodine number. Further analysis shows that iodine number can be related to the properties of the porosity AC materials [13], [14]. According to this research, the highest iodine number occurs at a carbonization temperature of 600°C which was 691.25 mg/g, although it was not in accordance with the SNI standard where the minimum level of iodine number was 750 mg/g. Based on TABLE 1, the iodine numbers of AC samples are decrease if the carbonization temperatures are increased. Carbonization temperature that is too high can cause damage to the pore structure, pore size widening occurs, so that the iodine number decreases.

The carbonization method performs an important role in the fabrication of porous activated carbon material, especially the carbonization temperature variable. Because, it has a significant effect on the porous activated carbon produced. The carbonization methods were used the high temperatures, it is possible thar these results may have been skewed by high levels of ash content and the fixed carbon, but the volatile matter standard was decreased [15]. There is a strong possibility that the condition will improve in the long term. The product of PAC structure also depends on the activating agent. The HCl activating agent can be a role in dehydrating the remaining materials, such as OH and CO, from the carbonization process.

The moisture content confirms the amount of water component in the PAC materials. According to TABLE 1, the moisture content was decreases if the high carbonization temperature. This finding is consistent with the SNI standard 06-3730-1995, which specifies a maximum water content of 15%. High temperatures during the carbonization process reduce moisture content and have an impact on the stability of the organic molecules in the PAC materials.

Referring to SNI standard 06-3730-1995**,** the maximum volatile matter content of activated carbon is 25%. In TABLE 1, the impact of the carbonization temperature process on the PAC product from the rise husk was at the point of maximal content. Overall, these studies indicate that volatile matter content are often important predictors of PAC materials. The highest carbonization temperature process can be caused to decrease the amount of volatile matter [16].

Volatile matter content was released at high temperatures. In the research decreased significantly from 21.40% to 15.71%. This happens because at high temperatures, volatile substances dehydrated and devolatilized. Degradation of lignocellulosic tissue will release volatile substances in the form of condensable and non-condensable gases.

Fixed carbon content indicates the amount of pure carbon contained in activated carbon. Generally high fixed carbon content and low ash content must be owned by a good precursor material. The TABLE 1 show, fixed carbon content for the highest temperature of carbonization process at 900ºC for this research did not conform with SNI standards. The fixed carbon content obtained less than 65%. Carbonization process at the temperature 600-800°C has produced a fixed carbon content conform to SNI standard. At the high temperatures, the structure of carbon can be damaged so that the fixed carbon content decreases. The high concentration of activator can also damage the micropores on the carbon surface, thereby reducing the fixed carbon content.

Study of The Characteristic Activated Carbon

To determine the spectra of functional groups in activated carbon, an analysis was carried out using FTIR. The correlation between the effect of carbonization temperature and the component involved in activated carbon product was tested using the FTIR spectra of OH, C=O, and C-H functional group.

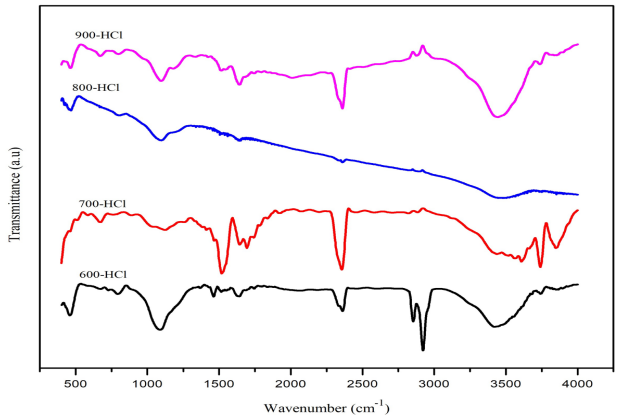

FIGURE 1. FTIR spectra of porous activated carbon with HCl activator

Figure 1 present the wavenumber obtained from the peak of functional groups analysis by the spectra infra-red for the sample with HCl activator agent. In Fig. 1 with HCl activation agent was illustrate of the spectra data of activated carbon with different carbonization temperature. In FTIR data spectra, all activated carbon samples did not show a significant difference.

For the sample with HCl activation agent, the peak of the OH stretching of hydroxyl groups was found on the band at 3441 cm^{-1}, weak absorption at 3435 cm^{-1}, 3439 cm^{-1}, and 3443 cm^{-1} for the effect carbonization temperature respectively [17]. As mentioned in the literature research, the functional groups vibration of C=O hydroxyl was indicated at the wavenumber 1693-1639 cm^{-1} [10].

One the question of FTIR spectra data for the sample with H_3PO_4 activation agent, OH stretching of hydroxyl groups was represent on the band at 3435-3423 cm^{-1} for the carbonization temperature at 600, 800, and 900°C. At the temperature 700°C, OH stretching was slightly shifted at the wavenumber 3614 cm^{-1}. The band spectrum peaks at the wavenumber 1122- 1091 cm^{-1} corresponding to Si-O groups. It is mean that the activated carbon sample contained a silica component [5].

TABLE 2. Physisorption data analysis of activated carbon

Sample		S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
Activator agent	**Temp variable (ºC)**			
HCl	600	204,95	0,085	0,824
	700	504,03	0,258	0,896
	800	270,20	0,111	0,826
	900	40,67	0,016	0,832

One of the aims of this study was to analyse the physisorption characteristic of activated carbon samples. This study set out to evaluate the importance of porous properties in the effect of activator agent and carbonization temperature variable.

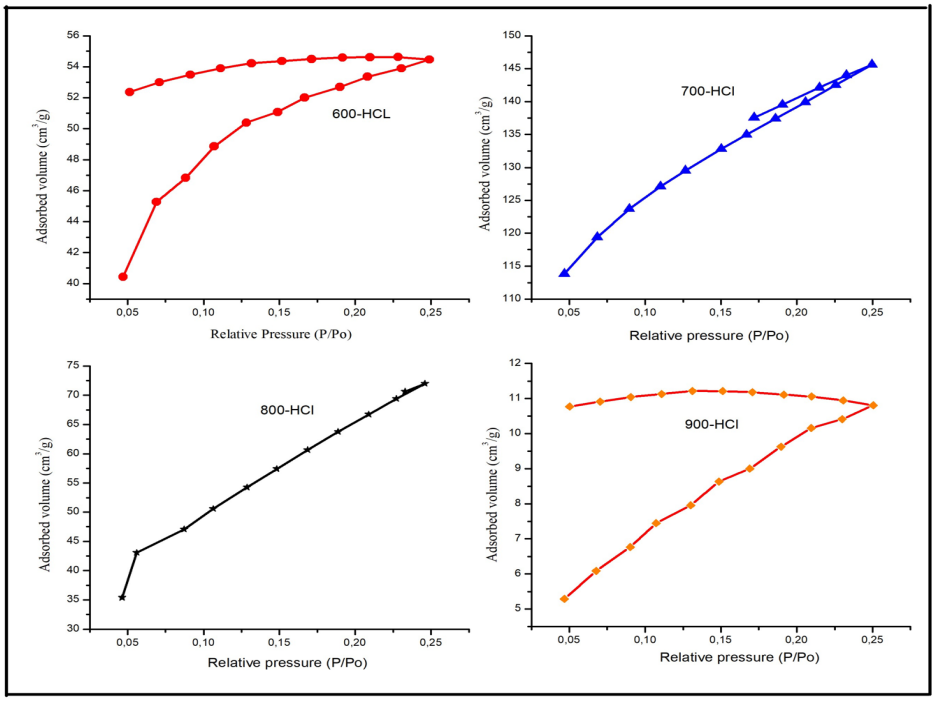

FIG. 2. Physisorption analysis of PAC sampel with HCl activator

TABLE 2 compare the results obtained from the properties analysis of porous activated carbon sample such as surface area by BET method, diameter and volume of the pore sample. This study found that HCl as activator agent have the larger surface area at 700°C the carbonization temperature. But pore diameter and pore volume not significant for the value variable of carbonization temperature. With respect to the first research question, it was found that the pore diameter of PAC sample was not significant with the increased the temperature of carbonization process (stable at 0,8 nm) and the pore volume were 0,02-0,258 cm^3/g. In Fig. 2, these initial results are suggestive of a link between the effect of high temperature carbonization process and physisorption analysis. To produce the PAC materials (high specified surface area, high pore volume and pore diameter), further project are required to develop reliable analytical methods for porous materials from natural source

CONCLUSION

The study also evaluated the impact of carbonization temperature and HCl as an activated chemical reagent on the quality standard of porous activated carbon (PAC) material based on SNI 06-3730-1995. Overall, this study strengthens the idea that carbonization temperature at 700°C has a suitable quality standard for PAC and has conformed to physisorption analysis. This is the first study that has measured high specific surface area (S_{BET} 507 m^2/g), pore diameter (0,896 nm), and high pore volume (0,258 cm^3/g). Future studies should explore the effects of carbonization temperature at the range 400-700°C without a chemical activation agent.

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