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Preparation and Characterization of Activated Carbon From Cacao Shell (*Theobroma cacao L.*)

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Abstract:

The purpose of this experiment was to prepare and characterize activated carbon from cocoa shell (*Theobroms cacao L*). Carbon from cacao shells was prepared by pyrolysis method at 300°C for 1 hour. This carbon was activated by chemical activation process with various activating reagent and concentration. The activated carbon was characterized using Indonesian Industry Standard (SII No. 0258-88), that is maximum water content of 15%, maximum vapor content of 25%, maximum ash content of 10% and bounded carbon content at least 65%. The results showed that the highest bounded carbon content obtained from pyrolysis was 74.5%. The best activating reagent was HCl with concentration of 4N that improved the bounded carbon to 91,78%. The water content, ash content, and vapor content of activated carbon was obtained as follows, 1,59%, 0,0598%,and 8,33%. Based on this results, activated carbon of cacao shell conformed the SII No.0258-88 values and will be applied as a thermoelectric material.

Keywords — **Pyrolysis, cocoa shell, activated carbon, chemical activation, SII No.0258-88**

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I. INTRODUCTION

Along with the growth of large and small industries in Indonesia, the need for activated carbon was increasing. At present, activated carbon was still imported from various countries in order for life necessities. Activated carbon can be used as an ingredient in deodorizers (deodorizing), fuel, filters, energy producers (batteries, solar panels), fine arts media, fillers and dyes [1] and as a material for thermoelectric [2]. Activated carbon can be produced from agricultural waste such as fruit peels, bark, shell, husk and others [3]. Journals that have discussed the use of activated carbon are: coconut (*Cocos mucifera*) [4], cocoa shell and seriguela seeds [5], kapok banana peel [6]. One of the wastes produced from the cocoa fruit industry in Indonesia was cocoa shells. Cocoa shells produces about 70% of wet weight waste from one kilogram of cocoa fruit. Generally, cocoa shells contains very high lignin around 14-28%, cellulose 19.7-26.1%, hemicellulose 8.7-12.8% which can be made carbon after the pyrolysis (carbonization) process [7].

Making activated carbon can be done in two stages. The first stage was carbonization of raw materials by pyrolysis to produce carbon. The second stage was activated process to remove hydrocarbons that line the carbon surface so as to increase carbon porosity [8]. Carbonization wass an imperfect combustion process of organic matter

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which composes the structure of the material in the form of cellulose, hemicellulose and lignin with a limited amount of oxygen that produces carbon [9]. Activated carbon was a solid containing 85-95% carbon produced from carbon-containing materials by heating at high temperatures [10]). Activated carbon was shaped like amorphous which has a large surface area and porous volume [11]. The amount of activated carbon produced was determined by the initial composition of biomass, the more volatile substances the more active carbon was produced because many parts are released into the air. Activated of forming and composing carbon so that the pores become larger and remove impurities in the pores of the activated carbon by breaking the hydrocarbon bonds. Carbon activation can be done in two ways, namely physical activation and chemical activation. On physics activation, carbon was activated at temperatures between 800°C - 1000°C by using steam or gas such as water vapor. In chemical activation, carbon was activated through a process of soaking with chemicals before being heated. Chemicals that can be used are H_3PO_4, NH_4Cl, $AlCl_3$, HNO_3, KOH, NaOH, $KMnO_4$, SO_3, H_2SO_4, K_2S and HCl [8],[12]. Actived carbon quality requirements according to Indonesian Industry Standards (SII No. 0258-88) can be seen in table 1 [1].

TABLE 1.
ACTIVE CARBON QUALITY REQUIREMENTS INDONESIA (SII NO.0258-88)

Test type	Requirements	
	Granules	Solids
Water content	Max. 4,4%	Max. 15%
Subtances Evaporates	Max. 15%	Max. 25%
Ash content	Max. 2,5%	Max.10%
Fixed Carbon	Min. 80%	Min. 65%

The purpose of this research is to utilize alternative raw materials, determine the activation temperature, determine the activating reagents and the concentration of the best activator to obtain high-quality, environmentally friendly activated carbon.

II. RESEARCH METHOD

A. *Preparation of Activated Carbon from Cocoa Shell*

Cocoa shell were obtained in the Biaro area, Ampek Angkek District. Cocoa shell was dried to dry in sunlight to reduce their water content to produce good activated carbon.

B. *Carbonization and Activation of Cocoa Shell*

The carbonization stage, cacao shells was weighed 500 grams, the pyrolysis process was carried out in the furnace at temperatures of 250^0C, 300^0C and 400^0C for 1 hour. The cacao shell of the carbonization stage was smoothed using mortar and pestle, then filtered using a 150 µm sieve.

The Activation was done by soaking 6 grams of carbon of cacao shells into 25 mL of different activator reagents (HCl, $ZnCl_2$ and KOH) with concentration of 4 N for 24 hours. Then these activated carbon were filtered using whatmann filtered paper and washed with aquades until neutral condition obtained, then heated at 110^oC for 2 hours. The optimized activated carbon reagent was obtained by applying Indonesian National Standard measurement, SII No.0258-88 (water content, ash content, vapor content and bounded carbon). Then variations in concentration of optimized activated carbon reagent were carried out from 2 N, 4 N, and 6 N to produce optimized activated carbon.

C. *Characterization Of Activated Carbon*

The activated carbon obtained is tested with the following parameters:

a. *Water Content Analysis*

The activated carbon was weighed 1 gram and put into a dried crucible porcelain, then was heated in the oven at 105°C for 1 hour. The activated carbon was then cooled in the desiccator and weighed.Water content can be calculated by the following equation:

Water content = **Error! Reference source not found.** x 100%

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Where:
a = initial activated charcoal weight (gram)
b = weight of activated charcoal after drying (gram)

b. Ash Content Analysis

The Activated carbon was weighed 1 gram and put into dried crucible porcelain, Then it was tarnished into furnace and heated slowly until ashes appeared. The flame of furnace was enlarged up to 800^0C and kept it at that temperature for 2 hours. When all the carbon has been changed to ashes, cool it in a desiccator and then weighed to obtain permanent weight. Ash content can be calculated by the following equation:

Ash content = **Error! Reference source not found.**eight ash / weight ash sample × 100%

c. Vapor Content Analysis

The activated carbon was weighed 1 gram and put into a dried crucible porcelain, then was heated up to 310°C and then turn off the furnace. After the temperature of the furnace reached below 100°C, the activated carbon was removed and then put in to desiccator and cooled. Vapor content can be calculated by the following equation:

Vapor Content = **Error! Reference source not found.** x 100%

Where:
a = initial activated carbon weight (gram)
b = activated charcoal weight after heating (gram)

d. Bound Carbon Content Analysis

The bounded carbon content of activated carbon was obtained from the results of the reduction of parts lost on heating 310^0C (vapor content) and ash content.

Pure activated carbon = 100% - (A + B)

Where:
A = ash content (%)
B = vapour content (%)

III. RESULTS AND DISCUSSION

A. Preparation of Activated Carbon from Cocoa Shell

The preparation of activated carbon from cacao shells carried out through two stages: carbonization and activation stage. Sample preparation was the first action to carry out this research. The shell of cacao (*Theobroma cacao L)* which has been collected, diced and then cleaned from dirt with water. After washing, the sample from the cocoa shells was dried under the sun for 1 week before taken into pyrolyzed process. The aimed was to reduce the water content of the cocoa shells and was to reduce smoke during the pyrolysis process. The carbonization process was an incomplete combustion process of cacao shells into carbon that was pyrolyzed at temperatures of 250°C, 300°C, and 400°C for 1 hour and several tests are carried out, namely: water content, ash content , vapor content and are bound carbon.

B. Carbonization and Activation of Cocoa Shell

a. Temperature Variation

The carbonization stage was a change in the cacao shells into carbon. Cacao shell samples were pyrolyzed at temperatures of 250^0C (CA), 300^0C (CB) and 400^0C (CC) for 1 hour and were tested: water content, ash content, vapor content and bound carbon content. CA was symbolized for cacao shell carbon by pyrolysis process at 250^0C for 1 hour. And CB was symbolized for cacao shell carbon by pyrolysis process at 300^0C for 1 hour, and CC was symbolized for cacao shell carbon by pyrolysis process at 400^0C for 1 hour.

1. Water Content Analysis

Water content analysis was carried out to determine the content of water remaining in carbon after going through the carbonization process.

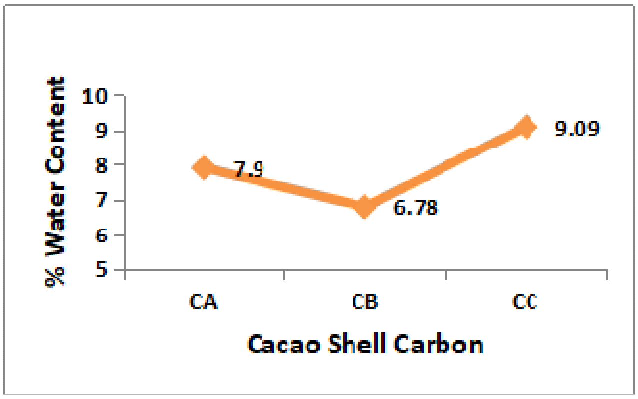

Fig 3. 1 Water content analysis of carbon from pyrolysis process of cacao shells for 1 hour

Fig 3.1 showed the water content analysis of carbon from pyrolysis process at three different temperature for 1 hour. Higher the pyrolysis temperature, the greater water content obtained for cacao shell carbon. At temperture of 300⁰C the water content was found at 6.78% and at 250⁰C, 350⁰C was 7,9 and 9,09%. Several factors can affect the water content of carbon, was; pyrolysis temperature and time and storage conditions where humid conditions can cause absorption of surrounding water vapor.

2. ***Ash Content Analysis***

The ash content analysis aimed to determine the metal oxide content which was still present in the carbon.

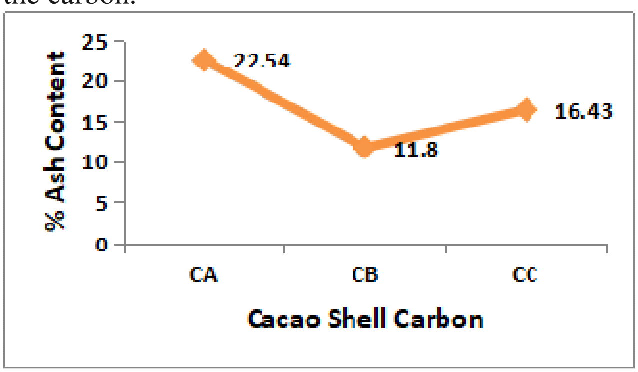

Fig 3. 2 Ash content analysis of carbon from pyrolysis process of Cacao Shell at 800 C for 2 hours

Fig 3.2 showed the ash content analysis of carbon from pyrolysis process at three different temperature for 2 hour. Higher the pyrolysis temperature, the greater ash content obtained for cacao shell carbon. At temperture of 250⁰C the ash content was found at 22,54%, at 400⁰C was 16.4% and at 300⁰C was 11,8%. ash content was related to the formation of mineral salts and other particles due to carbon oxidation during pyrolysis [3] and the silicate content of 0.47% in cocoa skin which can increase ash content [13].

3. ***Vapor Content Analysis***

Vapor content analysis aimed to determine the amount of substances or compounds that have not evaporated in the carbonization process.

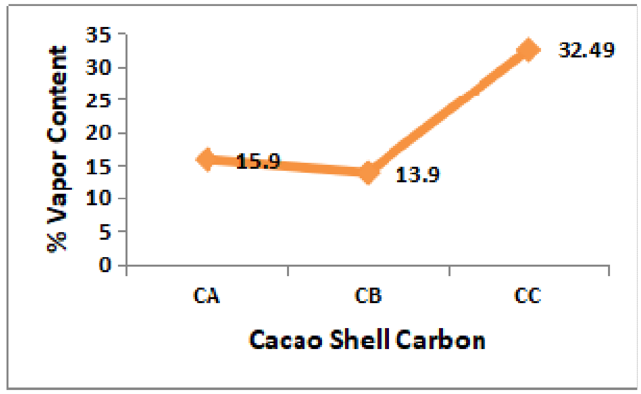

Fig 3. 3 Vapor content analysis of carbon from pyrolysis process of cacao shells

Fig 3.3 showed the vapor content analysis of carbon from pyrolysis process at three different temperature. Higher the pyrolysis temperature, the greater vapor content obtained for cacao shell carbon. At temperture of 250⁰C the vapor content was found at 15.9%, at 400⁰C was 32,49% and at 300⁰C was 13,9%. Temperature of 300°C decreases steam because most volatile compounds are released or wasted so that they have an impact on decreasing steam content.

4. ***Bounded Carbon Content Analysis***

Bounded carbon content analysis aimed to determine the carbon content after carbonization process.

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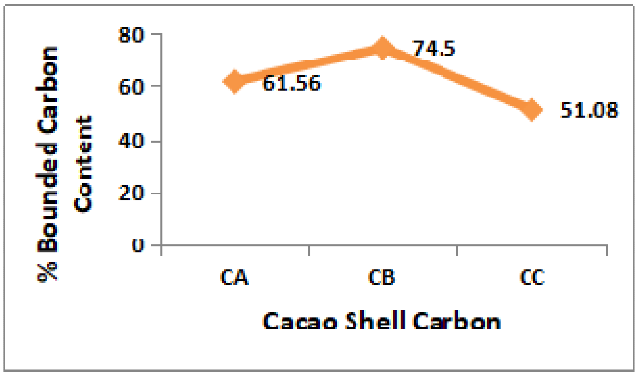

Fig 3. 4 Bounded carbon content analysis of carbon from pyrolysis process of cacao shell

Fig 3.4 showed the bounded carbon content analysis of carbon from pyrolysis process at three different temperature. Higher the pyrolysis temperature, the greater bounded carbon content obtained for cacap shell carbon. At temperture of 250^0C the bounded carbon content was found at 61,56 % , at 400^0C was 51,08% and at 300^0C was 74,5%. Bounded carbon was obtained from 100% reduced by ash content, steam content. The higher the carbon bound that is produced the better the carbon is obtained. Generally, cocoa skin is a material of low density which requires a faster time in the process of drying.

b. Variation of Reagents

From the process pyrolysis, obtained the best carbon from cacao shell at 300^0C was obtained. After that, carbon from cacao shell was activated by various activated reagent.

The activation stage was a change in carbon into activated carbon. Cacao shell samples were activated reagent at HCl, $ZnCl_2$ and KOH for 24 hours with 4N concentrations and were tested: water content, ash content, vapor content and bound carbon content.

1. ***Water Content Analysis***

Water content analysis was carried out to determine the content of water remaining in activated carbon after going through the activation process .

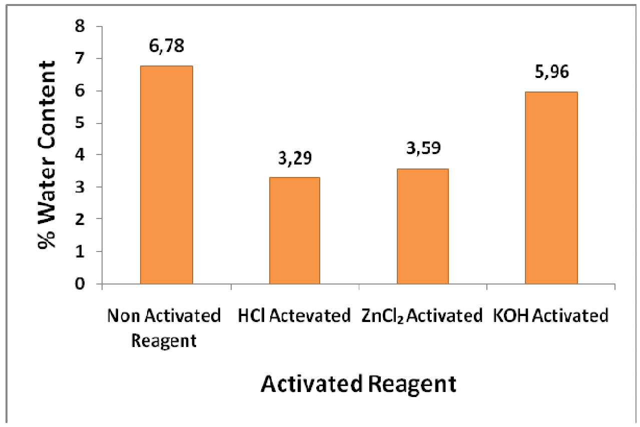

Fig 3. 5 Water content analysis of cacao shell CB at various activated reagent at 4N concentration

Fig 3.5 showed the water content analysis of activated carbon from various activated reagents at 4N concentration with HCl, $ZnCl_2$ and KOH. At activated reagent of HCl the water content was found at 3,29% and at non activated carbon was 6,78%. The Water content of activated carbon according to SII No.0258-88 which is lower than 15%.

2. ***Ash Content Analysis***

The ash content analysis aimed to determine the metal oxide content which is still present in the cacao shell activated carbon after going through the carbonization process and activation.

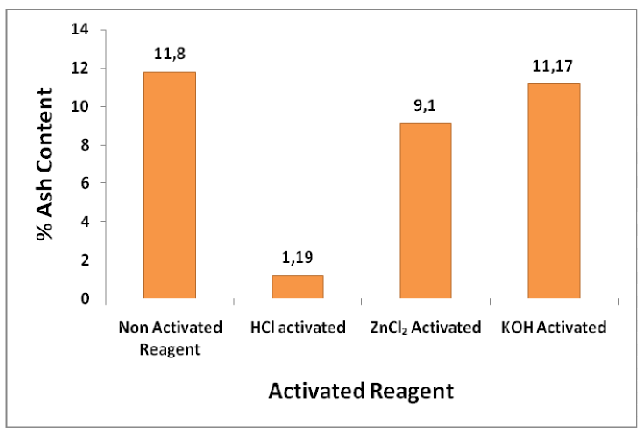

Fig 3. 6 Ash content analysis reagen of cacao shell CB at various activated reagent at 4N concentration

Fig 3.6 showed the ash content analysis of activated carbon from various activated reagents at 4N concentration with HCl, $ZnCl_2$ and KOH. At activated reagent of HCl the ash content was found

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at 1,19% and at non activated carbon was 11,8%. The ash content of activated carbon according to SII No.0258-88 which is lower than 10%.

3. ***Vapor Content Analysis***

Vapor content analysis aimed to determine the amount of substances or compounds that have not evaporated in the carbonization and activation process but evaporate at 310 ^{0}C.

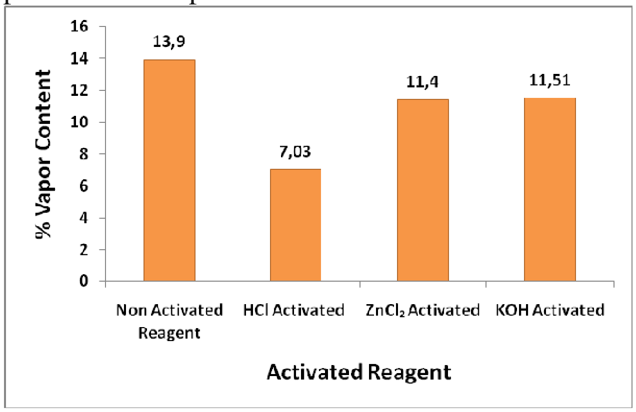

Fig 3. 7 Vapor content analysis of cacao shell CB at various activated reagent at 4N concentration

Fig 3.7 showed the vapor content analysis of activated carbon from various activated reagents at 4N concentration with HCl, $ZnCl_2$ and KOH. At activated reagent of HCl the vapor content was found at 7,03% and at non activated carbon was 13,9%. The ash content of activated carbon according to SII No.0258-88 which is lower than 25%.

4. ***Bounded Carbon Content Analysis***

Bounded carbon content analysis aimed to determine the carbon content after carbonization and activation process.

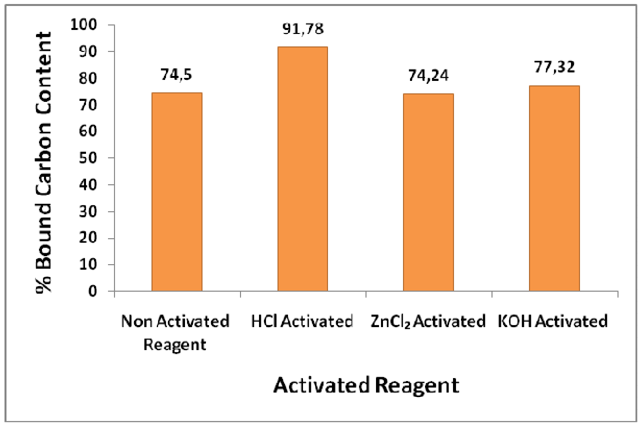

Fig3. 8 Bound carboncontent analysis of cacao shell CB at various activated reagent at 4N concentration

Fig 3.8 showed the bounded carbon content analysis of activated carbon from various activated reagents at 4N concentration with HCl, $ZnCl_2$ and KOH. At activated reagent of HCl the bounded carbon content was found at 91.78% and at non activated carbon was 74,5%. The bounded carbon content of activated carbon carbon according to SII No.0258-88 which is greater than 60%.

c. Variations in Concentration

From the various activated reagent, obtained the best activated reagent from banana peel carbon used H_2SO_4 was obtained. After that, various activated reagent from banana peel was activated by various concentration. HCl activating reagents were varied in concentration, which were 2N, 4N, and 6N.

1. Water Content Analysis

Water content analysis is carried out to determine the content of water remaining in activated carbon after going through the activating process using variations in activator concentration.

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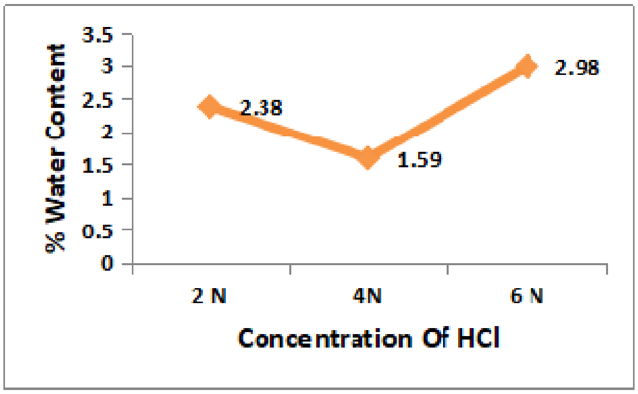


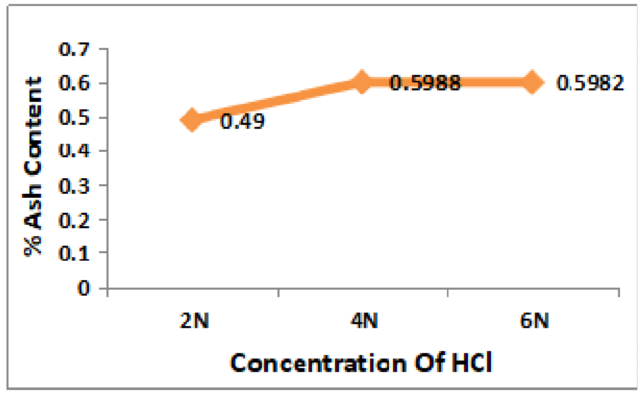
Fig 3. 9 Water content analysis of activated cacao shell CB with HCl at various concentration

Fig 3.9 showed the water content analysis of the activated carbon from various concentration at activated reagent HCl with 2N, 4N and 6N. At various concentration activated carbon HCl 4N the water content was found 1,59% and the activated with HCl 6N is at most 2,98%.The greater the concentration of the activated carbon pores will be greater, but the water content value increases with increasing concentration of activator substances, because too many activator substances from chemical compounds will cause clogged pores in activated carbon causing the characteristics of the activated carbon to increase [13]. Based on SII No. 0258-88 the water content of cacao shell carbon without activation and with activation allowed is a maximum of 15%.

2. *Ash Content Analysis*

The ash content analysis aimed to determine the metal oxide content which is still present in the banana peels activated carbon after going through the variations process in activator concentration.

Fig 3.10 showed the ash content analysis of activated carbon from various concentration at activated reagent HCl with 2N, 4N and 6N. At various concentration activated carbon HCl 4N the ash content was found 0,5988% and the activated with HCl 6N is at most 1,0582%. The greater the concentration of the pores of the activated carbon will be greater, but with increasing concentration of the activator reagent, it can cause clogging of the pores on the carbon and damage. Based on SII No. 0258-88 the ash content of cacao shell carbon without activation and with activation allowed is a maximum of 10%.



Gambar 3. 10 Ash content analysis of activated cacao shell CB with HCl at various concentration

3. *Vapor Content Analysis*

Vapor content analysis aimed to determine the amount of substances or compounds that have not evaporated in the variations process in activator concentration.

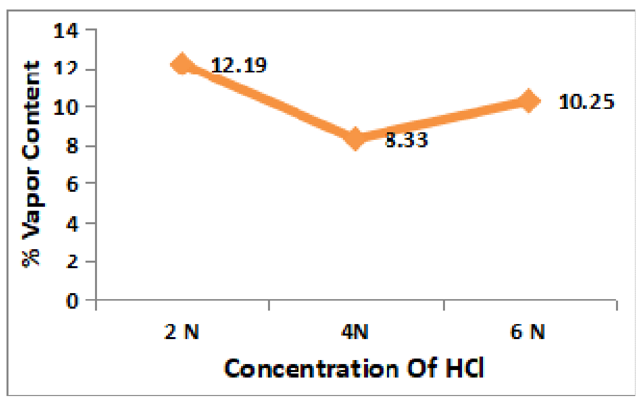


Fig 3. 11 Vapor content analysis of activated cacao shell CB with HCl at various concentration

Fig 3.11 showed the vapor content analysis of activated carbon from various concentration at activated reagent HCl with 2N, 4N and 6N. At various concentration activated carbon HCl 4N the vapor content was found 8,33% and the activated with HCl 2N is at most 12,19% and the activated with HCl 6N is at most 10,25%. The larger the size

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of the activated carbon, the higher the volatile contained in it. Imperfections in the decomposition of non-carbon compounds such as CO_2, CO and H_2 and the length of activation can result in high levels of volatile in activated carbon [1]. Based on SII No. 0258-88 the vapor content of carbon without activation and with activation allowed is a maximum of 25%.

4. Bounded Carbon Content Analysis

Bounded carbon content analysis aimed to determine the bounded carbon content after in the variations process in activator concentration.

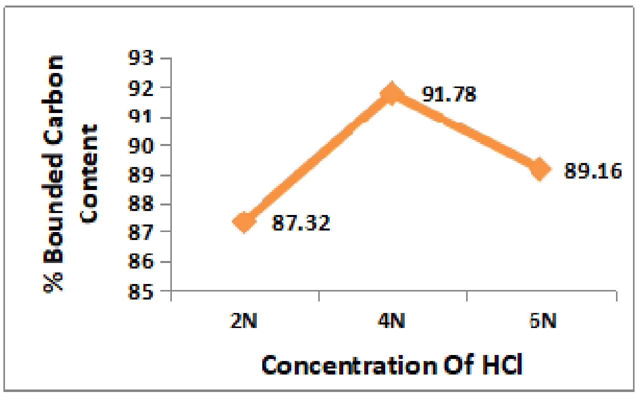

Fig 3. 12 Bound carbon content analysis of activated cacao shell CB with HCl at various concentration

Fig 3.12 showed the bounded carbon content analysis of activated carbon from various concentration at activated reagent HCl with 2N, 4N and 6N. At various concentration activated carbon HCl 4N the bounded carbon content was found 91,78% and the activated with HCL 2N and 6N is at lowest 87,32% and 89,16%. The greater the concentration of the pores of the activated carbon will be greater, but with increasing concentration of the activator reagent, it can cause clogging of the pores on the carbon and damage. Based on SII No. 0258-88 the bounded carbon content of carbon without activation and with activation allowed is a minimum of 65%.

IV. *CONCLUSION*

Activated carbon made by cacao shells apply SII No. 0258-88 quality standards. The optimal temperature for making carbon by pyrolysis process is 300^0C for 1 hour. HCl 4N is better activated reagent with produces 1,59% water content, 0,0589% ash content, 8,22% vapor content and bounded carbon 71,78%.

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