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## Preparation and Characterization of Cacao Waste As Cacao Vinegar And Charcoal

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**Abstract**—Potential waste are still abundant cocoa that has not been widely used by most people, especially farmers who are in the cacao plantations. One way to reduce the building of waste biomass pyrolysis technology which produces smoke that can be inserted into the fluid (liquid smoke and other organic materials) charcoal and some gas (hydrocarbon and methane, H<sub>2</sub>, and CO<sub>2</sub>). The purpose of this research is to produce cacao vinegar, activ carbon and charcoal. The results of this research that the pod husks produce ethanol of benzene of 1: 2 at 12.89%, content of hemicellulose 19,97%, cellulose 21,80% and lignin 47.96%. GC MS analysis for cacao waste Majene produce n -Buthane 8.72%, acetic acid 64.11%, 3.67% cyclopentane, 2 (3H) furanone 2.74%, 1.59% 2 furan methanol, and Mequinol 3.40%. FT-IR analysis for cacao waste Majene district showed that the wave number 1153.43 cm<sup>-1</sup> indicated to dehydration and depolymerization of cellulose and hemicellulose content. Changes aromatic peak at 1737.86 cm<sup>-1</sup> indicates the presence of C-H, lignin. While the wave number 3448.72 cm<sup>-1</sup> indicate the presence of hydroxyl group (O-H) and the absorbance of 717.52 to 617.22 cm<sup>-1</sup> indicates the presence of C = C-H (Aromatic H). XRD analysis results will be obtained the degree of crystallinity charcoal pod husks of 26.60% Waste cocoa with pyrolysis technologies to reduce carbon emissions on the environment in order to be sustainable development and environmental conservation in order to maintain and sustainably.

**Keywords**—Cacao Waste , Pyrolysis , charcoal and cacao vinegar

### INTRODUCTION

The development of the national cocoa plantations have not reached the optimal level, including decreased productivity due to less maintenance cocoa plants and pests, as well as the poor quality cocoa beans that have not been in accordance with the provisions required. The low quality of cocoa beans due to postharvest handling unfinished and most of the cocoa beans produced had not fermented. Biomass pyrolysis is a process in which biomass decomposes at temperature pyrolysis of about 500°C and has short reaction times in the absence of oxygen to produce liquid product with solid chars and gases. Biomass waste content in cellulose, hemicellulose and lignin and the pyrolysis conditions are the primary factors that pyrolysis reactions and resulting products. Pyrolysis compounds undergo decomposition into hemicellulose, cellulose and lignin in the wood that produce cacao vinegar, tar, charcoal and gas. Differences in the composition of the components of the timber is expected to affect the composition and type of compound pyrolysis results. Several typical wood biomass contains 40–50% cellulose, 25–35% hemicellulose and 10–40% lignin [1]. Reaction conditions for pyrolysis are more moderate and simple than in other thermochemical conversion technologies such as gasification and liquefaction. thermo-chemical decomposition behavior was assessed using a thermogravimetric (TGA) system by heating the sample from 50°C to 700°C at the heating rates of 10, 30 and 50 min under nitrogen. Evaluate phenolic compound produced from the catalytic pyrolysis of pine sawdust by commercial catalysis [2]. On pyrolysis of Napier grass stem in a fixed bed reactor with effect of nitrogen flow (20 to 60 mL/min) and reaction temperature (450 to 650° C) were investigated [3]. Pyrolysis of corn stalk a solid heat carrier was research with under temperature from 430 to 620° C. Solid heat carrier used was temperature ash from a CFB Boiler [4].

Observed in this research will use one types of pyrolysis of waste cacao from cacao shell and cacao wood. This paper study is related pyrolysis of deperature with rate reaction. The main objectives this research were (1). Get the yield of cacao vinegar and charcoal cacao in the pyrolysis process, (2) Identification of the fractions of potential chemical components of cacao vinegar and charcoal based on the above, this research is designed to make cacao vinegar through a pyrolysis process to produce a potential chemical components bioactive which product is environmentally friendly.

### EXPERIMENTAL METHODS

#### a. Manufacture of Cacao Vinegar

Samples consisting of cacao waste put into the kiln is made of stainless steel which is equipped with electric heaters, three capacitors and two pumpkins distillate reservoir. Burning carried out at a temperature of 120 - 500°C for 5 hours for each sample. Increase in temperature after no smoke issued again. Cacao vinegar at any combustion temperature taken with two replications, tar separated from the condensate by precipitation for 24 hours. Analysis was conducted on the cacao vinegar and tar yield (% w / w), pH, and acetic acid levels.

#### b. Identification of Chemical Compounds Cacao Vinegar

Chemical compounds of each fraction cacao vinegar temperature in the identification using GC-MS (*Gas Chromatography Mass Spectrometry*). Further chemical constituents were identified by GC-MS technical use BB 5 MS capillary column with a length of 50 m and a diameter of 0.25 mm with injector temperature of 125° C, and the helium carrier gas flow rate of 0.6 mL / min and injection volume of 0.2 mL. GC-MS results of the chemical components of the calculation in the form of cacao vinegar concentration of each fraction. The characteristic of charcoal cacao waste were analyzed. The testing included ultimate analysis, ash ratio, fixed carbon, Fly ratio and composition of the char ash. Also Analysis FT IR, SEM and XRD for active char cacao shell Majene Distric.

### RESULT AND DISCUSSION

Biomass waste raw material analysis showed that The results of this research that the pod husks produce ethanol of benzene of 1: 2 at 12.89%, content of hemicellulose 19,97%, cellulose 21,80% and lignin 47.96%. Pure biomass composition comprising cellulose content of 42%, 31.5% hemicellulose, and lignin 6.5% at 650k pyrolysis temperature, 700 K and 750 K [5]. So the lignin content cacao Wajo district 34,06%, 46,43% holoselulosa levels, 23,75% α cellulose and hemicellulose content of 22,68% [6]. Identification GC-MS results it appears that the content of Cacao vinegar produced as -3,4-diphenylisoxazolin-5-one , Boric Acid , n-Butane, Acetic acid, Ethylic acid, Cyclopentane, Propanoic acid , 2-Pentanone, Methylpyrazin, Cyclopentanone, 2-Methylcyclopentanone, 2-Propanone, 2-Methyl-2-cyclopentenone, ethanone, butyrolactone, 3-Methyl-2-cyclopentenone, 2-Furanmethanol, tetrahydro-, 2-Cyclopenten-1-one, 2,3-dimethyl, Mequinol , 4-Hexen-3-one, 4,5-dimethyl-

(CAS). Pyrolysis products Cassava Cassava rhizome and stalk for phenolic compounds, ketones, aldehydes and alcohol to bio oil for example acetaldehyde, acetone, methanol, 2 furan methanal, 2-methoxy phenol, 2,6 dimethoxy phenol syringyl. [7]. The chemical composition of the liquid smoke containing acids, in particular acetic acid is a derivative of a compound of acetyl groups during pyrolysis [8]. According to research by [9]. the chemical composition of pine wood liquid smoke on GGM (Galactoglucomannan) was 6.7% acetic acid, 1-hydroxy 2 - propylene 5.2%, and 2 4-methoxy propyl phenol 3.5% . Compared with the product distribution from 300 C, the relative content of 2 hydroxybenzaldehyde and 2 methoxybenzaldehyde increased [10]. Table 1. Pyrolysis process from cacao shell waste produced compound cacao vinegar by characterization cacao.

Table 1. Pyrolysis process from Compound cacao Vinegar shell

No	Compound cacao Vinegar shell	Concentration (%)
1	4-(3,4 difenil lisoksazolin) 5 on 2	0,44
2	Boric Acid	2,67
3	n Butane	8,72
4	Methyl ester	2,30
5	Methyl siklopentana	3,67
6	Propanoic acid	1,93
7	2-Pentanone,	0,12
8	5 methyl siklopentanon	0,44
9	1 asetiloksi 2 propanon	0,58
10	2-Methylcyclopentanone	1,33
11	1(2 furanil) etanon	0,62
12	2(3H)Furanon	2,74
13	3-Methyl-2-cyclopentenone	0,95
14	Mequinol	3,40
15	4-Hexen-3-one, 4,5-dimethyl- (CAS) 4,5-	0,55

FTIR analysis results for Analysis result FT IR from Cacao shell Majene distric (Figure 1), Shows that the wave number of 1153,43 cm<sup>-1</sup> indicated to dehydration and depolymerization of cellulose and hemicellulose content. Changes aromatic peak at 1531,48 cm<sup>-1</sup> indicates the presence of C-H, lignin. While the wave number 3448,72 cm<sup>-1</sup> indicates the presence of hydroxyl groups (O-H) and the uptake from 717,52 to 663,51 cm<sup>-1</sup> indicates the presence of C = C-H (Aromatic H). indicates the presence of C = C-H (Aromatic H). The results of this study are supported by [11]. That analysis FTIR To Coir pith Black Liquor (CBL) shows 3420 cm<sup>-1</sup> shows OH, absorption 1610 cm<sup>-1</sup> indicate the presence of CH lignin, absorption 1247 cm<sup>-1</sup> indicates the CO group and 586-891 cm<sup>-1</sup> showed the group C = CH (aromatic H).

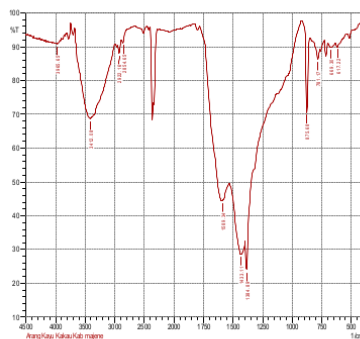
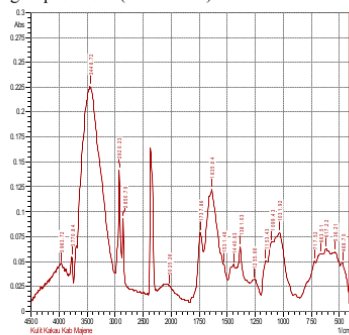


Figure 1 Analysis result FT IR from Cacao shell Majene distric and char wood Cacao Majene distric

The activation process uses heat activator, an increase in the activation temperature of 550-750°C temperature causes the degree of crystallinity of activated charcoal increases. According to the regularity have due to a shift. Using porosity charcoal cocoa leaf Majene district, at the cross-over visually performed using Scanning Electron Microscope (SEM) power 20 kV. Increased temperatures will cause the formation of a new micropores and micro damage grew larger. SEM analysis showed that the structure has a pore natural morphology. POFA have the original cellulose material has pore system interconnect, which relatively very high surface area According to [12]. Show SEM images of the polpar charcoal sintered at 800 C three pore sizes were analyzed 30 to 150 m, 3 to 15 m, and approximately 1,5 m. The first pore originated from the vessel , and the fibers sintered at 800 C, in N2 exhibited pit membranes that were cracked and weakened to form the pit pores [13].

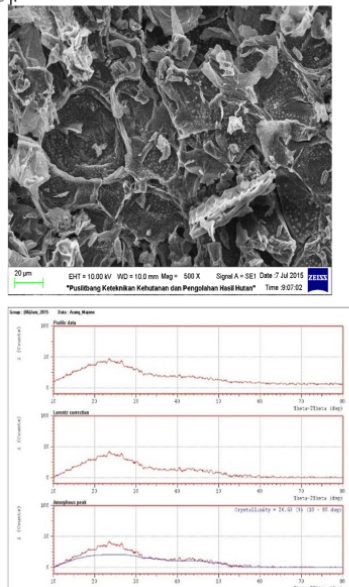


Figure 2 Analysis SEM for shell cacao char Majene distric and analisis X Ray Difrraction (XRD) cacao bean and shell cacao Majene District

Analysis result XRD for shell cacao chars taken from Majene District produced cristalinity degree of 26,60% . Research other [13][14] Analysis result XRD for coconut waste sawit for DS raw material do not give a horizontal line, This is due to the amorphous form, which

is essentially a line approaching the crystalline form. So as to give a diffraction angle 38.5353 and reticular distance 2.71274 with a ratio N cellulose and H cellulose.

### CONCLUSION

Charcoal characteristics resulted of cacao sawdust pyrolysis with electrical reactor indicated that the higher the pyrolysis temperature the lower content of flying matter and the lower of flying matter the higher of the carbon content. Biomass waste raw material analysis showed that The results of this research that the pod husks produce ethanol of benzene of 1: 2 at 12.89%, content of hemicellulose 19,97%, cellulose 21,80% and lignin 47,96%. From result of GC-MS, Compound bioactive for cacao vinegar produced as -Boric acid, n-Butane, acetic acid, Propanoic acid, 2-pentanone, methylpyrazine, ethanone, butyrolactone, 3-methyl-2-cyclopentenone, 2-Furan methanol, and mequinol, Although it was not possible to find any study fully devoted to study of the environmental impact of modern fast pyrolysis technologies, several reports on the impact of traditional charcoal kilns can be found in the literature.

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