

## **CHARACTERIZATION CHEMICAL COMPOUND BASED PYROLYSIS PROCESS FROM CACAO WASTES**

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### **ABSTRACT**

The research aim is to produce cacao vinegar through pyrolysis technology of potential chemical compounds from cacao shell wastes. Results of this research are expected to give benefits as follows: Liquid smoke produced from cacao shell wastes through pyrolysis process is able to diversify fertilizer and new products, The results research showed that the fat content of fermented for Luwu district 35.21. Results of pyrolysis of cacao waste that gave the highest liquid smoke as much as 40,36% in pyrolysis temperature of 500°C. In terms of the charcoal produced from pyrolysis process containing the highest yield was cacao shell waste Luwu district as 42,08%. Identification of GC-MS of cacao shell could provide compounds that mostly derived from acetone 13,01%, acetate acid 73,86%, 2-butanone 6,60%, methyl ester 2,46%, and propanoic acid 4,07%. Usually, Result X-RD analysis for cacao shell char with Luwu District as crystallinity degree 22,83%. Content of N for cacao vinegar rind Luwu district of 175.53 ppm and 1.39% charcoal, greater than nitrogen element content the better for plants as fertilizer organic. The technology of integrated cacao vinegar-charcoal production hence deserves its dissemination throughout Indonesian.

**Key Words :** *Cacao wastes, fermentation, pyrolysis, and Cacao Vinegar*

### **INTRODUCTION**

Cocoa production increased by 325 thousand tons in 2013, by replanting cocoa, rehabilitation and intensification through Gernas Cocoa, a program of the National Movement of Production and Quality Improvement of Ministry of Agriculture. Cocoa is still considered not optimal, and have not been able to increase productivity and farmers' welfare people. Low price of cocoa beans, is also a problem for increased production. Results of other studies indicate that cocoa is dried in the sun and then milled then be used as animal feed. Cocoa beans are rich in polyphenols. Cocoa and its derivatives (*Cocoa powder, Cocoa liquor and chocolate*) containing varying concentrations polyphenol. The polyphenols in cocoa beans contribute about 12-18% of the dry weight of the whole duty (Misnawi, 2012). Potential skin cocoa pods in the degradation of petroleum hydrocarbons contaminated with crude oil, which contained two kg of soil in a plastic bucket 36 contaminated with 250 mL of crude oil (Agbor, *etal.* 2012).

Pyrolysis is the best method (excellent) to realize a clean and efficient conversion of biomass to the source, where the product gases, liquids and solids have a high value to be used (Yemen 2004), in addition to the normal heating method (electrical heating), plasma (Xiu *etal.* 2005), heating technology is able to apply for the pyrolysis of biomass. In general, there are four stages used to convert plants include bamboo as an other advance of bioethanol pretreatment, hydrolysis enzymatic, ethanol fermentation and purification, to find a way to benefit from natural resource-based biomass for the supply of renewable energy and

sustainable development. Application of slow pyrolysis process that can be used to reduce electricity by between 31-33% recovery

The purpose of this study is as follows cocoa bean fermentation process to remove the pulp. .Conduct of liquid smoke from pyrolysis of waste cocoa shell Luwudistrict analysis and testing of chemical compounds contained in the cocoa waste,.

**RESEARCH METHOD**

**Raw Material**

Cocoa beans are dried by the drying method used by producers of cocoa. Cocoa beans are sun dried at different times ranging from3-5 days, the drying time is approximately 9 hours per day. Preparation of samples of cocoa beans each treatment, then washed and dried for 3 days, and then analyzedt he fat content.

**Method**

Fruit peel waste cocoa and cocoa leaves put into the kiln with the temperature and time setting, capacity (liquid smoke and charcoal). Determine the value of charcoal yield, moisture content, volatile matter, ash content, calorific value and carbon value..

**Analysis Date**

Cocoa fruit skin samples analyzed Klason lignin content, holoselulosa levels, and Cellulose.,TGA and Analysis charcoal cocoa rind with FTIR, SEM, XRD, andGCMS.

**RESULT OF RESEARCH AND DISCUSSION**

Based on the research results that have beenfermentedcocoa beans originating from Luwu district has a fat content of 35.21%, with apH of 5.61and FFA of 0.09. Water content in cocoa beanst hat have been fermented by 5.81. In the previous study. Thermal decomposition process has been carried out for the pyrolysis of biomass and its constituent mainly contains cellulose, hemicellulose and lignin are different. The content of hemicellulose, cellulose and lignin on cocoa waste can be seen inTable1.

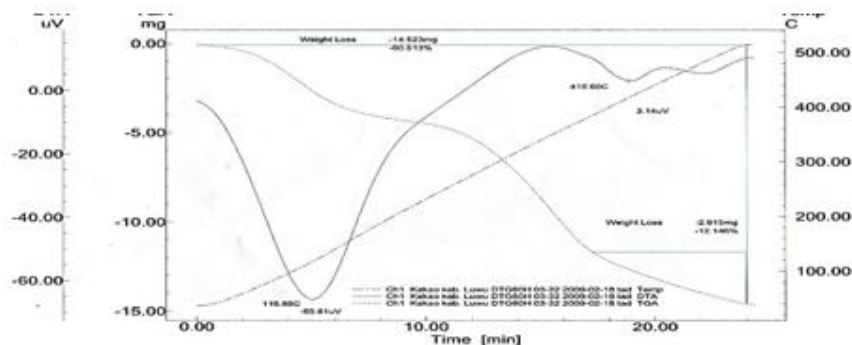


Figure 1. Analysis TGA/DTA for cacao waste

Table1. Content (% b/b) hemicellulose , cellulose and hemicellulose cacao shell

Cacao waste	Content (% b/b)			
	Hemisceluloce	Celuloce	Lignin	Holoceeluloce
Cacao Shell sawdust	16,81	12,12	64,72	28,93

Based on the decomposition of lignin content in the skin known cacao shell Luwu district 64.72 % , 16.81 % of hemicellulose , cellulose and hemicellulose 12.12 % 27.83 % . ( Table 1 and Figure 1 ) . Lignin is one of the determinants of the components to produce a quality liquid smoke ( Nurhayatiet al . 2005 ) ] . Lignin content depends on the different types of raw materials

. This suggests that the pine wood lignin structures are formed by koniferil alcohol alone , while by teak wood lignin prepared by koniferilsinapil alcohol and alcohol with a certain ratio ( Yemen 2004 ) . Chemical components contained in the liquid smoke is very dependent on the process conditions and raw materials used According Fengel&Wegener . 1995, the chemical composition of teak wood contains 39-57 % cellulose , 7-13 % hemicellulose, and lignin 29-39 % . The chemical composition of corn stalks used containing 42.4 % cellulose , hemicellulose and lignin 29.6 % 21.7 % ( Lv. et al . 2010) . The chemical composition of rice straw containing cellulose 34.94 % , 36.06 % hemicellulose and 12.3 % lignin ( Tewfik *et al .* , 2011) .

Table 2. Analysis result GC-MS for cacao vinegar shell district Luwu

Cacao Waste	Compound chemical	Prosentase(%)
Cacao Shell	Aceton	13,01
Luwu district	Methyl Ester	2,46
	Asetic Acid	73,86
	2 buthanone	6,60
	Propanoic Acid	4,07

GC - MS analysis was conducted to determine the types of compounds contained in any liquid smoke . Compounds that passed the GC - MS will be separated into its component chemical liquid smoke cocoa rind Luwu district ( Table 2 ) , ie 13.01 % acetone , methyl acetate 2.46 % , 73.86 % acetic acid , 2 butanone 6 , 60 % and 4.07 % propanoic acid . This is due to the presence of liquid smoke kandundan rind of 40.36 % cocoa and cocoa rind charcoal Luwu District of 42.08 % ..and lignin content in cocoa rind Luwu district at 64.72 % , the study was supported by the dominant compound results of the pyrolysis of wood and acacia wood toothpick consisting of acetic acid and vanillin . The chemical composition of the liquid smoke containing acids , especially acetic acid is a derivative of a compound of acetyl groups during pyrolysis ( Ratanapisit *et al .* 2009). The results of XRD analysis for charcoal cocoa rind Luwu district ( Figure 2 ) shows that the degree of kristanilitas of 22.83 % . XRD for natural pits with cellulose (  $C_6H_{12}O_6$  ) , Xylan (  $C_{10}H_{12}O_9$  ,  $2H_2O$  ) or hemicellulose provide crystallographic data with the number of Bragg diffraction of 5.5712 ( Zhao *et al .* 2010] . This is supported by the results of XRD analysis for oil palm waste material for DS do not give a horizontal line , this is due to the amorphous form wherein crystalline forms approaching the bottom line. diffraction angle 38.5353 So to give a ratio of 2.71274 reticular distances N and H celcel .



Figure 2. .Analysis result XRD for identification crystallinity degree  
With charcoal cacao shell sawdust DistrictLuwu

Results of FTIR analysis for charcoal powder cocoa shellLuwu district ( Figure3 ) shows that the wavenumber  $1111.000\text{ cm}^{-1}$  indicated dehydration and depolymerization of cellulose and hemicellulose content. Changes in aromatic peak at  $1583.49\text{ cm}^{-1}$  indicates the presence of CH , lignin . While the wave number  $3473.80\text{ cm}^{-1}$  indicates the presence of hydroxyl group absorption from  $873.75$  to  $750.31\text{ cm}^{-1}$  indicate the presence of C = CH ( aromatic H ) . While the wavenumber  $381.21\text{ cm}^{-1}$  indicates the presence of hydroxyl groups ( OH ) and uptake from  $873.75$  to  $748.38\text{ cm}^{-1}$  indicate the presence of C = CH ( aromatic H ) is supported by the results of this study ( Shanceset *al.* 2014 ) . that the FTIR analysis for waste fruits show  $3298$  ,  $3275$  and  $3292\text{ cm}^{-1}$  shows the OH vibrations of alcohol and pectic acid . FTIR analysis is used to change the structure of the waste identification fruits with chemical and biological treatment .. FTIR analysis for sugar cane Strawn suggests that the region  $3500\text{-}3400\text{ cm}^{-1}$  and the presence of hydroxyl groups hydrogenbond . Between  $2900\text{-}288\text{ cm}^{-1}$  the presence of aliphatic CH ring .  $1430\text{ cm}^{-1}$  shows the deformation of CH2 groups ( Meloet *al.* 2013)

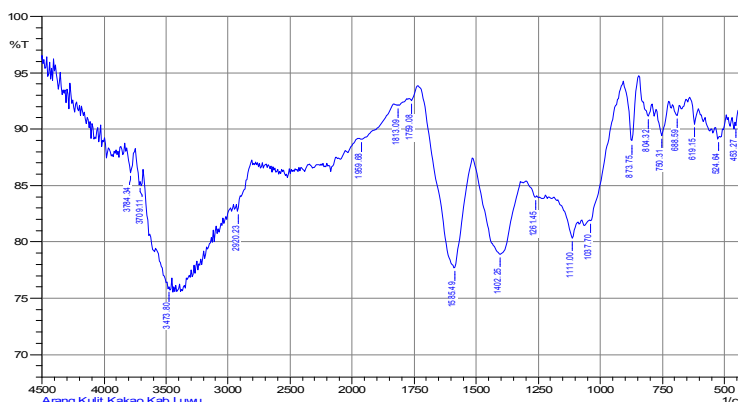


Figure .3 Analysis result FT-IR for charcoal cacao shell sawdust .

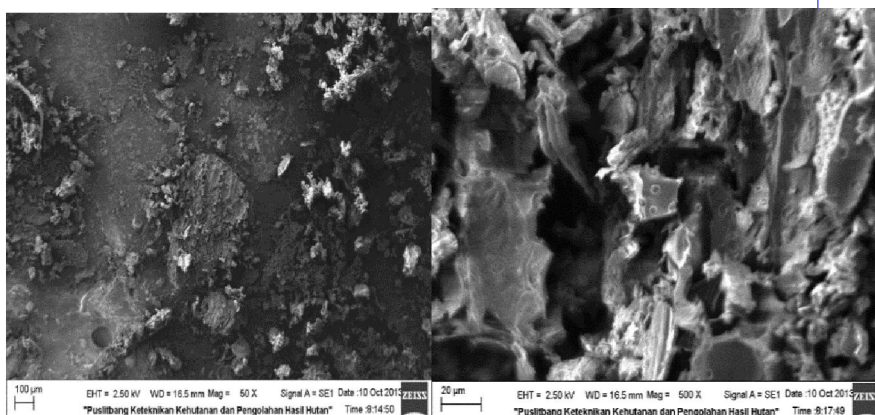


Figure4 .Analysis result SEM micrograph With cacao shell sawdust District Luwu 50x and 500x

Table3 .Content nutrient element into cacao shell waste.

Sampel	pH	C org	N	P	Ca	Mg	K	C/N
Cacao shell Luwu District	6,30	43,92	1,62	0,18	0,51	0,58	1,25	27,11

Information : Analysis C c(%) with Walkley & BlackMethodode  
N Total (%) with Kjeldhal.Methodode

pH for saw dust and bark cocoa shell between 6.30 to 7.80. Element content of organic C in the saw dust largest cocoa District Luwu at 54.88, while the largest N Elements for skin cocoa shell Luwu district of 1.62, 0.18 Elements P, Ca elements and nutrients of 0.51Mg of Element K 0.68 and 1.25. C / N ratio for sawdust largest cocoa Luwu District 90.63, can be seen in Table 3.

### CONCLUSION AND SUGGESTION

Based on the objectives and results of the research that has been done a few conclusions can be drawn as follows (1). Lignin content in cocoa rind Luwu district 64.72%, (2). The results of XRD analysis for charcoal powder cocoa rind Luwu districts shows that 22.83% of kristalinitas degrees. (3). Production of acetic acid obtained from the pyrolysis of waste liquid smoke where cocoa shell Luwu. district to 73.86%.

### SUGGESTION.

Further research needs to be done for other raw materials, the temperature is relatively high and then need for separation of compound so that the product of acetic acid and other compounds as potential anti-oxidant and anti-bacterial.

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