ISBN : 978-979-8452-71-0

Proceedings of International Conference of Indonesia Forestry Researchers III-2015

"Forestry research to support sustainable timber production and self-sufficiency in food, energy, and water"

MINISTRY OF ENVIRONMENT AND FORESTRY
RESEARCH, DEVELOPMENT AND INNOVATION AGENCY
2016

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IPB International Convention Centre, Botani Square Bogor, Indonesia

21-22 October 2015

PROCEEDINGS OF INTERNATIONAL CONFERENCE OF INDONESIA FORESTRY RESEARCHERS III – 2015

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Research, Development and Innovation Agency
Ministry of Environment and Forestry - Republic of Indonesia
2016

POSTER B1 - Characterization Compound Cacao Waste with Pyrolysis Process by Biomass Energy Resources

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ABSTRACT

Cacao biomass 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 liquid smoke, tar, bio char and gas. The main objectives this study were get the yield of liquid smoke in the pyrolysis process, (2) identification of the fractions of potential chemical components of liquid smoke, based on the above, this study is designed to make liquid smoke through a pyrolysis process to produce a potential chemical components such as acetic acid which is environmentally friendly. Biomass waste raw material analysis showed that the lignin content cacao Wajo district 34,06%, 46,43% holoselulosa levels, 23,75% α cellulose and hemicellulose content of 22,68%. Identification GC-MS results it appears that the content of liquid smoke Cacao produced aceton, acetic acid, 2 buthanone, 2 metoxy phenol, 1,1 methyl metocxy buthana and 3 methyl 2 cyclopentena Analysis EDX for cacap bean Wajo district produced element C : 72,13, O 27.50 dan P 0,38 and cacao shell sawdust district Wajo produced element C : 61,12, O : 36,65%, Si : 0,59%, P : 1,48 and Al : 17%. 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.

Keywords: Biomass waste, Pyrolysis, cacao vinegar, char dan bioenergy

1. INTRODUCTION

Potential cacao waste to be used as liquid smoke has gained attention in recent years, which is produced by pyrolysis. Biomass pyrolysis is a process in which biomass decomposes at moderate temperature of about 500°C and has short reaction times in the absence of oxygen to produce liquid product with solid chars and incondensate gases. Cacao biomass 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 liquid smoke, tar, bio char 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 (Mohan, *et al.,* 2006; Yaman, 2004). Pyrolysis conditions including temperature, pressure, vapor-phase residence time and heating rate affect the chemical reactions responsible for producing various chemical compounds present in bio-oils (Antal & Gronli. 2003).

Pyrolysis technology for biomass use has been studied recently because it has several advantages (Balat *et al.* 2009). It can be used to convert biomass resources is product liquid oil, char and gas. Reaction conditions for pyrolysis are more moderate and simpler than in other thermochemical conversion technologies such as gasification and liquefaction. Observed in this study will use one types of pyrolysis of waste cacao from cacao shell and cacao wood. Pyrolysis-based observations to determine the kinetics of activation energy and pre-exponential factor of the pyrolysis temperature has not been done. Thermo-chemical decomposition behavior was assessed using a thermo-gravimetric (TGA) system by heating the sample from 50°C to 700°C at the heating rates of 10, 30 and 50 °C/min under nitrogen. The activation energy was calculated for various fractional conversion values using the isoconversion method. (Wenjin *et al.,* 2013). Pyrolysis of corn stalk a solid heat carrier was studied with under temperature ranging from 430 to 620° C. The solid heat carrier used was temperature ash from a CFB Boiler (Guo *et al.* 2015). Temperature is most critical parameter influencing the performance of biomass fast pyrolysis (Angin, 2013). Evaluate phenolic compound produced from the catalytic pyrolysis of pine sawdust by commercial catalysis (Wang *et al.* 2014). 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 (Mohammed et al. 2015).

This paper study is related pyrolysis of temperature with rate reaction The main objectives this study were (1). get the yield of liquid smoke in the pyrolysis process, (2) identification of the fractions of potential chemical components of liquid smoke, based on the above, this study is designed to make liquid smoke through a pyrolysis process to produce a potential chemical components such as acetic acid which is environmentally friendly.

2. EXPERIMENTAL METHOD

2.1 Manufacture of liquid smoke

Samples consisting of cacao waste put into the kiln were 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. Liquid smoke at any combustion temperature taken with two replications, tar separated from the condensate by precipitation for 24 hours. Analysis was conducted on the liquid smoke and tar yield (% w / w), pH, and acetic acid levels.

2.2 Identification of chemical compounds liquid smoke

Chemical compounds of each fraction liquid smoke temperature in the identification using GC-MS (Gas Chromatography Mass Spectrometry), and then further analyzed by PCA (Principal Component Analysis) to obtain group compounds based on similarity properties. 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 liquid smoke concentration of each fraction liquid smoke.

2.3 Analysis

The characteristic of solid char cacao waste were analyzed. The testing included ultimate analysis, ash ratio, fixed carbon, Fly ratio and composition of the char ash. Also Analysis SEM and XRD for active char cacao shell Wajo Distric.

3. RESULT AND DISCUSSION

3.1 Identification of chemical compounds liquid smoke

Biomass waste raw material analysis showed that the lignin content cacao Wajo district 34,06%, 46,43% holoselulosa levels, 23,75% α cellulose and hemicellulose content of 22,68%. Identification GC-MS results it appears that the content of liquid smoke Cacao produced aceton, acetic acid, 2 buthanone, 2 metoxy phenol, 1,1 methyl metocxy buthana and 3 methyl 2 cyclopentena. Compounds teak sawdust pyrolysis results containing p-guaiacol, 2 methoxy 4 propenyl phenol, 2 methoxy 4 methyl phenol, 3,4,5 trimetoksi toluene and 1,3 dimethoxy syringol (Fatimah & Jake 2005). Dominant compound wood pyrolysis results of acacia wood toothpick and consists of acetic acid and vanillin (Kartal *et al.,* 2004). The chemical composition of the liquid smoke containing acids, in particular acetic acid is a derivative of a compound of acetyl groups during pyrolysis (Ratanapisit *et al*., 2009). According to research by Aho *et al*., (2008), the chemical composition of pine wood liquid smoke on GGM (Galactoglucomannan) was 6.7% acetic acid, 1-hydroxy 2 - propanone 5.2%, and 2 4-methoxy propyl phenol 3.5%.

3.2 Analysis result of cacao sawdust

Pyrolysis process from cacao shell waste produced char, active char by characterization compound for water ration, fly, ash and fixed carbon.

Table 1: Compound char cacao shell and cacao left

Sampel	Water	Fly Ratio	Ash Ratio	Fixed Carbon
Active char shell cacao Wajo District	4,06	14,39	31,11	54,45
active char shell cacao Wajo Ditsrict KOH 5 %	4,76	9,4	22,96	67,68
active char shell cacao Wajo District H_3PO_4 5 %	4,89	9,06	20,50	70,44

Analysis result fixed carbon (Table 1), which active char shell cacao Wajo District 54.45%. Also active char shell cacao sawdust Wajo District with activation solvent KOH 5% have 67.68% and active char shell cacao sawdust Wajo District H_3PO_4 5% have 70.44%. Yield active char cacao wood Wajo District 30%. With activation process solvent H_3PO_4 10% (700/steam 60 min) with weight 100 g. Analysis result XRD for shell cacao chars taken from *Wajo District* produced cristalinity degree of 21.20%. Research result other have was analysis XRD for natural pits with cellulose ($C_6H_{12}O_6$), and Xylane ($C_{10}H_{12}O_{9,2}H_2O$) or Hemicellulose produced crystallography date with diffraction Bragg number was 5.5712 (Zhao *et al*., 2007). Research other Abed *et al.* (2012), 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 celluloce and H celluloce.

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 Stevens (2007), the formation of crystalline growing tendency increasing regularity stereo. The regularity have due to a shift in the crystalline structure of activated charcoal (Schukin *et al.* 2002). The shift occurred in the addition of high aromatic layer followed by a narrowing of aromatic layers as well as an increasing number of aromatic layers (Kercher & Nagle, 2003). According to Pari *et al.* (2004), activated charcoal crystallinity increases with increasing activation temperature. Activation using KOH and H3PO4 showed increased crystallinity. The use of porosity charcoal cocoa leaf Wajo district, at the cross-over visually performed using Scanning Electron Microscope (SEM) berkuatan 20 kV. Increased temperatures will cause the formation of a new micro-pores and micro didnding damage grew larger. According to Aziz et al. 2014, that POFA consists of the contents of Al, Ca, P, and Si high mengidentiskasi used for the active compound to absorb into the absorbent (Mohamed et al. 2006). SEM analysis showed that the structure has a pore natural morphology. POFA have the original cellulose material has pore system interconnect, which relativity is very high surface area (Hubbe *et al.* 2011) According to Foo & Hameed (2009), that palm oil in characterization as spongy and pore structure emempunyai surface area and volume pore width, according (Bonelli *et al.* 2001), that the formation of enlarged pores caused by the evaporation of components degraded and the release of volatile matter. With the reduction of hydrocarbons, the activated carbon surface more clearly visible. The overall diameter of the pores on the surface of activated charcoal and charcoal cocoa leaf SEM analysis results into the micro-pore structure (5μ) is more dominant

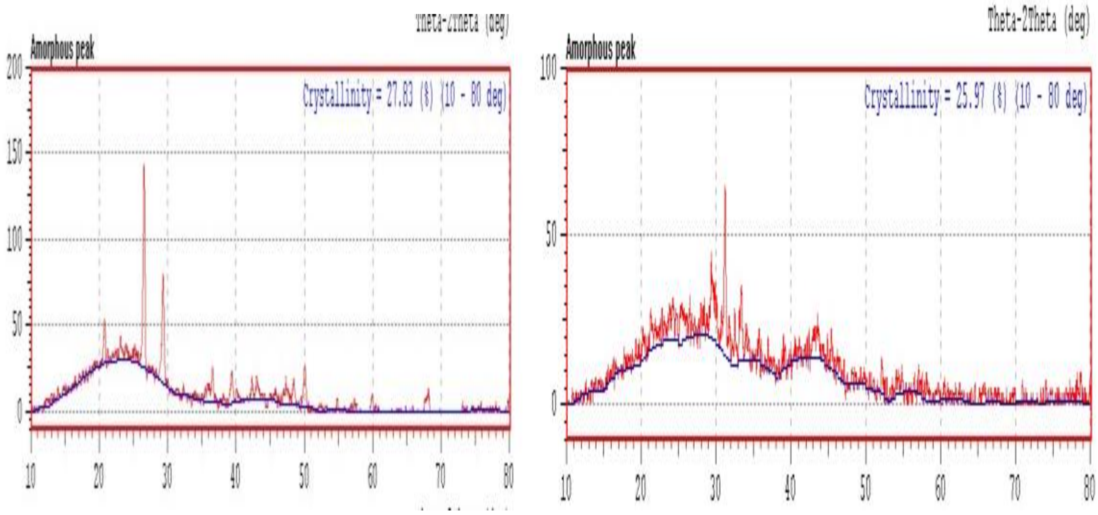

Figure 1: Analysis result XRD from Cacao leaf Wajo district and active char shell Cacao Wajo district

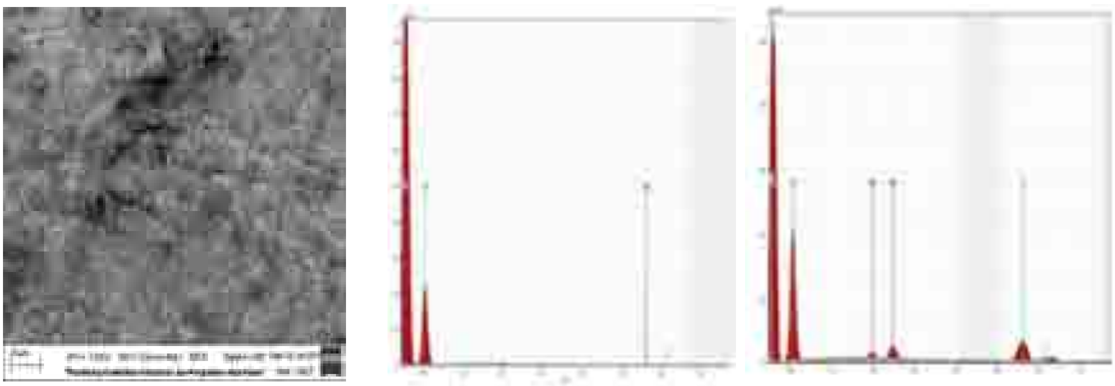

Figure 2: Analysis SEM for shell cacao char Wajo district and analisis Energy Dispersive X Ray (EDX) cacao bean and shell cacao Wajo District

Analysis EDX for cacap bean Wajo district produced element C : 72,13, O 27.50 dan P 0,38. Analysis EDX for cacao shell sawdust district Wajo produced element C : 61,12, O : 36,65%, Si : 0,59%, P : 1,48 and Al : 17%. (Table 3). According to Aziz et al. 2014, that the identification elements in the surface structure Pofa (Palm Oil Mill Boiler Fly Ash) showed that Pofa constituent is carbon, oxygen and silicon. Carbon in which the highest was 29.96% and amounted to 49.11% oxygen, so Pofa has a porous carbon. The CaO alumino silica compound for cation exchange reaction with heavy metals in a solution of distilled water. Additions can be made as an alkaline neutralizing agent (Visa et al., 2012, Bayat 2002). According to Wang et al. 2010, that the process of absorption and kapasity with physical and chemical absorbent characteristics such as particle size, pore diamteter, specific surface area and chemical surface characteristics.

Table 2: Analysis Element cacao bean and shell cacao District Wajo with method EDX

Component	Cacao bean	Cacao Sell
	Initial wt (%)	**Final wt (%)**
C	72,13	61,12
O	27,50	36.65
P	0,38	1,48
Si		0,59
Al		0,17
Total	100	100

Table 3: Proximate and Ultimate Analyses of the Raw Material

Sampel	pH	C org	N	P	Ca	Mg	K	C/N
Cacao Leaf Wajo	7,20	42,97	1,67	0,21	0,80	0,50	0,60	25,67
Cacao wood Wajo	7,00	52,73	0,61	0,19	0,57	0,47	1,15	86,44

Information: Analysis C organic (%) with Walkley & Black Method
N Total (%) with Kjedhal Method.

Analysis nutrient showed that the cocoa leaf Wajo districts have C organic of 42.97, N 1.67, P: 0.21%, Ca : .80%, Mg : 0.50% , and K : 0.60%. (See Figure 2)

4. CONCLUSION

Pyrolysis process of teak and pine wood sawdust at temperature of 120 until 500°C during 5 hours produced liquid smoke, charcoal and tar. 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. From result of GC-MS, Identification of GC-MS of cacao could provide compounds that mostly derived from acid is group of dominant volatile compounds. Biomass waste raw material analysis showed that the lignin content cacao Wajo district 34,06%, 46,43% holoselulosa levels, 23,75% α cellulose and hemicellulose content of 22,68%. Identification GC-MS results it appears that the content of liquid smoke Cacao produced aceton, acetic acid, 2 buthanone, 2 metoxy phenol, 1,1 methyl metocxy buthana and 3 methyl 2 cyclopentena Analysis EDX for cacap bean Wajo district produced element C : 72,13, O 27.50 dan P 0,38 and cacao shell sawdust district Wajo produced element C : 61,12, O : 36,65%, Si : 0,59%, P : 1,48 and Al : 17%. 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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