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Production of charcoal and chemicals from cocoa waste by pyrolysis process with analysis Transmission Electron Microscopy (TEM)

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Abstract. Cocoa and derivative products (Cocoa powder, cocoa liquor and chocolates) consist of polyphenols and different potential levels of antioxidants. Polyphenols in cocoa beans contribute 12-18% dry weight. Naturally, the greater content of polyphenols provides benefits to human health. The potential of cocoa peel waste is abundant and not yet widely utilized, even though it has considerable potential as compost charcoal and alternative animal feed ingredients. The results of processing cocoa produce cocoa waste. with the use of pyrolysis technology is able to overcome the accumulation of plantation waste. The results of this combustion produce liquid smoke of cacao waste into distillates, charcoal. In this study the pyrolysis temperature was 112-512 ° C. The decomposition process of the analysis of raw materials for cacao fruit skin in Soppeng district revealed that lignin content was 46.82%, α cellulose was 26.73%, and the hemicellulose content was 4.86%. Analysis GC MS cacao fruit skin in Soppeng district 3.02 Butane (CAS) n-Butane, 10.72 Acetic acid (CAS) Ethylic acid, 2.42 2-Propanone, 1-hydroxy- (CAS) Acetol , 3.80 Acetic acid (CAS) Ethylic acid 1.25 Acetic acid, pentyl ester (CAS) n-Amyl acetate , 2.21 Acetamide (CAS) Ethanamide , 9.42 2(3H)-Furanone, dihydro- (CAS) Butyrolactone , 2.20 Butanoic acid, 2-propenyl ester (CAS) ALLYL N-BUTANOATE , 6.46 Phenol (CAS) Izal, 3.50 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- (CAS) Corylon , 8.26 Phenol, 4-methoxy- (CAS) Hqmme , 4.47 Pentanal (CAS) n-Pentanal, 1.11 4H-Pyran-4-one, 3-hydroxy-2-methyl- (CAS) Maltol, 0.74 Butanoyl chloride (CAS) Butyryl chloride, SEM analysis for the morphological structure of Soppeng Regency cocoa pod charcoal with a magnification of 500x, 1000x, 3000x and 5000 x., Showed a small porous structure. EDX analysis of cocoa pod charcoal produced element C of 92.47%, MgO: 0 , 36%, K2O: 0.38%, CaO: 1.14%, and ZrO2: 1.58%. Analysis of TEM of 500 nm Cocoa charcoal with an intensity of 44.55%, while 200 nm has an intensity of 42.50% and 50 nm of 41.87%. The monitoring of cacao fruit skin charcoal with pyrolysis technology can reduce the potential for environmental pollution and increase the economic value marketed with cocoa charcoal products.

Keyword : Cocoa waste, *Pyrolysis, Liquid smoke, Charcoal and TEM*

1. Introduction

Biomass waste content in lignin, cellulose, and hemicellulose the pyrolysis conditions are the primary factors that pyrolysis reactions and resulting products. Several typical wood biomass contains 40%–50% cellulose, 25%–35% hemicellulose and 10%–40% lignin [1]. Pyrolysis conditions including temperature, heating rate affect , pressure, vapor-phase residence time the chemical reactions responsible for producing various chemical compounds present in bio-oils. In other research, liquid smoke from bamboo could be used as ingredients of supplement, healthy drinks and cosmetics [2].

Pyrolysis of Humulus Inpulus of the bio oil are phenolic compound straight chain and cyclic alkanes, alkenes, ketones and acids. That 25,81% of all peaks are due to aromatics, 21,55% for alkanes, 18,03% for alkenes and rest is for ketones anodic acids [4]. Thermochemical processes pyrolysis is considered as the most promising and important technology for liquid smoke, gaseous fuels and also solid char. Observed in Pyrolysis technology for biomass can be used for various products including electricity, transportation fuel, chemicals, fertilizers and bio charcoal [3].

Using of biomass waste as an eco friendly renewable energy source. Many concerns point out to the need to use of renewable feedstock, composting, and replacing as much as possible the fossil fuels; among them could be mentioned the depletion of fossil oil reserves, constant uncertainties as far as price is concerned, unsecured supplies, and environmental pollution [5]. This research will use two types of pyrolysis of waste biomass derived from cocoa waste. Testing of physical and chemical properties of cocoa waste determine compression test and depend ability and long burning. The main objectives of this study were (1) to get the yield of liquid smoke and charcoal on pyrolysis process, (2) Identification of the fractions of potential chemical components of liquid smoke

2. Methods

2.1. Manufacture of Cocoa Vinegar

Samples consisting of cocoa sawdust put into the kiln is made of stainless steel which is equipped, Burning carried outat a temperature pyrolysis of 115-515°C for 5 hours for each sample. Increase in temperature af terno smoke issued again. Cocoa vinegar and charcoal separated from the condensate by precipitation for 24 hours. Analysis chemical was conducted on the cocoa vinegar and charcoal yield (% w/ w), pH, and analysis raw material : acetic acid levels.

2.2.Characterization

Analysis GC-MS results ofthe chemical components of the calculationin the form of acetic acid concentration of each fraction liquid smoke. Analysis XRD for cocoa charcoal showed that the degree crystallinity. While Analysis FT IR, TEM dan SEM for charcoal cocoa

3. Result and Dissucion

3.1. Identification of compound chemical

Analysis GC MS cocoa vinegar by pyrolysis process 3.02 n-Butane, 10.72 Acetic acid, 2.42 2-Propanone, Acetol , 3.80 Acetic acid n-Amyl acetate , 2.21 Ethanamide , 9.42 2(3H)-Furanone, dihydro- (CAS) Butyrolactone , 2.20 Butanoic acid, 2-propenyl ester (CAS) ALLYL N-BUTANOATE , 6.46 Phenol, 3.50 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- (CAS) Corylon , 8.26 Phenol, 4-methoxy- (CAS) Hqmme , 4.47 n-Pentanal, 1.11 4H-Pyran-4-one, 3-hydroxy-2-methyl- (CAS) Maltol, and 0.74 Butyryl chloride, From these cocoa vinegar resulted from pyrolysis of raw materials, that gave the highest yield of liquid smoke was liquid smoke of pine wood sawdust by 49.60% and teak wood sawdust 43.78%.[6]. Lignin content depends on the different types of materials separation processes raw material also performed to determine the acetic acid compounds that have the potential as a natural preservative. Substances produced from corn stalk pyrolysis at 450° C containing compounds ketones , furans , carboxylic acids and alcohols. Acids are a group of

volatile compounds were dominant in number. Identification of the phenolic compounds, acids, esters, ketones, alcohols, furans and so on , then the separation process is carried out to determine the furfural compounds, phenol and toluene potential as a renewable bioenergy. pyrolysis of waste pine wood , Oak red and sweet gum at a temperature of 371-871° C from 109 species and 49 species of liquid smoke gases were identified , obtained by chemical compounds comprising 59 species 35 and 24 gas liquid smoke [7]. Compounds resulting from the pyrolysis of 2 types of coffee waste (TR1 and TR2) at 300 , 400 , 500 , and 600° C contains several groups of compounds such as phenols , alkanes , alkenes , steroids , acids , esters, ketones, benzene derivatives, and alcohol [8]. The formation of acetic acid teak and pine wood on the result experiment optimal temperature increase at 400-500 C. The highest yield of liquid smoke obtained from pine wood was 49,60% and teak wood was 42,78% [9].

3.2. Characterization

The results of XRD analysis for cocoa rind (Figure 1) showed that the type of cacao in Hedenbergite form was 69.0% with the formula form CuFeO6Si2, monoclin crystal system, density of 3.786 g / cm3. Other types of Vaterite crystals were 16.6%, CaO3 formulas, hexagonal crystalline systems, 2.568 g / cm3 density, and Quartz 14.5% with O2Si formula, density 2.802 g / cm3, trigonal crystal system. So the degree of crystallinity of cocoa pods in Soppeng Regency is 24.7%. This is supported by research %.[10]. that the results of XRD analysis for oil palm waste material for the DS does not give a horizontal line, This is due to the amorphous form , wherein crystalline forms approaching the bottom line. So for the diffraction angle reticular distance According to%. [11]. The results of XRD analysis were used to calculate the crystalline size of Fe3O4 using Formula Debye-Scherrer. The crystalline size for FeC-H and FeC-P is 9.7 and 25.1, smaller than Fe3O4 particles (33.2 nm).

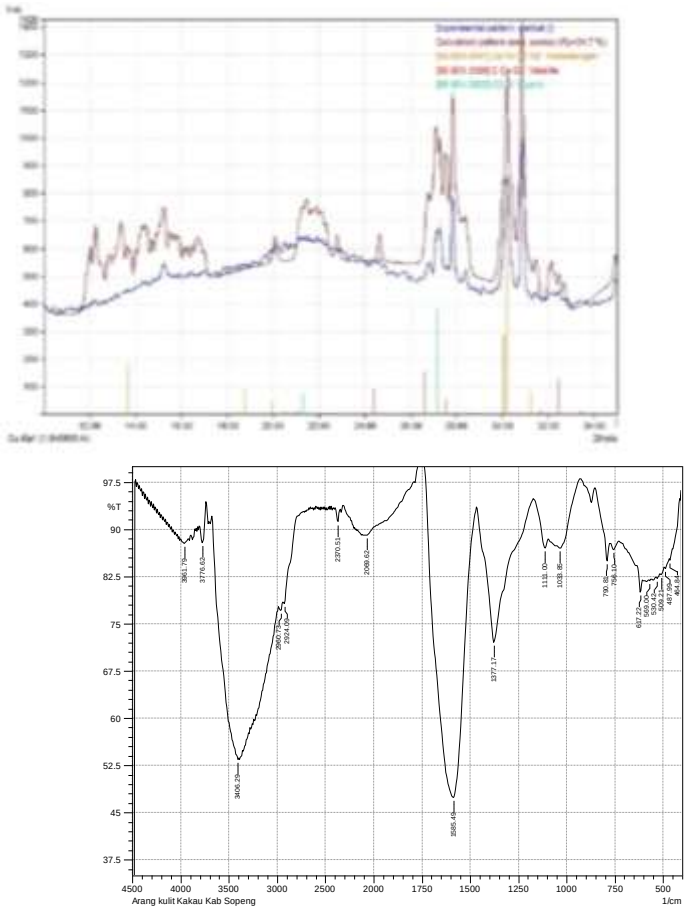

Figure 1**. Characterization structure by analysis** XRD and FT IR cocoa Charcoal

While the results of FTIR analysis for bio char to indicate that cocoa pods 1111.50 cm-1 indicated dehydration and depolymerization of cellulose and hemicelluloses content. Changes in aromatic peak at 1585 cm-1 indicate the presence of lignin. While the wave number 3406 cm-1shows and hydroxyl group (OH) (Figure 1). Typically, broad band related with O-H stretching vibration between 3200 and 3600 cm-1 indicate the prevence of phenol, alcohol, and moisture in the raw material. The presense of alkanes is indicated by absorbance peak of C-H stretching vibration between 300 and 2800 cm-1 and the by bending C-H vibration between 1490 and 1325 cm-1. The absorbance peak between 1775 and 1650 cm-1 shows the C=O the stretching vibration indicating the presense of aldehydes, ketones, and carboxylic acids. C-O stretching and O-H bending vibration s between 1300 and 950 cm-1 are due to the presense of primary, secondary and tertiary alcohols and phenols. Functional group of Humulus Inpulus , bio oil and char by FT IR and their related compound classes of the oils [3]. SEM Analysis for the morphological structure of Cocoa Charcoal with a Magnification of 500x, and 5000 x. (Figure 2), shows a small pore structure. This is supported by. Analysis of micrograph SEM on powder Silicon carbide (SiC) shows SiC particles at a distance of 0.2 to 1 μm [12]

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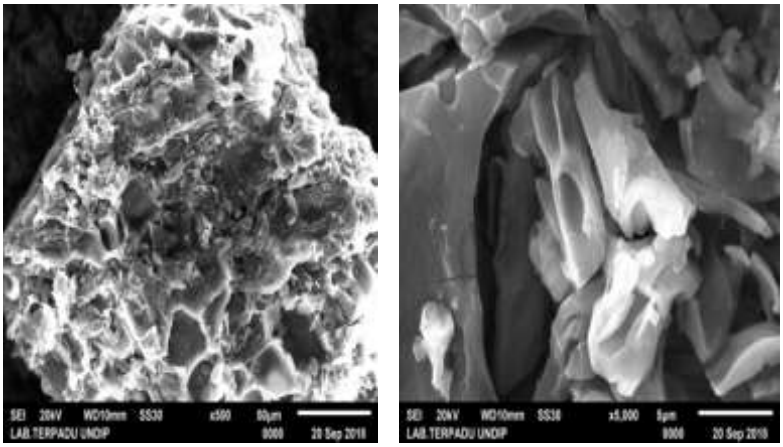

Figure 2**. Analysis** SEM for cocoa Charcoal with biggest 500x, and 5000 x.

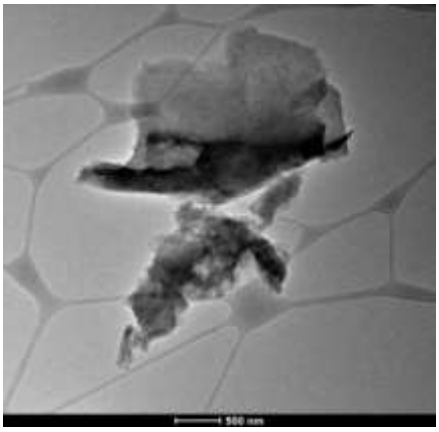

Figure 3**. Analysis** TEM for Cocoa Charcoal with size 500 nm

Mode TEM uP SA Zoom Image, so defocus 0.000 um, magnification 9900 x, Spot size : 3, Intensity as 44.553 %, with bjective lens : 92.097 % and Diffraction lens is 8.107 %

4. Conclusion

Based on the objectives and results of the research thath as beendonea number of conclusionsas follows. : raw material for cocoa waste analysis showed that the lignin content cacao waste 46,82%, so 26,73% so alpha cellulose and hemicelluloses content of 4,86%. 2. Mode TEM uP SA Zoom Image, so defocus 0.000 um, magnification 9900 x, Spot size : 3, Intensity as 44.553 %, with bjective lens : 92.097 % and Diffraction lens is 8.107 % The results of XRD analysis for cocoa rind. showed that the type of cacao in Hedenbergite form was 69.0% with the formula form CuFeO6Si2, monoclin crystal system, density of 3.786 g / cm3. Other types of Vaterite crystals were 16.6%, CaO3 formulas, hexagonal crystalline systems, 2.568 g / cm3 density, and Quartz 14.5% with O2Si formula, density 2.802 g / cm3, trigonal crystal system. So the degree of crystallinity of cocoa pods in Soppeng Regency is 24.7%. Identification of cocoa vinegar from the hazelnut shell by GC-MS yield potential chemical components including products as Biofuel and chemicals.

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