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Using pine and cocoa waste with pyrolysis technology by liquid smoke, charcoal and bio char

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Abstract. In this research, the pyrolysis proceeded at five destilate temperature, ie. 115 until 515°C. Targeted results of this study was to use liquid smoke, charcoal, oil, and gas produced from Biomass (Pine wood and Cacao shell) waste through fast pyrolysis technology, so the charcoal can be used potentially as bio fuel. Raw material analysis showed that leather raw material for wood pine analysis showed that the lignin content 26,06%, and so, 49,23% alpha cellulose and hemicelluloses content of 23,62%. and lignin content cacao waste 46,82%, so 26,73% alpha cellulose and hemicelluloses content of 4,86%. GC-MS results showed that liquid smoke each source contains different compounds. Different types of compounds found in liquid smoke from pine waste condensate such as acid (4 types), keton (10), alcohol(1), phenol(1), esters(3), quaiacol(1), aldehyde (1).furfural (1) and so on. And Cacao waste such acid (3 types), keton (7), alcohol (3), Alkana (1), Levoglucosan (1), resorcin (1), and so on. Identification of liquid smoke from the hazelnut shell by GC-MS yield potential chemical components including products levoglucosan and hydroxy methyl furfural as Biofuel and chemical raw material. FTIR analysis results for charcoal pine shell can be seen in Table 1 shows. Changes in aromatic peak at 1579 cm^{-1} shows that it contains lignin. 1159, 1cm^{-1} indicated dehydration and depolymerization of cellulose and hemicelluloses content. Wave number 3423 cm^{-1} shows hydroxyl group. FTIR analysis results for charcoal cacao l can be seen Changes in aromatic peak at 1585 cm^{-1} shows that it contains lignin. 1111 cm^{-1} indicated dehydration and depolymerization of cellulose and hemicelluloses content The wave number 3406 cm^{-1} shows hydroxyl group. Pyrolysis technology may reduce carbon emission. Each of the ten challenges was presented with a review of relevant literature followed by future directions which can ultimately lead to technological eco friendly that would facilitate commercialization of pyrolytic biochar.

1. Introduction

Potential biomass waste to be used as liquid smoke has gained attention in recent years [12], which is produced by pyrolysis process. Pyrolysis compounds undergo composition into lignin, hemicellulose, and cellulose in the biomass waste that produce liquid smoke, tar, charcoal and bio oil. Differences in the



composition of the components of the raw material is expected to affect the composition and type of compound pyrolysis results.

Biomass waste content cellulose, hemicellulose and lignin and 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, pressure, vapor-phase residence time and heating rate affect 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 cosmetics, supplement and healthy drinks [2].

Thermochemical processes pyrolysis is considered as the most promising and important technology for liquid smoke and 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]. Pyrolysis of *Humulus lupulus* of the bio oil are phenolic compound straight chain and cyclic alkanes and 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 and carboxylic acids [4].

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 wood pine and cacao waste. Testing of physical and chemical properties of wood pine and cacao waste determine compression test and dependability 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 (3). Testing the persistence and bio-char and long press the test firing.

2. Methods

2.1. Manufacture of Liquid Smoke

Samples consisting of pine wood and cacao sawdust put into the kiln is made of stainless steel which is equipped. Burning carried out at a temperature of 115–515°C for 5 hours for each sample. Increase in temperature after smoke issued again. Liquid smoke or tar separated from the condensate by precipitation for 24 hours. Analysis was conducted on the liquid smoke 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 a length of 50 m and a diameter of 0. Of 125°C, and gas flow rate of 0.6 mL/min and injection volume of 0.2 mL. Analysis GC-MS results of the chemical components of the calculation in the form of acetic acid concentration of each fraction liquid smoke. Analysis XRD for pine wood charcoal showed that the degree of crystallinity. While Analysis FT IR for cacao shell, charcoal cacao and charcoal pine wood,

2.3. Made bio char

Bio char can be made in two ways, namely organic matter derived from waste biomass pyrolysis (wood pine) or by printing organic material first and then charred briquettes printing equipment needs to be designed manually. So easily applied by people who live in rural areas with low cost. Drying process of the raw materials can use the sun, according to the condition of the material. Thus simplifying the implementation and the costs were economically. Test charcoal briquettes to determine moisture content, long burning, heating value, density and mechanical properties test (test of courage and puzzle test).

3. Result and Dissucion

3.1. Identification of compound chemical

Analysis GC MS for liquid smoke for Wood pine (Figure 1) was acetone, acetic acid, methyl ester, propanoic acid, 2-Butanone, Butanoic acid, Methyl butyrate, Vinyl crotonate, n-Butyric acid, Succinaldehyde, Dumasin, Dodecadien-2-one, Ethanediol, diacetate, Cyclopenten-1-one, 2-methyl-, Ethanone, 1-(2-furanyl)-, Butyrolactone, Furanone, Acetoxy-2-propionoxyethane, urancarboxaldehyde, 5-Methyl-2-furfural, 2-Cyclopenten-1-one, 3-Methyl-2-cyclopentenone, Corylon, 3-Dimethyl-2-cyclopenten-1-one, Guaiacol, Phenol, 2-methoxy-4-methyl. Analysis GC MS for Cacao vinegar was n-Butane, Ethylic acid, 2-Propanone, Acetol, Acetic acid, n-Amyl acetate, Ethanamide, Butyrolactone, Phenol, 2-Cyclopenten-1-one, Corylon, Phenol, n-Pentanal, Maltol, Butyryl chloride, 2,3,4,5-Tetramethyl-2-cyclopenten, 1-Cyclohexen-1-methyl ketone, p-Ethylguaiacol, 2-Cyclopenten-1-One, 3-acetyloxy, 2,6-Dimethoxyphenol, 1,4-Benzenediol, 2-methyl- Resorcin, 2-Propanone, 4-Hydroxy 3-Methoxy, Levoglucosan, 2-Hexyl acetate, 4-Allyl-2,6-dimethoxyphenol, and Myristic acid. Bioactive chemical compounds derived from liquid smoke from pine wood waste are acetic acid, butyrolactone, methyl-2-furfural, phenols and their derivatives. While bioactive chemical compounds derived from liquid smoke from cocoa waste are n-Amyl acetate, Resorcin, Levoglucosan functions as bio fuel. This is supported by other studies, that pyrolysis of corn cobs with a hot carrier at a temperature of 430-620 °C, gives a maximum bio-oil yield of 14.24% at a temperature of 510 °C. [6]



Figure 1. Comparison liquid smoke for wood pine and cacao shell

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. Results of this study are supported by [7]. that the compound produced from corn stalk pyrolysis at 450°C containing compounds ketones, furans Substances produced from 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 [8]. 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 [9]. Pyrolysis products from biomass waste products levoglucosan and hydroxy methyl furfural (HMF) as Biofuel 2012 [10]. Product Biochar ipreparasi preparation using corn waste to degradation with solvent as i treatment and time preparation 5 clock at temperataure 170° C [11]. From these two liquid smoke 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%. [12].

3.2. Characterization

While XRD analysis for pine wood charcoal showed that the degree crystallinity mixture of 20,09 % . This is supported by research % [13], 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.

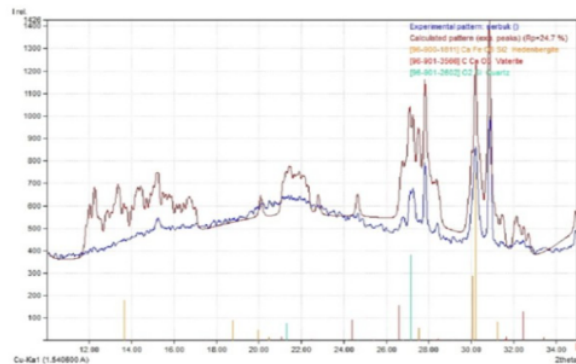


Figure 2. Analysis XRD for cacao shell charcoal

The results of XRD analysis for cocoa rind (Figure 2) showed that the type of cacao in Hedenbergite form was 69.0% with the formula form $\text{CuFeO}_6\text{Si}_2$, monoclin crystal system, density of 3.786 g/cm^3 . Other types of Vaterite crystals were 16.6%, CCaO_3 formulas, hexagonal crystalline systems, 2.568 g/cm^3 density, and Quartz 14.5% with O_2Si formula, density 2.802 g/cm^3 , trigonal crystal system. So the degree of crystallinity of cocoa pods in Soppeng Regency is 24.7%. According to%. [14]. The results of XRD analysis were used to calculate the crystalline size of Fe_3O_4 using Formula Debye-Scherrer. The crystalline size for FeC-H and FeC-P is 9.7 and 25.1, smaller than Fe_3O_4 particles (33.2 nm)

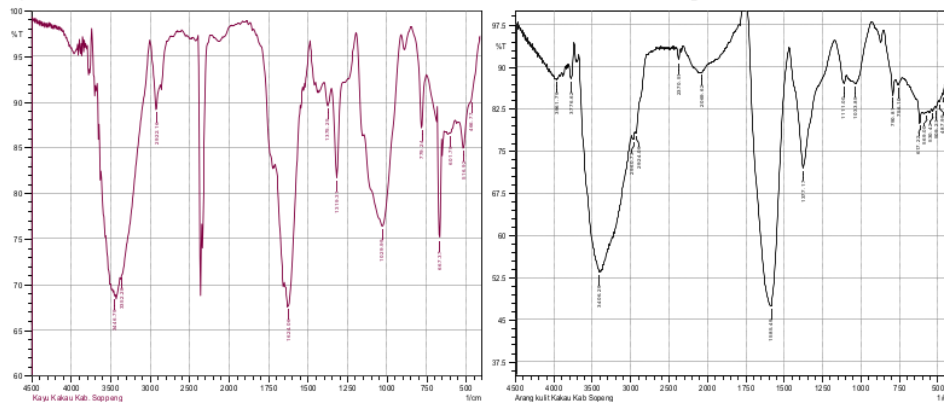


Figure 3. Analysis FTIR cacao wood and charcoal

Typically, broad band related with O-H stretching vibration between 3200 and 3600 cm^{-1} indicate the presence of phenol, alcohol, and moisture in the raw material. The presence 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} show the C=O the stretching vibration indicating the presence of aldehydes, ketones, and carboxylic acids. C-O

stretching and O-H bending vibrations between 1300 and 950 cm^{-1} are due to the presence of primary, secondary and tertiary alcohols and phenols. Functional group of *Humulus lupulus*, bio oil and char by FTIR and their related compound classes of the oils % [4].

Table 1. Functional group composition of raw material (cacao shell) and charcoal

Wave number (cm ⁻¹)	Functional groups	Compound class	CacaoShell	Char Cacao	Charcoal Pine
3600-3200	-OH stretching	Polymeric OH, water content	3446, 3352	3406	3423
3100-3010	C-H stretching	Aromatic ring	-	-	-
3000-2800	C-H stretching	Aliphatic	2922	2960, 2924	-
1775-1650	C=O stretching	Ketones, aldehydes, carboxylic acid	-	-	-
1680-1575	C=C stretching	Alkenes	1624	1585	1579
1490-1325	C-H bending	Alkanes	1375	1377	-
1300-950	C-O stretching	Alcohol, phenol, ester	1029	1111, 1033	1159

FTIR analysis results for charcoal pine shell can be seen in Table 1 shows. Changes in aromatic peak at 1579 cm^{-1} shows that it contains lignin. 1159 cm^{-1} indicated dehydration and depolymerization of cellulose and hemicelluloses content. Wave number 3423 cm^{-1} shows hydroxyl group. FTIR analysis results for charcoal cacao I can be seen Changes in aromatic peak at 1585 cm^{-1} shows that it contains lignin. 1111 cm^{-1} indicated dehydration and depolymerization of cellulose and hemicelluloses content. The wave number 3406 cm^{-1} shows hydroxyl group. While the results of FTIR analysis for bio char to indicate that cacao pods 1151.50 cm^{-1} indicated dehydration and depolymerization of cellulose and hemicelluloses content. Changes in aromatic peak at 1807.30 cm^{-1} indicate the presence of lignin. While the wave number 3477.55 cm^{-1} shows and hydroxyl group (OH). And uptake from 871.82 to 748.45 cm^{-1} indicate the presence of C=CH (aromatic H). Results of this study are supported by % [15]. that the FTIR analysis for Coir pith Black Liquor (CBL) shows the 3420 cm^{-1} showed OH, absorption in 1610 cm^{-1} indicate the presence of lignin CH, absorption in 1247 cm^{-1} indicate the presence of CO group and 586-891 cm^{-1} showed the presence of group C=CH (aromatic H).

4. Conclusions

Based on the objectives and results of the research that has been done a number of conclusions as follows. :1. Leather raw material for wood pine analysis showed that the lignin content 26,06%, and so, 49,23% alpha cellulose and hemicelluloses content of 23,62%. and lignin content cacao waste 46,82%, so 26,73% alpha cellulose and hemicelluloses content of 4,86%. 2. GC-MS results showed that liquid smoke each source contains different compounds. Different types of compounds found in liquid smoke from pine waste condensate such as acid (4 types), keton (10), alcohol (1), phenol (1), esters (3), quaiacol (1), aldehyde (1), furfural (1) and so on. And Cacao waste such as acid (3 types), keton (7), alcohol (3), Alkana (1), Levoglucosan (1), resorcin (1), and so on. Identification of liquid smoke from the hazelnutshell by GC-MS yield potential chemical components including products levoglucosan and hydroxy methyl furfural as Biofuel and chemical raw material.

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