Characterization compound chemical from cocoa waste as acetic acid and phenol

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Abstract. Potential Cocoa bean and derivative products consist compound of polyphenols and different potential levels of antioxidants. The greater content of polyphenols provides benefits to human health, cosmetic and food functional. Pyrolysis compounds under go decomposition into lignin, hemicellulose, and cellulose in the biomass waste that produce liquid smoke, tar, charcoal and other. The results of produce liquid smoke, tar and charcoal. Analysis of the lignin content of the cocoa pod husks from Barru District was 44.98%, cellulose was 60.03%, hemicellulose 15.54%, while the lignin content analysis of cocoa pod husks from Sidrap was 43.17%, cellulose was 43.26%, hemicellulose is 3.13%, and other is 31.3%. At a pyrolysis temperature of 514 °C, the acetic acid content was 8.94% and the phenol content was 1.23% for the liquid smoke of the fruit skins of Barru Regency, while the acetic acid content was 4.37% and the phenol content was 9.34% for liquid smoke Sidrap Regency, From the separation of chemical compounds from the liquid smoke of cocoa pod skin in Barru Regency, it turns out that the highest content of acetic acid is 42.61% and phenol by 5.56% compared to other chemical compounds. From the separation of chemical compounds from the liquid smoke of the cocoa pods in Sidrap Regency, it turned out that the highest content of acetic acid was 42.51% and phenol by 5.54% compared to other chemical compounds.

1. Introduction
Potential biomass waste to be used as liquid smoke has gained attention in recent years, which is produced by pyrolysis process. Pyrolysis compounds under decomposition into lignin, hemicellulose, and cellulose in the biomass waste that produce liquid smoke, tar, charcoal and other. Differences in the composition of the components of the raw material is expected to affect the composition chemical and type of compound pyrolysis results.

Biomass waste content in cellulose, hemicellulose and lignin and the pyrolysis conditions are the primary factors that pyrolysis reactions and resulting products. Several typical wood biomass contains 25%–35% hemicelluloses, 40%–50% cellulose, and 10%–40% lignin [1]. The pyrolysis process can be conducted at low temperature (300 °C–450 °C), medium temperature (450 °C–600 °C) or high temperature (>600 °C) [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, chemicals, fertilizers, and
bio charcoal [3]. In addition, the pyrolysis technology also can be divided into moving bed, fluidised bed, rotary kiln and fixed bed pyrolysis processes according to different pyrolysis devices[4].

Cocoa pod husk represents between 70 to 75% of the whole cocoa fruit weight where each ton of cocoa fruit will produce between 700 to 750 kg of cocoa pod husks (5). Many concerns point out to the need to use of renewable feedstock, composting, fertilizer, 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 [6]. This research will use two types of pyrolysis of waste biomass derived from cacao shell district Barru and Sidrap. Testing of physical and chemical properties of cacao waste determine compression test and depend ability and long burning. The main objectives of this research 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 cacao shell district Barru and Sidrap (3). Determine the characterization of the morphological structure of the cocoa pod husk from Barru and Sidrap.

2. Methods

2.1. Manufacture of Liquid Smoke

Samples consisting of cacao shell district Barru and Sidrap put into the kiln is made of stainless steel which is equipped, Burning carried out at a temperature of until 515°C for 5 hours for two sample. Increase in temperature after smoke issued again. Liquid smoke or ter separated from the condensate by precipitation for 24 hours. Analysis was conducted on the liquid smoke yield (% w/w), calor value, 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), 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.

2.3. Characterization

The surface morphology of the charcoal cacao shell were visualized in a JEOL JSM-6380LA analytical Scanning Electron Microscopy (SEM). The materials were treated with 8% NaOH solubility to remove impurities and placed in vacuum dry oven at 60°C for overnight. A small piece of specimen (0.5 cm²) was placed into double-sided tape of the specimen stub. The specimen was lightly pressed by release paper and coated with a thin layer of gold-palladium film before submitted to SEM for visualization the surface morphology characteristic of the charcoal cacao shell

3. Result and Discussion

3.1. Identification of compound chemical

Analysis of the lignin content of the cocoa shell from Barru Regency was 44.98%, cellulose was 60.03%, hemicellulose 15.54%, while the lignin content analysis of cocoa shell from Sidrap Regency was 43.17%, cellulose was 43.26%, hemicelluloid is 3.13%, and other is 31.3%. At a pyrolysis temperature of 514 °C, the acetic acid content was 8.94% and the phenol content was 1.23% for the liquid smoke of the fruit skins of Barru Regency, while the acetic acid content was 4.37% and the phenol content was 9.34% for liquid smoke of the fruit skins of Sidrap Regency.
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. 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].

Analysis GC MS for liquid smoke for Cacao waste Distric Barru at temperature 314º C (Table 2) as 2-Octylamine, n-Butane, Acetic acid, Pyridine, 2-Methylpyridine, 1,3-Butadiene, 2-methyl-, 2(3H)-Furanone, dihydro- (CAS) Butyro lactone, Carbamic acid, phenyl ester, Phenol, 2-methoxy, n-Pentanal, 2(3H)-Furanone, dihydro- (CAS) Butyro lactone, 7-Octabicyclo[4.1.0]heptane (CAS) Cy clohexene oxide, Pyrrolidine, 1-nitro-, Phenol, 2,6-dimethoxy- HEXA-2,4-DIYNE-1,6-DIOL, NERYL ACETONE, 1,6-ANHYDRO-BETA-D-GLUCOPYRANOSE, (LEVOGLUCOSAN), 3-Methyl-anticyclo[4.3.1]undec-3-en-10-one, Hi-oleic safflower oil (CAS) Safflower oil, 4-N-BUTYL-1,3-CYCLOPENTANEDIO, 1,5-Heptadiene, 3,6-dimethyl-3-(methyl-d)- (CAS) Androst-1-en-3-one, 17-hydroxy-1-methyl-, (5.alpha.,17.beta.). From the separation of chemical compounds from the liquid smoke of cocoa pod skin in Barru Regency, it turns out that the highest content of acetic acid is 42.61% and phenol by 5.56% compared to other chemical compounds.

### Table 1. Ratio acetic acid and phenol cacao vinegar shell District Barru and Sidrap

| No  | Type Sample                        | Acid Acetic Ratio (%) | Phenol Ratio (%) |
|-----|-----------------------------------|-----------------------|------------------|
| 1   | Cacao Vinegar Shell District Barru | 8,94                  | 1,23             |
| 2   | Cacao Vinegar Shell District Sidrap| 4,37                  | 9,34             |

### Table 2. Analysis GC MS for liquid smoke for Cacao shell Distric Barru at 314º C

| Peak# | Retention Time | Area       | Concentration (%) | Chemical Composition                          |
|-------|----------------|------------|-------------------|-----------------------------------------------|
| 1     | 6.617          | 18163319   | 1.07              | Acetic acid (CAS) Ethylic acid                |
| 2     | 7.658          | 45216014   | 2.66              | Acetic acid (CAS) Ethylic acid                |
| 3     | 8.017          | 17956873   | 1.06              | Acetic acid (CAS) Ethylic acid                |
| 4     | 8.206          | 37695435   | 2.22              | Acetic acid (CAS) Ethylic acid                |
| 5     | 12.225         | 16238303   | 0.96              | 2(3H)-Furanone, dihydro- (CAS) Butyro lactone |
| 6     | 12.793         | 15141929   | 0.89              | 3-CYCLOPROPENOIC ACID,-1-BUTYL, METHYL ESTER   |
| 7     | 13.064         | 94920528   | 5.59              | (E)-Hex-2-en-4ynal                            |
| 8     | 13.605         | 24175493   | 1.42              | 4-Heptenal, (Z)- (CAS) cis-4-Hepten-1-al     |
| 9     | 14.002         | 42598268   | 2.51              | Phenol, 2-methoxy- (CAS) Guaiacol             |
| 10    | 14.506         | 17500346   | 10.30             | 1-Hexyn-3-ol (CAS) 1-Hexyne-3-ol              |
| 11    | 14.977         | 112564724  | 6.62              | Lauric acid, 2,3-bis(trimethylsiloxy)propyl ester (CAS) 1-DODECANOYL, BIS 2-BUTYL-1-OL, 4-METHOXY-2-Propanone, methyl-2-propynylhydrazone (CAS) |
| Peak# | Retention Time | Area     | Concentration (%) | Chemical Composition                                      |
|-------|----------------|----------|-------------------|----------------------------------------------------------|
| 1     | 3.869          | 490990   | 0.11              | Ammonium bicarbonate                                     |
| 2     | 6.499          | 47548787 | 10.21             | Acetic acid (CAS) Ethylic acid                           |
| 3     | 6.692          | 14587013 | 3.13              | Acetic acid (CAS) Ethylic acid                           |
| 4     | 7.615          | 198078746| 42.51             | Acetic acid (CAS) Ethylic acid                           |
| 5     | 8.908          | 9201128  | 1.97              | 3(2H)-Pyridazinone, 4,5-dihydro-6-methyl- (CAS) 2,3,4,5-TETRAHYDRO-6-M | |
| 6     | 10.408         | 4975307  | 1.07              | 2-Cyclopenten-1-one (CAS) Cyclopentenone                 |
| 7     | 11.208         | 2158140  | 0.46              | 2,4-PENTADIENOIC ACID                                     |
| 8     | 11.486         | 4903776  | 1.05              | 4-VINYL-4,5-DIHYDRO-3H-PYRAZOLE                           |

Table 3. Analysis GC MS for liquid smoke for Cacao shell Distric Sidrap at temperature 314°C
Bioactive chemical compounds produced from pyrolysis of banana peel waste produce liquid smoke of the cocoa pods in Sidrap Regency, it turned out that the highest content of acetic acid was 42.51% and phenol by 5.54% compared to other chemical compounds.

Bioactive chemical compounds from the liquid smoke of the cocoa pods in Sidrap Regency, it turned out that the highest content of acetic acid was 42.51% and phenol by 5.54% compared to other chemical compounds.
chemical compounds derived from liquid smoke from pine wood waste are acetic acid, butyrolactone, methyl-2-furfural, phenols and their derivatives. [9]. 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. [10]. 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%. [11].

3.2. Characterization

While SEM analysis for charcoal cacao shell district Barru and Sidrap showed the surface morphology analysis was carried out by Scanning Electron Microscopy (SEM). This is supported by research while SEM analysis for charcoal cacao shell district Barru and Sidrap with magnification (a) 100 x (b) 250x dan (c) 1000 x. (seen in Figure 1 and Figure 2)

![Figure 1](image1.png)

Figure 1. While SEM analysis for charcoal cacao shell district Barru with magnification (a) 100 x (b) 250x and (c) 1000 x.

Figure 1 and 2 display the SEM images of charcoal cacao shell district Barru observed under different magnification level. The study on surface morphology was significant in understanding the distribution and fibre arrangement of the charcoal Cacao wastes. The surface morphology of charcoal Cacao wastes shows major structure of micro pores (Figure 1 (a)) and consist of abundant and long fibres Figure 2 (b) and (c). Slight impurities indicate by the white speckles were present on the surface as seen in Figure 1. SEM images of charcoal cacao shell district inside as shown in Figure 2(b). Besides that, the presence of encrusting substances causes the fibre to have an irregular appearance as shown in Figure 1(c). In addition, Figure 1(c) and 2(c) shows the fibrillar arrangements are linear.

Supported by research, Analysis scanning electron microscopy (SEM) was used to visualize the surface morphological of materials. In order to propose the suitability of the studied plant as alternative fibre resources in pulp and paper making, [12]. So [13]. stated that fibre surfaces have waxes and other encrusting substances such as pectin, hemicelluloses, and lignin that form a thick layer to protect the important substances, There are irregular void spaces between the fibrilles and enhance the strength properties of paper produced[14].
Figure 2. While SEM analysis for charcoal cacao shell district Sidrap magnification (a) 100 x (b) 250x and (c) 1000 x

4. Conclusions
Based on the objectives and results of the research that has been done a number of conclusions as follows: Leather raw material for cacao shell district Barru analysis showed that the lignin content 44.98%, and so 60.03% alpha cellulose and hemicelluloses content of 15.54%, and lignin content cacao shell district Sidrap 43.17%, so 43.26% alpha cellulose and hemicelluloses content of 3.13% .
Identification of liquid smoke from cacao shell by GC-MS yield potential chemical components including products acetic acid and phenol as preservative natural. From the separation of chemical compounds from the liquid smoke of cocoa pod skin in Barru Regency, it turns out that the highest content of acetic acid is 42.61% and phenol by 5.56% compared to other chemical compounds. 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%.

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