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Identification of chemical compound from cocoa waste and cocoa vinegar resulting from the pyrolysis process

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Abstract. Cocoa and derivative products consist of compound of polyphenols and different potential levels of antioxidants. The greater content of polyphenols provides benefits to human health, cosmetics, and food functional. Cocoa waste can be reused by pyrolysis to overcome the accumulation of plantation waste. This research aims to identify the fraction of the chemical compound and determine the yield of cocoa vinegar. Cocoa shell and leaves were determined by the lignin, cellulose, and hemicellulose content and further processed by pyrolysis at range 115-515°C. The chemical compound was determined using GC-MS. The result showed that cocoa shells contained lignin about 50.68%, cellulose 49.06%, and hemicellulose 19.06%, whereas analysis of cocoa leaves contain lignin 48.21%, cellulose: 61.98%, and hemicellulose 25.44%. The yield for liquid smoke of cocoa shell produced the largest liquid smoke product at a pyrolysis temperature of 215 ° C, about 16.16 %. Analysis GC MS from cocoa vinegar shell and leaves waste showed that acetic acid was the highest compound with 33.67% and 47.87% respectively. The next compound was 1, 6-anhydro-beta-d-glucopyranose (7.76%), 1-Hexyn-3-ol (6.60%), and Phenol, 2-methoxy (4.69%). The results of the identification of chemical compounds that have the potential for fiber and food ingredients are acetic acid, benzenesulfonic acid, and caffeine.

1. Introduction

Biomass waste used as liquid smoke has gained attention in recent years, produced by the pyrolysis process. Pyrolysis compounds undergo decomposition into hemicellulose, lignin, and cellulose. Biomass waste produces cocoa vinegar, tar, charcoal, and others. Differences in the composition of the raw material components are expected to affect the composition and type of compound pyrolysis results. Biomass waste content such as cellulose, hemicellulose, and lignin as well as the pyrolysis conditions are the main factors in the occurrence of pyrolysis reactions and resulting products. Several typical wood biomass contains 25%–35% hemicelluloses, 40%–50% cellulose, and 10%–40% lignin [1].

Pyrolysis of *Humulus inpulus* bio-oil produces 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 anodic acids [2]. 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 cosmetics, supplements, and healthy drinks [3]. Woody biomass waste (*Pinus radiata*) coming from forestry activities has been pyrolyzed to obtain charcoal and, at the same time, a hydrogen-rich gas fraction. The pyrolysis has been carried out in a laboratory-scale continuous screw reactor, where carbonization takes place, connected to a vapor treatment reactor, at which the carbonization vapors are thermo-catalytically treated. Different peak temperatures have been studied in the carbonization process (500–900°C), [4].

The utilization of biomass waste is an environmentally friendly renewable energy source. Many concerns point out to the need to use renewable feedstock, compost, and replace 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 types of pyrolysis of cocoa waste derived from cocoa shells and cocoa leaves in the district of Bantaeng. Testing of physical and chemical properties of cocoa waste determines compression test and dependability and long burning. The main objectives of this research were (1) to get the yield and pH of cocoa vinegar on pyrolysis process, (2) to identify the fractions of potential chemical components of liquid smoke cocoa shell district Bantaeng.

2. Materials and methods

2.1. Raw material

Cocoa shells and leaves from Bantaeng district were used as the material. Previously, the cocoa shell and leaves were tested for Klason lignin content (SNI 0492:2008), then cellulose and hemicellulose content determined using the modified hydrochloric acid method. Samples put into the kiln was made of stainless steel which is equipped. Burning was carried out at temperature pyrolysis of 115-515°C for 5 hours for each sample. Increase in temperature after no smoke was issued again. Cocoa vinegar or ter separated from the condensate by precipitation for 24 hours. The analysis was conducted on the cocoa vinegar yield (% w/ w), pH. Analysis TGA/DTG (DSC Q series) of raw material for thermal decomposition

2.2. Identification of chemical compounds

Chemical compounds of each fraction cocoa vinegar were identified by GC-MS (QP 5050 A Shimadzu) with a length of 30 m and a diameter of 0.255 mm. Operation condition at a temperature of 125°C, gas flow rate of 0.6 mL/min and injection volume of 0.2 mL.

3. Result and discussion

3.1. Identification of compound chemical

The analysis of cocoa shell lignin content from Bantaeng was 50,68%, cellulose : 49.06%, hemicellulose : 19.06%, whereas analysis of cocoa leaves lignin content from Bantaeng : 48.21%, cellulose : 61.98%, hemicellulose : 25.44%,: 6.40%, and others 10.38%.%.(table 1).

Table 1. Different Analysis of Content Lignin, Cellulose and Hemicellulose.

No	Type sample	Lignin (%)	Cellulose (%)	Hemicellulose(%)
1	Cocoa leaves waste	48,21	61,98	25,44
2	Cocoa shell waste	50,68	49,06	19,06

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Acids are a group of volatile compounds that were dominant in number. Identification of the phenolic compounds, acids, esters, ketones, alcohols, and furans then the separation process is carried out to determine the furfural compounds, phenol, and toluene potential as renewable bioenergy. The results of this study are supported by [6]. Compounds resulting from the pyrolysis of 2 types of coffee waste (TR_1 and TR_2) at 300, 400, 500, and 600°C contained several groups of compounds such as phenols, alkanes, alkenes, steroids, acids, esters, ketones, benzene derivatives, and alcohol [7]. From these two liquid smokes resulting from the pyrolysis of raw materials, the highest yield of liquid smoke was liquid smoke of pine wood sawdust by 49.60% and teak wood sawdust 43.78% [8].

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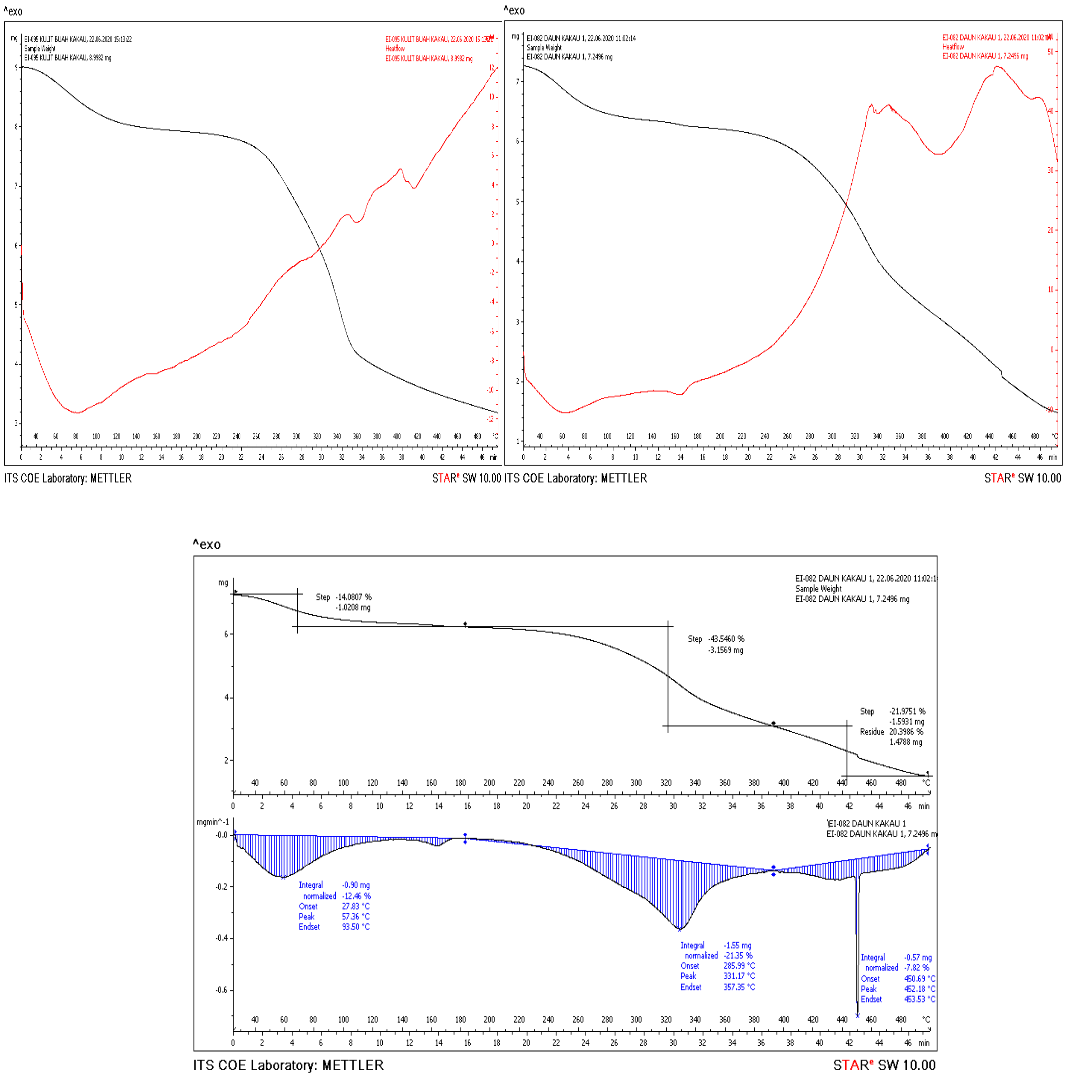

Figure 1. Analysis TGA and DTG from Cocoa waste Bantaeng District.

From the analysis of TGA and DTG from Cocoa waste Bantaeng District (figure 1), the pyrolysis process had been divided into seven stages. The first stage was a slow reduction of 1.6% of mass observed from 40 to 113.1°C. This event was most likely a result of evaporation of free water enclosed in the resin. Starting at 113.1°C and ending at 556.6°C, a significant drop in mass was observed. This stage could be divided into three sub-stages. The first one occurred between 113°C and 331°C and was connected with a small release of heat observed on the DSC curve – we hypothesize it to be a result of dehydration which is an exothermic reaction and can result in cross-linking of the resin [9]. The second and third stage corresponded to two maxima of the complex exothermic peak observed on a DSC curve at approximately 355.0°C and 480.1°C, indicating an ongoing chemical reaction resulting in a release of heat (such as crystallization, oxidation or combustion) [10].

Figure 2. Liquid Smoke for Cocoa Shell (left) and Leaves (right).

The yield for liquid smoke of cocoa shell (table 2), produced the largest liquid smoke product at a pyrolysis temperature of 215 ° C, obtained 16.16 followed by a temperature of 315 ° C of 11.97%, then the pyrolysis temperature was 415 °C of 11.09%. The appearance of liquid smoke can be seen on figure 2. The yield for liquid smoke of cocoa leaves shown in table 3.

The gases obtained at very high temperatures (700–900°C) in the presence of Ni-containing catalysts are rich in H_2 and CO, which makes them valuable for energy production, as hydrogen source, producer gas or reducing agent. Aiming to make the process of obtaining charcoal from biomass more sustainable and profitable, an essential aspect to investigate is the use of the derivate co-products, gas and liquids [11]. If charcoal production is carried out at very high temperatures (700–1000 °C) and slow heating rates (carbonization), the process yields more gas than liquid fraction, and the properties of the gas are more promising than those of the liquid fraction, which is mainly composed of tars and water [12]. The objective of the optimization of charcoal production must focus on maximizing the production of gas together with the reduction of the generated tars and water.

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Table 2. Yield cocoa shell vinegar for time and temperature of pyrolysis.

No.	Time (min)	Temperature (°C)	CocoaVinegar	
			Weight(gr)	Yield(%)
1.	07.25-08.58	115	45	3,43
2.	08.58-10.07	215	212	16,16
3.	10.07-10.43	315	157	11,97
4.	10.43-11.11	415	145	11,09
5.	11.11-13.10	515	42	3,20

Table 3. Yield cocoa leaves vinegar for time and temperature of pyrolysis.

No.	Time (min)	Temperature (°C)	Cocoa Vinegar	
			Weight((gr)	Yield(%)
1.	07.12–08.94	115	52	10,83
2.	08.94 -10.00	215	63	13,13
3.	10.00-10.35	315	31	6,45
4.	10.35-11.06	415	7	1,46
5.	11.06-13.03	515	5	1,04

The pH analysis for the liquid smoke of cocoa shells in Bantaeng Regency (table 4) for a temperature of 115 ° C was 2.60 for a temperature of 215 ° C of 3.18, for a temperature of 315 ° C of 3.46, for a temperature of 415 C of 4.95 and finally 515 C of 6.98. The pH analysis for liquid smoke of cocoa leaves in Bantaeng Regency was for a temperature of 115 ° C was 2.66. for a temperature of 215 ° C of 3.56, for a temperature of 315 ° C of 3.67, for a temperature of 415 C of 4.27 and finally 515 C of 5.18.

Table 4. The pH analysis.

No	Temperature °C	pH	
		Cocoa shell	Cocoa leaves
1	115	2.60	2.66
2	215	3.18	3.56
3	315	3.46	3.67
4	415	4.95	4.27
5	515	6.98	5.18

Analysis GC MS cocoa vinegar leaves (table 5) as acetic acid, 2-Cyclopenten-1-one. Methyl ButyricAcid, 2-Cyclopenten-1-one,2-methyl-, 1-Propanamine,N,2-dimethyl-N-nitroso, 2-

Butanone,1-(acetyloxy)--butanone, Tetrahydrofurfurylalcohol, 2-Cyclopenten-1-one,2-hydroxy-3-methyl, Phenol,2-methoxy-, 1-Hexyn-3-ol, 2-Pyrrolidinone, 2-Methoxy-4-methylphenol, n-Heptanal, cyclopenten-3,4,5-triol, 2(3H)-Benzofuranone,3a,4,7,7a-tetrahydro-3a-methyl, Phenol,2,6-dimethoxy, 2,5-Cyclohexadiene-1,4-dione,compd.with1,4-benzenediol(1:1), 2-isopropenyl-2,5-dimethylcyclohexanone-6,6-D2 n-Amylacetate, 2,4-Dioxa-6,8-, dithiaadamantane,1,3,5,7-tetramethyl, 1,6-anhydro-beta-d-glucopyranose, 4-Pyridinecarboxaldehyde, 3-hydroxy-5-(hydroxymethyl)-2-methyl-, 1H-Azepin-1-amine, hexahydro-, 2-Decene, 3-methyl-, (Z)-5,10-diethoxy-2,3,7,8-tetrahydro-1h, 6h-dipyrrolo[1,2-A;1',2'-D], 2-Cyclopenten-1-one, Methyl from the identification of liquid smoke from cocoa pod husks, chemical compounds that have the potential as food ingredients (fiber) are acetic acid, n Amyl acetate and others.

While bioactive chemical compounds derived from liquid smoke from cocoa waste are n-Amyl acetate, Resorcin, Levoglucosan functioned as biofuel. 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 [13]. The results showed that the pyrolysis of camphorwood in the conversion rate range from 0 to 0.85 might be considered as a one-step process. The study can provide guidance for the design and optimization of industrial reactors and the selection of target biofuels or chemical raw materials [14].

Table 5. GC-MS Analysis for Cocoa Vinegar Leaves from Bantaeng District.

Peak#	Retention Time	Area	Concentration (%)	Chemical Composition
1	8.230	884179155	47.87	Acetic acid
2	10.074	17599904	0.95	2-Cyclopenten-1-one
3	10.921	26354214	1.43	MethylButyricAcid
4	11.292	21312667	1.15	2-Cyclopenten-1-one,2-methyl-
5	11.913	27253494	1.48	1-Propanamine,N,2-dimethyl-N-nitroso-
6	12.267	21470934	1.16	2-Butanone,1-(acetyloxy)--butanone
7	12.699	49399835	2.67	Tetrahydrofurfurylalcohol
8	13.649	44374649	2.40	2-Cyclopenten-1-one,2-hydroxy-3-methyl
9	14.066	86550942	4.69	Phenol,2-methoxy-
10	14.611	63494383	3.44	1-Hexyn-3-ol
11	14.943	29979997	1.62	2-Pyrrolidinone
12	15.248	19133464	1.04	2-Methoxy-4-methylphenol
13	15.434	50048984	2.71	n-Heptanal
14	15.820	40893768	2.21	cyclopenten-3,4,5-triol
15	16.092	19315733	1.05	2(3H)-Benzofuranone,3a,4,7,7a-tetrahydro-3a-methyl-
16	16.930	17402180	0.94	Phenol,2,6-dimethoxy-
17	17.267	33629350	1.82	2,5-Cyclohexadiene-1,4-dione,compd.with1,4-benzenediol(1:1)(CAS)Quin

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18	17.693	83828813	4.54	2-isopropenyl-2,5-dimethylcyclohexanone-6,6-D2
19	17.967	43711701	2.37	n-Amylacetate
20	18.292	41085399	2.22	2,4-Dioxa-6,8-dithiaadamantane,1,3,5,7-tetramethyl
21	18.944	143388434	7.76	1,6-anhydro-beta-d-glucopyranose
22	20.342	18361999	0.99	4-Pyridinecarboxaldehyde,3-hydroxy-5-(hydroxymethyl)-2-methyl-
23	20.520	16983496	0.92	1H-Azepin-1-amine,hexahydro-
24	21.267	20465078	1.11	2-Decene,3-methyl-,(Z)-
25	21.968	26671080	1.44	5,10-diethoxy-2,3,7,8-tetrahydro-1h,6h-dipyrrolo[1,2-A;1',2'-D]P
26	10.074	17599904	0.95	2-Cyclopenten-1-one
27	10.921	26354214	1.43	MethylButyricAcid
		85489635	100.00	

Table 6. GC-MS Analysis for Cocoa Vinegar Shell Waste from Bantaeng District.

Peak#	Retention Time	Area	Concentration (%)	Chemical Composition
1	8.728	1003472153	33.67	Aceticacid
2	9.374	129834441	4.36	aceticacid,anhydride with formicacid
3	11.242	42912258	1.44	2-Furanmethanol
4	11.743	153775917	5.16	1-deuterobutane
5	12.780	52529828	1.76	3-Hepten-2-ol,(Z)-
6	13.431	37282270	1.25	Benzenesulfonicacid,4-hydroxy-
7	14.108	118964393	3.99	Phenol,2-methoxy-
8	14.585	178816977	6.00	1-Hexyn-3-ol
9	15.122	45303886	1.52	Butanoicacid,2-propenylester(CAS)allyln-butanoate
10	15.475	57250716	1.92	1-Pentanol
11	15.831	125490864	4.21	1,4-butandial
12	16.624	97351527	3.27	3-Nonyne
13	17.282	63003277	2.11	n-(1-cyano-propenyl)-formamide
14	17.608	50077263	1.68	6-methyl-2-pyrazinylmethanol
15	17.700	138126510	4.63	Phenol,3,5-dimethyl-4-(methylthio)-,methylcarbamate
16	18.353	120591598	4.05	4,4,6-Trimethyl-2-phenylamino(imino)-5,6-dihydro-4H-1,3-thiazine
17	18.987	171024573	5.74	1,6-anhydro-beta-d-glucopyranose(levoglucosan)
18	19.375	62946207	2.11	5H-1,4-Dioxepin,2,3-dihydro-
19	19.742	15708512	0.53	-
20	19.863	28133731	0.94	2,5-dioxo-3-isopropyl-6-methylpiperazine

21	20.202	115993499	3.89	Spiro[5.5]undecane,1-methylene-
22	20.842	10942859	0.37	
23	20.975	17247780	0.58	1,4-diaza-2,5-dioxo-3-isobutylbicyclo[4.3.0]nonane
24	21.295	71599586	2.40	Caffeine
25	21.947	72226000	2.42	5,10-diethoxy-2,3,7,8-tetrahydro-1h,6h-dipyrrolo[1,2-A;1',2'-D]P
			100	

GC-MS analysis cocoa vinegar shell waste from Bantaeng District (table 6) were Acetic acid, anhydride with formicacid, 2, uran methanol, 1-deuterobutane, 3-Hepten-2-ol,(Z)-Benzenesulfonicacid,4-hydroxy-, Phenol,2-methoxy-, 1-Hexyn-3-ol, Butanoicacid,2-propenylester1-Pentanol, 1,4-butandial, 3-Nonyne, n-(1-cyano-propenyl)-formamide, 6-methyl-2, pyrazinylmethanol, Phenol,3,5-dimethyl-4-(methylthio)-,methylcarbamate, 4,4,6-Trimethyl-2-phenylamino(imino)-5,6-dihydro-4H-1,3-thiazine,1,6-anhydro-beta-D-glucopyrano (selevoglucosan), 5H-1,4-Dioxepin,2,3-dihydro-, , 2,5-dioxo-3-isopropyl-6-methylpiperazine, Spiro[5.5]undecane,1-methylene-, 1,4-diaza-2,5-dioxo-3-isobutylbicyclo[4.3.0]nonane, Caffeine, 5,10-diethoxy-2,3,7,8-tetrahydro-1H,6H, ipyrrolo[1,2-A;1',2'-D]. The results of the identification of chemical compounds that have the potential for fiber and food ingredients are acetic acid, benzenesulfonic acid, and caffeine.

Some components of the hardener/catalyst can either undergo degradation into acetone [15] or into acetic acid. Laino [16] conducted pyrolysis of pure triacetin and found that after 30 s at 526.85 °C it constitutes in 79% of the pyrolysis products. However, some components of hardener/catalyst either do not undergo any thermal decomposition (e.g adipic acid, dimethyl ester) at all or do so to a very small degree, and thus, their concentration in the pyrolysis product is high (e.g. glycerol 1,2-diacetate). Cocoa beans originating from Bantaeng Regency with the following composition; Water content of 30.76%, crude protein content of 17.93%, fat content of 33.98%, crude fiber of 21.11%, BETN content of 20.495, and ash content of 6.46%.

4. Conclusions

Cocoa shells from Bantaeng contained lignin about 50, 68%, cellulose 49.06% and hemicellulose 19.06%, whereas analysis of cocoa leaves was lignin content 48.21%, cellulose 61.98%, hemicellulose 25.44%,: 6.40%, and others 10.38%. The results of the identification of chemical compounds that have the potential for fiber and food ingredients are acetic acid, benzenesulfonic acid, and caffeine.

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