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Synthesis and characterization of bioactive compound from Cocoa fruit shell by pyrolysis process

M Wijaya^{1*} and M Wiharto²

¹ Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Makassar, Indonesia

² Department of Biology, Faculty of Mathematics and Natural Sciences, Universitas Negeri Makassar, Indonesia

*Corresponding author: wijasumi@yahoo.co.id

Abstract. Cocoa contain polyphenols and potential antioxidants. Polyphenols is beneficial to human health and used for cosmetic and food manufacturing. The production of cocoa and its derivative products resulted liquid smoke, tar and charcoal. Pyrolysis is able to overcome the accumulation of those production waste. In this study, pyrolysis was conducted at temperature 114-514°C. Analysis of cocoa shell content from Bulukumba district was lignin (42.28%), cellulose (44.55%), hemicellulose (10.02%). Analysis of cocoa shell content from Enrekang district was lignin (45.61%), cellulose (37.61%), hemicellulose (6.40%), and others (10.38%). GC-MS analysis for liquid smoke of cocoa shell from Bulukumba resulted acetic acid (18.39%), butyrolacton (6.27%), oxetane, 2-propyl (4.45%), 2,6-dimethyl-7-octen-3-ol (6.48%), and hexadecanoic acid (4.36%). GC-MS analysis for liquid smoke for cocoa shell Enrekang resulted acetic acid (25.78%), propane diamide (2.18%), acetamide N-methyl (4.0%), cyclopropyl carbinol (12.57%), 2-propanoic acid-2-methyl (7.83%), phenol 2,6-dimethoxy (2.72%), 1,6-anhydro-beta (5.83%), alpha-beta-D ribopyranose (1.76%). While XRD analysis for cocoa shell from Bulukumba and Enrekang showed that the degree crystallinity are 40.15% and 22.22%, respectively. The use of pyrolysis of cocoa shell can reduce carbon emission as environmental pollution and increase the economic value.

1. Introduction

Pyrolysis compounds under go decomposition into lignin, hemicellulose, and cellulose in the biomass waste that produce liquid smoke, tar, charcoal and others. Differences in the composition of the components of the raw material is expected to affect the chemical composition 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. Sawdust wood wastes sample were obtained from Morocco, and the chemical compositions contains 26.7% of hemicelluloses, 40.1% of cellulose, and 33.2% of 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. Thermochemical conversion such as pyrolysis could be a viable option for environmentally acceptable way to manage waste wood biomass and agricultural [2].

Thermochemical reaction is considered as the most promising and important technology for liquid smoke, fuels and also solid char. Pyrolysis process for biomass waste can be used for various products



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including chemicals, electricity, fuel, 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 composting, renewable feedstock 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 [4]. Cocoa shell (*Theobroma cacao* L) which is the residue from the production of cocoa fruit, after extracting from cocoa beans, approaches 74-76% of the cocoa fruit and the rest is cocoa waste [5]. Pectin extracts from different methods of cocoa shell produce a pH below the water activity, so they can be made as acidic products [6].

This research will use two types of pyrolysis of waste biomass derived from cocoa shell Bulukumba and Enrekang district. Testing of physical and chemical properties of cocoa waste determine compression test and depend ability and long burning. The main objectives of this research were (a) to get the yield of liquid smoke and charcoal on pyrolysis process, (b) identification of the fractions of potential chemical components bioactive of liquid smoke from cocoa shell Bulukumba and Enrekang district.

2. Methods

2.1. Manufacture of Liquid Smoke

Samples consisting of cocoa shell from Bulukumba and Enrekang district put into the kiln which is made of stainless steel. The burning carried out at a temperature of 114-514°C for 5 hours for each sample. Increase in temperature after no 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 chemical based on similarity properties. Further chemical constituents were identified by GC-MS a length of 50 m and 125°C, and gas flow rate of 0.6 mL/min and injection volume of 0.2 mL. GC-MS analysis results of the chemical components of the calculation in the form of acetic acid concentration of each fraction liquid smoke. Analysis XRD for cocoa shell charcoal showed that the degree crystallinity. While FT-IR analysis for charcoal cocoa shell from Bulukumba and Enrekang districts for functional group.

3. Results and Discussions

3.1. Identification of compound chemical

Analysis of cocoa shell from Bulukumba district was lignin (42.28%), cellulose was 44.55%, hemicellulose was 10.02%, whereas analysis of cocoa shell lignin content from Enrekang was 45.61%, cellulose was 37.61%, hemicellulose was 6.40%, while analysis of lignin content of cocoa shells from Enrekang was 45.61%, cellulose was 37.61%, hemicellulose was 6.40%, and others 10.38% (Figure 1). 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. Corn stalk pyrolysis process 450° C produced containing compounds furans, ketones, 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 research are supported by [7]. Liquid product from pyrolysis of MSW are very complex and usually contain water. However, the thermal decomposition of polymers produce oils, which can be used either as a liquid fuel or as source of chemicals. [8]. The yield wood cylinder at pyrolysis temperature 450 to 1050° C, the main gas (CO, CO₂, CH₄, H₂ dan C₂H₄) and tars (acetic acid, hydroxyl acetone, levoglucosan, phenol, quaiacol, and syringol)

have been determined [9]. Pyrolysis products from biomass waste products levoglucosan and hydroxy methyl furfural (HMF) as Biofuel [10].

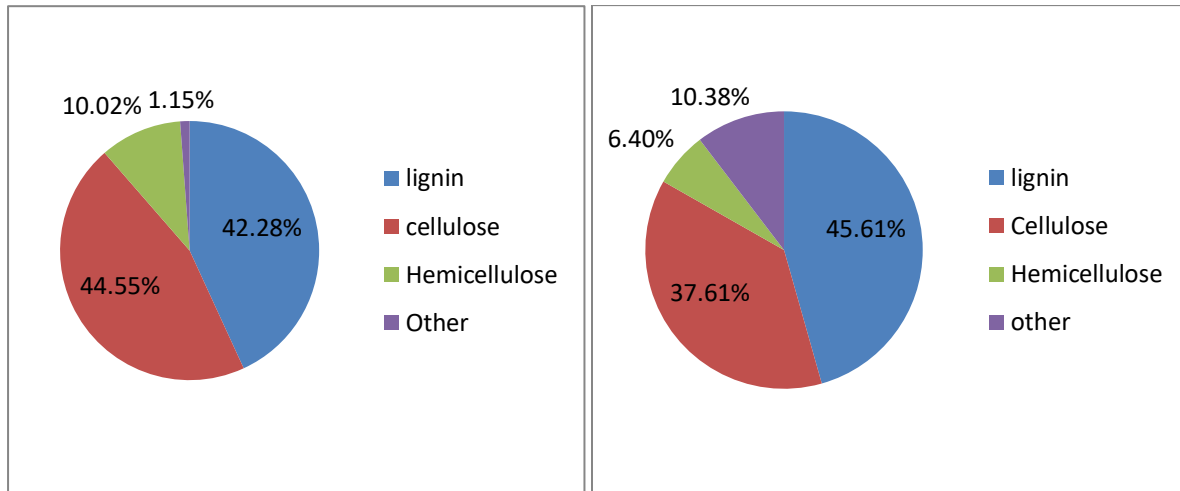


Figure 1. Comparison liquid smoke cocoa Shell from Bulukumba and Enrekang District

Table 1. Analysis of liquid smoke cocoa shell from Bulukumba and Enrekang District

No.	Pyrolysis Temperature (°C)	Liquid smoke cocoa shell Bulukumba District		Liquid smoke cocoa shell Enrekang District	
		Weight (g)	Percentage (%)	Weight (g)	Percentage (%)
1	114	45	11,19	25	8,04
2	214	135	33,58	89	28,62
3	314	89	22,14	86	27,65
4	414	98	24,38	78	25,08
5	514	35	8,71	33	10,61
Total	-	402 g	100	311 g	100

GC-MS analysis for liquid smoke for cocoa shell from Bulukumba district (Table 1) was acetic acid 18,39%, butyrolacton 6,27%, oxetane, 2 propyl 4,45%, 2,6 dimethyl 7 octen 3 ol 6,48%, levoglucosan 5,36%, 1,6 anhydro beta 6,75% and hexadecanoic acid 4,36%. Analysis GC MS for liquid smoke for cocoa shell from Enrekang district (Table 2), was acetic acid 25,78%, propane diamida 2,18%, acetamida N-methyl 4,0%, cyclo propyl carbinol 12,57%, 2 propanoic acid 2 methyl 7,83%, phenol 2,6 dimethoxy 2,72%, acetic acid penthyl ester 2,72%, 1,6 anhydro beta 5,83%, alpha beta-D ribopyranose 1,76%. 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 [7].

Table 2. GC-MS analysis for liquid smoke for cocoa shell from Bulukumba District

Peak#	Retention Time	Area	Concentration (%)	Chemical Composition
1	6.027	302236	0.35	Acetone
2	8.306	15718669	18.39	Acetic acid
3	9.603	2189260	2.56	Propanoic acid
4	10.530	5589514	6.54	Acetic acid
5	11.258	1212382	1.42	Pentanoic acid
6	12.585	5356812	6.27	Butyrolactone
7	13.589	1871645	2.19	Pentanoicacid,4-methyl
8	14.094	2079821	2.43	Phenol
9	14.898	2881545	3.37	Guaiacol
10	15.291	3802586	4.45	Oxetane,2-propyl
11	15.829	2502931	2.93	Butanoicacid,2-propenylester
12	16.537	5542494	6.48	2,6-Dimethyl 7-Octen -3-OL
13	17.358	977247	1.14	3-Nonen-5-one
14	17.663	1319491	1.54	Phenol,2,6-dimethoxy
15	18.060	1386419	1.62	9-Oxabicyclo[6.1.0]non-3-ene
16	18.474	1422649	1.66	Phenol,3,5-dimethyl-4-(methylthio)-,methylcarbamate
17	18.785	1659508	1.94	Silane,[1,4-dioxane-2,5-diylbis(oxy)]bis[trimethyl
18	19.192	886575	1.04	Acetovanillone
19	19.612	4579475	5.36	Levoglucosan
20	20.752	5772160	6.75	1,6-anhydro-beta-
21	21.425	2049333	2.40	Heptyloctanoate
22	22.168	3724659	4.36	Hexadecanoic acid
23	23.094	1332935	1.56	2-Dodecenal
24	23.607	1928466	2.26	9-Hexadecenoic acid
25	24.325	1409612	1.65	3-Dodecanol(CAS)
26	31.739	4465202	5.22	Pregn-16-en-20-one,3-(acetyloxy)-5,6-epoxy(3.beta.,5.alpha.,6.alpha.)-(C
27	32.855	371284	0.43	2,6,10,14,18,22-23-hexamethyl-
		85489635	100.00	

Table 3.GC-MS analysis for liquid smoke for cocoa shell from Enrekang District

Peak#	Retention Time	Area	Concentration (%)	Chemical Composition
1	5.567	1389036	1.29	Ammonium carbamate
2	9.209	27720851	25.78	Acetic acid
3	9.675	1035913	0.96	1H-Pyrrole
4	10.175	696572	0.65	tert-Butylacrylate
5	11.875	6001935	5.58	Acetic acid
6	12.384	2343945	2.18	Propane diamide
7	12.522	4305282	4.00	Acetamide,N-methyl
8	13.225	109357	0.10	Propan amide(
9	13.590	1191593	1.11	3-Penten-2-ol,(z)-
10	14.385	543181	0.51	Corylon
11	14.652	1043822	0.97	5-Valerolactone
12	14.849	1630866	1.52	Phenol,4-methoxy-
13	15.045	1752958	1.63	2,5-Pyrrolidinedione,1-methyl-
14	15.257	13515230	12.57	Cyclopropyl carbinol
15	16.075	5150252	4.79	2-Propanamine,N-(1-methylpropylidene)
16	16.505	8441505	7.85	Ethylester
17	17.276	2881666	2.68	1,2-Oxaborole,2,3,4-triethyl-2,5-dihydro-5,5-dimethyl
18	17.591	2924396	2.72	Phenol,2,6-dimethoxy-
19	17.921	3270405	3.04	1,4-Benzenediol
20	18.703	2928988	2.72	Acetic acid,pentyl ester
21	19.021	2171430	2.02	cyclohexenecarboxylate
22	19.300	812503	0.76	2-Propanone,1-(4-hydroxy-3-methoxyphenyl)
23	19.671	6266159	5.83	levoglucosan)
24	20.125	1891058	1.76	Alpha.-.beta.-d-ribopyranose,1,3-di-o-acetyl-
25	22.158	841964	0.78	hexadecanoic acid
26	23.618	279557	0.26	1,10-decanediol
27	31.835	1080977	1.01	Aacetyloxy
28	32.846	217555	0.20	tetracosahexaene
		107521235	100.00	

3.2. Characterization

While XRD analysis for cocoa shell from Bulukumba and Enrekang district showed that the degree crystallinity mixture of 40.15% and 22.22%. This research other analysis XRD for pine wood charcoal of 20.09% [11]. This is supported by previous research [12]. 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.

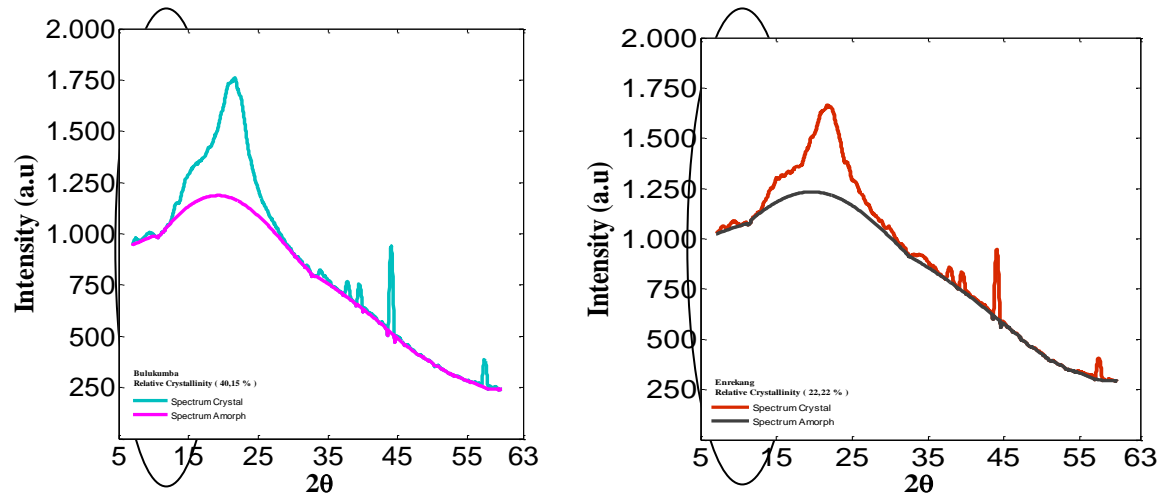


Figure 2.XRD analysis for cocoa shell charcoal from Bulukumba and Enrekang district

The results of XRD analysis for charcoal cocoa shell from Bulukumba and Enrekang district (Figure 2). According [13]. 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).

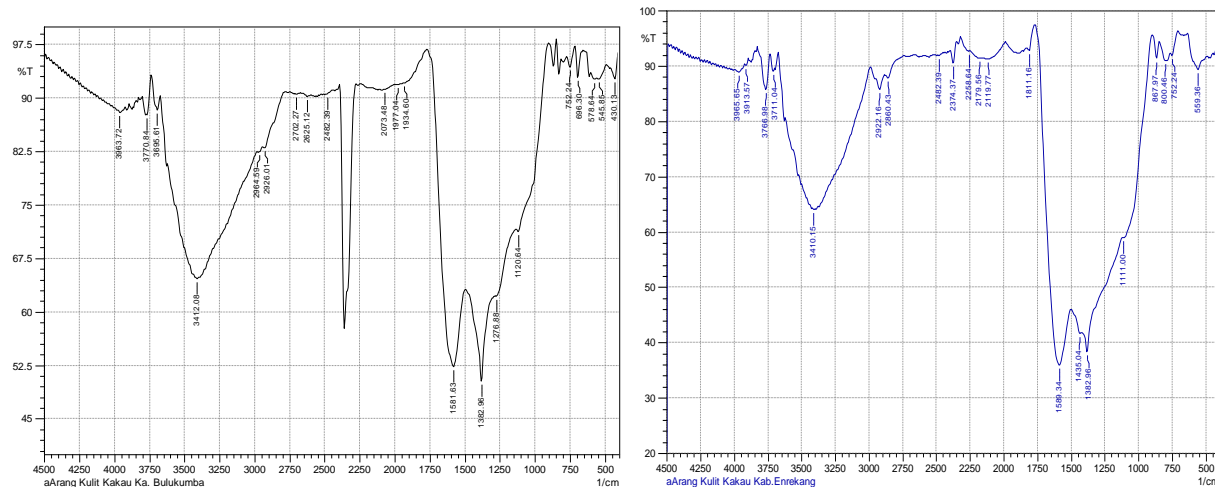


Figure 3.Functional group composition of charcoal Cocoa Shell from Bulukumba and Enrekang District

FTIR analysis results for charcoal, cocoa shell from Bulukumba district can be seen in (Figure 3). Changes in C-H bending peak at functional group alkanes at 1394 cm^{-1} shows that it contains lignin. 1138 cm^{-1} indicated dehydration and depolymerization of cellulose and hemicelluloses content. Wave number 3439 cm^{-1} shows hydroxyl group. FTIR analysis results for charcoal cocoa shell Enrekang district can be seen Changes in Changes in C-H bending peak at functional group alkanes at 1421 cm^{-1} shows it contains

lignin. 1114 cm^{-1} indicated dehydration and depolymerization of cellulose and hemicelluloses content. The wave number 3417 cm^{-1} shows hydroxyl group. Results of this study are supported by %.[14].the functional group on the surface of pyrolysis char were characterized. The peak at 3470 cm^{-1} was assigned to OH (Fuel) group, and the peak at 1000 cm^{-1} was corresponded to C-O stretching .In the low temperature (below 500° C), CO_2 was formed via decarboxylation reaction and carboxyl group (peak at 1730 cm^{-1} was disappeared when the temperature was above 400°C [15].]. The peak at 728 cm^{-1} corresponded to $-(\text{CH}_2)_n$ in plane rocking vibration and the peak at 1418 cm^{-1} corresponded to $-\text{CH}_3$, $-\text{CH}_2$ bonding. Which could explain to formation of hydrocarbon such as CH_4 , C_2H_4 during tyre pyrolysis [16].

4. Conclusions

Based on the objectives and results of the research that has been done a number of conclusions as follows. Raw material of cocoa shell content from Bulukumba district was 42.28% of lignin, 44.55% of cellulose, 10.02% of hemicellulose, whereas analysis of cocoa shell content from Enrekang was 45.61% of lignin, 37.61% of cellulose, 6.40% of hemicellulose. GC-MS analysis for liquid smoke of cocoa shell from Bulukumba resulted acetic acid (18.39%), butyrolacton (6.27%), oxetane, 2-propyl (4.45%), 2,6-dimethyl-7-octen-3-ol (6.48%), and hexadecanoic acid (4.36%). GC-MS analysis for liquid smoke for cocoa shell Enrekang resulted acetic acid (25.78%), propane diamide (2.18%), acetamide N-methyl (4.0%), cyclopropyl carbinol (12.57%), 2-propanoic acid-2-methyl (7.83%), phenol 2,6-dimethoxy (2.72%), 1,6-anhydro-beta (5.83%), alpha-beta-D ribopyranose (1.76%). FT-IR analysis results for charcoal from cocoa shell from Bulukumba district can be observed. Changes in C-H bending peak at functional group alkanes at 1394 cm^{-1} shows that it contains lignin. Absorption at 1138 cm^{-1} indicated dehydration and depolymerization of cellulose and hemicelluloses content. Wave number 3439 cm^{-1} shows hydroxyl group,

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