Al-Kimia, 12-1-2024, 9-14
Available online at: http://journal.uin-alauddin.ac.id/index.php/al-kimia

Characteristic and Chemical Compound of Charcoal Cocoa Wasted by Pyrolysis Process

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Received: April, 18, 2024/Accepted: June, 29, 2024
doi: 10.24252/al-kimiav12i1.46588

Abstract: *Indonesia continues to experience a decline in cocoa production due to the aging of cocoa plants, conversion of cocoa plantations, pests and diseases, and the government's focus on food crops which are the causes of the decline in production which is considered to be a problem of decreasing cocoa yields. The objectives of this research are 1. To apply the production of cacao tea from cocoa leaves which will be used as a natural herbal drink and 2. To determine bioactive chemical compounds from the pyrolysis results of cocoa waste by controlling temperature and time. The method used in this research is. Analysis of lignin, cellulose and hemicellulose content from cocoa leaves. Then the pyrolysis process was carried out with pyrolysis temperatures of 300,400 and 500 C. Extraction was carried out with an extractor where the cocoa leaf waste was mixed with heated water at a temperature of 80°C for 3 hours. Analysis of flavonoid and antioxidant levels for pinrang cocoa leaves, obtained lignin levels of 43, 13%, holocellulose content of 47.11%, alpha cellulose content of 31.13% and cellulose content of 43.13%. Proximate analysis, Kolaka Regency cocoa leaves were, phenol 529.52 mg/Kg, catechin 615.71 mg/Kg, glucose = 6.68%, caffeine = 329.56 mg/Kg, carbon 52.20%, nitrogen 1, 24%, hydrogen 17.55% and oxygen 29.01%. Cocoa leaf extract, for Pinrang Regency, total flavonoids were 6.01% w/w. Cocoa leaf extract, for Kolaka Regency, total flavonoids were 35.10% w/w. Utilization of cocoa leaves from Kolaka Regency had the best antioxidant content compared to the Regency. Pinrang for cacao tea products as a herbal drink product is very good to be developed, no one has carried out this research, especially from cocoa waste for cacao tea products. There is a need to utilize cocoa waste to reduce carbon emissions.*

Keywords: *Antioxidants, Cocoa Leaf, Extraction, Flavonoids*

INTRODUCTION

As stated in the Paris Agreement, Indonesia is realizing its national target of reducing GHG emissions by 29% independently and 41% with international support by 2030. Indonesia is targeting Net Zero Emissions by 2060. Indonesia's cocoa bean production continues to decline because cocoa plants are generally old, and the conversion of cocoa plantations, pests, and fertilizers, as well as the government's focus on food crops, are the causes of the decline in production. The Central Statistics Agency (BPS) stated that the export volume of cocoa beans in 2020 decreased by 7 per cent to 28,678 tons from 30,835 tons in 2019. The fermentation process in cocoa beans forms aroma and taste compounds and forms bioactive compounds for health (Vásquez et al., 2019). Fermented cocoa beans produce hygienic food and beverages and healthy functional food products. The product contains alcohol, phenol, furan compounds, and chemicals that add value to pyrolysis. (Ouattara et al. 2021). Stepwise pyrolysis uses the lignin technique with a catalyst via Py GC-MS at 260-650ºC for the bio-oil process and produces phenolic compounds (Shao. et al. 2017). The link between the food sector and cocoa waste processing by calculating the value of carbon emissions from pyrolysis technology, an innovative and sustainable product

National cocoa plantations have not yet reached optimal levels, including a decrease in cocoa plant productivity due to the low quality of cocoa beans due to incomplete post-harvest handling and most of the cocoa beans produced have not been fermented, lack of maintenance and pest attacks and there has been no effort to reduce the carbon emissions on cocoa plantations. Innovative use of cocoa bean production can be done through fermentation, drying, and extraction processes. Using cocoa waste for cacao tea as a herbal drink product is perfect for development. This research has yet to be carried out, especially on cocoa waste for cacao tea products, and carbon emissions resulting from the pyrolysis process and processing of cocoa waste can be calculated in carbon content to reduce pollution. Environment to support the G20 program. So that cocoa production can be developed in an integrated, innovative, and sustainable manner. This research aims to apply the production of cacao tea as a herbal drink product derived from cocoa leaves, which has been carried out by separating potential chemical compounds. 2. This policy will impact the behaviour of industry and society in producing and consuming products with low greenhouse gas emissions.

RESEARCH METHODS

Materials and Instruments

The raw materials come from cocoa waste, which comes from cocoa leaves from the three districts of Pinrang, Polman and Kolaka); the tools used are a pH meter, Soxhlet extractor, pyrolysis reactor, Bomb colourimeter, thermometer, Erlenmeyer, and glassware.

Methods

Proximate analysis of coca leaves in the form of caffeine, catechin and dietary fibre levels. Perform TGA/DTG analysis for thermal decomposition and Tensile strength testing (Stress and Strain). Cocoa Liquid Smoke analysis was conducted using GC MS, followed by FT IR and cellulose, hemicellulose, lignin, and water content analysis. The carbon content of biomass is obtained by calculating the carbon content of liquid smoke and charcoal at each pyrolysis temperature.

RESULTS AND DISCUSSION

The raw material comes from cocoa leaves with a 40-60 Mesh powder size. They are dried until the water content reaches 10-20% (w/w). The results of this study showed that the proximate analysis of Pinrang Regency cocoa leaf extract showed that the phenol content was 756.80 mg/Kg, the catechin content was 856.22 mg/Kg, the glucose content was 10.55% and the caffeine content was 323.55 mg/Kg. , proximate analysis of cocoa leaf extract from Polman Regency shows that the phenol content is 655.67 mg/Kg, catechin content is 722.63 mg/Kg, glucose content is 9.75% and caffeine content is 323.55 mg/Kg, proximate analysis of the extract Kolaka Regency cocoa leaves showed that the phenol content was 529.52 mg/Kg, the catechin content was 615.71 mg/Kg, the glucose content was 6.68% and the caffeine content was 329.56 mg/Kg. Based on the results of this research, the caffeine content from Pinrang Regency cocoa leaves is higher than the caffeine content from Polman and Kolaka Regencies. The bioactive chemical compounds produced from the pyrolysis of banana peels to produce liquid smoke and tar are 68.6% acid, 62.5% alcohol, 27.6% ketones, 25.7% phenol and 21.8% furans (Omulo et al., 2017). With a large composition of bioactive chemicals, such as organic acids, phenols, ketones, aldehydes, furans and guaiacol, pyrolysis liquid protects the wood from fungi and termites (Temiz et al., 2013). GC-MS results show that liquid smoke contains various types of compounds found in pine waste condensate liquid smoke, including acids, ketones, alcohol), phenols, esters, guaiacol, aldehydes and furfural (Wijaya et al., 2019)

Figure 1. Flavonoid content of cocoa leaf extract, for Pinrang and Polman Regencies

Cocoa leaf extract, for Pinrang Regency, has a total flavonoid content of 6.01% w/w and antioxidant IC50-DPPH = 18.10 ppm, while cocoa leaf extract, for Polman Regency, has a total flavonoid content of 6.47% w/w and antioxidant IC50-DPPH = 10.23 ppm, Cocoa leaf extract, for Kolaka Regency, total flavonoids of 35.10% w/w and antioxidant IC50-DPPH = 18.38 ppm, Utilization of cocoa leaves from Kolaka Regency has the best antioxidant content compared to the District. Pinrang and Polman for cacao tea products as herbal drink products are excellent to develop; no one has carried out this research, especially from cocoa leaf waste for cacao tea products; the development of cocoa production can be done in an integrated, innovative and sustainable manner. The research results show that. The natural organic material in sweet cherry (Prunus avium L.) leaves contains hemicellulose, cellulose and lignin, essential oils, crude fat, crude protein and minerals (Dziadek et al., 2018). Phenol production is produced from the pyrolysis of cocoa pod skin, which is used as an antiseptic (Wijaya et al., 2020). The chemical properties and morphological characteristics of cocoa pod shells can be used as an alternative fibre material for making pulp and paper. (Daud et al. 2013)

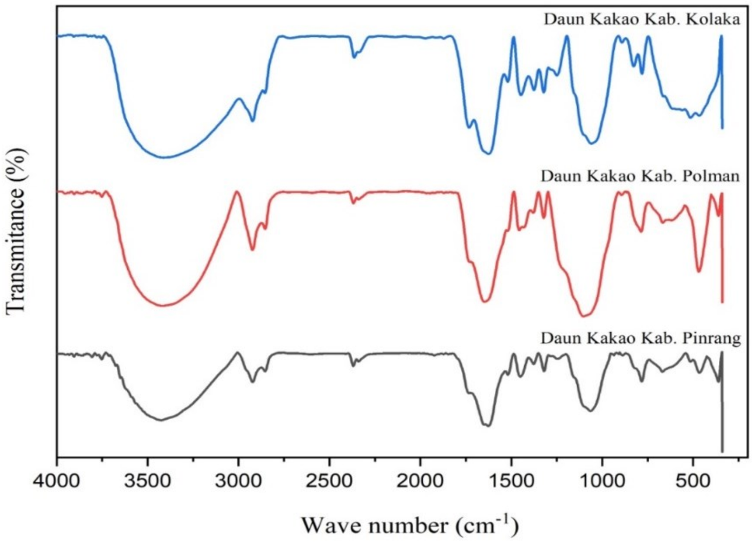

Figure.2 Results of FT IR analysis for cocoa leaves in 3 regions (Pinrang, Pinrang and Kolaka Regencies)

The results of this invention show that FTIR analysis for Pinrang Regency cocoa leaves, an absorption of 1488 cm-1, shows the presence of C-H bending alkane groups. A wave number of 1625 cm-1 shows an alkene group -C=C-stretching, a wave number of 1734.01 cm -1 indicates the presence of ketone, aldehyde, carboxylic acid groups, and the wave number 2922.16 cm-1 indicates the aliphatic stretching C-H group. The wave number 3423.65 cm-1 indicates the presence of a hydroxyl group (O-H). The results of this invention show that FTIR analysis for Kolaka Regency cocoa leaves, absorption of 1446.61-1375.25 cm-1 indicates the presence of C-H bending, alkane groups, then the wave number 1626.06 cm-1 indicates the alkene group -C=C- stretching, the wave number 1732.06 cm-1 indicates the presence of ketone, aldehyde, carboxylic acid groups, and the wave number 2922.16 cm-1 indicates the aliphatic stretching C-H group. The wave number 3423.65 cm-1 indicates the presence of a hydroxyl group (O-H).

Table.1. Functional group composition of Cocoa leaves for Pinrang, Polman and Kolaka Regencies

Wave number (cm-1)	Functional groups	Compound class	Daun kakao Kabupaten Pinrang	Daun kakao Kabupaten Polman	Daun kakao Kabupaten Kolaka
3600-3200	-OH streching	Polymeric OH, water content	3423,65	3419,19	3412,08
3100-3010	C-H streching	Aromatic ring	-		
3000-2800	C-H streching	Aliphatic	2922,16 2854,65	2922,16	2922,16
1775-1650	C=O streching	Ketones, Aldehydes, carboxylic acid	1734,01	1728,21	1732,06
1680-1575	C=C streching	Alkenes	1625	1647,21	1626,06

1490-1325	C-H bending	Alkanes	1488 1377,17	1456,26 1379,1	1446,61 1375,25
1300-950	C-O streching	Alcohol,phenol,ester		1103,28	1058,92

The results of this research show that FTIR analysis for Polman Regency cocoa leaves, absorption of 1456.26-1379.1 cm-1 indicates the presence of C-H bending, alkane groups, then the wave number 1647 cm-1 indicates the alkene group -C=C-stretching, The wave number 1726.29 cm-1 indicates the presence of ketone, aldehyde, carboxylic acid groups, and the wave number 2922.16 cm-1 indicates the aliphatic stretching C-H group. The wave number 3419.79 cm-1 indicates the presence of a hydroxyl group (O-H). The results of this study are supported by [8]. that FTIR analysis for Coir Pith Black Liquor (CBL) shows 3420 cm-1 indicating OH, absorption of 1610 cm-1 indicates the presence of C-H lignin groups, absorption of 1247 cm-1 indicates the presence of C-O groups and 586-891 cm-1 indicates the presence of C groups =C-H (aromatic H).

CONCLUSIONS

The research findings indicate that the caffeine content in cocoa leaves from the Pinrang Regency is higher than that found in the Polman and Kolaka Regencies. Additionally, cocoa leaves from Kolaka Regency exhibit the highest antioxidant levels among the three areas. Consequently, cacao tea products derived from cocoa leaves in Pinrang and Polman Regencies present excellent opportunities for development as herbal beverages.

ACKNOWLEDGMENTS

Thank you for funding assistance through the Directorate of Advanced Indonesian Innovation Research 3 and the Chair of the Institute for Research and Community Service, Makassar State University for collaboration in this research activity.

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