Study of Antioxidant Liquid Smoke Cacao Fruit Peel Waste at Different Water Content and Pyrolysis Temperatures

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Abstract: Cocoa pod husks are agricultural waste whose management has not been done much. This waste is only used as animal feed and many are left alone. This research uses cocoa waste as raw material for making liquid smoke. This study aims to determine the antioxidant activity of liquid smoke of cocoa pod skin with differences in raw material water content and pyrolysis temperature. The moisture content of the raw material for cocoa pods is around 10-25% and the pyrolysis temperature is 200 - 400°C. Antioxidant analysis using the DPPH method by calculating the IC_{50} value of the liquid smoke of cocoa pods. The results showed that liquid smoke with low moisture content of raw materials and high pyrolysis temperatures produced high antioxidant activity values. IC_{50} value of liquid smoke of cocoa pods ranged from 107.33 - 268.97 ppm and AAI values ranged from 0.186 to 0.466. Treatment of 10% water content and pyrolysis temperature of 400°C is the best treatment.

1 INTRODUCTION

Cocoa is an agricultural product from the plantation sector which is a leading commodity in the Indonesian state. The results of processing cocoa from plantation land produce biomass waste in the form of cocoa pods, cocoa leaves and cocoa wood. One of the waste originating from plantation products is the cocoa pods which have only been thrown away and burned (Wijaya, Wiharto and Anwar, 2017). At the time of harvest also produced fruit skins with volumes almost the same as seeds (Mulyatni, Budiani and Taniwiryono, 2012).

Cocoa pod waste produced in large quantities will be a problem if not handled properly because the production of solid waste reaches more than 60% of the total fruit production, this will be a great potential to pollute the surrounding environment (Harsini and Susilowati, 2010).

Cocoa pods contain phenolic compounds and flavonoids (Jusmiati, Rusli and Rijai, 2016). The polyphenol content includes cinnamic acid, tannin, pyrogalol, quercetin, resorcinol and epikatekin-3-galat (Fapohunda and Afolayan, 2012). This compound is a natural antioxidant found in the skin of cocoa fruit.

Seeing the potential of the cocoa pod skin, this study utilizes the cocoa pod skin to produce liquid smoke. Liquid smoke is the result of condensation process or condensation of steam from combustion directly or indirectly using materials that contain lignin, cellulose, hemicellulose, and hydrocarbon compounds (Kondo, Gunawan and Rizke, 2017). The purpose of this study is to utilize the cocoa pods as raw material for making liquid smoke and to know the antioxidant activity of liquid smoke produced.

Based on the description above, it has been tested the antioxidant activity and liquid smoke of cocoa pod skin using DPPH method (2,2-diphenyl-1-pikrihidrazil) by calculating the value of inhibition concentration of 50% (IC_{50}).

2 MATERIALS AND METHODS

The research has been carried out at the Agricultural Product Technology Laboratory of the Ekasakti University and the Agricultural Microbiology and Biotechnology Laboratory of the Andalas University in April - May 2019. This research is an explorative study with differences in the level of water content of

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raw materials and the temperature of liquid smoke pyrolysis.

Liquid smoke can be obtained by using a pyrolysis tool. The material used in this study is the cocoa shells that have been regulated according to the water content and the process of pyrolysis is carried out to obtain liquid smoke of cocoa pods, methanol p.a, distilled water, DPPH.

The equipment used is a series of pyrolysis apparatus, oven, UV-Vis spectrophotometer, 250 ml erlenmeyer, 500 ml cup glass, test tube, test tube rack, 1 ml micro pipette, 0.1 ml micro pipette tissue and spray bottles.

2.1 Research Procedure

2.1.1 Sample Preparation

The raw materials in this study are the cocoa pods obtained from Padang Pariaman and Lubuk Minturun Regencies, Padang City. The procedure for making liquid cocoa pod smoke includes: Washing cocoa shells, reducing cocoa shells with a diameter of 5-9cm. Then the cocoa skin is dried by being dried in the sun until the water content reaches 25%, 20%, 15%, and 10%.

2.1.2 Pyrolysis (Budaraga et al., 2016)

Each sample of cocoa shell was weighed as much as 1000 g based on treatment starting from water content (10%, 15%, 20%, and 25%) and then put into a pyrolysis reactor equipped with a series of condensing equipment and condenser coolers. The reactor is equipped with a temperature gauge. Electric heating in the form of a reactor envelope with a current of 10 amperes. Pyrolysis runs at temperatures of 200-400 ° C. Pyrolysis is stopped after no liquid smoke has dripped into the shade. The results of pyrolysis in the form of liquid smoke are collected in dark bottles and then left standing, then filtered using filter paper and activated carbon and gauze to separate tar and liquid smoke. After being stored for 1 (one) week, an analysis of antioxidant activity was carried out.

2.1.3 Determine the Antioxidant Activity of the DPPH Method (Tristantini et al., 2016)

Prepare 1 ml of liquid smoke of the cocoa pod skin and make each parent solution. Furthermore, dilution using PA methanol solvent by making variations in the concentration of 50 ppm, 100 ppm, 150 ppm, 200 ppm and 250 ppm in each sample. Prepare a stock solution of DPPH 50 ppm. The DPPH stock solution is prepared by dissolving 5 mg of DPPH solid into 100 ml of methanol PA. Then a comparison solution is prepared, a control solution containing 2 ml of methanol PA and 1 ml of a 50 ppm DPPH solution. For the test sample, 2 ml of each sample solution is prepared and 2 ml of DPPH solution is prepared respectively. Then, it was incubated for 30 minutes at 27 ℃ until the discoloration of DPPH activity occurred. All samples, ie incubated liquid cocoa smoke smoke samples were tested for their absorbance values using a UV-Vis spectrophotometer at a wavelength of 517 nm.

Analysis of DPPH method antioxidant testing is done by looking at the color changes of each sample after incubation with DPPH. If all DPPH electrons are paired with electrons in the extract sample, the sample color changes from dark purple to bright yellow. Then the absorbance value was measured using a UV-Vis spectrophotometer at a wavelength of 517 nm.

3 RESULTS AND DISCUSSION

The DPPH method is an effective and fast colorimetric method for estimating antiradical / antioxidant activity. This chemical test is widely used in natural product research to isolate antioxidant phytochemicals and to test the capacity of extracts and pure compounds to absorb free radicals. The DPPH method is used to measure a single electron as a hydrogen transfer activity as well as to measure the inhibitory activity of free radicals (Prakash, Rigelhof and Miller, 2001).

Antioxidant activity by DPPH method is expressed by 50% inhibition concentration or IC50, which is a sample concentration that can inhibit DPPH activity by 50%, so the value of 50 is substituted for the value of y. After substituting the value of 50 on the value of y, we will get the value x as the value of IC50.

The results showed that the moisture content of raw materials in making liquid smoke affects the IC50 value of the resulting liquid smoke. Low water content results in lower IC50 values, which means high antioxidant activity values. Similarly, the pyrolysis temperature used, the higher the pyrolysis temperature, the lower the IC50 value obtained. A compound is said to be a very strong antioxidant if the IC50 value is less than 50, strong (50-100), moderate (100-150), and weak (151-200). The smaller the IC50 value the higher the antioxidant activity (Badarinath et al., 2010). IC50 values of liquid smoke of cocoa pod peels are listed in Table 1.

Table 1: IC_{50} values of liquid smoke of cocoa pod husks.

Treatment	Temp	Antioxidant IC_{50} (ppm)	AAI
Water level 10%	200°C	156,04	0,32
Water level 15%		189,33	0,26
Water level 20%		218,56	0,23
Water level 25%		268,99	0,19
Water level 10%	300°C	148,54	0,34
Water level 15%		162,27	0,31
Water level 20%		170,67	0,29
Water level 25%		191,92	0,26
Water level 10%	400°C	107,33	0,47
Water level 15%		109,85	0,46
Water level 20%		114,87	0,44
Water level 25%		165,29	0,30

Based on Table 1, it can be seen that the IC50 value of liquid smoke of cocoa pod skins ranges from 107.33 - 268.97 ppm. This value is included in the moderate to weak group. From the results of the study it was found that liquid smoke with pyrolysis temperature of 200 OC at 10-25% raw material moisture content obtained IC50 values ranged from 156.04 - 268.97 ppm and included in the weak category. At pyrolysis temperature 300 OC, IC50 values ranged from 148.54-191.92 ppm. At the moisture content of raw materials 10% included in the medium category, while at the moisture content of raw materials 15-25% included in the category of weak. At pyrolysis temperature of 400 OC, IC50 values ranged from 107.33-165.29 ppm. In the moisture content of raw materials 10-20% included in the medium category, while the moisture content in raw materials 25% included in the category of weak. According to (Chen, 2014), the results of lignin pyrolysis will determine the stability of samples of the phenolic compounds making up liquid smoke. The compounds in liquid smoke vary, depending on the type of material, water content and temperature used during the pyrolysis process. Antioxidant testing is in Figure 1.

In this study also observed the value of Antioxidant Activity Index (AAI) which aims to determine the antioxidant activity index of liquid smoke of cocoa pods. From the research results obtained AAI values ranged from 0.186 to 0.466. This value is included in the weak category. This is consistent with the statement (Scherer and Godoy, 2009); (Faustino et al., 2010) which stated antioxidant

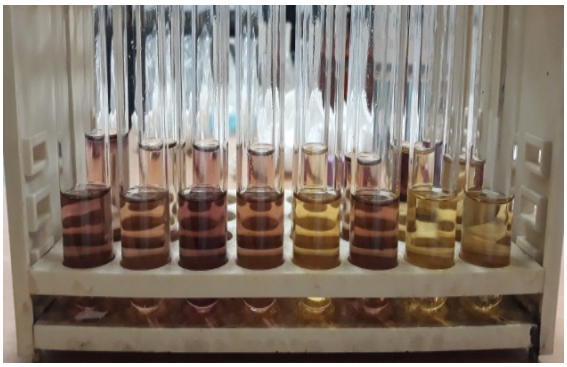

Figure 1: Testing the antioxidant activity of liquid smoke of cocoa pod skin DPPH method.

activity based on AAI values was said to be weak as antioxidants if the AAI value <0.5. Moderate antioxidant activity if the AAI value is 0.5 - 1. Strong antioxidant activity if the AAI value is 1.0 - 2.0. Antioxidant activity is very strong if the AAI value> 2.0.

When the purple DPPH solution meets the electron donor material, the DPPH will be reduced, causing the purple color to fade and replaced by the yellow color from the picril group. A decrease in absorbance and color change in the test sample indicates the presence of electrons or hydrogen atoms donated by the test solution as an antioxidant to DPPH. The higher concentration of the test solution means that more electrons or hydrogen atoms will be donated to DPPH free radicals (Sumpono, Putri and Sari, 2017). The DPPH radical reduction reaction by antioxidants is shown in Figure 2.

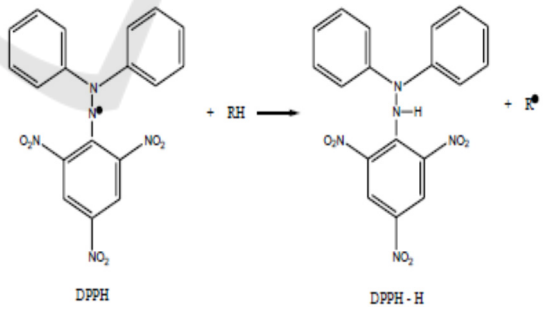

Figure 2: DPPH radical reduction reaction by antioxidants.

Cocoa pods are known to have secondary metabolites which act as antioxidants. According to (Loppies and Yumas, 2014), cocoa pods contain a number of compounds from the polyphenol and flavonoid classes. The presence of phenol groups with hydroxyl groups from polyphenols and flavonoids allows this compound to be a preservative. In addition (Burhanuddin, 2004), reported cocoa skin

contains tannins, polyphenols, flavonoids, alkaloids and steroids which are active components that are very beneficial for health.

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4 CONCLUSION

The results showed that liquid smoke with low moisture content of raw materials and high pyrolysis temperatures produced high antioxidant activity values. IC50 value of liquid smoke of cocoa pods ranged from 107.33 - 268.97 ppm and AAI values ranged from 0.186 to 0.466. Treatment of 10% water content and pyrolysis temperature of 400OC is the best treatment.

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