

# Pyrolysis\_and\_Characterization \_of\_Liquid\_Smoke\_from\_Cacao. pdf *by*

---

**Submission date:** 11-Mar-2022 11:18AM (UTC+0800)

**Submission ID:** 1781605572

**File name:** Pyrolysis\_and\_Characterization\_of\_Liquid\_Smoke\_from\_Cacao.pdf (616.68K)

**Word count:** 3259

**Character count:** 16863

**PAPER · OPEN ACCESS**

## Pyrolysis and Characterization of Liquid Smoke from Cacao Pod Husks

To cite this article: R E Putri *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **327** 012011

View the [article online](#) for updates and enhancements.

## Pyrolysis and Characterization of Liquid Smoke from Cacao Pod Husks

R E Putri<sup>1(1)</sup>, A Kasim<sup>2</sup>, Emriadi<sup>3</sup>, and A Asben<sup>2</sup>

<sup>1</sup>Postgraduated Doctoral Program, Andalas University, Padang

<sup>2</sup>Faculty of Agricultural Technology, Andalas University, Padang

<sup>3</sup>Faculty of Mathematics and Natural Science, Andalas University, Padang

Corresponding author:rahmistppmedan@gmail.com

**Abstract.** Cacao pod husks were treated by the pyrolysis process to produce liquid smoke. Cacao pod husks can be utilized to produce their useful chemicals by pyrolysis. The reactor of pyrolysis used is made from cylindrical steel reactor with a small capacity, rust resistant and portable. A sample was pyrolyzed for 5 hours. The parameters measured to determine the quality of liquid smoke are the yield of pyrolysis products, pH, the concentration of acetic acid and phenol concentration. The quality of liquid smoke also tested by looking at the chemical components of liquid smoke by using gas chromatography-mass spectroscopy (GC-MS). The pyrolysis process produced products in the form of liquid smoke, charcoal, tar, and gas. The yield of pyrolysis products are 14.77; 40.43; 1.67; and 43.13%, respectively. Liquid smoke obtained has a pH of 3.2 levels, acetic acid 9.306 ppm, and phenol levels 1.688 ppm. GC-MS measurement result showed that methanol, acetic acid, and acetol are the highest concentration of chemical obtained in liquid smoke.

### 1. Introduction

These Liquid smoke is the process of vapors condensation from the combustion of raw materials which containing lignin, cellulose, hemicellulose and other carbon compounds. Liquid smoke is known to be useful as a preservative and latex coagulation material. This is because of the functional properties of liquid smoke such as antifungals, antibacterials, and antioxidants. Sources of liquid smoke producing can come from coconut shells [1], palm oil waste [2], waste wood-based composites [3], and the waste of fruit and cocoa leaf skin [4]. In this study, Indonesian waste of cacao is used, which the cacao production ranks is third highest in the world [5].

Cacao is an industrially important plant because it produces cocoa beans which are the basic ingredients in making chocolate as a popular food in the world. However, in addition to the production of cocoa beans, are also produced the waste of cacao pod husks. According to [6] every 1 ton of dry cacao production produced 10 tons of wet cacao husks. This cacao pod husks cause odors that are not good for the environment. Cacao pod husks waste is only used as a substitute for firewood, animal feed, or as compost. To increase economic value and reduce the risk of environmental impact, technology is needed to process them.

Cacao pods husks potentially to be used as liquid smoke because they contain lignocellulose. The chemical composition of cacao pods husks, are lignin 60.67%, holocellulose 36.47%, alpha cellulose 17.57% and hemicellulose 18.90% [4]. While the research from [6] published that the composition of



Content from this work may be used under the terms of the [Creative Commons Attribution 3.0 licence](https://creativecommons.org/licenses/by/3.0/). Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Published under licence by IOP Publishing Ltd

cacao pods is cellulose 35%, hemicellulose 10.8-11%, lignin 14.6%, pectin 6.1%, crude fiber 22.6-32.5%, crude protein 5.9-7.7% and ash 9.1-10.1%. Pyrolysis can be used to decompose organic compounds from biomass to produce various products such as liquid smoke, biochar, tar, and gas. Compared to the combustion process pyrolysis requires low temperatures and results in low air pollution emissions [7].

In this study, cacao pod husks were converted by pyrolysis. The pyrolysis process uses a reactor made from cylindrical steel reactor. The pyrolysis equipment used is applicable and can scale up to a larger scale or industrial scale.

## 2. Material and Methods

### 2.1. Materials

Cacao pod husks used comes from the cacao plantations of West Sumatra, Indonesia. The cacao pods were separated from beans, and then sun-dried for a week. Before being fed into the pyrolyzer, the cacao pod was reduced in size about 3 cm x 4 cm. The water content of the cacao pod was analyzed using Moisture Meter.

### 2.2. Pyrolysis process of the cacao pod husks [8]

The pyrolysis of cacao pod husks was carried out in cylindrical steel reactor. The length and diameter of the pyrolyzer were 38 cm and 28 cm, respectively. 3 kg of cacao pod husks were placed in the pyrolyzer. The sample is pyrolyzed for 5 hours until there is no more liquid smoke dripping into the container.

### 2.3 pH measurement of liquid smoke

Measuring the pH of liquid smoke using a pen type pH meter, pH-009 (I) before measuring, the pH meter is calibrated first.

### 2.4 Measurement of total phenol

Total phenol levels were determined by the Folin-Ciocalteu method. Standard gallic acid curves are made with a variation of 4 concentrations; 250; 500; 1000; and 1250 ppm and absorbance measured at  $\lambda = 765$  nm. The sample measurement procedure was carried out by inserting 1 mL of sample and 1 mL of Folin-Ciocalteu reagent into a 10 mL flask. The mixture is then shaken for five minutes. After that, 7.5 %  $\text{Na}_2\text{CO}_3$  is added aligned with distilled water to a volume of 10 mL. The solution was incubated for 1 hours at room temperature. Absorbance measured at  $\lambda = 765$  nm using a Shimadzu UV 1800 spectrophotometer. Total phenol levels were determined by the Folin-Ciocalteu method. Standard gallic acid curves are made with a variation of 4 concentrations; 250; 500; 1000; and 1250 ppm and absorbance measured at  $\lambda = 765$  nm. The sample measurement procedure was carried out by inserting 1 mL of sample and 1 mL of Folin-Ciocalteu reagent into a 10 mL flask. The mixture is then shaken for five minutes. After that, 7.5 %  $\text{Na}_2\text{CO}_3$  is added aligned with distilled water to a volume of 10 mL. The solution was incubated for 1 hours at room temperature. Absorbance measured at  $\lambda = 765$  nm using a Shimadzu UV 1800 spectrophotometer.

### 2.5 Measurement of total acid by titration [9]

As much as 2 mL of liquid smoke was added to aquadest until the volume was 100 mL. Then add phenolphthalein indicator 3 drops. Titrate with 0.1N NaOH until the solution change colour to pink. Record the volume of NaOH used for titration. Calculate the acid content in liquid smoke with the formula:

$$\text{Acid Levels} = \frac{\text{mL titrant} \times N.\text{NaOH} \times \text{Acetic Acid (g/mol)}}{\text{Liquid Smoke (mL)}} \quad (1)$$

Information:

mL titrant

= NaOH volume for titration

N NaOH = Normality of solution  
 Molecular Weight of acetic acid = 60 g/mol

### 2.6 Analysis of Liquid Smoke Chemical Content

Liquid smoke prepared from pyrolysis was qualified by Gas Chromatography-Mass Spectrometry (GC-MS). GC-MS brand Shimadzu QP 2010 plus with the operational condition of injection temperature of 210 ° C, the column temperature of 100 ° C, the temperature rise of 10°C/min, helium carrier gas, the pressure of 111 KPa, Rtx\_5MS column type (30m x 0.25mm).

## 3. Result and Discussion

### 3.1. Pyrolysis Process of Cacao Pod Husks

The raw material is put into a pyrolyzer with the amount of material filled as much as 2/3 of the height of the pyrolyzer. The material in the pyrolyzer is heated so that the phase changes to vapor/gas. Steam/gas that has come out of the material will flow to the top of the pyrolyzer and exit through the pipe then flow into the condenser for the condensation process. Liquid smoke that has changed phase into a liquid phase goes out through the condenser and enters the storage tube. Charcoal as residue will remain in the pyrolyzer.

The products of this pyrolysis process are liquid smoke, tar, charcoal, and gas. The yield of pyrolysis products is shown in Table 1. The yield of liquid smoke from cacao pod husks is 14.77%. The biggest result from pyrolysis is charcoal with yield 40.43%. While from the results of measurements of water content and cacao pod husks density, the results were 14.34% and 0.8 g/mL respectively. This is caused by the water content in the raw materials which only sun-drying, not oven drying before pyrolysis. The yield of liquid smoke produced by the pyrolysis process will be affected by the raw materials used, including water content and density of raw materials.

Pyrolysis at high and long temperatures will cause the formation of liquid smoke to decrease because the temperature in the cooling water increases so that the smoke produced does not condense completely. The condensation process in this study does not use continuously water flowed on the cooling system so the condensation process does not take place perfectly. This condition is in accordance with [10] that liquid smoke by wood material processes can be produced maximally if the condensation process happens perfectly. The percentage of yield also depends on the pyrolysis temperature used and characterization of raw material. Besides climate, season, the age of the plant, type of the plant, raw materials and the way of burning also influence the liquid smoke yield on pyrolysis process [11].

**Table 1.** Yield of pyrolysis products from cacao pod husks

Biomass	The weight of Material (kg)	Temp Max (°C)	Pyrolysis Products			
			Liquid Smoke (%)	Ter (%)	Charcoal (%)	Gas (%)
Cacao pod husks	3	147	14.77	1.67	40.43	43.13

### 3.2. Characterization of Liquid Smoke

#### 3.2.1. Acidity (pH)

Liquid smoke products from the pyrolysis process contain acidic compounds. pH value is one of the quality parameters of liquid smoke. Measurement of pH value in the liquid smoke is to determine the level of pyrolysis decomposition of raw materials. The measurement results of the pH value of the liquid smoke from cacao pod husks are 3.2. The pH value obtained from the pyrolysis process at 147°C is higher than the liquid smoke of rubber fruit shells which pyrolyzed at 300°C is between 1.96-2.65 [12]. High temperatures will cause the compounds in the rubber shell to break down into acidic compounds [13]. This low pH value indicates that liquid smoke quality is high, especially in terms of

as a food preservative. Low pH value has an effect on long-lasting value and storage power of the smoke product [14].

### 3.2.2. Total Acetic Acid

From the measurement of the liquid smoke's pH value, it can be seen that the liquid smoke of cacao pod husks contains acetic acid compounds. The level of acetic acid from the liquid smoke in this study was 9.306 ppm. This acidic liquid smoke was the major contribution to food preservation activity that effects its storage time and flavor. The quality of liquid smoke influenced by the composition of chemical compounds in liquid smoke. The chemical compounds in liquid smoke influenced by pyrolysis conditions and type of raw material [15]. According to [16], bio-oil compounds contain hydroxyl (-OH) or carboxylic (-COOH) groups.

### 3.2.3. Phenol Levels

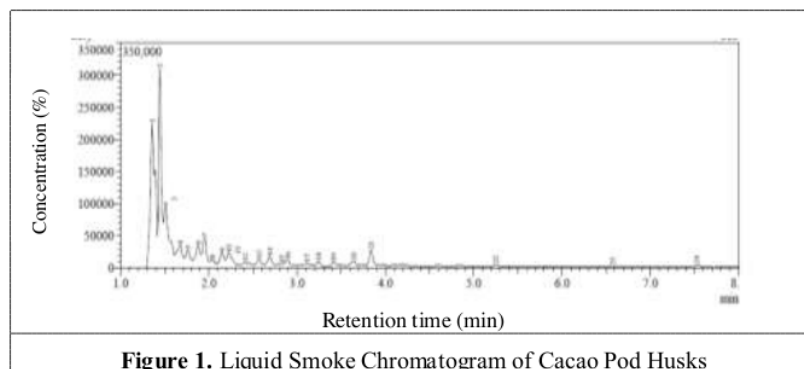
In the liquid smoke of cacao pods husks, contain phenol groups which derived from lignin degradation. Identification of phenol in liquid smoke is expected to represent the quality criteria so that the target user is more appropriate. Determination of phenol in this study using UV: 1800 spectrophotometer at 725 nm. Total phenol content obtained from the liquid smoke of cacao pods husks is 1.688 ppm. The phenol content obtained was lower than the phenol content of the 2.5098 ppm rubber fruit shell which was pyrolyzed at 300°C [12].

The temperature of cacao pods husks pyrolysis in the study was only 147°C. This low temperature causes lignin to not decompose completely. The quality of liquid smoke produced depends on the characteristics of the raw material and the temperature achieved during the pyrolysis process [15]. According to [13], the decomposition of chemical components in wood gradually decomposes hemicellulose starting at 200°C, at 240°C decomposition of cellulose into pyrolygnite solution, CO, and CO<sub>2</sub>; at a temperature of 240-400°C the decomposition process of cellulose and lignin occurs into pyrolygnite solution, CO, CH<sub>4</sub>, H<sub>2</sub> gas and more tar and at temperatures above 400°C aromatic layer formation occurs.

### 3.2.4. Components of Liquid Smoke

The components in liquid smoke were assumed to consist of thermally degraded products of biomass components such as cellulose, hemicellulose, and lignin. The components of liquid smoke chemistry from cacao pod husks were analyzed using GC-MS. The chromatogram can be seen in Figure 1.

Figure 1 shows that liquid smoke from pyrolysis of cacao pod husks shows the separation of chemical components through the chromatogram peaks that appear. The peaks began at a retention time of 1.359 to 7.524 minutes and based on system data identified as many as 24 compounds in the liquid smoke of cacao pod husks. These compounds are thought to have names and concentrations as listed in Table 2.



**Table 2.** The chemical content of liquid smoke from cacao pods husks

No.Peak	Retention Time (minute)	Compound	Concentration (%)
1	1.359	Methanol	25.78
2	1.445	Acetic Acid	20.57
3	1.511	Acetol	10.15
4	1.764	Cyclopentanone	3.14
5	1.879	2-Cyclopentene-1-one	3.70
6	1.953	Furfuryl alcohol	4.43
7	2.040	3-Methylpyridine	1.21
8	2.148	Butyrolactone	2.42
9	2.227	2-Methyl-2-cyclopentenone	2.60
10	2.414	3,4-Dimethylpyridine	0.83
11	2.568	3-Methyl-2-cyclopentenone	1.37
12	2.690	Benzene sulfonic acid	1.52
13	2.825	2,3,3-Trimethyl-1,4-pentadiene	0.45
14	2.896	Tetrahydrifurfuryl alcohol	0.77
15	3.110	Corylon	0.35
16	3.242	2,3-Dimethyl-2-cyclopentene-1-one	0.63
17	3.441	o-Cresol	1.49
18	3.838	phenol	1.97
19	5.250	2-Methoxy-4-methylphenol	0.23
20	6.574	p-Ethylquaiacol	0.08
21	7.524	2,6-Dimethoxyphenol	0.39

From GC-MS spectra data, the dispersed liquid smoke of cacao pod husks consist of 24 components. The highest compounds in liquid smoke was Methanol 25.78%, Acetic Acid 20.57%, and Acetol 12.40%. From 24 compounds identified in the liquid smoke of cocoa pods, there was 1 carboxylic acid group compound, 4 alcoholic compounds, 7 ketone group compounds, 4 phenol group compounds, 2 pyridine compounds, 1 benzene compound, 1 corylon, 1 butyrolactone and 3 unidentified compounds. This result is the decomposition of lignocellulose from cocoa pod husks which consists of cellulose, hemicellulose, lignin, and extractive substances. The decomposition of hemicellulose biomass was acetic acid, methanol, furfural, aldehydes, ketones, and o-acetyl groups [17].

Pyrolysis products from lignin are derivatives of phenol, guaiacol, and syringol [16]. This result is not much different from the material obtained by Mansur et al., (2014), that the chemical composition of liquid smoke from cacao pod husks is carboxylic acids, ketones, phenolic compounds, aldehydes, furans, benzenediols, heterocyclic aromatics, and heavy components. Meanwhile, the persistence of phenolics in liquid smoke from coconut shell from 2.48% to 23.40% at each varied temperatures [1]. The most chemical content in liquid smoke from the shell, away, and the length of palm oil is acetic acid and phenol [2].

#### 4. Conclusion

Cacao pod husks have the potential to be developed as liquid smoke containing useful chemicals. The pyrolysis process produced products in the form of liquid smoke, charcoal, tar, and gas. The yield of pyrolysis products are 14.77; 40.43; 1.67; and 43.13%, respectively. Liquid smoke has a pH of 3.2 levels, acetic acid 9.306 ppm, and phenol levels 1.688 ppm. GC-MS measurement result showed that methanol, acetic acid, and acetol are the highest concentration of chemical obtained in liquid smoke. To get a quality pyrolysis product is influenced by the operational conditions of pyrolysis. So that in this study there needs to be further developed in the heating process. The optimum temperature of pyrolysis is achieved to degrade lignocellulose biomass if condensation process happens perfectly.

## 5. References

- [1] S. Yuniningsih and S. P. A. Angraini, 2013, "Characterization of Liquid Smoke from Coconut Shell to Be Applied as Safe Food Preservatives for Human Health," vol. 3, no. 2, pp. 1–5,
- [2] A. G. Haji, 2013 "Komponen Kimia Asap Cair Hasil Pirolisis Limbah Padat Kelapa Sawit," *J. Rekayasa Kim. dan Lingkung.*, vol. 9, no. 3.
- [3] Y. Feng, S. Chen, and J. Mu, 2010. "Characterization of Products from Pyrolysis of Waste Wood-based Composites Containing Urea-formaldehyde Resins," pp. 185–189.
- [4] M. Wijaya, 2014, *Pemanfaatan limbah kakao sebagai bahan baku produk pangan*. Jurusan Kimia FMIPA Univ. Negeri Makasar.
- [5] Departemen Perindustrian, 2007, "Gambaran Sekilas Industri Kakao," [Online]. Available: <https://kemenperin.go.id/290/Paket-Informasi-Kakao>.
- [6] D. Mansur, T. Tago, and H. Abimanyu, 2014, "Conversion of Cacao Pod Husks by Pyrolysis and Catalytic Reaction to Produce Useful Chemicals," *Biomass and Bioenergy*, vol. 66, no. July, pp. 275–285.
- [7] D. Czajczyńska *et al.*, 2017, "Potential of pyrolysis processes in the waste management sector," *Therm. Sci. Eng. Prog.*, vol. 3, pp. 171–197.
- [8] R. E. Putri, A. Kasim, Emriadi, and A. Asben, 2018, "Characterization Of Liquid Smoke From Coconut Shell Based Pyrolysis Process," in *International Conference on Advance and Scientific Innovation*.
- [9] Prasetyowati, M. Hermanto, and S. Farizy, 2014, "Pembuatan Asap Cair Dari Cangkang Buah Karet Sebagai Koagulan Lateks," *J. Tek. Kim.*, vol. 20, no. 4, pp. 14–21.
- [10] A. Demirbas, 2005, "Pyrolysis of ground beech wood in irregular heating rate conditions," vol. 73, pp. 39–43.
- [11] I. K. Budaraga, Y. Marlida, and U. Bulanin, 2016, "Liquid Smoke Production Quality from Raw Materials Variation and Different Pyrolysis Temperature," vol. 6, no. 3, pp. 306–315, .
- [12] Prasetyowati, A. P. Novianty, and M. R. Haryuni, 2014, "Pembuatan Asap Cair dari Limbah Kulit Singkong (Manihot Esculenta L. SKIN) untuk Bahan Pengawet Kayu," *Tek. Kim.*, vol. 20, no. 1, pp. 64–75.
- [13] C. E. Byrne and D. C. Nagle, 1997, "Wood monoliths-characterization," *Carbon N. Y.*, vol. 35, no. 2, pp. 267–273.
- [14] Haji, Abdul Gani, Z. A. Mas'ud, B. W. Lay, and S. H. Sutjaho, 2006, "Karakterisasi Asap Cair Hasil Pirolisis Sampah Organik Padat," *J. Agroindustrial Technol.*, vol. 16, no. 3, pp. 1–9, .
- [15] T. Nakai, S. N. Kartal, T. Hata, and Y. Imamura, 2007, "Chemical characterization of pyrolysis liquids of wood-based composites and evaluation of their bio-efficiency," vol. 42, pp. 1236–1241.
- [16] E. A. Smith, S. Park, A. T. Klein, and Y. J. Lee, 2012, "Bio-oil Analysis Using Negative Electrospray Ionization: Comparative Study of High-Resolution Mass Spectrometers and Phenolic versus Sugarc Components," .
- [17] D. Fengel and Gerd Wegener, 1984, *Wood: Chemistry, Ultrastructure, Reaction*. New York, .



# Pyrolysis\_and\_Characterization\_of\_Liquid\_Smoke\_from\_Caca...

---

## ORIGINALITY REPORT

---

**25%**

SIMILARITY INDEX

**16%**

INTERNET SOURCES

**20%**

PUBLICATIONS

**5%**

STUDENT PAPERS

---

## MATCH ALL SOURCES (ONLY SELECTED SOURCE PRINTED)

---

7%

★ A R Irfansyah, M P Koentjoro, Isdiantoni, I Ekawati, E N Prasetyo. "Utilization of Moringa oleifera seed waste as substrate in lipase production under different pretreatments", IOP Conference Series: Earth and Environmental Science, 2021

Publication

---

Exclude quotes  On

Exclude matches  < 1%

Exclude bibliography  On