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The Rate of Formation of Main Compounds in the Pyrolysis of Cinnamon Wood

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Abstract - Cinnamon wood has chemical and physical properties that can be optimized for use other than firewood. Lignocellulose compounds and a high density of raw materials would produce beneficial new compounds through pyrolysis. This research aims to make liquid smoke from cinnamon using pyrolysis and identify the concentration of the chemical compounds in liquid smoke and the rate of formation of the main compounds of liquid smoke. The Pyrolysis process was done twice, and the results were observed every 30 minutes. Chemical compounds of liquid smoke were analyzed using Gas Chromatography-Mass Spectroscopy (GC-MS). The crystal structure of charcoal produced from pyrolysis was analyzed using an X-ray diffractometer (XRD). The results showed that the liquid smoke, tar, charcoal, and the content lost after 150-minutes of pyrolysis was 28.94; 3.6; 42.92, and 24.54 %, respectively. Chromatography yielded ten peaks corresponding to compounds present in each stage of the process after 30 mins of pyrolysis up to 150 mins. GC-MS analysis showed five chemical compounds, methanol, acetic acid, furfural, phenol, and guaiacol, as always present during the pyrolysis processes. Methanol, acetic acid, and phenol reached their highest concentration at the end of pyrolysis. The rate of formation of these compounds, particularly the methanol, continuously increased during the pyrolysis process. The length of the pyrolysis was proportional to the speed of methanol formation and the total yield.

Keywords— Cinnamon; pyrolysis; liquid smoke; GC-MS analysis.

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I. INTRODUCTION

According to the FAO, in 2005, Indonesia was the second-largest cinnamon producer after China and exports cinnamon to many countries. In West Sumatra, cinnamon is the fourth largest plantation commodity after oil palm, rubber, and coconut. Based on data from the Central Statistics Agency in 2017, the total area of cinnamon plantations in West Sumatra is 21,222 hectares; total production is 15,878.99 tons/year and 8,987.48 tons/year for dry skin. When harvesting, only 15% of the dry bark is used, and the rest is thrown away.

The remaining wood is mostly used as firewood. However, to significantly increase farmers' income, it is necessary to find ways to optimize the use of all cinnamon trees, including leaf branches, twigs, and trunks. Currently, even the trunks have limited use as firewood as many of them are just discarded in the forest. Cinnamon wood has good physical and mechanical properties with a density of 0.63 g/cm³ and of a 13.73% moisture content [1]. He found the cinnamon wood could be categorized as a class II hardwood. Chemical

analysis of cinnamon wood has shown it contained 62.64% holocellulose, 49.39% cellulose, 26.39% lignin, 15.44% pentosan, 0.95% ash and 0.18% silica [2].

Based on these physical and chemical properties, especially the high density, cinnamon wood could be processed into liquid smoke using pyrolysis. The wood's hardness affects the pyrolysis product quality along with water content, particle size, temperature, time, material, and type of pyrolyzer [3]. Lignocellulose compound of raw materials would produce beneficial new compounds through pyrolysis [4],[5]. Cellulose pyrolysis produces glucose and acetic acid. Hemicellulose, which is composed of pentosan and hexose, will produce furfural, furans, and carboxylic acid. Lignin, which is composed of phenylpropane units, will produce phenolic compounds guaiacol and syringol through the pyrolysis process.

Liquid smoke produced from pyrolysis of hardwoods produces a more distinctive scent, has a richer aromatic compound content and more acidic compounds compared to that from softwood or a resinous wood [4], [6], [7]. Pyrolysis

of wood produces charcoal, tar, and non-condensable gas along with the liquid smoke. Therefore, this research pyrolyzed cinnamon wood and identified the chemical compounds in the liquid smoke products using GC-MS. The chemical analysis data was then processed to discover the rate of formation of the 5 main chemical compounds during the pyrolysis process.

II. MATERIAL AND METHODS

A. Sample Preparation

The cinnamon wood was obtained from firewood sellers in the city of Lubuk Sikaping, Pasaman district, West Sumatra province. The samples were cleaned, chopped into small pieces of about $3 \times 2 \times 0.1 \text{ cm}^3$, and solar dried for ± 1 week. 4 kg of this raw material was used to 2/3 fill tubes for pyrolysis. This was done to ensure optimal combustion in the pyrolysis tube because the combustion process is complete with limited oxygen.

B. Pyrolysis Process

The pyrolysis process used a pyrolyzer like that made by Putri et al., 2018, as shown in Figure 1. The pyrolyzer used a 12 kg gas cylinder body size made of steel plate sheets and hot-rolled coils [9]. The gas cylinder was modified by making a hole in the neck and adding a chimney to it. The diameter and length of the tubes were 28 cm and 38 cm. The smoke distribution pipe was made of a 2 mm thick 0.75-inch diameter stainless steel pipe 100 cm long. The condenser pipes were spiral pipes made of 2mm thick 0.75-inch diameter stainless steel with a 35 in diameter spiral coil and 9 spiral loops.

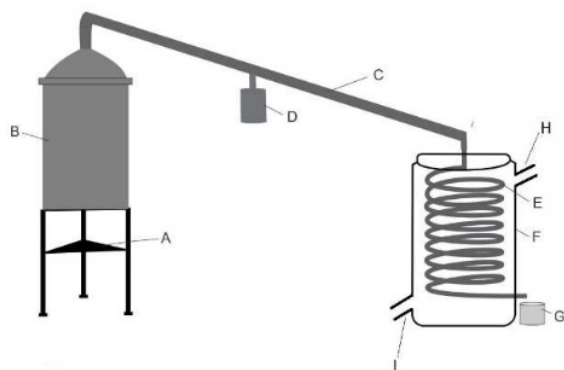


Fig. 1 Diagram of the pyrolyzer complete. A. heater, B. pyrolysis tube, C. smoke conduit pipe, D. tar container, E. condenser, F. condenser tub, G. liquid smoke container, E. inlet pipe, and F. outlet water pipe.

The liquid smoke production from cinnamon wood followed an experimental method. Each treatment was carried out with two replications with a pyrolysis duration of 30, 60, 90, 120, or 150 minutes. Four kilograms of the dried and chopped cinnamon wood were poured into the pyrolysis tube and then tightly sealed. The stove was then lit so that the material in the container would heat up and pyrolyze. Smoke came out of the container and went into the condenser pipe containing running water and was finally the condensed liquid dripped into the container. The pyrolysis duration was

calculated from the time the first drop of the liquid smoke formed until no more condensation liquid was dripping into the container.

C. Identification of Liquid Smoke Chemical Compounds Using Gas Chromatography-Mass Spectrometry

Liquid smoke samples were taken after the pyrolysis process of 30, 60, 90, 120, and 150 minutes. They were analyzed using GC-MS Shimadzu QP 2010 Plus at Bapelkes Gunung Pangil of Padang, West Sumatra. Operating condition was injection temperature of $210 \text{ }^\circ\text{C}$, column temperature of $100 \text{ }^\circ\text{C}$, the temperature rise of $10 \text{ }^\circ\text{C} / \text{minute}$, helium carrier gas 111 Kpa, and using a column type Rtx_5MS (30m x 0.25mm).

D. Pyrolysis Effectiveness

To determine the effectiveness of pyrolysis, the charcoal's carbon concentration produced after 150 minutes pyrolysis within was examined and then compared with the carbon concentration of cinnamon. The organic carbon concentration determination used the gravimetric method where the charcoal water concentration was measured, and a 5 g sample weighed carefully and placed in a porcelain cup then put into the furnace. It was first reduced to ash at 300°C for 1.5 hours and then heated at $550 - 600^\circ\text{C}$ for 2.5 hours. The furnace was turned off and left overnight. Afterward, the sample was cooled off in a desiccator and weighed. In order to observe the crystal structure of the sample after pyrolysis, it was analyzed using XRD.

Calculation: $\frac{4}{100}$
 Ash content (%) = $\frac{W_2}{W \times f_k \times f_{ki} \times 100}$
 Organic matter content (%) = $\frac{(W - W_2)}{W \times f_k \times f_{ki} \times 100}$
 C-organic content (%) = Organic matter content $\times 0.58$
 Key:
 W_2 = weight of ash in grams
 W = sample weight in grams
 f_{ki} = correction factor for the non-ash material
 = $(100 - \% \text{ non-ash material}) / 100$
 f_k = water content correction factor
 = $100 / (100 - \% \text{ water content})$
 0.58 = conversion factor of organic matter to carbon

III. RESULTS AND DISCUSSION

A. The Pyrolysis Process Observation

After the pyrolysis process had been set up, the heat source in the form of LPG gas was ignited. Pyrolysis smoke was observed after 12 minutes, and 15 minutes later, the first drop of liquid smoke fell. Smoke flowed through the smoke pipe, then the heavy fraction of the smoke was captured by the tar catcher, and the lighter fraction flowed into the condenser pipe and condensed as liquid smoke. The average time needed to get the first drop of cinnamon liquid smoke was 27 minutes. The process ended when no more liquid smoke was being formed after 177 minutes from the starting point. The pyrolysis process observations can be seen in Table 1.

During the pyrolysis process, the temperature increased continuously and the liquid smoke was production increased as shown in Table 2. The increase in liquid smoke yields because of the higher rate decrease of mass and heat transfer [6]. The liquid smoke was brownish-yellow. On standing for

1 week, two layers of liquid smoke were formed. The brownish-yellow top layer was the liquid smoke and the thick black bottom layer was the tar. According to Girrard, the brown color of coconut oil liquid smoke is influenced by carbonyl content. The higher the carbonyl content, the browner the product. The lignocellulose component decomposes more completely as the pyrolysis temperature increases.

TABLE I
PYROLYSIS TEMPERATURE AND THE TIME REQUIRED FOR PRODUCT FORMATION

Product	Time (Min)	Temperature at different positions of the pyrolysis tube (°C)*		
		Sealed section	Middle section	Bottom section
first smoke produced	12	66.5	99.5	368.5
first liquid smoke formed	27	102.5	126.5	393

Information: * The average temperature of pyrolysis from two observations.

TABLE II
PYROLYSIS TEMPERATURE AND THE LIQUID SMOKE AND ITS INCREASE

Pyrolysis time (min)	Pyrolysis Temperature (°C) *	Liquid smoke produced (mL)	Liquid smoke increase (%)
30	249 ± 3.479	223.50 ± 0.948	0
60	259 ± 2.529	352.50 ± 1.581	57.72
90	268 ± 1.881	441.50 ± 4.111	25.24
120	280 ± 3.123	539.00 ± 2.529	22.08
150	283 ± 1.144	582.50 ± 1.581	8.07

* The pyrolysis temperature is the average temperature measurement of the middle and bottom of the pyrolysis tube.

Table 2 shows that the highest amount of the liquid smoke produced after 150 minutes was 582.5 mL at 283°C while the lowest amount was 223.50 mL after 30 minutes at 249°C. Charcoal, tar, and non-condensed gas are also produced during the pyrolysis process. During the pyrolysis process, these organic compounds decompose into liquid or gas [10].

TABLE III
PYROLYSIS PRODUCTS OF 4.000 G OF CINNAMON WOOD

Pyrolysis products	Weight (g)	Percentage (%)
Liquid smoke	1157.6	28.94
Tar	114	3.6
Charcoal	1716.8	42.92
Gases	981.6	24.54
Total	4000	100

Information:

Weight of lost materials = Weight of gas that did not condense
= Cinnamon wood weight - (liquid smoke weight + tar weight + charcoal weight)

The cinnamon pyrolysis products after 150 minutes can be seen in Table 3. The yield of liquid smoke from cinnamon was 28.94% at the highest pyrolysis temperature of 283°C. Besides charcoal (3.6%) and tar (42.92%), lost material (24.54%) also produced. The material lost is volatile and does not condense. This material consists of CO₂ gas and several

flammable gases such as CO, CH₄, H₂, and light molecular weight hydrocarbons such as C₂H₄ and C₂H₆ [11], [12].

B. Pyrolysis Effectiveness

Carbon concentration can be an indication of the completeness of the pyrolysis process. The carbon concentration of cinnamon wood is 51.86% while the carbon concentration of cinnamon charcoal after being hydrolyzed for 150 minutes is 75.90%, as shown in table 4. Thus, there has been an increase in carbon concentration of 46.36% as shown in table 4.

TABLE IV
PROXIMATE ANALYSIS OF CINNAMON CHARCOAL

Sample	Water concentration (%)	Ash Concentration (%)	Carbon concentration (%)
Cinnamon wood	9.31	0.39	51.86
Cinnamon Charcoal	3.88	1.40	75.90
Wood Charcoal [13]	Max.6	Max.4	-
Wood charcoal briquettes [14]	Max.8	Max.8	-
Active Charcoal [15]	Max. 25	Max. 10	Min.65
Active Charcoal of Mangium Wood[16]	4.33	8.17	83.77

The carbon concentration of cinnamon charcoal when compared to the carbon concentration of activated mangium charcoal is lower because mangium charcoal is activated with a combination of gas and chemicals [16]. The C contents of charcoal formed depend on temperatures and characteristic of feedstock [17]. Table 4 shows a comparison with other charcoal-based products along with some Indonesian National Standard (SNI).

By using x-ray diffraction analysis, the diffraction pattern was obtained from a powder sample with diffraction angles (2θ) measured every 0.1° between 10° and 80° at the wavelength of CuKα = 1.54060 Å as shown in the following figure 2. The irregular peak pattern from the x-ray diffraction shows that the carbon structure of cinnamon charcoal is amorphous.

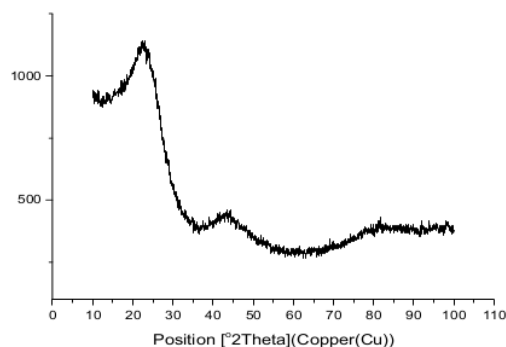


Fig. 2 X-Ray diffraction pattern of cinnamon charcoal

C. GC-MS to Identify Chemical Composition of Cinnamon Liquid Smoke

Table 5 shows the chromatography data from the cinnamon liquid smoke formed every 30 mins up until 150 mins using GC-MS analysis. Methanol, acetic acid, furfural, phenol and guaiacol are the dominant compounds in liquid smoke that were formed during the observation period. There were 10 compounds formed, methanol, acetic acid, furfural, butyrolactone, 5-methyl-2-furfural, 2-furan methanol, 2,3-Dimethyl-2-cyclopentene-1-one, phenol, guaiacol and 2-methoxy-4-methyl phenol, which were always present throughout the process. The highest percentage of acetic acid was in the cinnamon liquid smoke formed after 60 minutes while the highest percentage of methanol, furfural, phenol and guaiacol after 120 minutes.

The formation of the five dominant chemical compounds during the pyrolysis process can be seen in Figure 3. The highest concentration of acetic acid was 40.50% after 60 minutes at 259°C. The pyrolysis process occurs in stages

initiated by the removal of water from biomass at temperatures below 150°C. Then decomposition of cellulose and hemicellulose forming acetic acid and lignin forming furans and phenols in the temperature range 150 – 400°C [5], [18].

The highest concentration of furfural compounds was 9.55% produced after 120 minutes at 280°C. The highest concentration of phenol compounds was 8.70% after 120-minute pyrolysis at 280°C. Phenol is a decomposition product of lignin compounds in biomass that is decomposed at 200 – 500°C [19],[7]. Moreover, lignin is also decomposed to form phenolic ester compounds such as guaiacol and syringol [20]. Based on the highest concentration of acetic acid in cinnamon liquid smoke, it can be concluded that cinnamon wood has more cellulose than hemicellulose and lignin. Liquid smoke can be used as a latex coagulant, odor reducer, and raw material for organic fertilizers. Butyrolactone content in liquid smoke can stimulate the growth of roots, seeds, flowers, and as a natural pesticide in plants [21], [22].

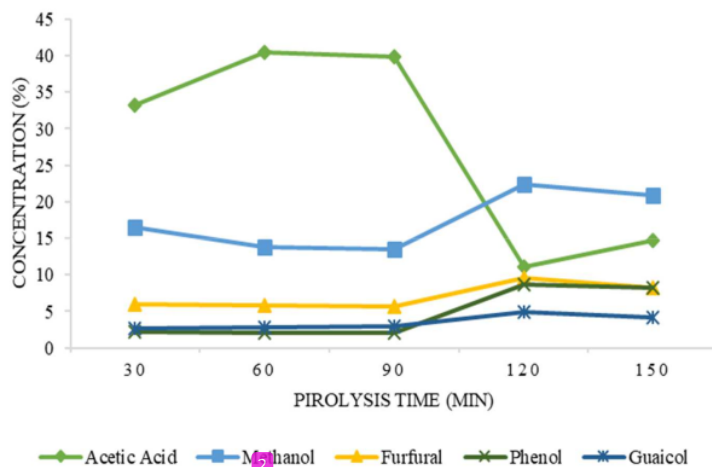


Fig. 3 Trend of spreading concentration of 5 main chemical compounds in cinnamon liquid smoke in every 30 minutes of pyrolysis

The chromatogram of cinnamon liquid smoke which the highest acetic acid content represented in Figure 4. The most abundant of acetic acid was formed at 60 minutes of pyrolysis. Acetic acid peaks formed at a retention time of 1.215 as much as 40.50%. Pyrolysis at 60 minutes of this research resulted in temperatures above 200°C. The hemicellulose and cellulose from the decomposed material produce organic acids such as acetic acid at this temperature. Acetic acid in liquid smoke affects the taste (bitterness), color, and shelf life of the preserved product [23], [24].

Figure 5 shows a liquid chromatogram of cinnamon at 120 minutes of pyrolysis. Phenol mostly formed in liquid smoke, compared to other pyrolysis times. Phenol peaks formed at a retention time of 2.916 as much as 8.70%. Another phenol derivative compound formed is guaiacol as much as 4.95%. Phenolic compounds are an important group of smoke constituents have antibacterial and antioxidant properties [25].

Table 6 shows the amount of the five main chemical compounds in cinnamon liquid smoke. The data were obtained by multiplying the percentage of the decomposition results using GC-MS with the liquid smoke volume produced. The highest production of methanol and phenol was reached after 150 mins of pyrolysis, acetic acid after 90 minutes, and furfural and guaiacol after 120 minutes. The longer the pyrolysis, the more methanol and phenol compounds formed. The three compounds produced in the highest volumes are shown in Table 6. The length of pyrolysis was proportional to the rate of methanol formation and the total yield. The rate of acetic acid formation keeps increasing from 30 minutes to 90 minutes then decreases at 120 minutes and increases again at 150 minutes although the yield is less than at 90 minutes of pyrolysis. The pattern also occurs in the formation of furfural during the pyrolysis process.

TABLE V
CHEMICAL COMPOSITION OF THE CINNAMON WOOD AT EACH STAGE OF PYROLYSIS.

No	Retention time (min)	Compound	Concentration (%)				
			30 min	60 min	90 min	120 min	150 min
1	1.142	Methanol	16.48	13.75	13.46	22.4	20.91
2	1.215	Acetic Acid	33.22	40.50	39.85	11.09	14.65
3	1.421	1-penten-3-ol	-	-	-	5.78	5.26
4	1.475	Hex-3-ene	-	-	-	-	4.51
5	1.269	Acetol	13.15	12.36	12.2	-	-
6	1.411	Erythrol	3.38	3.07	3.05	-	-
7	1.475	Dumasin	3.00	2.70	-	3.79	-
8	1.569	Furfural	6.01	5.79	5.59	9.55	8.16
9	1.629	1-cyclohexanol	-	-	-	5.22	-
10	1.634	5-methyl-5-hexen-2-one	3.77	-	-	-	5.66
11	1.801	Butyrolactone	1.30	1.29	1.37	2.62	2.44
12	1.861	2-Methyl-2-cyclopentenone	2.88	-	-	-	-
13	1.993	2-cyclohexenone	0.25	0.27	0.29	-	0.58
14	2.072	1-Acetoxy-2-butanone	1.18	-	1.11	-	1.44
15	2.156	5-Methyl-2-Furfural	1.28	1.13	1.22	2.29	2.11
16	2.230	Methyl-2-Furoate	0.44	-	0.43	-	0.8
17	2.272	Benzenesulfonic acid	0.72	0.76	0.78	-	-
18	2,451	2-Furanmethanol	1.83	5.33	5.2	3.75	3.67
19	2,592	Cyclooctene	0.23	-	0.2	-	-
20	2.661	Corylon	-	0.33	0.4	1.05	1.06
21	2.760	2,3-Dimethyl-2-cyclopenten-1-one	0.96	0.87	0.94	1.88	1.78
22	2.916	Phenol	2.13	2.07	2.03	8.70	8.24
23	3.015	2,3,4-Trimethylcyclopenten	-	0.23	0.22	0.58	-
24	3.021	Cyclopentan-1-Al	0.23	-	-	-	0.58
25	3.228	4-Hexen-3-one	-	0.21	0.23	-	-
26	3,231	4,5-Dimethyl-4-hexen-3-one	0.27	-	-	-	0.47
27	3.304	Guaiacol	2.61	2.82	3.00	4.95	4.19
28	3,781	Cyclohexanone	0.15	-	-	0.83	0.77
29	3,883	Veratrol	-	-	-	0.47	0.47
30	4,45	2-Methoxy-4-methylphenol	1.02	0.07	0.65	1.65	1.45
31	9,594	Toluene	0.08	-	-	0.14	0.12

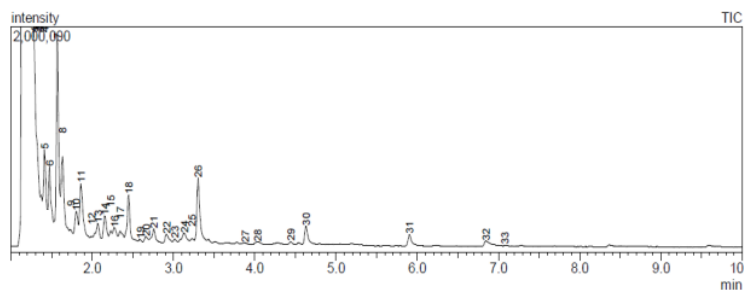


Fig. 4 GC-MS chromatograms of cinnamon liquid smoke after 60 minutes.

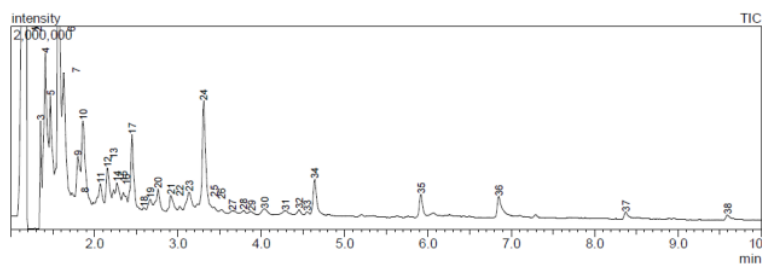


Fig. 5 GC-MS chromatograms of cinnamon liquid smoke after 120 minutes.

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