agriTECH, 43 (2) 2023, 187-198

Identification and Composition of Volatile Compounds in Liquid Smoke Derived from Betara Variety of *Areca catechu* Husk

Kamalia Muliyanti[1], Chusnul Hidayat[2], Supriyadi Supriyadi[2*]

[1]Assessment Institute for Agricultural Technologi (AIAT) Jambi, Ministry of Agricultural, Jl. Samarinda, Paal Lima Village, Kota Baru District, Jambi, Indonesia
[2]Department of Food and Agricultural Products Technology, Faculty of Agricultural Technology, Universitas Gadjah Mada, Jl. Flora No. 1. Bulaksumur, Yogyakarta 55281, Indonesia
[*]Corresponding author: Supriyadi Supriyadi, Email: suprif248@ugm.ac.id

Submitted: January 26, 2021; Revised: February 7, 2022, March 8, 2022, June 20, 2022, August 9, 2022, August 22, 2022; Accepted: August 22, 2022; Published: May 31, 2023

ABSTRACT

The seeds of *Areca* nut plants hold significant economic value, with a remarkable total production of 65,295.89 tons. However, the husk, constituting 50% to 75% of the fruit, are persistently discarded. This study aims to explore the conversion of *Areca* nut waste into liquid smoke with specific physical properties and chemical composition. It uses GC-MS to identify volatile chemicals in liquid smoke and carries out a distillation process using a glass column containing natural zeolite for purification. Furthermore, the pyrolysis method is employed at a varying temperature of 150 °C, 250 °C, 350 °C, and 450 °C for 3 hours to process the waste into liquid smoke. The study determines the chemical composition of total acid, phenol, and carbonyl, which range from 1.34% to 3.09%, 0.37% to 0.42%, and 6.84% to 7.46%, respectively. The physical properties of crude liquid smoke in terms of yield range from 16.93% to 31.49%, while the color brightness varies from 25.02 to 57.46. The result shows that liquid smoke comprises 13 acidic, 20 carbonyl, and 6 phenolic compounds, contributing to the aroma. In addition, temperature of the pyrolysis process affects the formation of liquid smoke and the corresponding compounds contained in *Areca* husk.

Keywords: Betara variety of *Areca Catechu* husk; liquid smoke; pyrolysis; temperature

INTRODUCTION

Areca catechu betel nut is a prominent plantation crop in Sumatra, with a total area of 146,271.73 ha and production output of 65,295.89 tons (Ministry of Agriculture, 2019). The fruit consists of 25% - 50% seeds and 50% - 75% husk, which are usually wasted, and considered garbage (Das & Singh, 2015). Furthermore, betel nut husk contains important components, such as hemicellulose 35% - 64.6%, lignin 13.0% - 26.0%, and cellulose 53.20% used as liquid smoke material (Ramachandra et al., 2004, Yusriah et al., 2012). Liquid smoke is produced by the chemical decomposition of organic matter through the pyrolysis, and some studies have explored the use of agricultural waste for this purpose. For instance, Oramahi & Diba (2013) found that the optimal conditions for the pyrolysis of durian husk were a temperature of 421 °C for 72.9 minutes. Handojo et al. (2018) also observed that the pyrolysis temperature of 450 °C produced higher phenolic compounds in cocoa

DOI: http://doi.org/10.22146/agritech.63605
ISSN 0216-0455 (Print), ISSN 2527-3825 (Online)

bean shell waste. Liquid smoke can be produced from coconut fiber at a temperature of 150 °C, with a lignin decomposition at 400 °C. Meanwhile, the quantity of lignins contained in the material is directly proportional to the yield of liquid smoke (Badin et al., 2017, Budaraga et al., 2016). A study by Gokul et al. (2019) found that decomposition occurs in the mass of *Areca* husk by 44.40% at temperature of 225 °C to 350 °C.

Liquid smoke obtained from the pyrolysis contains various compounds such as tar, phenolic compounds, acid compounds, and carbonyl compounds. These include Polycyclic Aromatic Hydrocarbons (PAH), rendering them unsuitable for direct use as food additives. According to (Darmadji, 2002) it is necessary to purify liquid smoke through distillation to eliminate unwanted components like tar compounds and PAHs. Besides distillation, other techniques such as the use of zeolite adsorbent have proved highly effective in absorbing benzo(a)pyrene content in liquid smoke (Fauzan & Ikhwanus, 2017). It is important to note that single distillation or adsorption treatments may not be adequate in reducing PAH content to acceptable levels. Nendissa (2005) demonstrated that a combination of distillation and adsorption with zeolite successfully purified coconut shell liquid smoke, resulting in a decrease in phenol and acid components, while carbonyl and PAH compounds were eliminated. Even though *Areca* husk has the potential to be a source of liquid smoke, optimal conditions for the pyrolysis are unknown. Therefore, this study aims to investigate the optimal conditions and chemical properties after purification using a combination of distillation and adsorption.

MATERIALS AND METHODS

Material

Betara Variety of *Areca catechu* husk obtained from the ripe nuts was used in the experiment. They were prepared by farmers in Siau District, Tanjung Jabung Timur Regency, Jambi Province. Zeolite (Bratachem) was used at a ratio of 1:2, which had undergone chemical and physical activation using 0.5 N NaOH and a funnel furnace at a temperature of 400 °C for 2 hours. The chemicals employed were solely used for analysis purposes and comprised KOH 1 N, NaOH 0.1 N, Na2CO3, Folin-Ciocalteu reagent, phenolphthalein indicator, methanol, 2,4-dinitrophenyl hydrazine, distilled water (Aquades), and concentrated HCl.

Equipment

The instrument utilized for the pyrolysis, as referenced in Kadir's (2011) study, comprises a set of cylindrical tube reactors, measuring 40 cm in height and 20 cm in diameter. The pyrolysis tool is furnished with a thermocouple that is connected to a readout meter. The tool is heated by electricity with a capacity of 3 kW. The distribution pipe used for smoke is 2.5 cm in diameter and 150 cm long. The spiral pipe connects to the distribution pipe, leading to the cooling column, which measures 100 cm in height and 20 cm in diameter. The cooling column is designed to circulate water through a pump, and liquid smoke is collected in a 1000 mL Erlenmeyer flask, which is shown in Figure 1.

The distillation series consists of several apparatus, including a 600-watt electric stove, a 1000 mL Erlenmeyer flask equipped with a thermometer, an 80 cm-long condenser with an inner pipe diameter of 1.5 cm, an outer pipe diameter of 5 cm, a cooling hose diameter of 3/8 inches, and a liquid smoke reservoir, which yields the distillation results. Liquid smoke was extracted using a glass column measuring 50 cm long and 2.5 cm in diameter, stative, test tubes, and 20 mL glass bottles. Furthermore, Erlenmeyer flask, micropipette, WM 41 filter paper, pH meter, desiccator, oven, burette, spectrometer, vortex, test tube, measuring flask, and dropper pipette were used to conduct chemical analysis. In this study, RAL with 4 temperature levels, namely 150 °C, 250 °C, 350 °C, and 450 °C, was used, and the process was repeated three times. The resulting data were analyzed using One-Way ANOVA with IBM SPSS Statistics 25 software, followed by Duncan's analysis with a significant level of 5%.

Liquid Smoke Production

Crude liquid smoke was manufactured by adjusting the heating temperature at 150 °C, 250 °C, 350 °C, and 450 °C using the pyrolysis reactor. The process involved adding 1500 grams of *Areca* nut husk into the reactor, which was equipped with a cooling column, and maintaining it for 2 hours until no liquid smoke dripped into the reservoir. Meanwhile, the entire process took approximately 3 hours, as depicted in Figure 2.

Liquid Smoke Purification

Liquid smoke purification involved distilling the sample obtained from the pyrolysis process in a 1000 mL Erlenmeyer flask. The distillation was carried out at a constant temperature of 100±2 °C for two hours. Furthermore, the resulting liquid smoke was collected in a measuring cup and left to settle until no condensate drops were observed. The purification process continued by passing the condensate through a natural zeolite (60 mesh) in a glass column, following the method outlined by Kadir (2011), with a ratio of 2:1 (w/w). The purified liquid smoke was then collected in a glass bottle, as

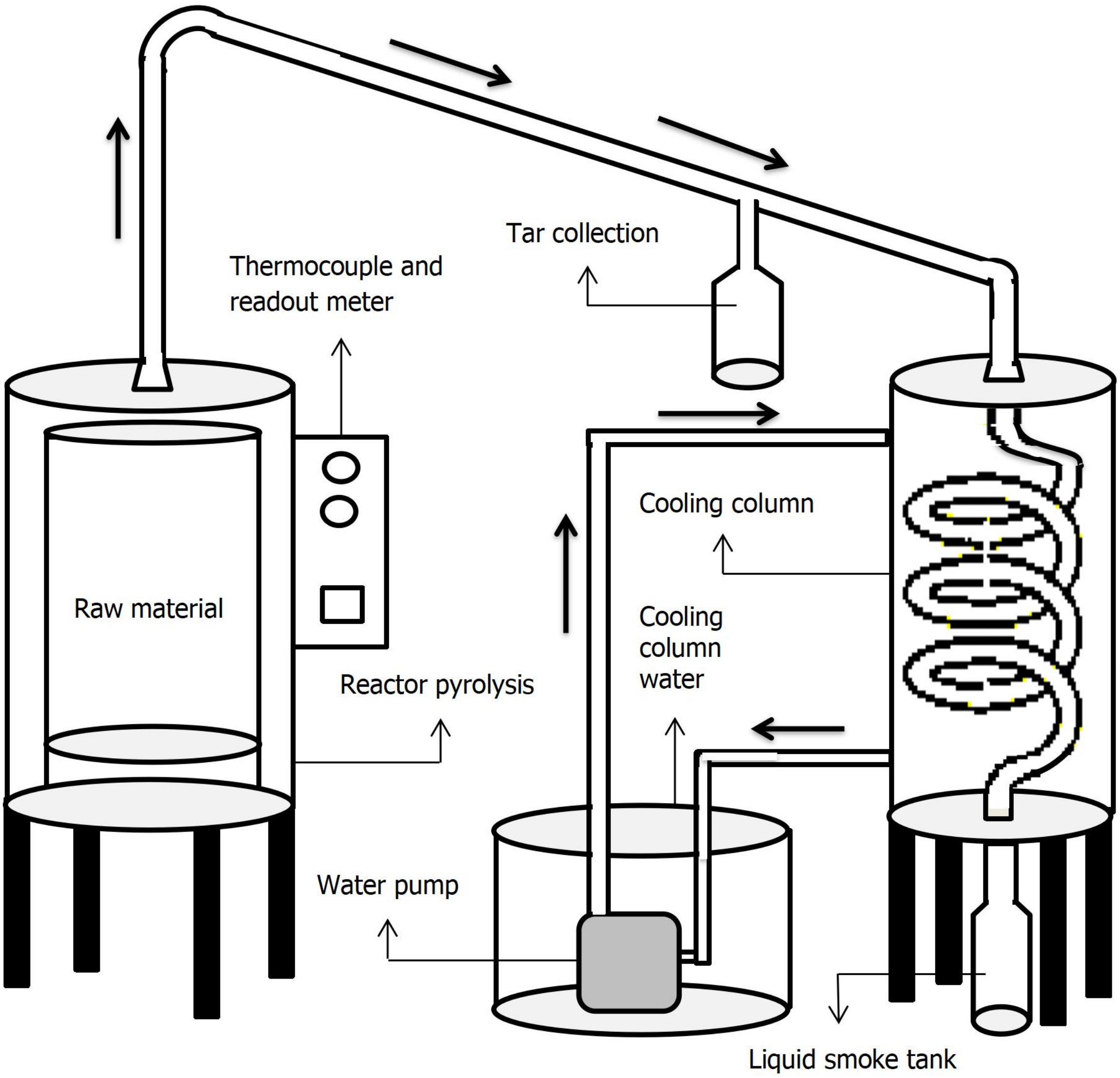

Figure 1. Schematic diagram of experimental apparatus

shown in Figure 3. The Chesson method was used to analyze the chemical components of Betara Variety of *Areca catechu* husk, namely Hemicellulose, cellulose, and lignin content (Datta, 1981).

Analysis of Chemical Components of Coarse Liquid Smoke, Distillation, and Adsorption

The color of the crude and refined liquid smoke samples was analyzed using a Chroma Meter CR-400 (Konica Minolta, Japan). The pH value was determined using a pH meter, and the total acid content was measured using the titration method (AOAC, 1990). Subsequently, the carbonyl and phenolic contents were determined using spectrometric methods, as described by Lappin and Clark (1951) and Senter et al. (1989), respectively.

Identification of Volatile Compounds (GC-MS)

To identify volatile compounds present in liquid smoke, GC-MS-QP2010S Shimadzu was used with an Agilent DB-624 column, 30 meters in length and 0.25 mm in diameter. The samples were ionized using El (Electron Impact) ionization at 70 Ev. The initial and final column temperature was set at 40 °C and 190 °C with an increase of 4 °C/min. Furthermore, the detector used was FID, with a detector and injector temperature of 240 °C and 250 °C. Helium was used as the carrier gas at a pressure of 40 kPa and a flow rate of 36.0 mL/minute. The data obtained from the analysis were processed using the GCMS solution software, and compounds were identified based on their retention time and mass spectra. The results were compared to the Spectra Standard Library analysis data and were expressed as a percentage of similarity.

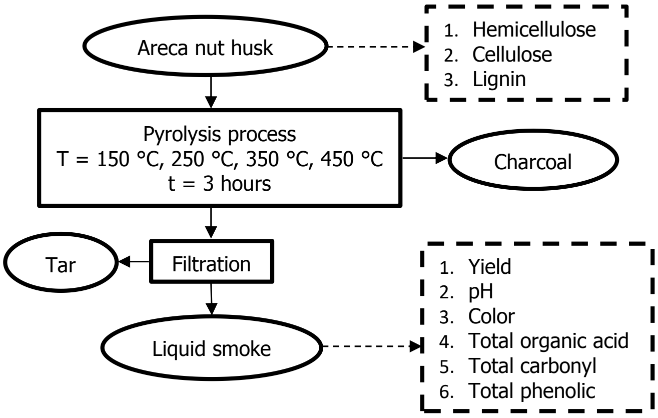

Figure 2. Flowchart of the production stage of liquid smoke *Areca* nut husk

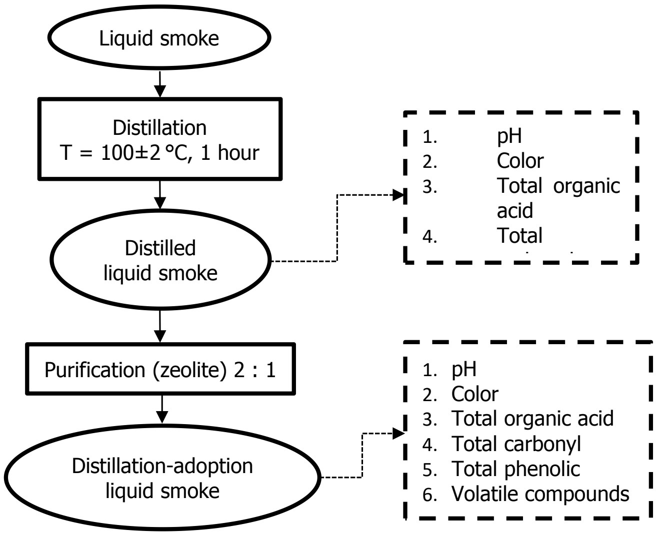

Figure 3. Flowchart of liquid smoke purification process

RESULTS AND DISCUSSION

Betara Variety of *Areca Catechu* Husk Analysis

Areca nut husk was used as a raw material for liquid smoke, which presented a distinct composition of constituent components compared to wood or shell-based raw materials. Sarwendah et al., 2019; Andy et al., 2021; Darmadji, 1996 demonstrated that raw materials significantly impacted the chemical and physical components of the equipment and the number of compounds generated during the pyrolysis process to produce liquid smoke. *Areca* nut husk had an average composition of 12.68% moisture, 12.66% hemicellulose, 46.94% cellulose, and 21.21% lignin contents. However, composition varied for different raw materials, ultimately determining the acid, carbonyl, and phenol levels in the resulting liquid smoke. The water content was measured to determine the quantity in *Areca* nut husk while measuring the levels of hemicellulose, cellulose, and lignin showed the content of compounds formed during the pyrolysis process.

Maga (1987) reported that the decomposition of hemicellulose produced furan and its derivatives, such as aliphatic carboxylic acid. Cellulose produced carbonyl groups, hydroperoxides, carbon monoxide, carbon dioxide, and charcoal, while lignin degradation yielded phenolic and phenolic ester components.

Physical Characteristics of Liquid Smoke

Yield

The desired results in the pyrolysis process were achieved through appropriate temperature conditions, and the variation resulted in different outcomes. Demirbas (2005) reported that temperature conditions affected the percentage of liquid smoke produced. Temperature is directly related to the yield of liquid smoke but inversely proportional to the production of charcoal. The chemical components in the raw material broke down due to high temperature during the pyrolysis process. Table 1 showed that a temperature of 350 °C produced a higher yield of liquid smoke than 150 °C, 250 °C, and 450 °C. At a temperature of 150 °C, only water biomass was removed from *Areca* nut husk, and few components were degraded. At 250 °C, hemicellulose degraded to yield volatile CO and CO2, reducing the volume of liquid smoke formation. Furthermore, at 350 °C, the lignocellulose decomposition process occurred, causing low molecular weight compounds to evaporate and condense into liquid smoke. At 450 °C, compounds in *Areca* nut husk degraded to produce more volatile CO, CO2, and H. Lombok et al. (2014) reported that the amount of the pyrolysis decreased at temperature between 351 °C and 450 °C in coconut shells due to the degradation of components to produce CO, CO2, and H.

In the study, the yield of liquid smoke was observed to increase between 16.93% and 31.49% as the pyrolysis process temperature was raised to 350 °C. However, the yield decreased to 29.71% when temperature was increased to 450 °C. It was higher than cocoa bean shells, which ranged from 17% to 24% (Handojo et al., 2018), and was comparable to coconut coir without the pyrolysis process, approximately 28% (Fatimah, 2011). The yield of charcoal produced decreased as temperature was increased from 150 °C to 350 °C, but it increased when temperature was further raised to 450°C. This was attributed to the degradation of the main components of the raw material caused by the increased pyrolysis. Furthermore, Gokul et al. (2019) reported that the highest mass decomposition of

Table 1. The yield of charcoal, liquid smoke, and tar of *Areca* nut husk with the several pyrolysis temperature treatments

Temperature (°C)	Charcoal (%)	Liquid Smoke (%)	Tar (%)
150	61.56±7.07^{c}	16.93±7.07^{a}	10.00±2.78^{a}
250	47.99±2.52^{b}	25.26±2.00^{b}	12.36±3.33^{a}
350	35.11±1.84^{a}	31.49±3.83^{b}	9.58±0.84^{a}
450	37.04±3.11^{a}	29.71±2.33^{b}	9.64±0.93^{a}

Note: Different letters on the same line indicate a significant difference (p<0.05)

Areca nuts occurred at temperature ranging from 220 °C to 370 °C. The yield of tar produced was defined as the weight fraction of the remaining product that melted when passed through the cooling pipe. Meanwhile, the resulting tar had a thickened liquid form, black with a strong aroma, and was sticky. It was noted that tar in the pyrolysis process produced liquid smoke, often considered as waste. The yield ranged from 9.58% to 12.36% when the pyrolysis was carried out between temperature of 150 °C and 450 °C.

Color

The crude liquid smoke condensate (ACK) that was produced from the pyrolysis process of *Areca* husk had a dark brown color due to the carbonyl content. The study showed that the pyrolysis temperature did not significantly affect the color of liquid smoke.

The color parameter (L) was used to determine the brightness value of the material, ranging from 0 to 100. In Figure 1, the ACK graph illustrated that the color parameter (L) ranged from 49.04 to 52.58, and a decrease was observed with an increase in the pyrolysis temperature. In addition, the color parameter (L) in liquid smoke fraction after distillation ranged from 56.22 to 57.46. The color parameter (L) in liquid smoke fraction after distillation and adsorption ranged from 25.02 to 49.48. These results indicated that the distillation process resulted in a lighter color (L) of the distilled liquid smoke fraction. According to Budaraga et al. (2016), a higher value of the color parameter (L) showed a brighter liquid smoke. The decrease after distillation and adsorption was due to the use of active zeolite as an adsorbent with a neutral pH. The study also found that the pH of the adsorbent had a significant effect on the intensity of the aroma

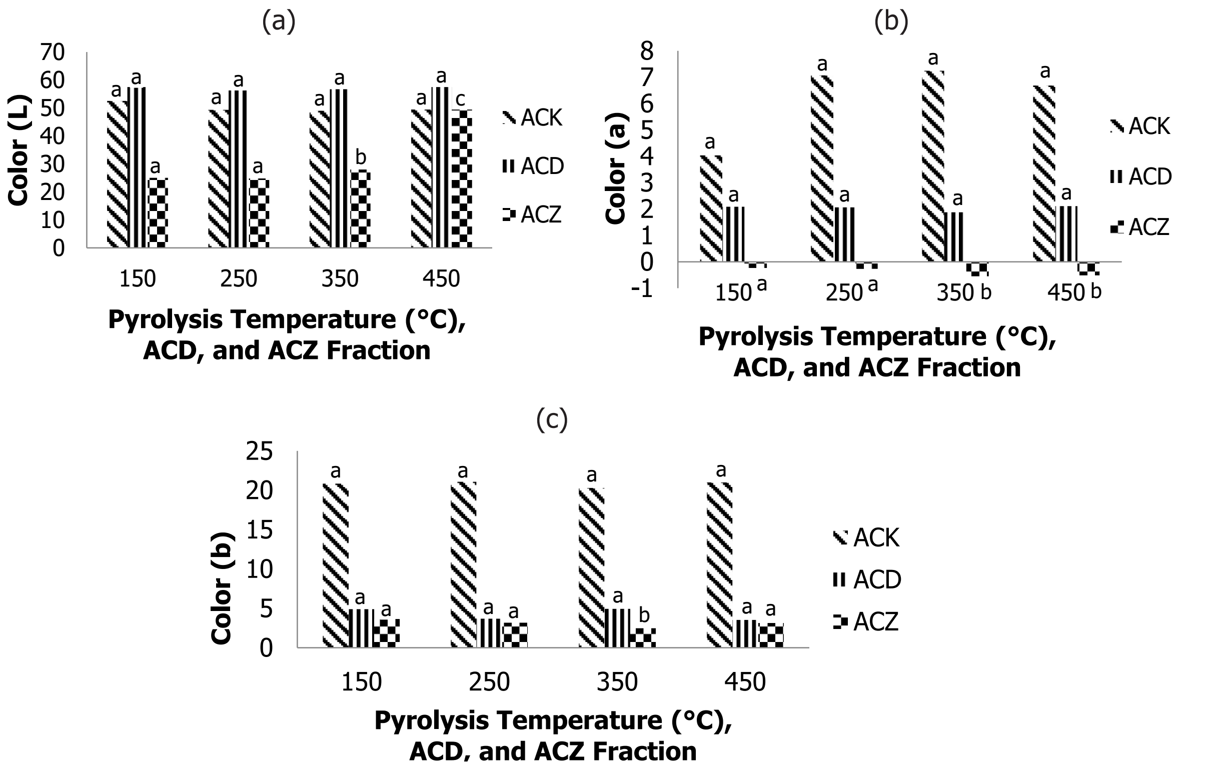

Figure 4. Comparison of the color of the ACK with the pyrolysis temperature of 150 °C, 250 °C, 350 °C, and 450 °C, with the distilled liquid smoke fraction (ACD) and liquid smoke fraction with zeolite adsorbed (ACZ). (a) L value; (b) a value; and (c) b value

and color of liquid smoke, and was consistent with the findings of Kadir et al. (2015).

The color parameter (a) represented the redness or mixture of red (a positive) to green (a negative). In Figure 4, the graph of liquid smoke resulting from the pyrolysis process showed the difference in parameters ranging from 4.04 - 7.24. Meanwhile, the positive color parameter resulting from the pyrolysis process showed that liquid smoke was close to red. The value resulting from the process decreased after the distillation process was carried out, indicating that the color parameters were close to yellow, namely a mixture of (a) positive (red) with (a) negative (green), with (a) between 1.88 - 2.11. The adsorption process using active zeolite with a neutral color pH decreased the color parameter (a) until it became negative, ranging from (-0.55) - (-0.23).

The color parameter (b) showed the yellowness or a mixture of yellow (b positive) to blue (b negative). In Figure 3, the graph of liquid smoke showed that the results of the pyrolysis process had color parameters ranging from 20.3 - 21.08. Furthermore, liquid smoke resulting from the pyrolysis process after the distillation process had a decreased color parameter (b) between 3.54 - 4.94. The distilled liquid smoke fraction was passed to the active zeolite with a neutral pH, and the color parameter (b) decreased in the range of 2.48 - 3.65. The value of liquid smoke resulting from the pyrolysis, distillation, as well as distillation and adsorption of *Areca* nut husk was still positive and contained a yellow color.

During the pyrolysis process, temperature played a significant role in determining the color of liquid smoke. This was due to the breakdown of cellulose, hemicellulose, and lignin present in the raw material (Wijaya et al., 2008). Furthermore, the resulting liquid smoke was subjected to a color change as temperature varied. Brighter and more transparent liquid smoke was considered superior in quality compared to the darker variant. Distillation was utilized to obtain clearer liquid smoke by separating components with different boiling points. Additionally, active zeolite acted as a filter in the production process by capturing carcinogenic compounds such as tar and benzo(a)pyrene (Fauzan & Ikhwanus, 2017).

Chemical Characteristics of Liquid Smoke

pH

The pH measurement of liquid smoke aimed to determine the extent of raw material decomposition by the pyrolysis and the production of natural acids. Lower acid values were indicative of good-quality liquid smoke, functioning as a food preservative with antibacterial properties. Meanwhile, the pH was closely related to

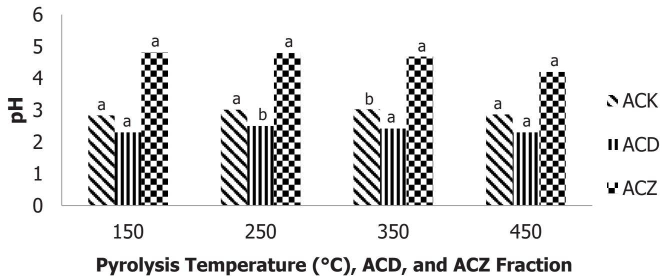

Figure 5. Comparison of the pH of the ACK with the pyrolysis temperature of 150 °C, 250 °C, 350 °C, and 450 °C, with the ACD and liquid smoke fraction with ACZ

the decomposition of the hemicellulose fraction, which produced acetic acid.

Figure 5 illustrated that the pH value was influenced by temperature of the pyrolysis, distillation, and purification processes involving a zeolite column. The crude liquid smoke obtained had a pH range of 2.83-3.03, which was consistent with the findings of Badin et al. (2017). In addition, the study on coconut coir at a temperature range of 150 °C-400 °C produced a pH of 2.62. In the distillation liquid smoke fraction, the pH dropped to between 2.3-2.42, and the result demonstrated that the acidic components had a boiling point of more than 100±2°C (Fachraniah et al., 2009).

The implementation of purification treatment using a zeolite column resulted in the pH value being observed within the range of 4.81 – 4.2. The pH value exhibited an increase due to the usage of a zeolite adsorbent with a pH of 7, indicating an affinity of liquid smoke towards polar adsorbents. Furthermore, an increase in the pH of the zeolite led to larger pores, resulting in a higher value of the solute due to its polarity, as described by Kadir et al. (2015). The study conducted by Tóth & Potthast (1984) found that the pH range of liquid smoke typically varied between 1.5 to 5.5.

Total Organic Acid

Acetic acid played a crucial role in the utilization of liquid smoke, as it is an organic acid essential for this process. The acidity was derived from the hemicellulose and cellulose components present in the raw materials. Figure 6 demonstrated that the total organic acid content increased with an increase in temperature during the pyrolysis process. This phenomenon occurred due to the decomposition of elements present in the raw materials, leading to the formation of acidic compounds (Silia & Maulina, 2017). The formation of organic acids from cellulose and hemicellulose components affected the organoleptic quality of liquid smoke and served as natural preservatives (Budaraga et al., 2016). The total

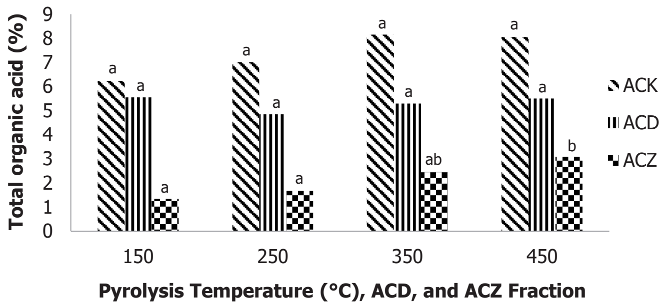

Figure 6. Comparison of the total organic acid of the ACK with the pyrolysis temperature of 150 °C, 250 °C, 350 °C, and 450 °C, with the ACD and liquid smoke fraction with ACZ

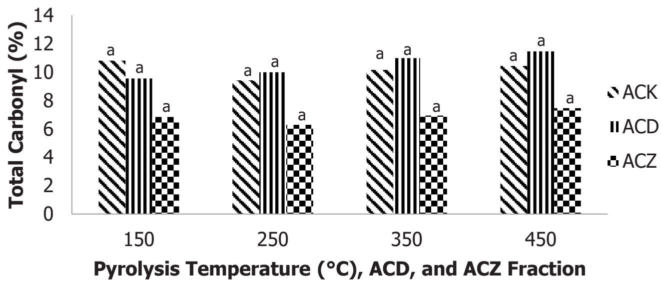

Figure 7. Comparison of the total carbonyl of the ACK with the pyrolysis temperature of 150 °C, 250 °C, 350 °C, and 450 °C, the ACD and liquid smoke fraction with ACZ

acid and pH were inversely proportional, with the higher concentration of acid in liquid smoke leading to a lower pH value (Rinaldi et al., 2015). The analysis of the acid content in liquid smoke derived from the pyrolysis and distillation at 100±2 °C showed that the former had a higher total acid value. However, the total acid value decreased further after the adsorption process using active zeolite.

The reduction in the total acid value was attributed to the presence of free water and organic acids with high boiling points in liquid smoke. During the distillation process, a significant portion of water was distilled, leaving only a small portion of organic acids, resulting in a decrease in the total acid value. Darmadji and Triyudiana (2006) reported that smoke component in liquid smoke consisted of medium-chain acids with a boiling point of 141 °C to 162 °C.

The adsorption process used active zeolite, which was polar in nature. The high affinity between liquid smoke and zeolite reduced the acid level in the distillation and adsorption of liquid smoke fraction. Meanwhile, the separation of compounds in coconut shells effectively reduced the levels of acid, carbonyl, and phenolic compounds by using zeolites in the adsorption method (Kadir, 2011).

Total Carbonyl

The cellulose in feedstock was subjected to thermal degradation and produced carbonyl and acetic acid. As shown in Figure 7, the crude liquid smoke resulting from the pyrolysis increased the total carbonyl value (Iskandar & Rofiatin, 2017). According to Darmadji (2002), the carbonyl component had the lowest boiling point. Compounds easily evaporated and produced a liquid smoke fraction with a higher content through the distillation process. The boiling point of compounds is inversely proportional to the volume and vapor point (Henrickson, 2005).

After the adsorption process was carried out using activated zeolite, the total carbonyl decreased. This was probably due to the increased ability of the activated zeolite previously activated. The zeolite was activated using NaOH to clean its pore cavity from any impurities, which expanded the active surface and increased its working ability as an adsorbent (Johnson & Arshad, 2014).

Total Phenolic Content

This study showed a significant effect on the coarse liquid smoke produced by the differences in temperature of the pyrolysis process. Figure 8 indicated that the total phenol production in the ACK increased with temperature of the pyrolysis process. At 450°C, the phenolic compounds produced through thermal processes were 1.20%. This finding suggested that temperature of the pyrolysis process is directly related to the total phenolic compounds. According to Darmadji (2002), the pyrolysis process at high temperature produced phenolic compounds with high antioxidant activity above 300°C. Furthermore, liquid smoke fraction obtained after the distillation of total phenolics showed an insignificant result at a temperature of 100±2°C. Only a few phenolic components could be distilled and most phenolic compounds showed high boiling points. Therefore, compounds were not distilled with the re-distillation process at temperature below 200 °C. (Darmadji, 2002).

In the process of purifying the distillation liquid smoke fraction through adsorption, a decrease in the total phenolic amount was observed. This was consistent with the results reported by Jaya et al. (1997), who found a reduction in phenol compounds after passing through active zeolite. The physically and chemically activated zeolite had a higher capacity to adsorb polar phenol compounds.

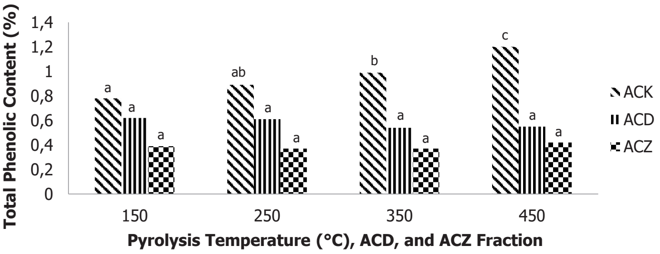

Figure 8. Comparison of the total phenolic content of the ACK with the pyrolysis temperature of 150 °C, 250 °C, 350 °C, and 450 °C, with the ACD and liquid smoke fraction with ACZ

Volatile Compounds Components of Distillation and Adsorption Liquid Smoke Fraction

The identification of compounds components was performed on liquid smoke fraction obtained from the distillation and active zeolite adsorption, using GC-MS. To obtain the fraction of *Areca* husk liquid smoke, the pyrolysis process was conducted at temperature of 150 °C, 250 °C, 350 °C, and 450 °C. Subsequently, a distillation process was carried out at 100±2 °C, followed by adsorption using a chemically and physically activated zeolite, as shown in Table 2.

The results of the identification of volatile compounds indicated that the number of compounds formed was different, as shown in Table 2. Specifically, 32 compounds were identified in the results of liquid smoke fraction of distillation and adsorption with the pyrolysis at a temperature of 150 °C. At 250 °C and 350 °C, 30 and 26 compounds were detected, with nearly the same results, respectively. At 450 °C, 27 compounds were found, indicating that temperature is inversely proportional to the production of compounds. Furthermore, the table showed that several compounds had the same weight and molecular formula but different compounds names. Liquid smoke resulting from the distillation and adsorption of *Areca* nut had the most compounds, specifically Methylamine-D2 compounds, which were also present in eucalyptus and teak wood (Suryani et al., 2020). Meanwhile, a significant number of constituents were produced in the distillation and adsorption fraction of liquid smoke, containing carbonyl, acid, and phenolic compounds. Benzo(a)pyrene compounds were not detected since they were considered as components of polycyclic aromatic hydrocarbons (PAHs).

Table 2. The fraction of *Areca* coir crude liquid smoke fraction of the pyrolysis process at 150 °C, 250 °C, 350 °C, and 450 °C

Name of compounds	Molecular weight (g/mol)	Molecular formula	% Relative component			
			ACZ 150	ACZ 250	ACZ 350	ACZ 450
Phenolic						
Phenol	94	C_6H_6O	11,77	12,07	12,02	11,18
Guaiacol	124	$C_7H_8O_2$	-	2,14	2,24	-
Mequinol	124	$C_7H_8O_2$	2	-	-	2,16
p-Kresol	108	C_7H_8O	-	-	0,4	-
m-Kresol	108	C_7H_8O	-	0,45	-	-
Phenol, 3-methyl	108	C_7H_8O	0,38	-	-	0,25
Total			14,15	14,66	14,66	13,59
Carbonyl						
Acetaldehyde	44	C_2H_4O	1,03	1,34	0,82	1,1
Propional	58	C_3H_6O	0,16	0,16	0,12	0,17
Acetone	58	C_3H_6O	-	4,42	3,56	3,11
2,3-Butanedione	86	$C_4H_6O_2$	1	0,87	1,01	1,18
2-Butanone	72	C_4H_8O	0,98	1,16	0,94	0,94
Butanal	88	$C_4H_8O_2$	-	0,29	-	-
3-Butanolal	88	$C_4H_8O_2$	-	0,29	-	-

2-Pentanone	86	$C_5H_{10}O$	0,12	-	-	-
2,3-Pentanedione	100	$C_5H_8O_2$	0,25	-	-	-
Hydroxyacetone	74	$C_3H_6O_2$	1,74	-	-	-
1 Hydroxy-2-Butanone	88	$C_4H_8O_2$	1,06	0,96	1,09	1,05
Cyclopentanone	84	C_5H_8O	0,53	0,64	0,55	0,48
2-Methyl-2- cyclopentenone	96	C_6H_8O	0,45	0,53	0,52	0,5
Vinyl butyrate	114	$C_6H_{10}O_2$	-	-	-	0,13
Formaldehyde	96	$C_5H_8N_2$	0,31	-	-	-
3-Methyl-2-cyclopenten-1-one	96	C_6H_8O	0,19	0,22	0,2	0,14
Propenyl butyrate	128	$C_7H_{12}O_2$	-	0,28	0,23	0,15
Allyl butyrate	128	$C_7H_{12}O_2$	0,13	-	-	-
2,3-Dimethyl-2- cyclopenten-1-one	110	$C_7H_{10}O$	-	0,2	-	-
Total			7,95	11,36	9,04	8,95
Furan dan pyran						
Furanidine	72	C_4H_8O	-	0,22	-	-
Furan	72	C_4H_8O	0,2	-	-	-
Tetrahydro-2-methyl-furan	86	$C_5H_{10}O$	-	0,09	-	-
2-Furfural	96	$C_5H_4O_2$	-	3,11	-	-
2-Furaldehyde	96	$C_5H_4O_2$	2,85	-	3,26	4,27
2-Acetylfuran	110	$C_6H_6O_2$	0,38	0,41	0,4	0,44
Butyrolactone	86	$C_4H_6O_2$	0,27	-	-	-
Furfural, 5-methyl	110	$C_6H_6O_2$	-	-	-	0,37
Total			3,7	3,83	3,66	5,08
Alkohol, ester, and acid						
Propanone	58	C_3H_6O	2,75	-	-	-
Methyl acetate	74	$C_3H_6O_2$	6,67	4,42	4,38	5,26
Propanoic acid	88	$C_4H_8O_2$	-	-	-	0,21
Methyl propionate	88	$C_4H_8O_2$	0,34	0,22	-	-
Acetic acid	60	$C_2H_4O_2$	21,38	7,84	13,42	16,32
2,3-Pentanedione	100	$C_5H_8O_2$	-	0,11	0,22	0,28
Acetol	74	$C_3H_6O_2$	-	-	1,81	1,65
2-Propanone, 1-hydroxy			-	1,36	-	-
Propanoic acid	74	$C_3H_6O_2$	2,15	1,1	1,66	1,94
Butyric acid	88	$C_4H_8O_2$	0,36	0,19	0,28	0,32
Acetic acid ethenyl ester	86	$C_4H_6O_2$	0,25	0,27	0,36	0,28
Butanoic acid	114	$C_6H_{10}O_2$	0,1	0,12	0,11	-
Butyrolactor	86	$C_4H_6O_2$	-	-	0,33	-
2,3-Pentanedione	100	$C_5H_8O_2$	-	-	0,4	-
Total			34	15,63	22,97	26,26

Miscellaneous						
(S)-(+)-1- Cyclohexylethylamine	127	$C_8H_{17}N$	-	0,55	-	-
1-Methyldecylamine	171	$C_{11}H_{25}N$	0,45	-	-	-
Methylamine-D2	31	CH_3D_2N	39,56	54,27	49,65	45,99
Propenyl Butyrate	128	$C_7H_{12}O_2$	0,1	-	-	
1,4-Dioxin	86	$C_4H_6O_2$	-	-	-	0,15
Z-Citral	152	$C_{10}H_{16}O$	0,11	-	-	-
Total			40,22	54,82	49,65	46,14

Note :
ACZ 150 = Distillation and Adsopsy Liquid Smoke Fraction at 150 °C pyrolysis
ACZ 250 = Distillation and Adsopsy Liquid Smoke Fraction at 250 °C pyrolysis
ACZ 350 = Distillation and Adsopsy Liquid Smoke Fraction at 350 °C pyrolysis
ACZ 450 = Distillation and Adsopsy Liquid Smoke Fraction at 450 °C pyrolysis

CONCLUSION

The results obtained from the pyrolysis process of *Areca* nut husk at temperature of 150 °C, 250 °C, 350 °C, and 450 °C show a noteworthy trend. Temperature of the pyrolysis process is directly proportional to the production of crude liquid smoke. However, the amount of yield produced decreases when a specific temperature threshold is reached. Temperature during the pyrolysis process is directly related to the brightness of liquid smoke color. After the distillation at 100±2 °C and purification through the zeolite column, the pH of liquid smoke decreases as the total acid and carbonyl concentrations increase. Further analysis through GC-MS of liquid smoke fraction obtained from the distillation and adsorption of *Areca* husk, shows the presence of volatile compounds in the group of phenolic, acid, and carbonyl compounds. Notably, the absence of benzo(a)pyrene, which is a class of polycyclic aromatic hydrocarbon (PAH), was detected.

ACKNOWLEDGE

The authors are grateful to the Research and Development of the Ministry of Agriculture which has helped finance study and research.

CONFLICT OF INTEREST

This study does not have any conflict of interest.

REFERENCES

Andy, Malaka, R., Purwanti, S., Ali, H. M., & Aulyani, T. (2021). Liquid smoke characteristic from coconut shell and rice husk. *The 3rd International Conference of Animal Science and Technology IOP Conf. Series: Earth and Environmental Science IOP Publishing*. https://doi.org/10.1088/1755-1315/788/1/012078

AOAC. (1990). *Official Methods of Analysis* (Vol. 1). Washington D. C.

Badin, Y. R., Anggraini, S. P. A., & Yuniningsih, S. (2017). Pengolahan sabut kelapa menjadi asap cair dengan menggunakan proses pirolisi. *EUREKA : Jurnal Penelitian Teknik Sipil dan Teknik Kimia 1*, *2*.

Budaraga, I. K., Arnim, Marlida, Y., & Bulanin, U. (2016). Analysis of liquid smoke chemical components with GC MS from different raw materials variation production and pyrolysis temperaturelevel. *International Journal of ChemTech Research*, *9*(6), 694–708.

Darmadji, P. (1996). Aktivitas antibakteri asap cair yang diproduksi dari bermacam-macam limbah pertanian. *Agritech*, *16*(4), 19–22. https://doi.org/10.22146/agritech.19317

Darmadji, P. (2002). Optimasi Pemurnian asap cair dengan metoda redistilasi. *Jurnal Teknologi dan Industri Pangan*, *13*(3), 267–271.

Darmadji, P., & Triyudiana, H. (2006). Proses Pemurnian asap cair dan simulasi akumulasi kadar benzopyrene pada proses perendaman ikan. *Majalah Ilmu dan Teknologi Pertanian*, *26*(2), 94–103.

Das, N., & Singh, S. (2015). The potential of arecanut husk ash as supplementary cementitious material. *Concret Research Letters*, *6*(3), 126–135.

Datta, R. (1981). Acidogenic fermentation of lignocellulose–acid yield and conversion of components. *Biotechnology and Bioengineering*, *23*(9), 2167–2170. https://doi.org/10.1002/bit.260230921

Demirbas, A. (2005). Pyrolysis of ground beech wood in irregular heating rate conditions. *Journal of Analytical and Applied Pyrolysis*, *73*(1), 39–43. https://doi.org/10.1016/j.jaap.2004.04.002

Fachraniah, F., Fona, Z., & Rahmi, Z. (2009). Peningkatan kualitas asap cair dengan distilasi. *Jurnal Sains dan Teknologi Reaksi*, *7*(1), 1–11. https://doi.org/10.30811/jstr.v7i1.133

Fatimah, F. (2011). Komposisi dan aktivitas antibakteri asap cair sabut kelapa yang dibuat dengan teknik pembakaran non pirolisis. *Agritech*, *31*(4), 305–311. https://doi.org/10.22146/agritech.9638

Fauzan, & Ikhwanus, M. (2017). Pemurnian asap cair tempurung kelapa melalui distilasi dan filtrasi menggunakan zeolit dan arang aktif. *Prosiding Semnastek*, 1–5. https://jurnal.umj.ac.id/index.php/semnastek/article/view/1976

Gokul, P. V., Singh, P., Singh, V. P., & Sawarkar, A. N. (2019). Thermal behavior and kinetics of pyrolysis of areca nut husk. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*, *41*(23), 2906–2916. https://doi.org/10.1080/15567036.2019.1582733

Handojo, L., Cherilisa, & Indarto, A. (2018). Cocoa bean skin waste as potential raw material for liquid smoke production. *Environmental Technology (United Kingdom)*, 1–23. https://doi.org/10.1080/09593330.2018.1520306

Henrickson, C. (2005). *Chemistry*. Canada Wiley Publishing.Inc.

Iskandar, T., & Rofiatin, U. (2017). Karakteristik Biochar berdasarkan jenis biomassa dan parameter proses pyrolisis. *Jurnal Teknik Kimia*, *12*(1), 28–34. https://doi.org/10.33005/tekkim.v12i1.843

Jaya, I. K., Darmadji, P., & Suhardi. (1997). Penurunan Kandungan benzo(a)pyrene asap cair dengan zeolit dalam upaya meningkatkan keamanan pangan. *Prosiding Seminar Teknologi Pangan*, 11–18.

Johnson, E. B. G., & Arshad, S. E. (2014). Hydrothermally synthesized zeolites based on kaolinite : A review. *Applied Clay Science*, *97–98*, 215–221. https://doi.org/10.1016/j.clay.2014.06.005

Kadir, S. (2011). *Teknologi Pemisahan Senyawa Aroma Keras Menyengat Pada Asap Cair Tempurung Kelapa dengan metode Redistilasi dan Adsorpsi*. Gadjah Mada University.

Kadir, S., Darmadji, P., Hidayat, C., & Supriyadi. (2015). Sifat Sensoris asap cair tempurung kelapa hasil adsorpsi pada zeolit. *J. Agroland*, *22*(1), 1–8.

Lappin, G. R., & Clark, L. C. (1951). Colorimetric Method for determination of traces of carbonyl compounds. *Analytical Chemistry*, *23*(3), 541–542. https://doi.org/10.1021/ac60051a050

Lombok, J. Z., Setiaji, B., Trisunaryati, W., & Wijaya, K. (2014). Effect of pyrolisis temperature and distillation on character of coconut shell liquid smoke. *Asian Jurnal of Science and Technology*, *5*(6), 320–325. http://www.journalajst.com/sites/default/files/1576.pdf

Maga, J. A. (1987). The flavor chemistry of wood smoke. *Food Reviews International*, *3*(1–2), 139–183. https://doi.org/10.1080/87559128709540810

Ministry of Agriculture. (2019). *Pusat Data dan Sistem Informasi*. https://aplikasi2.pertanian.go.id/bdsp/id

Nendissa, D. M. (2005). *Daya hambat asap cair tempurung kelapa yang sudah dimurnikan dengan cara redestilasi dan adsorbsi dalam zeolit aktif terhadap bakteri halofilik pada ikan tatihu (Thunnus sp) Asap*. Gadjah Mada University.

Oramahi, H. A., & Diba, F. (2013). Maximizing the production of liquid smoke from bark of durio by studying its potential compounds. *Procedia Environmental Sciences*, *17*, 60–69. https://doi.org/10.1016/j.proenv.2013.02.012

Ramachandra, T. V., Kamakshi, G., & Shruthi, B. V. (2004). Bioresource status in Karnataka. *Renewable and Sustainable Energy Reviews*, *8*(1), 1–47. https://doi.org/10.1016/j.rser.2003.09.001

Rinaldi, A., Alimuddin, & Panggabean, A. S. (2015). Pemurnian Asap cair dari kulit durian dengan menggunakan arang aktif. *Molekul*, *10*(2), 112–120.

Sarwendah, M., Feriadi, Wahyuni, T., & Arisanti, T. N. (2019). Pemanfaatan Limbah komoditas perkebunan untuk pembuatan asap cair. *Jurrnal Littri*, *25*(1), 22–30. https://doi.org/http://dx.doi.org/10.21082/littri.v25n1.2019.

Senter, S. D., Robertson, A., & Meredith, F. I. (1989). Phenolic compounds of the mesocarp of cresthaven peaches during storage and ripening. *Journal of Food Science*, *54*, 1259–1268. https://doi.org/https://doi.org/10.1111/j.1365-2621.1989.tb05968.x

Silia, F., & Maulina, S. (2017). Pengaruh Suhu, waktu, dan kadar air pada pirolisis pelepah kelapa sawit. *Jurnal Teknik Kimia*, *6*(2), 14–18.

Suryani, R., Rizal, W. A., Pratiwi, D., & Prasetyo, D. J. (2020). Karakteristik dan aktifitas antibakteri asap cair dari biomassa kayu putih (*Melaleuca leucadendra*) dan kayu jati (*Tectona grandis*). *Jurnal Teknologi Pertanian*, *21*(2), 106–117.

Tóth, L., & Potthast, K. (1984). Chemical aspects of the smoking of meat and meat products. *Advances in Food*

Research, *29*(C), 87–158. https://doi.org/10.1016/S0065-2628(08)60056-7

Wijaya, M., Noor, E., Irawadi, T. T., & Pari, G. (2008). Karakterisasi Komponen kimia asap cair dan pemanfaatannya sebagai biopestisida. *Bionature*, *9*, 34–40.

Yusriah, L., Sapuan, S. M., Zainudin, E. S., & Mariatti, M. (2012). Exploring the potential of betel nut husk fiber as reinforcement in polymer composites : effect of fiber maturity. *Procedia Chemistry*, *4*, 87–94. https://doi.org/10.1016/j.proche.2012.06.013