

Conversion of Cardamom By-product into Liquid Smoke and Biochar by Pyrolysis

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Most cardamom by-products have not been utilized yet, and by conducting pyrolysis, they can have added value. Pyrolysis is a heating process of biomass without oxygen that produces liquid smoke and biochar. The liquid smoke can be applied as a preservative, and the biochar can be used as an energy source. Cardamom seed residue after oil distillation and the husks were pyrolyzed at 350 – 550 °C with a heating rate of 0.36 - 0.45 °C/s for 1 hour using an N₂ carrier gas. The higher yield of liquid smoke (63.91%) was produced after pyrolysis of the husks at 550 °C. At the same time, 51.69% of liquid smoke was produced from pyrolysis of the seed residue at 450 °C. The liquid smoke consisted of chemicals grouped into alcohols, aldehydes, ketones, carboxylic acids, furans, and phenols, with methanol, acetic acid, 1-hydroxy-2-propanone, and furfuryl alcohol as the main compounds. Moreover, 44.86% and 41.86% of biochar were produced from pyrolysis of the husks and the seed residue at 350 °C. The yield of biochar decreased by increasing pyrolysis temperature. After being converted into biochar, the calorific value of the husks and the seed residue increased from 12.95 and 16.24 MJ/kg to 16.79 and 23.07 MJ/kg, respectively.

Key words: Biochar; cardamom husks; cardamom seed residue; liquid smoke; pyrolysis

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Indonesia is one of the countries rich in spice plants. One of them is cardamom plants, with many benefits and high economic value. Cardamom, the queen of spices, is widely used in the food, pharmaceutical, fragrance, and cosmetic industries so that it dominates the global spice trade and is a source of foreign exchange earner for several countries, e.g., India, Indonesia, Guatemala, Vietnam, etc. According to the Tridge-Globaltrade Platform, in 2016, India, Indonesia, and Guatemala produced 104,514 MT of cardamom from 121,939 MT of the total world production. In 2016, Indonesia produces 31,039 MT of cardamom [1] and in 2021 increase to 124,000 MT [2]. Generally, cardamom is sold in dried fruit (capsule), powder (ground dry seeds), or essential oil [3]. Cardamom essential oil has functioned as an antiseptic, anti-microbial, aphrodisiac, astringent, digestive, stomachic, and stimulant used in the food and pharmaceutical industries [4]. Cardamom essential oil is usually obtained from seed distillation and produces by-products called the seed residue (spent biomass) and the husks (pericarp) that have not been utilized much. Cardamom husks (pericarp) contain about 31% fiber, and the cardamom fruit and rhizome mainly contain starch. Cardamom fruit also contains essential oils, pigments, proteins, cellulose, sugars, silica, potassium oxalate, and minerals [5]. The chemical composition of cardamom depends on the variety, place of growth,

and age. Cardamom is primarily cultivated in India, Sri Lanka, Tanzania, Guatemala [6]. In Indonesia, it is widely cultivated in Java and Sumatera islands [5]. In India, some pericarp (husks) is used for garam masala or curry powder. The utilization of husk in research was conducted by Naik (2004) to produce pericarp oil by hydrodistillation and distillation by Clevenger [7]. The seed residue remaining after oil extraction can be processed to recover antioxidants [8]. Usually, solid waste generated by the herbal industries (for example, cardamom or vetiver spent cake after oil distillation) becomes an environmental issue due to being thrown on the road. There is almost no systematic waste management to reuse the waste. A small quantity of the waste was used as boiler fuel [9].

The seed residue (spent biomass after oil distillation) and cardamom husks as solid biomass can be utilized by pyrolysis to enhance their added value. As the simplest and easiest process, pyrolysis can convert solid biomass into liquid smoke and solid biochar with less pollution to the environment. Pyrolysis of biomass is the thermal decomposition of solid biomass through contactless heating with direct flames in the absence of oxygen or inert conditions, usually using N₂ gas to affect the partial pressure of pyrolysis vapor and shorten the residence time in the reactor [10 - 11].

Liquid smoke produced from biomass pyrolysis has antimicrobial and antioxidant properties because it is composed of compounds derived from cellulose, hemicellulose, and lignin, such as acetic acid, carbonyl-containing compounds, furans, and phenolic compounds. Liquid smoke has low acidity due to the acidic compounds. The liquid smoke also contains carbonyl that affects staining (browning) and inhibits microbial growth by penetrating the cell wall and disabling enzymes located in the cytoplasm and cytoplasmic membranes. Moreover, the liquid smoke contains furan and furfural compounds that make sweet, fruity, and grassy flavors and soften the heavy taste of smoky aromas associated with phenols [12 - 15]. The presence of phenols, carbonyls, and organic acids causes liquid smoke to have antimicrobial properties [16], so that it can be used as a food preservative that is more environmentally friendly, eliminates potentially toxic compounds, and easy to control the concentration of smoke than traditional smoking, while still imparting the desired flavors and aromas. Liquid smoke is applied to meat, fish, poultry, cheese, tofu, and even pet food. Liquid smoke is suited for use in marinades, sauces, or brines to processed meat items such as hot dogs, sausage, ham, and bacon [15]. Liquid smokes with high carbonyl compounds are applied as browning agents in food systems. Refined liquid smoke to reduce levels of color and flavor active compounds are used as color preservatives in raw tuna and salmon or as an antimicrobial additive in frankfurters [13].

Biochar or charcoal is produced from biomass pyrolysis containing carbon residues, organic solids, and inorganic materials [10]. Biochar can be burned as a solid fuel similar to coal. Its sulfur content is low compared to coal, while the ash content is high [17]. As a solid fuel, steam gasification of biochar could produce synthetic gas (H₂, CO) [18]. Biochar can be activated to produce activated carbon to improve sorption capacity performance [19]. The activated carbon with a porous structure has many applications, such as an absorbent in industry, medical, agricultural and environmental.

Based on the cardamom essential oil market, global industry trend analysis from 2012 to 2017, and forecast 2017 - 2025, the essential oil market is projected to grow by 5.9% [4]. With the increasing

demand for essential oils, including cardamom oil, which produced 2.8% of oil from the extraction of the seed [20], it is estimated that cardamom husks and seed residue as by-products also increase. Therefore, cardamom husks and the seed residue were utilized into value-added products such as pyrolysis to produce liquid smoke and biochar to reduce environmental pollution. In addition, liquid smoke can be applied as food preservatives and biochar as solid fuel. In the present study, the results of studies on pyrolysis for liquid smoke and biochar production of cardamom husks and the seed residue have been reported for the first time.

MATERIAL AND METHODS

1. Material

Cardamom was purchased from Padang, West Sumatera, Indonesia. The cardamom husks (0.5 cm of width, 1 cm of length) and the seed residue (a by-product of hydrodistillation) were used as the raw material of pyrolysis.

2. Methods

2.1. Pyrolysis Process

The pyrolysis process of the cardamom husks and the seed residue was carried out in a fixed bed reactor made of grade 304 stainless steel material with a diameter of 33 mm and a length of 560 mm. An external electric heater equipped with a temperature controller was used to heat the reactor, as shown in Figure 1 [21]. About 5 g of cardamom husks or about 10 g of the seed residue were inserted into the reactor, then heated from room temperature to specified temperature variations of 350, 450, and 550 °C with heating rates of 0.36 - 0.45 °C/s in the N₂ atmosphere. The vapor produced from pyrolysis was condensed in a condenser and a trap which cooled with ice cubes and a mixture of ice cubes and ethanol, respectively. Incondensable gas was called a gas product, and the residue remained in the bed of the reactor called biochar. The yield of pyrolysis products was determined based on the different weights of certain parts of the device before and after the process and then divided by the feed weight. At the same time, the overall mass balance was used to calculate a gas product, as shown in Eqs. 1-3.

$$Yield_{Biochar} = \frac{W_{reactor\ after\ pyrolysis} - W_{reactor\ before\ pyrolysis}}{W_{feed}} \times 100\% \quad (Eq. 1)$$

$$Yield_{Liquid\ smoke} = \frac{W_{downstream\ after\ pyrolysis} - W_{downstream\ before\ pyrolysis}}{W_{feed}} \times 100\% \quad (Eq. 2)$$

$$Yield_{gas} = 100\% - (Yield_{biochar} + Yield_{Liquid\ smoke}) \quad (Eq. 3)$$

where, W = weight; downstream = connection pipes, condenser, and trap.

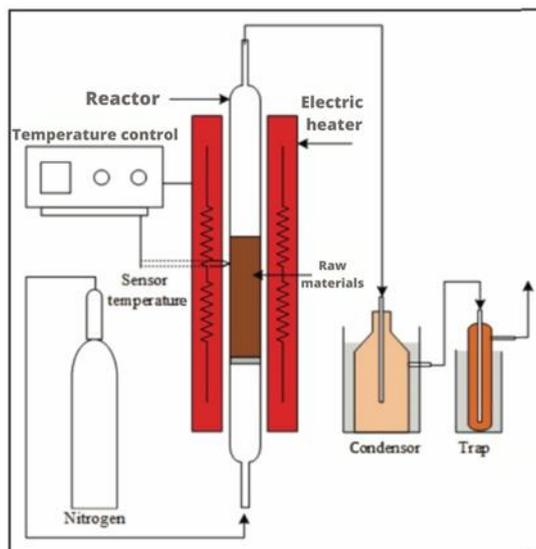


Figure 1. Schematic diagram of pyrolysis system.

2.2. Characterization of Raw Material, Liquid Smoke, and Biochar

Before pyrolysis, raw materials were analyzed using an elemental analyzer (Leco-CHN 628 refer to the ASTM D 5373 method), a moisture balance (VWR series), and a bomb calorimeter (Parr 6400) to determine the elemental composition, moisture content, and calorific value, respectively. Moreover, the characteristic thermal information of the raw material was determined by a thermogravimetric analyzer (THE STA Platinum License Serial). The analysis was carried out by heating the sample from room temperature to 600 °C with a 10 °C/min rate in the N₂ atmosphere [22]. Cellulose, hemicellulose, and lignin compositions in raw material were analyzed using the National Renewable Energy Laboratory (NREL) method [23].

The liquid smoke was analyzed by gas chromatography-mass spectrometry (GC-MS) to determine the chemical composition. The GC-MS instrument (GC-2010/QP2010S, Shimadzu) was equipped with a DB-624 column (Agilent Technologies, Inc. 30 m × 250 μm × 1.40 μm) using helium as the carrier gas. The injector temperature was 250 °C, and the initial oven temperature of the column was 40 °C which was maintained for 5 min, then raised to 190 °C with a rate of 4 °C/min, and finally held for 17.5 min at 190 °C. The ion source temperature and interface temperature were 240 °C. Ionization energy was 70 eV, and the mass ranged from m/z 28 AMU to 600 AMU. The total flow was 36 mL/min, the column flow was 0.85 mL/min, and the linear velocity was 33.2 cm/s. The chemicals in the samples were identified by comparing the spectra and retention time of individual compounds with the authentic reference compounds stored in the mass spectral data library. Presented compounds have a similarity index (SI) higher than 80%. Then, biochar produced from the pyrolysis

process was analyzed using a bomb calorimeter (Parr 6400) to determine its calorific value. The color of liquid smoke was examined by a chroma meter (CIE Lab 3nh).

RESULTS AND DISCUSSION

1. Characterization of Raw Material

The cardamom husks and the seed residue have calorific values of 12.95 MJ/kg and 16.24 MJ/kg with 11.40 wt.% and 10.40 wt.% of moisture contents, respectively. Moreover, the seed residue contained 40.99% carbon, 6.23% hydrogen, 1.98% nitrogen, and 50.84% oxygen based on elemental analysis. Then, the husks had 34.34% carbon, 6.02% hydrogen, 1.51% nitrogen, and 58.13% oxygen. The cardamom husks contained 24.83%; 10.41%; 19.23%; 1.50% of cellulose, hemicellulose, lignin, and ash. The seed residue had 37.16%; 3.00%; 40.20%; 2.62% of cellulose, hemicellulose, lignin, and ash.

The thermal characteristics of the seed residue and cardamom husks as raw material are shown in Figure 2 through the thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) curves. At temperatures <120 °C, the cardamom husks started to degrade (Figure 2a) due to evaporation of moisture content. Furthermore, in the range of 120 – 220 °C, there was a slow depolymerization process. Due to decomposition, a drastic decrease in sample mass occurred at 220 – 325 °C. Once it reached 500 °C, the husks mass decreased slowly because almost all of the volatile compounds were removed, so there was a slight decrease in sample weight. Moreover, at a temperature of <120 °C, the cardamom seed residue began to degrade (Figure 2b). Furthermore, in the range of 120 - 250 °C, there was a slow depolymerization process. Thermal decomposition of the cardamom seed residue occurred at temperatures of 250 – 340 °C,

where the mass of the sample decreased dramatically. Based on the increase in temperature, the pyrolysis process could be divided into four stages, namely: evaporation of moisture content and mild volatiles (< 120°C); degradation of hemicellulose (220 - 325°C); decomposition of some lignin and cellulose (325 - 400 °C); lignin degradation (> 450 °C) [24]. Based on TGA and DTG curves, as shown in Figure 2, pyrolysis of seed residue and cardamom husks was carried out at various temperatures of 350, 450, and 550 °C to identify the optimum yield of liquid smoke and biochar production.

2. Yield of Pyrolysis

Many factors influence the yields of pyrolysis products and chemicals contained in the liquid smoke. Temperature is one of the parameters associated with the thermal degradation of biomass. Figure 3 shows the product distribution of cardamom husks pyrolysis

grouped into biochar, liquid smoke, and gas. Pyrolysis at 550 °C produced a higher yield of liquid smoke (63.91 wt.%), whereas a higher biochar yield (41.86 wt.%) was obtained after pyrolysis at 350 °C. Lower temperatures tend to result in higher biochar. At higher temperatures, more significant primary decomposition of the biomass or the secondary decomposition of the biochar itself caused more volatile materials were being forced out of the biochar [25]. At lower temperatures, lesser primary and secondary decomposition occurred, resulting in a high proportion of biochar. The pyrolysis yield of cardamom husks can be compared with coffee husks that were pyrolyzed at 350–450 °C. Increasing temperature from 350 - 450 °C, liquid smoke yield increased from 27.77 to 31.94%, and the yield of biochar decreased from 39.82 to 34.68% [26]. Moreover, in the production of biochar from coffee husks, an increase in pyrolysis temperature from 350 - 550 °C decreased the biochar yield from 35.09 to 29.90% [25].

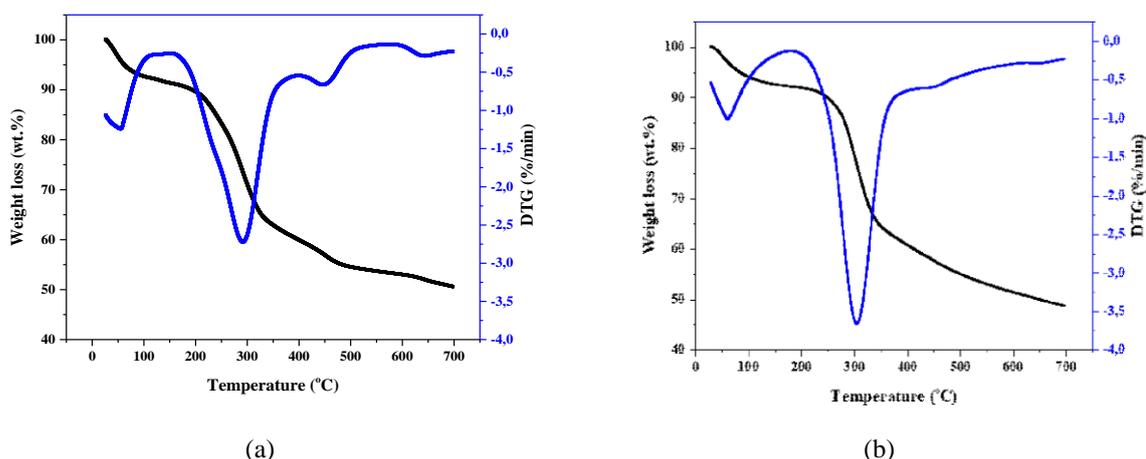


Figure 2. TGA-DTG curves of cardamom husks (a) and seed residue (b).

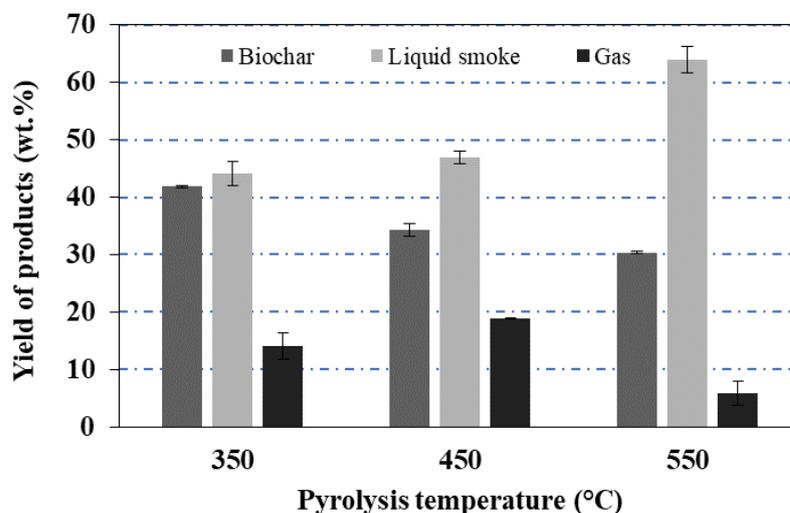


Figure 3. The pyrolysis product distribution of cardamom husks.

On the other hand, Figure 4 shows the pyrolysis distribution products of the seed residue. A higher yield of liquid smoke (51.69 wt.%) was obtained after pyrolysis at 450 °C, and a higher yield of biochar (44.86 wt.%) was produced at 350 °C. Based on the results shown in Figure 3, a higher yield of liquid smoke from cardamom husks was produced at 550 °C. While the production of liquid smoke after pyrolysis of seed residue at 450 °C was higher than at 550 °C that was predicted, a secondary reaction occurred and caused much vapor uncondensable or, in other words increasing the yield of gas and decreasing the liquid smoke. The DTG graph in Figure 2 illustrated the yield of liquid smoke, which depicted the change in mass per time. The much higher of peak was formed on the DTG graph, the higher decomposition of biomass. At a temperature of around 300 °C, there were peaks for cardamom husks and seed residue. However, the peak of seed residue was higher, which means at 300 °C,

the seed residue decomposed more than the cardamom husks. After a temperature of 400 °C, almost no peak was formed for the seed residue. Meanwhile, a peak formed at 450 °C for cardamom husks indicated more volatile materials were being forced out of the biomass at a higher temperature than the seed residue. Therefore, the amount of liquid smoke from cardamom husk increased when the pyrolysis temperature was increased to 550 °C. Whereas increasing the pyrolysis temperature of the seed residue to 550 °C did not increase the amount of liquid smoke.

Chemicals contained in the liquid smoke produced from pyrolysis of seed residue and cardamom husks were analyzed by a gas chromatography-mass spectrometer (GC-MS), as shown in Table 1. The detected chemicals in the liquid smoke are grouped into alcohols, aldehydes, ketones, carboxylic acids, furans, phenols, and others.

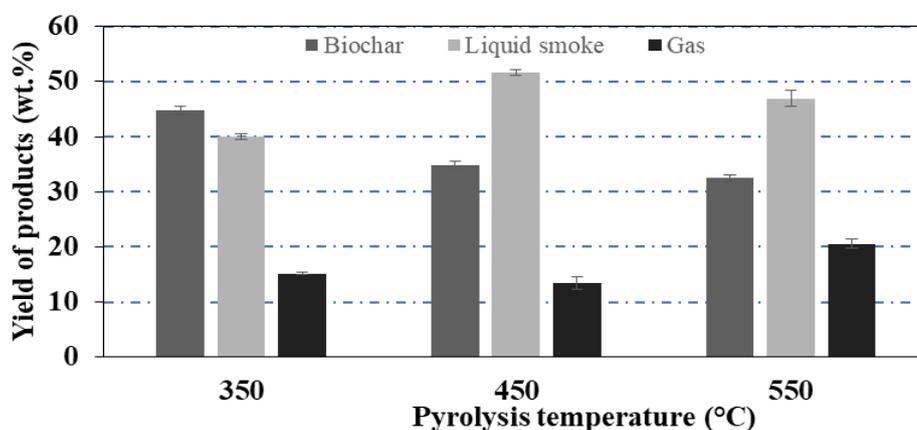


Figure 4. The pyrolysis product distribution of cardamom seed residue.

Table 1. Chemicals composition in the liquid smoke of cardamom husks and seed residue

Group	Chemicals	Cardamom husks (area of peak chromatography, %)				Cardamom seed residue (area of peak chromatography, %)			
		350 °C	450 °C	550 °C	SI*	350 °C	450 °C	550 °C	SI*
Alco- hols	Methanol	28.32	25.27	25.16	98-99	10.18	13.55	14.51	98-99
	Ethanol	0.86	0.62	-	98-99	0.17	-	-	85
	1,2-Ethanediol	-	-	0.43	97	-	-	-	-
	1,2-Ethanediol, diacetate	1.69	1.60	1.77	96-97	1.79	1.08	1.07	96
	2-Propenol	-	-	0.44	86	-	0.52	0.46	85
	2 α -Hydroxy-1,8-cineol	0.55	0.49	0.60	84-89	-	-	-	-
	2-Butene-1,4-diol, (Z)-	-	-	-	-	-	0.48	-	82
	3-Heptanol, 2-methyl-	-	-	-	-	-	1.55	1.62	80
	Total	31.42	27.98	28.40		12.14	17.18	17.66	

Aldehydes	Acetaldehyde	1.26	1.38	0.61	97-98	0.85	0.50	-	98
	Pentanal	1.35	2.57	2.70	86-87	-	3.51	-	87
	Propanal	-	-	-	-	0.16	-	-	84
	2-Heptenal, 2-methyl-	-	-	-	-	-	1.40	1.16	82-83
	Total	2.61	3.95	3.31		1.01	5.41	1.16	
Ketones	Acetone	5.79	6.97	2.12	98	4.59	5.88	6.05	98
	2,3-Butanedione	0.93	0.68	-	98	-	-	-	-
	2-Butanone	-	0.51	-	96	-	0.88	0.96	97
	2,3-Pentanedione	0.36	0.58	-	92-95	-	-	-	-
	2-Propanone, 1-hydroxy-	11.71	12.76	11.64	97	19.33	14.09	15.07	97
	2-Butanone, 3-hydroxy	0.42	-	-	95	-	-	-	-
	1-Hydroxy-2-butanone	3.36	3.12	3.29	96	1.34	1.00	1.03	95-96
	Butyrolactone	1.95	2.34	2.72	94-95	4.52	3.50	3.40	94
	1,3-Cyclopentanedione	1.76	2.33	4.21	81	-	3.39	2.79	81-82
	1,2-Cyclopentanedione, 3-methyl-	0.80	1.26	1.61	90-94	1.73	2.24	2.15	91-94
	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	-	0.70	0.82	88-89	-	-	-	-
	Cyclopentanone	-	-	-	-	-	0.39	0.45	96
	Cyclopentenone	-	-	-	-	1.89	1.58	1.64	82-86
	3-Methyl-2-cyclopenten-1-one	-	-	-	-	-	0.49	0.47	92
	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy	-	-	-	-	0.67	-	-	86
Total	27.08	31.25	26.41		34.07	33.44	34.01		
Carboxylic acids	Acetic acid	25.02	22.87	25.72	98	26.74	19.42	19.52	98
	Propanoic acid	2.99	2.95	3.65	96	2.77	2.88	2.85	96
	Butyric acid	-	-	0.55	97	0.52	0.62	0.62	92-97
	Formic acid	-	-	-	-	-	0.36	-	98
	2-Butenoic acid, (Z)-	-	-	-	-	-	0.37	-	91
Total	28.01	25.82	29.92		30.03	23.65	22.99		
Furans	Furfural	1.35	1.67	1.85	85-88	-	-	-	-
	Furfuryl alcohol	4.31	4.05	4.43	96-98	15.41	11.46	11.75	97-98
	2(5H)-furanone	-	-	0.42	87	-	1.66	1.52	88-90
	2-Furanmethanol, tetrahydro	0.93	0.82	0.78	92-93	-	1.87	1.76	90-91
	Ethanone, 1-(2-furanyl)-	-	-	-	-	0.33	0.49	0.47	88-92
	2(3H)-Furanone, 5-ethylidihydro-	-	-	-	-	-	0.62	0.82	84-85
Total	6.59	6.54	7.48		15.74	16.10	16.32		
Phenols	Phenol, 2-methoxy-	1.31	2,08	2.46	94	-	0.64	0.7	84-86

(Guaiacol)									
Others	Acetic acid, methyl ester	0.42	0.71	-	99	0.62	-	-	89
	Butanoic acid, 2-propenyl ester	-	0.57	0.67	91-92	-	-	-	-
	Pyridine	0.37	-	-	97	0.57	0.44	-	97
	Aminotriazole acetate	-	0.53	0.71	83-85	-	-	-	-
	2,5-Pyrrolidinedione	-	-	-	-	-	0.47	0.44	90
	2-Hydroxypyridine	-	-	-	-	-	0.41	0.46	86-88
	Acetonitrile	-	-	-	-	-	0.91	1.54	99
	1H-Imidazole	-	-	-	-	0.64	-	4.10	85-87
	2,3-Dimethylheptane	-	-	-	-	-	0.34	-	82
	Unknown	2.20	0.55	0.63	<80	5.18	1.03	0.62	<80
	Total	2.99	2.36	2.01		7.01	3.60	7.16	

*SI = a similarity index

Based on Table 1, the main components in the liquid smoke were methanol, acetic acid, 1-hydroxy-2-propanone, and furfuryl alcohol. 28.3% of methanol was contained in liquid smoke after pyrolysis of cardamom husks at 350 °C and 14.5% after pyrolysis of seed residue at 550 °C. Among the liquid smoke, the dominant composition was acetic acid in a range of 19.4 – 26.7%. The acetic acid can be recovered from the liquid smoke. Acetic acid, one of the simplest carboxylic acids, is widely used in various chemical industries such as soft drink bottle production, photographic film, wood glue, and synthetic fabric fibers. After dilution, acetic acid is also often used as a cleaning agent in households. Acetic acid is also used as an adjuster of acidity levels in the food industry to suppress the growth of microorganisms [27]. The presence of ketones (carbonyl group) and furan in a liquid smoke was influenced by cellulose content in

the seed residue and cardamom husks. Moreover, the acid derived from hemicellulose and phenolic compounds was produced from lignin decomposition [13]. The liquid smoke contained 28% methanol based on GC-MS analysis (Table 1). For food preservatives application, separation of methanol by distillation at the boiling point methanol can be carried out because of a hazardous substance.

The liquid smoke produced from pyrolysis of seed residue and cardamom husks was characterized by a chroma meter to identify the color difference. Table 2 shows the results of the color measurement by using distilled water as a blank.

Based on Table 2 total color difference of liquid smoke produced from pyrolysis of cardamom husks and the seed residue was not significantly

Table 2. The color measurement of liquid smoke from pyrolysis of cardamom husks and cardamom seed residue

Index	Aquadest	Cardamom husks			Cardamom seed residue		
		350°C	450°C	550°C	350°C	450°C	550°C
L*	51.5	46.3	46.3	46.6	46.5	46.4	46.3
a*	0.2	0.2	0.7	1.5	1.2	0.9	1.1
b*	-0.7	-1.2	-1.1	-0.9	-1.0	-1.1	-1.1
ΔE	-	5.2	5.3	5.1	5.1	5.1	5.3
Image							

Nomenclature : L* (CIE lightness coordinate), a* (CIE red(+)/green(-) color attribute), b* (CIE yellow(+)/blue(-) color attribute), ΔE (total color difference)

Table 3. The calorific value of biochar produced from seed residue and cardamom husks

Pyrolysis temperature (°C)	Calorific value (MJ/kg)	
	Seed residue	Cardamom husks
350	21.46	16.79
450	22.60	16.56
550	23.07	16.55

different, and the value was in the range of 5.1-5.3. All liquid smoke products looked brownish-red color in the direct vision. Color measurement of the liquid smoke is needed to determine the appropriate concentration in applications because it affects the intensity of the color parameters in the final product. The industry uses information on the liquid smoke concentration to produce standard colors for consumers.

Biochar can be burned as a solid fuel produced from pyrolysis because it has a high calorific value. The calorific values of the biochar are shown in Table 3.

Table 3 shows that the caloric value of biochar produced from seed residues was higher than the cardamom husks because carbon content (based on an elemental analysis) in the seed residue was higher than the cardamom husks. The carbon content was also indicated by higher cellulose and lignin contents in the seed residue. Increase in pyrolysis temperature, the caloric value of biochar from seed residue was also increased, and at 550 °C, the value reached 23.07 MJ/kg. While the caloric value of biochar from cardamom husks slightly decreased by increasing pyrolysis temperature. Biochar produced after pyrolysis at 350 °C had a value of 16.79 MJ/kg. Because the calorific value of biochar produced from cardamom husks was 27% lower than that of biochar derived from the seed residue, biochar from the seed residue was preferable for solid fuel applications.

CONCLUSION

Pyrolysis can increase seed residues and cardamom husks' added value by converting them into liquid smoke and biochar. The liquid smoke and biochar yield was influenced by several parameters such as temperature and the nature of biomass feedstocks. The optimum yield of liquid smoke resulted from pyrolysis of cardamom husks and seed residue at 550 °C and 450 °C, respectively. In contrast, a higher biochar yield was produced at low pyrolysis temperature. The liquid smoke consisted of chemicals dominated by acetic acid, methanol, and 1-hydroxy-2-propanone. Acetic acid has the potential as anti-microbial. Moreover, biochar can be used as solid fuel due to a high calorific value of 21.46 – 23.07 MJ/kg derived from seed residue.

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REFERENCES

1. International Cardamom Association (2019) Report: Cardamom, Dubai. [https://cardamomassociation.com/report/cardamom/#:~:text=According to Tridge-Globaltrade Platform, 78.21% 25 of world cardamom export. \[March 25th, 2022\].](https://cardamomassociation.com/report/cardamom/#:~:text=According to Tridge-Globaltrade Platform, 78.21% 25 of world cardamom export. [March 25th, 2022].)
2. Badan Pusat Statistik (2021) Production of medicinal plants by province and kind of plant, Statistics Indonesia. *Agricultural Statistic for Horticulture SPH, Indonesia*. [https://www.bps.go.id/indikator/indikator/view_data_pub/0000/api_pub/UVMzY2pGV3kyWjhLYm9UTEdtYk52Zz09/da_05/1. \[March 25th, 2022\].](https://www.bps.go.id/indikator/indikator/view_data_pub/0000/api_pub/UVMzY2pGV3kyWjhLYm9UTEdtYk52Zz09/da_05/1. [March 25th, 2022].)
3. National Institute of Food Technology Entrepreneurship and Management (2022) Reading manual for cardamom processing under PMFME scheme. *Ministry of Food Processing Industries, India*. [http://niftem.ac.in/site/pmfme/lmnew/cardamomwriteup.pdf. \[March 25th, 2022\].](http://niftem.ac.in/site/pmfme/lmnew/cardamomwriteup.pdf. [March 25th, 2022].)
4. Persistence Market Research (2017) Cardamom Essential Oil Market, Persistence Market Research. [https://www.persistencemarketresearch.com/market-research/cardamom-essential-oil-market.asp#:~:text=The world production of cardamom, followed by India and Tanzania. \[March 25th, 2022\].](https://www.persistencemarketresearch.com/market-research/cardamom-essential-oil-market.asp#:~:text=The world production of cardamom, followed by India and Tanzania. [March 25th, 2022].)
5. Syafitri, M. H. and Fazadini, S. Y. (2020) Analisis mutu minyak atsiri biji buah kapulaga lokal (*Amomum cardamomum*) berasal dari Pulau Jawa dan Bali. *Inovasi*, **22**, 74–80.
6. Morsy, N. F. S. (2015) A short extraction time of

- high quality hydrodistilled cardamom (*Elettaria cardamomum* L. Maton) essential oil using ultrasound as a pretreatment. *Industrial Crops Products*, **65**, 287–292.
7. Naik, J. P., Rao, L. J. M., Kumar, T. M. M. and Sampathu, S. R. (2004) Chemical composition of the volatile oil from the pericarp (husk) of large cardamom (*Amomum subulatum* Roxb.). *Flavour Fragrance Journal*, **19**, 441–444.
 8. Navarrete, A., Herrero, M., Martín, A., Cocero, M. J. and Ibáñez, E. (2011) Valorization of solid wastes from essential oil industry. *Journal of Food Engineering*, **104**, 196–201.
 9. Sen, S., Sharma, R. and Katyal, A. (2018) Cluster diagnostic report Kannauj Attar & Essential Oil Cluster, Technology Cluster Manager Technology Centre Systems Program (TCSP) Office of DC MSME, Ministry of MSME. Kanpur, India
 10. Yaman, S. (2004) Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Conversion and Management*, **45**, 651–671.
 11. Xin, X., Dell, K., Udugama, I. A., Young, B. R. and Baroutian, S. (2021) Transforming biomass pyrolysis technologies to produce liquid smoke food flavouring. *Journal of Cleaner Production*, **294**, 125368.
 12. Saloko, S., Darmadji, P., Setiaji, B. and Pranoto, Y. (2014) Antioxidative and antimicrobial activities of liquid smoke nanocapsules using chitosan and maltodextrin and its application on tuna fish preservation. *Food Bioscience*, **7**, 71–79.
 13. Montazeri, N., Oliveira, A. C. M., Himelbloom, B. H., Leigh, M. B. and Crapo, C. A. (2013) Chemical characterization of commercial liquid smoke products. *Food Science & Nutrition*, **1**, 102–115.
 14. Varlet, V., Prost, C. and Serot, T. (2007) Volatile aldehydes in smoked fish: Analysis methods, occurrence and mechanisms of formation. *Food Chemistry*, **105**, 1536–1556.
 15. Lingbeck, J. M., Cordero, P., O'Bryan, C. A., Johnson, M. G., Ricke, S. C. and Crandall, P. G. (2014) Functionality of liquid smoke as an all-natural antimicrobial in food preservation. *Meat Science*, **97**, 197–206.
 16. Mansur, D., Sugiwati, S., Rizal, W. A., Suryani, R. and Maryana, R. (2021) Pyrolysis of cajuput (*Melaleuca leucadendron*) twigs and rice (*Oryza sativa*) husks to produce liquid smoke-containing fine chemicals for antibacterial agent application. *Biomass Conversion and Biorefinery*, 0123456 789.
 17. Laird, D. A., Brown, R. C., Amonette, J. E. and Lehmann, J. (2009) Review of the pyrolysis platform for coproducing bio-oil and biochar. *Biofuels, Bioproducts and Biorefining*, **3**, 547–562.
 18. Kajita, M., Kimura, T., Norinaga, K. Li, C. Z. and Hayashi, J. I. (2010) Catalytic and non-catalytic mechanisms in steam gasification of char from the pyrolysis of biomass. *Energy and Fuels*, **24**, 108–116.
 19. Tan, X. F., Liu, S. B., Liu, Y. G., Gu, Y. L., Zeng, G. M., Hu, X., Wang, X., Liu, S. H., and Jiang, L. H. (2017) Biochar as potential sustainable precursors for activated carbon production: Multiple applications in environmental protection and energy storage. *Bioresource Technology*, **227**, 359–372.
 20. Hassan, A., Redha, A. A. and Adel, Z. (2020) Extraction, antioxidant activity and characterization of essential oils of different spices. *International Journal Science Research in Chemical Science*, **7**, 21–29.
 21. Simanungkalit, S. P., Mansur, D. and Fitriady, M. A. (2018) Effect of plastic blends on slow pyrolysis of oil palm empty fruit bunch. *AIP Conference Proceeding*, **2024**, 020003.
 22. Simanungkalit, S. P. and Mansur, D. (2020) Co-pyrolysis cangkang kelapa sawit dan limbah plastik kemasan. *Widyariset*, **6**, 62–74.
 23. Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D. and Crocker, D. (2012) Determination of structural carbohydrates and lignin in biomass. *Laboratory Analytical Procedure (LAP), National Renewable Energy Laboratory (NREL), United States*.
 24. Sanchez-Silva, L., López-González, D., Villaseñor, J., Sánchez, P. and Valverde, J. L. (2012) Thermogravimetric-mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis. *Bioresource Technology*, **109**, 163–172.
 25. Kiggundu, N. and Sittamukyoto, J. (2019) Pyrolysis of coffee husks for biochar production. *Journal of Environmental Protection*, **10**, 1553–1564.
 26. Setter, C., Silva, F. T. M., Assis, M. R., Ataíde, C. H., Trugilho, P. F. and Oliveira, T. J. P. (2020) Slow pyrolysis of coffee husk briquettes: Characterization of the solid and liquid fractions. *Fuel*, **261**, 116420.
 27. Njateng, G. S. S., Zaib, S., Chimi, L. Y., Feudjio, C., Mouokeu, R. S., Gatsing, D., Kuate, J. -R., Adewole, E. and Iqbal, J. (2018) Antidiabetic potential of methanol extracts from leaves of *Piper umbellatum* L. and *Persea Americana* Mill. *Asian Pac. J. Trop. Biomed.*, **8**, 160–165.