Effect of Pyrolysis Temperature and Time on Liquid Smoke Yield in Coconut (*Cocos nucifera L.*) Shells Pyrolysis Process

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Abstract. Biomass pyrolysis is an emerging method to manage solid biomass from agricultural activity, which transforms solid organic materials thermally to create solid, liquid, and non-condensable gases as its product. This research was conducted to understand the effect of pyrolysis temperature and time on the yield of liquid smoke from coconut shell biomass. In this work, the pyrolysis was performed with temperatures of 350°C, 450°C, and 550°C, with a pyrolysis time of 2, 3, and 4 hours. Based on this work, it is known that both pyrolysis temperature and time affected the yield of liquid smoke. The liquid smoke obtained at temperature pyrolysis of 350°C for 4 hours yields 46,5%, with density of 1.025 g/ml, viscosity of 1,555 cP, and pH of 2. GC-MS characterization revealed the 20 components in obtained liquid smoke, including organic acids, carbonyl compounds, phenolic compounds, and another compound. Acetic acid is the dominant component, up to 51.40%.

1 Introduction

One new method for producing liquid smoke is biomass pyrolysis, a rapidly expanding field of study in bioresource technology. By using heat to break down solid organic materials, biomass pyrolysis produces liquid, solid, and non-condensable gases [1]. To create these compounds, pyrolysis requires fast heating in the absence of oxygen. The amount of biomass utilized, the kind of pyrolysis, and process factors including pre-treatment settings, pyrolysis temperature, and heating rate all affect how much of each of these products is produced [2].

Water evaporation and the degradation of cellulose, hemicellulose, and lignin are the four steps in the pyrolysis process. Between 180°C and 350°C, hemicellulose and cellulose decompose to form carboxylic acids and carbonyl compounds, whereas lignin decomposes to form phenols between 300°C and 500°C. In addition to phenols, acids, and carbonyls, biomass pyrolysis frequently yields unwanted substances including polycyclic aromatic hydrocarbons (PAHs), which are created at temperatures ranging from 500°C to 900°C and some of which are naturally occurring. Others, on the other hand, are the outcome of incomplete combustion. Unwanted PAHs may be eliminated during the purification process, and the liquid smoke's flavor and color intensity can be altered [3].

Condensing the pyrolysis vapour product yields liquid smoke, which is composed of oxidized organic components such phenol, aldehyde, ketone, and carboxylic acid. Liquid smoke gets its unique flavor and smell from these ingredients, which also have antibacterial and antioxidant properties [2]. At present, liquid smoke has been employed for a variety of applications, such as natural preservatives for food products [4][5], fertilizer for plant [6], pesticide [7], natural rubber coagulant [8][9], and etc.

Coconut shells are an example of easily found biomass in Indonesia. According to the Indonesian Ministry of Agriculture [10], there is 3,355,535 Ha of coconut plantations in Indonesia in 2021, with 2,877,504 tons of coconut production generated. Ahmad et al. [11] states that a fully ripe coconut has 35% fiber, 12% hard shell, 28% white flesh, and 25% coconut water. Biomass from coconut shells is produced during the processing of coconuts to make various items. Valuing the shells into value-added goods is an alternative approach to managing solid waste from Indonesia's coconut industry. This is particularly effective when using the shells as sources of multipurpose liquid smoke.

The purpose of this work is to explore how temperature and time during pyrolysis affect the amount of liquid smoke produced from coconut shells. In order to determine the composition of the liquid smoke that was collected, GC-MS characterization had been carried out along with quality analyses of density, viscosity, and pH.

2 Methodology

Coconut shell was the material employed in this study. A digital scale, pycnometer, pH meter, viscosimeter Ostwald, filter paper, measuring cup, and gas

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chromatography-mass spectrometry (GC-MS) were among the tools utilized. Figure 1 displays the pyrolysis reactor design. The coconut shells underwent thorough separation and cleaning to remove any contaminants. Next, the coconut shells were weighted up to 2 kg and subjected at various pyrolysis time (2, 3, and 4 hours) and different temperatures (350, 450, and 550 degrees Celsius). After pyrolysis, the liquid smoke was collected and its yield, density, viscosity, pH, and chemical content were examined.

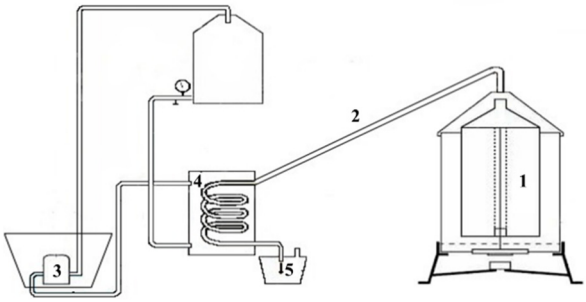

Fig. 1. Schematic of pyrolysis reactor
Note: (1) pyrolysis reactor; (2) condenser; (3) cooling water pump; (4) cooling water tank; (5) liquid smoke tank

3 Results and Discussion

3.1 Effect of Pyrolysis Temperature and Time on the Liquid Smoke Yield

Yield analysis was done to see the percentage of resulting liquid smoke from the coconut shells after pyrolysis. Fig 2 shows the effect of pyrolysis temperature and time on the yield of liquid smoke. In general, increasing pyrolysis temperature and time impacts liquid smoke yield. The yield of liquid smoke produced at 350°C ranges from 36.30-46.50%. There was variation in the liquid smoke yield at 450°C, namely 43.70%, 47.70%, and 43.50%. Ultimately, the liquid smoke production climbed to 46.50–51.00% when the pyrolysis temperature was raised to 550°C.

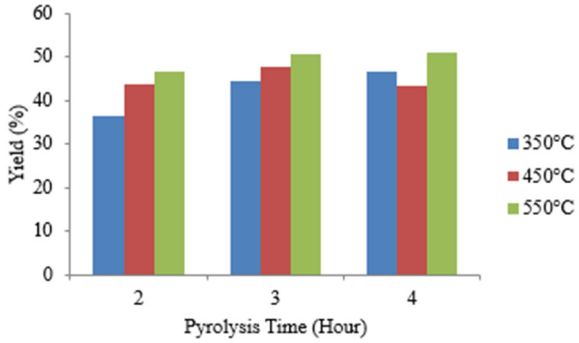

Fig. 2. Effect of pyrolysis temperature and time on the yield of liquid smoke

Elevated temperatures and extended pyrolysis times result in a more thorough breakdown of the starting components, producing more liquid smoke. [12]. Temperature is one of the critical variables affecting pyrolysis yield. Liquid smoke yield consistently increases at the beginning of the process, increasing temperature to a certain maximum temperature, after which the yield drops when the temperature rises further. At temperatures higher than optimum values, the liquid smoke yield is reduced, and the production of non-condensable gases is increased. On the other hand, liquid smoke yield has been observed to increase slightly with an increase in retention time [13].

3.2 Effect of Pyrolysis Temperature and Time on the Liquid Smoke Density

The quantity of components present in the liquid smoke is indicated by its density or specific gravity, which has an impact on the liquid smoke's weight [14]. For combustion applications, liquid smoke density is crucial since it represents the quality of atomization, vaporization, ignition, and combustion properties [15]. The effect of pyrolysis temperature and time on the liquid smoke density is depicted in Fig 3. The liquid smoke density decreases when the temperature is raised but increases when the pyrolysis time is extended. Specifically, the density of liquid smoke ranges from 1.024-1.027 g/ml at a pyrolysis temperature of 350°C, 0.933-1.021 g/ml at a pyrolysis temperature of 450°C, and 0.917-0.931 g/ml at pyrolysis temperature of 550°C.

According to the Japanese Quality Liquid Smoke Standard, the density requirement for liquid smoke is > 1.005. On the other hand, Indonesian National Standard (SNI) [16] set the density requirements for grade I-liquid smoke at 1.005-1.050 g/ml. Based on this research, only five samples of liquid smoke met this density requirement: all liquid smoke obtained at a temperature of 350°C and liquid smoke obtained at a temperature of 450°C for 3 and 4 hours.

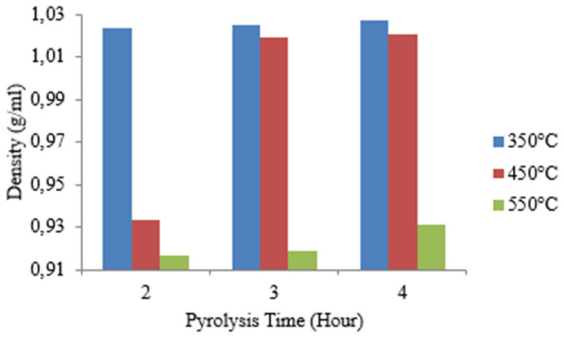

Fig. 3. The effect of pyrolysis temperature and time on the density of liquid smoke

3.3 Effect of Pyrolysis Temperature and Time on The Viscosity of Liquid Smoke

Fig 4 presents the viscosity of liquid smoke at various temperature and time of pyrolysis. Based on Fig 4, the viscosity of liquid smoke is ranging from 1.395-1.555 cP at 350°C, 1.265-1.398 at 450°C, 1.036-1.115 cp at pyrolysis temperature of 550°C. It's clearly seen that increasing temperature will produce the liquid smoke with lower viscosity. Higher temperatures during pyrolysis promote a more severe breakdown of biomass or pyrolysis vapour, leading to the synthesis of smaller molecules or lower molecular weight substances [15].

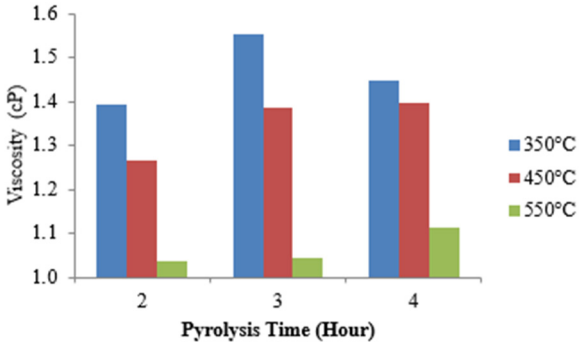

Fig. 4. Viscosity of liquid smoke

3.4 pH of Liquid Smoke

One of the quality criteria for the liquid smoke is the pH level. The measurement of liquid smoke pH aims to establish the degree of pyrolysis decomposition and to generate the smoke's natural acid. If the liquid smoke has a low pH, it shows good quality and can be used as a food preservative. The durability, shelf life, and organoleptic qualities of the liquid smoke are all impacted by the low pH value overall [14].

In this research, the pH measurement results show that the produced liquid smoke has an acidic pH of about 2-3. This pH value had met the Japanese Quality Liquid Smoke Standards, ranging from 1.5 to 3.7. More specifically, liquid smoke produced at 350°C has a pH of 2 and meets the SNI No. 8985:2021 [16]. The liquid smoke product is acidic from this work, based on the resultant pH. At temperatures higher than 200°C, pyrolysis is an exothermic reaction that generates heat. The decomposition rate is increasing at this point, and the biomass components that break down throughout the pyrolysis process significantly impact the liquid smoke product's acidity [17].

3.5 Composition of Liquid Smoke

In this work, the liquid smoke collected after 4 hours of pyrolysis at 350°C was submitted to a composition analysis. Twenty components have been determined through GC-MS analysis, as Fig. 5 and Table 1 demonstrate. Temperature may have an impact on how the chemicals in raw materials break down during pyrolysis. As the temperature rises, the average rate at which chemical bonds break increases [18]. From an application standpoint, the components were categorized into three functional groups: carbonyls, phenols, and carboxylic acids. This helped to depict the chemical composition of liquid smoke. These functional classes are not the only products; there are also hydrocarbons, lactones, and alcohols [19].

The obtained liquid smoke in this work contains aldehyde, organic acids, carbonyl, phenolic, aromatics, and another compound, with the highest component being acetic acid, 51.40%. In another investigation, the main ingredient in liquid smoke derived from coconut shells that were pyrolyzed for eight hours was acetic acid, which was found to be 51.6% at 200°C, 50.88% at 250°C, and 39.98% at 300°C [3]. Carbonyl compounds and acetic acid are the results of cellulosic pyrolysis. Furfural, furan, and its derivatives are the products of hemicellulose pyrolysis. Finally, phenol will be produced as lignin breaks down [12]. Acetic acid can act as an antimicrobial. Several factors, including concentration, pH, ambient factors, contact time, contact temperature, and species of bacteria, might affect the antibacterial activity of acetic acid. On the other hand, the development of the odour, texture, and colour of liquid smoke products is significantly influenced by other substances, such as phenols, that are present in liquid smoke [18]. Furthermore, phenolic compounds have antibacterial and antifungal effects of eliminating bacteria that cause rot and break down proteins into amino acids, stopping the offensive odour. Because they are capable of making cell membranes more permeable, phenols act as bactericides by inactivating vital enzymes and damaging or inactivating genetic material. [7]. After being refined using adsorption or distillation techniques, the liquid smoke from this research exhibits significant potential for use as a food preservation agent.

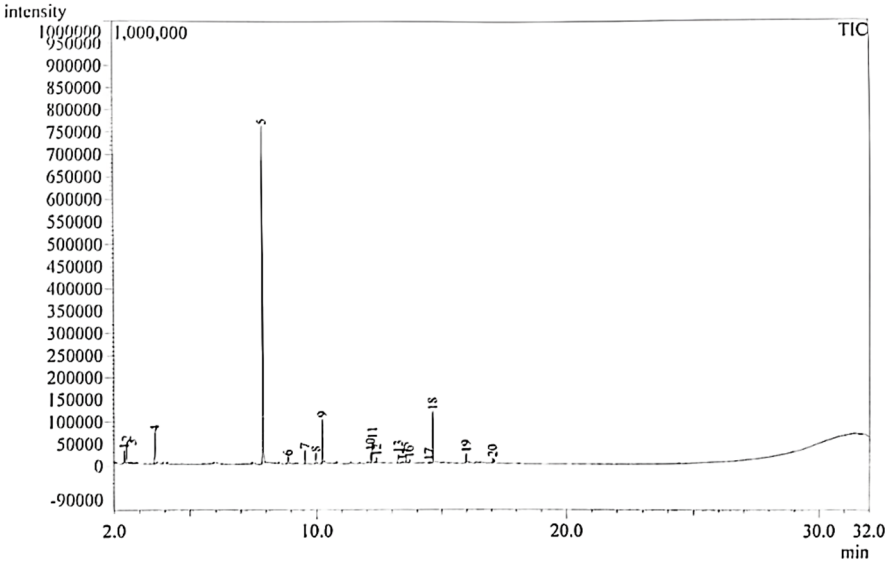

Fig. 5. Chromatogram of liquid smoke

Table 1. Composition of obtained liquid smoke

Component	Area (%)
2,2-dimethoxybutane	1.98
1-Hydroxy-2-Butanone	3.27
Propanal (CAS) Propionaldehyde	0.66
Acetic acid, Hidroxy	6.77
Acetic acid	51.40
2-Cyclopenten-1-one,2 hydroxy-3-methyl-(CAS) Coryclon	1.26
Phenol, 2-methyl-(CAS) o-Cresol	2.28
Phenol, 3-methyl- (CAS) m-Cresol	2.25
Phenol, 2-methoxy- (CAS) Guaiacol	6.60
2-Methoxy-4-methylphenol	1.87
1,2 Benzenediol (CAS) Pyrocathecol	4.31
III-Imidazole, 1-(1-oxooctadecyl)-	1.01
Benzene, (methylsulfinyl)- (CAS) Methyl phenyl sulfoxide	2.35
1,3-Benzenediol (CAS) Resorcin	1.09
Phenol, 4-ethyl-2-methoxy- (CAS) p-Ethylguaiacol	1.37
4 Methyl catechol	0.72
2-Methoxy-5-methyl pyrazine	0.67
Phenol, 2,6-dimethoxy- (CAS) 2,6-Dimethoxyphenol	7.92
Benzene, 1,2,3-trimethoxy- (CAS) 1,2,3-Trimethoxybenzene (CAS) Methylsy	1.36
Ethanone,1-(2,6-dihydroxy-4-methoxyphenyl)-(CAS) 2,6-Dihydroxy-4-methyl	0.85

4 Conclusion

The outcomes of this investigation indicate that the yield and characteristics of liquid smoke derived from coconut shells, particularly its density, viscosity, and pH, were impacted by both temperature and yield. After 4 hours of pyrolysis at 350°C, 46.5% of the liquid smoke was produced. It had a density of 1.025 g/ml, a viscosity of 1,555 cP, and a pH of 2. GC-MS analysis identified 20 components in the liquid smoke, with acetic acid contributing 51.40% of the total.

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