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Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

Upgrading of slow pyrolysis *Eleocharis Dulcis* bio-oils through vacuum distillation

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ARTICLE INFO

Article history:
Available online xxx

Keywords:
Bio-oil
Eleocharis Dulcis
Distillation
Phenol

ABSTRACT

The goal of this research is to develop and characterize bio-oil upgrading from pyrolysis *Eleocharis Dulcis* (ED) using the vacuum distillation process. Bio-oil from slow-pyrolysis *Eleocharis Dulcis* (ED) was employed as the feedstock. The distillation experiments were performed at temperatures ranging from 96, 97, 98, 99, and 100 °C, respectively. After that, the feedstock was distilled to separate the different fuel components. Gas chromatography-mass spectrometer (GC-MS) analysis was used to properly quantify a typical bio-oil component. The findings indicate that a common critical point was widely present during the distillation process, which may be attributed to a stable system generated by hydrogen bonding. The result showed that Acetic acid, propanone, and phenol were dominant with the concentration ranges of 20–50%, 12–20%, and 13–39.6%, respectively. The extensive distillation characteristics and product distribution contribute to a deeper understanding of the reaction process and component enrichment patterns, which helps with design and parameter optimization.

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1. Introduction

The world's reliance on fossil fuels for energy has remained high. This presents several critical economic, energy supply security, and environmental concerns [1]. As a result, growing interest in renewable energy development has prompted concerns about climate change as well as the continued growth for fossil fuels. Academic institutions have been working to improve and create renewable energy technologies and ideas, particularly those that may be utilized to replace fossil fuel resources, due to worries about energy use and pollution [2]. Biofuel production employing resources such as palm oil, fat, and other biomass is one of the most important renewables for biofuel production. Biomass or its wastes are a great choice among renewable energy sources that are not competing with food because they are relatively inexpensive, freely available, sustainable, and capable of significantly lowering greenhouse gas emissions [3,4]. Biomass, commonly known lignocellulosic biomass, is natural matter obtained from biological organisms such as crops or tree products that is not intended for

human use or feed. As a major agricultural and forestry country with the world's largest swampland, Indonesia is likely to generate vast amounts of agricultural wastes, forestry leftovers, and tidal swamp plants, all of which are classed as wet biomass. As a result, biomass can be used to replace fossil fuel resources in Indonesia to produce energy and high-value compounds. The biomass is composed of hemicellulose (19–25%), cellulose (32–45%), and lignin (14–26%) [5]. As a result, it may be converted into gas, liquid, and solid fuels, as well as biofuel, to generate heat and electricity. Biomass energy has numerous advantages over conventional fossil fuels, including shorter life cycles, more excellent dispersion, and reduced greenhouse gas emissions [6].

Thermochemical conversion, biochemical conversion, and physicochemical conversion are some of the technologies that have been utilized to convert biomass to energy. Because it is rapid and has no constraints for processing combinations of different types of the biomass, thermochemical conversion is the most used technology for converting biomass. Pyrolysis has been established as the most promising thermochemical conversion method for producing energy products from biomass, such as bio-oil, char, and biogas, for decades. Bio-oil is the primary product of the pyrolysis process, with a low energy content that may be used as a low-grade fuel

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<https://doi.org/10.1016/j.matpr.2022.02.494>

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for a variety of purposes and a higher energy content that can be utilized as a good feedstock for power production after upgradation [7,8]. Pyrolysis processes can be classified as fast or slow depending on the heating rate and solid/vapor residence time. When liquid production is the target, fast pyrolysis is used with short solid/vapor residence times (e.g. 12 s) and rapid heating rates (e.g. 500 W/m² K) [9,10]. Slow pyrolysis employs lower temperatures (300–600 °C), slower heating (5–20 °C/s), and longer solid residence times (10–60 min) [11]. The composition of biofuel products varies based on the process variables, such as temperature, heating rate, and vapor residence time [12]. This process involves the breakdown of a more complex chemical molecule into a simpler one at highish temperatures and almost no oxygen [13]. The end product of this process can be a gas, a solid (char), or a liquid (bio-oil). Utilizing such methods for value-added biomass products, for instance, holds incredible potential for various financial and power sectors, allowing for the production of high-value minerals, chemicals, and fuels. Pyrolysis bio-oil is a liquid that derives from the condensation of vapor created during pyrolysis. It has the potential to be utilized as a fuel oil replacement, with heating values of 40–50% that of hydrocarbon fuels [14]. The pyrolytic oil produced by slow pyrolysis of *Eleocharis Dulcis* (ED) is a complicated combination with valuable hydrocarbon components. It includes ketone, acid, phenol, and aromatic compounds with a wide variety of boiling points. Recently, Cong et al. [15] analyze the product property, energy balance, and ecological impact based on different biomass slow pyrolysis. They indicated that the heating plants based on biomass slow pyrolysis have promising application prospects. Slow pyrolysis of agro-food wastes and physicochemical characterization of biofuel products was conducted by Patra et al. [10]. Temperature, reaction time, and heating rate have all been optimized in the slow pyrolysis process to achieve the highest bio-char and bio-oil production. For liquid fuel applications, the bio-oil must have a low water, ash, and solids content, as well as a high energy content and acceptable pH and viscosity [16].

Depending on the intended enhancement in bio-oil qualities, it can be handled either physically or chemically. Filtration procedures can be used to remove ash, while solvents additive can be used to standardize and minimize the viscous of the bio-oil [17]. Realistically, producing bio-oil of high quality by adding solvent or chemical reagent is relatively costly. Therefore, increasing the value of bio-oil into value added product is essential and has gained attention. Wang et al. [18] used molecular distillation at 130 °C to separated bio-oil into three section. Guo et al. [19] used 60 Pa and 50 °C extract carboxylic acids from pine bio-oil. They were able to improve the bio-oil characteristics by lowering the acid level in the crude bio-oil.

The research above implies that distillation can improve the qualities of bio-oil by separating the components. However, complex distillation apparatus is required. Furthermore, bio-oil generated from biomass such as *Eleocharis Dulcis* (ED) was used in these investigations, which may have a different composition than other biomass and thus a different distillation characteristic. However, to the best of our knowledge, a plausible mechanism of pyrolytic bio-oil from *Eleocharis Dulcis* (ED) under vacuum distillation have yet to be reported. Therefore, this study aims to investigate the behavior of pyrolytic bio-oil *Eleocharis Dulcis* (ED) via vacuum distillation thoroughly. More specifically, this study examines the temperature effect on product distribution and characteristics of pyrolytic oil *Eleocharis Dulcis* (ED) biomass. Hence, the thorough investigation of pyrolytic bio-oil *Eleocharis Dulcis* (ED) via vacuum distillation would be beneficial not only for environmental mitigation but also for producing bioenergy and value-added chemicals and providing a more profound understanding for future research and implementation.

2. Materials and method

2.1. Materials

Eleocharis Dulcis (ED) biomass used in the pyrolysis process was obtained from Danau Seran, Banjarbaru, South Kalimantan,

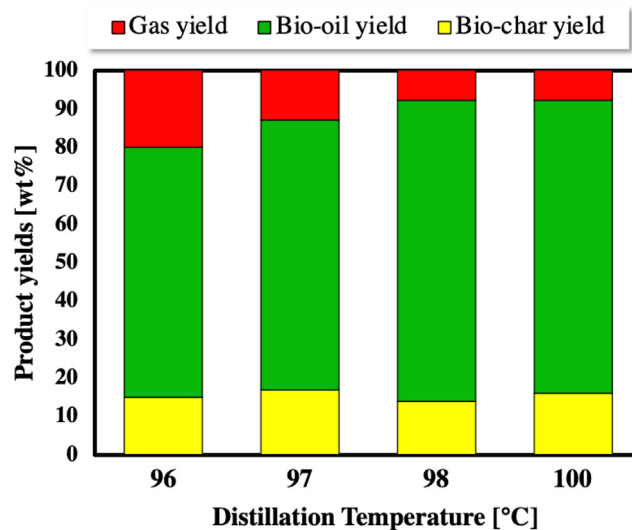


Fig. 2. Product distribution of distilled bio-oil at various temperature.

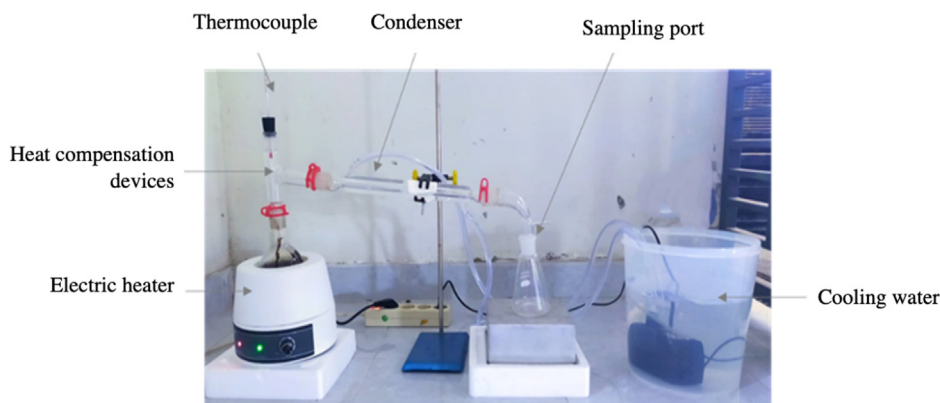


Fig. 1. Schematic diagram of the distillation equipment.

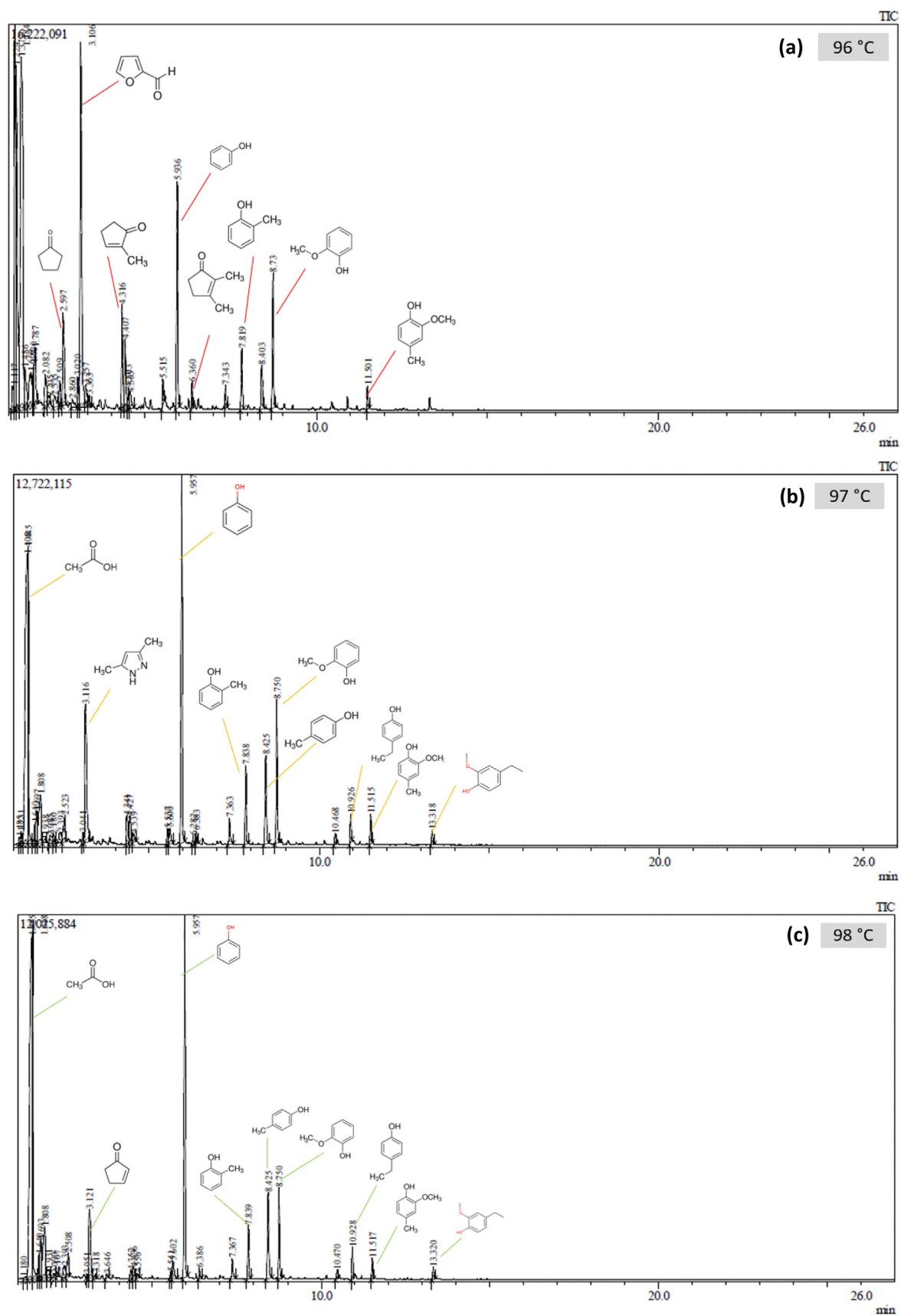


Fig. 3. GC-MS chromatographic separation of distillation pyrolytic bio-oil produced at (a) 96 °C, (b) 97 °C, (c) 98 °C, (d) 99 °C, and (e) 100 °C.

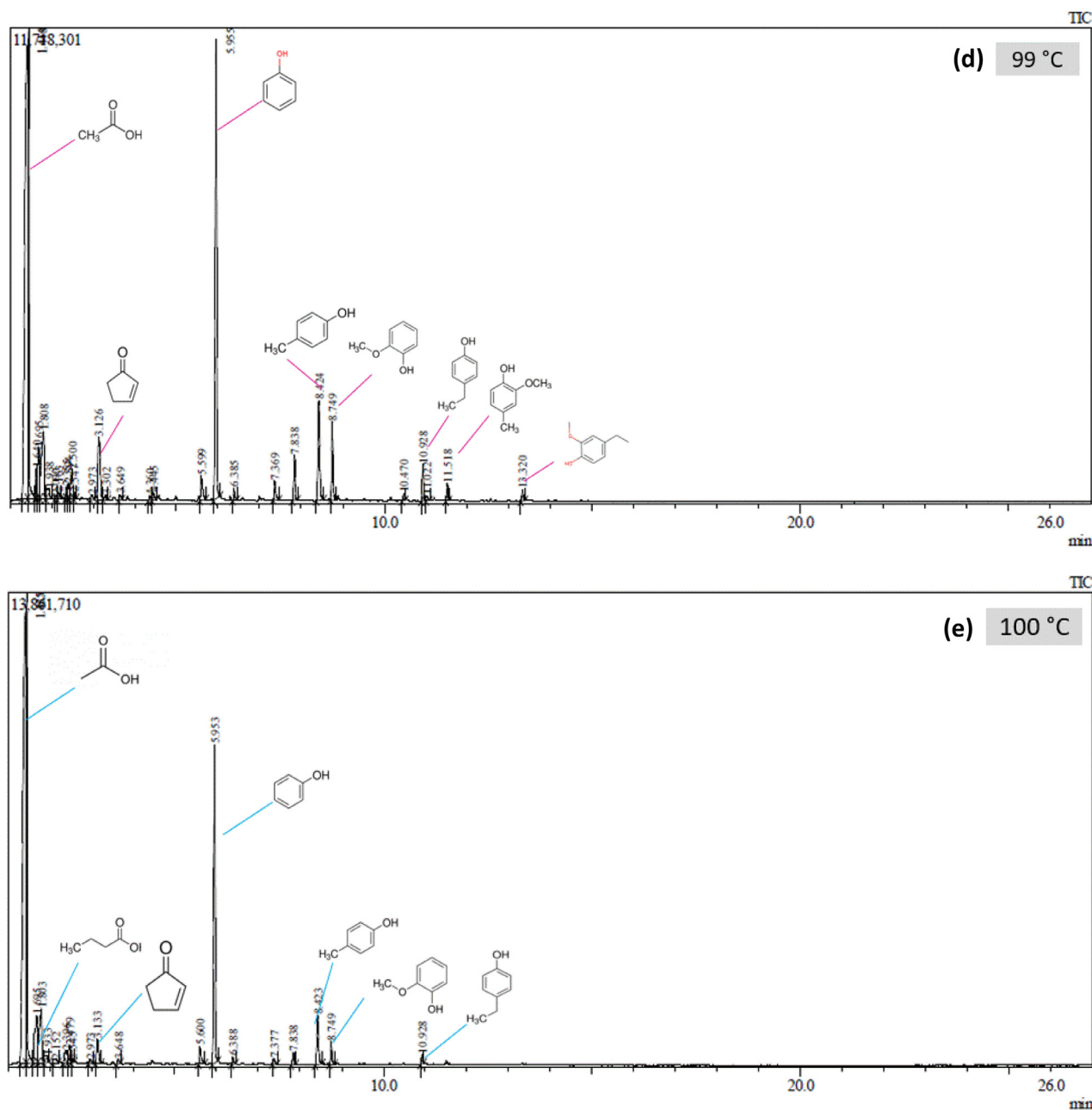


Fig. 3 (continued)

Indonesia. The feedstock used in this study was obtained from slow pyrolysis of *Eleocharis Dulcis* (ED) at 500 °C. The slow pyrolysis was conducted in a laboratory-scale reactor with a heating rate of 15 °C/min.

2.2. Experimental

A schematic diagram of the distillation process employed in this investigation is depicted in Fig. 1. The electric heater is power adjustable and has a 5 KW power rating. The flask has a 500 mL capacity. The capillary has a diameter of 2 mm. The thermometer's temperature range is 0–200 °C. The time from the first drop of distillate to the last 500 mL of distillate was recorded for an hour, as well as the volume of the distillate. In a dark place, the distillate was stored in a glass bottle. The distillation experiments were performed at temperatures ranging from 96, 97, 98, 99, and 100 °C,

respectively. All of the distillation experiments were done twice, and all of the observations were made twice, with the average values supplied.

2.3. Analysis

A GC-MS (QP-2010) with a capillary column coated with white Rtx-5MS was used to investigate the composition of bio-oil samples (i.d. 60 m 0.25 mm and film thickness of 0.25 μm). The sample was dissolved in methanol and inserted into the column at a volume of 1 mL. The temperature program on the GC started at 150 °C and lasted 5 min. The temperature was then raised to 300 °C. The usual solution was then used to identify each component. An electric balance was used to weigh the solid product after it had been dried.

3. Results and discussion

3.1. The impact of product distribution on distillation temperature

The temperature of a chemical process, particularly those involving an endothermic reaction, was the most important operating parameter in the distillation process. When it comes to delivering the heat required for biomass decomposition, temperature is critical. In this work, the distillation temperature was varied at 96, 97, 98, 99, and 100 °C. The bio-char, bio-oil, and gaseous product were evaluated as shown in Fig. 2.

Temperature changes have a favorable impact on bio-oil and gaseous yield. The percentage of bio-oil produced grew from 80 to 89%, followed by a temperature increase from 96 to 100 °C. Meanwhile, increasing the temperature from 96 to 100 °C reduced solid (bio-char) yield from 10 to 8.9%. The results and prior research by [20,21], hypothesized that the reduction of volatile matter, which are subsequently broken down into small molecules organic liquids and gaseous chemicals when lignocellulosic biomass degrades, could be linked to a drop in char yield as temperature rises. Nazari et al. [22] concluded that at a higher temperature of the distillation process, the primary cracking of lignin molecules could generate liquid hydrocarbons.

3.2. Effect of distillation temperature on bio-oil content

The chemical composition of bio-oils from pyrolytic bio-oil of *Eleocharis Dulcis* (ED), was studied using a GC–MS due to the complexity of the chemical content of bio-oil and the limitations of the GC approach. Fig. 3 shows a representative GC–MS chromatogram of sample distillation oils of *Eleocharis Dulcis* (ED) at the different temperature. Acetic acid is the most common component in the bio-oil product in this investigation. When the temperature was increased, the production of acetic acid improved from 17 to 60 %, showing that lignin and hemicelluloses were destroyed throughout the acetic acid production process. [23]. The breakdown of lignin can create not just acid but also phenol. The general chemical compounds identified by GC–MS were showed in Table 1.

From the table above, aldehydes, ketones, and phenols were found in bio-oil, as well as a wide range of other organic substances. Phenol and its compounds are used to make resins, fungicides, and preservatives, among other things. Lignin is decomposed into various phenolic compounds in two steps to generate phenol from hydrothermal treatment of biomass: first,

lignin is converted into diverse phenolic compounds; second, phenol compounds are subjected to demethylation, decarboxylation, and other phenol processes to yield phenol [24]. The effect of distillation temperature on phenol generation was investigated in this study. The yield of identified phenol increased when the distillation temperature was raised. At 98 °C, the proportion of phenol was found to be 39.6%. This outcome was better than our pyrolysis process result. Fig. 4 shows the comparison percentage of phenol obtained from distillation and pyrolysis process [5] by the same feedstock.

Fig. 4 depicts the percentage of phenol produced during the distillation and pyrolysis processes. The percentage of phenol produced by distillation is two times higher than that produced by pyrolysis. This could be because of the varying boiling points and solubilities of aromatic chemicals in different fractions. This result agreed well with previous study by Wang et al. [25]. They mentioned that phenol and guaiacol are mainly transferred from the liquid distillate. It can be confirmed that the upgrading process by distillation was enhanced the percentage of phenolic compounds. The highest phenol content as 39.6% was obtained at a temperature of 98 °C. It's because phenolic chemicals are mainly produced from the decomposition of lignin; this could be attributable to the variable lignin concentration of biomass.

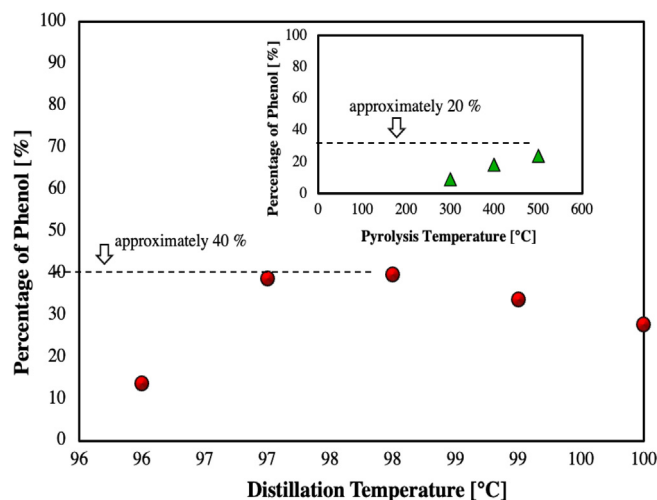


Fig. 4. Percentage of phenol during distillation and pyrolysis of *Eleocharis Dulcis* at different temperature.

Table 1

The general compounds of distillation bio-oil identified by GC–MS.

No	Compound name	Formula	Percentage under different distillation temperature [%]					Group
			96 °C	97 °C	98 °C	99 °C	100 °C	
2	Acetic acid	CH ₃ COOH	17.73	31.14	35.29	42.81	59.56	Acid
3	Propanal	C ₃ H ₆ O	23.40	n.a	n.a	n.a	n.a	Aldehyde
4	Furan	C ₄ H ₄ O	0.87	0.77	n.a	n.a	n.a	Furan
5	Butane	C ₄ H ₁₀	2.61	2.57	2.57	2.15	2.51	Alkane
6	2-Pentanone	C ₅ H ₁₀ O	1.03	n.a	1.97	0.30	0.33	Ketone
8	Propanoic acid	C ₃ H ₆ O ₂	0.06	4.42	4.34	4.10	3.94	Acid
10	Pentanoic acid	C ₅ H ₁₀ O ₂	1.15	4.42	n.a	n.a	n.a	Acid
11	Cyclopentanone	C ₅ H ₈ O	3.93	2.24	n.a	n.a	n.a	Ketone
12	2-Furancarboxaldehyde	C ₅ H ₄ O ₂	11.21	0.77	0.36	n.a	n.a	Aldehyde
13	Pyrazine	C ₄ H ₄ N ₂	1.94	2.58	0.70	n.a	n.a	Ketone
15	2-Cyclopenten-1-one	C ₅ H ₆ O	2.67	2.24	5.83	4.69	2.89	Ketone
16	Ethanone	C ₂ H ₂ O	2.88	2.19	0.88	0.37	0.81	Ketone
17	Phenol	C ₆ H ₆ O	13.68	38.73	39.60	33.78	27.65	Phenol
18	2,3-Dimethyl-2-cyclopenten	C ₇ H ₁₀ O	0.77	0.81	0.67	0.48	0.19	Ketone
19	2-Methoxy-4-methylphenol	C ₈ H ₁₀ O ₂	0.48	1.01	0.76	0.47	0.49	Phenol

4. Conclusion

Distillation of pyrolytic bio-oil has been carried out to enhance the concentration of phenol-rich bio-oil at different distillation temperatures (96, 97, 98, 99, and 100 °C). Five classes of compounds were identified by GC–MS, namely, acids, aldehyde, furan, ketones and phenolic. The result showed that Acetic acid, propanone, and phenol were dominant with the concentration ranges of 20–50%, 12–20%, and 13–39.6%, respectively. The phenol yield was increased to 39.6% was observed at 98 °C. The boiling point and solubility affected the production of the aromatic compounds in different fractions. The high-value compounds, including phenols, would begin to distill in areas with high concentrations only when the temperature increased over the crucial stage. As a result, successfully reducing the temperature point and breaking the hydrogen atoms in bio-oil was a valuable research topic for the future in terms of energy savings and cost reduction.

CRedit authorship contribution statement

Apip Amrullah: Conceptualization, Writing – original draft, Methodology, Validation, Formal analysis, Supervision. **Muhammad Rifky:** Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

AA thanks to Faculty of Engineering, Lambung Mangkurat University South Kalimantan, Indonesia, provided funding for this research.

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