COMMUNICATIONS IN SCIENCE AND TECHNOLOGY
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Evaluation of stirring rate and pH on phenolic compounds recovery from palm kernel shell heavy phase bio-oil

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Article history:
Received: 22 January 2023 / Received in revised form: 4 April 2023 / Accepted: 2 May 2023

Abstract

This study aims to develop an efficient separation method for phenolic compounds derived from the heavy phase of bio-oil produced by the pyrolysis of palm kernel shell. Two variables were investigated during phenolic compound extraction using dichloromethane, i.e., stirring rate and pH of the solution. In both variables, the composition, yield, and distribution coefficient of the extracted phase were investigated. The results showed that the phenolic compounds' extraction favors high stirring rate and it obtained more results at more acidic conditions (lower pH). The best conditions for phenolic compounds were at 300 rpm of stirring rate and pH 4, which resulted in 77.88 % of yield and a 1.13 distribution of coefficient for the total phenols. The findings of this research will contribute to the better separation of phenolic compounds in bio-oil for improving its fuel characteristics as well as producing value-added chemicals.

Keywords: palm kernel shell; pyrolysis; bio-oil; extraction; phenolic compounds

1. Introduction

Asia, particularly Southeast Asia, dominates palm oil production [1] in which Indonesia and Malaysia make up nearly 90 % of global palm oil exports [2]. The existence of palm oil industries is also followed by the environmental issues, one of which is the waste. Malaysia and Indonesia produce a lot of palm oil waste, like palm kernel shells and fibres, empty fruit bunches, palm oil trunks, and palm oil fronds [3].

The utilization of biomass, particularly lignocellulosic biomass from different sectors such as agriculture, forest, wood processing, and municipal waste [4], has attracted a lot of interest because it can increase added value and reduce environmental problems caused by waste. Biomass mainly comprises hemicellulose, cellulose, and lignin [5]. Some biomass is utilized using thermochemical methods [6] and one of promising options is to convert it using pyrolysis technology [7].

Pyrolysis can convert biomass into bio-oil as the feedstock of fuel and value-added products for chemicals. It is the high-temperature thermal decomposition of organic compounds in biomass in the absence of oxygen. Commonly used to refer to the temperature range of 300 to 800°C [8], pyrolysis products include char (solid), liquid (bio-oil), and gas [9,10]. Temperature, type of reactor, type of biomass, catalyst used, and rate of heating all have an impact on pyrolysis product yield and chemical composition [11].

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https://doi.org/10.21924/cst.8.1.2023.1119

The problem in bio-oil upgrading and utilization was related to the existence of many compounds such as hundreds of chemicals, including acids, alcohols, ketones, and phenols [12] that are thermally and chemically unstable [13]. Because of its inferior characteristics, such as its high water content, low heating value, and corrosiveness, its direct use as fuel is not as satisfactory as fossil fuels [14]. As a consequence, various techniques for improving its fuel properties, as well as research for separating value-added chemicals due to its various compositions, have been developed [15].

Because of its phenolic nature, lignin found in biomass such as palm kernel shell, is of particular interest because it can be utilized to produce a wide variety of phenolic and aromatic chemicals. Lignin cracking produces phenolic compounds [16]. Previous research has shown that palm kernel shell contains a high concentration of phenolic compounds [16,17,18]. The production of high-phenol bio-oil is appealing because it could be directly used to a synthesis of phenolic resins [12].

In general, bio-oil is divided into two phases: aqueous/light and dark/heavy, which can be separated by a density difference [19]. The components of light phase are high reactivity low molecular-weight acids, aldehydes and ketones, while the heavy ones consist of lignin-derived products such as monophenols and phenolic oligomers [20]. Separating the components from bio-oil will increase the efficiency of subsequent processes [21]. Solvent extraction has been suggested as a promising separation technique as it can be performed at room temperature and atmospheric pressure [13]. The chemicals in bio-oil can be grouped by their polarity differences using various organic solvents such as hexane, chloroform, toluene, methanol, methylene chloride, or acetone

[22]. Furthermore, dichloromethane is widely used as a solvent in the extraction of bio-oil [20,22].

Wang et al. [20] separated monophenols and pyrolytic lignins from the heavy phase of bio-oil and Tao et al. [15] separated different groups in the heavy phase of bio-oil through a series of separation process. Both of these previous research conducted the separation process via extraction reaction with dichloromethane as an organic solvent at fixed pH solution, pH 6 and pH 7 respectively. However, the effect of stirring rate and pH solution during the extraction process of bio-oil, particularly the heavy phase, has so far received little attention. The approach of this work involves the pyrolysis of palm kernel shell to produce bio-oil, bio-oil separation to the heavy phase and aqueous phase followed by extraction of phenolic compounds from the heavy phase of bio-oil produced from palm kernel shell pyrolysis. The specific goal is to separate phenolic compounds from bio-oil to be capable of producing phenolic compounds that can be used as fuel-based phenol substitutes in future. The findings of this study will contribute to the better utilization of bio-oil.

2. Materials and Methods

2.1. Materials

Palm kernel shell of palm oil (PKS) was obtained from a local palm oil processing plant in Tanah Laut District, South Kalimantan, Indonesia. The water content of PKS was 6–9 % and PKS composed cellulose (33.04 wt. %), hemicellulose (23.82 wt. %), lignin (45.59 wt. %), and extractives (9.89 wt. %) [16]. Prior to pyrolysis, the PKS was powdered to a particle size of less than 0.5 mm (30 mesh). Sodium hydroxide (NaOH, ACS certified grade) and hydrogen chloride (HCl, ACS certified grade) were used to adjust pH during the separation process and dichloromethane (CH_2Cl_2, ACS certified grade) was used as an extraction solvent. Meanwhile, Folin Ciocalteu reagent (ACS certified grade) was used in UV Vis spectroscopy analysis by using Thermo Scientific spectrophotometer Genesys 10S.

2.2. Pyrolysis of palm kernel shell

PKS was pyrolyzed in a fixed bed pyrolysis reactor to produce a bio-oil sample. More information about this pyrolysis reactor can be found elsewhere [23]. Pyrolysis was performed using 500 grams of PKS. The pyrolysis reaction was conducted at 400ºC for 1 hour since the temperature was reached. After the reaction was complete, the reactor was cooled. The resulted liquid product or bio-oil (BO) was separated by a separation funnel to obtain a dark phase (heavy phase) and a light phase (aqueous phase). The composition of the heavy phase (HBO) accounted for approximately 10 wt. % of the bio-oil sample. The separated HBO was used for phenolic compound separation via extraction in the next step.

2.3. Extraction of phenolic compounds from the heavy phase of bio-oil (HBO)

The extraction method performed in this study was a modified procedure of Wang et al. [20]. The modification was undertaken to investigate the effect of stirring rate and pH of solution on phenolic compound yield during the extraction process. The heavy phase of bio-oil was extracted with 20 mL of CH_2Cl_2 at a stirring rate of 250 rpm for 1 hour after being mixed with a 2.5 M NaOH solution to achieve a pH of 14. The extraction results produced two phases: the CH_2Cl_2 soluble phase and the CH_2Cl_2 insoluble phase. The CH_2Cl_2 soluble phase solution referred to the neutral phase, which was not studied in this study. The 1 M HCl solution was added to the CH_2Cl_2 insoluble phase until reaching pH 6. Then, the solution was filtered to obtain the filtrate and residue. While, the filtrate obtained was extracted with 20 mL of CH_2Cl_2 at various stirring rates of 200, 250, and 300 rpm for 1 hour to obtain a soluble CH_2Cl_2 phase, followed by an insoluble CH_2Cl_2 phase (raffinate). The CH_2Cl_2 soluble phase was then distilled at 40ºC to obtain a fraction rich in phenolic compounds (FB). To study the effect of pH, the same procedure was carried out for adding 1 M HCl solution to pH 4, 5, and 6, using a constant stirring rate of 300 rpm. The composition of bio-oil, HBO and phenol fraction (FB) was measured using GC-MS, while to determine the total phenol content, a UV-Visible Spectrophotometer at a wavelength of 765 nm was used [25].

To evaluate the effects of stirring rate and pH solution during the extraction, total phenols yield and distribution coefficient [26,27] were used. The mass concentration (g/L) ratio of total phenols in the FB and HBO phases was defined as the total phenol yield (Equation 1). The distribution coefficient, on the other hand, was described as the equilibrium mass fraction of the total phenols ratio in the FB and raffinate phases (Equation 2).

$$\text{Total phenol yield} = \frac{\text{Total phenol concentration in FB}}{\text{Total phenol concentration in HBO}} \times 100 \quad (1)$$

$$\text{Distribution coefficient} = \frac{\text{Total phenol concentration in the extract phase}}{\text{Total phenol concentration in rthe affinate phase}} \quad (2)$$

3. Results and Discussion

3.1. The compositions of bio-oil (BO) and heavy phase of bio-oil (HBO)

The bio-oil (BO) obtained from pyrolysis of palm kernel shells at 400°C as well as its heavy phase (HBO) were analyzed using GC-MS to determine their components. This study discovered more than 50 compounds in bio-oil. However, only 13 of them as the biggest compounds were considered. Table 1 shows the main components in bio-oil and its heavy phase HBO.

Table 1. The composition of bio-oil (BO) and heavy phase of bio-oil (HBO)

Chemical compounds	Peak area (%)	
	Bio-oil	Heavy Phase
2-propanone	9.01	
2,4-hexadiene	0.35	
Acetic acid	50.25	3.53
3-methyl-hexan-2-one	0.49	
1-hydroxy-2-butanone	2.38	
2-furancarboxaldehyde	5.02	4.20
Phenol	27.45	52.52
2-methoxyl-4-methylphenol		5.18
1,2,3-trimethoxybenzene		1.88
1,2-benzenediol	1.99	
1,2,4-trimethoxybenzene	0.53	
2-methoxy-4-propyl-phenol		2.60
3-methoxy-pyrocathecol	0.33	

According to the GC-MS results, 10 of the main group compounds in bio-oil (from the highest to the lowest peak area) included acetic acid, phenol and phenolic compounds, ketones, aldehydes, and alkene. Because more than 50 % (area) of acetic acid was identified in the bio-oil produced by PKS pyrolysis, it can be considered highly acidic. Phenolic compounds are the second most abundant one. In general, the phenol content of BO from PKS is higher than that of other feedstock [28,29]. The high lignin content in palm kernel shells could contribute to the higher yield of phenol and phenolic compounds in bio-oil [17,30,29].

This bio-oil composition is nearly identical to that of Kim et al. [16] result, but the results of this study showed that acetic acid was more dominant than phenolic compounds. This difference could be due to temperature differences in the pyrolysis reaction. This study was carried out at 400°C, which was lower than the pyrolysis temperature in the previous study. It could be due to the fact that lignin may not have completely decomposed into phenolic compounds. When temperature was below 500°C, lignin macromolecules were pyrolyzed incompletely, as observed by Lou et al. [32].

HBO had the same composition of three compounds as bio-oil after being separated from the light phase, containing a lot of water and water-soluble compounds. These are acetic acid, 2-furancarboxaldehyde, and phenol. The composition of the first two compounds decreased, and even acetic acid was significant. Because acidic compounds are polar and dissolve in water [15,20,27], they are easily moved to the light phase when separated from HBO. On the other hand, phenol increased by more than 90 % compared to the phenol content in bio-oil. Other phenolic compounds found in BO besides phenol are 1,2-benzenediol and 3-methoxy-pyrocathecol. After separation into HBO, alkyl phenol compounds, namely 2-methoxyl-4-methylphenol and 2-methoxyl-4-propylphenol, were observed. This is possible because HBO is composed of water-insoluble components [15], low polarity [27], and pyrolytic lignin [20].

The subsequent step was the extraction of phenolic compounds from HBO. It was preceded by raising the pH of HBO from 2.4 to basic pH (pH 14). For being water soluble and able to promote phenol extraction [30], a NaOH solution was mixed to create phenolates [30], which was then extracted with CH_2Cl_2 to separate the soluble neutral phase. Under alkaline conditions, after the addition of a strong base such as NaOH, neutral components including ketones, aromatics, and probably simple phenols (pKa > 10.35) will be carried away by the neutral phase by extraction with organic solvents such as CH_2Cl_2 [33]. To increase the extracted phenolic compounds, the insoluble CH_2Cl_2 phase was further acidified by adding HCl solution. The effect of stirring rate and acidity (pH solution) on the extraction of the insoluble CH_2Cl_2 phase will be discussed in the subsequent section of this study.

3.2. The effect of stirring rate on the extraction of phenolic compounds

To investigate the effect of stirring rate in the extraction, the previous step's insoluble CH_2Cl_2 phase was extracted with CH_2Cl_2 solvent at a constant pH of 6 with varying stirring rates of 200, 250, and 300 rpm. After being separated from the solvent, the extraction result (hereinafter referred to as FB) was analyzed for its chemical components using GC-MS and its total phenols content using UV-Vis. Figure 1 describes the composition of the heavy-phase bio-oil (HBO) and its extracted phase (FB) resulted from different stirring rates. Other compounds represented other phenolic compounds and their derivatives not belong to the mentioned compounds and were detected in low amount (< 1 % of relative area).

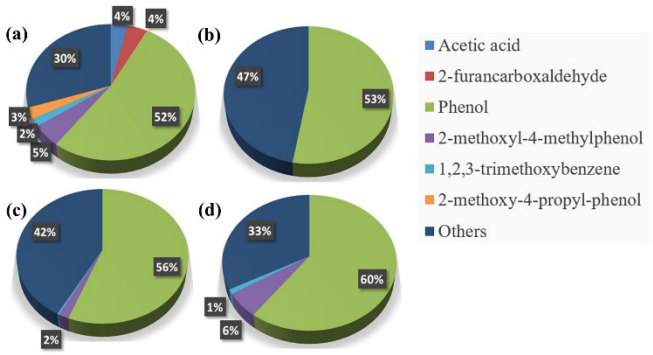

Fig. 1. The relative area (%) of components: (a) Heavy-phase bio-oil (HBO), and its extracted phase (FB) resulted from different stirring rates: (b) 200 rpm, (c) 250 rpm, and (d) 300 rpm.

When compared to HBO, FB had fewer compounds, which mostly consisted of phenol and phenolic compounds without acids, ketones, aldehydes, and alkenes, according to the GC-MS results in Figure 1. These compounds, as previously stated, were carried away in the neutral phase during the previous separation step. When the FB components were compared at different stirring rates, it was figured out that increasing the stirring rate from 200 to 250 rpm and then to 300 rpm increased the presence of phenol, alkyl-phenol compounds, and benzene, whose % area increased with the increasing stirring rate. This finding implied that increasing the stirring rate allowed for the extraction of more phenol and more complex phenolic compounds, including benzene compound.

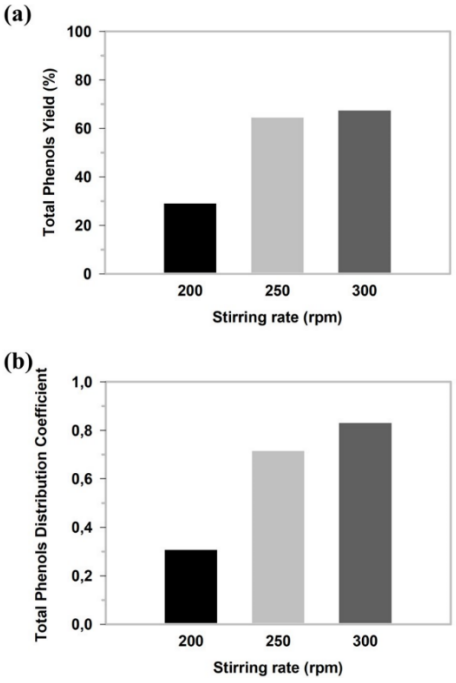

Fig. 2. (a) The total phenols yield (%) resulted from the extraction under different stirring rates, and (b) The total phenols distribution coefficient resulted from the extraction under different stirring rates.

Figure 2 shows the total phenols yield and total phenols distribution coefficient as a result of different stirring rates. Figure 2(a) shows that as the stirring rate increased from 200 to 250 rpm, the amount of total phenols increased approximately two-fold. The total phenols were then increased slightly as it approached 300 rpm. It implied that the extraction process's stirring promoted convective bulk movement in the solvent. This lowered the mass transfer barrier and improved extraction [34]. However, during the extraction of pyrolysis oil from forest residue, as observed by Vitasari et al. [26], the organic phase concentration rose with the stirring rate until reaching 300 rpm and then tended to stagnate. As a result, it was concluded that the stirring rate determined the time required to reach equilibrium but had no effect on the equilibrium composition. Fardhiyanti et al. [25] also observed that at too high stirring rate, there was back mixing process thus lowering extracted phenol from bio-oil of rice husk. Figure 2(b) depicts the effect of stirring rate on total phenol distribution coefficient. The highest phenol extraction distribution coefficient (0.83) was obtained at 300 rpm, while the lowest occurred at 200 rpm (0.31). This result showed that increasing the stirring rate during extraction increased phenolic compounds selectivity. As the rate of stirring increased, so did the distribution coefficient. It indicated that increasing the rate of stirring increased the amount of phenolic compounds that moved into the FB (extract) phase because increasing the rate of stirring enhanced the contact area between the solution and the solvent [30].

3.3. The effect of pH solution on the extraction of phenolic compounds

In the previous step, HBO neutralization, a NaOH solution was added to the HBO to generate sodium phenolates from phenols. Here, the extraction of phenolic compounds was highly determined by solution acidity. Other studies have found that a pH less than 7 is optimal for extracting phenols in the phenolate phase [35]. As a consequence, for this study, pH values of 4, 5, and 6 were chosen and obtained by adding HCl solution. The sodium phenolate compounds reacted with HCl at this point, producing phenols and sodium chloride. Furthermore, these phenols were extracted using an organic solvent, i.e., dichloromethane. The addition of the solvent to the aqueous phase appeared to create an equilibrium between both the phenolates and the free phenolics, allowing the free phenolics to be extracted as discovered [33].

In the present study, the stirring rate was maintained at 300 rpm for 1 hour. Figure 3 shows the pH solution effect on FB (extract) phase composition. Other compounds represented the other phenolic compounds and their derivatives not belong to the mentioned compounds and were detected in low amount (< 1 % of relative area).

Figure 3 depicts nearly identical trends as a result of increasing the stirring rate. The FB composition resulted from pH change was nearly identical to the one obtained from stirring rate variation. The presence of alkyl-phenol compounds and benzene, whose % area increased with the decreasing pH, contributed to the increase in phenolic compounds % area.

Figure 4 shows the total phenols yield and total phenols distribution coefficient as a result of different pH solutions. As shown in Figure 4(a), the total phenols yield increased slightly from about 67 % to 70 % when the pH was reduced from 6 to 5, and it increased significantly to approximately 78 % when the pH was reduced from 5 to 4. These findings suggested that the extraction of phenolic compounds is favored by acidic conditions (low pH) [15].

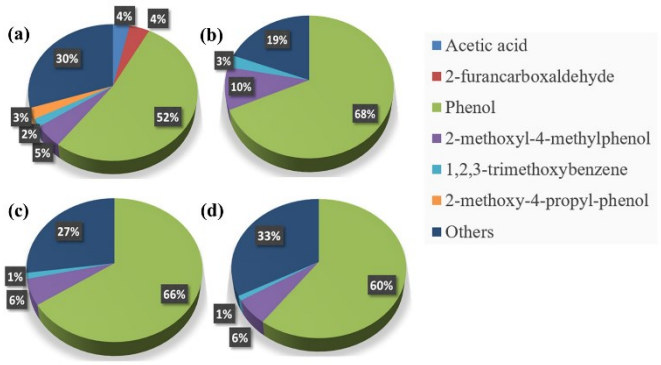

Fig. 3. The relative area (%) of components: (a) Heavy-phase bio-oil (HBO) and its extracted phase (FB) resulted from different pH solutions: (b) pH 4, (c) pH 5, and (d) pH 6

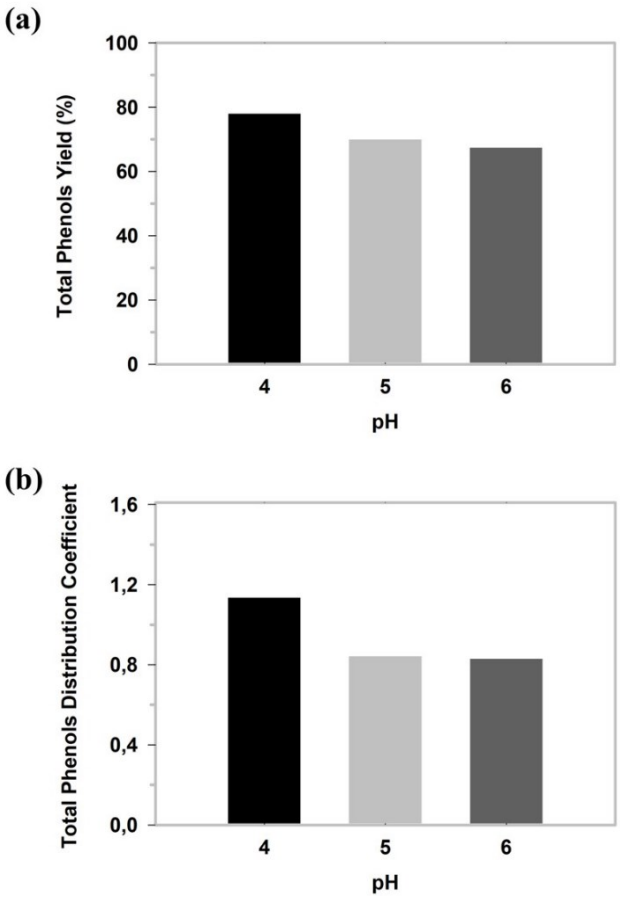

Fig. 4. (a) The total phenols yield (%) resulted from the extraction under different pH solutions, and (b) The total phenols distribution coefficient resulted from the extraction under different pH solution

The acid dissociation constant (pKa) value for the major phenolic compounds varies between 4 and 11 [33]. The lower the value of pKa, the greater its ability to donate its protons. Most of the phenolics are assumed to be present in their deprotonated form at pH 10 or higher, thus reducing their extraction by organic solvents. Lowering the pH value to 4 creates more acidic conditions, which improves phenolic compound extraction by increasing the mass transfer coefficient of phenolic compounds to dichloromethane. This

study's findings were supported by Badgujar and Rastogi [36] observation in phenol extraction via liquid membrane that the degree of dissociation was discovered to be the lowest when the pH of the sample was kept constant at 4, which resulted in the highest membrane mass transfer coefficient.

Figure 4(b) shows the effect of the pH of the solution on the distribution coefficient of total phenols. The trend shows that pH decreased will increase the distribution coefficient of total phenols. A very small increase was observed with the reduction of pH values from 6 to 5, but when the pH of the solution further decreased to 4, it resulted in a value of 1.13. The distribution coefficient of total phenols was more than 1. It suggested that phenolic compounds in the FB (extract) phase were greater than in the raffinate phase. Thus, this more acidic condition had successfully separated more phenolic compounds from the solution.

4. Conclusion

This research successfully conducted phenolic compound extraction using dichloromethane. As the stirring rate increased from 200 to 250 rpm, so did the amount of total phenols extracted, approximately two-fold. The total phenols then increased slightly as it approached 300 rpm. Furthermore, lowering the pH value from 6 to 5 only slightly increased the total phenols yield. However, at pH value of 4, creating more acidic conditions improved phenolic compound extraction, as shown from its total phenols' distribution coefficient that was more than 1. Further studies at a lower pH than 4 could be conducted to enhance the extraction result.

Acknowledgements

The authors would like to acknowledge financial support from Lambung Mangkurat University Indonesia through "Program Dosen Wajib Meneliti" Research University Grant Year 2022 (Number: 024. 95/UN8.2/PL/2022).

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