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Improving the Quality of Bio-Oil Produced from Rice Husk Pyrolysis by Extraction of its Phenolic Compounds

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Abstract

Rice husk is an agricultural waste which contains 50% cellulose, 25%-30% lignin and 15%-20% silica. It can be used as raw material of bio-oil. Bio-oil is liquid which produced by pyrolysis process. Bio-oil can be produced from the rice husk at 773 and 873 K. The main component of Bio-oil from rice husk pyrolysis at 773 and 873 K is phenolic compounds about 47.98% and 62.65%, respectively. It causes corrosive, low heating value, high acidity, high viscosity and unstable that causing an engine damage. The presence of phenolic compound decreases the quality of bio-oil. Therefore, it needs a process such as liquid-liquid extraction to reduce the phenolic compound using 80% methanol and 80% chloroform as a solvent. The extract and raffinate phase were analyzed using UV-Vis spectrophotometer. The aim of this research determine the effect of temperature pyrolysis for the characterization of bio-oil, the stirring speed and the temperature of the extraction for the distribution coefficient and the yield of phenolic compound. The results showed that the characterization of bio-oil produced from rice husk pyrolysis at 773 and 873 K are densities 1,040 and 1,042 Kg/m3; viscosities 9.3488 and 9.5007 cSt; acid numbers 46.75 and 52.45 mg KOH/g; pH 2.5 and 3; flash points 426 and 423 K and heating values 3.229 and 3.339 MJ/kg, respectively. The highest distribution coefficient and yield were obtained at 323 K and a stirring speed of 250 rpm. The distribution coefficient of bio-oil produced by pyrolysis at 773 and 873 K is 1.504, and 1.528, respectively. The yields of bio-oil produced by pyrolysis at 773 and 873 K are 58.885%, and 48.429%, respectively.

INTRODUCTION

About 95% of energy needs in Indonesia still provided by fossil energy such as 47% petroleum, 24% coal and 24% natural gas (ESDM, 2016). However, this is not supported by the availability of fossil fuels, so that the petroleum reserves will decrease in the near future. Special Task Force for Upstream Oil and Gas Business Activities of Republic Indonesia (SKK Migas) (ESDM, 2016) showed that the petroleum reserves are estimated to decrease from 4.3 billion barrels in early 2004 to 3.7 billion in 2014. Indonesia's alternative fuel consumption in 2011-2015 is 4.52 million kilo liters of biodiesel, 2.78 million kilo liters of bioethanol, 1.8 million kilo liters of bio-oil, and 9.84 million kilo liters of biofuels (Erawati et al., 2013). Depletion of the fossil fuels reserves made the development of alternative fuels such as bio-oil urgently needed.

Bio-oil is an inorganic liquid which produced by pyrolysis process (Erawati et al., 2013). Bio-oil can be produced from biomass. Biomass is a material derived from vegetables,

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fruits, weeds, grasses, agricultural waste, and forestry (Sahan et al., 2013). Various types of biomass can be used as raw materials for producing the bio-oil, such as corn cobs (Sahan et al., 2013), wood sawn dust (Wibowo, 2013), durian peel (Ismadji, 2012), coconut shell (Kongnum & Ratanawilai, 2014), rice husk (Guo et al., 2011), jatropha (Alfian, 2017) and coffee shell (Fardyanti et al., 2018).

One of the biomass that easily found in Indonesia is rice husk. The stockpile of rice husks in Indonesia is very abundant. It is showed from the data of rice production from the Central Statistics Agency (BPS) in 2011-2015 at Table 1.

Table 1. Data of Rice Production in Indonesia (BPS, 2018).

Year	Amount (Tons)
2011	9,391,959
2012	10,232,934
2013	10,344,816
2014	9,648,104
2015	11,301,422

Table 1 showed that the annual rice production was very large, although it decreased about 696,712 tons in 2014 and increased about 1,653,318 tons in 2015. The chemical components of rice husk are 50% cellulose, 25%-30% lignin and 15%-20% silica (Ismail & Waliuddin, 1996). High carbon compound, such as cellulose, makes it potentially to produce bio-oil as fuels.

Pyrolysis is a decomposition process of biomass from hydrocarbon compound that has a long chain into a simple molecule (Basu, 2010). The pyrolysis process produces liquid, gas, and solids. The solids are called as char while the liquid and gas can be used as bio-oil.

Pyrolysis of bio-oil from rice husk was carried out by several researchers such as Rahayu, et al. (2012) studied the pyrolysis of rice husks at 773 K, Suyitno et al. (2009) studied the pyrolysis process at 573, 673 and 773 K. Pyrolysis temperature above 973 K caused gasification process, then rice husk produced gas fuel. So this research will be done at 773 and 873 K for the pyrolysis process.

Phenolic compounds which is contained in bio-oil caused the low of heating value, corrosive, high acidity, high viscosity and unstable products. It also caused an engine damage (Muthia, 2011). So the extracting of phenolic compound is necessary for increasing the quality of the bio-oil.

The extraction of phenolic compound from bio-oil which produced by rice husk pyrolysis is carried out through liquid-liquid extraction methods using methanol 80% and chloroform 80% as solvents. Methanol has a good ability to carried out so many polar and nonpolar compounds. It has a cheaper price and has better ability to dissolve phenol compounds than other solvents such as ethanol, water and acetone (Fardhyanti et al., 2012). Some researcher has studied the extraction of phenolic compounds from bio-oil such as Jazbinsek (2008), Fardyanti et al. (2018; 2012; 2019), etc. The aim of this research is expected to reduce the phenolic compounds from bio-oil which produced by rice husk pyrolysis.

MATERIALS AND METHODS

Materials

Methanol, Ethanol, Chloroform, Folin & Ciocalteu reagent, Phenolphthalein, Sodium Carbonate, Potassium Hydroxide, Gallic acid, and Sodium Hydroxide were purchased from e-Merck (Germany). All reagents used here are A.R. grade and used as received without further purification. The distilled water and deionized water are available at the laboratory. Rice husk was obtained from public market in Semarang.

Experimental

Sample Preparation

Rice husk was washed using distilled water and then dried by the sunlight and further dried using an oven at 378 K until getting a constant weight. Dried rice husk was grinded using hammer mill and then sieved using sieved shaker to get similar size of particles in 35 mesh.

Pyrolysis Process of Rice Husk for Bio-Oil Production (Fardhyanti et al., 2018)

A fixed bed reactor was used to produce bio-oil by pyrolysis process. It is made of stainless steel. It has capacity 8 liters and dimensions of height 50 cm and diameter 20 cm. Pyrolysis reaction takes place at 773 and 873 K.

The 1000 g prepared rice husk was fed into a fixed bed reactor. The N_2 gas is fed vertically into a reactor at 200 ml/min from below until it passes through the top of the reactor. The pyrolysis reaction is anaerobic because there is no O_2 gas in the reactor, so N_2 gas serves as a substitute for air of the reactor. The steam formed during the pyrolysis process that flows with the N_2 gas toward the top of the reactor, then cooled with a water-filled condenser. From the condenser, the vapor containing the mixed gas turns into a liquid. The liquid product from the condenser is collected in a 500 ml sample bottle (it called Bio-oil), while the non-condensable gas, collected in a gas bag. The schematic experimental of rice husk reactor pyrolysis is shown in Figure 1.

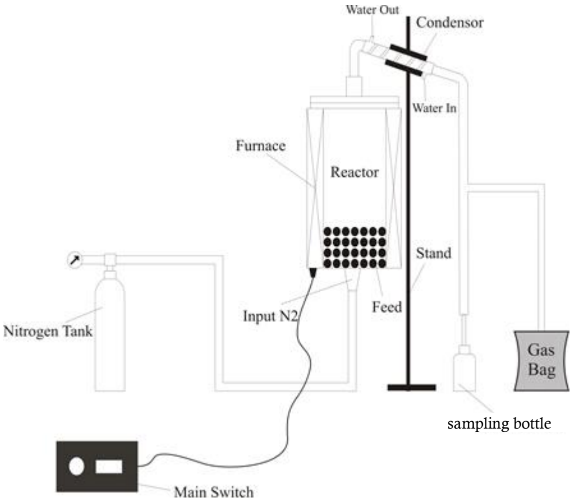

Figure 1. Fixed Bed Reactor Pyrolysis (Fardhyanti et al., 2018).

Table 2. The analysis condition of GC-MS (Fardhyanti et al., 2018).

GC-MS: Perkin Elmer		
GC Clarus 680		
MS Clarus SQ 8T		
Column:		
Inner diameter	[m]	2.5 x 10^{-8}
Length	[m]	30
Carrier gas	-	He
Split ratio	[-]	42.2 : 1
Holding time	[min]	5
Sample volume	m^3	1.10^{-6}
Injection temp.	[K]	583
Column temp.	[K]	333
Pressure column		vacuum
Column flow	[mL/min]	0.8
MS Scan	[K]	323 - 573
Hold	min	5

Bio-oil are stored in the refrigerator and used for the next step. GC-MS was used to analyze the compositions of bio-oil produced by rice husk pyrolysis (the principal conditions are shown in Table 2). The characteristic of bio-oil was also analyzed such as pH, viscosity, density, acid number, flash point, and heating value.

Extraction of Phenolic Compounds from Bio-oil

Bio-oil was neutralized using 2.5 M NaOH until pH 5. A 6.5 mL sample bio-oil was taken into three-neck rounded flask. The schematic experimental of extraction process is shown in Figure 2. It was extracted for 60 minutes at 303, 313, 323 K and 150, 200, 250 rpm, respectively using 6.5 mL 80% methanol as a polar solvent and 6.5 mL 80% chloroform as a non-polar solvent. Then they were poured into a separating funnel, settled for 60 minutes and separated into two phases. Then the two phases were weighed. Folin-Ciocalteu method was used to measure the total phenolic compounds in the extract and the raffinate phase of each extraction processes.

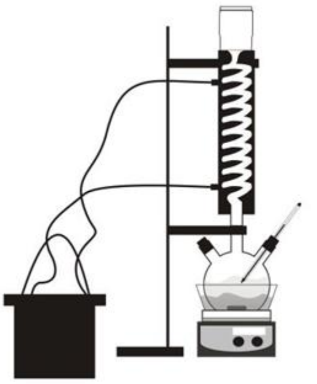

Figure 2. The Schematic Experimental of Extraction Process.

Folin-Ciocalteu Method

A 1 mL bio-oil sample, a gallic acid calibration standard and a blank (deionized water) were each taken in 2 ml cuvettes. A 0.5 mL Folin-Ciocalteu reagent was added, followed by deionized water (1.58 ml). Then it was mixed until homogeneous and incubated for 8 mins. A 4 mL 7.5% sodium carbonate solution was added, mixed, and incubated for 105 min at room temperature. The sample absorbance was measured at 765 nm with 1 cm cells and a 1.5 nm bandwidth using UV–visible Spectrophotometer.

A 100 ppm gallic acid calibration standards were made by dissolving 10 mg gallic acid and then diluted to 100 ml with water. Standards with 0, 50, 100, 150, 200, 250, and 300 ppm were made by diluting 0, 0.5, 1, 1.5, 2, 2.5, and 3 ml gallic acid calibration standards (100 ppm) to 10 ml with water, respectively. These can be stored up to 2 weeks at 277 K.

The 7.5% sodium carbonate solution was made by dissolving 7.5 g anhydrous sodium carbonate in 100 ml water and boiled. After reach rooms temperature, a few crystals of sodium carbonate were added. The solution was stored for 24 hours at room temperature. It was then filtered with Whatman #42 filter paper and water added to make 1 L. This solution can be stored indefinitely at room temperature.

All results are given in wt% gallic acid equivalents (GAE) as expressed by the FC method.

Total Acid Number

A 4 g bio-oil was added to 10 mL of methanol 99.9%, it was then heated and stirred for 10 minutes. Into the mixture, it was then added a 6 drops of phenolphthalein. Total acid number value was measured by Color Indicating Titration method using 0.1 N KOH. An appropriate pH color indicator e.g. phenolphthalein, is used.

RESULTS AND DISCUSSION

Characteristics of Bio-Oil Produced from Rice Husk Pyrolysis

The yields of bio-oil produced from rice husk pyrolysis at 773 and 873 K were 29.55% and 43.68%, respectively. The yield of pyrolysis process can be influenced by several factors, such as reaction temperature (Tsai et al., 2007), raw material (Kim et al., 2010), heating rate (Tsai et al., 2007), particle size (Sensoz et al., 2006) and type of reactor (Kockar et al., 2000). The yield of bio-oil produced by agricultural waste is less than wood material, i.e. 20-50% (Zhang et al., 2013).

Bio-oil produced from rice husk pyrolysis is yellowish brown and has sharp smell like smoke as shown in Figure 3. Physical properties of bio-oil produced from rice husk pyrolysis at 773 and 873 K are shown in Table 3.

Comparison of bio-oil physical properties between current research and the previous study conducted by Yu et al. (2009) is presented in Table 4. While, the physical properties comparisons between bio-oil from rice husk and other materials are presented in Table 5.

Table 3. Proximate analysis of rice husk.

Properties	Dried Base (%)
Water content	13.2
Ash	0.6
Volatile matter	58.4
Fixed carbon	23.6
HHV (MJ/Kg)	16.9


(a) (b)

Figure 3. Bio-Oil Produced by Rice Husk Pyrolysis at 773 K (a) and 873 K (b)

Table 4. The Comparison of Physical Properties of Bio-Oil and Bio-oil Conducted by Yu et al. (2009).

Parameter	**T 773 K**	**T 873 K**	**Yu et al. (2009)**
Density (Kg/m^3)	1,040	1,042	940 - 1,200
Viscosity (cSt)	9.3488	9.5007	4 – 78
Acid number (mg KOH/g)	46.75	52.45	0.5
pH	2.5	3	-
Flash Point (K)	426	423	48 – 67
Heating Value (MJ/kg)	3.229	3.339	16 - 19

There are 3 products of pyrolysis process, namely solid (bio char), liquid and gas. Two fluid fractions obtained from the liquid filtration process are a water-soluble fraction (bio-oil) and a water-insoluble fraction (tar) (Islam et al., 2010).

The pyrolysis process of 2.250 g rice husk at 773 and 873 K produced 425 mL and 675 mL of bio-oil and the product conversion was 20.02% and 31.56%, respectively. The process took 4 seconds, produced liquid compound called bio-oil. Decomposition of lignocellulose was occurred during the pyrolysis process. Hemicellulose produced acid, cyclopentanone, and furan at 472-

Table 5. The Comparison of The Physical Properties of Bio-Oil Produced From Rice Husk with The Other Biomass and The Petroleum Products.

Materials	Density (Kg/m^3)	Viscosity (cSt)	pH	Flash Point (°C)	Heating Value (MJ/Kg)
Rice Husk (773K)	1,040	9.3488	2.5	153	3.229
Rice Husk (873K)	1,042	9.5007	3	150	3.339
Sugarcane Bagasse (Nayan et al., 2013)	1,150	21.50	3.85	>72	23.50
Neem seeds (Erawati et al., 2014)	961	22.6	3.9	42	32.3
Broiled seeds (Erawati et al., 2014)	921	1.32	3.7	53	23.75
Glugu wood (Rout et al., 2016)	1,037.1	5.81	3	-	-
Diesel (Buttler et al., 2011)	820-850	2-5.5	-	53-80	37-40
Bio-diesel (Buttler et al., 2011)	880	4-6	5.6	100-170	42-45

573 K, cellulose produced sugar, aldehydes, and ketones at 573-673 K, and lignin produced phenols and aromatic compounds at 523-873 K (Zhang et al., 2013).

Density is an important parameter in fluid transportation. The density of bio-oil produced at 773 and 873 K were 1,040 kg/m^3 and 1,042 kg/m^3, respectively. The bio-oil density produced from pyrolysis that based on agricultural waste generally is 1,000-1,100 kg/m^3 (Rout et al., 2016). This result is lower than density of bio-oil which is obtained from Sengon wood with pyrolysis temperature of 500 – 600°C (Ozbay et al., 2008). The obtained bio-oil density is slightly higher than bio-oil from pyrolysis of rice husk where its density was ranged between 1.03–1.50 gr/mL (Ellens & Brown, 2012). The high density of bio oil was affected by the numbers of high molecular compound in bio-oil. High density of bio-oil also caused difficulty for pumping processes in the engine and decreased the quality of combustion bio-oil.

The density of bio-oil was measured at 313 K. The density of bio-oil produced by agricultural waste pyrolysis is generally between 1,000-1,100 kg/m^3 (Rout et al., 2016). The density of bio-oil is higher than the density of diesel and bio-diesel. High density causes the difficulties for the pumping and atomization process in the engine and also decreases the quality of bio-oil combustion.

The viscosity of bio-oil produced from rice husk pyrolysis at 773 and 873K were 9,3488 and 9,5007 cSt, respectively. It was so higher than viscosity of diesel and bio-diesel. High pyrolysis temperature caused high viscosity of bio-oil, because bio-oil produced from pyrolysis at 873K contains less water than bio-oil produced from pyrolysis at 773K (Rout et al., 2016). The viscosity is strongly influenced by water content. Higher water content in bio-oil will cause lower viscosity of bio-oil (Lin et al., 2013).

The heating value of bio-oil produced from rice husk pyrolysis at 773K is lower than 873K. The low heating value of bio-oil is caused by high water and oxygen content in bio-oil (Jahirul et al., 2012). However, the heating value of bio-oil from rice husk is lower than diesel and also bio-diesel.

Flash point of bio-oil at 773 K pyrolysis is higher than bio-oil at 873 K pyrolysis. It showed that bio-oil at 773 K pyrolysis was flammable. Flash point of bio-oil was as the same as flash point of bio-diesel but higher than flash point of diesel.

Acid number of bio-oil in this research is between 46.75 to 52.45 mg KOH/g. High acid number was caused by the presence of phenolic compound (carbolic acid or phenolic acid) from pyrolysis process that breaks the cellulose and lignin. It was also can caused by any acidic extractive substance.

The pH of bio-oil in this research is in accordance with the research conducted by Guo et al. (2012) that bio-oil has pH = 2.5 – 3.0 and it should be stored in anti-rust material such as stainless steel, glass bottle, plastic and fiberglass. Bio-oil can only be used directly as a fuel such as in boiler due to its high acidity value. Bio-oil is not recommended to be used as engine fuel because it corrosive and caused rusting in the engine. Upgrading bio-oil is needed to use bio-oil as an engine fuel such as hydro treating, hydrocracking, steam reforming, etc. (Mantilla et al., 2015). This process will break a high molecular weight compound into alkanes.

Heat of combustion is the amount of energy per mass of fuel. Heat of combustion of bio oil will increase as the increment of temperature at both different biomass particle size. As the increase of pyrolysis temperature, it will reduce the amount of oxygen and water in bio oil. The heat of combustion of bio oil was found between 9.3168 – 10.8173 MJ/kg.

GC-MS Results Analysis of Bio Oils

The bio-oil has so many various components and it depends on the time and temperature of the process. The components of bio-oil were also very complex which have various types of hydrocarbon compounds with a lot of molecular weight range.

The chromatograms of GC-MS analysis are showed in Figures 4 and 5. The results of GC-MS analysis of the bio-oil showed that it contained has more than 5 chemical compounds such as phenol, furfural, and others. The main components of bio-oil from rice husk are showed in Tables 5 and 6.

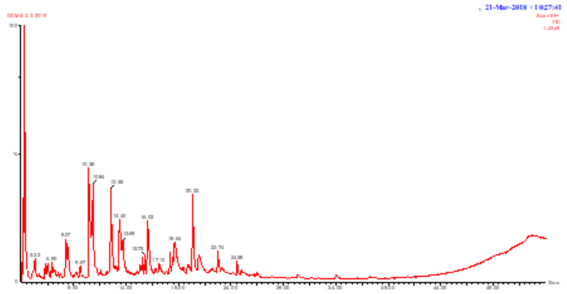

Figure 4. Gas Chromatogram-Mass Spectroscopy of the Components Produced by Rice Husk Pyrolysis at 773 K.

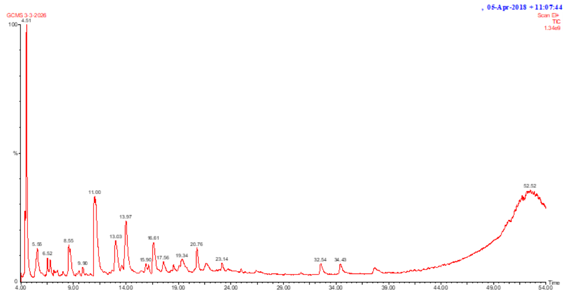

Figure 5. Gas Chromatogram-Mass Spectroscopy of the Components Produced by Rice Husk Pyrolysis at 973 K.

Table 6 and 7 showed that bio-oil contains more than 5 main components. The compositions of the bio-oil analysis by GC-MS was obtained from the percentage area of the peak or the height of the peak in the chromatograms. Using a method of GC-MS, this work presents a composition of the bio-oil generated in the experiment. The total phenolic compounds contained in bio-oil produced by rice husk pyrolysis at 773 K and 973 K are 47.98% and 62.65%, respectively. The presence of phenolic compounds is caused by thermal decomposition of lignin contained in bagasse during the pyrolysis process (Mantilla et al., 2015). A greater the amount of lignin contained in a biomass, a greater the yield of phenolic compounds will be produced from the biomass. the content of lignin in bagasse is 21.1% (Rocha et al., 2012). The composition of biomass such as hemicellulose, cellulose and lignin will be oxidized to phenol as the main component of the bio-oil (Fardhyanti et al., 2018). The decomposition of lignin produced phenol, derivatives of phenol, and aromatic compounds at 523-873 K (Zhang et al., 2013). More non-condensable gases will be produced such as CO, CO_2, methane, ethane, ethene, propane and propene at above 973 K (Treedet et al., 2017).

Sun et al. (2010) studied the content of bio-oils from various biomass and concluded that the main components of bio-oil attend to be the same, such as phenol, aldehyde, ketone, and organic acids.

Table 8 showed that the composition of bio-oil in this research is not much different from the research of Varma & Mondal (2017).

Table 6. The Compositions of Bio-Oil Produced by Rice Husk Pyrolysis at 773 K.

Retention Time	**Compounds**	**%**
4.313	Furfural	20.76
6.905	Butyrolactone	0.83
8.27	5-methyl-2-furancarboxaldehyde	4.67
8.46	3-methyl-2-cyclopentene	2.73
10.381	Phenol	16.42
10.841	3-methyl-1,2-cyclopentanedione	10.86
12.552	5-methyl-3-methylene	7.54
13.402	4-methyl-phenol	7.05
13.692	2,4-Octadienoic acid	3.48
15.748	2-methoxy-4-methyl-phenol	1.13
16.033	4-ethyl-phenol	7.72
18.159	4-ethyl-2-methoxy-phenol	1.31
18.639	1,2-Benzenediol	5.27
20.335	2,6-dimethoxy-phenol	6.79
22.736	4-methoxy-3-methyl-phenol,	2.29
24.581	2,4,5-trimethoxy-α-methyl-phenethylamine	1.14

Table 7. The Compositions of Bio-Oil Produced by Rice Husk Pyrolysis at 873 K.

Retention Time	Compounds	%
4.389	Furfural	4.41
5.554	2-Furanmethanol	8.09
6.524	3-methyl-2-cyclopentene	1.68
6.77	1-(2-furanyl)-ethanone	1.86
8.55	5-methyl-2-furancarboxaldehyde	4.66
8.69	4-ethyl-4-methyl-2-cyclohexene	4.11
11.001	Phenol	31.66
13.027	5-methyl-3-methylene-5-hexene	9.49
13.967	4-methyl-phenol	14.74
15.898	2,5-dimethyl-phenol	1.86
16.608	3-ethyl-phenol	9.09
19.345	3-cyclopentylpropionic acid	3.05
20.76	2,6-dimethoxy-phenol	5.30

Table 8. The Comparison of Bio-Oil Compositions between This Research and Previous Research (Varma & Mondal, 2017)

Component	Bio-oil 773 K (%)	Bio-oil 973 K (%)	Previous Research (%)
Furfural	20.76	4.41	12.12
Furan	4.67	8.09	8.49
3-methyl-2-cyclopentene	2.73	1.68	1.48
Phenol	34.79	40.75	35.57
Organic acid	3.48	3.05	1.12
2-metoxy-phenol	1.13	-	7.41
1,2-Benzenediol	5.27	-	5.37
2,6-dimetoxy-phenol	6.79	5.3	8.07
Phenethylamine	1.14	-	-

Extraction of Phenolic Compounds from Bio-oil Produced from Rice Husk Pyrolysis

The liquid-liquid extraction process is carried out at atmospheric conditions using methanol-water solvents as polar solvents and chloroform as non-polar solvents. Two solvents have different polarity for binding the different phases of bio-oil, aqueous and non-aqueous phases (Demirbas, 2007). Phenol as a polar in the aqueous phase will be dissolved to the methanol solution, while the other organic components as a nonpolar in the non-aqueous phase will be dissolved to chloroform (Mantilla et al., 2015). The purpose of using methanol-chloroform as mixture solvents is enlarge the contact surface area of solute molecules and solvents, so that solute molecules become more soluble in solvents (Widjanarko & Putri, 2012).

Methanol need to be mixed with water because it can increase the polarity of the solvent into a heterogeneous layer, so that the extract phase (aqueous phase) and raffinate phase (organic phase) can be completely separated (Fardhyanti et al., 2015).

The optimum time for phenolic compounds extraction from bio-oil is 50 minutes. Over the extraction time, it caused denaturation of phenolic compounds in the extract phase. The denaturation process was caused by the oxidation of the phenolic compounds in bio-oil which occurs because of the extraction needs long time process, so that it decreases the concentration of phenolic compounds in the extract phase (Juntachote et al., 2006).

The Effect of Stirring Speed and Temperature Extraction for The Yield of Phenolic Compounds

The yield of phenolic compounds that was shown at Figures 6 and 7 is about 40-60%. It was in accordance with the research that was conducted by Mantilla et al. (2015), the yield of total phenol is 40-60%. But for the pyrolysis temperature at 973 K and the extraction temperature at 298 K, the yield of phenol is 35-38%. It was in accordance with the research that was conducted by Patel et al. (2011), the yield of total phenol is 25-40%. The maximum yields for the pyrolysis temperature at 773 K and 973 K are 58.885% and 48.429%, respectively.

Figures 6 and 7 showed that the maximum yield of phenol is obtained at 303 K temperature extraction. The increasing of extraction temperature raises the yield of phenolic compounds, because it increases the concentration of phenolic compounds in the extract phase (Durling et al., 2007). Increasing the extraction temperature raises the kinetic energy of the solution and increase the diffusion of solvent into solute (Fardhyanti et al., 2017). When the extraction temperature is above the optimum temperature, it evaporated more volatile components in the solution during the extraction process which can reduces the solvent's ability for dissolving the solute (Durling et al., 2007).

Figures 6 and 7 showed the maximum yield of phenol is obtained at stirring speed of 250 rpm. The increasing of stirring speed raises the yield of phenolic compounds, because it increases the rate of mass transfer and more solute will be dissolved into the solvent. The increasing of stirring speed enlarges the contact surface area between solute and the solvent. But for the stirring speed of 300 rpm, back mixing process will occur because solute molecules are diffused into diluent. It caused to reduce the diffusion of solute into solvent (Zhou et al., 2014).

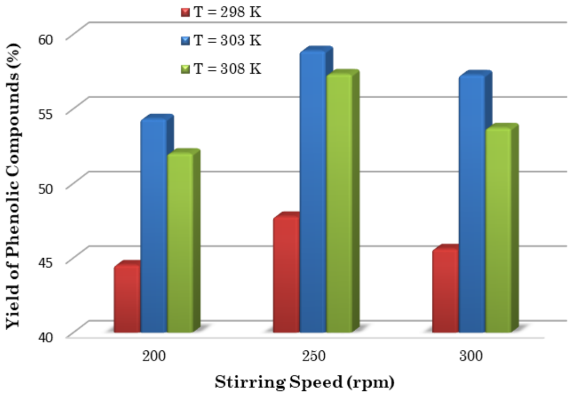

Figure 6. The Effect of Temperature and Stirring Speed for The Yield of Phenolic Compounds at 773 K Temperature Pyrolysis.

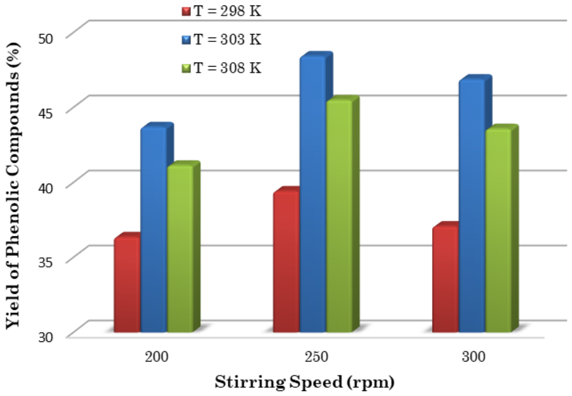

Figure 7. The Effect of Temperature and Stirring Speed for The Yield of Phenolic Compounds at 973 K Temperature Pyrolysis.

The Effect of Temperature and Stirring Speed for The Distribution Coefficient of the Extraction Process

Figures 8 and 9 showed that the distribution coefficients are between 1- 1.5. According to the research of Jieni (2013) which states that the calculation of the phenol extraction distribution coefficient is 0.75-1.75. The distribution coefficient is one of the important criteria for solvent selection. The distribution coefficients of phenolic compounds extraction are almost more than 1, it means that solute (i.e. phenolic compounds) which has been separated from diluent (i.e. bio-oil) are completely dissolved into methanol solution as a polar solvent (Fardhyanti & Damayanti, 2017).

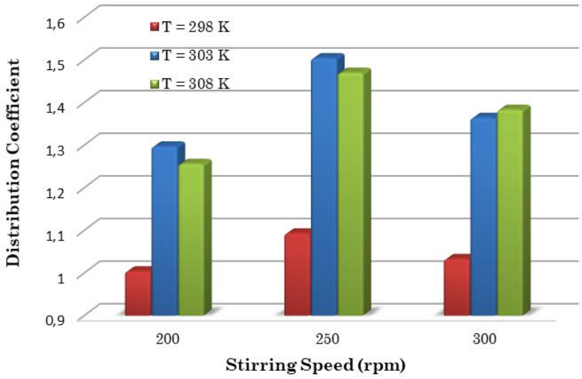

Figure 8. The Effect of Temperature and Stirring Speed for The Distribution Coefficient of the Extraction Process at 773 K.

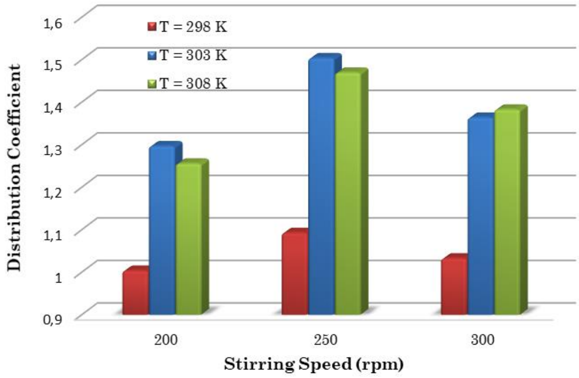

Figure 9. The Effect of Temperature and Stirring Speed for The Distribution Coefficient of the Extraction Process at 973 K.

The increasing of extraction temperature raises the mole fraction of phenol in the extract phase, but it is not in accordance with T = 308 K which is the mole fraction of phenol in the extract phase reduced. It caused by some molecules of the solvent turns into the vapor phase which can reduce the ability of the solvent to dissolve the solute (Fardhyanti et al., 2017).

The increasing stirring speed of the extraction process raises the distribution coefficient (Fardhyanti & Damayanti, 2017). It showed that the increasing stirring speed raises the mole fraction of phenol which is dissolved into the extract phase. The diffusion process will be faster when the distance of the solute molecule and the solvent molecule are smaller. Figures 8 and 9 showed that the maximum of distribution coefficient was obtained at 250 rpm. When the stirring speed is more than 250 rpm, it caused the solute molecule that have been dissolved in the solvent will be back to diffuse into the diluent (Zhou et al., 2014).

CONCLUSION

The characterization of bio-oil produced from rice husk pyrolysis at 773 and 873 K are densities 1,040 and 1,042 Kg/m3; viscosities 9.3488 and 9.5007 cSt; acid numbers 46.75 and 52.45 mg KOH/g; pH 2.5 and 3; flash points 426 and 423 K and heating values 3.229 and 3.339 MJ/kg, respectively. The total phenolic compounds contained in bio-oil produced by rice husk pyrolysis at 773 K and 873 K are 47.98% and 62.65%, respectively. The optimum conditions for phenolic compounds extraction from bio-oil produced by rice husk pyrolysis at 773 and 873 K were obtained at 303 K and 250 rpm to get the highest yield of phenol and the highest distribution coefficient are 58.885%, 48.429%, 1.504, and 1.528, respectively.

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