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Phenolic compound separation from bio-oil produced from pyrolysis of coffee shell at 700°C using liquid-liquid extraction

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Abstract. Coffee shell is an agricultural waste with high lignocellulose content which potentially produces bio-oil as an environmentally alternative fuel. Bio-oil was produced from agricultural waste (biomass) using pyrolysis process that was carried out at 700°C and 1 atm. Bio-oil contains about 28.4% of caffeine, an alkaloid compounds that contains nitrogen atoms from primary metabolites of amino acids. It formed gum in the fuel oil and caused the engine damaged. Separation of phenolic compound from bio-oil was done by liquid-liquid extraction using chloroform and n-hexane as a solvent for 10, 30, 50 minutes at 30°C and stirring speed 250 rpm with feed-solvent ratio 1:4, 1:6, 1:8. The phenolic compound in the extract and raffinate phase were analyzed using UV-Vis spectrophotometer. The aim of this research is to obtain the effect of solvent, time of extraction process and feed-solvent ratio on the yield of phenolic compound. The result showed that the highest yield is 77.93% which were obtained using chloroform as solvent for 50 minutes extraction process with feed-solvent ratio of 1:8.

1. Introduction

In recent years, the demand in energy sources from fossil fuel is gaining rapidly as the consequence of increased amount in human needs and also more advanced industrialization. From small kitchen in the households that use gas and cooking oil until machineries in the big factories, fossil fuels are still has a big role as the main energy source. Thus, this non-renewable energy is highly explored, despite of its limited amount. In order to fulfill the demand, alternative fuels with sophisticated properties are urgently needed.

Among all candidates of alternatives, natural renewable energy sources i.e. bio-oil, bioethanol, biodiesel, bio-briquettes and biogas can be sustainably and highly potential if managed properly [1]. The term bio-oil in this case is the one that obtained from various types of processes including hydrogenation pyrolysis, fisher tropsh, or gasification with lignocellulose as the raw materials. Indonesia as one of agrarian countries has huge amount of environmentally friendly lignocellulose-rich biomass sources which mostly come from natural plants, for example from wood powder [2], avocado seeds [3], corn cobs [4], coffee shells and coconut shells [5], durian shells [6], and oil palm [7].

Indonesia is the largest coffee producer after Brazil and Vietnam [8]. However, up until this date, the products from coffee plantation in Indonesia are still only used as raw material for ground coffee while the waste is immediately disposed as it is not utilized or threatened any further. This direct disposal could lead to the accumulation of waste which can cause the degradation of environment



quality. Hence, efforts to overcome the increasing number of coffee shell waste are needed. Several previous studies tried to transform coffee shell waste into more valuable products for organic fertilizers [9], livestock alternative feed [10], bioethanol [11][12], briquette fuel alternatives [13], natural soil ameliorations [14], and others. Meanwhile in this study, coffee shell waste was used as raw material for bio-oil.

Processing of biomass into bio-oil by means of rapid pyrolysis on coffee shell waste will produce charcoal, liquid (bio-oil), and gas. In this research, it is shown in the results from analysis using Gas chromatography–mass spectrometry (GC-MS) that coffee shell bio-oil contains high caffeine. In that case, liquid-liquid extraction using solvents was preferred to improve the quality of the bio-oil by purifying the components contained in bio-oil so that it can be used as alternative fuels.

The organic solvents used must be relatively selective against caffeine which included in polar compounds. Some previous studies reported that the extraction of caffeine had been successfully done using several solvents including Tautua et al. [15] with carbon tetrachloride, Roossenda [16] and Maramis et al. [17] with chloroform solvents, Aziz et al. [18] with n-hexane solvents, Mussato et al. [19] and Kartasasmita et al. [20] with methanol solvents. Among them, the most decrease in caffeine levels were extractions using chloroform and n-hexane solvents. Hence, these two solvents were used in this study.

2. Experiments

2.1. Materials

The research materials in this study were coffee shell biomass which was obtained from public market in Semarang. All reagents used here are of A.R. grade and used as received without further purification. Chloroform and n-hexane as the solvents, ethanol, sodium carbonate (Na_2CO_3), and sodium hydroxide (NaOH) were purchased from e-Merck (Germany). The distilled water is available at the laboratory.

2.2. Methods

2.2.1. Pyrolysis of Coffee Shells. The coffee shell was cleaned and then dried under the sun for 2 days. After that, the drying process was continued using oven to reduce the water content in the coffee shell. The dried coffee shell was then grinded and blended to obtain small and fair powder sized biomass. Pyrolysis was carried out in pyrolysis reactor under temperature of 700°C . The results of the pyrolysis process were liquid, tar, and charcoal fumes. The smoke from the combustion was condensed with a condenser in the form of a circular coil. Condensation was carried out with copper pipes installed in the cooling tub. Liquid smoke/bio-oil produced was stored in a vessel.

2.2.2. Extraction of caffeine. 5 mL of bio-oil obtained from pyrolysis process was added into solution which made of 10 ml of distilled water, 1 ml of Na_2CO_3 0.5 N. Into the mixed solution was also added solvent, chloroform or n-hexane, as much as the decided amount (ratio of solvent and bio-oil volume were 4: 1, 6: 1, 8: 1). All of the components were poured into separating funnels. The extraction process was carried out by shaking the separating funnel until it formed an organic phase (bottom) and water phase (top).

2.3. Analysis and Characterization

2.3.1. Gas chromatography–mass spectrometry (GCMS) and UV-VIS Spectrophotometer. Analysis using GC-MS was carried out in order to observe compounds that contained in the obtained bio-oil. Meanwhile, UV-Vis Spectrophotometer was used to measure the caffeine level in the extract solution.

2.3.2. Acid number measurement. The test was performed using titration process by weighing 5 grams of sample and add it into 50 mL of 95% ethanol solution. The solution was then mixed in a tightly

closed Erlenmeyer until the oil was homogeneously dissolved. Titration process was done using PP indicator and 0.1 N NaOH solutions.

2.3.3. Density measurement (at temperature of 40 °C). An empty pycnometer was weighed. After that, the pycnometer was filled with distilled water (40°C) until full and put into a beaker glass. The glass was heated it in a water bath at temperature of 40°C for 30 minutes. The pycnometer surface was then dried and weighed. Empty pycnometers are washed using alcohol and dried. The same step was performed using bio-oil samples instead of distilled water.

2.3.4. Kinematic velocity measurement (at temperature of 40 °C). Viscosity of the bio-oil samples were measured using viscometer Oswald.

2.3.5. Flash point measurement. The bio-oil samples were heated with a steady heating speed of 5-6°C/minute for the Cleveland test kit and Pensky Martens and 1°C/minute for Abel test equipment. The two devices were equipped with a pump and a gas tank. Every heat increase of 5°C for Cleveland test and 0.5°C for Abel test, the stirrer was set off and the light pin was put on the sample surface. The lowest temperature when the oil vapor was flashed is pointed as flash point.

2.3.6. Heating value measurement. Heating value of the bio-oil was measured using bomb calorimeter.

3. Result and discussion.

Coffee shell pyrolysis was carried out at the Energy Conversion and Heat Transfer Laboratory, Post Graduate Program, Universitas Gajah Mada, using semi batch pyrolysis reactor. The process was done under operating temperature of 700°C for 3 hours of combustion, producing a liquid yield of 46%. After doing several numbers of tests, it was found that after the pyrolysis process bio-oil obtained has brownish yellow color and has a strong smoke smell.

Table 1. Properties of coffee shell bio-oil (result of pyrolysis at temperature of 700°C)

Physical property	Standard	Bio-oil
Acidity	2.3 – 3.3 [21]	6
Kinematic viscosity (mm ² /s)	4 – 78 [4]	1.35
Density at 40°C (kg/m ³)	940-1,200 [4]	1037
Acid number (mgKOH/gr)	0.5 [4]	6.73
Heating Value (kal/gr)	Maks.9,938.76 [22]	973.612
Flash Point (°C)	Min. 100 [22]	132

The physical characteristics of bio-oil are shown in Table 1. Compared with the standard data, the obtained bio-oil from the coffee shell pyrolysis are already in the range of the standard, which means it can be used as an alternative fuel source. In addition to the physical properties, the chemical properties of the components contained in bio-oil are shown in GC-MS chromatogram results and its interpretation in figure 1 and table 2. It can be known from figure 1 and table 2 that the main component of bio-oil is caffeine (28.4%). The collection of caffeine compounds was carried out by a liquid-liquid extraction process with a shaking method using solvents i.e. chloroform and n-hexane.

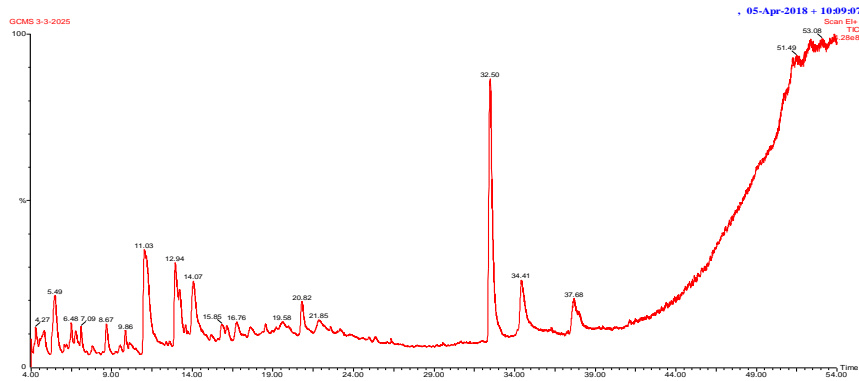


Figure 1. Chromatogram analysis of GC-MS from coffee shell bio-oil.

Table 2. List of components contained in coffee shell bio-oil

Retention Time	% Area	Component
4.27	3.47%	<i>Borazine, 1-methyl-</i>
4.82	5.86%	<i>Butanoic acid</i>
5.49	8.05%	<i>2-Furanmethanol</i>
8.67	2.27%	<i>2-Cyclopenten-1-one, 3-methyl-</i>
11.03	20.21%	<i>Phosphonic acid, (p-hydroxyphenyl)-</i>
12.94	7.69%	<i>Phenol, 2-methoxy-</i>
13.20	3.86%	<i>Phenol, 3-methyl-</i>
14.07	6.69%	<i>Phenol, 4-methyl-</i>
20.82	3.59%	<i>Benzenemethanol, 3-hydroxy-5-methoxy-</i>
32.51	28.40%	<i>Caffeine</i>
34.41	9.92%	<i>Oleic Acid</i>

As for analysis using UV-VIS spectrophotometry, the calibration curve as presented in figure 2 was obtained with 6 variations of concentration (1 ppm, 3 ppm, 6 ppm, 9 ppm, 12 ppm and 15 ppm) so that the results of the caffeine regression line equation were $y = 0.049x + 0.01862$ with a correlation coefficient (R^2) equal to 1.

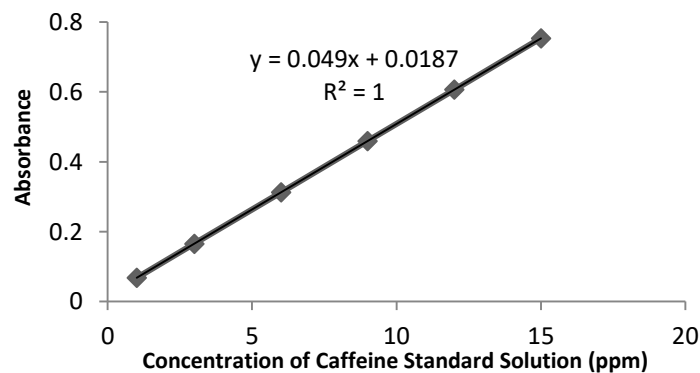


Figure 2. Calibration curve of standard caffeine solution.

After extracting the caffeine compound from coffee shell bio-oil shell pyrolysis results, a comparison of various types of solvents, extraction time at shaking, and the ratio of bio-oil and solvent volume ratio were obtained. It can be seen in figure 3 that the highest yield was obtained using chloroform solvent with a shaking extraction time of 50 minutes and the ratio of the volume of solvent bio-oil 1: 8.

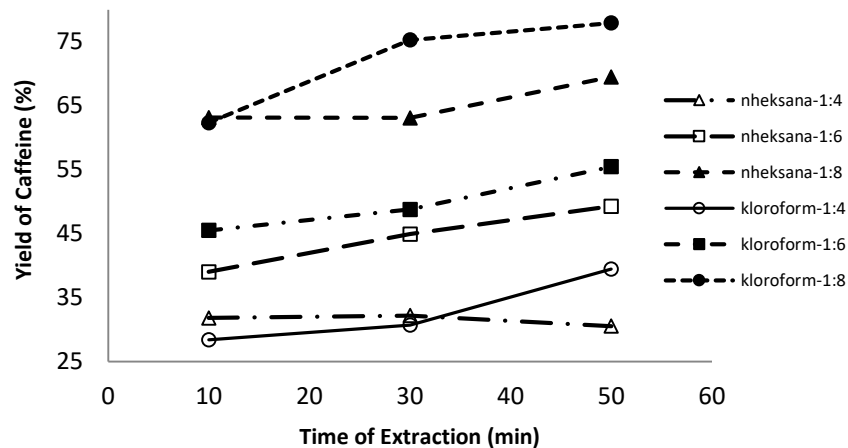


Figure 3. Effect of solvent variation, volume ratio, and extraction time on the caffeine extraction from coffee shell bio-oil.

The value of caffeine extraction yield is greater when using chloroform solvents than n-hexane solvents. The reason behind the phenomena is in accordance with the theory according to [23] namely "like dissolves like", which stated that caffeine which included in polar compounds will dissolve in polar solvents as well. Among the two solvents, chloroform has a slightly polar structure due to the presence of one hydrogen group and three chlorine groups [16]. In the opposite, n-hexane is not included in polar group as the hexane isomer is not reactive. In addition, n-hexane is commonly used as an inert solvent [18]. Further explanation, they can be seen from the boiling point of each solvent compounds, which is 61.2°C for chloroform and 68°C for n-hexane. The lower the boiling point of the solvent, the faster compounds will be dissolved in it [18].

According to Simbolon [24], if the ratio of solvent is bigger, the number of molecules of the compound that dissolve will also increase and leads to the increase of the compound extraction rate. Besides influencing the extraction rate, it also causes differences in concentration that becomes the driving force of the caffeine mass transfer [25]. While in the term of volume, the increasing volume of solvents will result in longer duration of contacting time between bio-oil and solvent. So that, caffeine content increases with the increasing volume of the used solvent.

The length of extraction process time is very influential on the yield produced because it will facilitate the penetration of solvents into bio-oil. Consistent with the theory according to Putri [26], the longer the extraction time, the more caffeine extracted obtained. The effect of extraction time also causes more caffeine mass transfer that occurs from the solute to the solvent [25]. In addition, with the longer process time, there will be components decomposition other than caffeine including impurities which can causes changes in the measured properties.

4. Conclusion

Coffee shell bio-oil was successfully produced and utilized as a potential alternative fuel source to replace fuel derived from fossil resources. The variations in solvent type, volume ratio, and extraction time are significantly influence the amount of yield obtained. The result from the study showed that

chloroform solvent gave better performance compared to n-hexane solvent. The ratio of the volume of bio-oil and solvent that produces the highest yield was 1:8. The shaking extraction time that produced the highest yield was 50 minutes.

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