Determination of Polycyclic Aromatic Hydrocarbon in Biochar

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Abstract. In certain concentration PAHs has hazardous effect to the environment particularly human. PAHs have hazardous effect as carcinogen and in long period persistent in the environment. Incomplete burning of biomass in biochar production process can resulted PAHs. In agriculture, biochar functioned as soil conditioner to increase soil fertility. We have to make sure that production of biochar contains low PAHs. Our department was setting some standard methods as reference methods in Indonesia for determination of PAHs, and involved in environment research, which was very important for Indonesia. Since the most of determination of PAHs used special commercial PAHs column that was expensive, our experiment carried out the determination of PAHs in biochar using HPLC and GC/MS with common column for various analyte of C18 for HPLC and (5%-Phenyl)-methylpolysiloxane for GC/MS. Furthermore, in this experiment, we used diode array detector and fluorescence detector in HPLC. The result showed that both HPLC and GC/MS can be used to determine PAHs only by using common column. Biochar that we produced contain 16 PAHs compound with concentration range from 0.07 to 9.36 µg/g while mean concentration of USEPA PAHs in reference biochar about 0.034 to 1.75 µg/g. Therefore, some PAHs compound were over the limit of USEPA standar in biochar

1. Introduction
Biochar is carbon resulted from biomass pyrolysis that contain some functional group in the surface such as carboxyl, phenolic hydroxy, anhydride and many others (Mayan 2012, Tang et al. 2013). Most common biomass to produce biochar is plant waste such as rice husk and straw, coconut shell and corn cob and many others. Positive impacts of biochar as soil conditioner are in increasing microorganism number and its activities and increasing crop productivity. Biochar also functioned as lime and contaminant absorbent. Negative impact of biochar is containing polycyclic aromatic hydrocarbons (PAHs) as a result of incomplete combustion. PAHs contamination may be caused by biochar production and application to soil. Some studies have already focused on the potential pollutants in biochar, and pyrolysis temperature were reviewed as the most important factors affecting the concentration of PAHs in biochar (Windeatt et al. 2014, Stefanie et al, 2011). Sixteen PAHs are classified as Priority Pollutants by US EPA due to their carcinogenic, mutagenic or teratogenic properties namely Naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[a]- anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene
(BaP), indeno[1,2,3-cd]pyrene (IPY), dibenzo[a,h]anthracene (DBA), and benzo[ghi]perylene (BPE) (US EPA, 2008).

Hale et al (2012) reported that with increasing pyrolysis time and temperature, PAHs concentrations generally decreased while. Quilliam et al (2013) found that soil contained biochar for 3 years had significantly higher levels of PAHs compared to unamended soil. Polycyclic aromatic hydrocarbons (PAHs) in the environment originate mainly from incomplete combustion of fossil fuels and pose a significant human health risk. Soils act as environmental sinks for PAHs, as they become strongly absorbed onto soil particles; degradation is mainly driven by microbial catabolism, although it is dependent on PAHs bioavailability. There is current interest in burying biochar in soil as a long-term soil carbon store; however, biochar inherently contains varying levels of PAHs and its application could contaminate soil, and its high sorptive capacity may facilitate the persistence of PAHs in the environment. Method analysis of biochar is very rare to find and usually need special column in chromatography on quantification. The objective of experiment is to find concentration of PAHs in biochar through easy and simple method analysis.

2. Material and Method

2.1. Chemical and material
Biochar was produced in Jakenan Experiment Field Station, Indonesian Agricultural Environment Research Institute (IAERI). PAHs calibration mix (sigma aldrich), acetonitrile, and n-Hexan were obtained from Merck KgaA, Darmstadt, Germany. Acetone was obtained from Mallincordt, Dublin, Ireland. Glass tube, micro pipet, glass pipet, plastic bottle, shaker, analytical balance, erlenmeyer, glass funnel, filter paper.

2.2. Biochar production
Biochar was made from corn cob that processed by pyrolysis method using closed chamber. Pyrolysis used temperature of 350 °C with 1-2% O₂ oxygen concentration. Closed chamber has special designed that contain 2 (two) components namely biomass burning chamber and distillation chamber in which beside produce biochar also smoke liquid as well.

2.3. Characterization of biochar using Fourier Transform Infra Red (FTIR)
Characterization of biochar by using FTIR the functioned to make sure that biochar contains aromatic functional group and also another chemical functional group. Chemical functional group of compounds is important to find out active chain in chemical reaction. FTIR was using Nicolet iS10 Thermo Scientific that equipped with ATR (Attenuated Total Reflectance) while data processing was using Thermo Electron OMNIC software. The procedure as follow : switch on the FTIR and computer, open OMNIC software, about 0.1 g of biochar (using small spatula) was put directly under ATR, click collect sample button and measure, the spectrum was appear in various frequency in which each frequency has characteristic as chemical functional group, and also can compare to library. After finishing, just log out from OMNIC software, turned off the computer and FTIR.

2.4. Identification of PAHs in biochar using GC/MS

2.4.1. Preparation of PAHs standard calibration curve
PAHs standard mix was diluted with acetonitrile at concentrations of 1 ppm, 0.5 ppm, 0.25 ppm, 0.125 ppm, 0.06 ppm dan 0 ppm. PAHs standar mix contained of Naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANÁ), fluorene (FLU), phenanthrene (PHE), fluoranthene (FLT), pyrene (PYR), benzo[a]- anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IPY), dibenzo[a,h]anthracene (DBA), and benzo[ghi]-perylene (BPE).
2.4.2. Gas Chromatographic (GC) condition
GC/MS was Agilent 5977b GC/MSD tandem with Agilent 7693a Autosampler. Column was DB5, 30 m x 0.25 mm df = 0.15 μm (Part number CP7462) with temperature of 70 °C (2 min), 40 °C/min to 180 °C (0 min), 7 °C/min to 230 °C (7 min), 20 °C/min to 280 °C (10 min), 5 °C/min to 325 °C (7 min). Injection volume was 1 μl and carrier gas was helium with constant flow of 2 ml/min. Injector temperature was 250 °C, Splitless mode, 1 min @ 50 ml/min. Detector was triple Quad, EI in SIM mode, ion source temperature 230 °C, transfer line temperature 300 °C and library was NIST 2017

2.4.3. Sample preparation and extraction
An amount of 5 gram of biochar was added by 15 ml mix of n-hexan:aceton (ratio 4:1) and Shaked up for 5 hours to homogenize the extract. Extract was precipitated for 24 hours and filtered by using filter paper to separate liquid and solid

3. Results and Discussion

3.1. Characterization of biochar using Fourier Transform Infra Red (FTIR)
According the identification by using FTIR showed at Table 1, the functional groups were detected namely aromatic ring, alkena, carboxylic acid, and alcohol. Aromatic ring was detected at frequency of 700 and 900 nm with strong intensity, and also at frequency of 1570 nm with fluctuate intensity. Alkena was detected at frequency of 1650 nm with fluctuate intensity. Carboxylic acid was detected at frequency of 2500 nm with broad intensity. Alcohol was deteted at frequency of 3650 nm with fluctuate intensity. From the table we can conclude that biochar contain PAHs due to existing of aromatic ring with strong intensity. PAHs are colorless, white or pale yellow-green. Solid organic compounds contained at least two fused six-sided aromatic rings that include only carbon and hydrogen.

| No. | Detected Frequency (nm) | Frequency area (nm) | Chemical Bond | Functional Group | Intensity |
|-----|-------------------------|---------------------|---------------|-----------------|-----------|
| 1   | 700, 900                | 690-900             | C-H           | Aromatic ring   | Strong    |
| 2   | 1570                    | 1500-1600           | C=H           | Aromatic ring   | Fluctuate |
| 3   | 1650                    | 1610-1680           | C=C           | Alkena          | Fluctuate |
| 4   | 2500                    | 2500-2700           | O=H           | Carboxylic acid | Broad     |
| 5   | 3650                    | 3590-3650           | O-H           | Alcohol         | Fluctuate |

The existing of functional groups are various depend on raw material of biochar and also production temperature. Biochar with highly loose and porous structure has the advantage of a large specific surface area. Besides, carboxy, phenolic hydroxy, anhydride and many other functional groups are contained in its surface (Mayan 2012, Tang et al. 2013). As a result, biochar has excellent adsorption performance, and can strongly adsorb the pollutants in environment and reduce their environmental risks, especially for heavy metals and organic pollutants. Heavy metals and organic pollutants can be strongly adsorbed and accumulated by biochar, and CO₂ in atmosphere can also be immobilized by it. Biochar would be a favorable soil amendment due to its alkalinity and high-carbon content, and when used for soil amendment, it not merely amended the contaminated soil but also improved the soil fertility and slowed down the greenhouse effect. So, it is wildly used for soil amendment and to immobilize CO₂ from the atmosphere to the soil (Xiao et al. 2014, Chen et al. 2014).
2015). Because of those benefits of biochar, it is gaining increasing attention on remediation of heavy metals and organic pollutants, combating climate change, water and wastewater treatment and soil amendment in recent years (Mohan et al. 2014).

![Figure 1. Determination of Biochar Using GC/MS](image)

**Table 2.** Linearity of calibration curve

| No | PAHs                          | Coefficient of Correlation (R) |
|----|-------------------------------|-------------------------------|
| 1  | Naphthalene                   | 0.985                         |
| 2  | Acenaphthylene                 | 0.990                         |
| 3  | Acenapthene                   | 0.986                         |
| 4  | Flourene                      | 0.987                         |
| 5  | Phenanthrene                  | 0.976                         |
| 6  | Flouranthenne                 | 0.986                         |
| 7  | Pyrene                        | 0.981                         |
| 8  | Benzo(a)Anthracene            | 0.981                         |
| 9  | Chrysene                      | 0.984                         |
| 10 | Benzo(a)Pyrene                | 0.982                         |
| 11 | Benzo(k)Flouranthenne         | 0.981                         |
| 12 | Benzo(b)Flouranthenne         | 0.977                         |
| 13 | Benzo(ghi)Perylene            | 0.983                         |
| 14 | Dibenzo(ah)Anthracene         | 0.978                         |
| 15 | Indeno(1.2.3-cd)Pyrene        | 0.978                         |
3.2. Linearity of standard (R)
Calibration curves were constructed by plotting integrated peak areas against concentrations of compounds. Linearity of standard were expressed by coefficient of correlation (R) value in which the value were 0.977 - 0.990 (Table 2). Those value fulfill the requirement as good coefficient of correlation. Peak areas have been reduced by the area of the peaks of compounds derived from blank to eliminate the matrix effect. Therefore, calibration curves were calculated without y-intercept, which the high value could significantly affect the calculation of the results making them inaccurate.

Standard area of each compound at 1 ppm was very high (Table 3). It is mean that chromatographic condition was good or ideal, and the preparation of standard was good also. The successful of determination is depend on chromatographic condition that were setting. The determination should be at suitable column and its temperature, suitable detector and its temperature, also suitable gas carrier and its flow.

Table 3. Area each compound at 1 ppm

| No. | PAHs Compound               | Area     |
|-----|-----------------------------|----------|
| 1   | Napthalene                  | 1121063  |
| 2   | Acenapthylene               | 1325939  |
| 3   | Acenaphene                  | 1786229  |
| 4   | Flourene                    | 1847151  |
| 5   | Phenanthrene                | 2101549  |
| 6   | Flouranthene                | 2146965  |
| 7   | Pyrene                      | 2440286  |
| 8   | Benzo(a)Anthracene          | 1661897  |
| 9   | Chrysene                    | 2995101  |
| 10  | Benzo(a)Pyrene              | 2175952  |
| 11  | Benzo(k)Flouranthene        | 2947060  |
| 12  | Benzo(b)Flouranthene        | 1969158  |
| 13  | Benzo(ghi)Perylene          | 1472612  |
| 14  | Dibenzo(ah)Anthracene       | 2084814  |
| 15  | Indeno(1.2.3-cd)Pyrene      | 2246289  |
According to result of analysis at Table 4, the concentration of PAHs in biochar were 0.07 until 9.36 ppm. Compared to US EPA standard, they 0.7 - 72 times higher in all compound. The highest concentration was reach by benzo (b) flouranthene while the lowest was chrysene. The chemical composition of biochar feedstock will greatly influence the amount and frequency of PAH reactions occurring during pyrolysis. In addition, the temperature and duration of pyrolysis can also make a significant difference to the concentrations of PAHs, e.g. PAHs are more likely be lost to the atmosphere as gases during a slower and longer pyrolysis residency time, whereas during a fast pyrolysis they are more likely to condense back onto the biochar surface (Hale et al. 2012). However, despite the concentration of PAHs in the rice husk biochar being nearly seven times greater than that in the wood biochar, the surface area available for PAHs adsorption were far lower than the rice husk biochar. The elevated concentrations of PAHs were due to the initial chemical composition of the feedstock (Hale et al. 2012).
Table 4. Concentration of PAHs in Biochar

| No. | PAHs Compound                  | Concentration (ppm) | US EPA standard (ppm) | Comparison |
|-----|--------------------------------|---------------------|-----------------------|------------|
| 1   | Napthalene                     | 3.6                 | 1.75                  | 2.1        |
| 2   | Acenapthylene                  | 1.19                | 0.026                 | 45.8       |
| 3   | Acenaphthene                   | 0.29                | 0.034                 | 8.5        |
| 4   | Flourene                       | 0.23                | 0.071                 | 3.2        |
| 5   | Phenanthrene                   | 6.29                | 0.71                  | 8.9        |
| 6   | Flouranthene                   | 0.72                | 0.30                  | 2.4        |
| 7   | Pyrene                         | 6.98                | 0.35                  | 19.9       |
| 8   | Benzo(a)Anthracene            | 7.25                | 0.35                  | 20.7       |
| 9   | Chrysene                       | 0.07                | 0.095                 | 0.7        |
| 10  | Benzo(a)Pyrene                | 9.18                | 0.19                  | 48.3       |
| 11  | Benzo(k)Flouranthene          | 1.44                | 0.10                  | 14.4       |
| 12  | Benzo(b)Flouranthene          | 9.36                | 0.13                  | 72.0       |
| 13  | Benzo(ghi)Perylene            | 6.18                | 0.15                  | 41.2       |
| 14  | Dibenzo(ah)Anthracene         | 0.46                | 0.056                 | 8.2        |
| 15  | Indeno(1.2.3-cd)Pyrene         | 0.62                | 0.15                  | 4.1        |

4. Conclusion
The result showed that GC/MS can be used to determine PAHs only by using common column. Biochar that we produced contain 16 PAH compound with concentration range from 0.07 to 9.36 µg/g while mean concentration of US EPA PAH in reference biochar about 0.034 to 1.75 µg/g. So, some PAH compound was over the limit of US EPA standard in biochar.

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