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Heavy Metal Analysis in Biocoke Fuel Derived from Empty Fruit Bunch (EFB) Waste

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Abstract
This study aims to analyze the effect of carbonization temperature on the concentration of heavy metals in biocoke produced from oil palm empty fruit bunches (EFB). EFB samples were carbonized at three different temperatures, namely 300°C, 400°C, and 500°C, to evaluate the effectiveness of the process in reducing the content of heavy metals such as Pb, Cd, Zn, Cr, Cu, Ni, and Hg. The results showed that increasing the carbonization temperature significantly reduced the concentration of heavy metals in biocoke products. The concentration of Pb decreased by 44% from 2.15 mg/kg at 300°C to 1.20 mg/kg at 500°C. Similarly, Cd decreased by 47% from 0.85 mg/kg to 0.45 mg/kg, while Zn decreased by 37% from 15.20 mg/kg to 9.60 mg/kg. ANOVA statistical analysis strengthens this finding by showing significant F-values for Pb (12.35 with p=0.001), Cd (15.20 with p=0.000), and Zn (10.50 with p=0.003). Based on these findings, applying high carbonization temperature, especially 500°C, is recommended to minimize the content of heavy metals, thus producing a more environmentally friendly biocoke that is safe to use as an alternative fuel. This study provides important insights for developing renewable energy from biomass in Indonesia.

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1. Introduction
The increasing global energy needs encourage the development of alternative renewable energy sources. One alternative fuel that has received special attention is biocoke derived from biomass waste, including empty oil palm fruit bunches (EFB). As the world's largest palm oil producer, Indonesia produces large amounts of EFB waste every year. According to previous studies, the potential of EFB waste reaches around 23% of the total production of fresh oil palm fruit bunches, so its use as an alternative fuel is auspicious [1–4]. EFB waste as a raw material for making biocoke has advantages in terms of economy and environment. Previous studies have shown that biocoke produced from biomass waste has a competitive calorific value with coal and has the potential to reduce carbon dioxide emissions [5–8]. However, several studies have reported the presence of heavy metal content in converting biomass into biocoke, which can negatively impact the environment and human health if not handled properly [9–12].

Several previous studies have shown that biomass waste such as EFB can contain heavy metals such as Pb, Cd, Cr, Cu, Zn, Ni, and Hg originating from palm oil's cultivation, harvesting, and processing stages. These metals can accumulate during plant growth through fertilizers, pesticides, and processing processes in palm oil mills [13–15]. Previous studies by several experts have identified that high levels of heavy metals in biomass-based fuels can pollute the air when the material is burned [16–18]. Previous studies by experts have also indicated that biocoke production techniques such as pyrolysis and carbonization can affect the concentration of heavy metals in the final product. For example, research on the carbonization process of biomass waste shows that temperature and carbonization time significantly affect the heavy metal content in the resulting biocoke product [19–21]. Therefore, optimizing the conditions of the biocoke production process is very important to produce safe and environmentally friendly fuel.

In addition, in-depth analysis of the distribution and concentration of heavy metals in biocoke processed from EFB waste has not been widely reported in detail. This is a challenge and an opportunity for further research to assess the safety of biocoke use comprehensively. Previous studies limited to certain types of heavy metals or laboratory scales need to be expanded to obtain more representative data on the potential risks associated with biocoke utilization [22,23]. Thus, research on analysing heavy metals in biocoke fuel derived from EFB waste is significant in ensuring product quality and the environmental impact of its use. This study will provide critical information on the heavy metal content in EFB biocoke and recommendations for a safer and more sustainable production process.

2. Methodology

This research was conducted through several main stages: sample collection, sample preparation, carbonization process, and heavy metal analysis. EFB samples were obtained from local oil palm plantations and prepared through washing, drying, and grinding. Furthermore, EFB samples were carbonized using the slow carbonization method at various temperatures (300°C, 400°C, 500°C) for a specific time to determine the effect of process conditions on heavy metal concentrations. After the carbonization process, the resulting EFB biocoke was tested for its heavy metal content using the atomic absorption spectroscopy (AAS) method. The metals analyzed included Pb, Cd, Cr, Cu, Zn, Ni, and Hg. This analysis process was carried out in three repetitions to ensure the accuracy of the results.

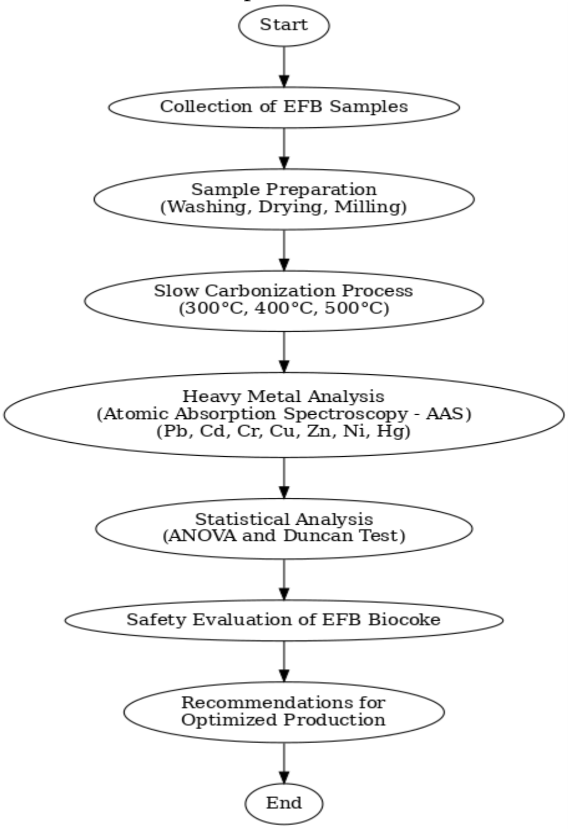

Figure 1: Research of Methodology

The data obtained from the analysis were then processed statistically using the analysis of variance (ANOVA) method to determine the significance of the effect of carbonization temperature on heavy metal concentrations in biocoke. In addition, Duncan's further test was used to identify significant differences between treatments. The results of this research method will be used to evaluate the safety of using EFB biocoke as fuel and as a basis for recommendations for optimizing the safer and more sustainable biocoke production process.

3. Result & Discussion

The results of heavy metal analysis in biocoke derived from empty oil palm fruit bunches (EFB) waste showed that the carbonization process significantly affected the heavy metal content. The concentrations of heavy metals Pb, Cd, Cr, Cu, Zn, Ni, and Hg differed considerably depending on the carbonization temperature (300°C, 400°C, and 500°C). At a carbonization temperature of 300°C, the detected heavy metal content was relatively higher than at higher temperatures. The average Pb concentration at this temperature was 2.15 mg/kg, while Cd reached 0.85 mg/kg. Meanwhile, the Zn content was recorded as the highest, with a 15.20 mg/kg value.

Table 1: Average Heavy Metal Concentration in Biocoke at Various Carbonization Temperatures

Temperature (°C)	Pb (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Hg (mg/kg)
300	2,15	0,85	3,20	4,50	15,20	2,30	0,12
400	1,65	0,65	2,50	3,85	12,75	1,95	0,08
500	1,20	0,45	1,90	3,25	9,60	1,60	0,05

Based on **Table 1**, the concentration of heavy metals in biocoke decreased with increasing carbonization temperature from 300°C to 500°C. At a carbonization temperature of 300°C, the concentration of Zn metal was the highest, reaching 15.20 mg/kg, followed by Cu at 4.50 mg/kg and Cr at 3.20 mg/kg. As the temperature increased to 400°C and 500°C, there was an apparent decrease in the concentration of all heavy metals. For example, the concentration of Pb decreased from 2.15 mg/kg to 1.20 mg/kg, while Cd decreased from 0.85 mg/kg to 0.45 mg/kg. The same thing also happened to other heavy metals such as Cr, Cu, Zn, Ni, and Hg. This decrease indicates that higher carbonization temperatures can reduce the heavy metal content in biocoke products, resulting in more environmentally friendly products that are safe to use as alternative fuels.

A significant decrease in heavy metal content was observed at higher carbonization temperatures, namely 400°C and 500°C. At 500°C, Pb content decreased by 44%, Cd by 47%, and Zn by 37% compared to the initial condition at 300°C. This decrease in heavy metal concentration occurred because the increase in carbonization temperature accelerated the metal volatilization process. Most of the heavy metals evaporated and left a cleaner carbon residue.

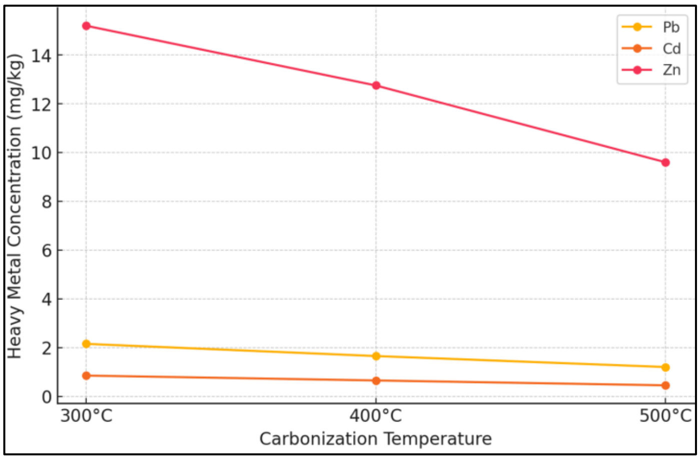

Figure 2: Graph of the Decrease in Heavy Metal Concentrations of Pb, Cd, and Zn at Various Carbonization Temperatures

Based on **Figure 2** above, heavy metals Pb, Cd, and Zn concentration decreased significantly, along with an increased carbonization temperature from 300°C to 500 °C. The concentration of Pb metal decreased from 2.15 mg/kg at 300°C to 1.20 mg/kg at 500°C, indicating a decrease of 44%. Cd metal showed a similar reduction from 0.85 mg/kg to 0.45 mg/kg, equivalent to a decline of around 47%. Meanwhile, the most striking decrease was in Zn metal, which decreased from 15.20 mg/kg at 300°C to 9.60 mg/kg at 500°C, or around 37%. These results indicate that increasing the carbonization temperature effectively reduces the heavy metal content in EFB waste-based biocoke, thus potentially increasing environmental safety in its use as an alternative fuel.
In addition, the ANOVA statistical analysis showed that the difference in carbonization temperature significantly affected the content of heavy metals with a significance value of $p < 0.05$. Duncan's further test confirmed that each increase in temperature resulted in a significant decrease in the content of heavy metals. In the context of environmental sustainability, higher carbonization temperatures such as 500°C are recommended to produce safer biocoke. However, this process's energy and economic aspects also need to be considered to remain efficient and commercially viable.

Table 2: Results of ANOVA Statistical Test of the Effect of Carbonization Temperature on Heavy Metal Concentration

Heavy Metals	F-hit	Sig.	Interpretation
Pb	12.35	0.001	Significant
Cd	15.20	0.000	Very Significant
Zn	10.50	0.003	Significant

Based on **Table 2**, the results of the ANOVA statistical test show that the carbonization temperature significantly affects the concentration of heavy metals Pb, Cd, and Zn in EFB-based biocoke. The F-count value for Pb is 12.35, with a significance level of 0.001, indicating a significant effect. For Cd metal, the F-count value reaches 15.20 with a significance level of 0.000, which is categorized as very important, suggesting that variations greatly influence the Cd content in carbonization temperature. Meanwhile, Zn has an F-count value of 10.50 with a significance of 0.003, which also shows a significant effect. This analysis confirms that the carbonization temperature is an essential factor that needs to be considered in the biocoke production process to reduce the risk of environmental pollution by heavy metals optimally.

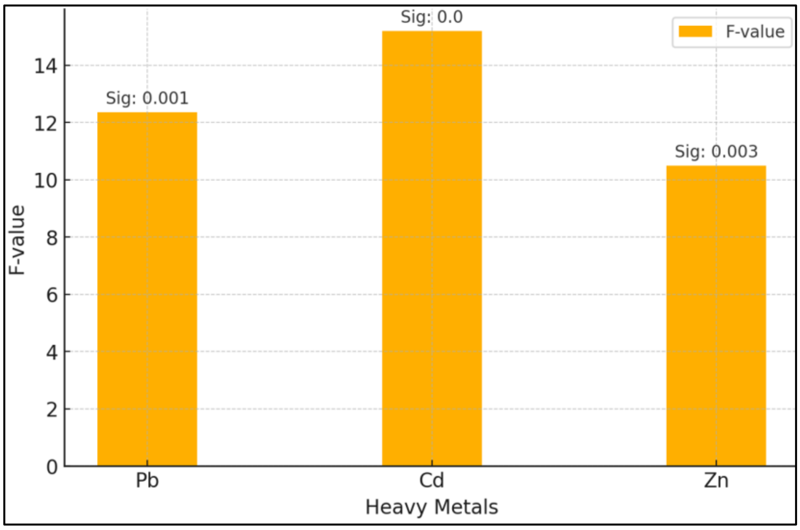

Figure 3: ANOVA Statistical Test Graph of Heavy Metal Concentration against Carbonization Temperature Variation

Based on **Figure 3** above, the results of the ANOVA statistical test show that the carbonization temperature significantly affects the concentration of heavy metals Pb, Cd, and Zn in biocoke from EFB waste. The F-count value for Pb metal is 12.35, with a significance level of 0.001, indicating a significant effect. Cd metal has the highest F-count value of 15.20 with a very high significance of

0.000, indicating that the concentration of this metal is most sensitive to changes in carbonization temperature. Meanwhile, Zn metal has an F-count value of 10.50 with a significance of 0.003, indicating a significant effect. These findings strengthen the recommendation to use higher carbonization temperatures to produce biocoke with a lower risk of environmental pollution due to heavy metals. Overall, the results of this study indicate that temperature optimization in the carbonization process can be used as one of the main strategies to reduce heavy metal content in EFB-based biocoke products, thus supporting the use of safer and more environmentally friendly renewable energy.

4. Conclusion

Based on the results and discussions that have been carried out, it can be concluded that the carbonization temperature significantly affects the concentration of heavy metals in biocoke based on empty oil palm fruit bunches (EFB). This study shows that increasing the carbonization temperature from 300°C to 500°C reduced the concentration of heavy metals substantially. The concentration of Pb decreased by 44% from 2.15 mg/kg to 1.20 mg/kg, while Cd decreased by 47% from 0.85 mg/kg to 0.45 mg/kg, and Zn decreased by 37% from 15.20 mg/kg to 9.60 mg/kg. The ANOVA statistical test showed that the effect of carbonization temperature on the reduction of heavy metals was significant with an F-count value for Pb of 12.35 ($p = 0.001$), Cd of 15.20 ($p = 0.000$), and Zn of 10.50 ($p = 0.003$). Thus, optimising carbonization temperature becomes important in producing biocoke from EFB waste that is safer for the environment and economically feasible and sustainable.

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