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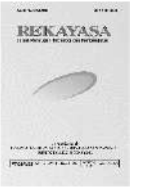

Optimizing Bio-Oil Yield from Pyrolysis of Spent Bleaching Earth for Liquid Fuel Production

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Abstract

Spent Bleaching Earth is an industrial waste generated primarily from vegetable oil processing and contains 20-40% oil by weight, which poses a fire hazard due to the risk of spontaneous combustion. Commonly, Spent Bleaching Earth is processed using extraction methods with solvents like n-hexane, methanol, or steam. However, transforming SBE into liquid fuel via pyrolysis remains underexplored. This research aims to convert into liquid fuel through pyrolysis. The process was conducted at 600 °C for 90 min, resulting in pyrolysis oil with a density of 992.8 kg/m^3, a viscosity of 31.21 cSt, a calorific value of 40.63 MJ/kg, and a flash point of 36 °C. Additionally, the oil contained 21.18% phenol compounds. The remaining material from the process, including char, constituted 54% of the original spent bleaching earth mass. These results demonstrate the feasibility of using pyrolysis to convert into a valuable liquid fuel, offering a sustainable approach to manage this hazardous industrial waste while producing energy-rich byproducts. This study underscores the potential of pyrolysis as a waste-to-energy solution and a safer alternative to traditional disposal methods for Spent Bleaching Earth.

Keywords: *extraction, n-hexane, energy,* phenol, hazardous waste

INTRODUCTION

The growing demand for non-renewable energy sources, coupled with the limited availability of resources (Athallah & Wulansari, 2022), can be partially addressed by utilizing Spent Bleaching Earth (SBE) waste, which can be processed into bio-oil. The vegetable oil refining industry generates large amounts of solid waste in the form of spent bleaching earth. All vegetable oils must undergo refinement to remove impurities before they can be used (Fattah et al., 2014). The refinement process involves several steps such as filtration, removal of phosphatides, neutralization of acids, bleaching, optional hardening, and deodorization. During the bleaching step, a natural absorbent such as bentonite clay, known as bleaching earth, is used (Sabour & Shahi, 2018). Bleaching earths are primarily bentonites, which are clays composed of aluminum silicates and various intermediate metal ions (Tang et al., 2015). The preparation of bleaching earth typically involves chemical activation using strong inorganic acid solutions to enhance its absorbent properties. Virgin bleaching earth, after removing undesirable elements like color and heavy metals from vegetable oil, becomes spent bleaching earth (Abdelbasir et al., 2023). Spent bleaching earth has been used in various environmental and industrial applications (Phey et al., 2022).

The pyrolysis process is one method used to regenerate spent bleaching earth. Regeneration of Spent bleaching earth can occur through pyrolysis at temperatures ranging from 250 to 800 °C (Naser et al., 2021). Studies have shown that SBE regenerated through pyrolysis, specifically between 300 and 800 °C in 100 °C increments, demonstrated good regeneration quality for vegetable oil bleaching (Pranowo et al., 2020). At 600 °C, the regenerated SBE achieved a bleaching efficiency of 65.4%, compared to 92.7% for fresh bleaching earth. Remarkably, the efficiency increased to 92.8% after the Spent bleaching earth was washed with 1 M HCl acid (Anom & Lombok, 2020).

Currently, SBE has limited options for beneficial reuse (Abdelbasir et al., 2023). Spent bleaching earth contains trapped crude oil and is often disposed of untreated, posing environmental risks. One method to address this involves oxide heat treatment, where oxygen is supplied in excess of the stoichiometric requirements to completely oxidize the organic matter in the spent bleaching earth, which is then blown through a stationary fluidized bed of inert granular material (Achaw & Danso-Boateng, 2021).

Pyrolysis, a thermal degradation process, converts polymer materials like plastics and organic materials like biomass into high-energy liquid and gaseous products through heating without oxygen (Novia, 2021). Biomass, which is a renewable organic material from plants and animals, is commonly used as feedstock for pyrolysis. It includes materials such as crops, trees, and agricultural waste and is composed primarily of carbon, hydrogen, nitrogen, oxygen, and trace elements (Tursi, 2019).

The aim of the study was to investigate the optimal pyrolysis conditions for processing Spent Bleaching Earth into valuable products such as pyrolysis oil and char, by evaluating the effects of pyrolysis temperature and time on density, viscosity, oil composition (especially phenol content), and char carbon content, as well as the overall yield. Pyrolysis offers an effective way to recycle energy from waste by converting it into valuable resources, thus generating economic benefits while reducing environmental impacts (Bridgwater, 2017). The process can operate at atmospheric pressure and temperatures around 500°C (Endang et al., 2016). Depending on factors such as temperature, heating rate, and residence time, pyrolysis can be categorized into fast and slow processes (Maqsood et al., 2021). Slow pyrolysis, characterized by lower heating rates, longer solid and vapor residence times (minutes to hours), and lower temperatures, offers advantages such as improved heat transfer and greater control over inlet and outlet flow rates (Al Arni, 2022).

METHOD

The main raw material used in this pyrolysis research is spent bleaching earth obtained from PT. Pertamina International RU

III Plaju Green Refinery, which has been collected over the course of one week.

SBE Pyrolysis Process

In the SBE Pyrolysis Process, the products, including bio-oil and biochar, are obtained at the end of the pyrolysis process. These products are weighed and added together, and the total is subtracted from the initial amount of Spent Bleaching Earth (SBE) used as input to determine the yield of each product. The SBE is first dried under the sun and then subjected to pyrolysis for varying durations of 30-90 min. The process is conducted at different temperature settings: 400-650 °C, using a predetermined mass of 300 g in the pyrolysis apparatus.

Measurement of Bio-oil Characteristic

In this research, the density of the bio-oil produced from the pyrolysis of Spent Bleaching Earth was measured using a pycnometer. Viscosity was determined following the ASTM D445 method. Flash point measurements were conducted according to the ASTM D93 method. The calorific value of the bio-oil was tested at the PT KPI RU III Laboratory, while the chemical composition and surface characteristics were analyzed using Gas Chromatography-Mass Spectrometry (GC-MS) and Scanning Electron Microscopy with Energy Dispersive X-ray (SEM-EDX) at the South Sumatra Regional Police Laboratory. The analysis of bio-oil samples from the pyrolysis process of the spent bleaching earth mixture includes several methods, such as the calculation of yield, density, viscosity, flash point, and calorific value, which aim to assess the quality of the bio-oil produced. The GC-MS test is a technique for compound analysis based on the separation of volatile substances, enabling the identification and quantification of individual compounds within the bio-oil. This method helps in determining the types and amounts of each compound present.

RESULTS AND DISCUSSION

Effect of Temperature Variation and Pyrolysis Time on the Yield of Bio-Oil Produced

The effect of temperature variation on the yield of bio-oil produced during the pyrolysis process. The results indicate that the temperature variations significantly influence the pyrolysis reaction of Spent Bleaching Earth, leading to the production of bio-fuel. The selected temperature ranges play a crucial role in optimizing the conversion of Spent Bleaching Earth into bio-oil, highlighting the importance of temperature control in achieving efficient bio-fuel production.

The highest yield of SBE pyrolysis oil was achieved at 400-600, and 650 °C with a pyrolysis time of 30-90 min. Achiving for 45 min pyrolysis has producing a yield of 53%. Conversely, the lowest yield was observed at 450 °C with a pyrolysis time of 45 minutes, yielding only 40 grams of oil. This indicates that the optimal conditions for maximum yield occur at 500 °C for 45 min. The results suggest that operating temperatures that are too low, coupled with shorter pyrolysis times, negatively impact the yield, as shown by the low yield at 450 °C. Similarly, excessively high temperatures and longer pyrolysis times can also reduce the yield of pyrolysis oil (Guedes et al., 2018).

At 500 °C, as shown in Figure 1, the results fluctuate depending on the pyrolysis time. The highest yield of 100 g of pyrolysis oil was achieved at 90 min, with a density of 986 g/cm^3 and a viscosity of 29.3 cSt. In contrast, the lowest yield of 110 grams was observed at 30 minutes, with a density of 948.2 g/cm^3 and a viscosity of 15.2 cSt. Although the yield at 30 min was greater than at 90 min., the density and viscosity values were notably lower, indicating that longer pyrolysis time enhances the quality of the oil in terms of density and viscosity.

At a temperature of 600 °C, there are noticeable fluctuations in the results obtained from the pyrolysis process. The highest yield of pyrolysis oil was recorded at a pyrolysis time of 60 min., producing 97 g of oil with a density of 960 g/cm^3 and a viscosity of 20 cSt. In contrast, the lowest yield occurred at a pyrolysis time of 75 min., with only 30 g of oil produced, though with a slightly higher density of 966.6 g/cm^3 and a viscosity of 16.8 cSt. These results indicate that a pyrolysis time of 60 min. at 600 °C is more effective for achieving a better yield compared to longer durations, such as 75 min.

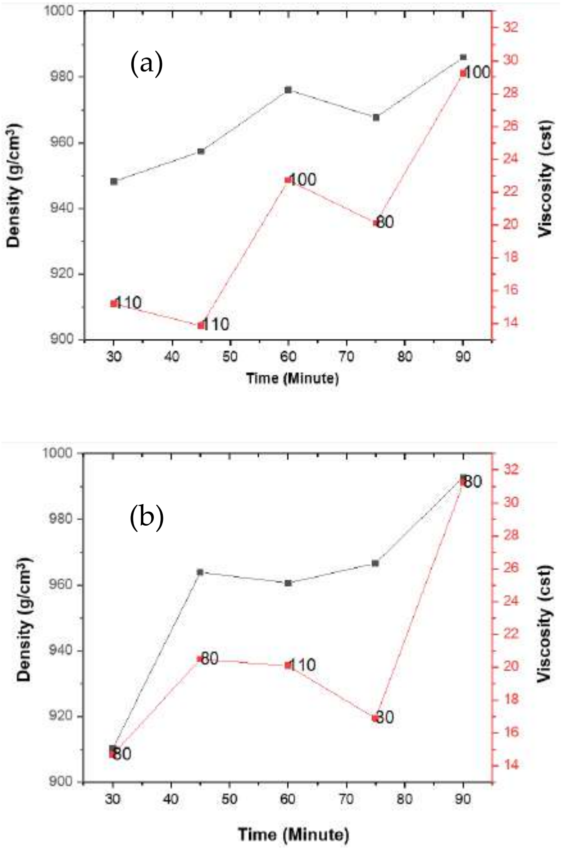

Figure 1. Spent Bleaching Earth Pyrolysis at (a) 500 °C and (b) 600 °C

At temperatures above 500 °C, fluctuations in viscosity and density were observed, and optimum results were not achieved under operating conditions of 550, 600, and 650 °C. The highest density and viscosity at 550°C occurred with a pyrolysis time of 75 minutes, yielding 972.5 g/cm^3 and 21.65 cSt, respectively. For 600 and 650 °C, the best results were obtained at a pyrolysis time of 90 min. At 600 °C, the density and viscosity reached 992.8 g/cm^3 and 31.21 cSt, while at 650 °C, they were slightly lower, at 983.6 g/cm^3 and 27.68 cSt. These findings suggest that while higher temperatures can increase density and viscosity, the optimal operating time is crucial to achieving the best results.

The findings of this study demonstrate a significant correlation between temperature and operating time on the resulting density and viscosity of the pyrolysis oil. As both temperature and operating time increase, the measured values of density and viscosity also rise, consistent with previous research (Rusdianasari et al., 2022). The optimal results were achieved at a temperature of 500 °C with a pyrolysis time of 60 min., and at 600 °C with a pyrolysis time of 90 min., where the highest values of density and viscosity were recorded. This indicates that specific combinations of temperature and time are critical for obtaining the best-quality pyrolysis oil.

Effect of Pyrolysis Temperature and Time on the Calorific Value of the Pyrolysis Oil Produced

At a temperature of 500 °C, as seen in Figure 2, there is fluctuation in the results, where the calorific value reached its optimum at a pyrolysis time of 60 min., with a value of 42.08 MJ/kg. Similarly, at higher temperatures, the calorific values fluctuated, with optimum heating values observed at different time intervals. The highest heating value at 500 °C and 60 min. was 42.08 MJ/kg. At temperatures of 600 and 650 °C, the highest results were achieved at operating times of 40 and 60 min., with heating values of 41.74 MJ/kg and 41.84 MJ/kg, respectively.

These results demonstrate that temperature and pyrolysis time significantly affect the calorific value. The best outcome was observed at 500 °C with a pyrolysis time of 60 min. However, variations in time and temperature at higher levels still produced substantial energy content, albeit with slightly lower heating values.

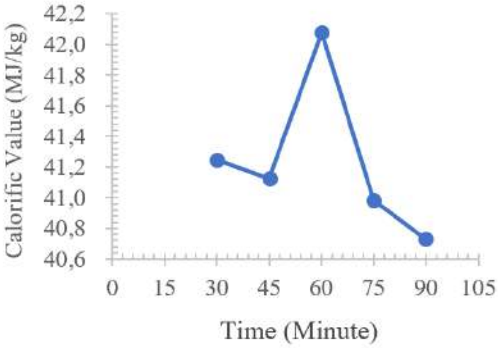

Figure 2. Calorific Value of Spent Bleaching Earth Pyrolysis at Temperature 500 °C

Effect of Pyrolysis Temperature and Time on Flash Point of Pyrolysis Oil Produced

At a temperature of 500 °C, as shown in Figure 3, the flash point results are linear, with a consistent flash point of 38 °C at all pyrolysis times. A similar linear pattern is observed at other temperatures, where the flash point values remain consistent across different operating times. The highest flash point recorded was 45 min at 650 °C, while temperatures of 550 °C and 600 °C both produced a flash point of 36 °C.

These findings indicate that both temperature and operating time significantly impact the flash point of the pyrolysis oil. The optimum flash point result in this study was achieved at 500 °C with a pyrolysis time of 60 min., suggesting that this combination of parameters produces the most stable and desirable flash point for bio-oil applications.

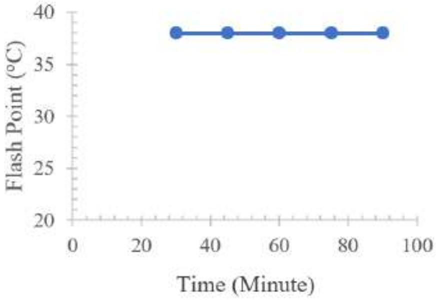

Figure 3. Flash Point of Spent Bleaching Earth Pyrolysis at 500 °C Temperature

Effect of Pyrolysis Temperature and Time on the Composition of Pyrolyzed Oil and Char

The study conducted a detailed composition analysis of the pyrolysis oil obtained at an optimal operating temperature of 500 °C with a pyrolysis time of 60 min. The Gas Chromatography-Mass Spectrometry analysis revealed that the composition of phenol in the pyrolysis oil exceeded 50%. This significant phenol content highlights the potential of producing bio-oil from Spent Bleaching Earth, with phenol as the primary compound. This finding demonstrates the capability of the pyrolysis process to transform SBE into a valuable product—bio-oil—dominated by phenol. The detailed composition analysis results are presented in Figure 4 and Table 3, illustrating the percentage of phenol and other compounds present in the bio-oil. This analysis not only shows the potential for bio-oil production but also opens avenues for using the resulting phenol-rich oil in industries that utilize phenol derivatives, such as in resins, plastics, and chemical intermediates.

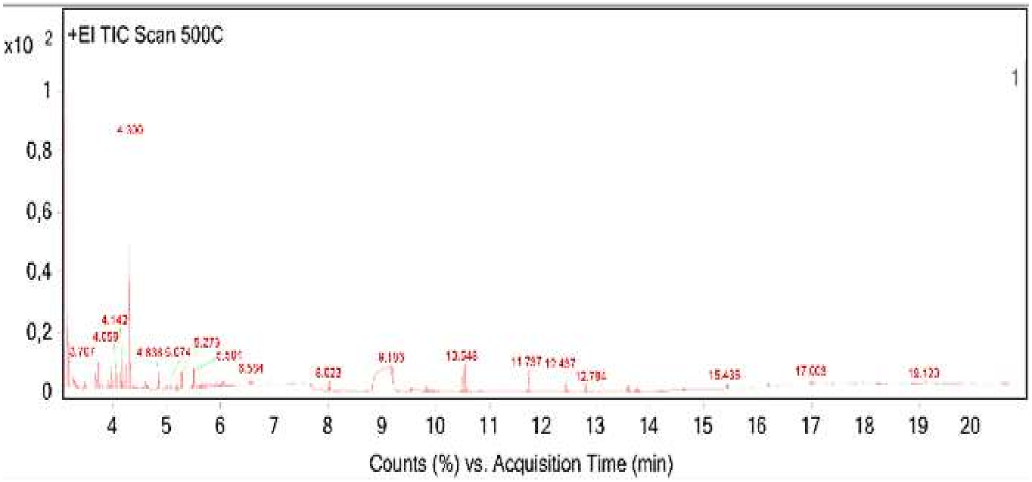

Figure 4

GC-MS Results of Pyrolysis Oil Temperature 500 °C for 60 min.

Table 1. Spent Bleaching Earth Pyrolysis Proces until 900 °C for 90 min

No.	Temperature (°C)	Time (Min.)	Initial Mass (g)	Final Mass (g)	Pyrolyzed oil (g)
1	400	30	300	100	90
2		45	300	100	85
3		60	300	90	100
4		75	300	90	100
5		90	300	100	100
6	450	30	300	100	120
7		45	300	80	40
8		60	300	80	60
9		75	300	110	120
10		90	300	80	110
11	500	30	300	100	150
12		45	300	90	160
13		60	300	100	130
14		75	300	90	100
15		90	300	90	130
16	550	30	300	100	120
17		45	300	80	140
18		60	300	90	100
19		75	300	100	130
20		90	300	100	110
21	500	30	300	80	120
22		45	300	100	100
23		60	300	80	150
24		75	300	100	50
25		90	300	100	110
26	650	30	300	80	110
27		45	300	80	140
28		60	300	70	140
29		75	300	100	120
30		90	300	80	120

Table 2. Pyrolysis Oil Compositions

No.	Components
1	(3E,5E)-Hepta-3,5-dien-2-one
2	Pyridine, 3,5-dimethyl-
3	2-Propanol, 1-(1,3-dimethylbutoxy)
4	(+-)-cis-3,4-Dimethyl-2-phenyltetrahydro-1,4-thiazine
5	3-Hexanone
6	2-Cyclopenten-1-one
7	Phenol
8	1,2-Cyclopentanedione
9	Phenol, 2-methyl-
10	Phenol, 3-methyl-
11	Phenol, 2-methoxy-
12	[1S-(1alpha.,5.alpha.)-6.alpha.-Methyl-6.beta.-(4-methyl-3-penten-1-yl)-3-azabicyclo[3.1.0]hexan-3-one
13	Phenol, 2,6-dimethoxy-
14	Cycloheptasiloxane, tetradecamethy 1-
15	Cyclododecasiloxane, tetracosamethyl-
16	Cyclononasiloxane, octadecamethyl-
17	Hexadecanoic acid, methyl ester
18	Cyclodecasiloxane, eicosamethyl-

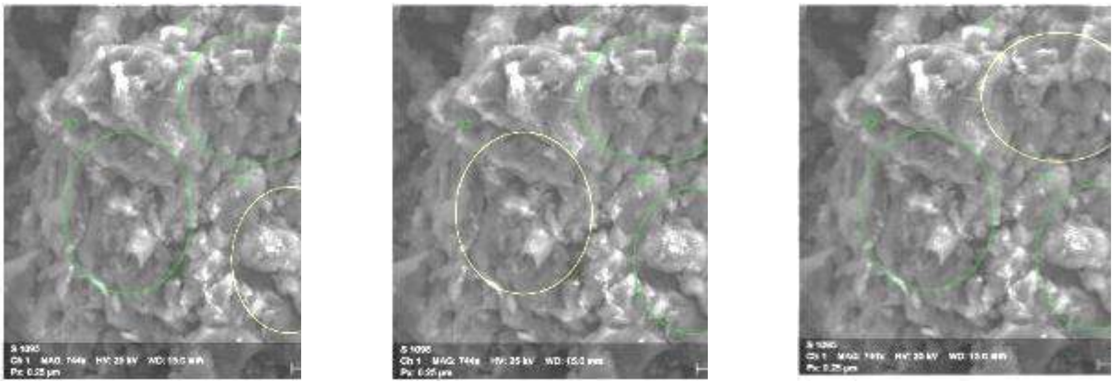
(a) (b) (c)

Figure 5. SEM Monograph of Char Pyroliysis at temperature and time (a) 400 °C, 60 min.; (b) 500°C, 60 min. (c) 650 °C, 90 min

In addition to analyzing the pyrolysis oil, the char produced from the pyrolysis process was examined using SEM-EDX to investigate its morphology and chemical composition. The SEM analysis revealed the structural characteristics of the char, while the EDX analysis provided insight into its elemental composition. The analysis demonstrated that the highest carbon content was found in the char produced at an operating pyrolisis temperature of 500 °C for 60 min. This indicates that under these specific conditions, the pyrolysis process was most effective at retaining carbon in the char, suggesting an optimal temperature and time for maximizing carbon yield from pent bleaching earth. These findings offer valuable insights into the utilization of SBE for both bio-oil and high-carbon-content char, which could have further applications in various industries such as energy and materials. Biochar yang disiapkan pada yang lebih tinggi sampai dengan 500 °C dari batang bambu dan batang kacang kapri memiliki pori-pori yang terbentuk dengan tepat dengan pori-pori kecil yang baru terbentuk (Sahoo et al., 2021).

In the SEM analysis of char samples produced at temperatures of 400, 500, and 650 °C, notable differences were observed in their morphology and microstructure, as shown in Figure 5. At 400 °C, the char surface displayed numerous porous structures and irregular particles, indicating incomplete thermal decomposition. This is supported by the EDX analysis, which showed a carbon content of 48.65% for the char produced at 400 °C with a pyrolysis time of 60 minutes.

In contrast, at an operating temperature of 500 °C with a pyrolysis time of 60 min., the carbon yield peaked at 54%. This indicates that both temperature and pyrolysis duration significantly influence the composition of the char. The results demonstrate that temperatures below 500 °C yield lower carbon content, while temperatures exceeding this threshold cause a decrease in carbon yield from its optimal level. These findings are consistent with research showing that temperatures above 500 °C result in declining carbon content, as observed by Üner & Bayrak (2022). In pyrolysis, the material exhibits distinct shapes and sizes, including large elongated particles with a fibrous texture and smaller particles that are more rounded with hollow structures (Wang et al., 2021).

CONCLUSION

The highest density and viscosity of the pyrolysis oil were achieved at 600 °C with a pyrolysis time of 90 min., with values of 992.8 kg/m^3 and 31.21 cSt, respectively. Phenol was identified as the dominant compound in the pyrolyzed oil, comprising 21.18% of the total composition. In terms of char residue, the highest carbon content was observed at 500 °C with a pyrolysis time of 60 min, reaching 54%. The optimal yield of pyrolysis oil, 53%, was recorded at 500 °C with a pyrolysis time of 45 min. These results demonstrate that the temperature and duration of pyrolysis play a crucial role in determining the physical and chemical properties of both the liquid and solid products from the process.

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