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Analysis of Heating Value of Hydro-Char Produced by Hydrothermal Carbonization of Cigarette Butts

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ABSTRACT

Hydrothermal carbonization is a thermal technique that offers numerous environmental benefits, particularly in managing solid waste streams by decomposing the raw materials of solid wastes and converting them into the renewable source of energy known as hydro-char.

This study evaluates the heating value of hydro-char produced through the hydrothermal carbonization of cigarette butts, taking into account influential factors such as time, temperature, and pressure, as well as its benefits and economic implications, using a novel approach involving simulations aimed at reducing the number of required tests, saving time, and cutting costs.

The range of 150 to 350 °C for temperature and 30 to 240 minutes for reaction time were considered and resulted in a thermal value range of 15.94 to 23.12 MJ/Kg for hydro-char, which makes its heat value greater than lignite coal and within the range of bituminous coal. The findings also indicated that temperature and time have a direct impact on the heat value, with time being the more influential factor, although high temperatures can expedite the reaction rate and should not be disregarded. Finally, the economic analysis of the project was conducted using the NPV method, which demonstrated that the viability of this method depends on the cost of coal, making it a promising alternative for accessing new and cost-effective fuel resources while considering environmental benefits.

Besides, this study highlights the potential of hydrothermal carbonization as a viable and advantageous method for producing fuel resources from biomass and organic waste, and provides quantitative and comparable evidence of the applicability and benefits of the proposed hydrothermal carbonization methodology in comparison to conventional methods.

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INTRODUCTION

In recent decades, countries have shifted towards reducing the use of fossil fuels and exploring new sources of energy, leading to the development of new techniques for energy production (Rajaeifar et al., 2015; Rahbari et al., 2019). One such technique is hydrothermal carbonization, a novel thermal conversion process that offers numerous environmental benefits, particularly in the management of solid waste streams (Berge et al., 2011; Ippolito et al., 2012). Hydrothermal carbonization shows promise as a reliable method for energy production (Ong et al., 2018; Libra et al., 2011), as it involves heating the raw material in subcritical water at temperatures typically ranging from 180 to 350□, with autogenic pressures.

As a result, the raw material undergoes a series of simultaneous reactions, including

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hydrolysis, dehydration, decarboxylation, aromatization, and recondensation, resulting in the formation of a carbonaceous residue known as hydro-char (Lu et al., 2012; Köchermann et al., 2018). Hydrothermal carbonization is a reliable technique that enhances the value of the raw material. Energy sources must meet three specifications: 1) reliability, 2) availability, and 3) sustainability (Hwang et al., 2012). Although solid waste was not considered an energy resource in the past, one of the modern methods used by municipalities to manage solid waste is by converting it into value-added products such as fuels using conversion methods such as pyrolysis, gasification, and hydrothermal (Lin et al., 2015).

Cigarette butts have been chosen among all solid wastes to produce hydro-char through hydrothermal carbonization (HTC) due to their abundance. However, cigarette waste is classified as hazardous waste (Novotny et al., 2009). Despite the common belief that cigarette waste is not harmful to the environment, it poses a dangerous environmental problem that the public is largely unaware of. Each cigarette butt can pollute an area of 1 square meter, and the non-degradable fibrous material of the waste contains up to 4,000 toxic substances. Furthermore, the remaining smoke filter contains toxic substances such as nicotine, lead, copper, and chromium, which are embedded in a package of 12,000 interconnected plastic fibers made of cellulose acetate and non-degradable acetone. These materials kill millions of birds and aquatic animals every year and enter the human food chain through the creeping cycle.

Releasing cigarette filters into flowing waters causes them to enter the reservoirs of dams that supply drinking water. Since they are non-degradable, their toxic substances are released into the water, posing a significant risk to human health. Collecting cigarette waste has numerous environmental benefits, and HTC is a proper method to utilize cigarette waste in the most useful way (Slaughter et al., 2011). It can also be used as a novel method to promote the value of the raw material, providing access to a new and cheaper fuel resource.

In the hydrothermal process, the physical state of the resulting product (i.e., solid, liquid, or gas) depends on the state of water during the reaction (Parsa et al., 2018). Water characteristics, operating conditions, and special additives are the main factors that control the reactions that break the bonds between C-C and C-O. The primary parameters of water that determine its physical and chemical characteristics are the ion product, dielectric constant, and hydrogen bonding. For instance, altering the ionic constant in water can change the output material, thereby allowing control over the reaction's direction and enabling the desired product to be obtained (Parsa et al., 2018).

Hydrothermal carbonization is a thermal conversion method which has been reported to convert biomass (and other organics) to a carbon-rich, energy-dense char. (Nizamuddin et al., 2017)

Comparison with Other Conversion Processes:

The hydrothermal method has several advantages over other thermal conversion methods, including lower operation temperatures, which leads to less fuel consumption. This method requires less solid processing, such as chemical or mechanical dewatering of biosolids. In contrast to other thermal conversion methods, HTC produces more solid yields and more water-soluble organic compounds. Gaseous oxidation products, particularly carbon dioxide, resulting from HTC, are minimal because, unlike combustion and gasification, exposure to oxygen is limited to that initially present in the reactor headspace and any dissolved oxygen in the water (Román et al., 2018). It should also be noted that the total gas produced during HTC is small compared to other thermal conversion processes, resulting in a smaller fraction of carbon being transferred to the gas (Lu et al., 2012).

Therefore, based on the literature review and considering the advantages of the novel and reliable HTC method and the potential of converting cigarette butts into a valuable fuel source, this study takes a novel approach to analyze the heating value of hydro-char produced by

Table 1. Experiment design

Experiments designed by design expert		
rows	time	temperature
1	100	220
2	30	240
3	135	300
4	135	240
5	240	240
6	135	240
7	100	260
8	170	260
9	170	220
10	135	240
11	135	240
12	135	240

hydrothermal carbonization of cigarette butts in terms of its effective factors, advantages, and economic viability.

MATERIALS AND METHODS

The waste material utilized in this study is cigarette butts, which have significant environmental implications. The cellulosic structure of cigarette butts makes them a suitable feedstock for obtaining useful output through hydrothermal carbonization. Cellulose acetate, the primary component of cigarette filters, is produced by esterifying bleached cotton or wood pulp with acetic acid. The amount of acid used is controlled to esterify between two and three of the three available cellulose hydroxy groups. The resulting ester is spun into fibers and formed into bundles called filter tow. Almost all cigarette filters, which are present in 90% of the world's cigarettes, are made from cellulose acetate (Luo et al., 2017).

To extract hydro-char through the hydrothermal process, preparations must be made for the sample (cigarette butt). The paper portion of the filter should be removed to examine only the cellulosic part. To ensure better and increased contact with water during the hydrothermal process, the raw materials should be cut into smaller pieces before being placed in a stainless steel 316 reactor with a volume of 90 mm^3. The reactor can withstand pressures of up to 600 bar and temperatures of up to 1000□.

The two key factors for the experiment were time and temperature. Based on scientific literature and initial experiments, the appropriate range for each factor was determined, and the experiments were designed using the RSM method with Design Expert software (Bezerra et al., 2008; Sharifi et al., 2018). The temperature range was set between 180°C to 300°C, and the time range was between 30 to 240 minutes. Ultimately, 13 tests were designed to investigate the effects of these factors on thermal energy and energy efficiency.

During each stage of the test, approximately 3 grams of cigarette butt were added to the reactor. Distilled water was then mixed with the cigarette butts in a volume ratio of 1 to 10, using approximately 30 mg of distilled water per stage.

The contents of the reactor produced three phases: gas, liquid, and solid. We transferred the solid and liquid phases to separate containers and dried them in an oven for 12 hours at 105 °C (Fernandez et al., 2019). The resulting solid is the desired hydro-char obtained from the hydrothermal carbonization process. We weighed the sample using a scale and obtained approximately 0.9 to 1.2 grams of hydro-char from every 3 grams of cigarette butt (Xu et al., 2021).

Table 2. Percentages of elements existing in the results

	elements				
row	O(%)	S(%)	N(%)	H(%)	C(%)
1	44.49	0	0.38	5.93	49.2
2	46.82	0	0.15	5.83	47.2
3	31.14	0	0.98	5.21	62.67
4	32.36	0	1.19	5.18	61.27
5	32.08	0	1	4.77	62.15
6	32.83	0	0.78	4.95	61.44
7	34.93	0	0.64	4.94	59.49
8	31.87	0	0.5	5.21	62.42
9	34.94	0	0.96	5.07	60.03
10	34.19	0	0.7	4.92	60.19
11	32.11	0	0.7	4.92	62.27
12	37.79	0	0.64	5.02	56.55

In the next step, we performed CHNS analysis[1] to determine the percentage of carbon, nitrogen, hydrogen, and sulfur in the hydro-char. The percentage of oxygen was calculated by subtracting the total percentage of the other elements from 100, using Equation (1):

$$O\% = 100\% - \left(C\% + H\% + N\% + S\%\right) \tag{1}$$

Formula (1) is a calculation of the oxygen percentage, which is obtained by lowering the total percentage of other elements from 100.

Using the percentages of each of the elements and the formula for Dulang, which is observed in equation (2), the thermal value of each sample of hydro-char is calculated:

$$HHV\left(\frac{MJ}{Kg}\right) = 33.86 \times C + 144.4 \times \left(H - \frac{O}{8}\right) + 9.428 \times S \tag{2}$$

Formula (2) is a calculation of thermal value according to the Dulang formula.

RESULTS AND DISCUSSION

The information presented in (Table 2) illustrates the percentages of carbon, hydrogen, sulfur, and oxygen in the sample. The oxygen percentage can be calculated by subtracting the total percentage of the other elements from 100. Besides, the thermal value of each sample is determined using the Dulang formula (Table 3).

Based on the results, the highest thermal value is related to a temperature of 300 and a time of 135 minutes, which is equal to 23.12 MJ / Kg.

Design expert

Each parameter was evaluated based on the responses obtained from the Design Expert software. The P-value was used to determine the statistical significance of the model by evaluating whether the F-value was large enough. According to Table 4, an F-value of 18.6 indicates that the model is significant, with only a 0.1% probability of the F-value occurring at this magnitude due to an error. A meaningful model is represented by P-values less than 0.05,

1 organic elemental analysis

Table 3. Thermal value results for the different samples

Results of heat value			
row	Heat value(MJ / Kg)	Time(min)	Temperature (C)
1	17.15	100	220
2	15.94	30	240
3	23.12	135	300
4	22.37	135	240
5	22.13	240	240
6	22.02	135	240
7	20.96	100	260
8	22.98	170	260
9	21.515	170	220
10	21.31	135	240
11	22.38	135	240
12	19.56	135	240

Table 4. ANOVA for Linear model

P value	F value	Mean square	Sum of squares	
0.000982	18.59664	22.9828132	45.9656264	model
0.000782	27.47616	33.9566453	33.9566453	A-time
0.024746	7.607286	9.40152889	9.40152889	B-temperature
		1.23585852	9.88686815	Residual
0.599192	0.765161	1.07143874	4.28575495	Lack of fit
		1.4002783	5.6011132	Pure error
			55.8524945	Core total

which is the case for factors A and B.

Disproportionate tests were conducted to determine the changes in data around the model. If the data changes around the model, then the misalignment test around the model will be meaningless. As shown in the table, the non-fitting test is meaningless, indicating that there is a significant relationship between the factors influencing the experiment and the obtained responses.

Furthermore, the R^2 value is a crucial indicator of the appropriateness of the linear model with laboratory data. A value of R^2 greater than 0.75 indicates the acceptability of the selected model. In this experiment, the R^2 value was calculated to be 0.78, demonstrating the acceptability of the model.

Heat value

According to the results of the experiments, the software has proposed a linear model for thermal value:

$$\text{HHV} = 4.04261 + 0.047810 \times A + 0.044025 \times B \tag{3}$$

The linear model for calculating thermal value is represented by formula (3). The significance of the model is confirmed by the value of P, which is 0.001 and less than the threshold of 0.05. The disproportion test also indicates a significant relationship between temperature and time as effective factors and thermal value as the response, with a value of 1.07. The Adjusted R^2 value is greater than 0.75, indicating that the linear model is acceptable. Furthermore, the difference between the R^2 adjusted and R^2 predicted is less than 0.2, which, according to the software's reference, indicates the reliability of the results.

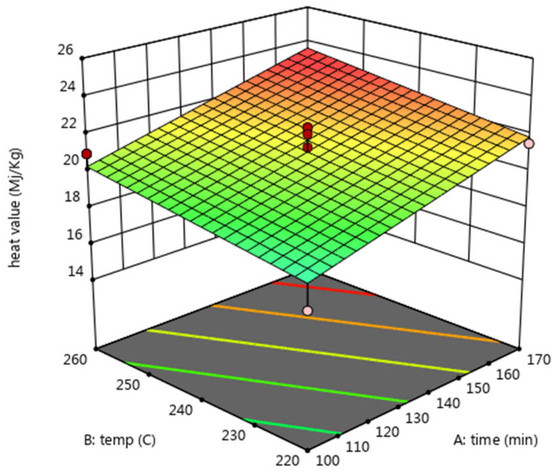

Fig. 1. Three-dimensional graph of surface response effect of temperature and time on thermal value

The Effect of Temperature and Reaction Time on Thermal Value

The three-dimensional graph presented in Figure 1 illustrates the combined influence of temperature and reaction time on the hydrothermal thermal value generated through the hydrothermal carbonization method. The graph clearly depicts that an increase in temperature and reaction time results in a corresponding increase in thermal energy. The peak thermal value is observed at 300°C and 135 minutes, which is 23.12 MJ/Kg, while the lowest thermal value is seen at 240°C and 30 minutes, which is 15.94 MJ/Kg. According to the Dulang formula (2), an increase in the percentage of carbon and a decrease in oxygen content is expected to raise the thermal value.

The decrease in the dielectric constant of water is one of the primary reasons for the increase in hydrothermal reaction efficiency with increasing temperature. Under subcritical conditions, the dielectric constant can drop significantly from 80 to 20, making water behave similarly to organic solvents. This enables it to dissolve other organic compounds and form a single-phase liquid, which offers advantages such as increased reactivity and no interphase mass transfer issues. The ionic constant of water increases by about three times the normal value in the subcritical region, creating an acidic environment that is ideal for hydrolysis. As shown in Figure 1, the effect of reaction time is more significant than that of temperature in this temperature range and time span, indicating that the completion of the hydrothermal process requires sufficient time for optimal reaction performance, and higher temperatures will expedite the process.

CONCLUSION

The thermal value of each of the designed experiments was calculated using the Dulang formula (2). Based on the experimental results, a linear model (3) for thermal value was developed. According to the Dulang formula, an increase in carbon percentage and a reduction of oxygen leads to an increase in thermal value with an increase in temperature and time. This is because the dielectric constant of water significantly decreases with an increase in temperature, with a decrease from 80 to 20 under subcritical conditions (Technology, n.d.). This decrease in dielectric constant makes water properties similar to organic solvents, enabling water to dissolve other organic compounds and become a single-phase liquid. The advantages of a single-phase liquid include a higher reactive concentration, which promotes better reaction, and no mass transfer issues between phases. Additionally, in the subcritical region, the ionic constant of water increases about three times the normal state, creating an acidic atmosphere for optimal hydrolysis of the reaction.

Based on the Design expert analysis, the effect of time is steeper than temperature within the given time span and temperature range, indicating that a sufficient amount of time is required to complete the hydrothermal process for optimal reaction. The higher temperature accelerates the process.

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CONFLICT OF INTEREST

The author declares that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy have been completely observed by the authors.

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LIFE SCIENCE REPORTING

No life science threat was practiced in this research

ABBREVIATIONS

%	Percentage
HTC	Hydrothermal carbonization
O	Oxygen
H	Hydrogen
N	Nitrogen
S	Sulfur
C	Carbon
HHV	Higher heating value

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