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Effect of Sulfuric Acid Immersion on the Carbon Characteristics of Cocoa Pod Husk

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A B S T R A C T

Indonesia faces the challenge of its reliance on fossil fuels, making the use of biomass as a renewable energy source increasingly important. Cocoa pod husk, an abundant agricultural waste, has the potential to be converted into high-quality solid fuel through torrefaction. This study aims to analyse the effects of sulfuric acid (H_2SO_4) solution concentration and torrefaction temperature on the characteristics of carbon produced from cocoa pod husk, and to compare the results with the Indonesian National Standard (SNI) 8675-2018. The methods used include biomass preparation, soaking with various H_2SO_4 concentrations (0, 0.4, 0.6, 0.8, and 1 M), and torrefaction at different temperatures (250, 275, 300, 325, and 350 °C). The product characteristics were analyzed using proximate analysis, calorific value testing, and SEM-EDX. The results showed that increasing acid concentration and torrefaction temperature significantly reduced moisture, ash, and volatile matter content, while increasing fixed carbon and calorific value. The optimum condition was obtained at 1 M H_2SO_4 soaking and 350 °C torrefaction, producing carbon with 0.17% moisture, 3.00% ash, 61.79% volatile matter, 35.04% fixed carbon, and a calorific value of 8071.34 cal/g. All parameters met the SNI 8675-2018 standard, indicating that acid-pretreated and torrefied cocoa pod husk has strong potential to be developed into high-quality solid fuel.

Contribution to Sustainable Development Goals (SDGs):

SDG 7: Affordable and Clean Energy

SDG 9: Industry, Innovation, and Infrastructure

SDG 12: Responsible Consumption and Production

SDG 13: Climate Action

1. INTRODUCTION

1.1. Research Background

Indonesia continues to rely heavily on fossil fuels as its primary energy source, raising serious concerns regarding the depletion of non-renewable resources and the intensification of environmental impacts. According to the Ministry of Energy and Mineral Resources (2023), fossil fuels account for approximately 74% of the national primary energy mix, while renewable energy contributes only 12.3%. This imbalance highlights the urgent need for a strategic transition to cleaner, more sustainable, and

environmentally friendly alternative energy sources. Among renewable energy sources, biomass has attracted significant attention due to its abundance, carbon-neutral characteristics, and potential to be converted into high-value solid, liquid, or gaseous fuels.

As the world's third-largest cocoa-producing country, Indonesia generates substantial quantities of cocoa pod husk waste, which constitutes up to 75% of the total cocoa fruit mass. Despite its large volume, cocoa pod husk remains underutilised, typically being used as organic fertiliser or animal feed, thus contributing minimally to the agricultural value chain. Its high



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lignocellulosic content—cellulose (35.4%), hemicellulose (37%), and lignin (14.7%)—however, positions it as a highly suitable feedstock for solid biofuel production.

Torrefaction, a mild thermochemical process conducted at temperatures between 200–300 °C, is widely recognised for improving the fuel characteristics of biomass by reducing moisture, reducing volatile matter, and enhancing calorific value and stability. Nevertheless, previous studies have reported that torrefied biomass often contains relatively high levels of ash, which can adversely affect combustion efficiency, slagging behaviour, and overall fuel quality. Chemical pretreatment has therefore emerged as a promising complementary approach capable of removing inorganic minerals such as potassium, calcium, and magnesium—key contributors to ash formation and fouling in thermochemical conversion systems. Several researchers have demonstrated that acid solutions can effectively reduce ash content, improve carbon yield, and enhance the combustion performance of biomass-derived solid fuels.

Although acid pretreatment and torrefaction have been studied independently across various biomass types, integrated investigations focusing specifically on cocoa pod husk remain limited. A more comprehensive understanding of how acid concentration interacts with torrefaction temperature to influence carbon quality is essential to optimise biomass utilisation in the cocoa sector. Therefore, this study examines the combined effects of sulfuric acid pretreatment and torrefaction on the proximate characteristics and calorific value of carbon derived from cocoa pod husk. The resulting biochar quality is further evaluated against the Indonesian National Standard (SNI 8675-2018). In addition, Response Surface Methodology (RSM) is employed to model and optimise process parameters, enabling the identification of optimal conditions for producing high-quality solid biofuel from cocoa-based biomass.

1.2. Literature Review

Biomass has been increasingly explored as a renewable energy source due to its abundance and potential to reduce dependency on fossil fuels, which still dominates Indonesia's energy mix at 74% [1]. Agricultural biomass waste utilization also contributes to environmental sustainability by reducing waste accumulation and creating value-added energy products [2].

Cocoa pod husk, representing approximately 75% of the cocoa fruit mass, is an abundant agricultural residue in Indonesia, the world's third-largest cocoa producer. Despite its abundance, its current use is limited to fertilizer and animal feed, resulting in low economic value. Cocoa pod husk's lignocellulosic composition—35.4% cellulose, 37% hemicellulose, and 14.7% lignin—makes it a promising raw material for solid biofuel production [2].

Torrefaction has been recognized as an effective thermochemical pretreatment process to improve biomass fuel properties by reducing moisture and volatile matter while increasing fixed carbon and calorific value [3]; [4]. This process promotes partial decomposition of hemicellulose and cellulose, enhancing the combustion performance of biomass. However, one major limitation of torrefaction is its tendency to produce biochar with relatively high ash content, which reduces its fuel quality and usability [5]. Further, higher torrefaction temperatures lead to increased decomposition of organic

components, concentrating the ash fraction [6], indicating the need for complementary methods to minimise ash content.

Chemical pretreatment has been investigated as a promising method to reduce ash in biomass. Inorganic acid solutions, such as sulfuric acid, have been shown to dissolve mineral components, including potassium (K), calcium (Ca), and magnesium (Mg), that contribute to ash formation in biomass (Pratama, 2021). Previous studies reported that acid pretreatment improved fuel quality and reduced ash content in biomass such as coffee grounds and palm residues [7]; [8]. Acid soaking promotes breakdown and removal of inorganic compounds, making it easier for subsequent thermal processes to yield higher carbon quality [8].

Several studies have evaluated either torrefaction or acid pretreatment independently; however, research combining both approaches on cocoa pod husk remains limited [3]; [9]. Moreover, very few studies have applied Response Surface Methodology (RSM) to optimize biochar production conditions, particularly involving interactions between sulfuric acid concentration and torrefaction temperature. Thus, systematic integration of acid pretreatment and torrefaction on cocoa pod husk represents a significant research opportunity to develop high-quality solid biofuel that meets national standards such as SNI 8675:2018 [10]

Table 1. Chemical Composition of Cocoa Pod Husk

| Component | Proportion, % |
|-----------|---------------|
| Ca | 25.8 |
| K | 66.4 |
| P | 1.7 |
| Mg | 1 |

1.3. Research Objective

This study aims to investigate and optimize the conversion of cocoa pod husk into high-quality carbon through a combined sulfuric acid pretreatment and torrefaction process. Specifically, the research seeks to evaluate the effect of different sulfuric acid (H₂SO₄) concentrations and torrefaction temperatures on the proximate characteristics and calorific value of the resulting carbon. In addition, this study examines the interaction between these variables using Response Surface Methodology (RSM) to determine the most effective operating conditions. The optimal treatment is further validated through SEM-EDX analysis to assess morphological and elemental changes. Overall, the goal of this research is to produce carbon that meets the requirements of the Indonesian National Standard (SNI 8675-2018), thereby demonstrating the potential of cocoa pod husk as a sustainable biomass-based solid fuel.

2. MATERIALS AND METHODS

2.1. Material and Tools

The primary raw material used in this study was cocoa pod husk waste obtained from a cocoa plantation in East Java, Indonesia. The chemicals used included technical-grade sulfuric acid (H₂SO₄) 98% and distilled water.

Proximate analysis (moisture content, ash content, volatile matter, and fixed carbon) was carried out in accordance with the Indonesian National Standard SNI 8675-2018. The calorific value

was measured using a bomb calorimeter. Morphological and elemental composition analyses were performed using Scanning Electron Microscopy–Energy Dispersive X-ray Spectroscopy (SEM-EDX). The torrefaction process was conducted in a horizontal tubular reactor equipped with a temperature control system and an inert nitrogen (N_2) gas supply.

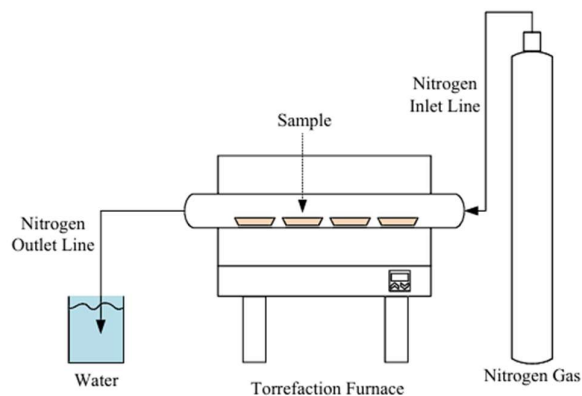


Fig. 1. Torrefaction Apparatus Setup

2.2. Methods

2.2.1 Biomass Preparation

Cocoa pod husk waste collected from a cocoa plantation in East Java, Indonesia, was used as the primary raw material. The biomass was thoroughly washed with distilled water to remove surface impurities and dried in the sunlight until a constant weight was achieved. The dried husks were then ground using a mechanical grinder and sieved to obtain a uniform particle size of 60 mesh.

2.2.2 Acid Pretreatment

A total of 20 g of prepared cocoa pod husk powder was immersed in 100 mL of sulfuric acid (H_2SO_4) solution with concentrations of 0, 0.4, 0.6, 0.8, and 1 M. The mixture was stirred using a magnetic stirrer at 400 rpm for 60 minutes at room temperature (25 °C). After soaking, the slurry was filtered, and the solid residue was rinsed repeatedly with distilled water until the pH was neutral. The treated biomass was then dried in an oven at 105 °C until a constant weight was obtained.

2.2.3 Torrefaction Process

Approximately 5 g of dried biomass was placed in a ceramic boat and inserted into a horizontal tubular reactor for torrefaction. Torrefaction was performed at 250, 275, 300, 325, and 350 °C for 30 minutes under a continuous flow of nitrogen (N_2) to maintain an inert atmosphere. The heating rate was set at 10 °C/min. After completion, the samples were cooled in a desiccator and weighed to determine the product yield.

2.2.4 Proximate Analysis

1. Proximate analysis was conducted to determine moisture content, ash content, volatile matter, and fixed carbon in accordance with SNI 8675:2018.
2. Moisture content: Samples were dried in an oven at 105 °C for 4 hours.

3. Ash content: Samples were heated at 800 °C for 2 hours in a furnace.
4. Volatile matter: Samples were heated at 950 °C for 7 minutes.

Fixed carbon: Calculated by subtraction:

$$\text{Fixed Carbon (\%)} = 100 - (\text{Moisture} + \text{Ash} + \text{Volatile Matter})$$

2.2.5 Caloric Value Measurement

The calorific value of the torrefied product was measured using a bomb calorimeter. The resulting energy values were compared with SNI 8675:2018 standards for solid biomass fuel.

2.2.6 SEM-EDX Characterization

Morphological characteristics and elemental composition of the optimum carbon product were examined using Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (SEM-EDX) to observe pore structure and mineral content changes after treatment.

2.2.7 Experimental Design and Data Analysis

The optimization of torrefaction temperature and sulfuric acid concentration was carried out using Response Surface Methodology (RSM) with a Central Composite Design (CCD). Analysis of Variance (ANOVA) was applied to evaluate the significance of the model and interaction effects between variables. The optimum conditions were validated experimentally.

2.3. Research Analysis

The analysis focused on evaluating the effect of sulfuric acid concentration and torrefaction temperature on the fuel characteristics of carbon produced from cocoa pod husk. The results showed that increasing acid concentration and torrefaction temperature significantly improved carbon quality by reducing moisture and volatile matter, while increasing fixed carbon and calorific value. This improvement was driven by enhanced dehydration, devolatilization, and carbonization processes.

Ash content decreased with higher acid concentrations due to the removal of inorganic minerals through acid leaching, but tended to increase at higher torrefaction temperatures as organic mass decreased and minerals became more concentrated. Statistical evaluation using Response Surface Methodology (RSM) confirmed that both variables had significant effects, with acid concentration being the dominant factor. The optimum condition was achieved at 1 M H_2SO_4 and 350 °C, resulting in high fixed carbon (35.04%) and calorific value (8071.34 cal/g), meeting SNI 8675-2018 standards.

Overall, the combined sulfuric acid pretreatment and torrefaction method effectively enhanced the energy properties of cocoa pod husk, demonstrating its potential as a high-quality renewable solid fuel.

3. RESULT AND DISCUSSION

3.1. Effect of Sulfuric Acid Concentration and Torrefaction Temperature on Proximate Characteristics

The experimental results showed that increasing sulfuric acid concentration and torrefaction temperature significantly affected the carbon quality of cocoa pod husk. Moisture content progressively decreased with higher acid concentration and temperature, reaching a minimum of 0.17% at 1 M H₂SO₄ and 350 °C, due to enhanced dehydration and thermal evaporation. This trend indicates that sulfuric acid pretreatment facilitates water removal by breaking internal hydrogen bonds and drawing moisture from the biomass matrix.

Similarly, volatile matter decreased as temperature and acid concentration increased, from 67.16% at 250 °C (0 M) to 61.79% at 350 °C (1 M). This reduction is attributed to greater devolatilization and thermal decomposition of hemicellulose and cellulose at elevated temperatures. Acid pretreatment further accelerated depolymerisation, resulting in higher volatile release during torrefaction.

Fixed carbon content exhibited the opposite trend, increasing with temperature and acid concentration. The highest fixed carbon value of 35.04% was obtained at 1 M and 350 °C, demonstrating improved carbonization. This improvement results from dehydration and devolatilization reactions that leave behind a carbon-rich solid residue.

3.2. Ash Content Behavior

Ash content showed two distinct trends. Increasing the acid concentration initially reduced ash content by dissolving mineral salts such as K, Ca, and Mg during acid soaking. The lowest ash content of 1.95% occurred at 1 M and 250 °C. However, ash content increased with increasing temperature, reaching 3.00% at 350 °C. This increase is linked to mass loss of organic components during torrefaction, resulting in a higher relative concentration of inorganic components in the final product.

3.3. Caloric Value

The calorific value increased in line with fixed carbon content, reaching 8071.34 cal/g at the optimum condition (1 M, 350 °C). This energy value greatly exceeds the minimum requirement of 4000 cal/g specified by SNI 8675-2018, confirming the excellent combustion potential of the processed biomass. The increased heating value reflects higher carbon density and lower moisture and volatile content, both of which improve fuel efficiency.

4. CONCLUSION

This study successfully demonstrated that the combination of sulfuric acid pretreatment and torrefaction significantly improves the carbon quality of cocoa shell waste. The optimum conditions were achieved at a torrefaction temperature of 350°C and a sulfuric acid concentration of 1 M, resulting in solid fuel characteristics that meet SNI 8675-2018 standards, with a moisture content of 0.17%, ash content of 3.00%, volatile matter of 61.79%, fixed carbon of 35.04%, and a calorific value of 8071.34 cal/g. The developed RSM model proved reliable, with minimal deviation between the predicted and experimental validation results. These findings indicate that cocoa shells processed using this method have strong potential as an alternative fuel for co-firing applications, supporting the transition to renewable energy.

3.4. Statistical Analysis and Optimization

Response Surface Methodology (RSM) confirmed that both sulfuric acid concentration and temperature significantly influenced carbon properties. Acid concentration had the strongest effect, followed by temperature. The high determination coefficient ($R^2 > 0.97$) demonstrated excellent model accuracy and predictive reliability. The experimental results closely matched the predicted optimum, validating the optimization approach.

Process optimization was carried out using Response Surface Methodology (RSM) with a Central Composite Design (CCD) to determine the optimal operating conditions. Analysis of Variance (ANOVA) was employed to evaluate the statistical significance of the developed model.

The ANOVA results indicated that the quadratic model was highly significant, with an F-value of 206.46 and a p-value $< 1.0 \times 10^{-4}$. A Prob $> F$ value below 0.05 confirmed that all model terms were statistically significant. The sulfuric acid concentration (B) was identified as the most dominant factor influencing the response, with an F-value of 856.77, followed by torrefaction temperature (A) with an F-value of 123.50. The interaction between temperature and acid concentration (AB) also showed statistical significance (p-value = 0.0063). The model exhibited a strong coefficient of determination ($R^2 = 0.9819$), indicating that the model explained 98.19% of the response variability. Furthermore, the close agreement between the Adjusted R^2 (0.9772) and Predicted R^2 (0.9711) values demonstrated excellent predictive accuracy.

Based on the RSM analysis, the quadratic prediction model in actual coded terms is expressed as:

$$FC = 2.30622 + 0.132394A + 17.07740B - 0.020125AB - 0.000161A^2 - 4.25467B^2$$

Numerical optimization resulted in optimal conditions of 348.53 °C for the torrefaction temperature and 1 M H₂SO₄ concentration, with a predicted fixed carbon content of 34.69%. Experimental validation under a closely similar condition (350 °C and 1 M) yielded a fixed carbon value of 35.04%, confirming the accuracy and reliability of the RSM model. Model validation was carried out by comparing the 25 predicted values generated from Equation (5) with the actual experimental results, as illustrated in Figure 2.

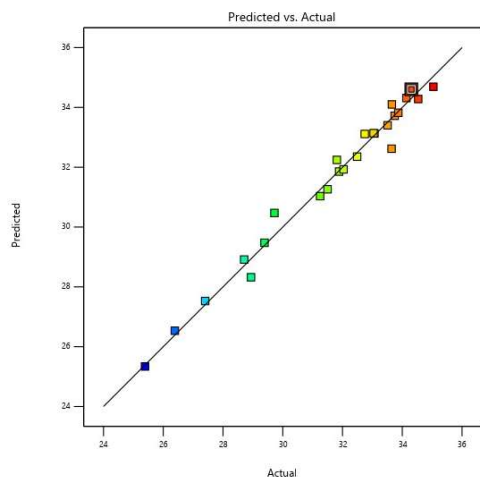


Fig. 2. Relationship Between Predicted Data and Actual Data for 25 Experimental Runs

From Figure 2, it can be observed that the plot of the 25 predicted and actual data points demonstrates good agreement between the model and the experimental results. This is indicated by the distribution of data points near the linear regression line ($y = x$), confirming that the developed model accurately represents the process. Conversely, if the data points were located far from the regression line, it would indicate lower model accuracy. The table below presents the optimisation results, including the optimum operating conditions.

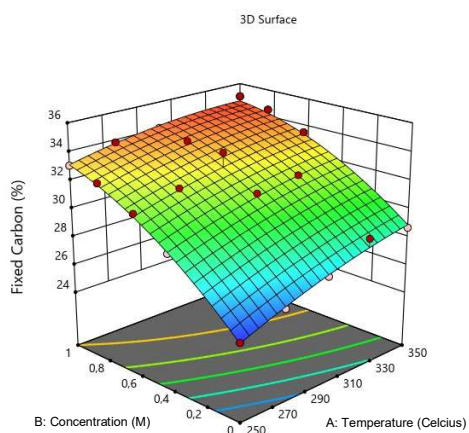


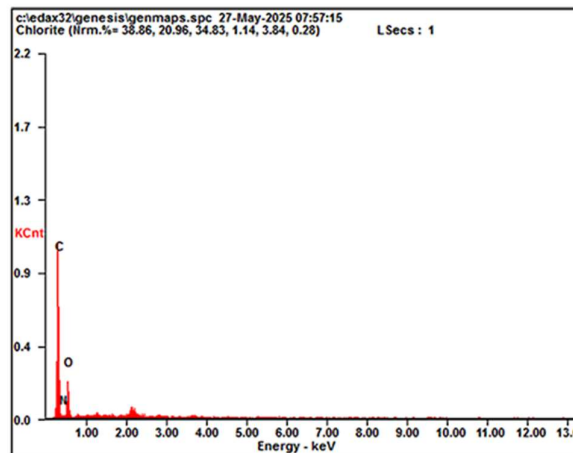
Fig. 3. 3D Surface Plot of the Effect of Temperature and Acid Concentration

3.5. SEM-EDX Characterization

SEM images of the optimal biochar displayed a porous, honeycomb-like structure, indicating effective volatilization and thermal degradation of biomass components. EDX analysis confirmed a reduction in inorganic mineral elements in acid-treated samples, which correlated with the lower ash content. Greater pore formation and cleaner carbon structure support enhanced energy performance and reactivity.

Table 1. Percentage of Organic Compounds from SEM-EDX

| Analysis | | | |
|-------------|-------|------|-------|
| Element | C | N | O |
| Content (%) | 53,11 | 5,84 | 41,05 |



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