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VALORIZATION OF *Ulva lactuca* VIA HYDROTHERMAL CARBONIZATION: EFFECTS OF TEMPERATURE, TIME, AND CONCENTRATION ON HYDROCHAR

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Abstract

The excessive proliferation of *Ulva lactuca*, a marine macroalga, contributes to eutrophication in many coastal areas and represents an underutilized biomass resource. This study aimed to evaluate the potential of *U. lactuca* as a feedstock for solid biofuel production through hydrothermal carbonization (HTC). Specifically, the effects of temperature, time, and feedstock concentration on the hydrochar yield and properties were investigated. HTC experiments were conducted in a batch reactor at 180–220 °C, with reaction times of 30–90 min and biomass loadings of 1% and 5% (w/w). The resulting hydrochars were analyzed for yield, water and ash contents, higher heating value (HHV), morphology using scanning electron microscopy (SEM), elemental distribution via SEM–energy-dispersive X-ray spectroscopy (EDX), and functional groups using Fourier transform infrared spectroscopy (FTIR). Statistical analysis using response surface methodology (RSM) was applied to optimize the process conditions, specifically focusing on the influence of temperature, residence time, and feed-stock concentration. The results showed that higher temperatures reduced the hydrochar yield owing to enhanced decomposition, whereas greater feedstock concentrations promoted the yield through polymerization. The maximum yield of 31.3% was obtained at 180 °C with 5% feedstock content. The water content decreased with increasing HTC severity, whereas the ash content varied. The HHV increased with temperature and time, reaching 21.22 MJ/kg at 220 °C, which is comparable to that of low-rank coal. RSM confirmed that temperature and feedstock concentration were the dominant factors influencing the yield. These findings demonstrate the potential of *U. lactuca* as a sustainable third generation biomass and provide insights into optimizing HTC to enhance hydrochar quality for bioenergy applications.

Keywords: green algae, optimization, solid fuel, RSM, sustainable biomass http://dx.doi.org/10.17844/f3kztf96

Valorisasi *Ulva lactuca* melalui Karbonisasi Hidrotermal: Pengaruh Suhu, Waktu, dan Konsentrasi terhadap Hidrokar

Abstrak

Pertumbuhan berlebih *Ulva lactuca*, salah satu makroalga laut, berkontribusi terhadap eutrofikasi di banyak wilayah pesisir dan sekaligus merepresentasikan sumber biomassa yang belum dimanfaatkan secara optimal. Penelitian ini bertujuan untuk mengevaluasi potensi *U. lactuca* sebagai bahan baku produksi bahan bakar padat melalui proses karbonisasi hidrotermal (*Hydrothermal Carbonization*/HTC). Secara khusus, penelitian ini mengkaji pengaruh suhu, waktu, dan konsentrasi bahan baku terhadap hasil dan karakteristik hidrokar. Eksperimen HTC dilakukan dalam reaktor *batch* pada suhu 180–220 °C, dengan waktu reaksi 30–90 menit dan konsentrasi biomassa 1% serta 5% (b/b). Hidrokar yang dihasilkan kemudian dianalisis mencakup rendemen, kadar air dan abu, nilai kalor atas (*Higher Heating Value*/HHV), morfologi menggunakan mikroskop elektron pemindai (SEM), distribusi unsur dengan SEM–EDX, serta gugus fungsi melalui spektroskopi inframerah transformasi Fourier (FTIR). Proses optimasi dilakukan menggunakan RSM dengan parameter suhu, waktu, dan konsentrasi bahan baku. Hasil penelitian menunjukkan bahwa peningkatan suhu menurunkan rendemen hidrokar akibat dekomposisi yang lebih intensif, sementara peningkatan konsentrasi bahan baku meningkatkan rendemen melalui reaksi polimerisasi. Rendemen maksimum sebesar 31,3% diperoleh pada suhu 180 °C dengan konsentrasi 5%. Kadar air menurun seiring dengan meningkatnya tingkat keparahan HTC, sedangkan kadar abu bervariasi. Nilai HHV meningkat seiring dengan suhu dan waktu, mencapai 21,22 MJ/kg pada suhu 220 °C, setara dengan batubara peringkat rendah. Analisis RSM menegaskan bahwa suhu dan konsentrasi biomassa merupakan faktor dominan yang memengaruhi rendemen. Temuan ini menunjukkan potensi *U. lactuca* sebagai biomassa generasi ketiga yang berkelanjutan dan memberikan wawasan untuk mengoptimalkan kondisi HTC guna meningkatkan kualitas hidrokar bagi aplikasi bioenergi.

Kata kunci: alga hijau, bahan bakar padat, biomassa berkelanjutan, optimasi, RSM

INTRODUCTION

In recent years, extensive research has focused on producing biofuels from various biomass sources, highlighting the potential of first- and second-generation biomass as feedstocks for renewable energy (Amrullah *et al.*, 2022). First-generation biomass, derived directly from food sources, includes crops such as corn and sugarcane. However, the widespread use of these crops for biofuel production has raised significant concerns, particularly regarding the potential competition between food and fuel production (Farobie *et al.*, 2022). This competition can lead to increased food prices and exacerbate food security problems. Second-generation biomass derived from non-food sources, such as lignocellulosic biomass and agricultural residues, offers a partial solution to this problem (Ragadhita *et al.*, 2023). However, the production of second-generation biomass still requires significant resources, including freshwater, fertilizers, and arable land, which may limit sustainability (Bharathiraja *et al.*, 2015).

To overcome these challenges, third-generation biomass, particularly macroalgae, has emerged as an attractive alternative feedstock for biofuel production. Macroalgae offer several distinct advantages over terrestrial plants, including faster growth rates, higher biomass yields, and shorter harvesting cycles (Farobie *et al.*, 2024). Furthermore, macroalgae can thrive in diverse aquatic environments, such as seawater, freshwater, and wastewater, thereby reducing their reliance on terrestrial resources (Farobie *et al.*, 2023). These attributes make macroalgae an attractive candidate for sustainable bioenergy production, potentially alleviating the environmental and resource constraints associated with first- and second-generation biomass (Farobie *et al.*, 2024).

One such macroalga, *Ulva lactuca*, commonly known as sea lettuce, has garnered attention owing to its rapid proliferation in coastal regions, often leading to overgrowth of water bodies and subsequent ecological imbalances (Allen *et al.*, 2013). This overgrowth poses a significant environmental challenge, particularly in island ecosystems, where sea lettuce accumulation can disrupt local marine habitats and water quality. To address this issue, harvesting *U. lactuca* for bioenergy production and extracting high-value chemicals is a viable solution (Nufus *et al.*, 2017). Utilizing this abundant and fast-growing resource mitigates its environmental impact and contributes to the development of sustainable energy alternatives.

Among the various thermochemical conversion techniques available for bioenergy production, hydrothermal processing has gained prominence owing to its ability to handle wet biomass, such as marine macroalgae, without the need for pre-drying (Babu *et al.*, 2022). Hydrothermal carbonization (HTC) is particularly suitable for converting wet feedstocks into valuable hydrochars, which can be used as solid biofuels or precursors for advanced materials. Compared to other thermochemical techniques, including gasification and pyrolysis, HTC operates under relatively mild conditions, making it an energy-efficient and environmentally friendly option for processing macroalgae such as *Ulva lactuca* (Farobie *et al.*, 2022).

Despite the potential of HTC to convert *U. lactuca* into valuable bioenergy products, there is limited understanding of how variables such as time, temperature, and feedstock concentration influence the yield and characteristics of the resulting hydrochars. For instance, Patel et al. (2021) studied the effects of temperature, time, and feedstock concentration during HTC, investigating waste seaweed growing on the surface of seawater near Summerside, Prince Edward Island, Canada. Moreover, previous studies have primarily focused on other biomass types, typically lignocellulosic biomass, or have not comprehensively examined the combined effects of these variables on *U. lactuca* (Khan *et al.*, 2019; Wang *et al.*, 2018). Hence, this study aims to address this knowledge gap by examining the effects of temperature, duration, and feedstock concentration on the product distribution and physicochemical properties of hydrochars produced from *U. lactuca* through hydrothermal carbonization. The findings of this study provide valuable insights into optimizing the HTC process for marine macroalgae and contribute to the broader development of sustainable bioenergy solutions.

MATERIALS AND METHODS

Sample Preparation

Ulva lactuca samples were collected from coastal regions in Lombok, Indonesia (8°52’12” S, 116°27’36” E) and thoroughly cleaned using municipal water to eliminate impurities such as sand and shells. The cleaned biomass was then oven-dried at 40 °C until a constant dry weight was achieved, with a moisture content of 7.18%. Following drying, the biomass was ground using a blender and sieved through a 60-mesh screen to achieve uniform particle size. The processed samples were stored in airtight zip-lock bags to prevent moisture absorption and contamination before further use.

Hydrothermal Carbonization of *Ulva lactuca*

The HTC of *U. lactuca* in this study was conducted based on the methodology described by Patel *et al.* (2021), with modifications to the reaction time and feedstock concentration. HTC was conducted in a preheated reactor, which was brought to target temperatures of 180, 200, and 220 °C before sample introduction. The PTFE reactor vessel containing the prepared U. lactuca sample was inserted into a preheated stainless-steel reactor assembly, as shown in Figure 1. The reactor was purged with nitrogen gas for 30 s to remove any residual oxygen, followed by pressurization to 80 bar using nitrogen. The HTC process was performed at the specified temperatures for 30, 60, and 90 min. Two different biomass concentrations (1 and 5% w/w) were used in the experiment. During the HTC process, the pressure was maintained between 8 and 10 MPa. After the HTC process, the reactor was rapidly cooled in a water bath to prevent further reactions. Once the reactor temperature decreased to below 50 °C, the process water and hydrochar were separated. The pH of the process water was measured immediately, and the hydrochar was dried

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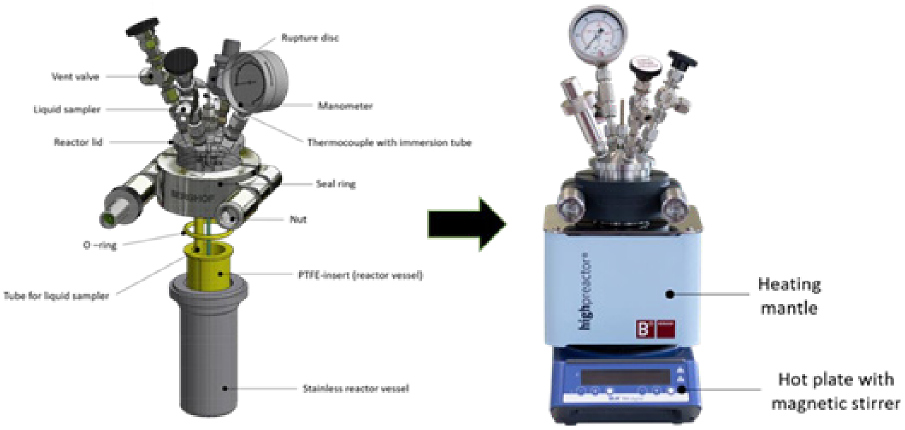


Figure 1 Hydrothermal carbonization reactor

overnight at 105 °C, weighed, and stored for subsequent analyses. Please note that all experiments were conducted in triplicate.

Morphological and HHV Analysis of Hydrochar

The morphologies of raw *U. lactuca* and hydrochar were examined using light microscopy and scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX). Light microscopy was performed at 100x magnification to observe changes in cell structure before and after HTC. For SEM–EDX analysis, the hydrochar samples were mounted on stubs, sputter-coated with gold, and analyzed under high vacuum. Detailed images were captured to assess the surface modifications, and EDX was used to determine the elemental composition, as described in our previous studies (Farobie *et al.*, 2024; Hartulistiyoso *et al.*, 2024). To evaluate the HHV of the hydrochar, measurements were performed using a Parr 6200 isoperibol bomb calorimeter following the ASTM D5865–04 procedure.

Functional Group Analysis using FTIR

Fourier-transform infrared (FTIR) spectroscopy was used to identify the functional groups present in the hydrochar. The samples were prepared by blending them with potassium bromide (KBr) powder and pressing them into pellets for analysis. FTIR spectra were recorded and compared with a background scan for baseline correction, following standard procedures Shrestha *et al.*, (2021).

Determination of Water and Ash Content

The water content of the hydrochars was determined according to the ASTM D1762-84 standard. Approximately 1 g of hydrochar was placed in a pre-weighed porcelain crucible and dried at 105 °C for 2 h. The samples were cooled in a desiccator and weighed, and the drying process was repeated until a constant weight was attained. The water content was calculated using Equation (1):

$$\text{Water content (\%)} = \frac{A-B}{A} \times 100$$

Where A initial sample weight (g) and B is the weight after drying (g).

For ash content determination, the dried samples were heated at 750 °C for 6 h in a muffled furnace. After cooling in a desiccator, the samples were weighed until a constant weight was obtained. The ash content was calculated using Equation (2):

$$\text{Ash content (\%)} = \frac{C}{B} \times 100$$

Where C is the residual weight after ashing (g) and B is the weight after drying at 105 °C (g).

Optimization Process

Response Surface Methodology (RSM) was applied to investigate and optimize the hydrothermal carbonization (HTC) of *Ulva lactuca*, with the goal of maximizing the hydrochar yield. A Box–Behnken design (BBD) with 17 experimental runs was selected as the experimental framework, as it provides an efficient quadratic model for evaluating the combined effects of three independent variables: temperature, residence time, and feedstock concentration (Amrullah *et al.*, 2024). The effects of these variables on the performance metrics were evaluated using analysis of variance (ANOVA). The regression model was analyzed by evaluating the regression coefficients, performing ANOVA, and examining the P-values and F-values. The coefficient of determination (R^2) was used to assess the quality of the polynomial model equations.

The use of RSM allowed for a systematic exploration of both the individual and interaction effects of these variables on the hydrochar yield, while reducing the number of experimental runs compared with full factorial designs. This approach is particularly useful in biomass valorization studies, where multiple process factors are interdependent. To ensure reliability, a split-plot design was employed in combination with optimization using the Design-Expert version 12 software. A thorough multi-step approach was adopted for model validation. Initially, cross-validation with experimental data verified the model accuracy by comparing the numerical predictions with the experimental results under similar conditions. Further validation was conducted through sensitivity and error analyses to identify and address potential discrepancies. Residual analysis was also performed to evaluate model stability and ensure consistency across various input variables. Additional information on the validation procedures has been included in the manuscript to improve clarity and robustness of the study.

RESULTS AND DISCUSSION

Product Fraction

The hydrothermal carbonization of *U. lactuca* demonstrated a clear influence of temperature, time, and feedstock concentration on the hydrochar yield. As shown in Figure 2, an increase in temperature led to a noticeable decrease in the hydrochar yield, whereas an increase in the feedstock concentration resulted in higher yields. These results are consistent with those of a previous study (Erdogan *et al.*, 2015), which reported a similar decrease in hydrochar yield with increasing temperature, attributed to enhanced deoxygenation reactions, such as decarboxylation and dehydration, and the formation of volatile compounds.

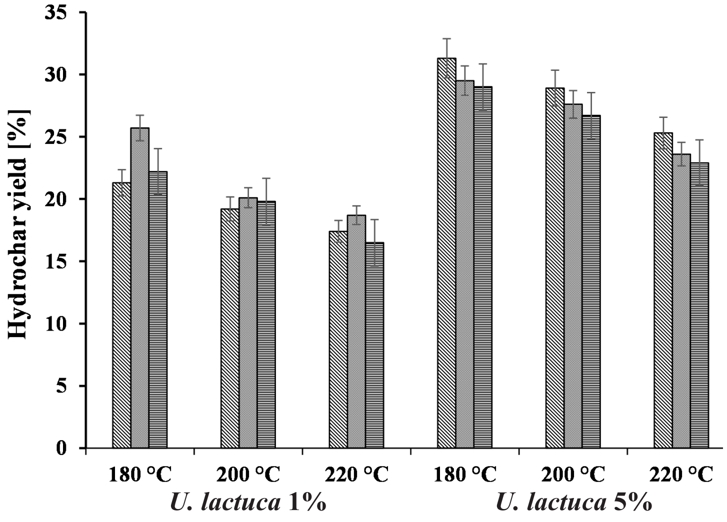


Figure 2 Effect of temperature and feedstock concentration on hydrochar yield through hydrothermal processes for 30 min (▧), 60 min (▩), and 90 min (▤)

The decrease in yield with increasing temperature may be linked to the more intense breakdown of organic materials at higher temperatures, leading to the formation of gaseous products and a reduction in solid hydrochar. This is consistent with the findings of Shrestha *et al.* (2021), who observed that significant portions of organic carbon were decomposed and dissolved in process water during the HTC of seaweed and watercress waste. In their studies, the yields were notably lower, ranging between 9.51% and 24.43%, further indicating that the severity of the HTC conditions plays a crucial role in determining the yield of the solid product.

Conversely, the observed increase in the hydrochar yield at higher feedstock concentrations can be explained by the saturation of the degradation products, which promotes polymerization reactions. As the feedstock concentration increased, the likelihood of these secondary reactions increased, resulting in greater solid formation. Prakoso *et al.* (2018) suggested that this phenomenon occurs because of the accumulation of derivative compounds during the degradation process, which eventually forms a hydrochar through polymerization. In this study, the highest hydrochar yield was obtained at a feedstock concentration of 5% and temperature of 180 °C, indicating the optimal conditions for the formation of hydrochar from *U. lactuca* under the tested parameters.

Morphological Features of Hydrochar

The hydrothermal carbonization of *U. lactuca* significantly altered the morphological features of the resulting hydrochar, as observed by optical microscopy and Scanning Electron Microscopy (SEM). These morphological changes provide insights into the structural transformations and decomposition mechanisms of biomass under varying HTC conditions, particularly temperature. Initially, *U. lactuca* exhibited well-structured and well-defined cell walls with intact cell content (Figure 3A). As the HTC temperature increased to 180 °C, the cell walls began to show signs of degradation, with partial leakage of cell contents (Figure 3B). This degradation became more pronounced at 200 and 220 °C (Figure 3C and 3D), where the cellular structures were further disintegrated, indicating that higher temperatures accelerated the hydrolysis of cell wall components, such as proteins, lipids, hemicellulose, and cellulose, ultimately leading to their conversion into carbon. The increased damage at higher temperatures is consistent with the thermal degradation pathways of these biopolymers,

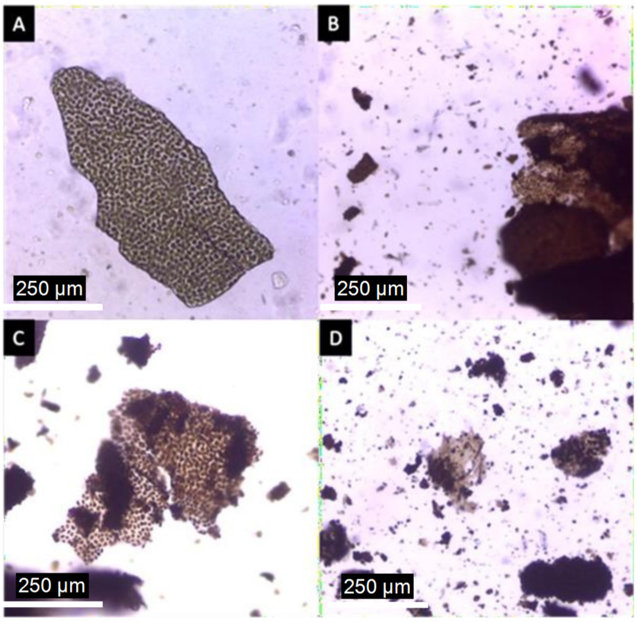


Figure 3 Surface morphology of *U. lactuca*: (A) before treatment and hydrochar samples from the 5% feedstock after hydrothermal processing at (B) 180, (C) 200, and (D) 220 °C (100× magnification)

which decompose into smaller molecules that may volatilize or condense into solids.

SEM analysis further revealed that the hydrochar produced under HTC exhibited a porous structure with irregularly shaped macropores and spherical carbon formations (Figure 4). The presence of these pores can be attributed to the removal of volatile compounds and water during the HTC process, which leaves behind a carbon-rich matrix. The yellow arrows in Figure 4 indicate the spherical carbon particles, which are critical features in the analysis. The formation of spherical carbon particles, which tend to aggregate into clumps, suggests a complex interplay between the polymerization and condensation reactions occurring within the hydrochar matrix. These observations are consistent with the findings of Steinbruch *et al.* (2020), who reported the formation of spherical carbon structures in *Ulva* sp.-derived hydrochars, suggesting a common mechanism for the carbonization of *Ulva* sp.

Chemical analysis using SEM-EDX highlighted the presence of various macrominerals and trace elements on the surfaces of hydrochar samples (Figure 5). Elements such as magnesium, calcium, phosphorus, potassium, and sodium were detected, along with trace amounts of iron and manganese. These elements are typically found in seaweeds, and their concentrations vary depending on the environmental conditions (Farobie *et al.*, 2021; Farobie *et al.*, 2024). The HTC process, which involves high temperatures and subcritical water, leads to changes in the dielectric constant of water, shifting it towards a nonpolar nature. This shift enhances the solubility of organic compounds while reducing that of inorganic compounds, leading to the precipitation of metal oxides, hydroxides, and salts on the hydrochar surface. The variability in metal content with temperature changes, such as the observed increase in calcium content from 180 °C to 200 °C, followed by a decrease at 220 °C, indicates a complex interaction between the solubility of salts and oxidative degradation products, such as CO_2.

However, it is interesting to note that the trend in sulfur (S) content differed from that of the metal content. This variation could be attributed to the temperature effects on the sulfur retention. The volatility of sulfur compounds may vary at different temperatures. At 180 °C, sulfur is likely to

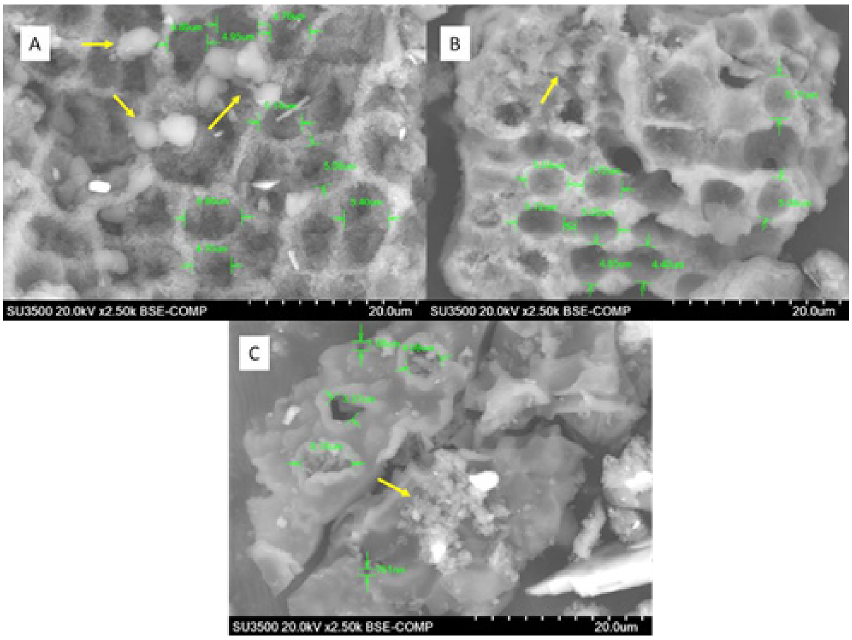
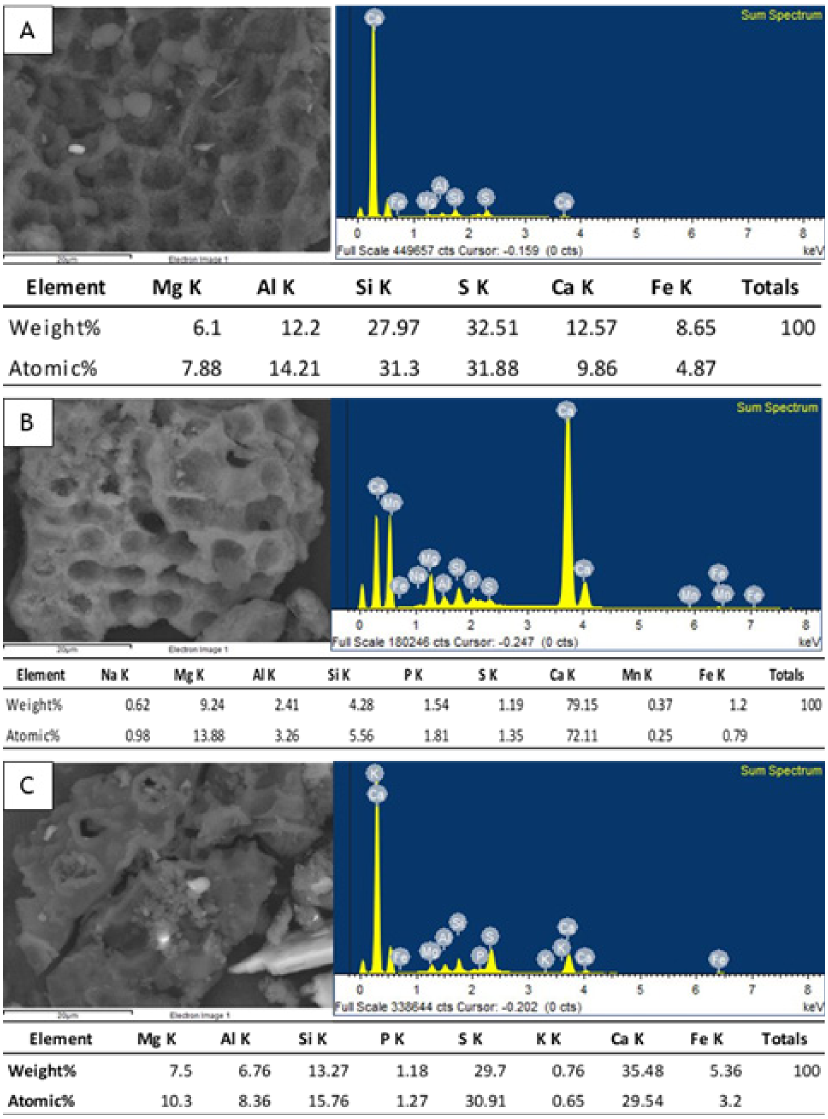


Figure 4 SEM images of hydrochar samples from the 5% feedstock after hydrothermal processing at (B) 180, (C) 200, and (D) 220 °C (2.50k magnification)

remain in the hydrochar, whereas at 200 °C, it may undergo partial volatilization or transformation into other sulfur compounds that are not detectable by SEM-EDX. The hydrolysis and decomposition processes could lead to the loss of sulfur at this specific temperature. Additionally, this variation may be associated with different thermal degradation pathways of the components. The presence of sulfur at 180 °C and 220 °C could be related to the thermal degradation of organic matter at these temperatures, which allows the retention of sulfur in the hydrochar. At 200 °C, a transition in the degradation pathway may occur, leading to lower sulfur retention. Further investigation into the sulfur content would be beneficial using additional analyses, such as X-ray fluorescence (XRF) or chemical digestion methods, which could provide more insights into the sulfur retention mechanisms at this temperature.

Interestingly, the SEM-EDX analysis of the hydrochar samples from the 200 °C treatment revealed the presence of manganese (Mn) and sodium (Na), which were not detected in the other treatments. This observation suggests that the hydrothermal carbonization (HTC) process at 200 °C may promote the release or mobilization of these elements from biomass. The increased



Element	Mg K	Al K	Si K	S K	Ca K	Fe K	Totals
Weight%	6.1	12.2	27.97	32.51	12.57	8.65	100
Atomic%	7.88	14.21	31.3	31.88	9.86	4.87	

Element	Na K	Mg K	Al K	Si K	P K	S K	Ca K	Mn K	Fe K	Totals
Weight%	0.62	9.24	2.41	4.28	1.54	1.19	79.15	0.37	1.2	100
Atomic%	0.98	13.88	3.26	5.56	1.81	1.35	72.11	0.25	0.79	

Element	Mg K	Al K	Si K	P K	S K	K K	Ca K	Fe K	Totals
Weight%	7.5	6.76	13.27	1.18	29.7	0.76	35.48	5.36	100
Atomic%	10.3	8.36	15.76	1.27	30.91	0.65	29.54	3.2	

Figure 5 SEM-EDX spectra of hydrochar samples from the 5% feedstock after hydrothermal processing at (B) 180, (C) 200, and (D) 220 °C

solubility of inorganic compounds at this temperature could lead to the incorporation of Mn and Na into the hydrochar, potentially through precipitation or complexation with other elements. This finding indicates that temperature plays a crucial role in the distribution and retention of metal elements in the resulting hydrochar, and further studies are required to understand the mechanisms underlying the selective retention of Mn and Na at this specific temperature.

Furthermore, the gradual degradation of hemicellulose, cellulose, and lignin during HTC aligned with the observed changes in the hydrochar structure and composition. Hemicellulose, which begins to decompose at approximately 180 °C, contributes to the formation of pores and spherical carbon particles. As the temperature increases to 200-230 °C, the degradation of amorphous cellulose further amplified these effects, whereas the degradation of crystalline cellulose and lignin at higher temperatures led to more pronounced structural changes. The selective degradation of these components, which is influenced by the stability of their chemical bonds, underscores the importance of temperature in controlling the properties of the resulting hydrochar.

Functional Groups of Hydrochar

Fourier-transform infrared (FTIR) spectroscopic analysis of the hydrochar samples derived from *U. lactuca* provided valuable insights into the chemical transformations that occurred during HTC. The FTIR spectra (Figure 6) demonstrate that while the main functional groups were consistent across the samples subjected to different temperatures, the absorption intensities varied, indicating changes in the chemical structure and composition as a function of temperature increase.

The specific band assignments of the hydrochars at various temperatures are listed in Table 1. One of the most prominent features observed in the FTIR spectra is the broad absorption band at 3500-3200 cm^{-1}, which corresponds to the O–H stretching vibrations of alcohol, phenol, or carboxylic groups (Farobie *et al*., 2024). The decrease in the absorption intensity of this band for the hydrochar produced at 200 °C suggests the occurrence of dehydration reactions, leading to the loss of hydroxyl groups and the subsequent formation of water molecules. This observation aligns with the known thermal degradation pathways of biomass, in which dehydration is a key step in the conversion of organic matter into carbon-rich solids. Conversely, the increase in absorption intensity at 220 °C could be attributed to the formation of reactive oxygen-containing groups on the hydrochar surface, likely owing to the re-adsorption of oxygen species during the carbonization process.

The absorption band at approximately 2900 cm^{-1} is indicative of C–H stretching vibrations, which are characteristic of aliphatic chains, such as those found in cellulose and hemicellulose. The reduction in the absorption intensity at 200 °C suggests the cleavage of these aliphatic chains, likely through the breakdown of cellulose, which is consistent with the expected thermal decomposition behavior of this polysaccharide. The weak absorption observed at approximately 1981

Table 1 Specific band assignments of hydrochar at various temperatures

Typical band assignment	Main peak (cm^{-1}) at various temperatures of hydrochar (°C)		
	180	200	220
OH stretching	3,310	3,298	3,286
aliphatic C-H stretching	2,940	2,890	2,910
aromatic C–H bending	1,981	1,978	1,980
aromatic C=C stretching	1,475	1,470	1,468
C–O stretching	1,100	1,093	1,098

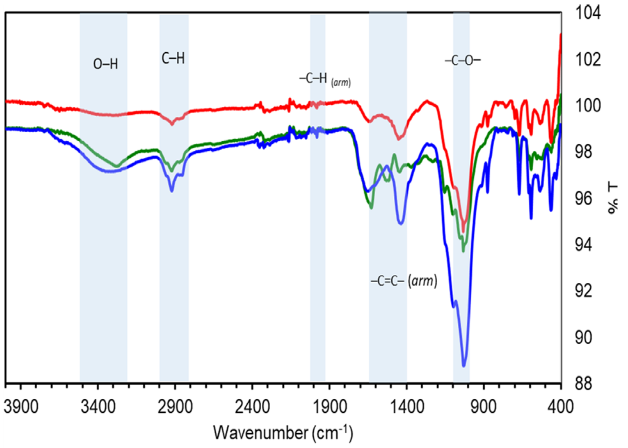


Figure 6 FTIR spectra of hydrochar samples from 5% feedstock after hydrothermal process at 180 °C (—), 200 °C (—), and 220 °C (—)

cm^{-1} is linked to the C–H bending vibrations of aromatic compounds, which became more pronounced as the temperature increased to 220 °C. This increase in absorption intensity suggests that polymerization reactions occur, leading to the formation of more complex aromatic structures in the hydrochar matrix. These findings are consistent with those of previous studies, which showed that higher temperatures facilitate the aromatization and condensation of carbon chains, resulting in the formation of stable aromatic rings.

In the region of approximately 1600 cm^{-1} and 1475 cm^{-1}, the paired absorption bands are indicative of C=C stretching vibrations, primarily from aromatic compounds. The decrease in the absorption intensity at 200 °C may be due to conjugation effects, where the overlap of π-electrons in adjacent bonds leads to a reduction in the bond energy. However, as the temperature increased to 220 °C, the absorption intensity increased, suggesting enhanced polymerization, aromatization, and dehydration reactions, which led to the formation of more C=C bonds. This transition reflects the gradual shift from aliphatic to aromatic dominance within the hydrochar as the HTC temperature increases, which is a hallmark of carbonization.

Finally, the absorption bands observed in the 1100-1000 cm^{-1} region correspond to C–O stretching vibrations, which can be associated with aliphatic ether or alcohol groups. The increase in the absorption intensity at 220 °C indicates that dehydration and aromatization processes occur actively, resulting in the formation of these functional groups in the char. The presence of these groups in the hydrochar suggests that, despite extensive carbonization, some oxygenated functional groups are retained, which could influence the reactivity and potential applications of the hydrochar, such as in adsorption processes or soil amendment.

Water and Ash Content of Hydrochar

The results of this study demonstrate a clear relationship between the HTC conditions and the water content of the resulting hydrochar. As the temperature and heating time increased, the water content of the hydrochar consistently decreased (Figure 7). This trend can be attributed to the enhanced dehydration reactions that occur under more intense HTC conditions, in which water molecules are released from the biomass and transferred to the process water. This reduction in water content, ranging from 6.67% to 3.16%, is significant because it meets the quality standards specified in SNI 4931:2010, which requires a water content of ≤12% for coal briquettes. Thus, the hydrochar produced under the conditions explored in this study is suitable for applications in which a low moisture content is critical, such as solid fuel production.

However, the ash content of the hydrochar tended to increase with variations

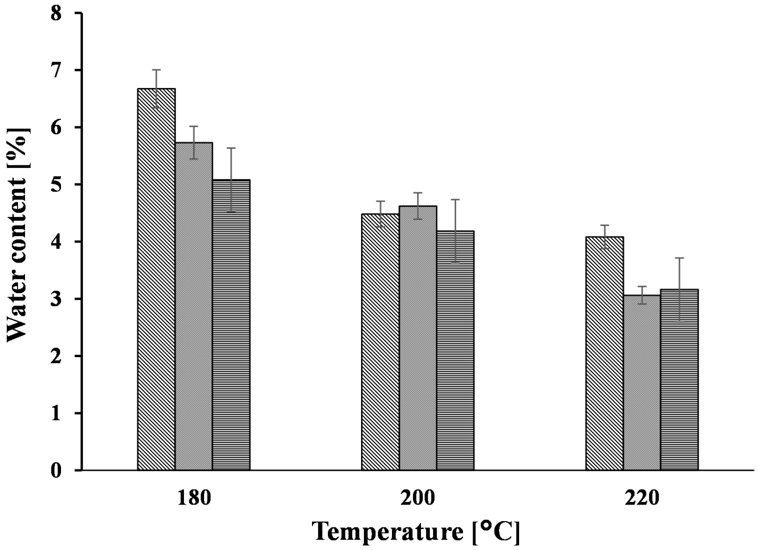


Figure 7 Effect of time and temperature on the water content of hydrochar samples with a feedstock concentration of 5% conducted at hydrothermal processes for 30 min (▧), 60 min (▩), and 90 min (▤)

in temperature and heating time (Figure 8). This observation aligns with previous studies, such as those by Liu *et al*. (2019), who suggested that higher temperatures can increase the rate of hydrolysis, thereby concentrating the inorganic mineral content as the organic matter is reduced. However, the decrease in ash content in some samples could be due to the partial dissolution of inorganic fractions, such as alkali and alkaline earth metals, in the process water. The ash content in the hydrochar samples from this study ranged from 9.48% to 23.22%. There is no specific standard for the ash content of hydrochars. However, SNI 4931:2010, which concerns the quality of new coal briquettes, requires an ash content of ≤15% for class A carbonized coal briquettes and ≤20% for class B carbonized coal briquettes. Therefore, only hydrochar samples from the 5% feedstock treatment with heating at 180 °C for 30 and 60 min, and at 200 °C for 60 min, met the

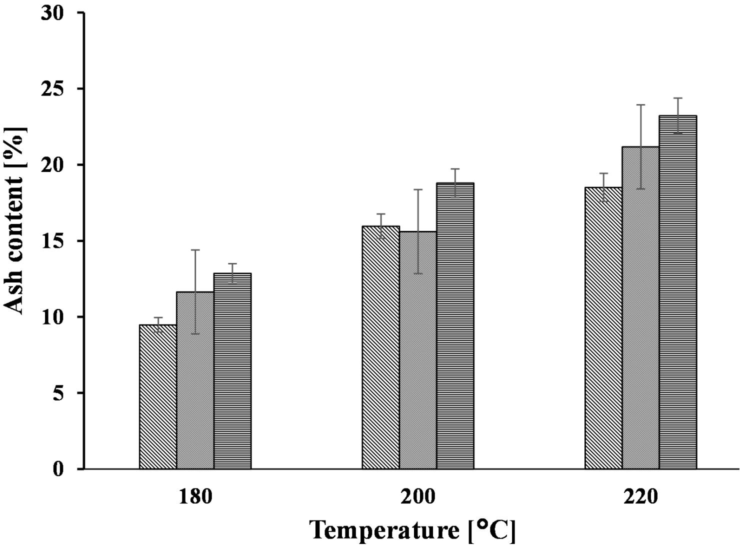


Figure 8 Effect of time and temperature on the ash content of hydrochar samples with a feedstock concentration of 5% conducted at hydrothermal processes for 30 min (▧), 60 min (▩), and 90 min (▤)

quality standards of SNI. The high ash content in other samples could pose challenges if the hydrochar is intended for use as a fuel, as it may lead to operational issues such as fouling, as noted by Patel *et al.* (2021).

Higher Heating Value

The higher heating value (HHV) of the hydrochar was clearly dependent on the HTC temperature. As shown in Figure 9, the HHV increased steadily with increasing temperature from 180 to 220 °C. At 180 °C, the HHV values ranged between 14.96 and 17.79 MJ/kg, whereas at 220 °C, the values increased significantly to 19.51–21.22 MJ/kg. This trend indicates that higher reaction temperatures favor the energy densification of hydrochars, which can be attributed to the enhanced thermal decomposition of labile components and the subsequent enrichment of carbon in the solid phase. The increase in calorific value with temperature is consistent with the removal of oxygenated groups through decarboxylation and dehydration, leading to a higher degree of carbonization (Cui *et al.*, 2020).

In addition to temperature, the reaction time also influenced the HHV of the hydrochar. At a given temperature, a prolonged residence time resulted in an incremental increase in HHV. For instance, at 180 °C, the HHV increased from 14.96 MJ/kg (30 min) to 17.79 MJ/kg (90 min), and at 220 °C, it improved from 19.51 MJ/kg (30 min) to 21.22 MJ/kg (90 min). Although the effect of time was less pronounced than that of temperature, it contributed to further stabilization of the carbon-rich structure. The extension of the reaction time promotes additional secondary reactions, such as dehydration, condensation, and aromatization, which collectively reduce the hydrogen and oxygen content relative to that of carbon (Seyedsadr *et al.*, 2018). This mechanism explains the observed stepwise improvement in the HHV with increasing holding time.

The combined effects of increasing the temperature and extending the reaction time highlight the role of HTC in enhancing the fuel quality of *Ulva lactuca*-derived hydrochar. The HHV values obtained in this study (14.96–21.22 MJ/kg) are comparable to those of low-ranked coals. Luo & Tao, (2017) reported that the HHV of low-rank coals typically averages around 15 MJ/kg, with a range between 12 and 25 MJ/kg. This indicates that the hydrochar produced under optimal HTC conditions approaches the calorific value of conventional fossil-based solid fuels. Compared to previous studies on macroalgal hydrochars, the values obtained in this study are within a favorable range, demonstrating the potential of *Ulva lactuca* as a viable feedstock for renewable solid fuel production. The HHV enhancement

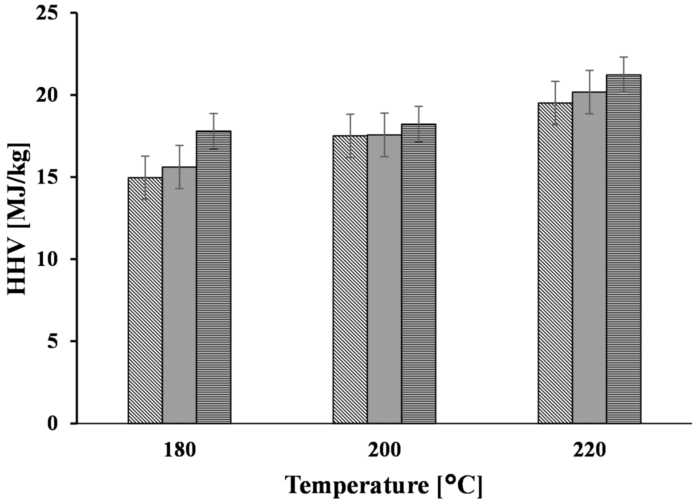


Figure 9 Effect of time and temperature on the higher heating value (HHV) of hydrochar samples feedstock concentration of 5% conducted at hydrothermal processes for 30 min (▧), 60 min (▩), and 90 min (▤)

confirmed that hydrothermal carbonization effectively transformed macroalgae into an energy-dense solid fuel, supporting its application in energy recovery and coal substitution.

Response Surface Methodology

RSM was employed to optimize the HTC process and evaluate the combined effects of temperature, residence time, and feedstock concentration on the hydrochar yield. The ANOVA results for the quadratic model are presented in Table 2. The overall model was statistically significant ($p = 0.0017$) with an F-value of 12.06, confirming that the quadratic regression equation adequately described the relationship between the process variables and hydrochar yield. Among the individual factors, temperature ($p = 0.0004$) and feedstock concentration ($p = 0.0008$) showed highly significant effects, indicating that these parameters strongly influenced the hydrochar yield. In contrast, the reaction time ($p = 0.5463$) did not exhibit a statistically significant effect within the tested range, suggesting that extending the residence time beyond 30 min did not substantially improve the hydrochar yield. This outcome highlights temperature and biomass loading as the dominant factors determining HTC efficiency for *U. lactuca*.

The interaction effects provided further insights into the process behavior. The combination of time and concentration (BC, $p = 0.0031$) was statistically significant, showing that higher yields could be achieved when the feedstock concentration was increased at longer reaction times. Conversely, the interactions between temperature and time (AB, $p = 0.3689$) and temperature and concentration (AC, $p = 0.2635$) were not significant, indicating that the effect of temperature on yield was largely independent and not strongly modified by other variables. Regarding quadratic terms, both time squared (B^2, $p = 0.0441$) and concentration squared (C^2, $p = 0.0283$) were significant, reflecting nonlinear relationships in which extreme values of these factors could reduce the yield. The lack-of-fit test ($p = 0.9383$) was not significant, validating the adequacy of the quadratic model for describing the experimental data (Amrullah & Farobie, 2023).

The three-dimensional response surface and corresponding contour plots (Figure 10) provide a visual representation

Table 2 One-way analysis of variance (ANOVA) for hydrochar yield

Source	Sum of squares	df	Mean square	F-value	p-value	
Model	449.72	9	49.97	12.06	0.0017	significant
A-Temperature	168.18	1	168.18	40.58	0.0004	
B-Time	1.67	1	1.67	0.40	0.5463	
C-Feed percentage	133.25	1	133.25	32.15	0.0008	
AB	3.82	1	3.82	0.92	0.3689	
AC	6.13	1	6.13	1.48	0.2635	
BC	80.46	1	80.46	19.41	0.0031	
A^2	2.76	1	2.76	0.66	0.4417	
B^2	24.89	1	24.89	6.01	0.0441	
C^2	31.46	1	31.46	7.59	0.0283	
Residual	29.01	7	4.14			
Lack of Fit	2.55	3	0.85	0.13	0.9383	not significant
Pure Error	26.46	4	6.62			
Cor Total	478.73	16				

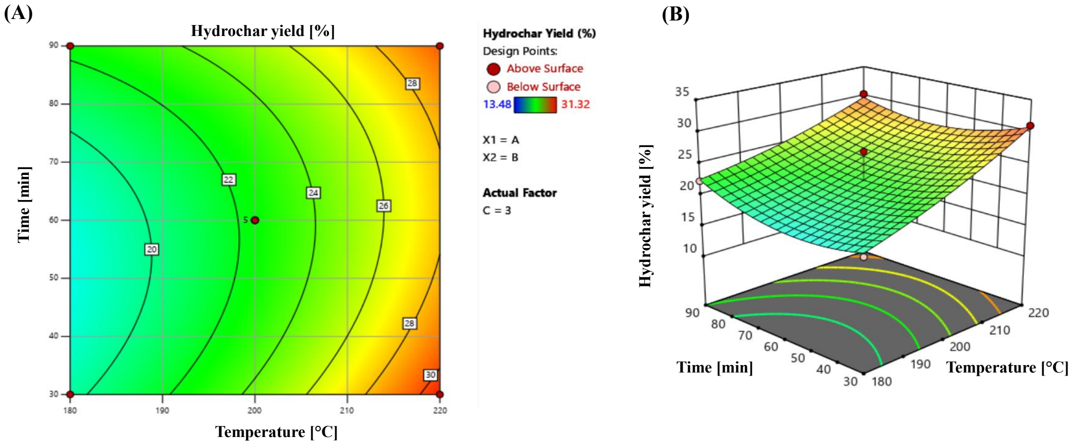


Figure 10 (A) contour plots of hdyrochar yield against time, temperature, and feedstock concentration, (B) three-dimensional surface) for hydrochar yield

of the combined effects of temperature, time, and feedstock concentration on the hydrochar yield. These graphical models derived from the quadratic equation of the Box–Behnken design allow for a more intuitive interpretation of the interaction between the process variables and the optimization region for maximum yield. The contour plot of hydrochar yield against temperature and time demonstrated that temperature exerted a more dominant influence on the yield than residence time. At lower temperatures (180 °C), changes in time from 30 to 90 min caused only minor variations in the yield. However, as the temperature increased to 200–220 °C, the yield decreased noticeably regardless of the holding time, confirming the strong negative correlation between temperature and hydrochar formation. This aligns with the ANOVA results, which indicated that temperature was the most significant factor, whereas time alone had no substantial effect.

The three-dimensional surface plot further illustrates the curvature of the response, highlighting the nonlinear interactions in the HTC process. The surface plot shows that the hydrochar yield reached its maximum at lower temperatures combined with higher feedstock concentrations and moderate retention times, consistent with the significant quadratic terms observed for concentration and time. At higher temperatures, the surface declined steeply, indicating intensified decomposition reactions that reduced the solid fraction. These observations reinforce the notion that optimal hydrochar production occurs under relatively mild HTC conditions, where decomposition is controlled and polymerization processes favor solid formation.

CONCLUSION

This study confirmed that HTC is an effective approach for converting *Ulva lactuca* into hydrochar, with the process conditions playing a decisive role in determining the yield and quality. Among the investigated parameters, temperature and feedstock concentration emerged as the most influential factors. The hydrochar yield was highest (31.3%) at 180 °C and 5 wt. % concentration. Microscopic and spectroscopic analyses demonstrated that elevated temperatures promoted structural degradation, pore formation, and the development of aromatic carbon structures, thereby improving the fuel quality through a higher energy density.

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