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Hydrogen and Hydrochar Production from *Ulva lactuca* via Subcritical and Supercritical Water Gasification with Formic Acid Addition

Novi Syaftika[1,*], Gissa Navira Sevie[2], Nirma Afrisanti Kinasih[2],
Nesha Adelia[2], Imron Masfuri[2], Tyas Puspita Rini[2], Abdul Hadi[2],
Asep Bayu[3], Apip Amrullah[4], Obie Farobie[5,*]

[1]Research Center for Process Technology, National Research and Innovation Agency (BRIN),
Building 625, KST BJ Habibie/PUSPIPTEK Serpong,
Tangerang Selatan, Indonesia, 15314
[2]Research Center for Fuel Technology, National Research and Innovation Agency (BRIN),
Building 625, KST BJ Habibie/PUSPIPTEK Serpong,
Tangerang Selatan, Indonesia, 15314
[3]Research Centre for Vaccine and Medicine, National Research and Innovation Agency (BRIN),
Jl. Raya Jakarta-Bogor KM 46 Cibinong, Bogor, West Java 16911, Indonesia
[4]Department of Mechanical Engineering, Lambung Mangkurat University, Banjarmasin,
Kalimantan, Indonesia, 70123
[5]Mechanical Engineering, Faculty of Engineering and Technology, IPB University (Bogor
Agricultural University), IPB Darmaga Campus, Bogor, West Java, Indonesia, 16002

*Author to whom correspondence should be addressed:
E-mail: novi.syaftika@brin.go.id; obiefarobie@apps.ipb.ac.id

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Abstract: Among biomass resources for bioenergy, marine macroalgae such as *Ulva lactuca* is highly productive, requires no land or freshwater, and remains underexplored compared to terrestrial biomass. Its high moisture content makes hydrothermal processing or subcritical and supercritical water gasification (SbWG and SCWG) well suited for conversion to bioenergy, eliminating the need for drying. Chemical additives such as formic acid can further enhance the process. This study investigated the effect of formic acid on SbWG and SCWG of *Ulva lactuca* for hydrogen and hydrochar production. Experiments were conducted in a 500 mL high-pressure reactor at 300–400 °C for 30–90 minutes, using feedstock concentrations of 1 wt% and 5 wt%, with and without 1 wt% formic acid. Gas, solid, and liquid products were collected and analyzed (proximate, ultimate, and HHV). Results showed that formic acid significantly enhanced hydrogen production, with a maximum yield of 39% v/v at 350 °C for 90 min. However, hydrogen yield declined at 5 wt% loading, likely due to inefficient mixing. Hydrochar quality deteriorated with formic acid, showing lower carbon content, higher oxygen, and greater moisture, producing a sticky, tar-like material. The Van Krevelen analysis confirmed that formic acid promotes the formation of gaseous products over solid carbon retention, making it more effective for enhancing gas yields rather than producing solid fuel.

Keywords: Hydrochar; Hydrogen; Macroalgae; Subcritical water gasification; Supercritical water gasification; *Ulva lactuca*

1. Introduction

Incorporating renewable energy into the power, heat, and transportation sectors is crucial for preventing the global average temperature from surpassing the 1.5°C threshold[1)]. Similar to other nations, Indonesia is actively addressing global warming by establishing a Net Zero Emission (NZE) goal for 2060, with bioenergy considered a substitute for fossil fuels in this initiative[2)]. Indonesia formulated the National Energy Policy as a strategic framework to direct its energy development until 2050. Established under Government Regulation No. 79 of 2014,

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the policy seeks to ensure national energy security and self-sufficiency by promoting sustainable and equitable energy management[3]**.** Nevertheless, the actual implementation of bioenergy is currently falling short of achieving the targeted share of Indonesia's energy mix. The achievement in 2024 indicates that Indonesia's renewable energy is only 14.1%, which is far below the set target of 23% that should be achieved in 2025[4]. The development of bioenergy in Indonesia began in the early 1990s and expanded significantly in the 2000s, primarily utilizing land-based resources, such as palm oil for biodiesel and cassava for bioethanol. Recently, research efforts have focused on investigating the agricultural residues, that do not compete with food resources as alternative feedstocks, including corn cobs[5], coconut shells[6], and oil palm waste[7,8]. However, a significant biomass resource in Indonesia remains underutilized and has yet to be fully explored for its potential as a bioenergy feedstock, particularly for macroalgae.

Macroalgae or seaweed as a marine biomass for bioenergy offers some advantages over terrestrial biomass[9]. First, macroalgae do not compete with terrestrial biomass in terms of land and freshwater use, because they can grow in the ocean. Seconly, macroalgal productivity is also known to be rapid and exceeds that of terrestrial plants[10]. Moreover, macroalgae are considered a promising option for bioenergy production due to exceptial photosynthetic efficiency, rapid growth rate, and high biomass yield compared to conventional energy crops such as rapeseed and soybean[11]. Most macroalgae produced at this time are utilized either as food for human consumption (approximately 47%) or for hydrocolloid production (over 50%), such as agar, carrageenan, and alginate[12].

Ulva lactuca is a green macroalgae species that grows in various regions of Indonesia and is not yet widely utilized in industry. Similar to other types of biomass, *Ulva lactuca* contains a high proportion of organic components that can be converted into energy products, such as gaseous products (syngas) and solid carbonaceous products (char), through thermochemical processes. As an aquatic biomass, macroalgae has a high moisture content[9]. *Ulva lactuca* in particular contains approximately 80% moisture[13]. This makes hydrothermal processes, specifically Subcritical and Supercritical Water Gasification (SbWG and SCWG) more suitable for its conversion[14]. These processes utilize water as a reaction medium, enabling a series of thermochemical reactions to occur without the need for energy-intensive drying, thereby improving cost and energy efficiency[15]. The solid product derived from SbWG and SCWG is referred to as hydrochar when produced through hydrothermal treatment.

In SbWG and SCWG, water exists below or above its critical temperature and pressure. The subcritical state occurs at temperatures up to 374 °C and pressures at or below 22.1 MPa, where water remains in the liquid phase. In contrast, the supercritical state is defined by operating conditions exceeding the critical point, specifically temperatures above 374 °C and pressures greater than 22.1 MPa[16]. Under subcritical region, water remains in a liquid state with high polarity, promoting mild hydrolysis and partial decomposition of biomass[17]. In contrast, supercritical water acts as a non-polar fluid that dissolves organic intermediates effectively, enabling near-complete gasification and higher hydrogen yields while suppressing solid byproduct formation[18].

Our earlier research indicated that *Ulva lactuca* is a promising feedstock for generating H_2 and hydrochar through the SbWG and SCWG process. Nevertheless, within the moderate temperature of 300–400 °C, the maximum yield of H_2 was only 8.09% at 400 °C and 90 min. It is anticipated that elevating the temperature within the supercritical water region may enhance hydrogen production. However, this entails substantial energy consumption because of the high temperature. Therefore, an alternative approach involves incorporating a catalyst or additive to boost H_2 yield during biomass gasification[14].

Formic acid, which is recognized for its versatility, low flammability, biodegradability, stability under ambient conditions, and cost-effectiveness, has emerged as a catalyst or additive in recent hydrothermal applications for converting organic compounds. Yemis et al., 2011 demonstrated that formic acid acts as a catalyst to convert xylose and xylan into furfural in the microwave-assisted[19]. Onwudili et al. observed an increase in the liquid product mass fraction of alkali lignin to 40% with formic acid compared to reactions without an addition of formic acid[20]. In gasification processes, studies by Yin et al., 2017, and Fan et al., 2016, highlighted the effectiveness of formic acid in enhancing sewage sludge gasification while reducing undesired phenol and char formation[21]. Recent literature, as indicated by Fan et al. (2018), also suggests that formic acid addition improves gasification and hydrogen efficiency[22]. However, to the best of our knowledge, the influence of formic acid addition on gasification and char production from the marine biomass *Ulva lactuca* has not been explored in the existing literature. Unlike terrestrial biomass and sludge, *Ulva lactuca* is characterized by high moisture content, distinct polysaccharide composition, and minimal lignin, which could lead to different decomposition pathways and interactions with formic acid under hydrothermal conditions. Hence, in this study, we investigated the role of formic acid on the SbWG and SCWG of *Ulva lactuca*, focusing on how it modifies product yields, gas composition, and hydrochar characteristics. This work provides new insights into the synergistic effects of formic acid on the conversion of marine macroalgae, offering a basis for optimizing hydrothermal processes to maximize hydrogen-rich syngas and tailor hydrochar properties. Such findings advance the development of carbon-neutral energy systems using underutilized marine biomass.

2. Material and methods

2.1. Materials

The macroalgae (*Ulva lactuca)* was collected from Ekas Beach, Lombok Island, West Nusa Tenggara, Indonesia. After collection, tap water was used to wash the macroalgae to ensure that debris and sand were removed, followed by rinsing with distilled water. The next step was the drying process using an oven at 50 °C to decrease the moisture content. Drying was conducted to ensure precise measurement and consistent feedstock quantities across all samples in this study. In future applications, the drying process could be omitted. Afterwards, the dried macroalgae were ground to gain a fine sample with uniform particle size. Meanwhile, the formic acid was prepared in a beaker glass using a weighing machine to ensure a concentration of 1 wt. The feedstock was characterized as described in our previous work, including proximate analysis (moisture content, volatile matter, and ash content), ultimate analysis (C, H, N, O, and S), and determination of the Higher Heating Value (HHV)14).

2.2. SbWG and SCWG Process

A high temperature and pressure reactor was used to conduct batch mode of SbWG and SCWG of macroalgae *Ulva lactuca,* with formic acid introduced as an additive. The reactor comprised an electric heating element, a detachable vessel, a magnetically driven agitator, a temperature controller. The reactor has a total volume of 500 mL and is capable of operating at conditions up to 500 °C in temperature and 34.5 MPa in pressure

To conduct SbWG and SCWG, the desired amounts of dried macroalgae (1wt% and 5 wt%) and liquid formic acid (1 wt%) were added to the reactor. Subsequently, the feedstock was loaded, the reactor was sealed, and pure nitrogen was flushed through the system to purge the air. The experiments were conducted at temperatures of 300 °C and 350 °C for SbWG, and 400 °C for SCWG, with holding times of 30, 60, and 90 minutes. The system was initially pressurized to 8 MPa with nitrogen gas, and agitation was maintained at a constant 100 rpm. After the holding time was achieved, cooling was performed using a water-cooled chamber. Samples of gas, solid, and liquid products were collected. Solid and liquid were separated through vacuum filtration, after which the solid residue was oven-dried at 60 °C for 24 h. To ensure reproducibility, each experiment was carried out in two replicates.

2.3. Characterization of syngas and bio-char

To characterize the gaseous products resulting from SbWG and SCWG of *Ulva lactuca*, Gas Chromatography (GC, Shimadzu 8A, Japan) with two different detectors was employed. The first system employs a Thermal Conductivity Detector (TCD) coupled with a Shincarbon ST 50/80 mesh column and helium (He) as the carrier gas to analyze CH_4, CO_2, and CO. The second setup uses a Flame Ionization Detector (FID) paired with a Porapak Q column, also with helium as the carrier gas, to measure C_2 hydrocarbons (C_2H_4 and C_2H_6). The column temperature of 50 ºC was maintained isothermally. On the other hand, the detector and injector were settled at 100 ºC.

For the solid product (hydrochar), characterization was carried out only for samples with a feedstock concentration of 5%. This is due to the very limited amount of hydrochar obtained from *Ulva lactuca* treated with a feedstock concentration of 1%. The solid product was washed with distilled water to remove residual formic acid, then oven-dried. Its ultimate properties, including oxygen content, were subsequently analyzed using a (C, H, N, and S) analyzer, following the same procedure used for feedstock characterization.

3. Result and discussion

3.1. Effect of temperature, time, feedstock concentration and formic acid addition on gas yield

The impact of temperature variation on the gas product yield from the SbWG and SCWG of Ulva lactuca was also evaluated (Figure 1). The percentages of 1% and 5% indicate the feedstock concentration, and the abbreviation FA refers to experiments with the addition of formic acid. In the Figure, the white bars with small dotted patterns represent experiments using 1% feedstock concentration with formic acid addition (FA), whereas the blue bars with cross patterns correspond to 5% feedstock concentration with FA. The red diamonds and green circles represent the experiments conducted without formic acid, where the red diamond corresponds to a 1% feedstock concentration, and the green circle corresponds to a 5% feedstock concentration. Without formic acid, the gas yield remained low at 300 °C and gradually increased from 14.70% to 55.17% upon increasing the temperature to 400 °C for both 1% and 5% feedstock concentrations. Moreover, in the absence of formic acid, extending the reaction time from 30 to 60 minutes enhanced gas yield for both feedstock concentrations. Extending the holding time to 60 min resulted in an increase gas yield to a range of 24.40–64.71%, which further to 26.08–72.00% at 90 min. Comparable temperature-dependent trends in gas yield have also been reported in previous studies on the hydrothermal treatment of macroalgae23). The increased gas yield at higher temperatures was attributed to enhanced thermal degradation, which breaks down biomass bonds24). Longer holding times also increased the gas yield, likely due to further decomposition of liquid-phase dissolved compounds, as seen in previous studies on *Ulva prolifera*25).

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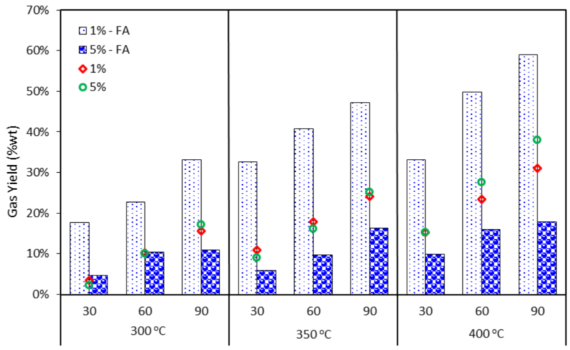


Fig. 1: Gas product yield distribution from *Ulva lactuca* via SbWG and SCWG at feedstock concentrations of 1wt% and 5 wt% (FA: formic acid added)

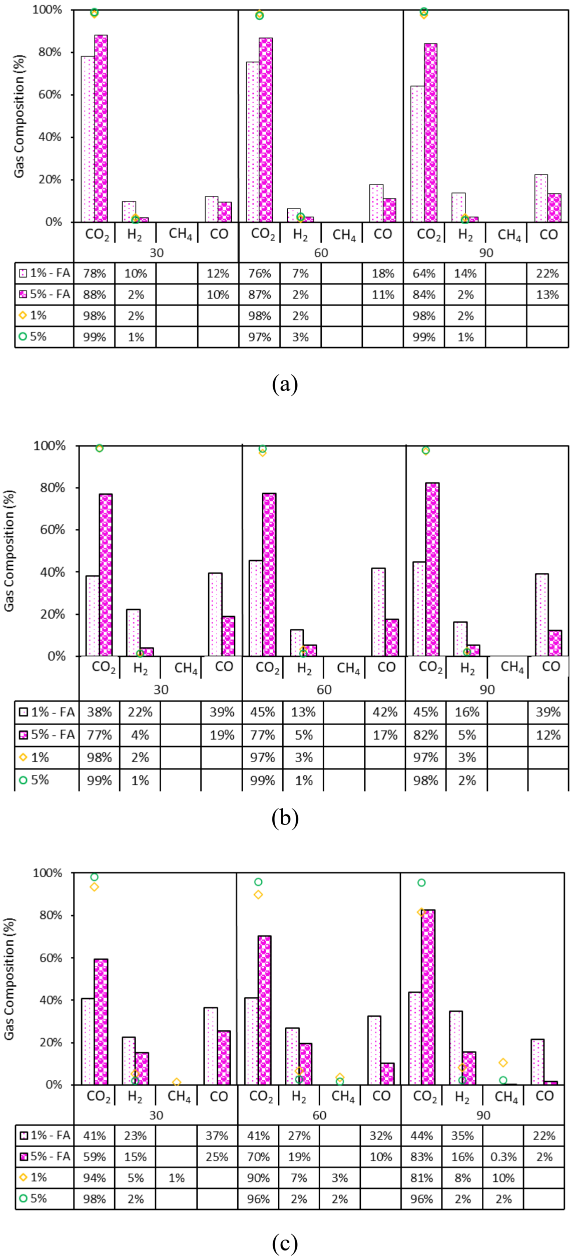
The temperature increase significantly affects gas formation at both 1% and 5% feedstock concentrations, with or without the addition of formic acid. This observation aligns with those of previous studies that water's physical properties including viscosity, density, and dielectric constant change dramatically near its critical point (374 °C). Consequently, water exhibits like nonpolar solvent characteristics, enhancing its miscibility with gases[26].

Interestingly, the experiment using a 1% feedstock concentration with formic acid produced substantially higher gas yields across the entire temperature range from 300 to 400 °C and holding times from 30 to 90 min. In contrast, the gas yield from the 5% feedstock concentration, even with formic acid addition, was lower than that obtained without formic acid, which may be attributed to the higher solid loading promoting the formation of solid residues owing to incomplete degradation. This trend is linked to the reduced water content at higher feed concentrations, which limits the progression of the gasification reactions. A study on rice husk gasification found that as feed concentration increased, char yield significantly increased due to the inhibition of gasification reactions caused by water deficiency[27]. Similarly, another study on wheat straw gasification found that higher feed concentrations led to decreased H_2 yields because the reduced water content suppressed reforming and water-gas shift reactions[17]. This result indicates that the addition of formic acid becomes less effective as the volume of water in the reaction medium decreases relative to the total mass and possibly forms char via re-polymerization. Future research may focus on identifying the optimal feedstock concentration ratio, along with appropriate mixing strategies and operating conditions, to enhance gas production and maximize the impact of formic acid addition under higher feedstock loading.

3.2. Effect of temperature, time, feedstock concentration and formic acid addition on gas composition

To investigate whether the higher gas yield contained higher H2, gas composition analysis was performed, as shown in Figure 2. Carbon dioxide (CO_2) followed by carbon monoxide (CO) was observed as the dominant gas component under all experimental conditions, this suggests that decarboxylation reactions are a dominant pathway in the gasification of Ulva lactuca under both subcritical and supercritical water conditions. As discussed in a previous study, during decarboxylation, biomass undergoes loss of carboxyl groups as part of the hydrothermal process. These fragmented carboxyl groups, along with any existing carbonyl groups, rapidly decompose at temperatures above 150 °C, leading to the formation of CO_2 and CO[28].

For the main target, which is H_2, it can be observed that, in general, the H_2 composition produced from *Ulva lactuca* increases with increasing temperature, both without (from 1% to 10%) and with the addition of formic acid (from 2% to 35%). This behavior can be attributed to the thermal characteristics of the reaction, where under elevated temperature and pressure, liquid water functions simultaneously as a reactant and a solvent or reaction medium for the biomass, facilitating its breakdown through various chemical reactions including hydrogen generation[9]. Interestingly, a higher feedstock concentration of 5% resulted in a lower H_2 content at 300, 350, and 400°C. This aligns with the previously mentioned lower gas-yield volume. It was also observed that increasing the reaction time, as well as the formic acid addition, did not significantly improve the H_2 content in the treatments with a 5% feedstock concentration. This is because higher biomass concentrations can cause inefficient mixing and reduced contact between the biomass and supercritical water, leading to incomplete gasification and lower H_2 production as observed in a previous study by Su et al., in 2019 who used food waste as a raw material to generate hydrogen under SbWG conditions[29]. The study revealed that increasing the feedstock concentration from 10 to 30 wt% led to a significant decrease in hydrogen yield, dropping from 1.1 to 0.6 mol/kg. As mentioned previously, the formic acid addition did not make a difference when the feedstock loading was high. At the lower feedstock concentration (1 wt%), both with and without formic acid, the excess water promotes the water-gas shift (WGS) and steam reforming reactions, enhancing H_2 production. Conversely, at a higher feedstock concentration (5 wt%), the reduced availability of water may constrain these reactions, potentially leading to lower H_2 yields. These findings align with those of previous studies by Graz et al. (2016), who examined macroalgae and found that increasing the *Ulva* sp from 7 to 16.4 wt% led to a significant decline in H_2 yield from 2.7 – 1.8 mol/kg[30]. Likewise, Ni et al. examined the effect of feedstock concentration on the SCWG of macroalgae (*E. intestinalis*), reported that an increase in *E. intestinalis* concentration from 1 to 2 wt% significantly



	30				60				90			
	CO_2	H_2	CH_4	CO	CO_2	H_2	CH_4	CO	CO_2	H_2	CH_4	CO
□ 1% - FA	78%	10%		12%	76%	7%		18%	64%	14%		22%
▨ 5% - FA	88%	2%		10%	87%	2%		11%	84%	2%		13%
◇ 1%	98%	2%			98%	2%			98%	2%		
○ 5%	99%	1%			97%	3%			99%	1%		

(a)

	30				60				90			
	CO_2	H_2	CH_4	CO	CO_2	H_2	CH_4	CO	CO_2	H_2	CH_4	CO
□ 1% - FA	38%	22%		39%	45%	13%		42%	45%	16%		39%
▨ 5% - FA	77%	4%		19%	77%	5%		17%	82%	5%		12%
◇ 1%	98%	2%			97%	3%			97%	3%		
○ 5%	99%	1%			99%	1%			98%	2%		

(b)

	30				60				90			
	CO_2	H_2	CH_4	CO	CO_2	H_2	CH_4	CO	CO_2	H_2	CH_4	CO
□ 1% - FA	41%	23%		37%	41%	27%		32%	44%	35%		22%
▨ 5% - FA	59%	15%		25%	70%	19%		10%	83%	16%	0.3%	2%
◇ 1%	94%	5%	1%		90%	7%	3%		81%	8%	10%	
○ 5%	98%	2%			96%	2%	2%		96%	2%	2%	

(c)

Fig. 2: Gas composition from UV via SbWG at feedstock concentrations of 1 wt% and 5 wt% (FA: formic acid-added) (a) 300 °C; (b). 350 °C; (c) 400 °C

reduced hydrogen yield from 4.07 to 2.55 mol H_2/kg feedstock[31)].

In treatments without formic acid, for both 1% and 5% feedstock concentrations at temperatures of 300°C and 350°C, H_2 was only detected in the range of 1–3%. A significant increase was observed at 400°C after 30 min; however, the H_2 content remained within the range of 2–8%. Interestingly, with the addition of formic acid, H_2 gas production increased significantly, as seen in the 1%-FA sample, the H_2 composition had already reached 10% at 300°C and just 30 min, and reaching 14% at 90 min. The increase in the H_2 composition became more apparent when the temperature was raised to 350°C, reaching 22–39%. At 400°C, the H_2 composition was still high, although it decreased slightly, but remained within the range of 23 to 35%. The highest H_2 content was also reported in another study using the macroalgae *Padina*, reaching 17.5% at 400 °C with a longest reaction time of 90 min[9)]. The high H_2 content at elevated temperatures is attributed to supercritical conditions, which enhance the solubility of organic compounds in aqueous phase and facilitate their conversion through gasification reactions[32)]. This condition promotes free-radical reactions that favor H_2 formation beyond water's critical point[14)]. Elevated H_2 yields observed at higher temperatures may also result from the thermal decomposition of intermediates, as observed by Acelas et al. 2014[33)].

At 400 °C, the presence of formic acid led to a slight decrease in H_2 yield from *Ulva lactuca*, which contrasts with the observation at 350 °C without formic acid, where the H_2 yield was four times higher. This possibly due to the reverse water-gas shift reaction facilitated by the presence of formic acid. We also noticed that CO decreases followed by CO_2 increases at 400°C, especially when the time is prolonged to 90 min. This is likely to occur due to the equilibrium of the water gas shift reaction that has been reached, preventing further conversion of biomass into H_2 while the decrease in CO is possibly caused by the oxidation of CO into CO_2.

Another contrast between the conversion of *Ulva lactuca* into H_2 with and without formic acid is that with formic acid, the reaction tends to shift more into CO, CO2, and H_2 formation at a high temperature (400 °C) instead of methanation. In subcritical water gasification of *Ulva lactuca* without formic acid, CH4 tends to be obtained at a higher temperature (400 °C)[14)]. In contrast, the formic acid addition tends to enhance CO formation via the dehydration pathway and CO_2 and H_2 generation via the decarboxylation pathway while suppressing methanation. Another study reported an enhancement in hydrogen production in the presence of organic acids. Matsumura et al. (2018) observed that acetic acid, when added to biomass gasification under supercritical water conditions, functioned as a radical scavenger, suppressing char formation and facilitating increased hydrogen production[34)]. Formic acid likely functions as a reactant, hydrogen donor, and radical scavenger, affecting the overall reaction mechanisms that show different behaviours compared to when formic acid is absence[20)].

3.3. Effect of temperature, time, feedstock concentration and formic acid addition on hydrochar

To further investigate the impact of formic acid addition on the behavior of Ulva lactuca under hydrothermal conditions, we analyzed the ultimate composition of the hydrochar, as shown in Figure 3. This analysis focused on the hydrochar generated from the treatment using a feedstock concentration of 5% owing to the very low

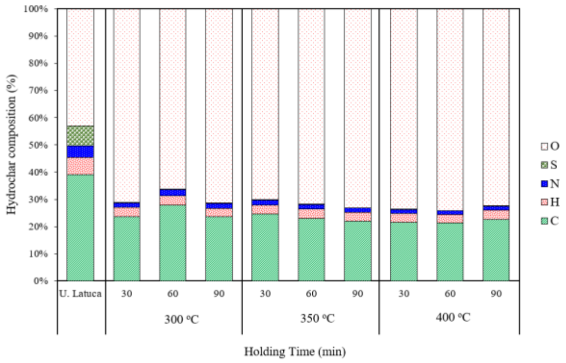


Fig. 3: Ultimate analysis characteristics of hydrochar obtained from *Ulva lactuca* via SbWG and SCWG with a feedstock concentration of 5% and formic acid addition

availability of hydrochar obtained from the treatment using a feedstock concentration of 1%. This implies that the conversion of feedstock into gaseous products when the feedstock is low is effective because water is sufficient to support the reaction[17, 27].

As shown above, the oxygen was the highest component in all the samples. This is reasonable because biomass naturally contains high amounts of oxygen. From the hydrochar perspective, especially when intended as a solid fuel, the carbon content becomes crucial as it is closely related to the calorific value. The ultimate analysis results show that oxygen content is the highest in all samples. This was expected because biomass naturally contains a high amount of oxygen[35]. From a hydrochar perspective, especially when intended as a solid fuel, the carbon content becomes crucial because of its strong correlation with the calorific value[36].

Intriguingly, this study indicated that the hydrochar obtained in the presence of formic acid exhibited a lower carbon content compared to the initial biomass feedstock. An interesting observation in our experiment was that the hydrochar produced in the presence of formic acid became extremely sticky or tar-like and was difficult to collect. This contrasts with the hydrochar from samples without formic acid, which is easily separable and nonsticky. Based on these observations, we suspect that formic acid mixed thoroughly with the formed char, making accurate carbon detection more challenging. For instance, formic acid may dilute the hydrochar, affecting the combustion efficiency during analysis and consequently lowering the measured carbon content per unit mass.

A study in 2020 on the hydrothermal co-liquefaction of biomass (lignite and lignocellulosic) reported that incorporating formic acid led the formation of by-products through secondary reactions, including levulinic acid and formic acid itself. These compounds have lower heating values than the original biomass components, potentially reducing the overall carbon content of the resulting hydrochar[37]. Furthermore, formic acid might interact with the surface functional groups of hydrochar, forming esters, carboxylates, other organic compounds, or structures that

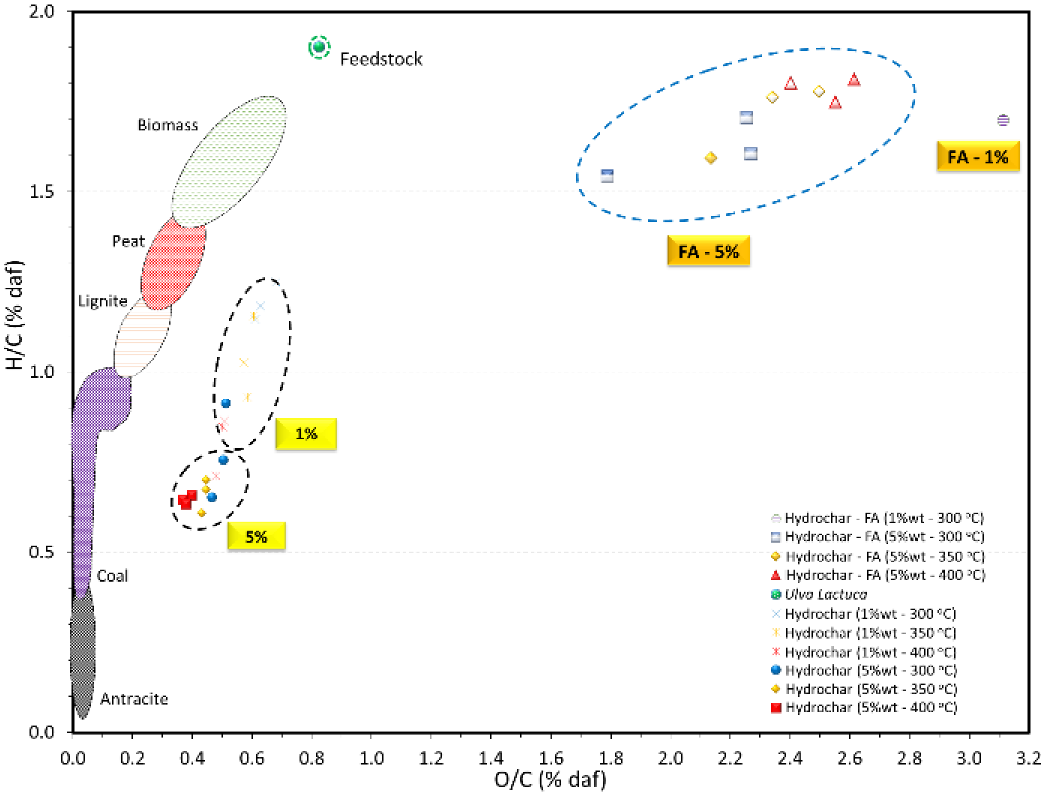


Fig. 4: Van Krevelen diagram of hydrochar (FA: formic acid added at feedstock concentration 1 wt% and 5 wt%)

interfere with carbon detection[38)]. However, these hypotheses remain tentative, as the hydrochar was washed but no additional methods were applied to ensure the complete removal of residual formic acid prior to carbon analysis, which represents a limitation of this study.

Next, both the untreated feedstock and hydrochar ultimate analysis data was plotted on a Van Krevelen diagram. As shown in Figure 4, this diagram compares the ratio of H/C and O/C, where lower values indicate the maturity of the material or a stronger resemblance to high-quality material (coal-like), which is desirable for fuel applications. In this study, the decrease in H/C and O/C ratios in the treatment with formic acid was not significant compared with the hydrochar obtained without formic acid. This suggests that formic acid promotes the gas yield and H_2 production. Formic acid can act as a reducing agent, promoting the generation of gaseous products including hydrogen during hydrothermal reactions. This may result in a reduction of the solid carbon content within the hydrochar[39)]. Thus, formic acid is not a suitable additive for hydrochar intended for use as a solid fuel, as its presence leads to lower carbon content and reduced calorific value. In addition, potential residual compounds from formic acid may be undesirable, and the resulting hydrochar was observed to be more moist and sticky, making it more difficult to handle. It is likely that when hydrochar is the target product, alternative operating conditions should be optimized, including the use of catalysts to enhance calorific value. For example, Shin et al. (2023) demonstrated that catalysts derived from inorganic metals and acids can increase the calorific value of hydrochar by 18% compared to coal for power generation[40)].

Since this study primarily focused on the gas and solid products, the liquid phase was not extensively analyzed. Further studies could explore the liquid products to provide deeper insights into how formic acid influences the behavior of *Ulva lactuca* under SbWG and SCWG conditions, which could support future applications, such as industrial-scale processes.

3.4. Kinetic modeling of *Ulva lactuca* degradation with the addition of formic acid

A kinetic model was developed to describe the degradation behavior of macroalgae during SbWG and SCWG, enabling the assessment of temperature effects on product distribution. This model follows the assumptions made by Arun et al. (2020) and Farobie et al. (2022), which suggest that a high feedstock concentration leads to incomplete degradation[14,41)].

Additionally, a kinetic model was developed to describe the yields of solid, liquid, and gas phases, based on the prior investigation conducted by Mainil and Matsumura (2019), where the kinetics of SCWG in processing palm oil mill effluent (POME)[42)]. By the equation (1) to (3), shows that the macroalgae decomposition pathways. The *Ulva lactuca* feedstock (solid) is converted into a liquid phase (k_1), while a portion of the solid biomass is directly transformed into a gaseous product (k_2). Simultaneously, the liquid intermediates further react to generating gas (k_3). The product yield variation rate can be mathematically expressed as

$$\frac{dY_{(solid)}}{dt} = -\left(k_1 + k_2\right).Y_{(solid)} \qquad (1)$$

$$\frac{dY_{(liquid)}}{dt} = k_1.Y_{(solid)} - k_3.Y_{(liquid)} \qquad (2)$$

$$\frac{dY_{(gas)}}{dt} = k_2.Y_{(solid)} + k_3.Y_{(liquid)} \qquad (3)$$

Here, t denotes the reaction time [s], k is the reaction rate constant [s^{-1}], and Y*(X)* represents the product yield *of component X*. The rate constant *k* was determined using the least-squares error (LSE) method, in line with approaches from previous studies. The fitted curve for a feedstock concentration of 1 wt% is shown in Figure 5, while the corresponding curve for the 5 wt% feedstock is shown in Figure 6. The parity plot in Figure 7 confirms the accuracy of the model, as evidenced by the high coefficient of determination (R^2), shows that the experimental data and model predictions value has a precise correlation. Moreover, the relationship between the temperature and rate constants was analyzed using the Eq (4):

$$k = A.exp^{\left(-\frac{E_a}{R.T}\right)} \qquad (4)$$

Figure 6 presents the Arrhenius plots for the SbWG and SCWG of *Ulva lactuca*. Consistent with expectations, a linear correlation was identified between ln k and the 1/T, which confirms that the reaction kinetics of the generated products conform to the Arrhenius behavior.

As summarized in Table 1, the activation energy required for SbWG and SCWG at a concentration of *Ulva lactuca* concentration of 5 wt% was higher than that required at 1 wt%. This indicates that higher energy input is required to decompose solid macroalgae at elevated concentrations compared to lower ones.

For 1 wt% feedstock concentration without formic acid, the activation energies varied from 14.36 to 34.98 kJ. When formic acid was introduced, the activation energy decreased to a range of 10.85–28.82 kJ. Similarly, at a 5 wt% concentration without formic acid, activation energies increased compared to 1 wt%, ranging from 22.27 to 45.14 kJ. However, the addition of formic acid reduced these values to a range of 15.56–37.07 kJ.

These findings confirm that formic acid lower the activation energy required for decomposition. Additionally, higher feedstock concentrations led to increased activation energy requirements, although the presence of formic acid can mitigate this effect. Among all the tested conditions,

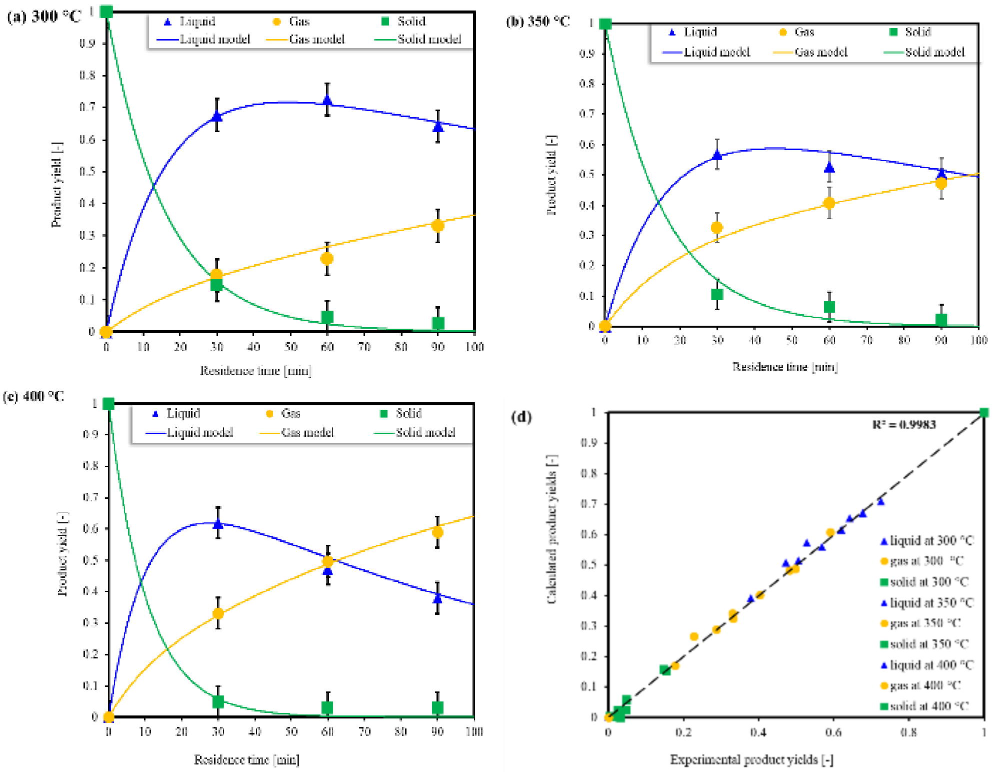


Fig. 5: Product distribution from the experiment (symbols) and kinetic model (lines) at various temperatures of (a) 300 °C, (b) 350 °C, (c) 400 °C, and (d) parity plot with the formic acid addition at a feedstock concentration of 1 wt%

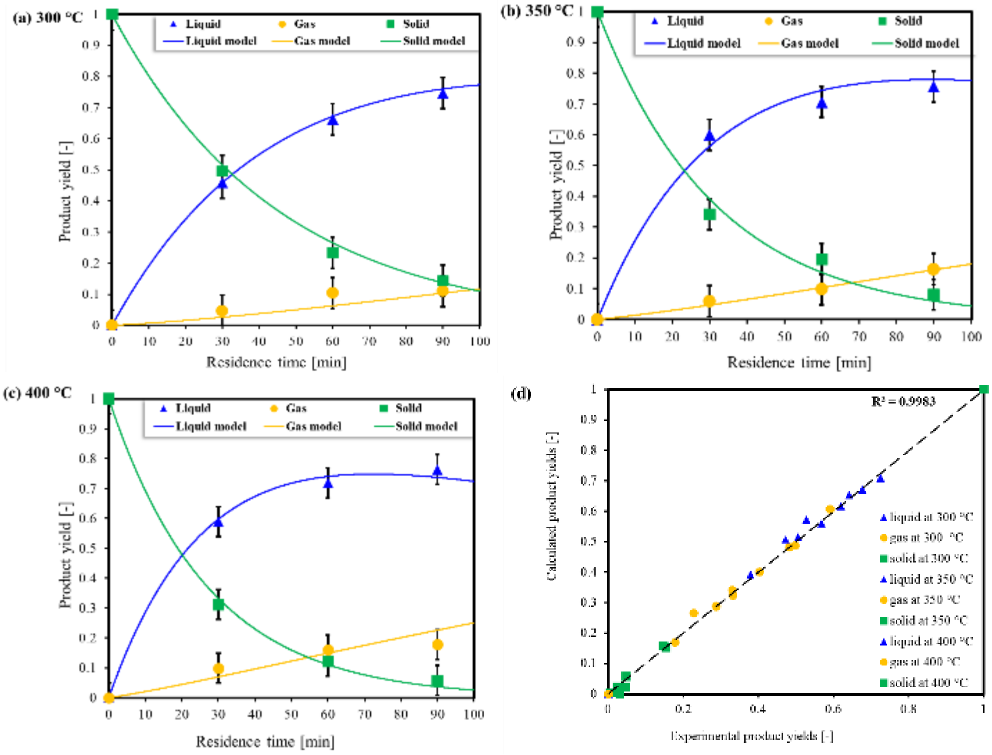


Fig. 6: Product distribution from the experiment (symbols) and kinetic model (lines) at various temperatures of (a) 300 °C, (b) 350 °C, (c) 400 °C, and (d) parity plot the formic acid addition at a feedstock concentration of 5 wt%

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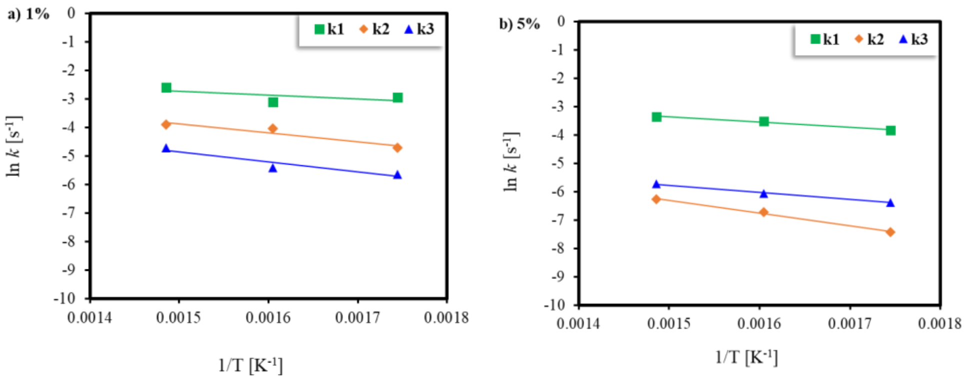

Fig. 7: Arrhenius plot of SbWG and SCWG of *Ulva lactuca* at feedstock 1wt% and 5%wt with formic acid addition

Table 1: Comparison of the activation energies (Ea) impact by formic acid addition on the for SbWG and SCWG of *Ulva lactuca* at 1 and 5wt% feedstock concentration

Reaction pathways	**Activation Energy, Ea (kJ.mol^{-1})**			
	1wt% feedstock		**5wt% feedstock**	
	Without FA	**With FA**	**Without FA**	**With FA**
k1 = S → L	14.36	10.85	22.27	15.56
k2 = S → G	29.93	26.01	45.14	37.07
k3 = L → G	34.98	28.83	23.79	20.92

the lowest activation energy range (10.85–28.83 kJ) was observed at 1 wt% feedstock concentration with formic acid.

Consistent with the observations of Farobie et al., 2022, it is notable that at low feedstock concentrations, the conversion of liquid to gas (k$_3$) requires the highest activation energy14). Conversely, at higher feedstock concentrations, the highest activation energy was observed for the conversion of solids to gas (k$_2$). This phenomenon is likely due to the dilution of macromolecules such as carbohydrates and proteins from the biomass into the liquid phase at lower concentrations, which facilitates further decomposition into non-condensable gaseous products.

4. Conclusions

This study highlights the significant impact of formic acid on syngas and hydrochar production from *Ulva lactuca* via subcritical and supercritical water gasification. The addition of formic acid was found to markedly enhance gas yield, particularly hydrogen production, which increased up to 39% at 350 °C and 90 min compared to significantly lower yields without formic acid. However, at a 5 wt% feedstock concentration, the positive effect of formic acid was less pronounced due to inefficient mixing and incomplete gasification, which limited H$_2$ production.

From a hydrochar perspective, the addition of formic acid negatively influenced fuel quality, resulting in lower carbon content, higher oxygen levels, and greater moisture retention, producing a sticky, tar-like material. The Van Krevelen analysis further revealed that the O/C and H/C ratios in hydrochar treated with formic acid remained relatively unchanged, indicating a preference for conversion into gaseous products rather than carbon-rich solids.

These findings have important implications for practical applications. The substantial increase in hydrogen content demonstrates that adding formic acid can be an effective strategy to produce hydrogen-rich syngas, supporting cleaner energy production and potentially reducing reliance on fossil-derived hydrogen. On the other hand, the deterioration in hydrochar quality suggests that formic acid is not suitable when the goal is to generate high-quality solid fuel or carbon materials. Therefore, process conditions including additive use, feedstock concentration, and operational parameters should be carefully optimized depending on whether the primary objective is to maximize renewable hydrogen generation or to produce solid biofuels with desirable carbon characteristics.

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