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Macroalgae and Microalgae as Mixed Feedstock to Produce Hydrogen Under Sub-Critical Water Gasification

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Abstract: The studies regarding macroalgae and microalgae treated under Sub-critical Water Gasification (SbWG) especially their behaviour as mixed feedstock to produce H_2 are still rarely found in the literature. Therefore, this study elaborated the characteristics of hydrogen gas production from single macroalgae *Padina* sp [P] and the impact of adding microalgae *Nanochloropsis* sp [N] or *Spirulina* sp [S] as mixed algae feedstock [NP] and [SP]. The SbWG were conducted in a high-temperature and pressure reactor at 300, 350, 400 ºC for 30, 60, and 90 minutes. It was found that the addition of microalgae to macroalgae feedstock under SbWG at 400 ºC and 90 minutes showed a negative impact on gas yield i.e 17.5% from single macroalgae feedstock [P] decreased to 4.75% and 14.34% for single feedstock [NP] and [SP] respectively. However, it is interesting that the hydrogen from the [NP] treated at 400 °C was higher (7.4%) than from single macroalgae [P] (3.5%). It is distinctly possible that the impact of microalgae addition to macroalgae feedstock in producing gas and H_2 under SbWG depends on the composition of the microalgae itself, microalgae with significant carbohydrate content leading to higher H_2 yield despite lower overall gas production compared to single feedstock of macroalgae.

Keywords: macroalgae; microalgae; hydrogen; Sub-critical Water Gasification.

1. Introduction

The impact of climate change has marked by unpredictable weather and air pollution in recent years[1)]. It is widely accepted that excessive consumption of fossil energy is the main source of this problem and that it has to be substituted with renewable energy to minimize its negative impact towards the environment. Moreover, considering fossil fuel price and its availability that is prone to be affected by the geopolitical situation[2–4)], renewable energy has become a necessity. Since Indonesia is committed to Net Zero Emission (NZE) target in 2050, this country has a strong motive to replace fossil energy using renewable energy. However, the implementation is only 12,3 % in 2023 and still far from the target (23 % in 2025)[5)]. Thus, Indonesia has to work more proactively in implementing renewable energy, including bioenergy.

Indonesia has the potential of bioenergy as much as 32

GWe. This calculated potential mostly come from terrestrial biomass such as palm oil waste, cattle dung and other crop waste[6]. On the other hand, Indonesia is an archipelagic country with various species and large amount of marine biomass resources that hasn't explored or utilized optimally[7]. Among marine biomass in Indonesia, algae has high organic content and known as a source of third-generation bioenergy with many advantages over terrestrial plants. They include the rapid growth rate, does not require land, does not require fresh water, and can decrease carbon dioxide as one of GHG emissions with more efficient photosynthesis (6-8%) compare to terrestrial biomass (1.8 – 2.2%)[8,9].

Algae are a diverse group of plant-like organisms classified under the kingdom Protista[10]. Algae can be categorized into two groups based on its size, namely macroalgae and microalgae. Macroalgae is popularly known as seaweed. It is multicellular, and visible with the naked eye. While microalgae are microscopic single cells. Naturally, both of them can grow rapidly and require only carbon dioxide and seawater. When cultivated, algae do not require special treatment; they only need water, simple salts, minerals, and sunlight[11]. However, macroalge is easier to be harvested than microalgae because of larger size[12,13].

Macroalgae and microalgae as aquatic species contain high amounts of water. Several techniques have arisen for harnessing biomass energy, covering both biochemical and thermochemical conversion processes[14]. Considering the aquatic characteristic, a thermochemical process using water is suitable to be used to convert this biomass into desired product so that drying process is avoidable. Sub-critical Water Gasification (SbWG) or hot compressed water has been known to use water as medium to dissolve biomass effectively and convert it to desired products under varied temperature between 150 to 374 °C [15–17]. Using this process, gas products can be derived containing hydrogen that can be utilized as an energy source. Hydrogen gas is known as an environmental friendly energy source because it produces water as final combustion product[18]. SbWG is also can be called with Hydrothermal Liquefaction (HTL). It uses the same principle as SbWG just with different target products. HTL usually applied to obtain bio-oil as main product that can substitute fossil oil for transport or being used directly for heat and power generation[19].

Exploration on macroalgae or microalgae conversion to hydrogen has been done in literature. One of the studies is carried out by Farobie et al, 2021[9] who found that using SbWG at elevated temperature 400 °C improved the yield of hydrogen from macroalgae *Ulva* sp 4 times larger compare to those treated at lower temperature. Studies on microalgae treated under SbWG is more limited compare to macroalgae. Instead, most of the studies focused on HTL to obtain bio-oil from microalgae. For example microalgae *Spirulina* sp was treated using HTL process at 240 – 320 °C and it was found that the bio yield could achieve optimum yield of bio oil 35.80 wt% when treated at 304 °C for 34.7 min[19]

As aquatic biomass, macroalgae and microalgae are often live co-excitingly in nature. The use of high value, co-production strategy is prospective to improve commercial implementation of biofuel in integrated system from algae[20]. However, studies on these two types of biomass as mixture feedstock for bioenergy is still rarely found in the literature. Jin et al, 2013[21] who investigated the co-HTL of microalgae *Spirulina platensis* (SP) and macroalgae *Enteromorpha prolifera* (EP) found a positive synergistic effect depending on the reaction conditions. SP and EP was found to promote the in-situ deoxygenation of bio-oil resulting in the higher heating value of bio-oil. Another study investigated the co-HTL process involving microalgae (*Chlorella vulgaris*) and macroalgae (*Enteromorpha clathrata*). It explored the impact of varying mass ratios of mixtures on the product yield, and the distribution of nitrogen-containing compounds. The results indicated that co-HTL positively influences the enhancement of bio-oil yield, demonstrating a maximum increase of 15.0 wt%[22]. Nonetheless, to the best of our knowledge, the observation on the impact of using macroalgae and microalgae as mixed feedstock with the focus on obtaining hydrogen is not explored yet in the literature. Therefore, in this study we elaborate on the possibility of using macroalgae and microalgae to produce hydrogen under SbWG.

2. Material and methods

2.1 Materials

This study investigated two different feedstock mixtures, namely macroalgae *Padina* sp mixed with microalgae *Spirulina* sp, and macroalgae *Padina* sp mixed with microalgae *Nannochloropsis*sp. For comparison, macroalgae (*Padina* sp) and microalgae (*Spirulina* sp and *Nannochloropsis* sp) as single feedstocks were also used. *Padina* sp was obtained from Ekas Beach, Lombok Island, Indonesia, and *Spirulina* sp was obtained commercially. *Nannochloropsis* sp was cultivated for 3 weeks using the seeds obtained from the Centre for Brackish Water Aquaculture Fisheries in Jepara, Central Java, Indonesia.

2.2 Preparation and the SbWG Process

The pretreatment of feedstock was carried out by a gradual drying process. Initially the feedstock was exposed to sunlight for 1-3 days, then dried at 105°C for 3-6 hours until it reached a constant weight. Drying step in the method was carried out in order to ensure the amount of feedstock is uniform between one experiments and another so that the data can be reliable and reproducible. In the future application level in which the fundamental mechanism is already well understood, drying method can be omitted and moisture can be measured instead to calculate the yield quantitatively when necessary. Moreover, in implementation level the

presence of water within the feedstock is expected to also become the medium of SbWG.

The moisture content was then measured using a moisture determination balance (FD 660), to ensure that the feedstock exhibited a moisture content below 10%. Once the desired dryness was attained, feedstock were crushed and sieved to obtain particle size of 60 mesh (approximately 250 μm).

2.3 SbWG process

The SbWG process was applied to the feedstock using a 500-mL autoclave (Fig. 1; Parr Instrument, batch reactor model 4575) at various temperatures (300, 350, and 400 °C) and an initial pressure of 80 bar to reach a reaction pressure of 280 bar. The desired amount single feedstock *Padina sp*. [P], single feedstock *Spirulina sp*. [S], single feedstock *Nannochloropsis*sp) [N] and mixed feedstock of *Spirulina* sp with *Padina* sp [SP] and *Nannochloropsis* sp with *Padina* sp [NP] was added to distilled water to obtain a fixed of 1% wt solid loading (3 gr of feedstock in 297 mL of distilled water). According to our previous work by Farobie et al., 2022[23], in which observe the amount of solid is in inversely proportional to the gas product yield. Therefore, this lower ratio is used since our focus is to obtain gas.

The autoclave's temperature was adjusted to the reaction condition after it was purged and filled with N_2 gas, and the process was held for 30, 60, 90 minutes. The whole process is agitated at 100 rpm to ensure a uniform mixture and temperature. After holding time was achieved, the autoclave was cooled down immediately to a temperature of 50 °C. Then, volumetric gaseous products were quantified in a sampling bag using a gas meter. The component mass of gaseous was estimated using the ideal gas equation. Besides, the yield was determined by comparing the moles of components with the mass of dry feed. Apart from the gas product, the liquid and solid (hydro-char) were collected and separated by vacuum filtration.

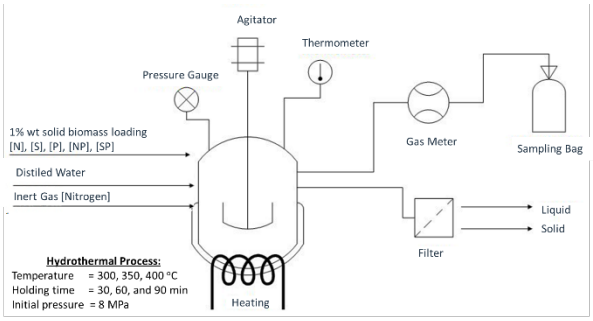


Fig. 1: Autoclave based experimental setup of SbWG process.

2.4 Characterization of Feedstock and Gas Product

The gaseous products of these experiments were analysed using a gas chromatograph (GC Bruker Scion 456) equipped with a thermal Conductivity Detector (TCD). This instrument is equipped with Shincarbon ST column 80/100 mesh. The column was heated to 100°C at 20°C/min for 12 minutes after being at 50°C for 7 minutes. Meanwhile the injector was set at 100^{O}C and the detector at 220^{O}C.

The proximate analysis involved estimating the chemical composition (carbohydrate, protein, and lipid) of algae utilized using the Food Energy – methods, 18-8-31/MU/SMM-SIG (Kjeltech) method and the 18-8-5/MU/SMM-SIG point 3.2.2 (Weilbull) method, respectively. The comparation of chemical composition of algae feedstock that used in this experiment is summarized in Table 1.

Table 1. Chemical composition of algae feedstock in the SbWG Process

Algae	Chemical composition (%)		
	Protein	Lipid	Carbohydrate
Padina sp [P]*	13.84	<0.02	46.37
Spirulina sp [S]*	63.17	4.89	13.31
Nannochloropsis sp [N][24]	43.00	30.00	35.00

*This study

3. Result and discussion

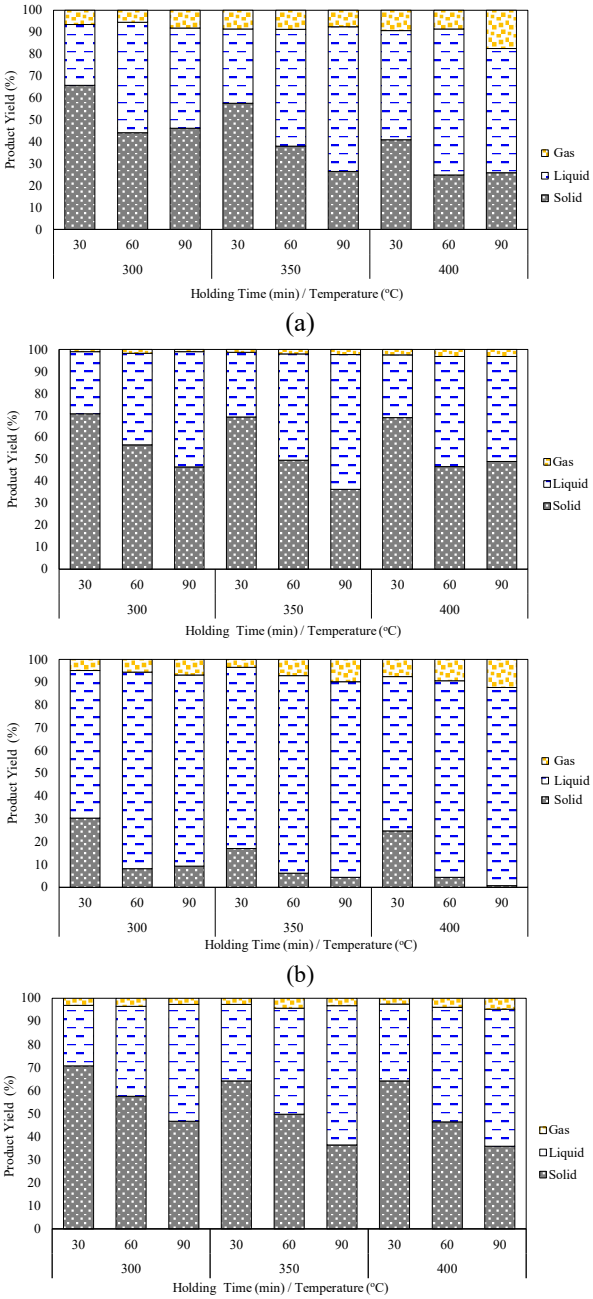
3.1 Product Distribution of SbWG Process

3.1.1 Single algae feedstocks

Figure 2 illustrates the effect of reaction conditions, specifically holding time and temperature on products distribution. Generally, there is a similar pattern of gaseous yield production for all kind of feedstock, including single feedstock [P], [S], [N], or mixed [SP], [PN]. As both the temperature and the reaction time increase, the tendency of gaseous product increases as well. The highest gas yield was obtained at the highest temperature (400ºC) and the longest reaction time (90 minutes), resulting in 3.19%, 10.03%, and 17.5% for single feedstock of [N], [S], and [P], respectively. These values increased about 3.22 times, 2.07, and 2.72 respectively compared to those gas yield obtained at lowest severity (300 °C for 30 minutes). This phenomenon can be attributed to the increased decomposition of intermediate compound such as polysaccharides, cellulose, and protein in the liquid phase at high temperature, resulting in the formation of non-condensable gas[23,25]. Furthermore, the increase in gas production is also linked to the appearance of supercritical-like characteristics in water, and its behaviour changes dramatically at near and above critical point of water (374 °C). As a result, it enables water to enhance the solubility of organic compounds, making them more accessible for gasification reactions to form gaseous products[26].

However, the highest gas yield obtained from these feedstocks were lower compare to those from other

macroalgae species as observed by Farobie et al., 2022[23] where the SbWG of U. *Lactuca* generated gas 31.10% at the same temperature range. This implies that different spesies of algae with different composition influence the gas yield in a different pattern. One reason may caused by the high mineral content of *Padina* sp that may interfere the gasification process [P][27].



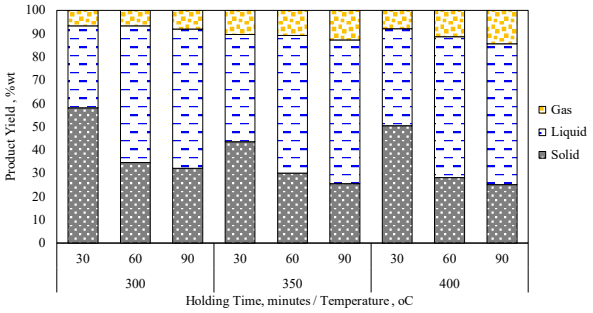


Fig. 2: Product yield of hydrothermal (a) macroalgae [P], (b) microalgae [N], [S], (c) mixed feedstock [NP], [SP]

3.1.2 Mixed algae feedstock

As for mixed feedstock, it was found that the product distribution pattern of mixed feedstock, both [NP] and [SP], is remarkably similar to that of single feedstock of each [N] and [S] respectively. However, when compared to the feedstock of macroalgae only [P], at the same temperature and reaction time (400 °C and 90 minutes), the presence of microalgae in the mixed feedstock slightly reduced gas production, from 17,5% for macroalgae alone [P] to 4.75% and 14.34% for [NP] and [SP], respectively. This is possibly because microalgae [N] and [S] contains high amount of protein, therefore the hydrophilic characteristic of protein allows the feedstock to dissolve more easily as a liquid phase in hot compressed water system instead of converted to gas[9,24]. As observed by Kruse et al., similar phenomenon was found when feedstock with high protein was gasified. The amount of gas generated by feedstock with protein is smaller compared to feedstock with fewer protein The causes could be whether protein is gasified in a lower rate compare to carbohydrates or the protein content and/or their following products become a hindrance to the degradation of carbohydrates, leading to an inhibition of gas formation[28]. Kruse et al. further investigated that when feedstock contains both carbohydrates and proteins, the degradation products of these components undergo Maillard reactions. In such reactions, free radical scavengers might be formed, which reduce the reaction rate of free radical chain reactions crucial for gas formation. Consequently, the gas yield is lower in the presence of proteins or amino acids compared to systems without these compounds[29].

On the other hand, yield of solid product showed the opposite trend compares to gas product. Most of solid products decreased significantly with increasing temperature and reaction time for all feedstocks. This outcome can be ascribed to two main factors. Firstly, a more pronounced primary breakdown of macroalgal biomass (involving carbohydrates, lipids, and proteins) occurs at elevated temperatures and prolonged reaction durations, resulting in the production of liquid and gas by-products[30] . Secondly, there a secondary decomposition of hydrochar during the carbonization process, particularly under rigorous conditions[31]. At the highest temperature

applied (400 °C), there was a significant reduction in hydrochar yield. It is likely due to the breakdown of macroalgae structure, leading to the production of liquid and gaseous phase instead of the solid phase. Similar behaviours were found in hydrothermal processed macroalgae *Ulva* sp where the yield of hydrochar decreased with reaction temperature and time[23].

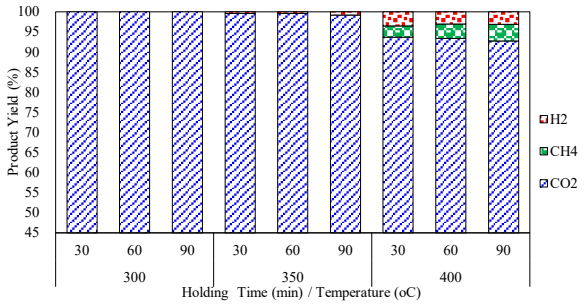
However, the solid yield for single macroalgae [P] has a slight increase from 24.8% to 26.93%, following further increased of holding time from 30 to 60 minutes at a temperature of 400 °C. Similar observation are presented by Xue et al,2016[32], that the certain compounds existing especially intermediate degradation products of biomass in the liquid phase could re-polymerize to char at high temperature and extended reaction time.

3.2 Gas Composition of SbWG Process

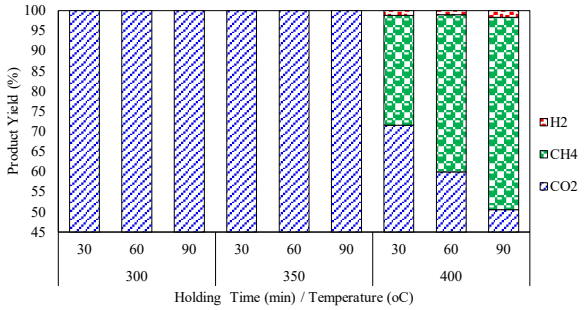
3.2.1 Single Algae Feedstock

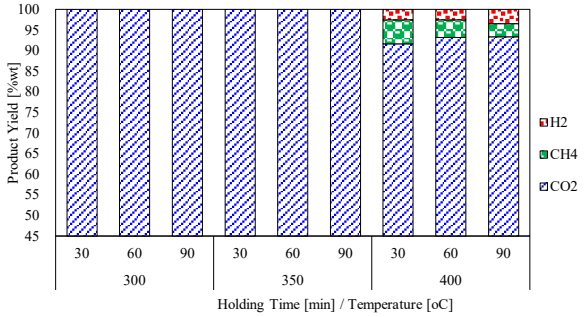
The temperature and holding time have been found to have a strong impact on the gas product composition as shown in Fig. 3. From all the feedstock type, the combustible product gas observed were CO_2, H_2 and CH_4. There was no CO present throughout the temperature range. Similar behavior was observed by Guan et al, 2012[33] and Farobie et al, 2021[23] that possibly due to the augmentation of water-gas shift and/or methanation reactions. The increase of temperature promoted hydrogen generation in all feedstocks. As we can see that at 400 °C, the hydrogen achieved the highest amount. This is likely because at high temperature above critical point of water (>374 °C), free radical reactions is more prevalent compare to ionic reaction resulting in more hydrogen formed[34]. On the other hand, the longer reaction time shows considerable improvement in hydrogen composition. This phenomenon can be elucidated by the increased decomposition of low molecular weight compounds in the liquid phase into non-condensable gas, a process that intensifies at higher temperatures and prolonged reaction durations[23].

In overall view, the gas composition from SbWG of single algae feedstock namely [P], [N] and [S], treated at 300 – 350 °C, contains mostly CO_2. This CO_2 was derived from decarboxylation reaction at a temperature of 300-350 °C[35]. At harsher conditions (400 °C), the reaction was altered and favors the production of H_2 and CH_4. On the other hand, the formation of hydrogen (0.8%) from macroalgae [P] started at a lower temperature of 350 °C and achieved the highest (3.5%) at 400 °C and holding time 90 minutes. This value of H_2 is higher than those from single feedstock of S and N obtained at the same reaction condition. There are two possible reasons for this. Firstly, the H_2 generation is likely facilitated by the carbohydrate-dominant composition of macroalgae *Padina* sp (see Table 1) that is faster to be gasified compare to protein[36]. In other words, the gasification reaction enhanced H_2 production at higher temperatures by converting carbohydrate components to gaseous products via steam reforming and water-gas shift reactions. Secondly, at the most severe treatment temperature 400 °C and holding time of 90 minutes, the water is above critical temperature (>374 °C) that enables it to act as both gas and liquid properties and become a non-polar solvent to dissolve organic matter and gases, releasing H_2[37]. In addition, CH_4 was generated in the near supercritical conditions (400 °C) from most of feedstock. This may be attributed by the methanation reaction that promoted at above supercritical temperature of water as presented by Farobie et al, 2022[23].



(a)





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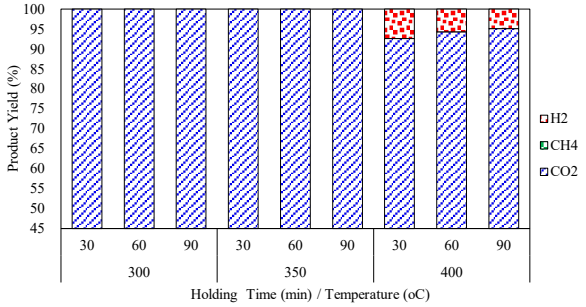
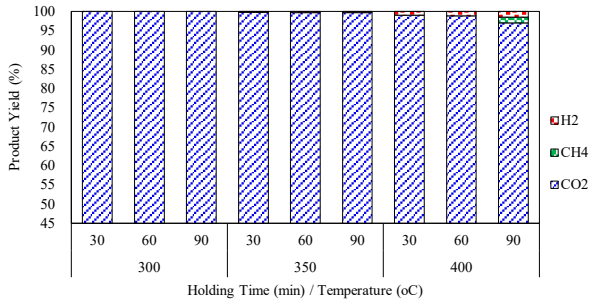




(c)

Fig. 3: Gas composition (a) macroalgae [P], (b) microalgae [N], [S], and (c) mixed algae [NP], [SP]

Interesting differences were observed when comparing SbWG using different species of microalgae [S] and [N]. Both of them only produced H_2 when the temperature was employed at 400 °C. However, as single feedstock of [N], the H_2 released is lower (1.6%) than H_2 generated from [S] (3.4%). Instead, single feedstock [N] released substantial amount of CH_4 at 400 °C. This is possibly due to the high content of lipid in *Nannochloropsis* sp (see Table 1). The high lipid content of [N] may lead to the degradation of the long-chain fatty acids and obtain the higher composition of CH_4[38]. This trend was investigated by Sherif et al., 2020[39] where the lipid content of *Nannochloropsis* sp is likely causing it to generate higher CH_4 compare to other microalgaes (*Scenedesmus* sp and *Spirulina* sp). Similarly, Brown et al, 2010[24] observed the SbWG of *Nannochloropsis* sp where the yield of CH_4 surpassed any other gas composition at high temperature.

3.2.2 Mixed Algae Feedstock

Interesting finding was investigated when we compare between the impact of using two different species of microalgae in the feedstock mixture towards the gas product. In Fig. 3 we can see that when *Nannochloropsis* sp., with its higher carbohydrate and lipid content, is used as a single feedstock, the methane composition in the resulting gas is dominant, while the hydrogen content is lower compared to *Spirulina* sp., a dominant protein feedstock, as discussed earlier. However, when *Nannochloropsis* sp. is mixed with *Padina* sp., the hydrogen composition in the gas product is higher (7.4%) or two times of H_2 from single feedstock of macroalgae *Padina* sp. alone, and five times of H_2 from mixture of *Padina* sp. with *Spirulina* sp. although the gas yield is low (4.75%) at temperature 400 °C and reaction time 90 minutes. In other words, these results indicate that although the lipid content of *Nannochloropsis* sp. is higher than that of *Spirulina* sp., when *Nannochloropsis* sp. is mixed with macroalgae, an interaction occurs, resulting in a higher hydrogen content in the [NP] mixture compared to [SP], [P], and [N]. A possible cause is that the major combustible CH_4 composition generated from *Nannochloropsis* sp. encouraged an alteration of the equilibrium methanation reaction, resulting in the formation of hydrogen ($CH_4 + H_2O \leftrightarrow CO + 3H_2$). Another possible cause is that the high composition of carbohydrate (35%) in *Nannochloropsis* sp (see Table 1) contributes to the forming of H_2 . A similar result was observed by Heeley et al., who indicated that a higher carbohydrate content in algae may enhance biomass conversion into gas, thereby facilitating higher hydrogen content[40].

In short, it is distinctly possible that the impact of microalgae addition to macroalgae feedstock in producing gas and H_2 under SbWG depends on the composition of the microalgae itself. When the microalgae mixed with macroalgae contain high carbohydrates, even though their protein and lipid contents are also high as in the case of *Nannochloropsis* sp., the impact on hydrogen production from the mixed feedstock is positive. Conversely, when the microalgae mixed with macroalgae contain high protein and low carbohydrates as in the case of *Spirulina* sp., hydrogen production from the mixed feedstock is lower. This further emphasizes that the composition of the feedstock significantly influences the characteristics of the resulting products.

3.3 Kinetic Modelling of SbWG Process

Kinetic models are crucial for obtaining the kinetic mechanisms involved in the algae decomposition during the sub-critical water gasification process[41,42]. Sub-critical water gasification products (including liquid, solid, and gas) are used to determine the kinetic, adapted from the previous study by Farobie et al., 2022[23]. To describe the decomposition process for *U. Lactuca* in catalytic sub-critical water at 300◦C – 400 °C with the irreversible reaction pathways.

In this work, the product yield from experiments was used to find kinetic parameters. The compounds yield change rate is describe by the differential rate equations: Eq. (1)–(3)

The rate of change solid yield:

$$\frac{d[S]}{dt} = -(k_1 + k_2)[S] \quad (1)$$

$$\frac{d[L]}{dt} = k_1[S] - k_3[L] \quad (2)$$

$$\frac{d[G]}{dt} = k_2[S] + k_3[L] \quad (3)$$

Integrating Eq (1-3), then solved this set of differential equations by using the given initial conditions:

$$[S^0] = \frac{W_{solid}}{W_{feedstock}};\ [L^0] = 0;\ [G^0] = 0, \qquad at\ t = 0$$

The calculated rate of change yield:

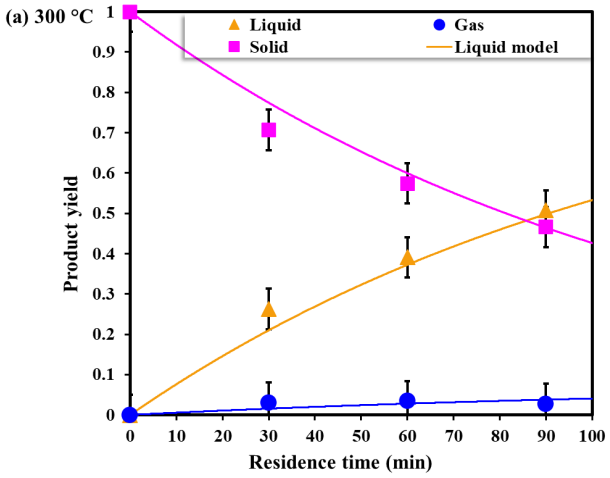
$$[S] = [S^0].e^{-(k_1+k_2).t} \quad (4)$$

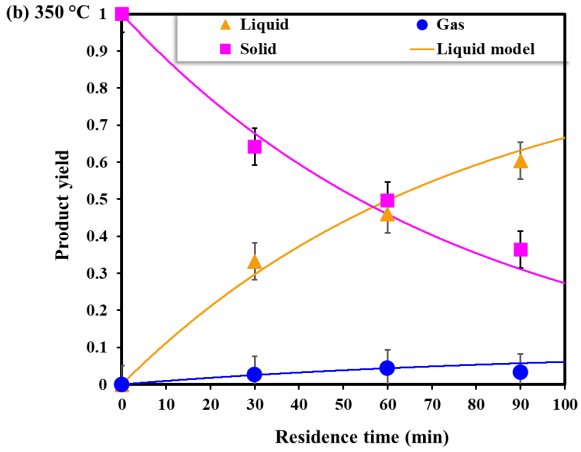
$$[L] = \frac{k_1[S^0]}{-(k_1+k_2-k_3).t}\left[\frac{e^{-(k_1+k_2-k_3).t}-1}{e^{k_3.t}}\right] \quad (5)$$

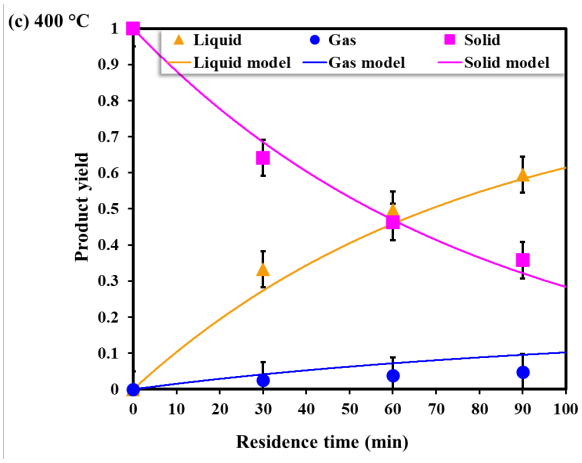
$$[G] = \frac{k_1[S^0]}{-(k_1+k_2-k_3)}\left[1 - e^{-(k_3).t}\right] + (k_2 - k_3)[S^0].\left[1 - e^{-(k_1+k_2).t}\right] \quad (6)$$

Furthermore, the kinetic rate constants (k_1, k_2, k_3) were

determined using a fitting approach by minimizing nonlinear least-squares errors between predicted values and experimental. In Fig. 4 and Fig. 5 (a)– (c) represented the results of the curve fitting, where the calculated yield product distribution is derived from equations (4)-(6) and compared to experimental data. As illustrated by the parity plot (see Fig. 4 and Fig. 5 (d), a coefficient of determination ($R^2 \geq 0{,}99$) was attained, this high fitting accuracy indicates that the developed kinetic model can represent the trends of SbWG product yields.







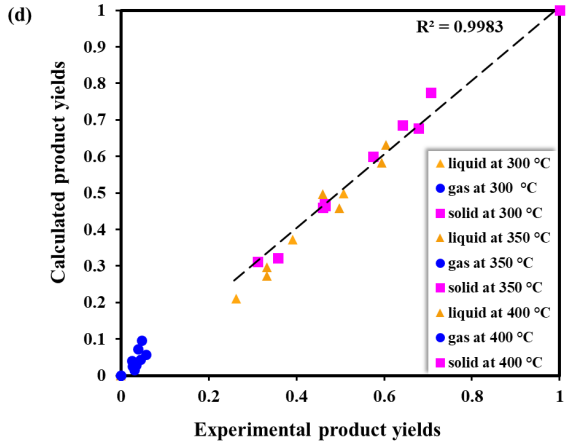
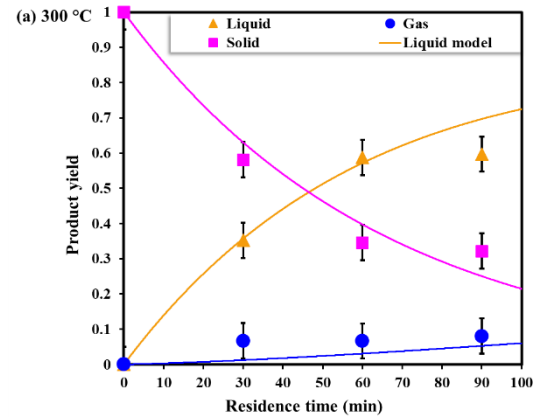
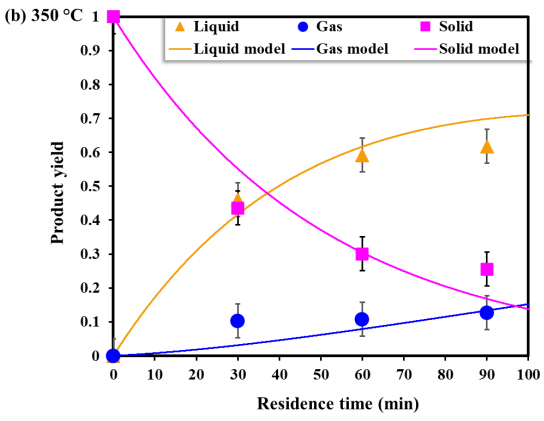


Fig. 4: Yield of product derived from kinetic model (line) and experiment (symbol) at temperature (a) 300 °C, (b) 350 °C, (c) 400 °C, and (d) parity plot for mix algae [NP]





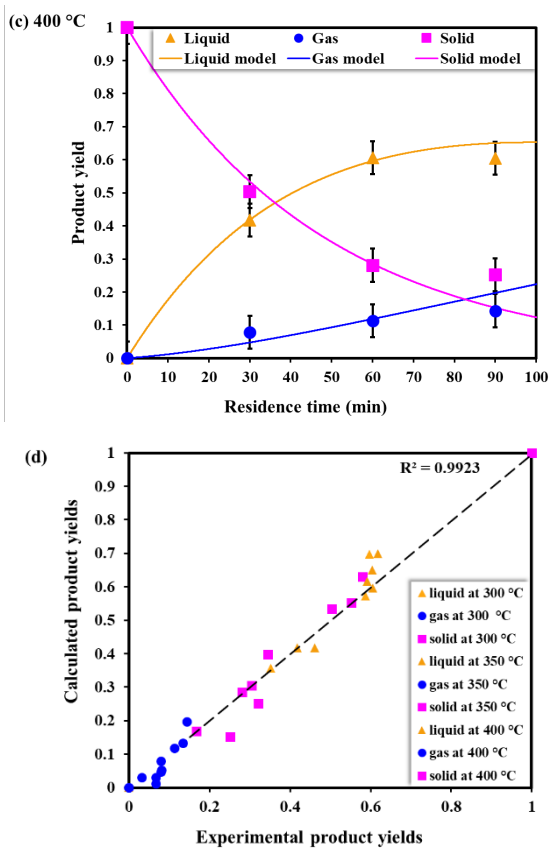
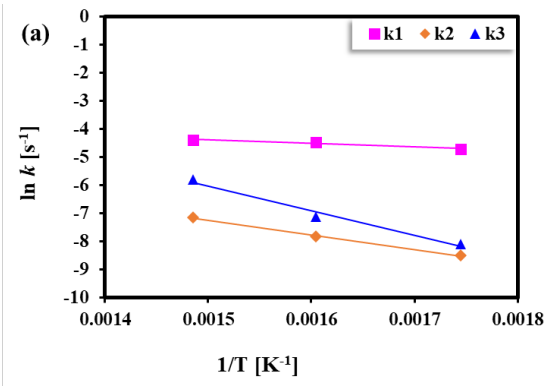


Fig. 5: Yield of product derived from kinetic model (line) and experiment (symbol) at temperature (a) 300 °C, (b) 350 °C, (c) 400 °C, and (d) parity plot for mix algae [SP]

The relevant processes activation energy (Ea) is determined by using the following Arrhenius law (Eq 7). The number of molecules involved in a chemical reaction is typically constrained by the fact that their combined kinetic energy must be greater than the activation energy at temperature T. To obtain the activation energy graphically, it is necessary to estimate numerous rate constants for the same reaction at various temperatures ranging from 300 to 400 °C, as previously mentioned.

$$k\,(T) = A\,e^{\frac{(-E_a)}{RT}} \qquad (7)$$



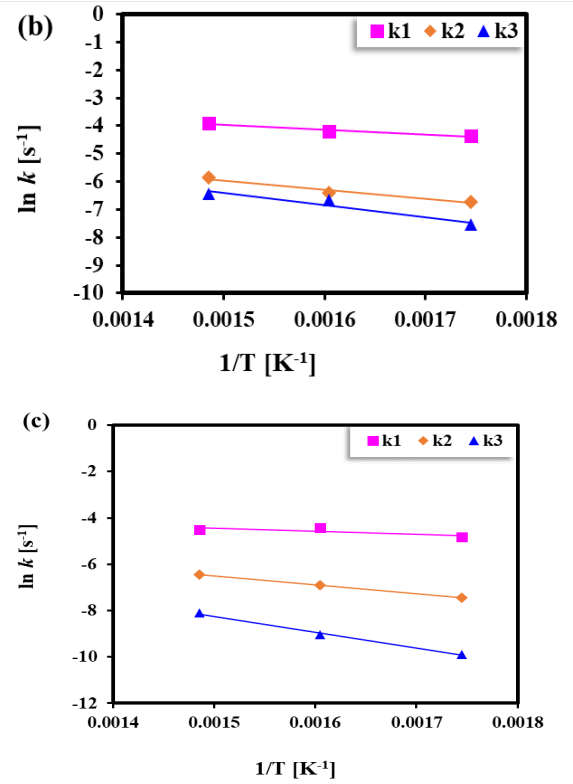


Fig. 6: Arrhenius plot of hydrothermal (a) microalgae [N], (b) macroalgae [P], and (c) mixed [NP]

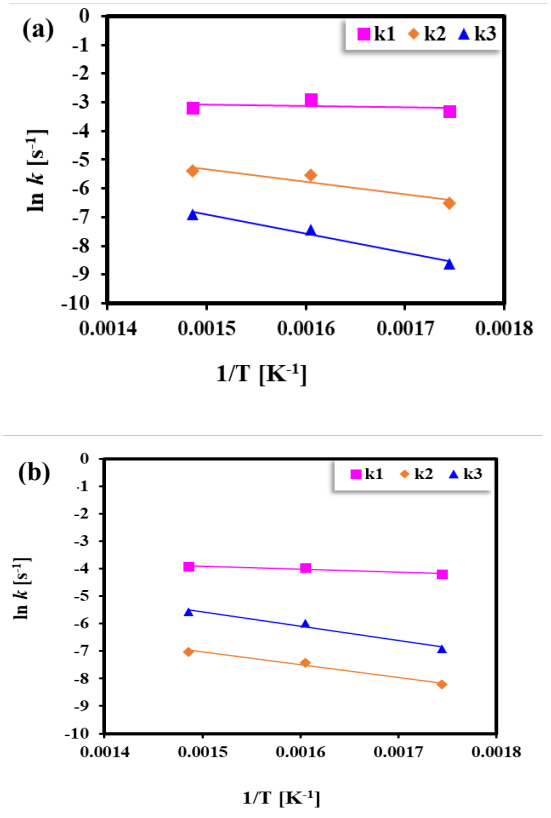


Fig. 7: Arrhenius plot of hydrothermal (a) microalgae [S], and (b) mixed [SP]

As illustrated in Fig. 6 and Fig. 7, according to the Arrhenius law, a straight line will be plotted against the inversed absolute temperature (1/T) for each kinetic rate constant. This shows that the temperature dependence of rate constants for the product produced from SbWG by various combination algae feedstock is an accurate approximation.

Table 2. Activation energies at experimental conditions: 300–400 °C; 1 wt% solid loading of [N], [S], [P], [NP], [SP]

Reaction pathway	Activation Energy, [kJ. mol $^{-1}$]				
	Microalgae		Macro -algae	Mixed	
	[N]	[S]	[P]	[NP]	[SP]
k_1 = S → L	10.59	4.21	14.46	10.86	9.15
k_2 = S → G	43.42	36.10	27.99	39.38	38.87
k_3 = L → G	73.41	55.56	36.38	57.32	43.39

As shown in Table 2, the SbWG reaction associated with k_1, k_2, and k_3 requires activation energy between 10.86 kJ mol^{-1} to 57.32 kJ mol^{-1} and 9.15 kJ mol^{-1} to 43.39 kJ mol^{-1} for mixed algae [NP] and [SP], respectively. The reaction pathway kinetics that convert from liquid to gas (k_3) has the highest activation energy required for all feedstock types, single and mixed. As reported by Farobie et al, 2022[23] there is a possibly diluted into the liquid phase of biomass macromolecule such as protein and lipid. Therefore, it is reasonable that the addition microalgae with high protein [S] or high lipid [N] content particularly enhances the kinetics of k_3 for mixed combination. In contrast, the ability of protein dilution means that less energy is needed to reach the transition state for solid to liquid (k_1) with low activation energies of 10.86 kJ mol^{-1} and 9.15 kJ mol^{-1} for mixed algae [NP] and [SP], respectively.

Moreover, the addition of microalgae as a mixture [NP] and [SP] leading to the high energy needed to decompose the solid into the gas phase directly in k_2. A higher content of recalcitrant compounds such as lignin-like substances and certain proteins that are more resistant to thermal and degradation. In contrast, macroalgae contain a higher proportion of easily degradable carbohydrates and lower amounts of resistant compounds, making their decomposition more straightforward in hydrothermal processes.

4. Conclusion

Identification of the impact of macroalgae [P] and microalgae [N], [S] as mixed feedstock [NP] and [SP] towards the production of gas particularly hydrogen and has been carried out through sub-critical water gasification. The findings show that the type of feedstock greatly influences the desired product. The gas yield of mixed feedstock has increased with increasing temperature (300 to 400^{o}C) and longer holding time (30 to 90 minutes). However, the addition of microalgae shows a negative impact on gas product yield from 17.5% for single macroalgae [P] decrease to 4.75% and 14.34% for [NP] and [SP], respectively. This possibly because microalgae [N] and [S] contain an extensive amount of protein, which is hydrophilic and dissolves more easily in hot compressed water instead of converted to gas. However, it is interesting that the hydrogen from the [NP] treated at 400 °C was higher (7.4%) than from single macroalgae [P] (3.5%). It is distinctly possible that the impact of microalgae addition to macroalgae feedstock in producing gas and H_2 under SbWG depends on the composition of the microalgae itself. When microalgae contain high levels of protein, but the carbohydrate content is also significant, then an interaction can occur and resulted in producing higher H_2 composition compared to single feedstock of macroalgae, even though with lower gas yield. On the other hand, the solid byproduct, hydrochar, can find utility as a material for solid fuel or in wastewater treatment.

The kinetics model of SbWG from mixed feedstock requires activation energy between 10.86 kJ mol^{-1} to 57.32 kJ mol^{-1} and 9.15 kJ mol^{-1} to 43.39 kJ mol^{-1} for mixed algae [NP] and [SP], respectively. The addition of high protein microalgae [N] or [S] particularly enhances the kinetics energy activation of k_3 (liquid to gas) for mixed combination algae.

Acknowledgements

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