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Torrefaction of biomass macroalga *Ulva intestinalis* using TGA

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Abstract. The torrefaction of Malaysian marine biomass specie called *Ulva intestinalis* was studied using thermogravimetric analyser (TGA). The torrefaction temperature and residence time were varied in the range of 200 – 300 ºC and 30 – 90 minutes, respectively. The chemical functional groups in the torrefied *U. intestinalis* were identified by Fourier transform infrared (FTIR). TGA results showed that the torrefaction temperature has a greater influence on the weight loss and changes in the *U. intestinalis*'s properties after the torrefaction as compared to the torrefaction time. The increased in fixed carbon (FC), and carbon (C) content and decreased in volatile matter (VM), moisture content (MC) and oxygen (O) with the severity of torrefaction reflects the improvement of calorific values for the torrefied *U. intestinalis*. Analysis of the FTIR showed that the torrefaction decreased the spectra intensity of the main functional groups (O-H, C=C, C-O and C-H) as a consequence of structural alteration within the biomass. The present findings may provide useful information for the development of industrial torrefaction processes to turn *U. intestinalis* into a carbon enrichment solid fuel.

1. Introduction

Malaysia has an extensive coastline surrounded by numerous islands thus providing an ideal habitat for the various species of aquatic organisms, including macroalgae. Due to their abundantly available, high growth rate and higher photosynthesis efficiency, macroalgae can be considered as biomass feedstock in thermochemical process reactor for biofuels productions. However, raw macroalgae having relatively low thermal values and depending on species, can have significantly high moisture, ash and sulphur content. Torrefaction is an effective approach to elevate such low quality biomass feedstock into coal-like solid fuel. Torrefaction pre-treatment of biomass is a mild thermal decomposition process under inert environment at a temperature range of 200 – 300 ºC [1], [2]. Previous studies have found that torrefaction could improve the quality of biomass raw materials by reducing the oxygen-containing functional groups, improving carbon content and high heating value, as well as enhancing the grinding performance and hydrophobicity [3], [4]. The improve in properties of the solid char after torrefaction offers better conversion efficiency in subsequent thermochemical processes such as combustion, pyrolysis and gasification. There is a significant amount of study reported the torrefaction pre-treatment of terrestrial biomass. Most these torrefaction studies use laboratory scale reactors, while for experimental pilot study or commercial plants rather include torrefaction furnaces [5], [6]. However, there are researchers who studied thermal decomposition of biomass by thermogravimetric analyser

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(TGA) to gain better understanding of the torrefaction process in a well-controlled environment [1], [2] and [7] .

The recent works of biomass torrefaction include woody Norway spruce [8] Jatropha seed kernel waste [9], olive tree pruning [10], empty fruit bunches, wood pellet and rice husks [11]. However, minimal works exists on torrefaction of marine biomass like micro- and macroalgae. Phusunti, Phetwarotai and Tekasakul [12] carried out the torrefaction of microalga *Chlorella vulgaris* in a fixed-bed tubular reactor with nitrogen inert environment atmosphere at temperature range of 150 to 300 ^{o}C and torrefaction time of 15 to 60 minutes. The results showed that torrefaction temperature has stronger influences compared to the process time on the mass yield and changes in the properties of the microalga after the torrefaction process. The same reactor type and torrefaction temperature have been used by Uemura et al. [13] in the study of torrefaction of macroalga *Laminaria japonica*. The study suggested that the major reaction during the torrefaction of this macroalgal biomass come from its alginate and the ratios of hydrogen to carbon as well oxygen to carbon are similar to trend of terrestrial biomass. In this work, torrefaction of biomass macroalgae specie that can be found in Malaysian shore, i.e. *Ulva intestinalis,*was performed using TGA. The objective is to investigate the effects of torrefaction temperature and torrefaction time on the fuel properties of resultants biochars. The results of chemical compositions and chemical functional group of *U. intestinalis* after torrefaction can be helpful for further utilization of *U. intestinalis* as biomass fuels.

2. Materials and Methodology

Sample of *U. intestinalis* was collected from Southern part of Peninsular Malaysia on August 2016. The samples were identified and catalogued at Marine Algal Reference Collection (MARC) in Central Laboratory, Universiti Malaysia Terengganu (UMT). The collected sample was washed and dried in a furnace at 60 ^{o}C for 24 hours. The sample then was milled and sieved to prepare sample size up to 120 microns. Torrefaction of about 80 – 85 mg was carried out in thermogravimetric analyser (TGA) under nitrogen flow at rate of 100 mL/min. The sample was heated up at a heating rate of 10 ^{o}C/min to three torrefaction temperature (200, 250 and 300 ^{o}C). For each torrefaction temperature, the torrefaction proceeded for 30, 60 and 90 minutes. JIS M8812 standards are used for the identification of moisture contents (MC), volatile matter (VM), and ash contents of both raw and torrefied *U. intestinalis*. The fixed carbon contents were determined by the difference, i.e. Fixed carbon content % = 100 – (MC+VM+ash). The carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) contents were determined by using Elementar, vario Macro cube CHNOS analyser. The oxygen (O) content were calculated from the difference from total and verified using the same analyser. The torrefied *U. intestinalis* were studied through Fourier transform infrared spectroscopy (FTIR) with range from 4000 to 400 cm^{-1}.

3. Results and discussion

3.1. Torrefaction process

Figure 1 shows TGA curves for torrefaction of *U. intestinalis* for three different torrefaction temperatures at three different torrefaction times. It can be observed from these curves that the torrefaction temperature of 200, 250 and 300 ^{o}C was reached around 17, 23 and 27 minutes after the heating process started from room temperature, respectively. The first decomposition region can be seen earlier as the time has increased from 0 to around 16 minutes, in which the temperature at this time has risen up to 180 ^{o}C. As many researchers agreed, in this region, biomass normally discharges its moisture content and some of its light volatile compounds [7], [14], [15], [4]. Then, the volatile compounds continue to be released in the second region until the torrefaction process end after 30, 60 and 90 minutes. According to Kim, et al. [16], the thermal degradation of macroalgae at temperature range of 180 to 270 ^{o}C is corresponds to decomposition of carbohydrates within the macroalgae.

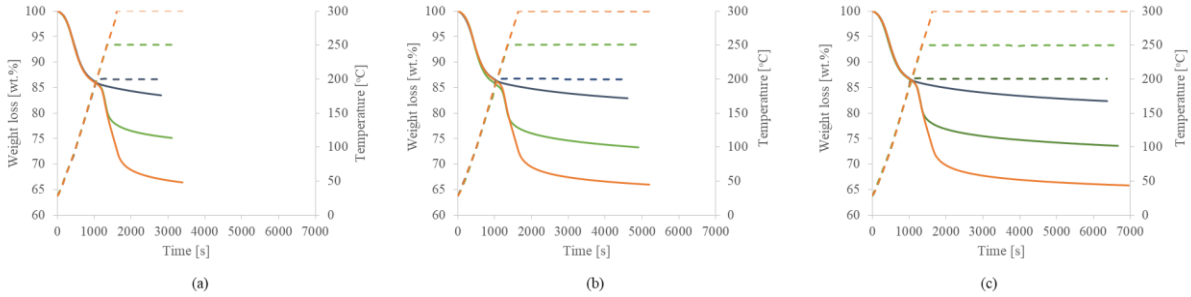


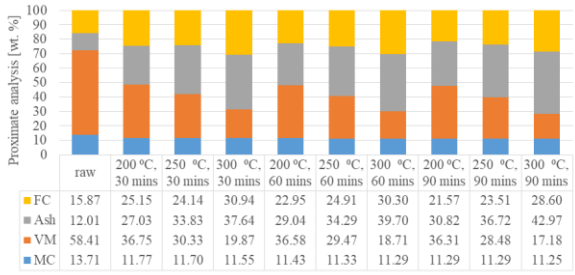
Figure 1. Thermogravimetric profiles for torrefaction of *U. intestinalis* at torrefaction temperature 200, 250 and 300 °C at time of (a) 30 mins, (b) 60 mins, and (c) 90 mins.

Figure 1 (a) to (c) also indicates that weight loss of *U. intestinalis* increases significantly with torrefaction temperature, which is to around 17, 27, and 34 wt.% for temperature of 200, 250, and 300 °C, respectively. This trend is almost similar for all torrefaction time considered in this study, indicating torrefaction time have unnoticeably influence on the thermal decomposition of *U. intestinalis*.

3.2. Proximate and ultimate analysis

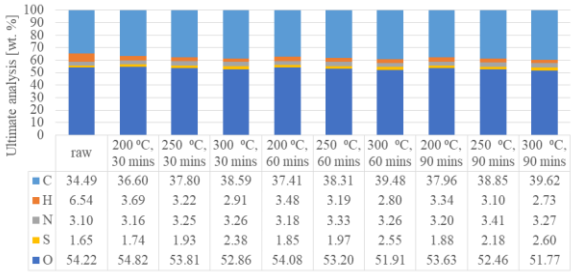
The results of proximate and ultimate analysis for raw and torrefied *U. intestinalis* are shown in Figure 2 (a) and (b), respectively. It can be seen that the torrefaction temperature exerts a significant effect on the properties of *U. intestinalis*. The VM of raw *U. intestinalis* was 58.41% and decreased by ~20% when torrefied at 200 °C. With the increase in temperature from 200 to 300 °C, the VM decreased rapidly from in the range of 7 to 11%. The increased in torrefaction time cause only a very small reduction of VM content. Meanwhile, the initial FC of *U. intestinalis* was increased by ~6 to 7% when torrefied at 200 °C and was increased at an average of 3 to 4% for every increment of 50 °C in the torrefaction temperature. However, the FC content decreased at an average of 1 to 2% when the torrefaction time extended from 30 to 90 minutes. The decrease of VM is a consequence of devolatilization, while the increase in FC of *U. intestinalis* can be attributed to the carbonization and thermal cross-linking reactions during the torrefaction process [2], [17]. The ash content in the torrefied *U. intestinalis* increased roughly 15% at temperature of 200 °C and residence time of 30 minutes. Ash content further increased to about 7 and 4% at temperature of 250 and 300 °C, and to 1 and 2% for residence time of 60 and 90 minutes, respectively. The initial MC in *U. intestinalis* was about 13.71%. The MC then was decreased around 2% with the increase in torrefaction temperature and residence time up to 300 °C and 90 minutes, respectively. The decrease in MC after torrefaction is in consistent with the weight loss presented by TGA curve in Figure 1.

The results of ultimate analysis exhibits that the C content in *U. intestinalis* was increased about 3% when being torrefied at 200 °C for 30 minutes and was increased at an average of 1% for every increment of 50 °C and 30 minutes in the torrefaction temperature and residence time, respectively. According to Granados et al. [18], the increase in C content has a significant increase in calorific value of the biochar. The H content of *U. intestinalis* was lessened to 3.69% from 6.54% when torrefied at 200 °C for 30 minutes. Further improved the torrefaction temperature and residence time cause only slightly decrease of the H content. The O content change a bit at the torrefaction temperature at 200 °C, and merely decreased at average of 1% when torrefaction temperature increased for 250 and 300 °C. Meanwhile, the increased in torrefaction residence time cause less than 1% decreased of O content. The reduction of H and O content with torrefaction temperature is due to the increased release of volatile compounds that consist of O and H content and thus in agreement with the reduction in VM content as discussed for proximate analysis. The S content for the raw *U. intestinalis* was 1.65%. At lower temperature of 200 °C and different resident times, the changes in S content was marginal around 0.09 to 0.23%; however, increasing the temperature to 250 and 300 and residence time to 60 and 90 minutes increased the S content between 0.14 to 0.58%. Lastly, the changes in torrefaction temperature and residence time slightly change the N content of *U. intestinalis*, in the range of 0.06 to 0.31%.



	raw	200 °C, 30 mins	250 °C, 30 mins	300 °C, 30 mins	200 °C, 60 mins	250 °C, 60 mins	300 °C, 60 mins	200 °C, 90 mins	250 °C, 90 mins	300 °C, 90 mins
FC	15.87	25.15	24.14	30.94	22.95	24.91	30.30	21.57	23.51	28.60
Ash	12.01	27.03	33.83	37.64	29.04	34.29	39.70	30.82	36.72	42.97
VM	58.41	36.75	30.33	19.87	36.58	29.47	18.71	36.31	28.48	17.18
MC	13.71	11.77	11.70	11.55	11.43	11.33	11.29	11.29	11.29	11.25

(a)



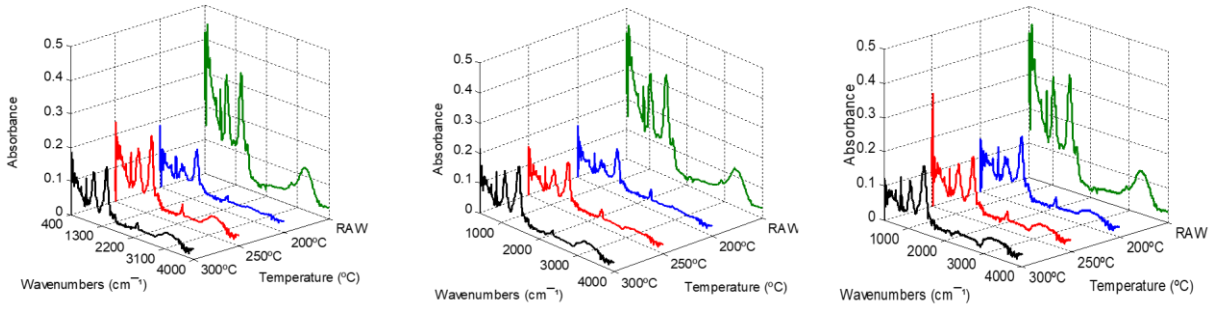
	raw	200 °C, 30 mins	250 °C, 30 mins	300 °C, 30 mins	200 °C, 60 mins	250 °C, 60 mins	300 °C, 60 mins	200 °C, 90 mins	250 °C, 90 mins	300 °C, 90 mins
C	34.49	36.60	37.80	38.59	37.41	38.31	39.48	37.96	38.85	39.62
H	6.54	3.69	3.22	2.91	3.48	3.19	2.80	3.34	3.10	2.73
N	3.10	3.16	3.25	3.26	3.18	3.33	3.26	3.20	3.41	3.27
S	1.65	1.74	1.93	2.38	1.85	1.97	2.55	1.88	2.18	2.60
O	54.22	54.82	53.81	52.86	54.08	53.20	51.91	53.63	52.46	51.77

(b)

Figure 2. Mass *U. intestinalis* before, during and at the end of torrefaction

3.3. Fourier transform infrared analysis

The changes of torrefied *U. intestinalis* functional group with the increase of torrefaction temperature and residence time were studied by FTIR and the spectra are presented in Figure 3. There are no obvious deviations in the functional group with the severity of torrefaction, but torrefaction process did weakened or removed some of the functional group. In the spectrum of raw *U. intestinalis*, the broad band at 3100 – 3600 cm^{-1} is ascribed to the O-H stretching and indicates the presence of alcoholic, hydroxyl and phenolic groups involved in hydrogen bonds and certain carbohydrates [19] [18]. This band disappeared after torrefaction temperature of 200 ºC for residence time of 30 and 60 minutes, but remained with reduce in intensity for other torrefaction conditions. According to Xin et al. [14], the reduction of O-H stretching band with the increase in severity of torrefaction can be attributed to a dehydration reaction and water evolved during the torrefaction process. A small peak at around 2900 cm^{-1} is attributed to C-H stretching of aliphatic groups methyl, methylene, or methane (CHal) in the lignin [18] was observed in the raw *U. intestinalis* but disappeared due to the heat treatment of torrefaction. The disappearance indicates the breaking of the weak bonds between the C and H atoms of the alkyl groups [20]. The C=C stretching peak which initially detected at 1623 cm^{-1} was also removed by the torrefaction process. The peak at 1465 cm^{-1} represented bending of C-H in some amorphous polysaccharides of lignin and cellulose [18]. Increase in torrefaction temperature and residence time decreased the intensity of this peak. C-O stretching bands originating from alcohol, phenols, ester or ethers observed between 1000 and 1300 cm^{-1}. The depletion or removal of peaks in this range after torrefaction is in agreement with the decrease in H and O content discussed in ultimate analysis [21]. In the raw *U. intestinalis*, the peak of 856 cm^{-1} which can be associated to aromatic C-H bending appeared. The absence of this peak in the torrefied *U. intestinalis* is replaced with aromatic C-H bending at slightly higher wavelength, around 910 cm^{-1}.



(a) (b) (c)

Figure 3. Comparison of FTIR spectra between raw and torrefied *U. intestinalis* at (a) 30 min, (b) 60 min and (c) 90 min residence time.

4. Conclusions

Thermal decomposition behaviours during torrefaction as well as the changes in compositions and functional groups of *U. intestinalis* at different temperature and residence time have been studied. The increased in weight loss of *U. intestinalis* was more pronounced when the torrefaction temperature

increases over a longer torrefaction residence time. This in consistent with the improvement in FC content and decline of VM and MC content with the increased in torrefaction severity. The C content in the torrefied sample increased slightly with increase in torrefaction while that of O and hydrogen decreased. This can improved the calorific value of the torrefied *U. intestinalis*. Functional groups of O-H and C=C were removed while C-O and C-H either reduced in intensity or removed after the torrefaction process. The level of torrefaction severity gave almost no changes to these function groups.

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