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Bio-oil production by pyrolysis of *Azolla filiculoides* and *Ulva fasciata* macroalgae

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ABSTRACT

BACKGROUND AND OBJECTIVES: In this study, the characteristics of bio-oil samples produced through slow pyrolysis of two different macroalgae, i.e. *Azolla filiculoides* and *Ulva fasciata*, at optimized conditions were determined and compared.

METHODS: For this purpose, the effects of temperature (300-500 °C), carrier gas flow rate (0.2-0.8 L/min), and heating rate (10-20 °C/min) on the final bio-oil production were optimized using response surface methodology established by a central composite design.

FINDINGS: The highest bio-oil yield from *U. fasciata* (34.29%) was obtained at the temperature of 500 °C, nitrogen flow rate of 0.2 L/min, and heating rate of 10 °C/min. As for *A. filiculoides* feedstock, the highest bio-oil yield (30.83%) was achieved at the temperature of 461 °C, nitrogen flow rate of 0.5 L/min, and heating rate of 20 °C/min. Both bio-oil samples contained saturated and unsaturated hydrocarbons. However, the average hydrocarbon chain length was relatively shorter in *U. fasciata* bio-oil (C4-C16) than in bio-oil from *A. filiculoides* (C6-C24). Although both bio-oils had almost identical heating values, the *U. fasciata* bio-oil showed more appropriate properties, i.e. lower viscosity and density. Furthermore, the energy recovery from *U. fasciata* pyrolysis was calculated as 56.6% which was almost 1.5 times higher than the energy recovery from *A. filiculoides* pyrolysis.

CONCLUSION: The results indicated that *U. fasciata* bio-oil, with its superior characteristics, could be proposed as a promising candidate for application in diesel-based automotive industries.

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INTRODUCTION

Pollution of the environment, over-reliance on non-renewable traditional fuels, shortage in fossil fuel supply, and global warming are among the great challenges in the world (Lam *et al.,* 2019). To maintain sustainability and meet current energy demands, production of renewable energy and neutral fuels seems to be imperative (Ho *et al.,* 2014). Among various alternatives, biomass has gained considerable attention as a renewable energy resource to replace the conventional fossil fuels, due to its potential for stable energy supply and inherent nature of being environmentally friendly (Akia *et al.,* 2014; Zeng *et al.,* 2013). However, due to several issues associated with some of these resources, there is a strong motivation to develop biofuel production from non-agricultural food crops (Ahmad *et al.,* 2011; Correa *et al.,* 2017; Suganya *et al.,* 2016). In this context, algae can provide a potentially renewable source for biofuel production due to their fast growth rate, efficiency in CO_2 biofixation, ability to grow in non-arable lands and non-potable water, no competition with agricultural food/land, and higher areal productivity compared to traditional/terrestrial sources (Kositkanawuth *et al.,* 2014; Pourkarimi *et al.,* 2020; Ullah *et al.,* 2015). Algae resources can be converted to environmentally friendly biofuels such as bio-oil (biodiesel), biohydrogen, bioethanol, biomethane, and many other bio-based products (Javed *et al.,* 2019; Ortigueira *et al.,* 2015). Among the techniques developed for biomass conversion, such as fermentation, transesterification, hydrothermal liquefaction, and gasification, pyrolysis has been known as an efficient and popular technology for biofuel production because of its simplicity, product diversity, operating at relatively mild conditions, cheapness, and potential to be used in industry (Isahak *et al.,* 2012; Lin *et al.,* 2014). This technique involves thermal degradation of organic components under a non-oxidative environment by which biomass resources can be converted to the carbon-rich solid residues (bio-char), liquid products (bio-oil) and gaseous products (syngas) (Jahirul *et al.,* 2012). The yields and compositions of pyrolysis products depend considerably on the type and composition of the feedstock, pyrolysis type, and operating conditions (Azizi *et al.,* 2018). Considerable efforts have been made to study the pyrolysis behavior of algae biomass (Francavilla *et al.,* 2015; Grierson *et al.,* 2009; Pan *et al.,* 2010). Recently, macroalgae have received much attention as promising sources for biofuel production owing to their availability, high growth rate, and high photosynthesis efficiency (Choi *et al.,* 2017). Azolla is a small aquatic fern growing very fast and is widely found at the surface of Anzali wetland in north of Iran (Sadeghi *et al.,* 2014). *Ulva fasciata*, belonging to the family Ulvuceue, is a green macroalga that proliferates fast and occurs abundantly worldwide (Khan and Hussain, 2015). This macroalga is usually detrimental to local ecosystems and economy as it can change the biological and physicochemical properties of aquatic ecosystems (Sadeghi *et al.,* 2013). Therefore, its proper utilization can be considered as a good strategy to tackle with the environmental issues associated with its high distribution. More importantly, the usage of macroalgae as potential sources of renewable bioenergy would pave the way for energy security in the country, mitigate the worldwide challenges related to fossil fuels scarcity and global warming, and improve the economy by creating more job opportunities (Chang *et al.,* 2018). Some studies have focused on biofuel production from Azolla and Ulva species using the pyrolysis process (Biswas *et al.,* 2017; Ma *et al.,* 2020; Pirbazari *et al.,* 2019; Zhang, 2017). Biswas *et al.,* (2017) investigated the effect of temperature range 300-450 °C on pyrolysis of water rich *Azolla pinnata* in a glass reactor using carrier gas nitrogen flow rate of 50 ml/min and heating rate of 25 °C/min. They finally reached the maximum bio-oil yield of 38.5% at 400 °C. Moreover, Ma *et al.,* (2019) studied the capacity of bio-oil production from water rich Ulva prolifera in a fixed bed reactor and obtained the maximum bio-oil yield of 38.5% at 400 °C and carrier gas nitrogen flow rate of 30 ml/min. However, these studies primarily focused on the effects of one or more process variables on quality and yield of bio-oil using the conventional methods. Response surface methodology (RSM) is a statistical method widely applied in modelling and optimization of the processes (Bobadilla *et al.,* 2017). In contrast to conventional methods, RSM can consider the effects of independent variables and their interaction on the response while keeping the number of experiments minimized. In this way, it saves the time and experimental costs of the production process. The present study aimed to study the simultaneous effects of three experimental parameters (temperature, carrier gas flow rate, and heating rate) on slow pyrolysis of two types of natural macroalgae, *Azolla filiculoides* (*A. filiculoides*) and *Ulva fasciata* (*U. fasciata*), in order

to achieve efficient biofuel production. To optimize the effects of process variables on bio-oil yield, a statistical analysis was performed using the RSM. The central composite design (CCD) of experiments was employed to develop the corresponding mathematical response surface equations. To the best of authors' knowledge, no study yet has been done on pyrolysis of Azolla or Ulva by RSM considering the optimal condition of the process. It should be noted that the authors will consider the experimental analysis of the mentioned parameters and cost analysis of bio-oil production through pyrolysis of *Azolla filiculoides* and *Ulva fasciata* in their future work. This study has been carried out in Biofuel Research Laboratory, Caspian Faculty of Engineering, College of Engineering, University of Tehran, Rezvanshahr, Iran during 2017-2019.

MATERIALS AND METHODS

Biomass preparation

Freshwater macroalga *A. filiculoides* was collected from Anzali wetland located in the northern part of Iran, and marine green alga *U. fasciata* was harvested from Makran Sea located at the southeast of Iran. Both macroalgae were harvested during the summer of 2019. The collected samples were thoroughly washed and dried under sunlight for 10 h. Afterwards, they were dried in an oven at 70 °C for 2 h. The feedstock was then pulverized by a grinding mill and sieved to an average particle size of 500-1000 µm. The ultimate analysis was performed using a Thermo Finnigan-CE Instruments Flash EA 1112 series elemental analyzer. The lipid and protein contents were determined by Soxhlet-extract method and Kjeldehl method, respectively. Moreover, the moisture and ash contents were obtained through ASTM E 1756 and ASTM E 1755, respectively. The obtained results are summarized in Table 1.

Experimental setup

The experimental system had three main parts: pyrolysis reactor (4), reformer (10), and condenser (11) (Fig. 1). The pyrolysis reactions were performed in a lab-scale fixed-bed reactor made of a stainless steel tube (23-cm long, 7.8-cm internal diameter) which was placed inside an electrical furnace (5). The stainless steel-made reformer had a length of 20 cm and diameter of 14 cm. The volumes of the pyrolysis reactor and the reformer were 1 and 0.45 L, respectively. The pyrolysis process was performed without using a catalyst in the reformer. Before pyrolysis, nitrogen (1) was fed into the system as an inert carrier gas with a controlled flow rate using a mass flow controller (3). The regulator (2) set the output gas pressure to 1 atm. An electric furnace was used to heat the reactor, and a K-type thermocouple connected with a temperature-controller system (8) was applied for measuring the temperature and controlling the heating rate. The algal feedstock (6) was loaded into the sample boat (7) inside the reactor. After completing the reaction, the pyrolysis products including biochar, bio-oil, and bio-gas were collected in the reactor, condenser (11-13), and gas bag (14), respectively.

Experimental procedure

To perform each experiment, 14 g dried biomass was placed in the reactor. Before the pyrolysis experiment, the nitrogen gas was passed through the system with a flow rate of 100 mL/min for 30 min to eliminate oxygen. The samples were heated from room temperature to different temperatures (300-500 °C) according to the designed heating rates (10 - 20 °C/min) and the nitrogen gas flow rates of 0.2-0.8 L/min. The reactor was kept at the desired temperature for 30 min. At the end of each run, the system was turned off and allowed to cool down to room temperature and then the solid fraction (bio-char) was collected from the reactor. The liquid phase (bio-oil) generated from the cooling down of condensable gases was collected in a falcon (13), weighed, and stored for further analysis. The non-condensable gases were stored

Table 1: Chemical composition and ultimate and proximate analyses of *A. filiculoides* and *U. fasciata* biomass samples

Element	Ultimate analysis					Biochemical composition			Proximate Analysis				HHV (MJ/kg)
	C	H	N	S	O[a]	Protein	Carbohydrate[b]	Lipid	Moisture	Volatiles	Fixed carbon[c]	Ash	
Azolla	42.5	7.12	3.15	0.12	47.11	18.34	56.38	6.98	10.90	75.38	6.32	7.40	16.13
Ulva	34.5	7.02	1.88	2.27	54.33	15.9	51.26	2.23	9.87	56.80	12.59	20.74	12.20

[a] Calculated by difference: % O = 100 - C - H - N - S
[b] Calculated by difference: % Carbohydrate = 100 - lipid - protein - ash – moisture.
[c] Calculated by difference: Fixed carbon = 100 - volatile - moisture – ash.

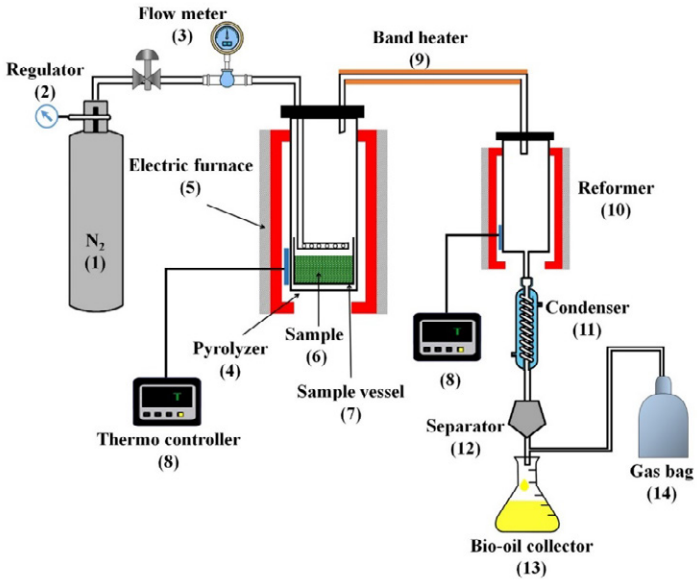

Fig. 1: Schematic representation of the pyrolysis experimental setup

Table 2: Variables and their levels used in the central composite design

Factor	Symbol	Levels				
		-α [a]	-1	0[b]	+1	+α [a]
Temperature (°C)	T	268	300	400	500	532
Carrier gas flow (L/min)	Q	0.1	0.2	0.5	0.8	0.9
Heating rate (°C/min)	H	9	10	15	20	22

[a] Axial points are equal to ±1.682 unit.
[b] Central point.

in a gas bag. All the experiments were performed in duplicates and the average values were reported. Finally, the pyrolysis performance was evaluated by measuring each fraction yield according to Eqs. 1-3 (Biswas *et al.*, 2017).

$$\text{Bio}-\text{oil yield, wt. \%} = \frac{\text{mass of bio}-\text{oil (g)}}{\text{mass of feed (g)}} \times 100 \quad (1)$$

$$\text{Bio}-\text{char yield, wt. \%} = \frac{\text{mass of bio}-\text{char (g)}}{\text{mass of feed (g)}} \times 100 \quad (2)$$

$$\text{Bio}-\text{gas yield wt. \%} = 100\% - (\text{Bio}-\text{oil yield, wt. \%} + \text{Bio}-\text{char yield, wt. \%}) \quad (3)$$

Experimental design

An experimental design combined with the RSM was used to optimize the pyrolysis process and minimize the number of experiments required. The experimental data and response surfaces were analyzed using the software package Design-Expert 11 trial version. A CCD was applied to evaluate the effects of three important factors, including temperature (T), carrier gas flow rate (Q), and heating rate (H), on bio-oil yields of *A. filiculoides* and *U. fasciata*. The variable ranges for the three parameters were determined based on previous studies and experimental setup specifications. Each independent variable was coded as high and low levels (+1 and -1, respectively) and the ranges were selected based on previous experiences. The factors and their variation levels are presented in Table 2.

The total number of experimental runs (N), suggested by CCD methodology, was calculated based on equation $N = 2^f + 2f + N_0$, where *f* is the number of variables, and N_0 is the replicate number of the center point. Therefore, 20 experimental runs (randomized) derived from three factors and six center points were

conducted to investigate and optimize the variables effecting the bio-oil yield (Table 3). The relationship between the response (*Y*) and experimental variables (x_i, x_j) can be predicted by a quadratic polynomial model as presented by Eq. 4.

$$Y = \beta_0 + \sum_{1}^{3} \beta_i x_i + \sum_{i,j,j=2}^{3} \beta_{ij} x_i x_j + \sum_{1}^{3} \beta_{ii} x^2 \quad (4)$$

Where, β_0, β_i, β_{ij}, and β_{ii} represent the intercept, linear, interaction and quadratic coefficients, respectively. The significance of the predicted models was evaluated using the analysis of variance (ANOVA) with 95% confidence level.

Analysis

To evaluate the thermal decomposition characteristics of the algal samples, the thermogravimetry analysis (TGA) and the derivative thermogravimetry analysis (DTGA) were performed using the Perkin Elmer TG/DTA STA 6000 model. The samples were heated from 30°C to 900 °C at a constant heating rate of 10 °C/min under N_2 atmosphere. The chemical composition of bio-oils was analyzed by an Agilent 7890-5975c gas chromatography-mass spectrometry (GC-MS) instrument. The separation was performed on a UA-5 column (30 m × 0.25 mm ID × 0.25 µm film thickness). Helium (> 99.999%) was employed as a carrier gas at a flow rate of 1.0 mL/min. The initial oven temperature was set at 40 °C for 10 min, and later it was increasing to 300 °C at a rate of 10 °C/min, and finally held at 300 °C for 30 min. The injection volume of the samples was 0.5 µL. Some of the important qualitative parameters of the produced bio-oils, such as cetane number (CN), iodine value (IV), density, and viscosity, were specified based on the results obtained by GC-MS analysis and Biodiesel Analyzer version 2.2 software tool. The higher heating value (HHV) was obtained according to Dulong's formula, using Eq. 5 (Pourkarimi *et al.,* 2019).

$$HHV\left[\frac{MJ}{kg}\right] = 0.338*C + 1.428*\left(H - \frac{O}{8}\right) + 0.095*S \quad (5)$$

Where, *C*, *H*, *O*, and *S* are the weight percentages of carbon, hydrogen, oxygen, and sulfur, respectively. The energy recovery (ER) was determined according to Eq. 6 (Babich *et al.,* 2011).

$$Energy\ Recovery\left(ER\right) = \frac{HHV_{bio-oil} \times m_{bio-oil}}{HHV_{biomass} \times m_{biomass}} \times 100 \quad (6)$$

Where, $m_{bio\text{-}oil}$ and $m_{biomass}$ are the weights of bio-oil and biomass, respectively.

Table 3: Central composite design arrangement and responses for Azolla and Ulv

Run No.	T (°C)	Q (L/min)	H (°C/min)	Bio-oil, wt. (%)		Bio-char, wt. (%)		Bio-gas, wt. (%)	
				Azolla	Ulva	Azolla	Ulva	Azolla	Ulva
1	400	0.5	22	27.86	23.93	44.29	50.07	27.86	26.00
2	400	0.5	15	29.57	25.91	41.43	50.36	29.00	23.73
3	532	0.5	15	23.79	31.36	37.21	45.71	39.00	22.93
4	300	0.2	20	15.36	21.12	48.29	53.93	36.36	24.95
5	500	0.8	20	27.86	27.00	37.71	46.57	34.43	26.43
6	268	0.5	15	18.71	18.29	56.57	58.21	24.71	23.50
7	500	0.2	10	21.71	34.43	44.00	49.00	34.29	16.57
8	400	0.5	15	30.64	26.86	42.21	50.36	27.14	22.79
9	400	0.5	15	28.07	26.43	43.29	50.79	28.64	22.79
10	400	0.5	15	29.29	26.00	40.71	50.57	30.00	23.43
11	400	0.5	9	26.43	25.90	42.86	50.00	30.71	24.10
12	300	0.8	10	13.29	21.29	51.14	52.43	35.57	26.29
13	400	0.5	15	28.14	26.21	42.07	50.43	29.79	23.36
14	400	0.9	15	18.86	23.00	45.00	49.57	36.14	27.43
15	500	0.8	10	18.36	29.50	37.36	47.71	44.29	22.79
16	300	0.2	10	21.07	22.43	51.86	59.00	27.07	18.57
17	400	0.1	15	24.64	27.71	43.00	50.29	32.36	22.00
18	300	0.8	20	15.57	19.29	60.86	52.86	23.57	27.86
19	400	0.5	15	30.00	25.29	40.00	50.29	30.00	24.43
20	500	0.2	20	26.43	31.50	44.14	48.57	29.43	19.93

RESULTS AND DISCUSSION

Biomass characterization

The results of chemical composition, ultimate and proximate analyses of the two macroalga samples have been shown in Table 1. According to the elemental analysis, the contents of C (42.5%) and H (7.12%) were higher in *A. filiculoides* than in *U. fasciata* (34.5 % C and 7.02% H). The carbon contents in both samples were higher than the carbon contents previously reported for green tide algae such as *U. fasciata* (25.64%) (Trivedi *et al.,* 2013), *Enteromorpha clathrata* (32.65%) (Wang *et al.,* 2013), and *Cladophorpha linum* (26.0%) (Bird *et al.,* 2011). The higher quantities of C and H and lower oxygen content in *A. filiculoides* led to a greater HHV, compared to *U. fasciata*. The higher HHVs obtained in this study can be comparable with the higher HHVs reported for other macroalgae, such as *Cladophora glomerata* (Norouzi *et al.,* 2016), *Laminaria japonica* (Choi *et al.,* 2015), *Enteromorpha clathrata* (Wang *et al.,* 2013), and *Porphyra tenera* (Bae *et al.,* 2011), ranging from 12 MJ/kg to 16 MJ/kg. *A. filiculoides* showed a higher nitrogen percentage (3.15%) compared to *U. fasciata* (1.88%), probably due to its higher protein content. Based on the proximate analysis, *A. filiculoides* macroalga had a low ash content of about 7.40 wt%, while *U. fasciata* had a high ash content of 20.74%. The ash content in Ulva was in the rang of the ash content previously observed in green algae *Ulva prolifera* (24.46%) (Ceylan and Goldfarb, 2015), brown algae *Saccharina japonica* (20.21%) (Kim *et al.,* 2012) and red macroalgae *Gracilaria gracilis* (19.98) (Francavilla *et al.,* 2015). Moreover, *A. filiculoides* had a higher volatile matter content (75.38%) compared to *U. fasciata* (56.80%). High volatile matter resulted in high efficiency in conversion of feedstock to products. The chemical composition analysis indicated that both macroalgae contained low amounts of lipid (<7%). However, the high contents of protein and carbohydrates as well as good volatile matters in both macroalgae made them suitable for bio-oil production through pyrolysis process.

Model analysis of CCD

Yields of pyrolysis products of *A. filiculoides* and *U. fasciata* based on the designed experiments with CCD have been presented in Table 3. It could be seen that the highest bio-oil yield for *A. filiculoides* (30.64%) was obtained at the temperature of 400 °C, heating rate of 15 °C/min, and N_2 flow rate of 0.5 L/min (experiment 8). Meanwhile, pyrolysis of *U. fasciata* at the temperature of 500 °C, heating rate of 10 °C/m, and N_2 flow rate of 0.5 L/min (experiment 7) led to the highest bio-oil yield (34.43%). Compared to the highest biochar yield for *A. filiculoides* (60.86%) (experiment 18), the highest biochar yield for *U. fasciata* (59%) (experiment 16) was observed at the same temperature (300 °C) but at lower heating rate and N_2 flow rate. The maximum syngas yields produced from the pyrolysis of *A. filiculoides* and *U. fasciata* were found to be of 44.29% (experiment 15) and 27.86% (experiment 18), respectively. The results revealed that the bio-oil yields of both biomasses enhanced with the increase of temperature to a certain point and then decreased at higher temperatures. According to Biswas *et al.* (2017), the maximum bio-oil yield of Azolla (38.5 wt.%) was achieved at the temperature of 400 °C, but the bio-oil yields decreased at the temperatures above 400 °C. Zhang (2017) and Ma *et al.* (2020) also reported that the bio-oil yield of *Ulva prolifera* improved with the increase of temperature and then gradually decreased at higher temperatures. It is generally believed that temperature is one of the significant factors affecting the bio-oil yield, since biomass depolymerization is extended with the increase of temperature. However, further increase of temperature above the specified optimum point does not usually lead to an improved bio-oil production. Two mechanisms can reduce the bio-oil production at high temperatures: 1) the secondary decomposition of pyrolysis vapors into non-condensable gases, which leads to the generation of more gaseous products; and 2) the repolymerization reaction of cracked species at high temperatures, which results in char formation (Pan *et al.,* 2010).

Analysis of variance

The results of ANOVA for bio-oil yields of *A. filiculoides* and *U. fasciata* are summarized in Table 4. According to the results, both models, with p values less than 0.0001, were significant. Besides, the lack of fit (LOF) values of 2.42 and 1.99 for *A. filiculoides* and *U. fasciata*, respectively, confirmed that the LOFs had no significant relationship with the pure errors and the models fitted well with the responses. The quality of fit of the models was also tested by determination coefficients (R^2, adjusted-R^2, and adequate precision). The R^2-values implied that the data variabilities for bio-oil yields of *A. filiculoides* and *U. fasciata* were 96.89% and 98.18%, respectively. Moreover, the good

agreement observed between the predicted R^2 values (Azolla = 0.8022, Ulva = 0.9639) and the adjusted R^2 values (0.9410, 0.9734) indicated the well-fit of the experimental data with the predicted values. The adequate precision ratios greater than 4 (16.130 for Azolla and 37.540 for Ulva) represented the adequate model discrimination. Based on the data analysis rendered by multiple regression analysis, a quadratic model and an interactive model (2FI) were suggested by the software for *A. filiculoides* and *U. fasciata*, respectively, as the satisfactory response surface models to fit the experimental data. The model terms are significant at $p < 0.05$. For *A. filiculoides*, all terms (A, B, C, AC, BC, A^2, and B^2), except AB and C^2 interactions, were significant model terms, while for *U. fasciata*, A, B, C, and AB variables, with p values less than 0.05, had significant effects on the bio-oil yields. The final predicted models for the bio-oil yield of *A. filiculoides* (AOY%) and *U. fasciata* (UOY%) were expressed using Eqs. 6 and 7:

$$AOY\% = +29.16 + 3.11\,A - 1.49\,B + 1.17\,C + 2.21\,AC + 1.60\,BC - 4.32\,A^2 - 3.96\,B^2 \quad (7)$$

$$UOY\% = +25.68 + 4.84\,A - 1.62\,B - 1.00\,C - 0.8064\,AB \quad (8)$$

The sign of the coefficient (+ or -) determines the direction of the relationship between the related

Table 4: Analysis of variance (ANOVA) for the bio-oils derived from Azolla and Ulva

Source	Sum of squares [a]	Df[b]	Mean square[c]	F-value [d]	p-value[e] Prob > F	Significance
Azolla:						
Model	556.63	9	61.85	34.67	< 0.0001	Significant
A [f]	111.38	1	111.38	62.43	< 0.0001	
B [g]	25.64	1	25.64	14.37	0.0035	
C [h]	15.42	1	15.42	8.64	0.0148	
AB	3.98	1	3.98	2.23	0.1661	
AC	38.91	1	38.91	21.81	0.0009	
BC	20.43	1	20.43	11.45	0.0070	
A^2	131.40	1	131.40	73.65	< 0.0001	
B^2	113.07	1	113.07	63.38	< 0.0001	
C^2	7.98	1	7.98	4.47	0.0606	
Residual [i]	17.84	10	1.78			
Lack of fit [j]	12.63	5	2.53	2.42	0.1770	Not significant
Pure error [k]	5.21	5	1.04			
Cor total [l]	574.47	19				
Ulva:						
Model	316.32	6	52.72	116.81	< 0.0001	Significant
A [f]	268.81	1	268.81	595.59	< 0.0001	
B [g]	30.23	1	30.23	66.99	< 0.0001	
C [h]	11.51	1	11.51	25.49	0.0002	
AB	5.20	1	5.20	11.53	0.0048	
AC	0.5618	1	0.5618	1.24	0.2848	
BC	0.0086	1	0.0086	0.0191	0.8921	
Residual [i]	5.87	13	0.4513			
Lack of fit [j]	4.47	8	0.5582	1.99	0.2325	Not significant
Pure error [k]	1.40	5	0.2804			
Cor total [l]	322.19	19				

[a] Sum of the squared differences between the average values and the overall mean.
[b] Degrees of freedom.
[c] Sum of squares divided by d.f.
[d] Test for comparing term variance with residual (error) variance.
[e] Probability of seeing the F-value if the null hypothesis is true.
[f] Temperature.
[g] Carrier gas flow rate.
[h] Heating rate.
[i] Consists of terms used to estimate experimental error.
[j] Variation of the data around the fitted model.
[k] Variation of the response in replicated design points.
[l] Totals of the whole information corrected for the mean.

variable and the response. The positive sign shows that the variable and the response move in the same direction. Conversely, when the variable and response move in opposite directions, the sign of the coefficient is negative. The strength of each relationship is measured by the absolute value of the related coefficient. As expressed by Eqs. 6 and 7, for both models, temperature variable (A) was the most effective factor in the bio-oil yields of both *A. filiculoides* and *U. fasciata* with absolute coefficients of 3.11 and 4.84, respectively. However, the effect of this variable on *U. fasciata* was greater. Gas flow rate (B) had almost the same negative effect on the bio-oil yields of both species. It meant that the bio-oil yields decreased with the increase of N_2 flow rate. The heating rate (C) had a positive effect on the bio-oil yield of *A. filiculoides* and a negative effect on the bio-oil yield of *U. fasciata*.

Response surface plots

The response surface plots of the models were used to display the graphical representation of the interactions between process variables and their effects on the bio-oil yield. These plots illustrated the effect of any two experimental factors while maintaining the third factor fixed at its central level. The related response surface plots of responses versus significant factors are shown for *A. filiculoides* and *U. fasciata* in Figs. 2 and 3, respectively. As illustrated in Fig. 2a, the bio-oil yield of *A. filiculoides* increased with the increase of temperature and carrier gas flow rate, and reached the maximum level at the temperature of 400 °C and gas flow rate of 0.5 L/min. However, a prolonged heating rate had a little positive effect on the response (Fig. 2b-c). Moreover, increase of temperature had a positive effect on the bio-oil yield of *U. fasciata*. In fact, it reached the maximum level at the temperature of 500 °C when the other two factors were kept fix at their lowest values (Fig. 3a-b). However, increase of carrier gas flow rate and heating rate led to the decrease of the bio-oil yield of *U. fasciata* (Fig. 3c).

Optimization of conditions

To achieve the optimum conditions for both *A. filiculoides* and *U. fasciata*, the maximum bio-oil yield was considered as the optimization goal. Based on the overall desirability function value of 1.0, the optimized conditions were determined as: a) temperature = 461 °C, heating rate = 20 °C/min, and N_2 flow rate = 0.5 L/min for *A. filiculoides*; and b) temperature = 500 °C, heating rate = 10 °C/min, and N_2 flow rate = 0.2 L/min for *U. fasciata*. Under these conditions, the optimum predicted bio-oil yields were found to be 30.64% and 34.43% for *A. filiculoides* and *U. fasciata*, respectively. Verification of the predicted results was performed by pyrolyzing of both biomasses under the optimized conditions. The experimental bio-oil yields of *A. filiculoides* and *U. fasciata* were obtained to be 30.83% and 34.29%, respectively. The results revealed that the experimental bio-oil yields were closely correlated with their model predictions with an error of 0.58% and 0.41% for *A. filiculoides* and *U. fasciata*, respectively. These obtained results were not in agreement with results reported by Biswas *et al.* (2017) for *Azolla pinnata* and by Ma *et al.,* (2019) for *Ulva prolifera* who reached the maximum bio-oil yield (38.5%) at the temperature of 400 °C.

Thermogravimetric analysis of Azolla and Ulva

Thermogravimetry and DTG analyses of *A. filiculoides* and *U. fasciata* seaweeds (Fig. 4a and 4b) were conducted to study the weight loss profile associated with thermal degradation, oxidation, and reaction with other gases. Fig. 4a and b showed the weight loss curves obtained from the pyrolysis of *A. filiculoides* and *U. fasciata*. The thermal degradation curves exhibited three different stages of weight loss. The first stage of weight loss occurred at temperatures lower than 180 °C, due to the removal of the adsorbed water in the macroalgae samples (Mulligan *et al.,* 2010). For *A. filiculoides* (Fig. 4a), the second and the third decomposition stages took place at 300 and 460 °C, corresponding with the decompositions of carbohydrates (cellulose, hemicellulose) and proteins, respectively (Kim *et al.,* 2013). This reflected that the pyrolysis of *A. filiculoides* should be performed at temperatures ranged 300-460 °C, since the thermal decomposition of organic matters occurred in this range. For *U. fasciata*, the main weight loss occurred in the second stage at the temperature of 220 °C, due to the volatilization of cellulose and hemicellulose materials present in the *U. fasciata* structure (Fig. 4b). Compared to the second stage, a lower DTG peak height in the third stage at the temperature of 630 °C was mainly due to the thermal degradation of lignin materials (Roslee and Munajat, 2018; Wu *et al.,* 2014). The lignin components in the biomass have a main role in biochar production. Higher lignin content produces more biochar yields and higher amounts

of ash. According to Ma *et al.* (2020), temperature range of 300-500 °C was responsible for main product formation via the pyrolysis of *U. fasciata*. This was in line with the results obtained in the present study.

Properties of biomasses and produced bio-oils

Table 5 shows the elemental contents of the bio-oils derived from the pyrolysis of *A. filiculoides* and *U. fasciata.* Both algae oils had high amounts of nitrogen (3.25% and 4.21%), and sulfur contents of 0.11% and 2.15 %. Moreover, the S/N ratio for Ulva oil (0.66) was much more than the S/N ratio for Azolla oil (0.02). The large nitrogen contents and S/N ratios observed in the bio-oils might be attributed to the initial biomass compositions which were mainly composed of chlorophyll and proteins (Miao *et al.*, 2004). Therefore, further treatment seemed to be necessary before using the bio-oils for combustion to reduce the nitrogen and sulfur contents, especially for Ulva bio-oil because of its high S/N ratio. The reported results also showed that the *U. fasciata* pyrolytic bio-oil had lower carbon contents and higher

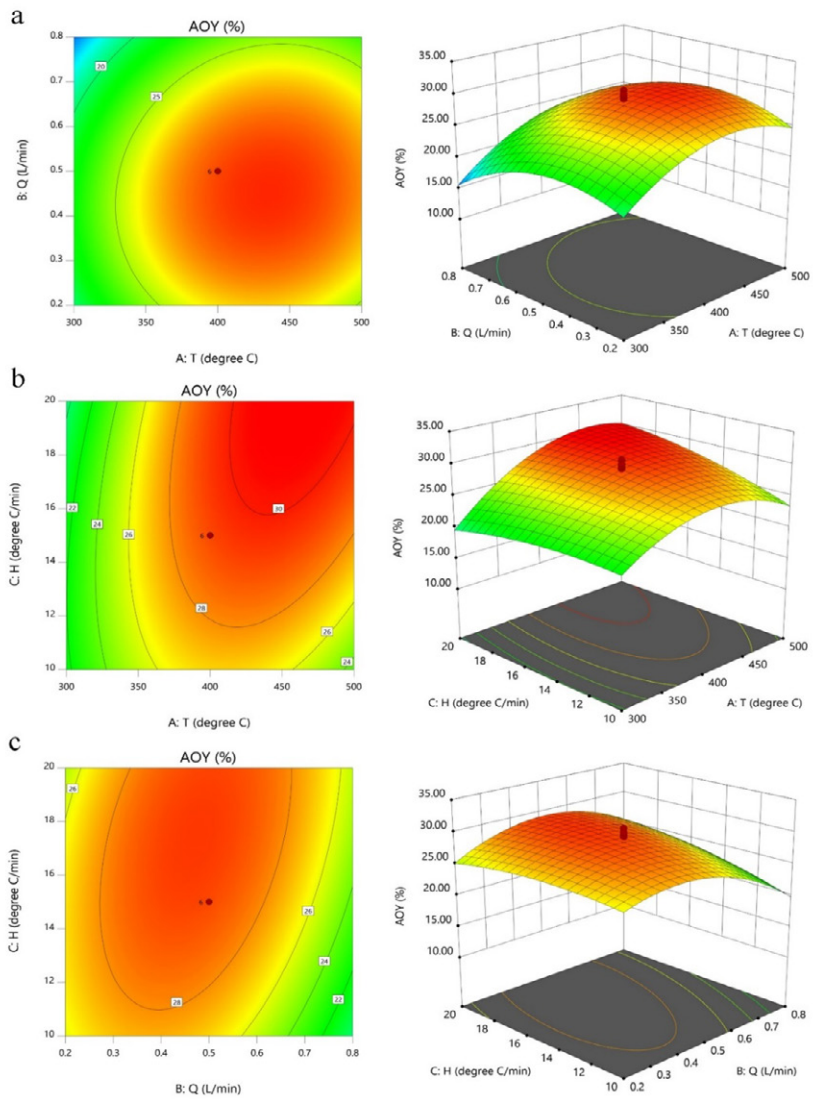

Fig. 2: The contour plots and three-dimensional response surface plots for the bio-oil yield of *A. filiculoide*: (a) temperature versus carrier gas flow rate; (b) temperature versus heating rate; (c) carrier gas flow rate versus heating rate

oxygen amounts, compared to *A. filiculoides.* This was probably due to the high concentration of cellulose in the initial *U. fasciata* biomass with a considerable amount of oxygen (Morris, 2011). The HHV, calculated by the Dulong's formula (Eq. 5), and the ER values of both bio-oil samples are also presented in Table 5. The bio-oil from *A. filiculoides* exhibited higher HHV values than the bio-oil derived *U. fasciata*, due to its relatively large carbon and hydrogen concentrations and small oxygen content. Conversely, the ER value of *U. fasciata* bio-oil (54.6%) was remarkably higher than that of *A. filiculoides* bio-oil (36.8%), because of its higher bio-oil yield and $HHV_{bio\text{-}oil}/HHV_{biomass}$ ratio. Table 6 shows the elemental contents of the biochars derived from the pyrolysis process. It can be seen the carbon amounts in both biochars are higher than the carbon amounts of both bio-oils. Moreover, the carbon amount of the Azolla-based biochar is higher than that of the Ulva-based biochar.

Effect of pyrolysis temperature on the products yield

As already discussed, temperature was the most effective parameter involved in the pyrolysis yields of *A. filiculoides* and *U. fasciata* biomasses. To compare

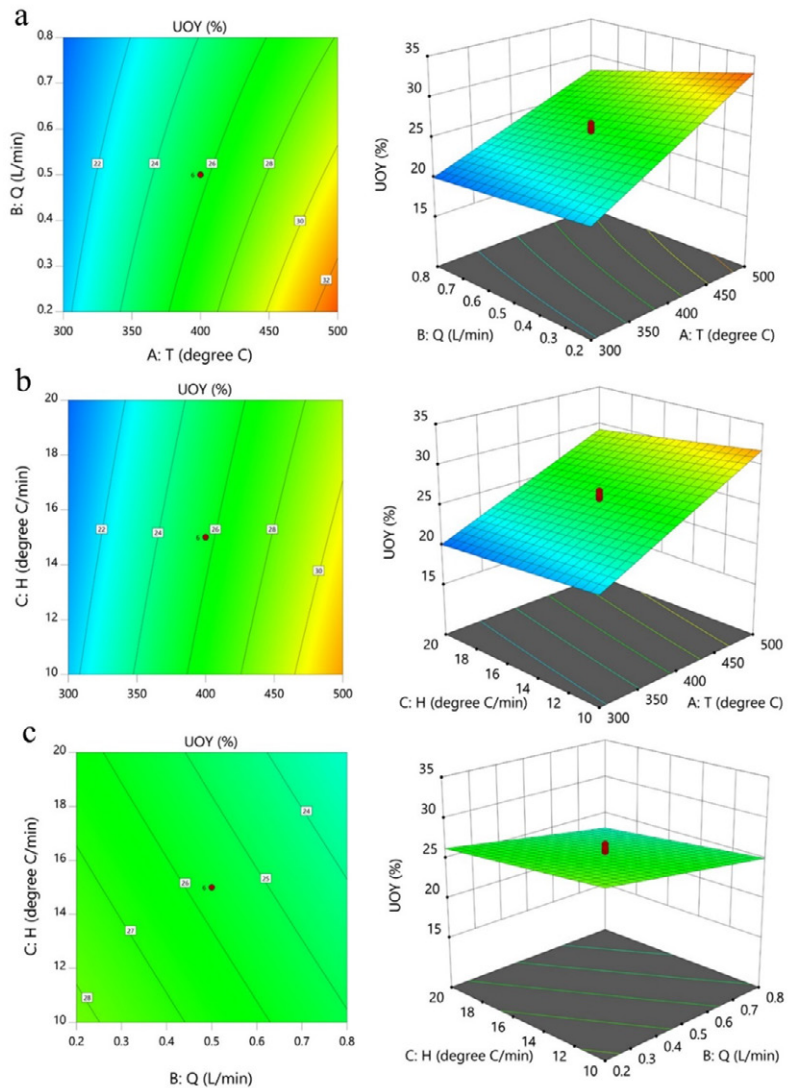

Fig. 3: The contour plots and three-dimensional response surface plots for the bio-oil yield of *U. fasciata*: (a) temperature versus carrier gas flow rate; (b) temperature versus heating rate; (c) carrier gas flow rate versus heating rate

the pyrolysis behavior of the two macroalgae, the yields of bio-oil, biochar, and biogas were investigated at several temperatures (268, 300, 400, 500, and 532 °C) (Fig. 4c and e). According to the presented plots, the bio-gas yields of *A. filiculoides* were significantly larger than those of *U. fasciata* at all temperatures. However, the yields of the bio-oil and biochar produced by *A. filiculoides* were lower than those of the bio-oil and biochar produced by *U. fasciata* at different temperatures. As shown in Fig. 4c, the maximum yields of bio-oils from *A. filiculoides* and *U. fasciata* were obtained at the temperatures of 400 °C (30.64 wt%) and 500 °C (34.43 wt%), respectively. At lower temperatures, the predominant reaction is carbonization and the bio-oil yields are small. When the temperature increases to the optimum point, more volatile components are formed during the algal pyrolysis, producing more liquid products. However, when the temperature exceeds this point, the secondary cracking of volatiles into more incondensable gases decreases the bio-oil yields. Therefore, the biochar yields of the two biomasses were significantly reduced as the pyrolysis temperature exceeded the temperature of 300 °C (Fig. 4d). However, the bio-gas yields of *A. filiculoides* and *U. fasciata* enhanced from 24.71 wt% and 23.5 wt% to 44.29 wt% and 27.43

Table 5: Ultimate analysis, high heating values and energy recovery values for the bio-oils obtained from the pyrolysis of *A. filiculoide* and *U. fasciata*

Element	Ultimate Analysis					HHV	Energy
	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O (wt%)	(MJ/kg)	Recovery (%)
Azolla oil	51.23	6.87	4.21	0.11	37.58	20.43	36.8
Ulva oil	49.25	6.65	3.25	2.15	38.7	19.44	54.6

Table 6: Ultimate analysis for the biochars obtained from the pyrolysis of *A. filiculoide* and *U. fasciata*

Elements	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O (wt%)
Azolla based biochar	62.43	4.19	2.71	0.08	30.59
Ulva based biochar	57.14	4.06	2.07	1.52	35.21

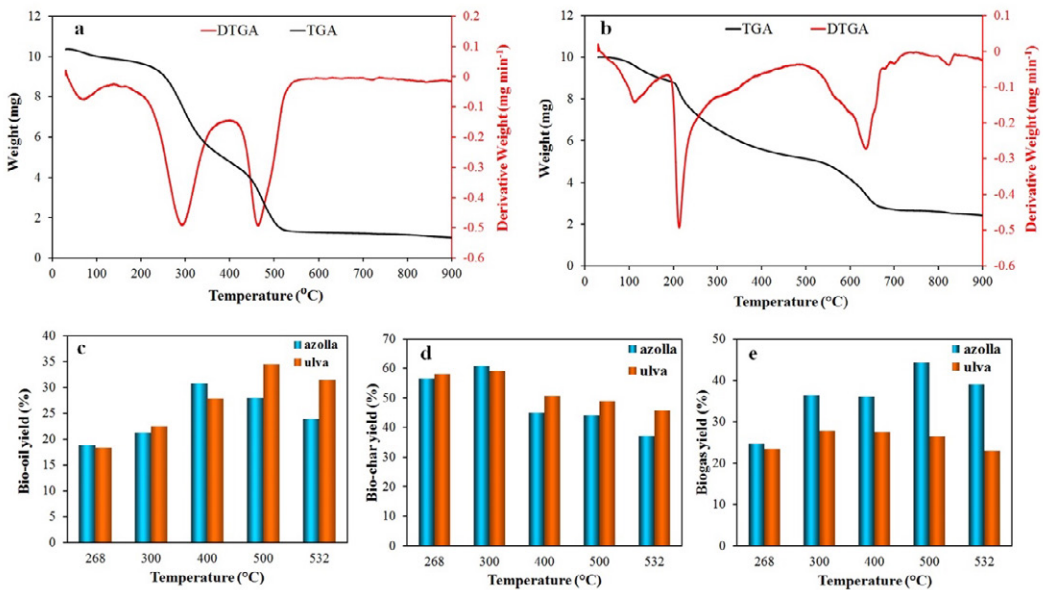

Fig. 4: Thermogravimetric curves for the pyrolysis process of (a) *A. filiculoide*; and (b) *U. fasciata* macroalgae, and yields of the products obtained from the pyrolysis of *A. filiculoide* and *U. fasciata* macroalgae at different temperatures: (c) bio-oil yield; (d) biochar yield; and (e) bio-gas yield

wt% by increasing the temperature from 260 °C to 500 °C, respectively (Fig. 4e). This could be explained by further thermal decomposition of the biochar and release of volatile components.

Qualitative analysis of the produced bio-oils

To evaluate the composition of organic compounds, the produced bio-oils were analyzed using a GC-MS instrument. As shown in Table 7, the produced bio-oils contained complex mixtures of aromatic and unsaturated hydrocarbons, alkanes, alkenes, and alcohols. Carbon distribution of the obtained bio-oil ranged from C_6-C_{24} to C_4-C_{16} for *A. filiculoides* and *U. fasciata*, respectively. Phenol (15.5%), p-Cresol (11.2%) and Catechol (9.2%) were mainly obtained from pyrolysis of *A. filiculoides*, while Ethyl acetate (11.9%), 1H-Pyrrole (9.9%) and 1-Tetradecene (7.2%) were largely obtained from pyrolysis of *U. fasciata*. This difference was probably due to the distinction of the chemical structures in the two biomasses. It should be noted that the higher contents of aromatics, phenols, and nitrogen-containing compounds in the *A. filiculoides* bio-oil rather than the *U. fasciata* bio-oil might be attributed to the higher protein content of *A. filiculoides* biomass (Table 1). According to Table 7, the aromatic hydrocarbons such as benzene, toluene, diol, and especially phenols were dominant components in the oil fraction of *A. filiculoides*. These products were associated with the degradation of the proteins containing the amino acids with aromatic rings in their structures. The majority of phenolic compounds, which are of great commercial importance, were typically present in the form of phenol, 4-methylphenol, 2-methyl phenol, 4-ethyl phenol, 2,4- dimethyl phenol, 3,5- dimethyl phenol, and 2,5- dimethyl phenol in the oil fraction of *A. filiculoides*. However, most of these compounds were absent in the pyrolytic oil of *U. fasciata* (Table 7).

Proteins were responsible for the formation of some nitrogenous compounds such as pyridines,

Table 7: Main compounds detected in the bio-oils of *A. filiculoide and U. fasciata*

No.	*A. filiculoide.*			*U. fasciata*		
	Formula	Component	Wt. %	Formula	Component	Wt. %
1	C_5H_5N	Pyridine	1.6	C_6H_6	Benzene	2.8
2	C_7H_8	Toluene	3.1	C_7H_8	Toluene	3.25
3	$C_5H_6O_2$	2-furan methanol	2.3	C_6H_6O	Phenol	2.7
4	C_6H_7N	3-methyl pyridine	1.6	C_8H_8	Styrene	3.3
5	C_8H_{10}	Ethyl benzene	2.0	$C_4H_8O_2$	Ethyl Acetate	11.9
6	C_6H_{10}	3-methyl-2- cycloPentene	0.8	C_4H_4N	1H-Pyrrole	9.9
7	C_8H_7N	Indole	7.6	$C_4H_8O_2$	2-Butene-1,4-diol	5.8
8	C_9H_{12}	1-Ethyl-3-methylbenzene	1.75	C_7H_5N	2-Ethynyl pyridine	3.7
9	C_9H_{12}	1,2,3-trimethylbenzene	1.2	C_6H_8O	2-Methylene-4-pentenal	2.3
10	$C_6H_8O_2$	3-methyl, 1,2-cyclopentanedione	1.5	C_5H_7N	1H-Pyrrole, 3-methyl	3.2
11	C_7H_{12}	2,3-Dimethyl-3-cycloPentene	0.7	C_7H_8O	Phenol,4-methylene	5.8
12	C_6H_6O	Phenol	15.5	$C_{10}H_{22}O$	1-Octanol,3,7-dimethyl	0.9
13	C_7H_8O	2-Methyl phenol	4.4	$C_6H_8O_3$	2,5-Dimethyl-4-hydroxy-3(2H)-furanone	2.4
14	C_7H_8O	p-Cresol	11.2	$C_{10}H_8$	1H-Indene, 1-methylene	3.2
15	$C_7H_8O_2$	2-Methoxyphenol	0.7	C_8H_7N	Benzonitrile, 3-methyl	1.1
16	C_5H_5NO	3-Pyridinol	2.6	$C_{11}H_{24}$	Nonane,2,6-dimethyl	0.8
17	$C_8H_{10}O$	2-Ethyl phenol	1.00	C_5H_9O	2-methyl-3-butenyl	2.5
18	$C_8H_{10}O$	2,4-Dimethyl phenol	2.7	$C_9H_{18}O$	Nonan-4-one	2.5
19	$C_8H_{10}O$	2,5-Dimethyl phenol	1.6	C_8H_7N	Indolizine	3.2
20	$C_8H_{10}O$	4-Ethyl phenol	3.1	$C_{14}H_{28}$	1-Tetradecene	7.2
21	$C_8H_{10}O$	3,5-Dimethyl phenol	2.0	C_8H_7N	Indole	0.8
22	$C_6H_6O_2$	Catechol	9.2	$C_{14}H_{28}O$	E-2-Tetradecen-1-ol	5.6
23	$C_9H_{10}N_2$	2-Ethyl benzimidazole	1.7	$C_{13}H_{24}$	1-Tridecyne	1.3
24	$C_{11}H_{10}$	2- Methyl naphthalene	1.3	$C_{16}H_{32}O$	Hexadecanal	3.2
25	$C_7H_8O_2$	4-Methyl-1,2-benzenediol	4.42	$C_{10}H_{20}O_2$	Decanoic Acid	1.1
26	$C_{13}H_{26}$	1-Tridecene	1.1	$C_{11}H_{21}N$	Undecanenitrile	1.1
27	$C_{14}H_{28}$	2-Tetradecene	1.6	$C_{12}H_{22}O_2$	Allyl nonanoate	2.8
28	$C_{16}H_{34}$	Hexadecane	1.6	$C_{12}H_{24}$	3-Dodecene	1.00
29	$C_{24}H_{38}O_4$	Bis(2-ethylhexyl) phthalate	1.0	$C_{14}H_{29}NO$	Tetradecanamide	3.8
30	$C_{19}H_{40}$	Nanodecane	1.5	$C_{12}H_{24}$	2-Undecene, 3-methyl	1.3

Table 8: Biodiesel properties of *A. filiculoide* and *U. fasciata* and the EU standards for biodiesel

Quality parameter	Azolla oil	Ulva oil	Standard EN14214 (2012)
Cetane Number (CN)	69.8	62.4	51<
Iodine Value (IV) g I_2/100g oil	140	125	120>
Density (g/cm^3)	0.95	0.84	0.86-0.9
Kinematic viscosity (mm^2/s)	4.3	3.9	3.5-5

furans, indoles, and imidazoles. Alkenes, such as 1-Tridecene, 2-Tetradecene, 3-methyl-2- cycloPentene, and 2,3-Dimethyl-3-cyclopentene, could be produced from the conversion of unsaturated fatty acids in *A. filiculoides*. Other components identified in the *U. fasciata* bio-oil (Table 7), besides aliphatics and aromatic hydrocarbons, were alcohols, esters, ketones, and fatty acids with relatively long carbon chain amide and nitrile. Some physicochemical properties of the produced bio-oils (CN, IV, density, Kinematic viscosity, and CP) were determined using the Biodiesel Analyzer v2.2 software, and the obtained parameters were compared with the European Diesel and Biodiesel Standard (EN14214) as presented in Table 8. The CN shows the time delay in the fuel ignition. The minimum CN recommended by the European standards EN 14214 is 51 for dieselbiodiesel. In the present study, the CN values for pyrolysis of the bio-oils derived from *A. filiculoides* and *U. fasciata* were found to be 69.8 and 62.4, respectively. Although both bio-oil samples had a good quality according to the European standards, the bio-oil from *A. filiculoides* had a higher CN compared to the bio-oil produced from *U. fasciata*. This could be due to higher amount of oxygenated compounds and long-chain hydrocarbons present in the *A. filiculoides* bio-oil, which improved the combustion rate and CN (Costa *et al.,* 2018). Oxygen helps the formation of air-fuel mixture and reduces the ignition delay in order to achieve a good combustion. IV, as a factor for biodiesel tendency to react with O_2, is used to evaluate the degree of unsaturation (Saber *et al.,* 2016). The lower the iodine value, the better the combustion quality. The maximum IV recommended by the European standards EN 14214 for biodiesel is 120 g I_2/100 g of a sample. According to Table 8, the *U. fasciata* bio-oil showed a lower IV compared to the *A. filiculoides* bio-oil, probably due to the lower content of unsaturated products such as benzene, phenol, and their derivatives. The kinematic viscosity of the bio-oil produced from *A. filiculoides* was about 4.3 mm^2/s at the temperature of 40 °C, whereas the kinematic viscosity of the bio-oil derived from *U. fasciata* was about 3.9 mm^2/s at the same temperature (Table 8). The obtained values (i.e. 3.5-5 mm^2/s) were almost in the middle of the acceptable range proposed by the European standards EN 14214, indicating that the produced bio-oils could be consumed as a fuel in the current diesel engines without any modification. As shown in Table 8 (supplementary material), the density of the bio-oil produced from *A. filiculoides* was higher than that of the *U. fasciata* bio-oil. The higher density and kinematic viscosity of the *A. filiculoides* bio-oil could be explained by the presence of longer-chain hydrocarbons and higher amount of unsaturated compounds in the oil (Nascimento *et al.,* 2013). Considering the density and kinematic viscosity parameters, it was concluded that Ulva macroalgae would produce a higher quality pyrolytic bio-oil compared to *A. filiculoides* algae. The *A. filiculoides* bio-oil with higher heating value, higher viscosity and higher density can be consumed in the boilers and generators burning heavy oil, while the low viscosity and low density of the *U. fasciata* bio-oil make it more suitable to be used, either in neat form or blended, as a fuel in diesel vehicles (Kumar *et al.,* 2015).

CONCLUSION

In this study, the non-catalytic pyrolysis experiments were performed in a fixed-bed reactor on two types of biomass, *Azolla filiculoides* and *Ulva fasciata*. The effects of main pyrolysis parameters, including pyrolysis temperature, carrier gas flow rate, and heating rate, on bio-oil yields were investigated, and an experiment design method (Response Surface Methodology) was employed to determine the test conditions and analyze their results. The results obtained from the mathematical models indicated that the effect of pyrolysis temperature was more significant than the effects of nitrogen flow rate and heating rate on the bio-oil yields. Accordingly, at the optimum operating conditions, the highest bio-oil yields of 30.83 % (at the temperature of 461 °C, nitrogen flow rate of

0.5 L/min, and heating rate of 20 °C/min) and 34.29% (at the temperature of 500 °C, nitrogen flow rate of 0.2 L/min, and heating rate of 10 °C/min) were obtained from the pyrolysis of *A. filiculoides* and *U. fasciata*, respectively. The results showed that the burning quality of Azolla fuel was higher than that of Ulva fuel. Moreover, the Azolla bio-oil, showing a higher heating value and higher density and viscosity, proved to be more suitable for application in boilers and turbines. Considering the physicochemical properties, the bio-diesel obtained from *U. fasciata* macroalgae, with their superior quality, was a good candidate for application in diesel vehicles, compared to the bio-diesel derived from *A. filiculoides*. Technically, the results indicated that both biomasses could be considered as potential sources for producing the third-generation biofuel. Since further studies seem necessary to deepen the overall knowledge about the bio-oil production through pyrolysis of *A. filiculoides* and *U. fasciata*, the effect of catalytic pyrolysis on the yield and properties of the bio-oil derived from these species will be systematically investigated in our future work.

AUTHOR CONTRIBUTIONS

S. Pourkarimi has performed experiments, experimental design and data collection as well as partial analysis. A. Alizadehdakhel performed data analysis in the study. A. Hallajisani contributed to the literature, supervision and writing of the original draft. A. Nouralishahi edited and corrected the manuscript.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest regarding the publication of this work. In addition, the ethical issues including plagiarism, informed consent, misconduct, data fabrication and, or falsification, double publication and, or submission, and redundancy have been completely witnessed by the authors.

ABBREVIATIONS

$\propto$	Level of significance
%	Percentage
<	Less than
=	Equal
>	Greater than
° C	Degrees Celsius
°C /min	Degrees Celsius per minute (Heating rate = H)
° K	Degrees Kelvin
AOY	Bio-oil yield of Azolla
β_i (1,2,3 ... k)	Regression coefficients
C	Weight percentage of carbon
Cm	Centimeter
CN	Cetane number
DTGA	Derivative thermogravimetry analysis
et al.	"and others" in Latin
Eq.	Equation
ER	Energy recovery
Fig.	Figure
G	Gram
g/cm^3	Gram per cubic centimeter (Density)
H	Weight percentage of hydrogen
HHV	Heating value
IV	Iodine value
Kg	Kilogram
L	Litre
L/min	Liter per minute (Carrier gas flow) = Q
M	Meter
Mg	Milligram
Min.	Minutes
mL	Milliliter
mL/min	Milliliter per minute
Mm	Millimeter
mm/s	Square millimeters per second (Kinematic Viscosity)
MJ/Kg	Megajoule per kilogram
O	Weight percentage of oxygen
P<0.05	Probability that the null hypothesis is rejected
p-value	Probability value
RSM	Response surface methodology
R^2	Coefficient of determination
S	Weight percentage of sulfur
T	Temperature
TGA	Thermogravimetry analysis
UOY	Bio-oil yield of Ulva
X_i (1,2,3 ... k)	Explanatory variables
Y_i	Value of each individual observation

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