ORIGINAL RESEARCH PAPER

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

S. Pourkarimi1, A. Hallajisani2,*, A. Alizadehdakhel1, A. Nouralishahi2

1 Department of Chemistry and Chemical Engineering, Rasht Branch, Islamic Azad University, Rasht, Iran
2 Biofuel Research Laboratory, Caspian Faculty of Engineering, College of Engineering, University of Tehran, Rezvanshar, Guilan, Iran

**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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*Corresponding Author:
Email: hallaj@ut.ac.ir
Phone: +9813 4460 3270
Fax: +9813 4460 8600

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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 CO₂ 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 Ulvaceae, 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 Kjeldahl 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 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 in a gas bag (14), weighed, and stored for further analysis.

**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 biogas were collected in the reactor, condenser (11-13), and gas bag (14), respectively.

<table>
<thead>
<tr>
<th>Table 1: Chemical composition and ultimate and proximate analyses of <em>A. filiculoides</em> and <em>U. fasciata</em> biomass samples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Azolla</td>
</tr>
<tr>
<td>Ulva</td>
</tr>
</tbody>
</table>

*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.
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).

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

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

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

**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.

$$Y = \beta_0 + \sum_{i=1}^{\bar{m}} \beta_i x_i + \sum_{i,j=1, i,j \geq 2}^{\bar{m}} \beta_{ij} x_{ij} + \sum_{i=1}^{\bar{m}} \beta_{ii} x_{i}^2$$

(4)

Where, $\beta_0, \beta_i, \beta_{ij}, \beta_{ii}$ 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).

$$HHV \left( \frac{MJ}{kg} \right) = 0.338 \times C + 1.428 \times \left( \frac{H-O}{8} \right) + 0.096 \times S$$

(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).

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

(6)

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

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

<table>
<thead>
<tr>
<th>Run No.</th>
<th>T (°C)</th>
<th>Q (L/min)</th>
<th>H (°C/min)</th>
<th>Bio-oil, wt. (%)</th>
<th>Bio-char, wt. (%)</th>
<th>Bio-gas, wt. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Azolla</td>
<td>Ulva</td>
<td>Azolla</td>
</tr>
<tr>
<td>1</td>
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<td>22</td>
<td>27.86</td>
<td>23.93</td>
<td>44.29</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
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<td>15</td>
<td>29.57</td>
<td>25.91</td>
<td>41.43</td>
</tr>
<tr>
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<td>23.79</td>
<td>31.36</td>
<td>37.21</td>
</tr>
<tr>
<td>4</td>
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<td>15.36</td>
<td>21.12</td>
<td>48.29</td>
</tr>
<tr>
<td>5</td>
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<td>27.00</td>
<td>37.71</td>
</tr>
<tr>
<td>6</td>
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<td>18.71</td>
<td>18.29</td>
<td>56.57</td>
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<tr>
<td>7</td>
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<td>44.00</td>
</tr>
<tr>
<td>8</td>
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<td>30.64</td>
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<td>42.21</td>
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<tr>
<td>9</td>
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<td>15</td>
<td>30.07</td>
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<td>43.29</td>
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<tr>
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</tr>
<tr>
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<td>31.50</td>
<td>44.14</td>
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</table>
RESULTS AND DISCUSSION

Biomass characterization

The results of chemical composition, ultimate and proximate analyses of the two macroalgae 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 *Cladophora clathrata* (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* macroalgae 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 range 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 N₂ 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 N₂ 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 N₂ 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 (R², adjusted-R², and adequate precision). The R²-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 $A. \text{ filiculoides}$ and $U. \text{ fasciata}$, respectively, as the satisfactory response surface models to fit the experimental data. The model terms are significant at $p < 0.05$. For $A. \text{ filiculoides}$, all terms (A, B, C, AC, BC, $A^2$, and $B^2$), except $AB$ and $C^2$ interactions, were significant model terms, while for $U. \text{ fasciata}$, 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 $A. \text{ filiculoides}$ (AOY%) and $U. \text{ fasciata}$ (UOY%) were expressed using Eqs. 6 and 7:

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

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

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

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

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>Df</th>
<th>Mean square</th>
<th>F-value</th>
<th>p-value Prob &gt; F</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Azolla:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model</td>
<td>556.63</td>
<td>9</td>
<td>61.85</td>
<td>34.67</td>
<td>&lt; 0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>A</td>
<td>111.38</td>
<td>1</td>
<td>111.38</td>
<td>62.43</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>25.64</td>
<td>1</td>
<td>25.64</td>
<td>14.37</td>
<td>0.0035</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>15.42</td>
<td>1</td>
<td>15.42</td>
<td>8.64</td>
<td>0.0148</td>
<td></td>
</tr>
<tr>
<td>AB</td>
<td>3.98</td>
<td>1</td>
<td>3.98</td>
<td>2.23</td>
<td>0.1661</td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>38.91</td>
<td>1</td>
<td>38.91</td>
<td>21.81</td>
<td>0.0009</td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>20.43</td>
<td>1</td>
<td>20.43</td>
<td>11.45</td>
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</tr>
<tr>
<td>$A^2$</td>
<td>131.40</td>
<td>1</td>
<td>131.40</td>
<td>73.65</td>
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</tr>
<tr>
<td>$B^2$</td>
<td>113.07</td>
<td>1</td>
<td>113.07</td>
<td>63.38</td>
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<td></td>
</tr>
<tr>
<td>Residual</td>
<td>7.98</td>
<td>10</td>
<td>0.798</td>
<td>4.47</td>
<td>0.0606</td>
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</tr>
<tr>
<td>Lack of fit</td>
<td>12.63</td>
<td>5</td>
<td>2.53</td>
<td>2.42</td>
<td>0.1770</td>
<td>Not significant</td>
</tr>
<tr>
<td>Pure error</td>
<td>5.21</td>
<td>5</td>
<td>1.04</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor total</td>
<td>574.47</td>
<td>19</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ulva:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model</td>
<td>316.32</td>
<td>6</td>
<td>52.72</td>
<td>116.81</td>
<td>&lt; 0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>A</td>
<td>268.81</td>
<td>1</td>
<td>268.81</td>
<td>595.59</td>
<td>&lt; 0.0001</td>
<td></td>
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<tr>
<td>B</td>
<td>30.23</td>
<td>1</td>
<td>30.23</td>
<td>66.99</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>11.51</td>
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<td>25.49</td>
<td>0.0002</td>
<td></td>
</tr>
<tr>
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<td>5.20</td>
<td>11.53</td>
<td>0.0048</td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>0.5618</td>
<td>1</td>
<td>0.5618</td>
<td>1.24</td>
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<td></td>
</tr>
<tr>
<td>BC</td>
<td>0.0086</td>
<td>1</td>
<td>0.0086</td>
<td>0.0191</td>
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<td></td>
</tr>
<tr>
<td>Residual</td>
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<td>13</td>
<td>0.4513</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of fit</td>
<td>4.47</td>
<td>8</td>
<td>0.5582</td>
<td>1.99</td>
<td>0.2325</td>
<td>Not significant</td>
</tr>
<tr>
<td>Pure error</td>
<td>1.40</td>
<td>5</td>
<td>0.2804</td>
<td></td>
<td></td>
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<tr>
<td>Cor total</td>
<td>322.19</td>
<td>19</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*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\textsubscript{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\textsubscript{2} flow rate = 0.5 L/min for A. filiculoides; and b) temperature = 500 °C, heating rate = 10 °C/min, and N\textsubscript{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
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-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](image-url)
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 biogas yields of *A. filiculoides* and *U. fasciata* enhanced from 24.71 wt% and 23.5 wt% to 44.29 wt% and 27.43 wt% respectively.

| Table 5: Ultimate analysis, high heating values and energy recovery values for the bio-oils obtained from the pyrolysis of *A. filiculoides* and *U. fasciata*
<table>
<thead>
<tr>
<th>Element</th>
<th>Ultimate Analysis</th>
<th>Energy Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azolla oil</td>
<td>C (wt%)</td>
<td>H (wt%)</td>
</tr>
<tr>
<td>Azolla oil</td>
<td>51.23</td>
<td>6.87</td>
</tr>
<tr>
<td>Azolla oil</td>
<td>Ulva oil</td>
<td>49.25</td>
</tr>
</tbody>
</table>

| Table 6: Ultimate analysis for the biochars obtained from the pyrolysis of *A. filiculoides* and *U. fasciata*
<table>
<thead>
<tr>
<th>Elements</th>
<th>C (wt%)</th>
<th>H (wt%)</th>
<th>N (wt%)</th>
<th>S (wt%)</th>
<th>O (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azolla based biochar</td>
<td>62.43</td>
<td>4.19</td>
<td>2.71</td>
<td>0.08</td>
<td>30.59</td>
</tr>
<tr>
<td>Ulva based biochar</td>
<td>57.14</td>
<td>4.06</td>
<td>2.07</td>
<td>1.52</td>
<td>35.21</td>
</tr>
</tbody>
</table>

Fig. 4: Thermogravimetric curves for the pyrolysis process of (a) *A. filiculoides*; and (b) *U. fasciata* macroalgae, and yields of the products obtained from the pyrolysis of *A. filiculoides* 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 aromatics. The carbon distribution of the obtained bio-oil ranged from $C_6$ to $C_{14}$ 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. filiculoides* and *U. fasciata*](image-url)
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 2 std. L/min, and an heating rate of 10 °C/min) were obtained from the Azolla filiculoides bio-oil. For the Ulva fasciata bio-oil, the optimum operating conditions were found to be 51 °C (nitrogen flow rate), 10 °C/min (heating rate), and 1 std. L/min (carrier gas flow rate), resulting in a bio-oil yield of 31.66%.

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).

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

<table>
<thead>
<tr>
<th>Quality parameter</th>
<th>Azolla oil</th>
<th>Ulva oil</th>
<th>Standard EN14214 (2012)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane Number (CN)</td>
<td>69.8</td>
<td>62.4</td>
<td>51&lt;</td>
</tr>
<tr>
<td>Iodine Value (IV) g l⁻¹/100g oil</td>
<td>140</td>
<td>125</td>
<td>120&gt;</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.95</td>
<td>0.84</td>
<td>0.86-0.9</td>
</tr>
<tr>
<td>Kinematic viscosity (mm²/s)</td>
<td>4.3</td>
<td>3.9</td>
<td>3.5-5</td>
</tr>
</tbody>
</table>

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.

**ACKNOWLEDGEMENTS**

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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**

- ∞: 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
- βi (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/cm³: 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)
- 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
- R²: Coefficient of determination
- S: Weight percentage of sulfur
- T: Temperature
- TGA: Thermogravimetry analysis
- UOY: Bio-oil yield of Ulva
- Xi (1,2,3 ... k): Explanatory variables
- Yi: Value of each individual observation
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**AUTHOR (S) BIOSKETCHES**

**Pourkarimi, S.,** Ph.D. Candidate, Department of Chemistry and Chemical Engineering, Rasht Branch, Islamic Azad University, Rasht, Iran. Email: sara.pourkarimi@phd.iaurasht.ac.ir

**Hallajisani, A.,** Ph.D., Assistant Professor, Biofuel Research Laboratory, Caspian Faculty of Engineering, College of Engineering, University of Tehran, Rezvanshar, Guilan, Iran. Email: hallaj@ut.ac.ir

**Alizadehdakhel, A.,** Ph.D., Assistant Professor, Department of Chemistry and Chemical Engineering, Rasht Branch, Islamic Azad University, Rasht, Iran. Email: alizadeh@iaurasht.ac.ir

**Nouralishahi, A.,** Ph.D., Assistant Professor, Biofuel Research Laboratory, Caspian Faculty of Engineering, College of Engineering, University of Tehran, Rezvanshar, Guilan, Iran. Email: nouralishahi@ut.ac.ir

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