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Bio-oil production from fast pyrolysis of *Cladophora glomerata* in a fluidized bed reactor

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Algae proved that are very good oil resource in recent years. Southern coast of Caspian Sea has good potential for reservoir of filamentous Macro-algae bearing oils such as, *Cladophora glomerata.* Among various auto thermal conversion routines for production of energy from biomass, fast pyrolysis (conversion of a solid/liquid carbon-based fuel into a large number of energetic components (gaseous component and small quantities of liquid) and solid residue (char and ash) in the absence of a fluidizing medium) is one of the methods that are receiving more attention from researchers. In this work, several experiments were carried out to evaluate the qualities of product yields especially bio-oil in *Cladophora glomerata* by a fluidized bed reactor. The data obtained showed that an increase in the Reaction time (RT) leads to significant increases in the gas yield and a considerable decrease in both bio-oil and char yield. The experimental runs also showed that the reaction temperature (T_p) has an effective role in the quality of the product yields; higher temperature is favorable for higher gas yield and lower char yield production from *Cladophora glomerata.*

Keywords: Algae, *Cladophora glomerata*, Fast pyrolysis, Bio-oil, Char, Fluidized bed, Farahabad Region, Iran

INTRODUCTION

In recent years Algae showed third generation of biodiesel and biofuel reservoir that economically has more yields than crops. For example proved that lipid content in algae (% of lipid content by dry weight), is as good as in other oil crops. In recent years, interest is growing in the production of bio-oil and bio-gas from autothermal conversion of biomass because it is renewable, CO_2 neutral, and abundantly available. Another reason is the present energy crisis due to dependency on fossil fuels and economic problems. Algae biofuels are important sources of renewable energy for production clean energy through auto thermal or biological conversion [1].

Among various autothermal conversion routines for production of energy from biomass, fast pyrolysis (conversion of a solid/liquid carbon-based fuel into a large number of energetic components (gaseous component and small quantities of liquid) and solid residue (char and ash) in the absence of a fluidizing medium) is one of the methods that are receiving more attention from researchers. The main purpose of fast pyrolysis is to convert solid feedstocks into a liquid fuel which contains water, organic acids, non-polar hydrocarbons and other oxygenated components [2]. In this process, feedstock rapidly heated to high temperature in the range of 500-700 ˚C to yield: solid residue, 10-15%; liquids, 70-80%; and light gaseous components, 10-15% [3].

The advantages of fast pyrolysis of biomass materials include availability and simplicity, and it has been studied by numerous authors using various kinds of reactors like bubbling fluidized beds (BFBs), circulating fluidized beds (CFBs), and fixed beds (FBs). For instance, Ali et al. [4] investigated the influence of working conditions (particle size, 1.0-2.0 mm and reaction temperature, 360-540 ˚C) on the yield of bio-oil from fast pyrolysis of biomass and concluded that the maximum yield of bio-oil obtains with a carrier gas flow rate of 11.0 m^3/h. Pattiya and Suttibak studied the effects of reaction temperatures and hot vapor filter on pyrolysis product yields and concluded that the optimum pyrolysis temperature for production of maximum bio-oil is about 475 ˚C [5]. The use of hot vapor also led to a decrease of 6.0-7.0 wt% of bio-oil yield. An experimental study for enhancing the yield of produced bio-oil from fast pyrolysis of microalgae biomass was carried out by Miao and Wu. The authors found that the yield of bio-oil produced from *Chorella protothecoides* is much higher than from autotrophic cells during the process [6].

Most of the studies reported above have been focused on biomass gasification at different working conditions and have not considered the influence of fuel particle size and reaction time, both having a major influence in the in kinetics of the fast pyrolysis process and thus on the yield of bio-oil. Thus, this work aims to study the effects of hydrodynamic characteristics on the yield of bio-oil. Given the

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relatively low emphasis on hydrodynamic parameters, the purposes are to achieve a better understanding of the fast pyrolysis under different hydrodynamic conditions, as well as to help establish the maximum yield of bio-oil from *Cladophora glomerata* grown in southern coast of Caspian Sea.

EXPERIMENTAL

Experiments

The experimental runs have been performed at the pyrolysis equipment shown in Figure 1. The pilot plant consists of a feeding system (K-Tron) which enables to control the algal biomass feeding ratio, a fluidized bed system (equipped with 150 μm gas distributor), and a hot gas filtering system. The reactor was indirectly heated by two electric heaters which enable to keep the pyrolysis temperature constant. Two K-type thermocouples have been installed at the outer wall to measure and control the process temperature.

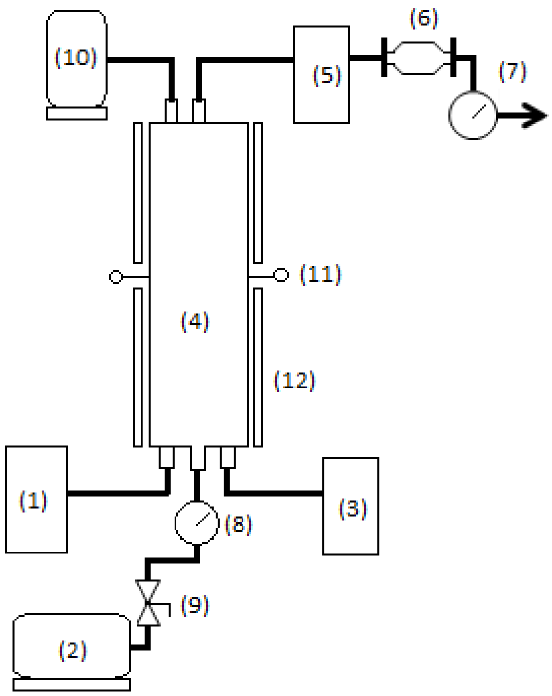

Fig. 1. A schematic diagram of fluidized bed; (1) bio-oil storage tank; (2) Nitrogen gas feeding system; (3) solid hopper; (4) fluidized bed reactor; (5) filtering system (6) pressure transducer; (7) gas meter; (8) nitrogen flow meter system (9) valve (10) feedstock feeding system (11) thermocouple (12) electric heater.

An solid hopper located at the bottom of the fluidized bed allows to collect the solid residues of the pyrolysis process including ash and char. The nitrogen (inert gas) and biomass feeding rates were about 20 L/min and 300 kg/h, respectively. The gas and liquid products were analyzed by a gas chromatograph (Model Agilent 428A) and a Py-GC/MS (Model TH-411), respectively.

Raw material

The feedstock used in this work is *Cladophora glomerata* which collected from Farahabad Region (Sari city of Mazandaran, 2016) located in Caspian Sea, Iran, according to standard method [7-8]. The *Cladophora glomerata* belong to filamentous Ulvophyceae (Chlorophyta-green algae) is the main and dominant macro algae in the southern coast of Caspian Sea that has extensive distribution in all seasons in this region (Figure 2). It mainly grown on the big stones (usually near to 80-90% covering) and near sea coast walls. Its appearance is tolerating permanent change so that it will depend directly on age, habitat and also environmental conditions. Prior to the pyrolysis experimental tests, the algae biomass has been dried under atmospheric conditions for 36 h and then crushed to a particle size below 7.0 mm. The properties of the algae biomass, such as the proximate and elemental analysis, and also feedstock caloric value are listed in Table 1.

Table 1. Detailed Properties of *Cladophora glomerata.*

Proximate analysis (wt %)	
Moisture	05.01
Volatile matter	77.71
Fixed carbon	16.94
Ash	0.34
HHV (MJ/kg)	19.97
Ultimate analysis (wt %), daf[a]	
C	50.26
H	06.72
O	42.66
N	00.16
S	00.20

[a] Dry and free ash

RESULTS AND DISCUSSION

In the first test series, the influence of process temperature (T_p) on product yields and higher heating value (HHV) was analyzed, where the particle size (PS) and reaction time (RT) were kept constant. Metrics can be expressed as follows [9]:

$$\mathrm{HHV\,(MJ/kg)} = 0.3491\mathrm{C} + 1.1783\mathrm{H} + 0.1005\mathrm{S} - 0.1034\mathrm{O} - 0.0151\mathrm{N} - 0.0211\mathrm{A} \qquad (1)$$

Fig. 2. *Cladophora glomerata* obtained from Farahabad region of Caspian Sea (November 2016).

$$Y(\%) = \frac{\text{Mass of fraction } i}{\text{Total mass in the feed}} \times 100 \qquad (2)$$

Here Y is the product yield (gas, solid, and oil) in %. C, H, S, O, N, and A also are the mass of carbon, hydrogen, sulfur, oxygen, nitrogen, and ash in the dry biomass. Summarized in Table 2 are the results of the experimental tests based on various working conditions during the fast pyrolysis of *Cladophora glomerata*. Major changes in the results occurred with changes made in the reaction temperature. The highest and lowest bio-oil yields were around 45.5 and 24.2 % which achieved at T_p of 360 and 520 °C. For the gas yield, the highest (24%) and lowest (7.0%) value are obtained at around 520 °C and 380 °C, respectively (Table 2).

Table 2. Effect of Tp on product yields (PS= 7.0 mm, RT = 10 min)

Run	T_p	Yields (%) Bio-oil	Char	Gas	HHV (MJ/kg)
1	360	26	65.0	9.0	15.28
2	380	59.2	52.2	7.0	14.73
3	400	57.0	47.5	9.5	14.07
4	420	47.5	39.8	12.7	13.52
5	440	54.5	30.1	15.4	12.88
6	460	55.0	26.7	18.3	12.16
7	480	59.1	20.8	20.1	11.72
8	500	62.1	15.4	22.5	11.24
9	520	65.5	10.5	24.0	10.87

Finally, process temperatures of 360 and 520 °C correspondingly attained the highest (65%) and lowest (10.5%) char yield. Although the yield of bio-oil obtained in this work is found to be slightly lower than those derived from agricultural residue (60-78%), the result is still higher than those of other works (26-43%) which used algae biomass as fuel for bio-oil production [10]. The results show that the present process is a promising method as a sustainable and clean way for the production of bio-oil; however, there is a relatively high quantities of char residue which leads to a reduction in the total efficiency. With increase of reaction temperature from 360 to 520 °C, the bio-oil production decreased due to the endothermic reactions occurring along the fluidized bed.

Table 3. Effect of PS on product yields (Tp = 520 °C, RT = 10 min)

Run	T_p (°C)	PS (mm)	Yields (%) Bio-oil	Char	Gas
1	520	7.0	65.5	10.5	24.0
2	520	6.5	65.4	10.3	24.3
3	520	6.0	65.5	10.1	24.4
4	520	5.5	65.5	10.0	24.5
5	520	5.0	65.8	09.5	24.7
6	520	4.5	66.0	08.9	25.1
7	520	4.0	66.3	08.4	25.3
8	520	3.5	66.8	07.6	25.6
9	520	3.0	67.0	07.2	25.8

Table 3 shows the product yields as a function of PS. As far as the PS is concerned, this hydrodynamic parameter has influence upon the product yields and emissions of the process. As can be seen, PS has a slight influence on the product yields (which is associated with a slight decrease in the heat and mass transfer restrictions); however, the use of small size particles as a feedstock entails environmental and socioeconomic benefits. Clearly, between 5.0 and 7.0 mm, the char yield (and thus the char conversion ratio) suffers a significant decrease, which shows that for fuel particles above 5.0 mm not only are thermal decomposition enhanced, but also are the char conversion ones, hence increasing gas production. Note that the effect of PS on the yield of bio-oil depends on the heating rate of the process; higher heating rates (smaller particles) favorable more bio-oil and gas production [11]. Among the different methods for improving economic aspects of the process, a reduction in the PS is more economical than those of other methods because it allows the reduction of reactor length.

In fact, a reduction in the particle size leads to an increase in the produced gas quality and a decrease in the residence time of particles to achieve a higher conversion of char. Wei et al [12] investigated the influence of the PS in the pyrolysis process in a free fall reactor, and they found that pyrolysis of smaller particles leads to a decrease in the solid residues and an increase in the yield of product gas.

Table 4. Effect of RT on product yields (PS = 3.0 mm, RT = 10 min)

Run	T_p (^{0}C)	RT (min)	Yields (%) Bio-oil	Char	Gas
1	520	10	67.0	07.2	25.8
2	520	12	68.8	05.1	26.1
3	520	14	69.5	03.2	27.3
4	520	16	67.5	03.0	29.5
5	520	18	66.8	02.8	30.4
6	520	20	66.4	02.7	30.9
7	520	22	64.8	02.5	32.7
8	520	24	64.6	02.3	33.1
9	520	26	64.5	02.0	33.5
10	520	28	64.0	01.8	34.2
11	520	30	63.7	01.5	34.8

Table 4 shows the product yields as a function of reaction time in the range of 10-30 min. Reaction time is another important variable which affects the gas composition, bio-oil quality and quantity, and char yield. As observed, with increasing the reaction time (RT), the yield of bio-oil increases and then decreases while the syngas yield continuously increases due to a significant improvement in the rate of endothermic reactions with increasing RT. Another reason is the expansion of char conversion and tar cracking reactions, as the RT improves. In this sense, Fonts et al. [13] suggested that biomass pyrolysis rates strongly depend on the reaction time, and that reactivity of a biomass fuel was related to the long of reaction time and heating rates.

CONCLUSION

The production of bio-oil from *Cladophora glomerata* biomass using fast pyrolysis in a fluidized bed reactor was studied. Effects of some important variables such as reaction temperature (T_p), Algae particle size (PS) and reaction time (RT) on product yields were evaluated by experimental and analyses. The data obtained show that an increase in the RT leads to a significant increases in the gas yield and a considerable decrease in both bio-oil and char yield. The experimental runs also showed that the PS has a slight influence on the product yields; however, it plays a major role in the economic aspects of the process.

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ПРОИЗВОДСТВО НА БИО-МАСЛО ЧРЕЗ БЪРЗА ПИРОЛИЗА НА *Cladophora Glomerata* В РЕАКТОР С КИПЯЩ СЛОЙ

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(Резюме)

През последните години водораслите са доказали, че са много добрър източник на масла. Южното крайбрежие на Каспийско море има добър потенциал като резервоар на филаментозни макро-водорасли, съдържащи масла като *Cladophora glomerata*. Сред различните начини за автотермична преработка за производство на енергия от биомаса, бързата пиролиза (преобразуване на твърдо/течно въглеродно гориво в голям брой енергийни компоненти (газообразен компонент и малки количества течност и твърди остатъци (въглен и пепел) в отсъствието на флуидизираща среда) е един от методите, които получават повече внимание от изследователите. В тази работа бяха проведени няколко експеримента за оценка на качествата на продукта, особено био-масло в *Cladophora glomerata* чрез реактор с кипящ слой. Получените данни показват, че увеличаването на реакционното време (RT) води до значително увеличение на добива на газ и до значителен спад както в добива на био-масло, така и на въглен. Експерименталните тестове също показват, че реакционната температура (T_p) има ефективна роля в качеството на продукта; По-високата температура е благоприятна за по-висок добив на газ и по-ниска производителност на добив на въглен от *Cladophora glomerata*