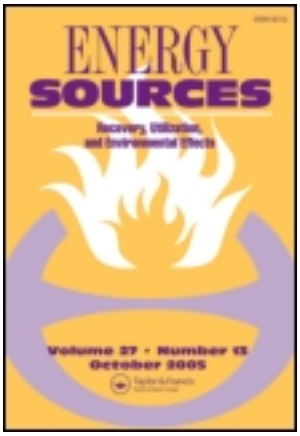

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The use of non-food biomass for bio-oils production appears to be an important trend for renewable energy in China. Biomass, in the form of marine macro-algae, is becoming popular among new renewable energy sources. Fast pyrolysis is one of the most important thermal conversion processes from biomass to bio-fuel. In this work, the marine green tide macroalgae *Enteromorpha prolifera* was converted into bio-oil by fast pyrolysis in a free-fall reactor at different temperatures ranging from 100 to 750°C. The bio-oil obtained was analyzed by elemental, gas chromatography-mass spectrometer, and Fourier transform infrared spectroscopy analysis. The results showed that the average heat value was 25.33 MJ kg^{-1} and the oxygen content was 30.27 wt%. The results suggested that *E. prolifera* presents as a good bio-oil feedstock candidate.

Keywords: biomass, bio-oil, *Enteromorpha prolifera*, fast pyrolysis, macroalgae

INTRODUCTION

The widespread use of fossil fuels, such as petroleum, coal, and natural gas, causes several environmental consequences that trigger the researches for finding alternative green bio-fuels. For the past few years, extensive researches have been performed on conversion from various types of terrestrial biomass into bio-fuels (Asadullah et al., 2007; Berrios et al., 2011; Feral et al., 2009). Nevertheless, terrestrial biomass may eventually be competitive with crop and food production. Therefore, many researchers have paid much attention to marine algae biomass, which are considered to be excellent candidates for bio-oil production because of their development superiorities of fast growth rate, great photosynthetic efficiency, superior biomass production, and lack of arable soil requirements (Pan et al., 2010). The marine macro-algae, *Enteromorpha prolifera*, pose no competition with food production on land and have a very high growth rate.

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Large-scale *Enteromorpha prolifera* green tides have occurred in Qingdao in the summers of 2007, 2008, 2010, and 2011. An unprecedented scale of *E. prolifera* green tide occurred in China's Yellow Sea just before the Olympics in 2008 and a large number of drifting *E. prolifera* biomass flocked to the regatta site and the shore, then became waste and soon began to decay, which not only did harm to the coastal ecological environment but also the seawater quality, and furthermore, became a blow to the local tourism (Zhao et al., 2011).

Fast pyrolysis is an effective method to harvest the energy in biomass. Many kinds of pyrolysis reactors have been researched in the literature. Jacques et al. (2007) have reported the properties of bio-oils produced by fast pyrolysis in a cyclone reactor, and they also compared these properties with other literature. Asadullah et al. (2007) also investigated the properties of bio-oil pyrolyzed in a fixed bed reactor. However, very little information is available on the process of conversion macro-algae *E. prolifera* into bio-oil and analysis of the characteristics of bio-oil.

The objectives of the present work are to evaluate the feasibility of using *E. prolifera* powder to provide bio-fuel by fast pyrolysis in one free-fall reactor and to find a new way to make full use of the macro-algae sources of marine green tides occurring frequently in China.

MATERIALS AND METHODS

Materials

E. prolifera samples were collected from Huiquan bay of Qingdao, China, in July 2008. The samples were air-dried and pulverized to a size <90 μm. Proximate analysis was measured by referring to the national standard GB212-91 and ultimate analysis was analyzed by the Elementar Analysensysteme GmbH vario EL cube. Cellulose, hemicellulose, and lignin analysis were conducted by hydrolysis of 72% sulphuric acid, 2 mol/l hydrochloric acid, and concentrated hydrochloric acid, respectively (Jiang et al., 2010). All tests were carried out in triplicate. The proximate, ultimate, and component analysis results are shown in Table 1.

Methods

Free-fall Reactor

The *E. prolifera* powders were pyrolyzed in a free-fall reactor for production of bio-oil, which was different from other pyrolysis reactors, such as a cyclone reactor or fixed bed reactor. A conceptual design of the process was shown in Figure 1. The reactor was set vertically and inert gases (e.g., N_2) were introduced inside the reactor at the rate of 50 cm^3/min with a pump from the top and passed through to the bottom. The heating medium was a kind of inert medium (sand), and according to many studies on the pyrolysis characteristics of *E. prolifera*, the temperatures of preheating section 1, preheating section 2, and preheating section 3 were 700–750, 400–450, and 100–200°C, respectively, and the temperature of the three sections were controlled strictly. A water-cooled condenser was used to condense the volatiles at temperature ranges between 140 and 400°C.

Physical Properties Analysis of Bio-oil

The bio-oil was obtained by the procedure as shown in Figure 2. The ash, density, and moisture of bio-oil obtained under optimal conditions were determined according to ASTM standard methods. pH of the bio-oil was obtained with a PHS-3E pH meter, and the main physical properties were shown in Table 2 and the elemental analysis of bio-oil was listed in Table 3. The experiments were replicated three times.

TABLE 1
Proximate Analysis, Ultimate Analysis, and Component Analysis of *E. prolifera* (wt%)

Parameters	E. prolifera
Proximate analysis[a] (%)	
Moisture	9.83
Ash	12.46
Volatile matter	68.79
Fix carbon[b]	8.92
Ultimate analysis[a] (%)	
Carbon	32.89
Hydrogen	4.67
Oxygen[b]	57.50
Nitrogen	2.51
Sulfur	2.43
Component analysis[a] (%)	
Hemicellulose	13.49
Lignin	8.81
Cellulose	29.03

[a]Weight percentage on dry basis.
[b]Calculated by difference.

Thermochemical Analysis of Bio-oil

A thermal analyzer (TGA/DSC1/1600LF, Mettler Toledo Co, Zürich, Switzerland) was used to analyze the thermal characteristics of the bio-oil. Ten milligrams of the bio-oil sample was pyrolyzed with a heating rate of 20°C/min. The temperature of the furnace was programmed to rise from 25 to 500°C. The volatiles were carried out by nitrogen gas of 99.99% purity with a flow rate of 50 cm^3/min. The analysis was carried out in triplicate.

FT-IR Analysis

Infrared analysis was used to determine the main organic components based on the peaks of the present functional groups using a Fourier transform infrared (FT-IR) spectrometer (NICOLET380-FT-IR).

GC-MS Analysis

The gas chromatography-mass spectrometer (GC-MS) spectra of the bio-oil were analyzed using a DSQ-GC-MS system with a DB-1 polysiloxane-coated capillary column (30 m × 0.25 m i.d., film thickness of 0.25 mm). Helium gas with 99.99% purity was used as a carrier gas with a flow rate of 1.2 cm^3/min. The column temperature was programmed from 20 to 240°C at a heating rate of 10°C/min after an initial 2 min isothermal period. The column was kept at the temperature of 60°C and the final temperature for 5 and 30 min, respectively. A sample injection was made in the split mode (1:40). The mass spectrometer was set at an ionizing voltage of 70 eV and a mass range of 30–500 u. The sweep time is 0.5 s. The identification of organic compounds was accomplished by comparing the mass spectra of the resolved components using electronic library search routines.

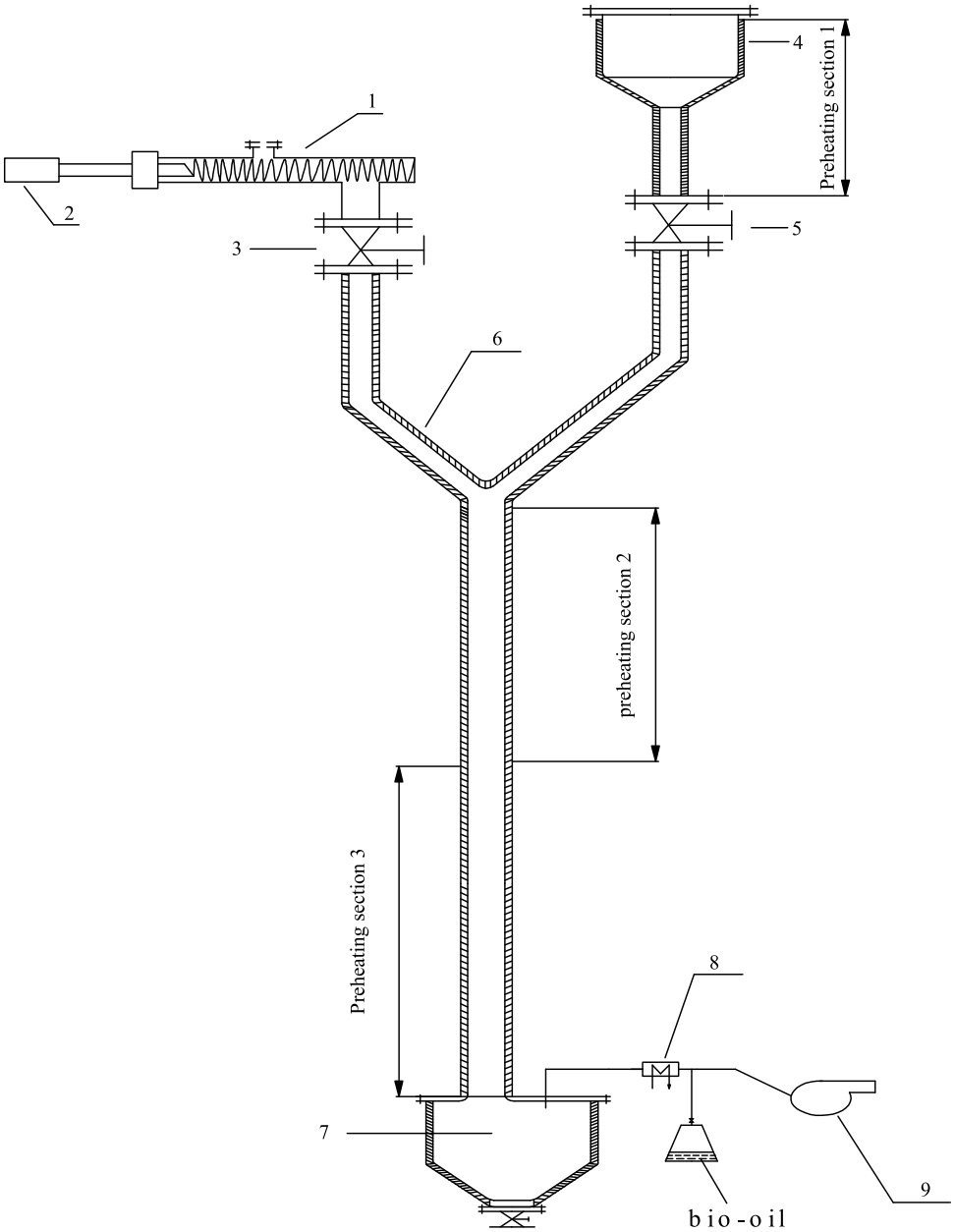

FIGURE 1 The schematic diagram of the free-fall reactor. (Note. 1: Screw feeder; 2: Electromotor; 3 and 5: Inlet valve; 4 and 7: Storage tank; 6: Thermal barrier; 8: Condensator; 9: Vacuum pump.)

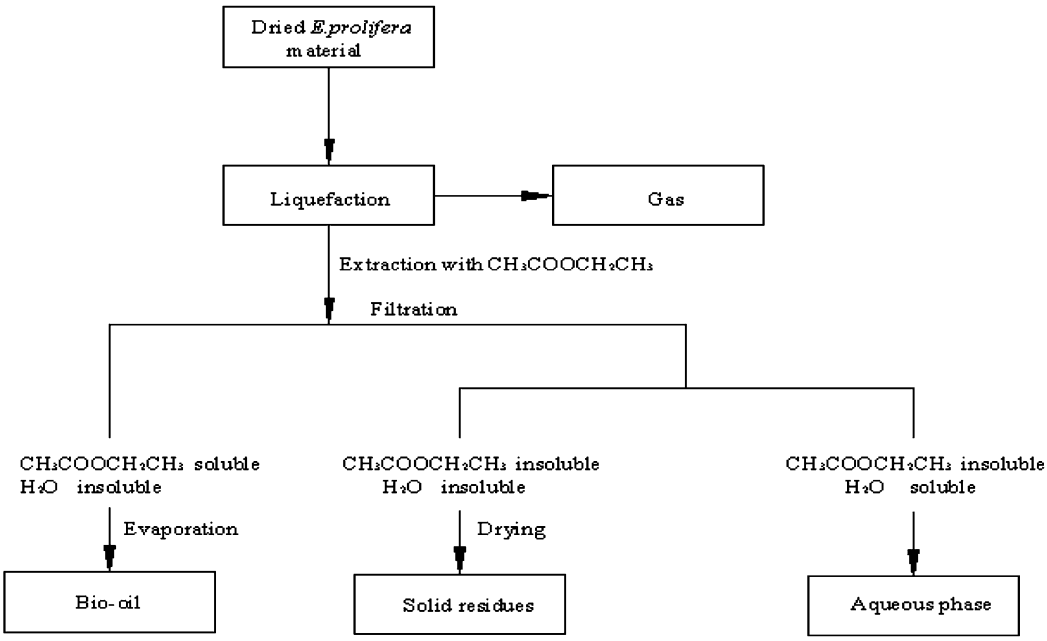

FIGURE 2 Procedure for liquefaction products.

TABLE 2
The Main Physical Properties of Bio-oil

Properties	*Bio-oil*
Ash (wt%)	2.29 ± 0.13
H_2O (wt%)	32.45 ± 2.55
Density (g/cm^3)	1.037 ± 0.02
pH	2.56 ± 0.11
Heat value (MJ/kg)	25.33 ± 3.01

TABLE 3
Elemental Analysis Results of Bio-oil (%)

Bio-oil						
C	*H*	*N*	*O*[a]	*S*	*C/H*	*C/N*
59.52 ± 2.65	7.96 ± 1.01	2.05 ± 0.31	30.27	0.20 ± 0.02	6.60 ± 0.42	25.62 ± 2.08

[a]Calculated by difference, O(%) = 100-C-H-N-S.

RESULTS AND DISCUSSION

Main Characteristics of *E. prolifera* Sample

Proximate, ultimate, and component analysis results of an *E. prolifera* sample were shown in Table 1.

Physical Properties of Bio-oil

The main physical properties of bio-oil were shown in Table 2, and the results of bio-oil elemental analysis were listed in Table 3. The results showed that the average heat value was 25.33 MJ kg^{-1}, which is bigger than 17.25 and 19.91 MJ kg^{-1} in batch feeding and the fixed bed reactor as researched by Asadullah et al. (2007), and the oxygen content was only 30.27 wt%.

Thermochemical Properties of Bio-oil

Figure 3 showed the weight loss and the rate of weight loss curve obtained during the pyrolysis of bio-oil sample under nitrogen atmosphere at a heating rate of 20°C/min. Two stages could be distinguished during the thermal degradation of bio-oil. The first stage went from room temperature to 240°C. The first stage was characterized by a major weight loss, which corresponded to the main pyrolysis process. This could be due to the fact that most water and organics with low boiling points were decomposed. The mass loss of this stage was more than 90% of total volatiles. The second stage went from 240°C to the final temperature of 500°C. In this stage, the carbonaceous and other residues continuously were decomposed at a very slow rate and a slight continued loss of weight was shown in the weight loss curve.

The analysis of the rate of weight loss curve showed that there were two strong peaks, and therefore two decomposition processes appeared during the degradation of bio-oil. The first peak appeared at the temperature of 68.61°C and the second peak appeared at the temperature of

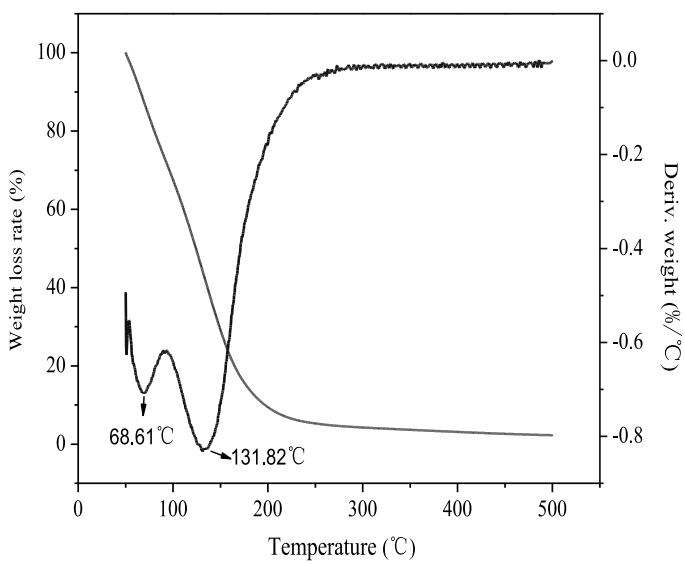

FIGURE 3 TG-DTG curves of bio-oil.

TABLE 4
The Thermal Degradation Characteristics of the Bio-oil

	Volatiles, %		
	I	II	*Char*
Bio-oil	94.51	3.25	2.24

131.28°C, which might correspond to the degradation of water and low boiling point organics, respectively. The results of main physical properties analysis were listed in Table 2. The degradation characteristics of the bio-oil in terms of devolatilization temperatures and total volatile matter content were shown in Table 4.

Chemical Composition of Bio-oil

The FT-IR spectra of bio-oil showed characteristic absorption peaks that reflected special functional groups and the presence of corresponding category compounds. Interpretation of the main bands was based on Socrates. The FT-IR analysis result of bio-oil was shown in Figure 4 and the functional groups were listed in Table 5. The peak at 3,383 cm^{-1} is related to O–H stretching vibration that was caused by water or alcohol in the bio-oil. The band appears at 2,928 cm^{-1}, which may attribute to C–H stretching, indicating the possible existence of alkyl C–H. The bands at 2,167 cm^{-1}, as a result of C≡C stretching vibration, show the presence of alkynes. The C=O stretching vibration at 1,715 cm^{-1} indicate the presence of ketones, aldehydes, esters, or acids. The bands at 1,261, 1,174, and 1,102 cm^{-1} are related to C–O stretching vibration, showing possible existence of acids or alcohols in the bio-oil from fast pyrolysis of *E. prolifera.*

A lot of peaks were detected in the spectra of the bio-oil using GC-MS and the standard in the NIST Mass Spectra database, showing the existence of some additional compounds that are difficult to be identified by FT-IR, for they are in trace amounts. Total ionic chromatograms (TIC)

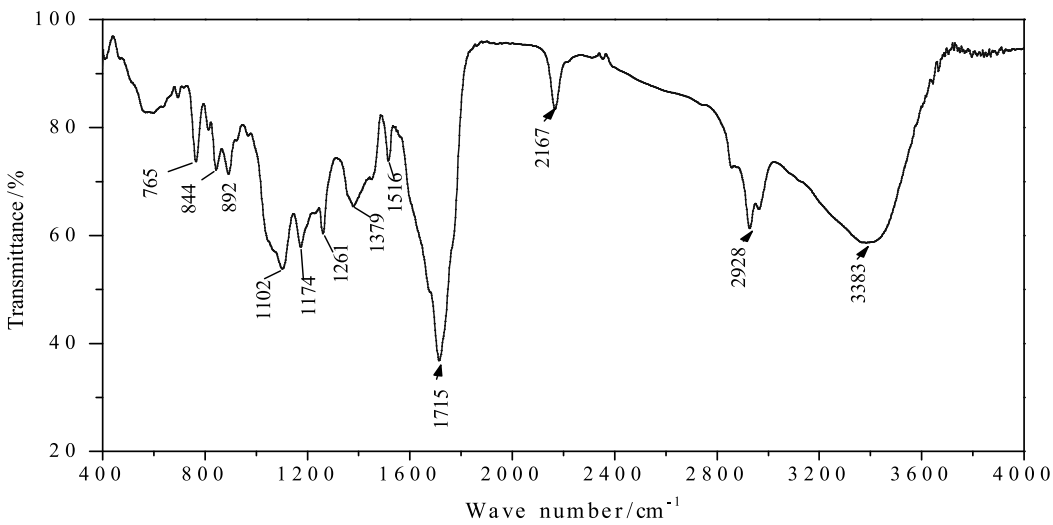

FIGURE 4 FT-IR spectra of bio-oil from fast pyrolysis of *E. prolifera*.

TABLE 5
FT-IR Functional Groups of Bio-oil from Fast Pyrolysis of *E. prolifera*

Frequency Range, cm^{-1}	*Frequency, cm^{-1}*	*Group*	*Class of Compound*
3,300–3,600	3,383	O–H stretching	Polymeric O–H, water impurities
3,050–2,800	2,928	C–H stretching	Alkanes
2,100–2,200	2,167	C≡C stretching	Alkynes
1,750–1,650	1,715	C=O stretching	Ketones, aldehydes, carboxylic acids
1,600–1,450	1,516	C=C skeletal vibration	Alkene
1,465–1,340	1,379	C–H bending vibrations	Alkanes
1,300–950	1,261, 1,174, 1,102	C–O stretching	Primary, secondary, and tertiary alchol
915–650	892, 844, 765	O–H bending	Phenol, esters, ethers, aromatics

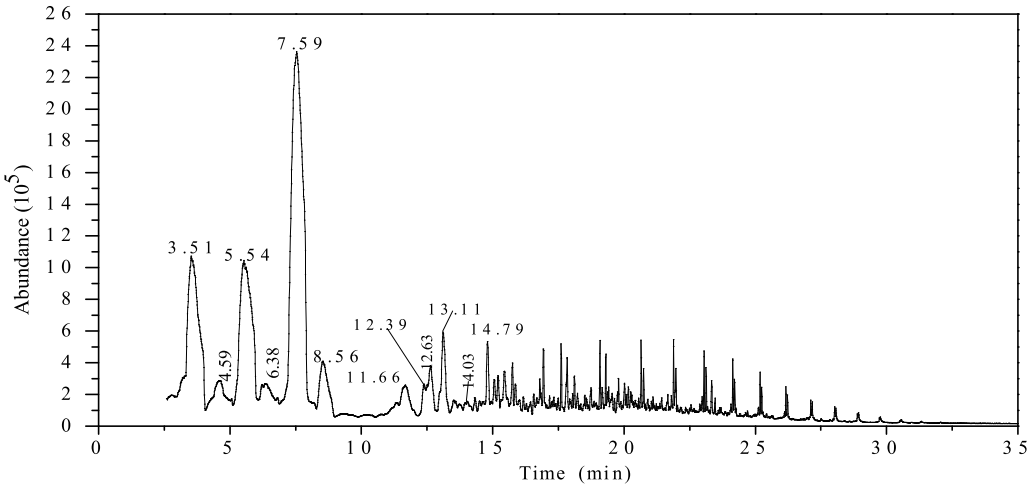

FIGURE 5 Total ionic chromatograms (TIC) of bio-oil obtained by pyrolysis of *E. prolifera*.

TABLE 6
Major Chemical Compositions of Bio-oil Analyzed by GC-MS Analysis

No.	*RT, min*	*Name of Compounds*
1	3.508	(rep lib)Furfural
2	4.592	(main lib)Pyridine,1,2,5,6-tetrahydro-1,2-dimethyl-
3	5.535	(main lib)2-Furancarboxaldehyde,5-methyl-
4	6.376	(main lib)2,3-Dihydrooxazole, 2-t-butyl-4(1-hydroxy-1-methylethyl)-3-methoxycarbonyl-5-methyl-
5	7.545	(rep lib)2-Furancarbox-aldehyde,5-methyl-
6	8.556	(rep lib)Phenol
7	11.658	(main lib)5-Methyl-5-octen-1-ol
8	12.388	(rep lib)Phenol,3-methyl-
9	12.631	(main lib)trans-8-Hydroxy-bicyclo(4,3,0) non-3-ene
10	13.107	(rep lib)Phenol,4-methyl-
11	14.030	(main lib)3,5-Dimethyl-cyclohexanone oxime
12	14.790	(rep lib)Benzyl nitrile

of the bio-oil analysis are shown in Figure 5, and 12 typical compounds of major chemicals categorized were found in the study, which are listed in Table 5. The results listed in Table 5, that is the compounds detected by GC-MS, correspond to the results listed in Table 6. In other words, the results detected by GC-MS make an excellent complement to the results obtained by FT-IR. According to the results, the categories of aldehydes, alkene, hydroxybenzene, alcohols, hydrocyanic esters, and fatty acids exist in the bio-oil. The results are much similar to those bio-oils obtained from other algae by the pyrolysis or hydrothermal liquefaction process. However, the main composition of the bio-oil obtained from the *E. prolifera* is different from that of lignocellulosic materials by fast pyrolysis process. The production of bio-oil is mainly converted by its main components, wherefore there are differences between bio-oils components composition.

CONCLUSIONS

E. prolifera was pyrolyzed and converted into bio-oil in one free-fall reactor. Pyrolysis characteristics of the bio-oil were investigated using a thermogravimetric analyzer. The bio-oil obtained was analyzed by elemental, GC-MS, and FT-IR analysis. The results showed that the average heat value was 25.33 MJ kg^{-1} and the oxygen content was 30.27 wt%. The results suggested that *E. prolifera* presents as a good bio-oil feedstock candidate.

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