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Pyrolysis of fast-growing aquatic biomass – *Lemna minor* (duckweed): Characterization of pyrolysis products

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ABSTRACT

The aim of this work was to conduct the experimental study of pyrolysis of fast-growing aquatic biomass – *Lemna minor* (commonly known as duckweed) with the emphasis on the characterization of main products of pyrolysis. The yields of pyrolysis gas, pyrolytic oil (bio-oil) and char were determined as a function of pyrolysis temperature and the sweep gas (Ar) flow rate. Thermogravimetric/differential thermogravimetric (TG/DTG) analyses of duckweed samples in inert (helium gas) and oxidative (air) atmosphere revealed differences in the TG/DTG patterns obtained for duckweed and typical plant biomass. The bio-oil samples produced by duckweed pyrolysis at different reaction conditions were analyzed using GC–MS technique. It was found that pyrolysis temperature had minor effect on the bio-oil product slate, but exerted major influence on the relative quantities of the individual pyrolysis products obtained. While, the residence time of the pyrolysis vapors had negligible effect on the yield and composition of the duckweed pyrolysis products.

1. Introduction

The growing demand for clean renewable energy is driving the worldwide efforts to develop environmentally benign and efficient technological processes for converting biomass to energy and transportation fuels. Biomass is considered to be a carbon neutral resource because an equivalent amount of CO_2 is absorbed from the atmosphere during its growth. Of particular importance is the potential of biomass-derived fuels to replace petroleum-based fuels such as gasoline, jet and diesel fuel, thus, reducing the dependence on imported oil. Hydrocarbon-based bio-fuels offer several advantages over oxygenated bio-fuels (e.g., bio-diesel, bio-ethanol) in that they have higher volumetric energy content and are compatible with the existing fuel delivery and distribution infrastructure.

One of the major concerns with regard to the development of sustainable land-based biomass energy production systems relates to a possible change in the arable land use. From this viewpoint, aquatic biomass offers the advantage over its terrestrial counterpart in that it does not compete with food for land usage. Besides, aquatic biomass has higher photosynthetic efficiency and faster growth rate compared to terrestrial lignocellulosic biomass. Much of the recent developments on bio-fuel production from aquatic biomass has been focused on microalgae (Miao and Wu, 2004; Amin, 2009; Mata et al., 2010; Brennan and Owende, 2010; Shuping et al., 2010). Thermochemical liquefaction and pyrolysis have been the main techniques used for generating bio-fuels from microalgae. Minowa et al. (1995) conducted thermochemical liquefaction of *Dunaliella tertiolecta* at 300 °C and 10 MPa to produce fuel oil like liquid. Dote et al. (1994) have liquefied *Botryococcus braunii* to a product similar to petroleum-based oil. Miao and Wu (2004) and Miao et al. (2004) have used fast pyrolysis to produce bio-oil from *Chlorella protothecoides*. Demirbaş (2006) has used various species of moss and algae to produce bio-oil via pyrolysis technique. One of the challenges with the practical realization of microalgae based systems is the energy intensive step of recovering relatively dry algal biomass from the aqueous medium. Duckweed (scientific name: *Lemna minor*) is one of the fastest growing aquatic plants and, advantageously, it can be easily recovered from the growing medium by a simple separation process. Duckweeds have traditionally been used to treat wastewater streams (Hammouda et al., 1995; Cheng and Stomp, 2009) for they have been known as excellent accumulators of trace elements and heavy metals (Prasad et al., 2001; Appenroth et al., 2010) from polluted industrial waste streams and landfill leachates. Duckweeds also have high protein content and have been used as an animal feed (Bairagi et al., 2002).

There is a paucity of data in the literature on thermochemical processing of duckweeds for liquid bio-fuel production. In this paper, we report the experimental results obtained from duckweed pyrolysis and its conversion to pyrolysis gas, bio-oil and char.

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The pyrolysis products were collected and analyzed using a number of analytical and materials characterization techniques.

2. Methods

2.1. Duckweed samples

The samples of dry duckweed were provided by Petroalgae Inc. (Melbourne, Florida, USA) and were used as received. The proximate analysis of dry duckweed is as follows (wt.%): moisture – 3.7; total volatiles (120–950 °C) – 78.0 (including volatiles evolved at 120–650 °C – 67); fixed carbon – 8.8; ash – 9.5. The ultimate analysis of a dry duckweed sample gave the following (%): C – 39.11; H – 6.13; O – 37.74; N – 5.52; S – 0.67; balance – mineral matter.

2.2. Duckweed pyrolysis experiments

The experimental setup consists of a quartz tube reactor with the internal diameter of 13 mm heated by a tube furnace ("Thermolyne"). Typically, a 2.27–2.53 g sample of duckweed (pre-dried at 120 °C overnight) was placed inside the reactor which was connected to an argon (Ar) tank having a delivery pressure of 34.5 kPa. The flow rate of Ar sweep gas was varied in the range of 36–150 mL/min using a metering valve and a calibrated flow metering rotameter. A *K*-type thermocouple was inserted into the center of the heated zone for controlling the temperature via a PID controller (Eurotherm 2116). The reactor outlet was connected to a Pyrex™ glass condenser which was cooled by ice. Prior to each run, the reactor and all connecting lines were purged with Ar. After the furnace temperature reached the desired level and stabilized, the section of the reactor containing the duckweed sample was inserted into the heated zone and kept there for 15 min. During the run, the pyrolysis liquid was condensed on the quartz tube walls outside the furnace and in the ice cooled condenser. The non-condensable gases were allowed to accumulate in a Teflon gas bag. The pyrolysis reaction was carried out at the temperature range of 400–700 °C. At the end of the run, the tube furnace was switched off and the gas collected in the sampling bag was analyzed gas-chromatographically. The pyrolytic liquid product was collected by rinsing the reactor with dichloromethane (DCM) and gathering the liquid in the condenser (which already had some portion of pyrolysis oil condensed there during pyrolysis). DCM with dissolved liquid products of pyrolysis was left overnight to evaporate (small amount of water formed during pyrolysis was also evaporated). The resulting bio-oil was weighed and analyzed on a gas chromatography–mass spectrometer (GC–MS) system. The solid residue (char, or bio-char) remaining after each test was collected and weighed.

The experimental data on the duckweed pyrolysis products yields were subjected to the one-way analysis of variance (ANOVA) as implemented in the GraphPad InStat 3 statistics platform. In order to ascertain that the observed variations in the yield of pyrolytic gas, bio-oil and bio-char as a result of changes in the residence time (expressed in terms of argon flow rate) and pyrolysis temperature are statistically significant, the probability (*P*) values were determined. If the *P* values were small (post-test following one-way ANOVA), then it is unlikely that the differences in the values of dependent variables (i.e., yield of gas, bio-oil and char) observed are coincidental and due to random sampling.

2.3. Analysis of duckweed pyrolysis products

Duckweed pyrolysis gases were analyzed by Varian 450 GC (Varian Inc., Palo Alto, CA, USA) with a thermal conductivity detector for permanent gases and a flame ionization detector for hydrocarbon gases; Ar was used as a carrier gas and three columns were employed for separation of components: PLOT alumina/KCL, Molecular sieve 13× and Haysep Q. Bio-oil was analyzed by GC–MS method using Agilent 6890 GC (Agilent Technologies Inc., Santa Clara, USA) coupled with JEOL GCmate-II MS (JEOL Ltd., Tokyo, Japan). Typical GC–MS parameters used in the analyses were as follows: Helium as carrier gas at a flow rate of 2 mL/min, column: HP-5 m/s (60 m × 0.32 mm × 0.25 μm), injection port temperature: 300 °C, GC-MS interface temperature: 250 °C, a sample injection volume: 10 μL, split ratio: 10:1.

The thermogravimetric (TG) and differential thermogravimetric (DTG) analyses of the duckweed sample were carried out in a Perkin-Elmer Diamond TG/DTA (PerkinElmer Inc., Waltham, MA, USA) instrument using helium or air as a carrier (sweeping) gas. In a typical TG analysis, about 10 mg of the sample was loaded into the instrument and heated from 50 to 950 °C at a heating rate of 20 °C/min in helium (during duckweed pyrolysis tests) or air (during duckweed combustion tests) flow.

3. Results and discussion

3.1. Duckweed pyrolysis

Two sets of duckweed pyrolysis experiments were conducted: one with the sweep gas flow rate and another with pyrolysis temperature as variables.

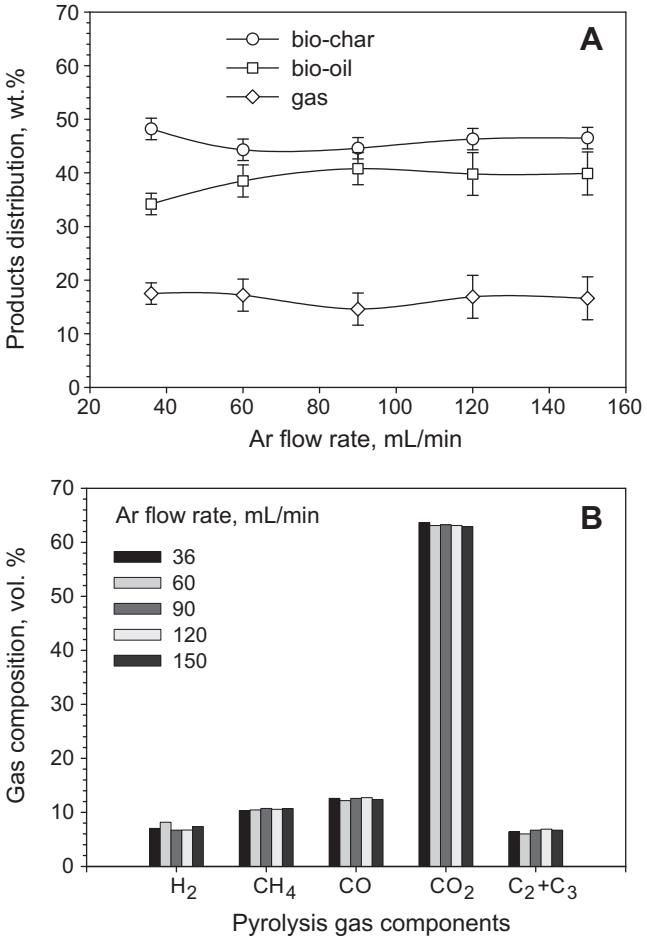

Fig. 1. Distribution of products (A) and composition of pyrolysis gas (B) produced by duckweed pyrolysis carried out at different flow rates of Ar sweeping gas. Temperature: 500 °C.

Effect of sweep gas flow rate. Fig. 1 shows the yield of the duckweed pyrolysis products (gas, bio-oil, char) (A) and the composition of pyrolysis gas (B) as a function of the sweep gas (Ar) flow rate varied in the range of 36–150 mL/min at pyrolysis temperature of 500 °C (Note that Ar flow rate is inversely proportional to residence time: higher flow rate – lower residence time; for the sake of simplicity, we will use Ar flow rate as an independent variable). The results presented in Fig. 1A show a trend towards increasing the bio-oil yield and decreasing pyrolysis gas yield at the lower range of Ar flow rates. This effect can be explained by relatively fast removal of pyrolysis products from the reaction zone that results in shorter residence time in the heated zone and over char as the char and oils are being formed. One should note the higher values for the error bars, especially for bio-oil, at the high flow rates, which can be attributed to the fact that at these conditions a small fraction of the oil product in the form aerosols passes through the condenser without being captured, and, thus, remains unaccounted for. The experimental data were subjected to statistical analysis (see Section 2.2), which indicated that the probability (P) values were well above 0.05 – implying that the observed variations in the measured values of gas, bio-oil and bio-char yields due to changes in the flow rate of the sweep gas in the range of 60–150 mL/min are not statistically significant.

The composition of pyrolysis gas as a function of Ar flow rate is depicted in Fig. 1B. The major gaseous products of duckweed pyrolysis are H_2, CO, CO_2 and CH_4, with small amounts of C_2H_6 and C_2H_4 hydrocarbons present. CO_2 is by far the major component of the gaseous mixture amounting to about 60 vol.%. Fig. 1B shows that there is no appreciable change in pyrolysis gas composition with the Ar flow rate.

Effect of temperature. Fig. 2 depicts the effect of pyrolysis temperature varied in the range of 400–700 °C on the yield of pyrolysis products (A) and pyrolysis gas composition (B) at constant Ar flow rate of 60 mL/min. The yield of pyrolysis gas, as expected, increases monotonously in the entire temperature range (Fig. 2A), which could be due to the secondary decomposition of both char and volatiles at high temperatures. A statistical analysis of the data of Fig. 2A seems to indicate that the variations in the measured values of bio-oil and bio-char yields in the range of temperatures 400–700 °C are not statistically significant. Fig. 2B depicts the changes in the composition of duckweed pyrolysis gas as a function of pyrolysis temperature. Unlike Ar flow rate, the temperature change has a profound effect on the composition of the pyrolysis gas. In particular, there was a significant drop in CO_2 concentration and rise in H_2 and CO concentrations in the gaseous products with increased pyrolysis temperature. The concentrations of hydrocarbon products such as methane and ethylene also increased with temperature. A sharp increase in H_2 yield signals the contribution of deep cracking reactions involving condensable and non-condensable products (the latter may explain a plateau for the methane yield) at elevated temperatures (Menéndez et al., 2007; Becidan et al., 2007). The increase in CO content in the pyrolysis gas may be contributed (at least, partially) to the reverse Boudouard reaction between CO_2 and carbon in char. This reaction also explains the reduction in CO_2 concentration in the pyrolysis gas (Yang et al., 2006; Menéndez et al., 2007).

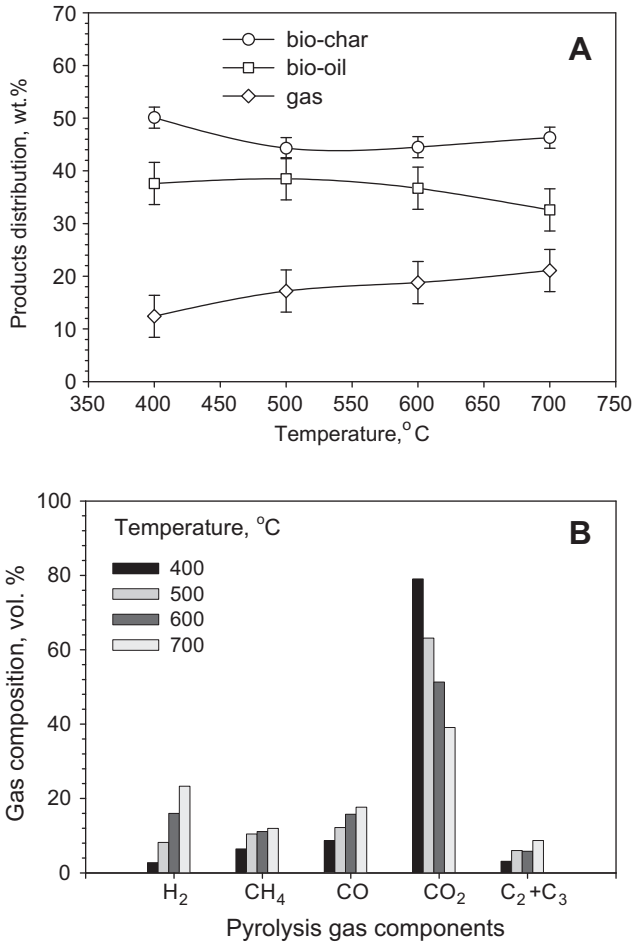

Fig. 2. Distribution of products (A) and composition of pyrolysis gas (B) produced by pyrolysis of duckweed as a function of pyrolysis temperature. Ar flow rate: 60 mL/min.

3.2. Thermogravimetric analysis of duckweed thermal conversion

The TG/DTG analyses of a pre-dried (at 120 °C) duckweed sample in helium and air atmosphere at a temperature range of 50–950 °C and heating rate of 20 °C/min was conducted. The TG pattern of the duckweed sample shows a significant weight loss in the temperature range of 200–350 °C. This is followed by an intermediate region at the temperature range of 350–450 °C, and rather slow rate of weight loss at temperatures above 500 °C. The DTG curve shows a rather intensive and broad trough in the temperature range of 275–325 °C and weak troughs at 160 °C, 460 °C and 760 °C. The comparison of TG/DTG profiles for duckweed with that of terrestrial biomass, e.g., poplar, willow (Mészáros et al., 2004), forest residue, saw dust (Skodras et al., 2006), shows significant differences. In particular, the intensive trough on the DTG curve for duckweed is shifted to lower temperature range by about 40–50 °C compared to the intensive troughs in DTG of a plant biomass. Secondly, the DTG thermogram of plant biomass distinctly shows the presence of a large trough and a rather intense shoulder about 50–80 °C apart (assigned to cellulose and hemicellulose, respectively), whereas, the DTG pattern for duckweed exhibits two almost fused troughs only 20–30 °C apart.

The above observations are consistent with the complex structure of duckweed biomass, comprising several classes of natural compounds (i.e., proteins, lipids, carbohydrates, etc.), each of which is characterized by a distinct thermal signature. The intensive double-trough in the DTG curve of duckweed (at 275–325 °C) is in the same temperature range as that of plant hemicellulose (e.g., Mészáros et al., 2004; Skodras et al., 2006) and raw protein. In particular, it has been reported recently (Shuping et al., 2010) that the DTG curve of a marine microalgae showed one intensive peak at 285 °C (at a sample heating rate of 20 °C/min), which was assigned to microalgae protein. Other authors also pointed at rather low thermal stability of proteins, e.g., according to Renugopalakrishnan et al. (2006), thermal stability of proteins is limited to about 200 °C. Cellulose decomposition peak, which

typically manifests itself in the temperature range of 350–370 °C (Mészáros et al., 2004; Skodras et al., 2006) is not seen on the duckweed DTG curve (although the weak peak could be hidden in the tail of the intensive peak). The weak peaks in the low temperature range (up to 200 °C) could result from degradation of thermally unstable functional groups of various organic compounds. The weak peak at about 465 °C lies in the high temperature range where thermal degradation of lignin typically occurs (Mészáros et al., 2004; Ranzi et al., 2008), so, this result may indicate the presence of lignin-like compounds in duckweed. A weak peak at very high temperature range (760 °C) may have originated from the thermal transformation of inorganic components (ash) present in duckweed.

The DTG profile of duckweed thermolysis in air at the temperature range of 50–950 °C and heating rate of 20 °C/min markedly differs from that obtained in inert helium atmosphere in that there are two areas of significant weight loss separated by about 270 °C. The low-temperature intensive peak (265 °C) on the DTG curve (in air) is slightly shifted to lower temperatures compared to that obtained in helium atmosphere. This observation implies that the presence of oxygen only slightly affects thermolysis of duckweed at temperatures below 400–450 °C. The high temperature peak at 540 °C is absent on the DTG thermogram of duckweed in He, and, presumably, it results from combustion of bio-char. Similar two-peak behavior related to oxidative thermolysis of straw and waste wood has been reported by Skodras et al. (2006) and Senneka et al. (2002), although in their cases the high temperature peak was observed at the lower temperature range of 460 °C and 440 °C, respectively (at a heating rate of 20 °C/min). The relatively weak peak at 430 °C located between two intensive peaks on the duckweed DTG curve can be assigned to thermal degradation of lignin-like compounds.

Mechanistically, three reaction pathways can be envisioned with regard to oxidative pyrolysis of biomass matter (e.g., Senneka et al. 2002), and those can also be applied to duckweed as follows:

(a) initial pyrolysis of biomass to volatile matter and char followed by their combustion,
(b) direct combustion of biomass to oxidation products, predominantly, CO_x, H_2O,
(c) combination of (a) and (b) pathways.

Each of these pathways would result in different DTG signature as shown in Fig. 3 (for simplicity, the DTG curve of biomass in an inert atmosphere is presented by a single peak). Comparing the DTG patterns of duckweed in air to those shown in Fig. 3, one can conclude that oxidative pyrolysis of duckweed, in all likelihood, follows along pathway (c), i.e., the combination of (a) and (b) with pathway (a) prevailing.

3.3. Analysis of duckweed pyrolysis bio-oil

Bio-oil produced by duckweed pyrolysis is a dark-brown viscous liquid. The GC–MS analyses of dichloromethane-dissolved bio-oil samples produced at pyrolysis temperature of 400 °C, 500 °C and 700 °C and Ar flow rate of 60 mL/min were conducted. The major components (identified by the search-match function of the GC–MS) of bio-oils are presented in Table 1. The results of the GC–MS analysis showed that pyrolysis temperature has minor effect on the pyrolysis product slate (i.e., a similar set of pyrolysis products is produced), however, the relative quantity of the individual products changes noticeably with the pyrolysis temperature. Particularly, the data show that the yield of lighter pyrolysis products such as phenol, 4-methylphenol, and 2-furanmethanol1H-imidazol-4-methanol increases at higher pyrolysis temperatures.

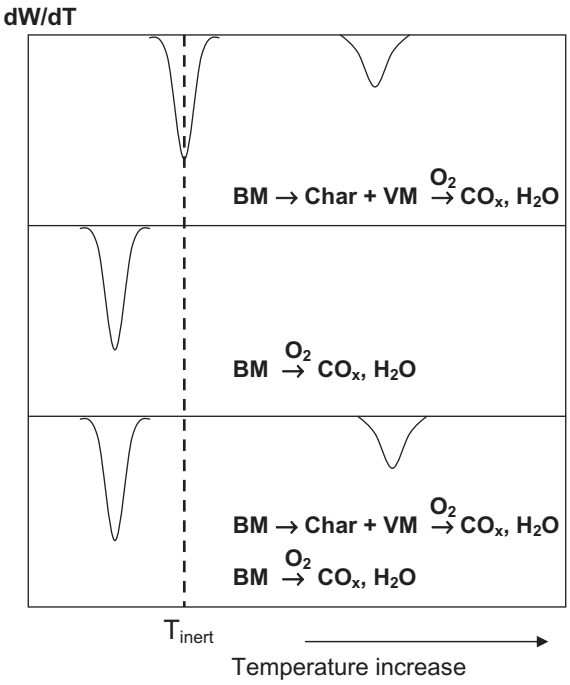

Fig. 3. DTG patterns related to three reaction pathways for oxidative pyrolysis of biomass. T_{inert} relates to DTG peak obtained in inert atmosphere. BM – biomass, VM – volatile matter.

Table 1
Main products (tentatively identified) of duckweed pyrolysis in Ar atmosphere found in the bio-oil analyzed by GC–MS method.

Retention time, min	Compound
4.3	Pyrrole
4.48	Toluene
5.2	3-Methyl-1H-pyrrole
5.38	2-Furanmethanol
5.56	Ethylbenzene
5.96	Styrene
6.2	Butyrolactone
6.45	2,5-Dimethyl pyridine
7.1	Phenol
7.54	4-Ethyl-2-methyl pyrrole
7.87	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
8.23	2-Methyl phenol
8.54	4-Methyl phenol
8.87	4-Pyridinol
8.99	3-Pyridinol
9.65	3,4,-Dimethyl phenol
9.91	4-Ethyl phenol
10.67	2,3-Dihydrobenzofuran
10.68	4-Tert-Butoxystyrene
11.11	Benzenepropanenitrile
11.88	Indole
13.16	3-Methyl-1H-indole
14.47	Levoglucosan
18.28, 18.72	3,7,11,15-Tetramethyl-2-hexadecen-1-ol (phytol)
21.59	N,N-Dimethyl-1-dodecamine
22.51	Z-11-Pentadecanol
24.30	Heptacosane
24.91	9-Octadecenoic acid
28.37	Squalene

The effect of the sweep gas flow rate on distribution of duckweed pyrolysis products was also investigated. In particular, GC–MS analysis of bio-oil samples obtained at 500 °C in Ar flow rates of 36 and 90 mL/min showed no significant differences in their GC–MS spectra. This implies that neither distribution nor relative quantity of duckweed pyrolysis products are much affected by the sweep gas flow rate.

It should be noted that pyrolysis products found in the duckweed bio-oil are quite similar to those of bio-oil derived from *Macrocystis pyrifera*, macroalgae as reported by Ross et al. (2008). Compounds like 2-furanmethanol, butyrolacton and 3-Methyl-2-hydroxy-cyclopenten-1-one are of carbohydrate origin. The phenolic compounds observed could be due to the lignin content though methoxyphenol compounds (typically found in terrestrial biomass) are completely absent. Long chain alcohol and acids can be attributed to the lipids content of duckweed. Duckweed bio-oil also contains abundant nitrogen containing compounds like pyrrole and indole.

4. Conclusions

This paper reports experimental findings for pyrolysis of one of the fastest growing aquatic biomass – duckweed (*Lemna minor*) with a special emphasis on the pyrolysis products (gas, bio-oil and char) characterization. It is shown that even at relatively low rates of pyrolysis (at 500 °C) it is possible to obtain in excess of 40 wt.% of bio-oil from dry duckweed. Faster pyrolysis rates would significantly increase the bio-oil yield. Major gaseous and liquid products of duckweed pyrolysis were identified. The TG/DTG analyses provided a means for the preliminary mechanistic interpretation of the duckweed pyrolysis process both in inert and oxidative atmosphere.

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References

Amin, S., 2009. Review on biofuel oil and gas production processes from microalgae. Energy Convers. Manage. 50, 1834–1840.

Appenroth, K.-J., Krech, K., Keresztes, Á., Fischer, W., Koloczek, H., 2010. Effects of nickel on the chloroplasts of the duckweeds *Spirodela polyrhiza* and *Lemna minor* and their possible use in biomonitoring and phytoremediation. Chemosphere 78 (3), 216–223.

Bairagi, A., Ghosh, K.S., Sen, S.K., Ray, A.K., 2002. Duckweed (*Lemna polyrhiza*) leaf meal as a source of feedstuff in formulated diets for rohu (Labeo rohita Ham.) fingerlings after fermentation with a fish intestinal bacterium. Bioresour. Technol. 85, 17–24.

Becidan, M., Skreiberg, Ø., Hustad, J.E., 2007. Products distribution and gas release in pyrolysis of thermally thick biomass residues samples. J. Anal. Appl. Pyrolysis. 78 (1), 207–213.

Brennan, L., Owende, P., 2010. Biofuels from Microalgae- A review of technologies for production, processing, and extraction of biofuels and co-products. Renew. Sustain. Energy Rev. 14 (2), 557–577.

Cheng, J.J., Stomp, A.-M., 2009. Growing duckweed to recover nutrients from wastewaters and for production of fuel ethanol and animal feed. Clean: Soil, Air, Water 37 (1), 17–26.

Demirbaş, A., 2006. Oily products from mosses and algae via pyrolysis. Energy Sources Part A 28, 933–940.

Dote, Y., Sawayama, S., Inoue, S., Minowa, T., Yokoyama, S., 1994. Recovery of liquid fuel from hydrocarbon-rich microalgae by thermochemical liquefaction. Fuel 73 (12), 1855–1857.

Hammouda, O., Gaber, A., Abdel-Hameeed, M.S., 1995. Assessment of the effectiveness of treatment of wastewater-contaminated aquatic systems with *Lemna gibba*. Enzyme Microb. Technol. 17, 317–323.

Mata, T.M., Martins, A.A., Caetano, N.S., 2010. Microalgae for biodiesel production and other applications: A review. Renew. Sustain. Energy Rev. 14, 217–232.

Menéndez, J.A., Domínguez, A., Fernández, Y., Pis, J.J., 2007. Evidence of self-gasification during the microwave-induced pyrolysis of coffee hulls. Energy & Fuels 21 (1), 373–378.

Mészáros, E., Várhegyi, G., Jakab, E., 2004. Thermogravimetric and reaction kinetic analysis of biomass samples from an energy plantation. Energy & Fuels 18 (2), 497–507.

Miao, X., Wu, Q., 2004. High yield bio-oil production from fast pyrolysis by metabolic controlling of *Chlorella protothecoides*. J. Biotechnol. 110, 85–93.

Miao, X., Wu, Q., Yang, C., 2004. Fast pyrolysis of microalgae to produce renewable fuel. J. Anal. Appl. Pyrolysis. 71, 855–863.

Minowa, T., Yokoyama, S., Kishimoto, M., Okakura, T., 1995. Oil production from algal cells of *Dunaliella tertiolecta* by direct thermochemical liquefaction. Fuel 74 (12), 1735–1738.

Prasad, M.N.V., Malec, P., Waloszek, A., Bojko, M., Strzalka, K., 2001. Physiological responses of *Lemna trisulca L* (Duckweed) to cadmium and copper bioaccumulation. Plant Sci. 161, 881–889.

Ranzi, E., Cuoci, A., Faravelli, T., Frassoldati, A., Migliavacca, G., Pierucci, S., Sommariva, S., 2008. Chemical kinetics of biomass pyrolysis. Energy & Fuels 22 (6), 4292–4300.

Renugopalakrishnan, V., Wei, X., Narasimhan, G., Verma, S., Li, P., Anumanthat, A., 2006. Enhancement of protein thermal stability: toward the design of robust proteins for bionanotechnological applications. In: Renugopalakrishnan, V., Lewis, R.V. (Eds.), Bionanotechnology: Proteins to Nanodevices. Elsevier, pp. 117–139.

Ross, A., Jones, J., Kubacki, M., Bridgeman, T., 2008. Classification of macroalgae as fuel and its thermochemical behavior. Bioresour. Technol. 99 (14), 6494–6504.

Senneka, O., Chirone, R., Salatino, P., 2002. A thermogravimetric study of nonfossil solid fuels. 2. Oxidative pyrolysis and char combustion. Energy & Fuels 16 (3), 661–668.

Shuping, Z., Yulong, W., Mingde, Y., Chun, L., Junmao, T., 2010. Pyrolysis characteristics and kinetics of the marine microalgae *Dunaliella tertiolecta* using thermogravimetric analyzer. Bioresour. Technol. 101 (1), 359–365.

Skodras, G., Grammelis, P., Basinas, P., Kakaras, E., Sakellaropoulos, G., 2006. Pyrolysis and combustion characteristics of biomass and waste-derived feedstock. Ind. Eng. Chem. Res. 45 (11), 3791–3799.

Yang, H., Yan, R., Chen, H., Lee, D.H., Liang, D.T., Zheng, C., 2006. Pyrolysis of palm oil wastes for enhanced production of hydrogen rich gases. Fuel Process Technol. 87 (10), 935–942.