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# Production and characterization of *Lemna minor* bio-char and its catalytic application for biogas reforming

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ABSTRACT

Pyrolysis of fast-growing aquatic biomass - *Lemna minor* (commonly known as duckweed) with the emphasis on production, characterization and catalytic application of bio-char is reported in this paper. The yield of bio-char was determined as a function of *L. minor* pyrolysis temperature and sweep gas flow rate. It was found that the pore development during *L. minor* pyrolysis was not significant and the changes in the reaction conditions (temperature and sweep gas flow rate) did not alter markedly the textural characteristics and BET surface area of the bio-char produced. Thermogravimetric/differential thermogravimetric (TG/DTG) analyses of *L. minor* and different bio-char samples in inert (helium) and oxidative (air) media showed substantial differences in their TG/DTG patterns. A comparison of scanning electron micrographs (SEM) of *L. minor*, bio-char and ash indicated that the basic structural features of *L. minor* remained intact and were not affected by thermolysis. The inorganic ash content of *L. minor* derived bio-char is significantly higher than that of typical terrestrial (plant) biomass. The energy dispersive spectroscopic (EDS) analysis of *L. minor* ash showed that it mostly consisted of silica, and small quantities of Na, K and Ca compounds. The treatment of bio-char with $CO_2$ at 800 °C increased its BET surface area. It was found that $CO_2$-treated bio-char exhibited appreciable initial catalytic activity in biogas reforming.



## 1. Introduction

Due to ever growing concerns over depleting fossil fuel resources and their negative ecological impact, the development of environmentally benign and efficient processes for converting biomass energy to clean transportation fuels, chemicals and other value-added materials has received a worldwide attention. The advantages of using biomass are three-fold: it is a distributed, abundant and carbon-neutral resource. However, the use of terrestrial biomass for energy and fuels production is frequently queried by the relatively low solar energy conversion efficiency of plants and potential undesirable effects on the arable land for food production. From this point of view, the utilization of aquatic biomass via thermochemical conversion processes (*e.g.*, liquefaction, gasification or pyrolysis) is more advantageous since it does not compete with agriculture for land usage [1–4]. In terms of solar energy utilization efficiency, some types of aquatic biomass are an order of magnitude more efficient than common crops and most terrestrial biomass.

*Lemna minor* (commonly known as duckweed) is one of the fastest growing aquatic plants and presents the advantage of more facile (*e.g.*, compared to microalgae) harvesting (for simplification, hereafter, *L. minor* will be referred to as

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duckweed). Duckweed has been used to treat wastewater streams, as a scavenger for trace elements and heavy metals from polluted industrial waste streams and landfill leachate, and even as an animal feed, due to its high protein content [5–9]. However, there is a paucity of information in the literature on thermochemical processing of duckweed to fuels, chemicals and other products. Recently, Muradov et al. reported on bio-oil production and characterization by duckweed pyrolysis [10].

Besides biofuels and chemicals, biomass is a resource for production of other value-added products such as bio-chars. Benefits of soil amendment by bio-chars are well known. Bio-char acts by enhancing moisture retention and nutrient holding capacity of the soil (which means less dependence on chemical fertilizers). Also, due to its chemical inertness, bio-char is considered a method for long-term (thousands of years) sequestration of carbon in soils. These considerations imply that conversion of biomass to biofuels and bio-char can become an important carbon-negative technology [11].

Bio-chars have traditionally been used for production of activated carbons (AC) and other carbonaceous products [12]. In general, AC produced from bio-chars can be used as adsorbents, catalyst supports or utilized directly as catalyst, due to their stability, availability and low cost. Among more recent applications of ACs and bio-chars are their use as catalysts for methane decomposition [13–20] and $CO_2$ reforming (or dry reforming) of methane [21–24].

Application of bio-char as catalyst for biogas reforming has many environmental benefits, such as the use of renewable, easily disposable non-metal catalyst and its value in converting greenhouse gases ($CO_2$ and $CH_4$) to value-added products (*e.g.,* transportation fuels) via Fischer-Tropsch synthesis. Another advantage of using bio-char-based catalysts for biogas reforming is that carbon-based catalysts are quite resistant to deactivation by $H_2S$ and other sulfur-containing gases [20]. Note that conventional catalysts for biogas reforming or dry reforming contain expensive noble metals (Pt, Rh, Ir) or Ni that are easily poisoned by sulfurous compounds, thus, an elaborate and costly desulfurization step is often necessary prior to reforming process [25].

There is a paucity of data in the literature with regard to production and characterization of bio-chars from fast-growing aquatic biomass such as duckweed and, especially, on their catalytic activity. This paper provides, for the first time, experimental data for the pyrolytic production and characterization (BET, TG/DTG, EDS, FTIR, XRD, and SEM) of duckweed-derived bio-char. Also, the catalytic activity of duckweed-derived bio-chars for biogas reforming has been carried out and findings are presented in this paper.

## 2. Materials and methods

### 2.1. *Duckweed samples*

The samples of duckweed were harvested from PetroAlgae, Inc. demonstration facility in Fellsmere, Florida (Latitude: 27° 46′ 4N, Longitude: 80° 36′ 5W). The samples were dried at ambient temperature and stored in a refrigerator at 5 °C prior to the experiments. No further pre-treatment of the duckweed samples was carried out. The proximate analysis of dry duckweed is as follows (weight fraction, %): moisture − 3.7; total volatiles (120–950 °C) − 78.0 (including volatiles evolved at 120–650 °C − 67.0); fixed carbon − 8.8; ash − 9.5. The ultimate analysis of a dry duckweed sample yielded (weight fraction, %): C − 39.11; H − 6.13; O − 37.74; N − 5.52; S − 0.67; balance − others.

### 2.2. *Bio-char production via duckweed pyrolysis*

A 2.3–2.5 g sample of duckweed, pre-dried at 120 °C overnight, was placed inside a quartz tube reactor with the internal diameter of 13 mm. All experiments were carried out at atmospheric pressure. Prior to each run, the reactor and all connecting lines were purged with Ar gas (used as sweep gas) at room temperature. The flow rate of Ar sweep gas was varied by means of a metering valve and a calibrated rotameter. Pyrolysis of dry duckweed samples occurred inside a tubular furnace ("Thermolyne") fitted with a K-type thermocouple located in the center of the heated zone that allowed temperature control via a PID controller (Eurotherm 2116). In a typical experiment, the furnace was heated to a pre-set temperature and allowed to equilibrate. After the furnace temperature had stabilized, the quartz reactor containing the duckweed sample was placed inside the heated zone and allowed to remain there for 15 min. The pyrolysis temperatures and argon sweep gas flow rates selected were in the range of 400–700 °C and 36–150 $cm^3\ min^{-1}$, respectively. At the end of each run, the remaining solid residue (bio-char) was carefully removed from the reactor, weighed and analyzed.

Duckweed-derived bio-chars were heated at 850 °C for 15 min in a $CO_2$ stream in order to increase their porosity; this treatment resulted in additional 14% weight loss (due to burn-off) and in increased bio-char surface area.

### 2.3. *Characterization of duckweed bio-char*

The textural characterization of the bio-chars produced was carried out by means of $N_2$ adsorption–desorption isotherms at −196 °C in a Micromeritics Tristar II 3020 apparatus. The BET method was applied to the $N_2$ adsorption isotherms in order to determine the BET surface area, $S_{BET}$ [26]. Total pores volume, $V_p$, contribution of mesopores and micropores, were calculated from the quantity adsorbed at saturation point, according to the Gurvistsh rule [27]. Volume of mesopores, $V_{meso}$, and micropores, $V_{mic}$, were determined by applying BHJ method to $N_2$ desorption isotherms [28] and Dubinin-Radushkevich method to $N_2$ adsorption isotherms [29], respectively. Besides, the helium density, or real density ($d_r$), was determined at 35 °C and 1 atm in a Micromeritics AccuPyc II 1340 gas pycnometer. The real density and textural parameters of duckweed pyrolytic bio-chars produced at different conditions are shown in Table 1. It is noted that in the Table 1, the sum of mesopores and micropores volumes slightly exceeds that of total pores, which can be attributed to the margin of error in determining these