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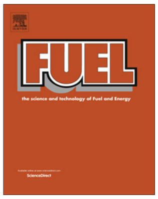

Full Length Article

Non-catalytic and catalytic fast pyrolysis of *Schizochytrium limacinum* microalga

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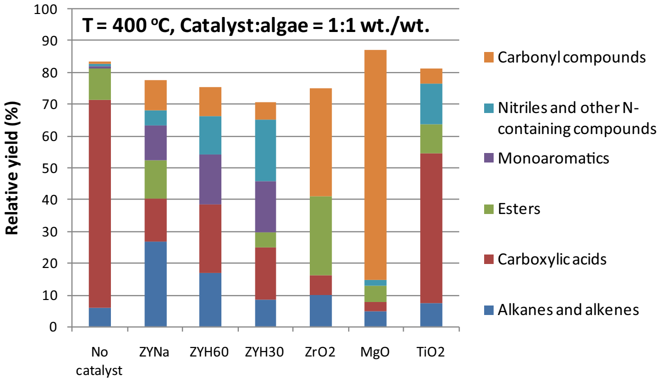
HIGHLIGHTS

- Fast pyrolysis of *Schizochytrium limacinum* alga was conducted in Py-GC/MS set-up.
- Non-catalytic fast pyrolysis resulted in tetradecanoic and hexadecanoic acids.
- ZYH, ZYNa, MgO, ZrO_2 and TiO_2 were used for catalytic fast pyrolysis.
- ZYNa, MgO and ZrO_2 promoted the formation of long chain ketones via ketonization.
- ZYH promoted the formation of aromatic hydrocarbons and nitriles.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, fast pyrolysis of lipid-rich microalga, *Schizochytrium limacinum*, is carried out to evaluate the potential of deriving valuable chemicals and fuel molecules from this algae variety. The alga was characterized for its proximate and elemental composition, and heating value. The pyrolytic mass loss profiles of the alga were obtained from thermogravimetric analyzer, and the apparent kinetic parameters of degradation were evaluated using advanced isoconversional method of Vyazovkin. Fast pyrolysis experiments were performed in analytical pyrolyzer coupled with gas chromatograph/mass spectrometer. Long chain carboxylic acids, primarily tetradecanoic and hexadecanoic acids, were observed as the major pyrolysates in the temperature range of 350–650 °C in the absence of catalyst. A clear increase in production of aromatics and cyclic hydrocarbons was observed at high temperatures owing to the cracking of long chain hydrocarbon portion of the carboxylic acids. Catalytic fast pyrolysis was performed at 400 °C using zeolite Y-hydrogen (ZYH), zeolite Y-sodium (ZYNa), and oxides like MgO, ZrO_2 and TiO_2. The production of polyaromatic hydrocarbons and nitriles increased, while that of long chain carboxylic acids decreased with increasing acidity of ZYH. Increasing the loading of ZYNa resulted in the formation of long chain ketones. The formation of ketones was more pronounced with MgO and ZrO_2 catalysts. The major ketones obtained include 16-hentriacontanone and 14-heptacosanone, which were formed via ketonization reactions of palmitic and myristic acids present in the algae. This study demonstrates that selective production of valuable chemical intermediates can be achieved from complex feedstocks like microalgae via catalytic fast pyrolysis using zeolites and metal oxides.

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1. Introduction

The escalated demand and usage of fossil fuels lead to their depletion, and also poses a severe threat to environment with higher greenhouse gasses emissions resulting in global warming. Lignocellulosic biomass, a promising renewable source of carbon on earth, remains the well studied feedstock for the production of fuels and chemicals via different routes including biochemical, thermochemical and thermocatalytic processes [1,2]. Microalgae are promising and emerging feedstocks for the production of biofuels and chemical intermediates [3]. Compared to lignocellulosic biomass, microalgae provide a number of advantages such as high growth rates (owing to higher photosynthetic efficiency of algae), high yield per unit area without any requirement of arable land for cultivation, and high carbon capture efficiency in the form of CO_2 or bicarbonate [4]. It is reported that 1.6–2 g of CO_2 is captured for every gram of algae produced. Moreover, many unicellular algae are reported to produce up to 60%/g dry weight of triacyl glycerol, a neutral lipid, which can be used to produce biodiesel [4].

Fast pyrolysis is a promising thermochemical conversion process to convert biomass to bio-oil, which can be further upgraded to liquid transportation fuels by catalytic hydrodeoxygenation technique [1,2,5]. Fast pyrolysis involves rapid heating of biomass in inert environment such that cracking occurs at short time scales of the order of a few seconds. The involvement of solid, melt and gas phases makes pyrolysis a complicated process. The product yields and their quality are controlled by various reaction conditions such as temperature, heating rate, residence time, influence of secondary cracking reactions, and the use of catalysts. Catalytic fast pyrolysis (CFP) aids in better deoxygenation of the biomass, and improves the quality of bio-oil in terms of better higher heating value, lower acidity and O/C ratio [2]. Venderbosch and Prins [6] reviewed fast pyrolysis technology from the view point of biofuels production, and concluded that the type of oxygen functionality in bio-oil (–OH, –C=O, –COOH, –C–O–C–, –COOR) should be controlled rather than the overall reduction in oxygen content. Moreover, the demonstration of the use of bio-oil in boilers, engines and turbines is very important for commercialization of this technology.

It is important to note that, unlike lignocellulosic biomass, which is made up of cellulose, hemicellulose, and lignin as the building blocks, algae contain proteins, carbohydrates and lipids as the major constituents. Therefore, the composition of the bio-oil from algae is significantly different from that of lignocellulosic biomass. Slow pyrolysis and (catalytic) fast pyrolysis of a number of algae species are reported in the literature. These include *Arthrospira platensis* (spirulina) [7,8], *Chlorella vulgaris* [9–13], *Nannochloropsis gaditana* [13], *Scenedesmus almeriensis* [13], *Laminaria digitata* [14], *Fucus serratus* [14], *Dunaliella salina* [12], *Nannochloropsis oculata* [15], and *Cladophora glomerata* [16]. Besides the presence of oxygenates such as carbonyl compounds, alcohols and carboxylic acids, algae bio-oil contains a number of N-containing organics (NCO) such as nitriles, amines, amides, pyrroles, indoles, and nitro compounds [7–9]. Importantly, the total acid number of algae bio-oil is found to be lower than that of bio-oil from wood fast pyrolysis [17]. A majority of the studies have shown that aromatic hydrocarbons, primarily BTX (benzene, toluene, xylene), styrene, naphthalene, indene, alkyl benzenes and alkyl naphthalenes, are the major products produced at high selectivities from CFP of different varieties of algae with zeolites [7–10]. Importantly, the carbon yield of BTX and its selectivity are found to be more from CFP of *Chlorella vulgaris* algae as compared to CFP of red oak biomass [9]. Literature suggests that CFP of algae using zeolites results in the release of nitrogen inherently present in algae in the form of ammonia gas [9], and the conversion of amides to nitriles [8]. Moreover, the use of HZSM-5 zeolite resulted in denitrogenation of NCOs like nitriles, amines and amides to form carbazoles [7]. The use of basic catalyst like Na_2CO_3 in CFP of *Chlorella vulgaris* is shown to improve the higher heating value (HHV) of the bio-oil (c.a. 32 MJ kg^{-1}), and simultaneously reduce the acid content [11]. Campanella and Harold [18] performed a detailed study on CFP of duckweed biomass in a falling solids reactor and investigated the effects of temperature, particle size, flow rate, gas atmosphere and ZSM-5 (H, Fe, Cu, Ni) catalysts. It was found that the use of protonated ZSM-5 improved the bio-oil yield besides improving the hydrocarbons in the organic fraction by 22%. The presence of steam atmosphere also improved the selectivity of hydrocarbons.

Schizochytrium limacinum (*S. limacinum*) is an important algae species in biofuel research owing to its high oil content (c.a.50–77% of dry biomass) [19]. This alga can be used to produce ω-3-polyunsaturated fatty acid (C22:6, n-3) using biodiesel-derived crude glycerol as an inexpensive substrate. Johnson and Wen [20] demonstrated the production of biodiesel from this alga via direct transesterification. The fuel was also able to meet a number of ASTM specifications. Recently, Li et al. [21] investigated fast pyrolysis of *S. limacinum* at different temperatures (300–800 °C) in the absence of catalysts and showed that tetradecanoic acid and hexadecanoic acid are the major products. A detailed study on thermal stability and the effect of catalysts on the product distribution from *S. limacinum* under fast pyrolysis conditions is not available in the literature. In this study, the effects of (a) zeolite Y catalysts of different Si:Al ratio, (b) algae:catalyst ratio, and (c) oxides like TiO_2, ZrO_2 and MgO on the production of various organic compounds in the pyrolysate are analyzed, and plausible mechanisms for the formation of major products are discussed. The characterization of algae bio-char is also reported.

2. Experimental

2.1. Materials

The alga, *S. limacinum*, was obtained in dried powdered form from Aqua World Pvt. Ltd., Chennai. The zeolites were obtained from Alfa Aesar. Aeroxide TiO_2 and MgO were purchased from Sigma Aldrich and Merck, respectively. Zirconyl nitrate and glycine, obtained from Merck, were used as the precursor and fuel, respectively, for the synthesis of ZrO_2 by solution combustion technique as described elsewhere [22]. The alga was used as-received, while the zeolites were calcined at 500 °C for 5 h before characterization and use in experiments.

2.2. Characterization of algae

Proximate analysis was carried out according to ASTM E1131-08 method in automatic thermogravimetric analyzer (TGA 2000A, Navas instruments), and elemental analysis was performed in CHNSO analyzer (Thermo Flash 2000). HHV of the alga was determined using a bomb calorimeter (IKA 2000). The characterization of the microalga is depicted in Table 1. Thermal stability of the alga was evaluated using TGA (SDT Q600, T.A. Instruments). Approximately 8 mg of the alga sample was heated from ambient temperature to 800 °C at different heating rates of 10, 15, 20 and 30 °C min^{-1} in presence of N_2 at a flow rate of 60 mL min^{-1}. All experiments were run in triplicate to confirm the repeatability of the data. The mass loss and differential mass loss data were collected, and the kinetic parameters for the decomposition of the alga were determined using integral isoconversional method of Vyazovkin. The methodology is described in Section 2.4.