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Catalytic fast pyrolysis of *Arthrospira platensis* (spirulina) algae using zeolites

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ABSTRACT

This study is aimed at characterizing the thermal stability and evaluating the conversion of *Arthrospira platensis* (*Spirulina platensis*), a species of microalgae, to various chemicals and intermediates via non-catalytic and catalytic fast pyrolysis using different zeolites. Thermogravimetric analysis was performed to evaluate the kinetics of decomposition of the algae using integral isoconversional method of Vyazovkin, and fast pyrolysis experiments were performed in a micropyrolyzer and the relative composition of the pyrolysates was analyzed in a gas chromatograph/mass spectrometer. The effects of (i) temperature during non-catalytic fast pyrolysis, and (ii) zeolite type, zeolite:algae mass ratio and temperature during catalytic fast pyrolysis on pyrolysate composition were analyzed. The formation of long chain organics like alkanes, alkenes, carboxylic acids and nitriles decreased, while that of CO_2 increased with increase in pyrolysis temperature from 350 to 800 °C. The addition of ZSM5, zeolite-β and zeolite-Y catalysts at 10:1 wt./wt. loading to algae at 600 °C significantly altered the product spectrum involving the formation of nitriles, aromatics, and cycloalkanes. Acetonitrile, benzene, toluene, xylene, cyclobutane and dimethyl cyclopropane were the major organics. Calorific value of the organic components in the pyrolysate (>30 MJ kg^{-1}) was significantly higher than that of the raw algae (20.75 MJ kg^{-1}). Increase in catalyst loading (from 2:1 to 50:1 wt./wt.) and temperature (from 350 to 600 °C) resulted in significant increase in production of monoaromatics, polyaromatics and cycloalkanes, whereas the formation of nitriles increased and decreased with catalyst loading and temperature, respectively. Plausible reactions leading to the observed product distribution are discussed. This study shows that useful organic intermediates can be obtained via catalytic fast pyrolysis of spirulina.

1. Introduction

Biomass, one of the most preferred modes of sustainable energy, is a potential candidate for solving environmental problems such as greenhouse effect and depletion of non-renewable energy resources. Biomass can be classified into lignocellulosic biomass such as woody plants, herbaceous plants/grasses such as agricultural residues, aquatic flora and manures [1]. There has been a phenomenal growth in the production of biofuels from the above renewable and sustainable feedstocks owing to the mitigation of CO_2 buildup in the atmosphere. Biofuels are one of the most promising options to reduce the planet's dependence on conventional fuels. One of the recent concerns with respect to increased biofuels production is the availability of land. According to World Energy Outlook of International Energy Agency, about 14 million hectares of land (about 1% of the world's arable land) are used for the production of biofuels, providing 1% of global transportation fuels [2]. Clearing land for the production of biofuels will possibly offset greenhouse gas benefits. Biofuels that could be produced with minimum requirement of arable land or reduction in tropical rainforests could be very attractive in the future. Algal biomass has a great potential of offering this opportunity. Algal biomass, both microalgae and macroalgae, have been studied for a myriad purposes including bioactives, food and feed, chemicals, bioenergy and biofuels [3]. Microalgae were among the first forms of life to exist on earth [4]. They can arguably fix large amount of CO_2 while contributing almost 50% of oxygen in the atmosphere thereby helping to support life in our planet. Owing to their high photosynthetic efficiency and tolerance to adverse environmental conditions, certain microalgae species that are rich in lipid content are projected

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Table 1
Properties of the various zeolites used in this study [32,33].

Sl. no.	Catalysts	Si/Al ratio	Notation	Total acidity from NH_3-TPD (mmol g^{-1})	Micropore area (m^2 g^{-1})	External surface area (m^2 g^{-1})	BET specific surface area (m^2 g^{-1})	Average pore diameter (Å)	Micropore volume (cm^3 g^{-1})
1	ZSM-5 ammonium	50:1	ZSM50	0.4752	251.62	83.85	335.47	88.73	0.122
2	ZSM-5 ammonium	200:1	ZSM200	0.1058	84.51	301.21	385.72	25.75	0.039
3	Zeolite β hydrogen	360:1	ZβH	0.1739	351.24	139.85	491.10	49.90	0.171
4	Zeolite β ammonium	38:1	ZβAm	0.4481	402.28	110.12	512.40	54.94	0.196
5	Zeolite Y ammonium	5.1:1	ZYAm	1.4373	589.32	55.22	644.54	54.57	0.288
6	Zeolite Y hydrogen	5.1:1	ZYH	1.3614	593.67	53.38	647.05	55.68	0.290

to yield oils per hectare that are many times higher than those from lignocellulosic biomass [5,6].

Conventional algae biofuel technologies involve specific steps which are broadly classified as cultivation, harvesting and concentration, oil extraction, and conversion [3]. Thermochemical conversion methods, such as pyrolysis [5,7,8], hydrothermal liquefaction and gasification [3,9,10], are among the most promising emerging techniques in the domain of both lignocellulosic and algal biomass conversion into biofuels. Fast pyrolysis, which is characterized by very high heating rates of c.a 1000 °C s^{-1} and very low residence times, has significant advantages owing to high oil yields that can be achieved over slow pyrolysis [8,11]. Recently, it was confirmed by both experiments and mechanistic modeling that the typical timescale involved in fast pyrolysis is 5–10 s [11–13]. The quality of bio-oil can be improved by performing catalytic fast pyrolysis in presence of deoxygenation catalysts such as zeolites. Apart from favorably altering the degradation mechanism, the addition of a catalyst also brings the product spectrum close the long chain hydrocarbon and/or aromatics range [14]. Besides conventional fast pyrolysis, microwave-assisted heating can also provide flash heating conditions by the formation of microplasma spots in presence of catalysts like metal oxides, carbonaceous materials, metal powders and SiC [15–17].

A variety of microalgae species such as chlorella, nannochloropsis, dunaliella, tetraselmis, synechococcus, chaetocerous, laminaria, fucus, schizochytrium, scenedesmus, and microcystis have been studied for bio-oil production via slow and fast pyrolysis techniques [5,14,18–27]. Among all the above species, chlorella species is very well studied by many researchers for bio-oil production and pyrolysis kinetics. Miao et al. studied fast pyrolysis of cultivated microalgae species [18,19]. They obtained oil yields of 17.5% and 23.7% from autotropic microalgae like *Chlorella protothecoides* and *Chlorella aeruginosa*, respectively, whereas the yield of bio-oil was 57.9% from heterotrophic *Chlorella protothecoides*. Thangalazhy-Gopakumar et al. [14] reported 25 wt.% (carbon yield) of aromatics from chlorella species via catalytic fast pyrolysis using HZSM-5 catalyst at high catalyst:algae mass ratio (9:1). Importantly, the aromatic fraction contained more monoaromatics like BTX (benzene, toluene, xylene), and the aromatic yield was significantly higher than that derived from red oak [5,14]. In another study, Rizzo et al. [23] reported that the organic phase of bio-oil from pyrolysis of chlorella was superior to that from lignocellulosic biomass in terms of low oxygen content, high heating value, low acidity and low density.

Arthrospira platensis (*Spirulina platensis*), commonly known as spirulina, is among the most popular blue green algae species, which is cultivated in a large scale. This species is primarily utilized for the production of bionutrients and food supplements owing to the highest content of carotenes and gamma-linolenic acid [3,28]. Lin et al. [29] studied microwave-assisted plasma pyrolysis of spirulina algae and demonstrated the production of H_2 among other gases like CO and CO_2. Hydrogen production was found to increase with microwave power. In another recent study, Lorenzetti et al. [30] evaluated the effect of H-ZSM5 on spirulina pyrolysis, and showed that the bio-oil contained significantly low amount of oxygen and nitrogen, and high amount of aromatics. Moreover, spirulina is nitrogen rich algae. Therefore, studying its thermocatalytic conversion will shed insights on the transformation of intrinsic nitrogen present in algae to various nitrogen-containing organic compounds. This work is focused on characterizing the thermal stability of spirulina, and its non-catalytic and catalytic fast pyrolysis using analytical pyrolyzer-gas chromatograph/mass spectrometer (Py–GC/MS) set-up. The effects of different parameters such as pyrolysis temperature, zeolite type and catalyst:algae ratio on the composition of pyrolysate are thoroughly evaluated.

2. Experimental

2.1. Materials

Arthrospira platensis was obtained in dried powdered form from Aqua World Pvt., Ltd., Chennai. The various zeolites were obtained from Alfa Aesar. The zeolites varied by Si:Al ratio, specific surface area, surface acidity and pore size distribution. The salient properties are given in Table 1. The alga was used as received, while the catalysts were calcined at 500 °C for 5 h before characterization and use in experiments.

2.2. Characterization of algae

Proximate analysis of the alga was performed in a thermogravimetric analyzer (TGA, SDT Q600, T.A. Instruments) according to an established procedure [31]. Approximately 10 mg of the sample was heated to 110 °C and held at this temperature in presence of N_2 (100 mL min^{-1}) to evaluate the moisture content. The sample temperature was then raised to 900 °C at a heating rate of 80 °C min^{-1} and held at this temperature to evaluate the content of volatile matter. The purge gas was then shifted to air (100 mL min^{-1}) and the sample was held isothermally at 900 °C for 45 min to evaluate the fixed carbon content. The final mass of residue was noted as ash content. Elemental analysis was carried out in an Elementar Vario Micro CHNS analyzer by taking c.a. 3 mg of the sample. Oxygen content was calculated by difference. Higher heating value (HHV) of the raw algae was measured in an isoperibolic bomb calorimeter (IKA 2000) by taking c.a. 0.5 g of sample. The algae sample was also subjected to Fourier transform infra red (FT-IR) analysis in Agilent Cary 660 FT-IR spectrometer to identify the predominant organic functional groups. The algae sample was initially heated to a temperature of 120 °C to remove physisorbed moisture, and then mixed with dry KBr at 1:100 wt./wt. to make transparent pellets. The FT-IR spectrum was obtained in transmittance mode in the mid-IR range from 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1}.

Thermal stability of algae was evaluated in the TGA. Approximately 8 mg of algae sample was heated from ambient temperature to 800 °C at different heating rates of 10, 20, 50, 100 and 180 °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. Mass loss and differential mass loss data