Bioresource Technology 118 (2012) 150–157

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Catalytic pyrolysis of green algae for hydrocarbon production using H^+ZSM-5 catalyst

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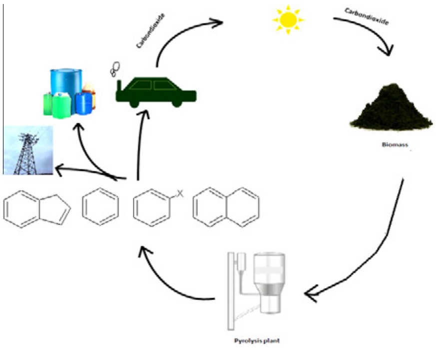
HIGHLIGHTS

- Fixed bed pyrolysis of *Chlorella vulgaris* produced 52.7 wt.% of bio-oil.
- Bio-oil from algae contained alkane compounds and aromatic hydrocarbons.
- A high yield of aromatics was obtained from catalytic pyrolysis of algae.
- About 25 wt.% of the carbon in algae was converted into aromatics.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 February 2012
Received in revised form 15 May 2012
Accepted 17 May 2012
Available online 24 May 2012

Keywords:
Algae
Bio-oil
Catalytic pyrolysis
Fixed-bed reactor
ZSM-5

ABSTRACT

Microalgae are considered as an intriguing candidate for biofuel production due to their high biomass yield. Studies on bio-oil production through fast pyrolysis and upgrading to hydrocarbon fuels using algal biomass are limited as compared to other terrestrial biomass. Therefore, in this study, a fresh water green alga, *Chlorella vulgaris,* was taken for pyrolysis study. The average activation energy for pyrolysis zone was found to be 109.1 kJ/mol. Fixed-bed pyrolysis of algae gave a bio-oil yield of 52.7 wt.%, which accounts for 60.7 wt.% carbon yield. In addition, analytical pyrolysis of *C. vulgaris* was carried out in a Py/GC–MS to identify major compounds present in bio-oil with and without catalyst (H^+ZSM-5). The study found that in catalytic-pyrolysis, as the catalyst loading increased from zero to nine times of the biomass, the carbon yield of aromatic hydrocarbons increased from 0.9 to 25.8 wt.%.

1. Introduction

Biomass, a renewable source for carbon based liquid fuels, has a potential to alleviate the dependency on fossil fuels, and related environmental problems. Therefore, biofuels are considered as an important candidate for the national energy security and energy sustainability. In addition, biofuels can be a major factor for the nation's economy in creating more job opportunities in rural areas. Biochemical and thermochemical techniques have been developed to convert biomass into electricity and liquid fuels. Fast pyrolysis, a thermochemical conversion, gives high liquid yield (*i.e.,* bio-oil) up to 70 wt.% (dry weight) from biomass. The liquid can be utilized as an energy carrier, source for many commodity chemicals, or can be upgraded as a transportation fuel. However, bio-oil has some negative properties such as high density, acidity, water content, and, oxygen content together with low heating value.

Catalytic pyrolysis is one of the methods to produce hydrocarbon fuels from bio-oil where C–C bonds in bio-oil compounds are ruptured in presence of some shape selective catalysts. Cracking reactions involve dehydration, decarboxylation, and

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http://dx.doi.org/10.1016/j.biortech.2012.05.080

decarbonylation of compounds to produce aromatic hydrocarbons, water, and carbon dioxide. Catalytic pyrolysis produces better quality of bio-oil at atmospheric pressure without of the need of hydrogen gas as opposed to hydrodeoxygenation process, which makes this process less expensive (Williams and Nugranad, 2000). Recently, a few micro-scale studies (Carlson et al., 2009; French and Czernik, 2010; Thangalazhy-Gopakumar et al., 2011b) have reported high aromatic yields (30–40 wt.% carbon yield) from the catalytic pyrolysis of lignocellulosic biomass or its structural units.

The major challenge for the utilization of biomass is the uncertainty on the continuous supply of biomass. Therefore, researchers have tested different types of biomass such as agriculture wastes, forest wastes, municipal wastes, animal manure, algae, and energy crops for different biomass conversion techniques. Currently, utilization of algae as a source of biofuel has attracted a great interest due to a number of reasons (Babich et al., 2011; Li et al., 2008; Miao et al., 2004). For example, algae have higher growth rate and higher efficiency for CO_2 fixation than terrestrial plants. Water consumption of algae is lower than terrestrial plants, and algae help to reduce eutrophication from water bodies by consuming nitrogen and phosphorus. Another advantage of algae is high temperature tolerance and can grow in a wide range of environmental conditions (Li et al., 2008).

Current algal biofuel research is mainly focused on extraction of lipids and transesterification to produce biodiesel. In biodiesel production, only a part of organic content of algae (lipid content) is utilized for biofuel production; rest is considered as waste. On the other hand, thermochemical treatment can utilize complete organic content of algae biomass for biofuel production. High ash content of algae (~10 wt.%) is considered as an inferior characteristic for biomass. However, fast pyrolysis has the flexibility over ash content of biomass, and both bio-oil and bio-char (products of fast pyrolysis) can be utilized for a number of applications. A number of studies (Radlein et al., 1991; Shafizadeh et al., 1972) have reported pyrolysis products from lignocellulosic biomass and its basic constituents (cellulose, hemicelluloses and lignin). The major components of algae biomass are proteins, lipids, and carbohydrates, which are different from the main components of lignocellulosic biomass. Therefore, the pyrolysis behavior and bio-oil components from algae biomass are expected to be different from terrestrial biomass. *Chlorella* species is a promising strain for biofuel production (Tran et al., 2010), and can be cultivated in industrial scale. *Chlorella vulgaris* is freshwater green algae which is cultivated in wastewater streams for the degradation of pollutants (Kim et al., 2010), and can fix around 18.3 mg CO_2 L^{-1} day^{-1} (Chinnasamy et al., 2009). In addition, *C. vulgaris* is one of the species which can give high yield of biomass and oil (Araujo et al., 2011).

Herein, *C. vulgaris* algae were taken for the pyrolysis study to investigate the possibility of producing hydrocarbons using catalytic pyrolysis process. The first objective was to find the possibility of producing bio-oil from microalgae that has very low lipid content. A fixed-bed reactor was used for algae pyrolysis and the chemical properties of bio-oil were studied. The quality of bio-oil produced from this study was compared with the bio-oil from woody biomass. The second objective of this study was to investigate the catalytic pyrolysis of algae biomass to produce hydrocarbons. An analytical pyrolysis of *C. vulgaris* was carried out to evaluate the major compounds in algae bio-oil with and without catalyst.

2. Methods

2.1. Sample characterization

Algal biomass (*C. vulgaris*) used for this study was obtained in dry powder and was purchased from an online store (http://www.nutsonline.com). Moisture content of a biomass sample (wet basis) was determined by calculating weight loss after heating in an oven at 103 °C for 16 h according to ASTM E 871 standard, and the ash content was measured using ASTM E 1755 standard. The higher heating value (HHV) of the biomass sample was measured using an oxygen bomb calorimeter (IKA, model C200). Ultimate analysis of biomass sample was analyzed in a CHNS/O analyzer (Perkin Elmer model 2400). Carbon, hydrogen, oxygen and nitrogen contents of a sample were reported on "as received" basis. Algae sample was sent to an outside laboratory (Midwest Laboratories, Inc., Omaha, NE) for analyzing fat and protein content.

2.2. Catalyst

ZSM-5 catalyst ($SiO_2/Al_2O_3 = 50$ and surface area = 425 m^2/g) used in this study was purchased from a commercial supplier (Zeolyst International, Conshohocken, PA, USA). ZSM-5 powder was received in ammonium cation form, and, in order to obtain in H^+ZSM-5 form, the catalyst was calcined in air at 550 °C for 2 h prior to use.

2.3. Thermogravimetric analysis

Pyrolytic behavior of algal biomass was analyzed in a thermogravimetric analyzer (Shimadzu, TGA 50H) under nitrogen environment. A known amount (approximately 10 mg) of biomass was taken for the analysis, and biomass was heated from 30 to 800 °C at different heating rates of 10, 20, 30, and 40 °C/min and held at final temperature for 10 min. Nitrogen flow rate of 30 mL/min was maintained during the pyrolysis. All experiments were run in triplicates to confirm reproducibility of the data.

If m_0 is the initial weight of the sample, m is the instantaneous weight for a specified time, t, and m_∞ is the weight remaining without decomposition, the biomass conversion (α) can be defined as $(m_0 - m)/(m_0 - m_\infty)$. The rate of degradation ($d\alpha/dt$) is a linear function of rate constant (k) and conversion (α), where the temperature dependency of the rate constant is given as $k = Ae^{(-E/\mathrm{RT})}$. The rate of degradation ($d\alpha/dt$) can be expressed as

$$\frac{d\alpha}{dt} = Ae^{(-E/\mathrm{RT})}f(\alpha) \tag{1}$$

where A is a pre-exponential factor, E is the activation energy, R is the universal gas constant, and T is the absolute temperature. Since the heating rate (β) is dT/dt, Eq. (1) can be expressed as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}e^{(-E/\mathrm{RT})}f(\alpha) \tag{2}$$

The integrated form of this Eq. (2) would be

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(x)} = \frac{A}{\beta}\int_{T_0}^{T} e^{(-E/\mathrm{RT})}dT \tag{3}$$

The apparent activation energy can be found out by two methods without knowing the reaction mechanism. The methods are Flynn–Wall–Ozawa (FWO) and Kissinger's (Kissinger–Akahira–Sunose or KAS). The Flynn–Wall–Ozawa equation (Flynn and Wall, 1966; Ozawa, 1965) is given as follows:

$$ln\beta = ln\left(\frac{0.0048AE_a}{RG(a)}\right) - 1.0516\frac{E_a}{\mathrm{RT}} \tag{4}$$

The KAS (Kissinger, 1957) equation is given as

$$ln\frac{\beta}{T^2} = ln\left(\frac{AR}{E_aG(\alpha)}\right) - \frac{E_a}{\mathrm{RT}} \tag{5}$$

From Eqs. (4) and (5), the linear plots of ln(β), $ln(\beta/T^2)$ vs $1/T$ at fixed α will give the apparent activation energy, E_a, for the given value of conversion.