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Non-isothermal pyrolysis of de-oiled microalgal biomass: Kinetics and evolved gas analysis

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HIGHLIGHTS

- Non-isothermal pyrolysis of de-oiled microalgal biomass were evaluated by TGA-MS.
- Iso-conversional and model–fitting kinetics were applied for thermal decomposition.
- Evolved gas analysis were evaluated during pyrolysis.
- Three-stage thermal decomposition & three-zone volatilization of organic matters.
- Pyrolysis involved multi-step reactions & 3D growth rate with random nucleation.

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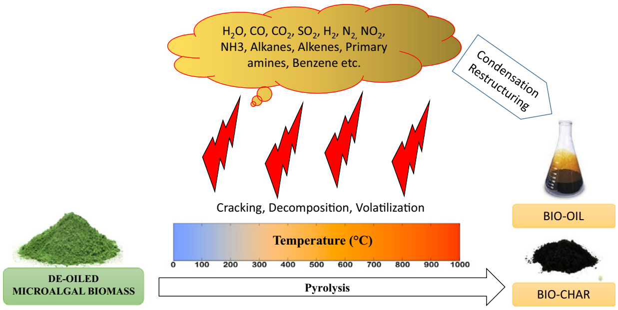
GRAPHICAL ABSTRACT



ABSTRACT

Non-isothermal ($\beta = 5, 10, 20, 35$ °C/min) pyrolysis of de-oiled microalgal biomass (DMB) of *Chlorella variabilis* was investigated by TGA-MS (30–900 °C, Argon atmosphere) to understand thermal decomposition and evolved gas analysis (EGA). The results showed that three-stage thermal decomposition and three volatilization zone (100–400 °C, 400–550 °C and 600–750 °C) of organic matters during pyrolysis. The highest rate of weight-loss is 8.91%/min at 302 °C for 35 °C/min heating-rate. Kinetics of pyrolysis were investigated by iso-conversional (KAS, FWO) and model-fitting (Coats-Redfern) method. For Zone-1 and 3, similar activation energy (E_a) is found in between KAS ($\alpha = 0.4$), FWO ($\alpha = 0.4$) and Avrami–Erofe'ev (n=4) model. Using the best-fitted kinetic model Avrami–Erofe'ev (n=4), E_a values ($R^2 = >0.96$) are 171.12 (Zone-1), 404.65 (Zone-2) and 691.42 kJ/mol (Zone-3). EGA indicate the abundance of most gases observed consequently between 200–300 °C and 400–500 °C. The pyrolysis of DMB involved multi-step reaction mechanisms for solid-state reactions having different E_a values.

1. Introduction

The biomass is becoming a valuable source of renewable energy, and amongst which microalgae is a very strong candidate due to its low content or lacking of most complex component

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hemicellulose and lignocellulosic (Chen et al., 2013; Ceylan and Kazan, 2015) which are mainly found in plant-derived biomass. Microalgal biomass has simple carbohydrate, proteins, lipids, minerals and value added pigments. Microalgae are widely discussed in the literature for its biofuel properties and very well known for biodiesel production. After lipid extraction, the remnant biomass is rich in carbohydrate, protein, and minerals, which could be used further for valuable applications to compensate the sustainability of microalgal biodiesel production (Maurya et al., 2016c). De-oiled microalgal biomass (DMB) can be fermented to produce bioethanol (Pancha et al., 2016), biogas and biohydrogen production. Protein rich DMB can be utilized as supplement to feed and fertilizer (Maurya et al., 2016a) while their protein-rich liquid hydrolysate can serve as good nutrient source (Maurya et al., 2016b) as well as growth stimulant for microbes like microalgae, bacteria and yeast for further production of value added products (Lactic acid, polyhydroxyalkanoate, bioethanol, lipids etc.) (Maurya et al., 2016c; Rashid et al., 2013). Recently, DMB was utilized to make biomaterials like nanoparticles (Chokshi et al., 2016), and also utilized directly as biosorbent for dye sorption (Maurya et al., 2014).

One another approach is to the thermo-chemical conversion of DMB to produce different valuable chemicals, fuels, bio-oil and biochar (Maurya et al., 2016c). There are three different approaches for thermo-chemical conversion of DMB: hydrothermal liquefaction (HTL), gasification and pyrolysis. HTL is suitable for high moisture biomass, which is treated at high temperature (250–350 °C) and pressure (5–15 MPa) while in gasification, biomass is treated at very high temperature (>700 °C) without combustion and controlled amount of oxygen and steam for the production of carbon monoxide, hydrogen, and traces of methane gas mixture called syngas (Minowa and Sawayama, 1999).

Pyrolysis is suitable for low moisture (<5%) or dry biomass, which are treated at high temperature (350–700 °C) in absence of oxygen, in which the organic compound of biomass decomposes to form volatile matter; the bio-oil phase is separated when volatile matter re-condenses into the aqueous phase. The bio-oil is mainly composed of aromatic compounds, hydrocarbons, amides, amines, carboxylic acids, phenols, and other substances. The remaining solid by-product is mainly char which may be used as fertilizer, activated charcoal or other applications (Libra et al., 2011). Pyrolysis is categorized into slow (0.1–1 °C/s), fast (10–200 °C/s) and flash (>1000 °C/s) pyrolysis on basis of heating rate (Demirbas and Arin, 2002). A very less energy input is required for DMB pyrolysis as compared to raw or fresh algae (Peng et al., 2001). During last few years, DMB pyrolysis of different species has been reported in literature including *Chlorella* (Miao et al., 2004; Demirbas, 2006; Bui et al., 2016), *Microcystis* (Miao et al., 2004), *Tetraselmis* (Grierson et al., 2011), *Nannochloropsis* residues (Pan et al., 2010), *Dunaliella tertiolecta* (Kim et al., 2015; Francavilla et al., 2015) and *Chlamydomonas* (Bui et al., 2016).

Thermal gravimetric analysis (TGA) and differential thermal gravimetric analysis (DTGA) are very important techniques for studying the thermal characteristics of biomass and its components (Agrawal and Chakraborty, 2013). By this analysis, thermal degradations of biomass are understood by real-time monitoring of weight loss of biomass with respect to temperature. In the present study, based on TGA and DTGA data obtained during non-isothermal (at heating rate) conditions, the different kinetics of biomass degradation are developed and tried to understand their thermal behaviour. Apart from TGA and DTGA, a component of evolved gases during thermal decomposition is monitored in real-time by coupling the TGA instruments with a mass spectrophotometer (MS).

2. Materials and methods

2.1. De-oiled microalgal biomass preparation

The preparation and characterization of DMB are described previously in Maurya et al. (2016a). The lipid was extracted from algal biomass (*Chlorella variabilis*) in soxhlet extractor using 3 L n-hexane per kg dry biomass. The residual algal biomass after lipid extraction was sundried for a day and powdered by grinding in mixture grinder.

2.2. Thermogravimetric analysis

A known amount of the oven dried *C. variabilis* biomass was weighed in high alumina (Al_2O_3) crucible of the thermal analyser NETZSCH TG 209F1 Libra. The pyrolysis of DMB was performed on different heating rates 5, 10, 20 and 35 °C min^{-1} in a flow (40 mL min^{-1}) of inert gas Argon. The temperature of furnace programmed from room temperature to 900 °C. The evolved gases produced during pyrolysis were analysed by Quadrupole Mass Spectrometer (QMS) 403 D Aëolos® which runs in couplings with NETZSCH thermal analysis instruments under Proteus® Software on Windows®.

2.3. Kinetics theory and modelling

The whole pyrolysis process might be worked in several phases and each phase can be elicited by different independent models (Liu et al., 2009). In the kinetic analysis, generally, each pyrolysis phase can be described by the rate of reaction (Chen et al., 2012). The rate of reaction expressed by a certain function f(α), of the reaction extent α by following equations.

$$\alpha_t = \frac{m_0 - m_t}{m_0 - m_f}$$

where α is defined by reaction extent or degree of conversion which is always between 0 and 1; m_t represents the mass of the sample at arbitrary time t (or temperature T); whereas m_0 and m_f are the mass of the sample at the beginning and at the end of the process, respectively.

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \tag{1}$$

where dα/dt is the degradation rate; k(T) is the rate constant which can be expressed by the Arrhenius equation:

$$k(T) = A\exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

where A is the pre-exponential factor, E_a is the apparent activation energy, R is the universal gas constant, T is the absolute temperature. Replacing k(T) with Arrhenius equation gives

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha) \tag{3}$$

For the non-isothermal experiment, the sample is heated with constant heating rate $\beta = dT/dt$, Eq. (3) is rewritten as

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha) \tag{4}$$

This equation is known as the general equation of TGA curve.

Above equations can be processed in two ways for kinetic parameters. One in which the knowledge of reaction model f(α) is not required are known as model-free or iso-conversional