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Iso-conversional kinetics of low-lipid micro-algae gasification by air

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ABSTRACT

This study investigates the non-isothermal (10, 15, 20 and 30 °C min^{-1}) gasification of chlorella vulgaris and spirulina under air stream via thermogravimetric analysis coupled with mass spectrometry (30–800 °C) to explore the application as feedstock for syngas production. The results showed four major peak conversion zones of organic matters in both chlorella vulgaris (60–100 °C, 280–305 °C, 390–420 °C, and 440–450 °C) and spirulina (280–305 °C, 380–410 °C, 430–450 °C, and 720–760 °C) during the gasification process. Thermogravimetric data via iso-conversional method was interpreted to achieve the kinetic parameters of the devolatilization reaction of algal biomass gasification. The kinetic investigation showed that the activation energy values (E_a) varied over the conversion values ($\alpha = 0.05–0.8$). The comparison of kinetic results obtained by the model and those reported in other studies for micro-algal biomasses was in agreement. Quantification of evolved gases was accomplished via a semi-quantitative method. The main evolved gases were H_2, CO and CO_2, implying that water gas reaction, water gas shift reaction and oxidation reactions were predominant. H_2 generation rate was supported with increase in lower heating rate (owing to its longest gasification time compared to higher heating rates). The obtained data are expected to facilitate the design and optimization of the gasification of low-lipid microalgae.

1. Introduction

The everlasting climate change effects due to the world's high dependency of fossil fuels is now being felt worldwide, which has led to search for sustainable alternative options of cleaner energy production (Azizi et al., 2017). Biomass has attracted much attention recently as an important renewable energy source by supplying more than 10% of world's energy supply (Raheem et al., 2017b; Welfle, 2017). The widespread availability and lower environmental impacts makes biomass an efficient alternative source to replace fossil fuels. According to estimations biomass will contribute approximately 38% of worldwide fuel supply by 2050 (Demirbas, 2000). Biomass encompasses three different groups: first generation, second generation and third generation biofuels sources. The first generation biofuels feedstocks are originated from terrestrial plants such as corn, wheat, maize, soybean, potato, oil palm, and sugarcane etc (Guo et al., 2015; Vassilev and Vassileva, 2016). However, their cultivation on arable land has destructive consequences on food security, large-scale deforestation and show poor energy balance (Guo et al., 2015; Ho et al., 2014; Mohr and Raman, 2013). These biofuel's development similarly entail potable water, fertilizers and a huge a huge (fertile) land area for their cultivation. This causes a further upsurge of net carbon emissions and also results in accumulation harmful contaminations (i.e. ammonia and nitrous oxide) into the atmosphere and in groundwater (nitrates and phosphates) due to their cultivation in such an open system (arable land).

The second generation biofuel feedstocks are mainly derived from non-food waste and lingo-cellulosic materials such as grasses, husk, wood, municipal solid waste and sewage sludge etc (Ho et al., 2014; Rodionova et al., 2017). These feedstocks do not threaten food/feed supplies; besides, they produce higher yields of biofuel and require lower land for their cultivation (Vassilev and Vassileva, 2016). Regardless of these benefits, they encounter certain limitations of not being economically viable at commercial-scale such as the transportation, collection networks and the cost-effective pretreatment development (Naik et al., 2010; Nigam and Singh, 2011).

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In recent years, microalgae are increasingly becoming a tenable solution to avoid the problems with aforementioned biofuel feedstocks. A vast research efforts are being devoted for developing algal based biofuel industry for its numerous advantages. The cultivation of algal biomass does not need the use of cultivatable land and thus they do not complete with traditional food crops (Hallenbeck et al., 2016; Laurens et al., 2017; Naik et al., 2010; Raheem et al., 2017b; Ruiz et al., 2016; Su et al., 2017). Compared to plants, microalgae have shown incomparable fast growth rates and outstanding photosynthetic efficiency (ca. they convert 3.8% solar energy into chemical energy against 0.5% for plants). Microalgal biomass is normally supplemented in their quantities of protein (7–55 wt %), carbohydrates (6–25 wt %) and lipids (8–25 wt %) (Ishika et al., 2017; Sanchez-Silva et al., 2013; Su et al., 2017). Microalgae barely comprise the lignin compared to lignocellulosic biomasses. Thus, these characteristics make microalgae an ideal feedstock for various biofuel conversion. Unlike first generation biofuel resources, microalgae can be grown without using agricultural resources (i.e. fertile land, fertilizer and potable water etc.) in ponds or photobioreactors with nutrients or wastewater supply.

Besides, integration of algae cultivation with coal based power plants not only will enable efficient reduction in the greenhouse gas (GHG) discharges but could be used for CO_2 capture and utilization. Recently, various studies have been conducted, demonstrating that microalgae cultivation systems aired by chimney gases added with few intermediate CO_2 quantities (3–6% v/v) have a tendency to enhance algal biomass yield (Anjos et al., 2013; Bhola et al., 2011). Therefore, the contribution of algal-based biofuels could become extremely crucial in contributing to environmental, social, cost-effective and sustainable biofuel production systems.

Microalgal biomass can potentially be transformed into a spectrum of bioenergy commodities (such as liquid, gas and solid) through thermochemical and biochemical conversion technologies. Thermal technologies include gasification, pyrolysis, liquefaction, and direct combustion methods. Gasification includes the partial oxidation of algal biomass into syngas at elevated temperatures (800–900 °C). Pyrolysis converts biomass into bio-oils, bio-chars and gases in the absence of oxygen (350–700 °C). Combustion converts biomass into useful energy under excess oxygen at high temperatures (>1000 °C) (Sanchez-Silva et al., 2013).

Conversely, biological methods enable the conversion biomass materials into biofuels via fermentation and anaerobic digestion, etc. Regardless of inherent potential of biochemical conversion technology, its commercial feasibility for algal biomass as feedstock has not been accomplished yet.

Of all thermochemical conversion processes, gasification is regarded as one of the potential technologies to turn a low value material into high-value products. Particularly, it is well recognized that the study of biomass thermal decomposition is necessary to evaluate the operation of gasification. The different gasifying agents for instance; steam, CO_2, steam and air are often applied based on the requirements and availability (Duman et al., 2014; Qadi et al., 2017). Thermogravimetric analysis (TGA) and differential thermal gravimetric analysis (DTGA) with an aid of mass spectrometer (MS) is the analytical technique, the least expensive and the most efficient to perceive decomposition behavior including evolved gas profiles of a material. TGA includes two major main classifications: non-isothermal and iso-thermal processes. To date, non-isothermal process is often employed due to the high sensitivity to experimental noise contrasted to later one. TGA and DTGA curves are very useful in providing quick and reliable information related to the kinetic parameters (i.e. conversion rate and activation energy etc.) over a varied range of parametric conditions. To mark microalgae as a future sustainable biofuel source, the potential of algal biomass via the pyrolysis and combustion have been widely evaluated using TGA-MS (Bach and Chen, 2017a; b; Chen et al., 2013; Chen et al., 2011; Gai et al., 2013; Kim et al., 2013; Li et al., 2011; Peng et al., 2015; Vo et al., 2017). Bach and Chen have published a comprehensive review on recent developments in pyrolysis of microalgae biomass mainly focusing on kinetics, pyrolyzer design, operating conditions and biofuel production. They infer that multiple parallel reaction models are more desirable to obtain comprehensive kinetic information rather than the kinetic-free models, as those provide inadequate kinetic information (Bach and Chen, 2017b).

The studies dealing with gasification behavior of microalgae in a TGA-DTGA coupled with MS under air stream has been rarely explored. Sanchez-Silva et al. reported the steam (H_2O + Argon) gasification characteristics of nannochloropsis gaditana microalgae by TGA coupled with MS. The gasification parameters were set to be temperature (550–850 °C), algal biomass loading (9 g), particle size (100–250 μm), argon flow rate (200 mL min-1), a stream concentration (5 vol% in argon) and a heating rate of 40 °C min^{-1}. Results showed temperature as a key parameter influencing conversion and reactivity of biomass. The main gas constituents were CO_2, CO and H_2 (Sanchez-Silva et al., 2013). Bach et al. studied the gasification and kinetics characteristics of raw and wet-torrefied chlorella vulgaris ESP-31. The sample was heated from 105 to 1200 °C in CO_2 atmosphere at a constant heating rate and flow rate of 10 °C min and 100 mL min^{-1}. Thermal decomposition showed two main devolatilization peaks. For kinetics, the wet torrefaction influences most of the kinetic parameters of the algal components, whereas temperature affects the kinetics parameters of carbohydrates and lipids but not on those of protein and chars (Bach et al., 2017). However, they did not used MS to evaluate the real time gas production. Furthermore, López-González et al. investigated the steam gasification of chars resulted from the pyrolysis of algae spices (i.e, chlorella vulgaris, nannochloropsis gaditana and scenedesmus almeriensis) using TG-MS at three different temperatures of 850, 900 and 950 °C. H_2, CO and CO_2 were found to be the major gases during gasification process (López-González et al., 2014). Figueira et al. also investigated the gasification of chlorella vulgaris (CV) microalgae in steam atmosphere through TGA connected with GC analyzer. The sample was heated from 125 to 850 °C under reactive gas mixture (argon and steam) at different heating rates of 10–40 °C. The main gas constituents were H_2, CO and CH_4, signifying the potential from producing syngas from algal biomass (Figueira et al., 2015a).

However, at the best of our knowledge; published studies on CV gasification are a few, whereas spirulina (SP) has never been studied as feedstock for gasification via TG-MS. Compared to high-lipid microalgae, high-protein microalgae, such as CV and SP, with higher biomass productivity are suitable feedstock for thermochemical conversion (Gai et al., 2013; Kumar et al., 2017; Zhang et al., 2015). In addition, none of published studies have considered air as a gasifying agent for TG-MS gasification. Thus, the microalgae gasification via TG-MS under air stream, and kinetic modeling has to be further explored to obtain useful information at real-time of weight loss and evolved gases. The kinetic analysis will provide the fundamental information for design and optimization of reactor and operating conditions, which will further help in standardizing, improving and developing microalgae based industry.

The present research thus aims to explore the gasification behavior of CV and SP by means of the TGA-MS and air as gasifying agent (use of air is beneficial over steam and pure oxygen, which make the process entirety complex, lengthy, and pricey) at different heating rates. Additionally, the influence of various heating rates conditions was investigated. The isoconversional method was used to establish the kinetic parameters and to understand the reaction mechanisms to support the algal biomass gasification. The obtained