



Microalgae hydrothermal liquefaction and derived biocrude upgrading with modified SBA-15 catalysts

Jing Li^{a,1}, Xudong Fang^{b,1}, Junjie Bian^{a,c,*}, Yuehong Guo^a, Chunhu Li^a

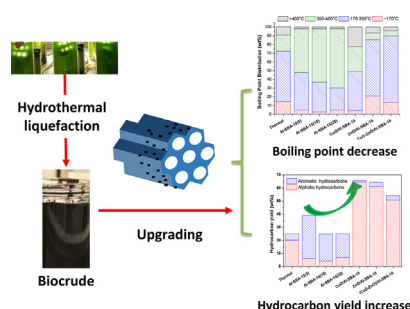
^a Key Laboratory of Marine Chemistry Theory and Technology of Ministry of Education, Ocean University of China, Qingdao, Shandong 266100, China

^b Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian, Liaoning 116023, China

^c School of Chemical, Biological, and Materials Engineering, University of Oklahoma, Norman, OK 73019, USA



GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Hydrothermal liquefaction
Bio-oil upgrading
SBA-15 catalyst
Methyl palmitate decarboxylation
Hydrocarbon yield

ABSTRACT

In this study, a novel route was proposed for microalgae biofuel production by catalytic upgrading of *Chlorella* hydrothermal liquefaction (HTL) derived biocrude. Al-SBA-15, CuO/Al-SBA-15, ZnO/Al-SBA-15, and CuO-ZnO/Al-SBA-15 catalysts were synthesized in a facile, one-pot way, and tested for methyl palmitate decarboxylation and biocrude upgrading without H₂ addition. These modified SBA-15 catalysts enhanced alkane selectivity of methyl palmitate decarboxylation from 7.6 wt% up to 79.6 wt% at 340–350 °C. FT-IR, TG and GC-MS characterizations were employed to identify the composition and properties of the upgraded bio-oils. Compared with thermal upgrading, modified SBA-15 catalysts enriched the yield of low boiling point compounds, and the content of heavy bio-oil (> 400 °C) declined from 9.57 wt% to 1.89 wt%. Hydrocarbon yield was greatly enriched on the catalysts, and aromatics predominant on Al-SBA-15 while aliphatics abundant on metal oxide(s) supported catalysts. The hydrocarbon yield was increased from 25.1 wt% (thermal) to 65.7 wt% on the CuO/Al-SBA-15.

1. Introduction

Biomass and biowaste conversion to biofuel or valuable chemicals offers a better approach to sustainable, renewable energy supply (Elliott

et al., 2015; Kruse and Dahmen, 2018). Compared with terrestrial plants, microalgae has been chosen as one of the promising feedstocks for thermochemical conversion for its faster growth rate, higher productivity, and flexible cultivating environment (Marcilla et al., 2013;

* Corresponding author at: Key Laboratory of Marine Chemistry Theory and Technology of Ministry of Education, Ocean University of China, Qingdao, Shandong 266100, China.

E-mail address: junjiebian@ouc.edu.cn (J. Bian).

¹ J. Li and X. Fang contributed equally to this paper.

<https://doi.org/10.1016/j.biortech.2018.07.008>

Received 11 May 2018; Received in revised form 2 July 2018; Accepted 3 July 2018

Available online 04 July 2018

0960-8524/ © 2018 Elsevier Ltd. All rights reserved.

Mallick et al., 2016), the significant increase in the microalgae supply has made the world ready to use bioenergy as an important part of our energy structure, while simultaneously slashing greenhouse gas emission. Biodiesel process that employs microalgae extracted lipid as the feed has been on its way to industrial-scale production (Su et al., 2017), and hydrothermal liquefaction (HTL) of medium and low lipid content microalgae would be the ideal technology for high-energy density transportation fuels, such as green diesel, jet fuel and gasoline. Due to its milder reaction conditions and magnified yield of liquid products, HTL route has been widely employed for wet microalgae slurry in a batch or continuous flow reactor (Yang et al., 2015). The bio-crude derived from microalgae has high oxygen content, leading to a low heating value and lower stability over the time. This instability is associated with the presence of reactive chemical species, notably aldehydes, ketones, carboxylic acids, and phenolic molecules (López Barreiro et al. (2013)). A sequential upgrading procedure is required to output transportation fuels (Biller et al., 2015; Ramirez et al. 2015).

The quality of biocrude can be improved by the partial or total elimination of the oxygenated functional groups. Deoxygenation is categorized into the two paths: hydrodeoxygenation (HDO) by metallic catalysts and decarboxylation/decarbonylation by solid acid catalysts. Despite its high cost and harsh reaction conditions, hydrodeoxygenation or hydrotreating may be a commonly used method for a decade (Ko et al., 2012; Tan et al., 2014; Sugami et al., 2016). For decarboxylation and/or decarbonylation process, precious metal based catalysts have been intensively explored, and showed reasonable activity for biofuel upgrading (Crossley et al., 2010; Yeh et al., 2015). Low-cost, high-capacity processes have been focused on microalgae conversion and bio-oil upgrading with non-precious metal catalysts, and series research on heterogeneous catalysts, mainly zeolites and mesoporous materials. Both model compounds and true biocrude conversion have been reported at present (Li et al., 2015). Zeolite catalysts, such as MoZSM-5 and HZSM-5 (Robin et al., 2017), H-Beta (Zhang et al., 2017), modified MCM-41 (Bian et al., 2017a), as well as active carbon (Hossain et al., 2018) and Ni/C (Wu et al., 2016) have been prepared and tested in a batch or continuous reaction for deoxygenation, and revealed good performance without H₂ addition. That provided a potential to affordable commercial conversion of fatty acids and fatty acids methyl ester to fuel-like hydrocarbons.

SBA-15 is an ideal candidate for large molecule's conversion in aqueous phase, which made it one of the best candidates for the bio-oil in situ upgrading due to its higher hydrothermal stability, desired morphology, and easily adjustable pore size and wall thickness (Chiriac et al., 2016). SBA-15 can be modified and functionalized to prepare acid and redox sites that are active for biomass decomposition and deoxygenation respectively. The gas phase decarbonylation of lactic acid was performed over SBA-15 supported heteropolyacids (Katryniok et al., 2010). Co/Al-SBA-15 was a promising catalyst for the production of biofuels in diesel range from vegetable oils with a remarkable HDO activity (Ochoa-Hernández et al., 2013). NiWC/Al-SBA-15 catalyst showed greater conversion of oleic acid and selectivity to heptadecane (Al Alwan et al., 2015).

Taking techno-economic analyses into consideration, further efforts should be concerned on the integrating microalgae HTL and in situ upgrading by designing and fabricating the high hydrothermal stable, virtually active catalysts for process intensification. In our group, microalgae non-hydrogenation conversion and the derived oil in situ upgrading process has been explored with Fe₂O₃/MCM-41 catalysts, and reaction kinetics of fatty acid decarboxylation and pathway of co-conversion with amino acid has been intensively studied (Bian et al., 2017b).

This study aims to intensify the *Chlorella* HTL conversion and sequential bio-oil upgrading by employing the made one-pot synthesized Al-SBA-15 and incorporating metal oxide(s) Al-SBA-15 catalysts. Methyl palmitate has been chosen as a model reactant for decarboxylation under an inert atmosphere, and these well performed catalysts

Table 1Proximate analysis and ultimate analysis of *Chlorella*.

Proximate analysis ^a (wt %)		Elemental analysis ^b (wt%)		Chemical composition analysis (wt %)	
Volatile matter	84.5	C	49.25	Protein	60.60
Fixed carbon	6.97	H	7.07	Lipid	12.80
Ash	4.28	N	9.15	Polysaccharide	3.70
Moisture	4.25	O ^c	34.53	Dietary fiber	13.0

^a Dry basis.^b Dry ash free basis.^c By difference.

were applied for deoxygenation upgrading of *Chlorella* HTL biocrude in subcritical water. The authors' efforts related to catalytic upgrading of bio-oil can be effectively used in advancing knowledge, and thereby creating potential value at the biorefinery.

2. Material and methods

2.1. Microalgae biomass characterization

As typical microalgae, *Chlorella* was picked as the feedstock to perform hydrothermal liquefaction experiments. The basic properties were identified with regard to proximate analysis and ultimate analysis, and the results listed in Table 1. *Chlorella* has a high content of volatile matter and a comparatively low content of ash. As it can be seen from ultimate analysis and chemical composition analysis, the relatively high contents of oxygen and nitrogen arise from the protein and lipid as well as carbohydrates.

2.2. Catalyst synthesis and characterization

A typical preparation procedure of Al-SBA-15 catalysts was one-pot method, as described by other researchers (Muthu Kumaran et al., 2008; Xing et al., 2017). A certain amount of PEO-PPO-PEO (P123) was dissolved in deionized water. Hydrochloric acid was quickly added to adjust the pH value to 1.5–3.0. Then added 7.0 mL tetraethyl orthosilicate (TEOS) and 1.7 g aluminum sulfate were hydrolyzed on the micelle surface and then polymerized to produce Al-SBA-15. The catalysts were designated as Al-SBA-15(number), and the number is the ratio of Si to Al in the mother liquid.

Metallic oxide(s) supported Al-SBA-15 catalysts were prepared by precipitation condensation method to get the well dispersed CuO and/or ZnO nanoparticles on the surface of Al-SBA-15. Firstly, ammonia water was quickly added to 0.3 mol/L CuSO₄ (zinc acetate, or 0.15 mol/L CuSO₄ and 0.15 mol/L zinc acetate) solution until pH reaching 10.0, and the fine precipitate was filtered, added to sodium citrate solution under vigorous stirring to get a suspension. Secondly, P123 was dissolved under pH 1.5–2.0, and introduced to the suspension; TEOS and aluminum sulfate were put in sequentially. Aging for 4 h, a colloidal solution was available. Then, the mixture was transferred into a Teflon-lined steel autoclave and statically heated at 120 °C for 48 h. The product was dried, washed, filtered and calcined at 550 °C for 5 h with a heat rate of 10 °C/min. Finally, the samples were designated as CuO/Al-SBA-15, ZnO/Al-SBA-15, and CuO-ZnO/Al-SBA-15 respectively.

The synthesized catalysts were characterized with X-Ray Diffractometer (Bruker D8 ADVANCE) for phase identification, TEM microscope (JEM 2100) for morphology observation with high resolution. Ammonia temperature programmed desorption (NH₃-TPD) profiles were measured on AutoChem II 2920 (Micromeritics) for acid sites strength determination.

Download English Version:

<https://daneshyari.com/en/article/7066149>

Download Persian Version:

<https://daneshyari.com/article/7066149>

[Daneshyari.com](https://daneshyari.com)