



Lewis acid-catalyzed in situ transesterification/esterification of microalgae in supercritical ethanol



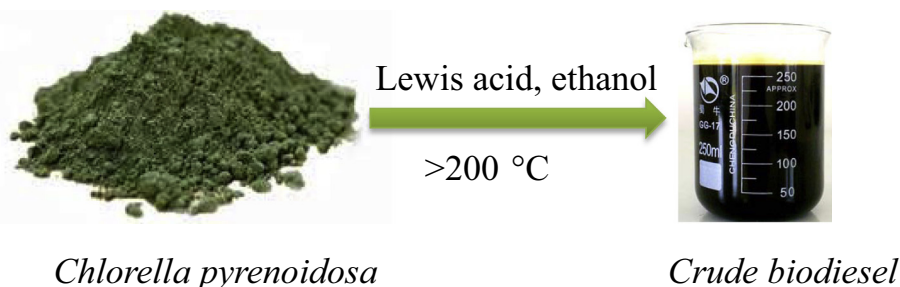
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HIGHLIGHTS

- Lewis acids significantly promote the production of crude biodiesel (CBD).
- Lewis acid makes the reaction much milder than that using supercritical ethanol alone.
- ZnCl₂ shows the highest performance toward the CBD production.
- Algae moisture is the most influential factor on the yield and quality of CBD.
- The CBD is rich in fatty acid esters which can be used as candidate for bio-fuels.

GRAPHICAL ABSTRACT



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ABSTRACT

The activities of several Lewis acid catalysts such as SnCl₂, FeCl₃, ZnCl₂, AlCl₃, and NbCl₅ for the in situ transesterification/esterification of lipid contained within a microalga (*Chlorella pyrenoidosa*) in ethanol at 350 °C were examined to identify the most suitable catalyst in term of crude biodiesel (CBD) yield. Of those catalysts tested, ZnCl₂ showed the highest performance toward the CBD production. Using ZnCl₂ as catalyst, effects of reaction temperature (200–370 °C), time (0–120 min), ethanol to microalga ratio (EtOH:MA) (5/5–40/5), catalyst loading (0–30 wt.%), and algae moisture (0–80 wt.%) on the yields of product fractions and the properties of CBD were studied. The presence of ZnCl₂ not only promoted the production of CBD but also showed activities toward the deoxygenation and denitrogenation of CBD. The moisture content in the starting material is the most influential factor affecting the yield and properties of CBD.

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1. Introduction

In the past few decades, biodiesel has received increased attention as renewable alternatives to petroleum diesel in the steadily growing transportation sector due to its non-toxic, biodegradable, energy efficient, and renewable merits (Ma and Hanna, 1999; Chisti, 2007; Salvi and Panwar, 2012). Currently, bio-

diesel is mainly derived from the lipid rich sources such as vegetable oils (Mittelbach, 1996; Demirbas, 2003), animal fats (Karmakar et al., 2010), waste greases (Kulkarni and Dalai, 2006; Canakci, 2007), and other plant oils (Durrett et al., 2008). However, production of biodiesel from these sources encountered many challenges such as high capital cost and limited availability of fat and oil resources. Therefore, efforts are being made to find low-cost, sustainable, and lipid rich feedstocks for the production of biodiesel. As an alternative energy source, microalgae are an economical choice for biodiesel production as many of algal species have been found to grow rapidly and accumulate substantial amounts of lipids and also have the potential to mitigate the competition for

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land-use and food-for fuel conflicts (Chisti, 2007; Hu et al., 2008; Mata et al., 2010). Furthermore, microalgae have the potential to produce higher biodiesel yields with about 25% reduction in production costs (Sani et al., 2013).

Methanol and ethanol are commonly used for the biodiesel production both in laboratory research and industry process due to their high reactivity. The low cost of methanol makes it the main choice for the esterification and transesterification reaction in commercial scales around the world. However, methanol is mainly derived from petroleum-based sources and has toxic properties. In contrast, ethanol is less toxic and renewably derived, and has superior dissolving power for oils, and produces biodiesel with improved fuel properties (e.g. higher energy density, larger cetane number, and stronger oxidation stability) (Stamenković et al., 2011). To avoid the mass transfer limitations and finish esterification and transesterification in relatively short time, subcritical/supercritical ethanol (SUE/SCE) was usually employed. SUE/SCE exhibited unique properties such as low dielectric constant, low viscosity, and high diffusion coefficients that allow it to be used in transesterification or esterification (Lu et al., 2002). The tunable properties of SUE/SCE with pressure and temperature allow a better control of the process. The SUE/SCE process can be even carried out in the presence of certain amount of moisture (Lotero et al., 2005). There has been some previous work that conducted the in situ transesterification/esterification of microalgae in SCE (Duan et al., 2013a; Huang et al., 2011). However, the process requires high energy consumption due to high temperature and is not economically feasible.

To enhance the reaction rate and improved the yield of biodiesel, a catalyst is necessarily needed. Lewis acids were proved to be active for both esterification and transesterification reactions (Di Serio et al., 2005; Hou et al., 2007; Cardoso et al., 2008; Soriano et al., 2009; Levine et al., 2012), most of which are alcohol-soluble, inexpensive, non-toxic, reusable, and insensitive to common heteroatoms (e.g., N, P, S), thus making the esterification and transesterification reactions free of diffusion or mass transfer restriction and the production of biodiesel more economical (Levine et al., 2012). A great advantage with Lewis acid-catalyzed esterification and transesterification is that it can directly produce biodiesel from the low-cost but free fatty acids (FFAs) rich (commonly have FFAs levels of $\geq 6\%$) feedstocks such as microalgae. Another advantage is that it avoids the soap formation as did for the base-catalyzed reaction, making it easier for the subsequent biodiesel purification and catalyst removal. Previous studies on the Lewis acid-catalyzed in situ transesterification/esterification of microalgae in SCE are rare. To the authors's knowledge, only Levine et al. have entered this arena (Levine et al., 2012). These investigators used rare-earth metal triflate catalysts (i.e., $\text{Sc}(\text{OTf})_3$ and $\text{In}(\text{OTf})_3$) to assist the transesterification/esterification of lipids within carbonized algal biomass using ethanol in the presence of water. Both Lewis acid catalysts are highly active between 200 and 235 °C and showed a high tolerance for moisture. Under optimal conditions, the highest fatty acid ethyl ester yields (85–98%) were achieved.

The purpose of the present study is twofold: first to screen the activity of different potential Lewis acid catalysts for the in situ transesterification/esterification of microalgae in SCE in terms of CBD yield; second using the identified catalyst (ZnCl_2) to study the influence of reaction temperature (200–370 °C), time (0–120 min), ethanol to microalga ratio (EtOH:MA) (5/5–40/5), algae moisture (0–80 wt.%), and catalyst loading (0–30 wt.%) on the yields of product fractions and the properties of CBD. Obviously, catalyst loadings employed in this work sometimes are far greater than the loading typically used for the transesterification/esterification reactions. However, previous study (Leung et al., 2010) suggested that catalyst loading affected the yield and quality of crude

biodiesel. So, rather than refusing to do experiments within the typical catalyst loadings, the authors opted to increase the catalyst loading beyond the typical ones wants to see the possible highest CBD yield and quality. It should be noted that high catalyst loading is undesirable in view of the economic implication. However, if the catalyst can be recycled, higher catalyst loading amount is not a problem. *Chlorella pyrenoidosa* (*C. pyrenoidosa*), a marine microalga with a lipid content of 19 wt.%, was used as the feedstock. Cheap and commercially available Lewis acid catalysts such as SnCl_2 , FeCl_3 , ZnCl_2 , AlCl_3 , and NbCl_5 were used. To the author's knowledge, this study is the only previous examination of Lewis acid-catalyzed in situ transesterification/esterification of microalgae in SCE in the presence of a range of catalysts. Finally, the CBDs were characterized by using a comprehensive collection of analytical techniques (e.g., Gas chromatography–Mass spectroscopy (GC–MS), Thermogravimetric analysis (TGA), elemental analysis).

It is known that design of experiment (DOE) is usually an efficient procedure to extract the maximum amount of information with the minimum experiments. However, there are two major drawbacks for DOE: (1) if numerous treatments are included in the experiment, the number of participants required can be prohibitive; (2) a factorial design lacks simplicity in the interpretation of results if interaction effects are present. Therefore, DOE was not employed in the present study.

2. Experimental

2.1. Materials

C. pyrenoidosa was commercially available (Shandong Binzhou Tianjian Biotechnology Co., Ltd., North China) and received in powdered form, which had a moisture content of 10 wt.%. Property details of this algae powder are available in previous publication (Duan et al., 2013a). To reduce the alcohol requirement for high efficiency during in situ transesterification/esterification, the algae powder was further dried prior to its use for most of the reactions. For those reactions conducted with algae at different moisture content, algal paste was prepared by mixing the algae powder with the desired amount of deionized water. All the catalysts and other chemicals were obtained from Aladdin Reagents (Shanghai) Co., LTD in high purity. SnCl_2 and FeCl_3 were obtained in the form of crystalline hydrate as $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, respectively.

A custom made high-pressure/corrosion-resistant mini autoclave, which provides an internal volume of 126 mL, was used to carry out all experiments. Prior to its use in experiments, the reactor was loaded with water and seasoned at 400 °C for 4 h to remove any residual organic material from the reactor and to expose the fresh metal walls to high-temperature water. After this condition, potential catalytic wall effects might be eliminated or reduced. However, they might also play a role in producing the observed results. The reactor in the present study was heated by using a molten-salts bath that consists of potassium nitrate and sodium nitrate at a mass ratio of 5/4.

2.2. In situ transesterification/esterification

Reactions of the dried *C. pyrenoidosa* powder with ethanol in the presence of different Lewis acids (SnCl_2 , FeCl_3 , ZnCl_2 , AlCl_3 and NbCl_5) were first performed to identify the activity of these catalysts in term of CBD yield. 5 g algae powder, 24 mL anhydrous ethanol, and 0.25 g (free of crystal water) catalyst were loaded into the reactor. Once loaded, the reactor was sealed tightly and submerged in a preheated molten-salts tank set at 390 °C. After about 22 min, the reactor reached 350 °C and was held at that temperature until a total time of 60 min had elapsed. The temperature was controlled

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