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Two-step *in situ* biodiesel production from microalgae with high free fatty acid content

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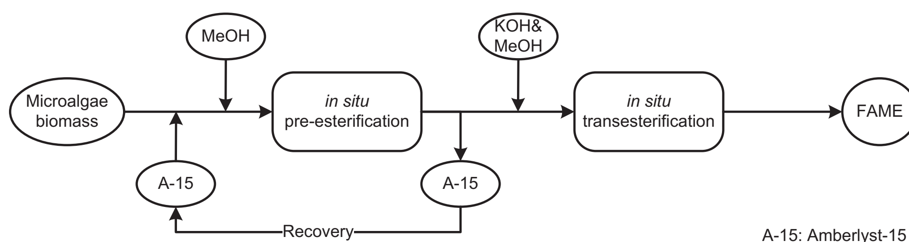
HIGHLIGHTS

- An efficient two-step *in situ* microalgal biodiesel production process is reported.
- The biodiesel yield was dramatically higher than one-step *in situ* process.
- Amberlyst-15 is suitable for the *in situ* pre-esterification and can be recycled.
- The use of recyclable Amberlyst-15 reduced catalysts (acid and base) requirement.
- This environmentally benign process has the potential to reduce production cost.

GRAPHICAL ABSTRACT



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ABSTRACT

The yield of fatty acid methyl ester (FAME) from microalgae biomass is generally low via traditional extraction-conversion route due to the deficient solvent extraction. In this study a two-step *in situ* process was investigated to obtain a high FAME yield from microalgae biomass that had high free fatty acids (FFA) content. This was accomplished with a pre-esterification process using heterogeneous catalyst to reduce FFA content prior to the base-catalyzed transesterification. The two-step *in situ* process resulted in a total FAME recovery up to 94.87 ± 0.86%, which was much higher than that obtained by a one-step acid or base catalytic *in situ* process. The heterogeneous catalyst, Amberlyst-15, could be used for 8 cycles without significant loss in activity. This process have the potential to reduce the production cost of microalgae-derived FAME and be more environmental compatible due to the higher FAME yield with reduced catalyst consumption.

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1. Introduction

Fatty acid methyl ester (FAME), also known as biodiesel, has been produced from vegetable oil, animal fat and waste cooking oil (Encinar et al., 2011; Hernandez-Martin and Otero, 2008; Ozbay et al., 2008). However, the high price and unsustainable supply of feedstocks are the major bottlenecks for increasing biodiesel production (Chen et al., 2012). Microalgae have been suggested as promising candidates of biodiesel feedstock because of their specific advantages of higher biomass productivity, faster growth rate and higher level of oil accumulation comparing with other energy crops (Guedes et al., 2011; Schenk et al., 2008).

Microalgae biodiesel has been produced from extracted lipids via a traditional extraction-conversion approach (Krohn et al., 2011; Miao and Wu, 2006; Umdu et al., 2009). However, the microalgae biodiesel production via the extraction-conversion route heavily relies on organic solvent extraction efficiency, which has been identified as a major drawback in several recent reports because of the incomplete extraction (Johnson and Wen, 2009; McNichol et al., 2012). Unlike extracting vegetable oils from various crops, which can be easily performed by crushing the oil seeds fol-

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lowed by a solvent extraction, lipid extraction from microalgae is hindered by the rigid cell wall structure and the fact that existing equipment is not suitable for mechanical crushing to extract microalgae oil (Johnson and Wen, 2009). It has been realized that one of the major hurdles for the commercial production of biodiesel from microalgae is the high costs associated with lipids recovery routes. Therefore any improvements in lipids extraction would have a significant impact on the economics of the process (Patil et al., 2011; Wahlen et al., 2011).

One of the alternatives to overcome the limitations of conventional extraction-conversion process is the '*in situ*' transesterification method, in which the lipids are simultaneously extracted and converted to FAME. Since the *in situ* approach integrates the extraction and conversion in one step, it eliminates the need to first isolate and refine the lipid before converting it into biodiesel which could lead to a reduction in cost. Moreover, besides serving as a reactant in the *in situ* process, the alcohol may weaken the cellular and lipid body membranes to facilitate the FAME conversion (Haas and Wagner, 2011). Recently, the *in situ* process has been applied to prepare biodiesel from various microalgae biomass with H_2SO_4 (Ehimen et al., 2010; Haas and Wagner, 2011; Johnson and Wen, 2009; Wahlen et al., 2011), KOH (Patil et al., 2011; Xu and Mi, 2011), and SrO (Koberg et al., 2011) as catalyst.

The base-catalyzed *in situ* process is preferred over acid-catalyzed process due to lower requirement of reagents, milder reaction conditions, and a substantially higher FAME yield (Haas et al., 2004). However, since microalgae oil has been characterized as high FFA content feedstock (as high as 70% of the total lipids) (Chen et al., 2012; Zhu et al., 2008), the *in situ* transesterification using base as catalyst might cause undesired saponification. In contrast, acid catalyst is suitable for high FFA content lipids, except for the fact that the transesterification efficiency of the acid catalyst is much lower (4000 times) than the base catalyst (Lotero et al., 2005). Alternatively, either removing FFA by solvent extraction before base-catalyzed transesterification (Zhu et al., 2008) or applying a two-step approach in which acid-catalyzed pre-esterification occurs prior to the base-catalyzed transesterification (Shiu et al., 2010; Vasudevan and Briggs, 2008) could lead to a high FAME yield in a short reaction time.

However, it would be extremely difficult to recycle homogeneous acid catalyst such as sulfuric acid after pre-esterification in the two-step *in situ* process, and neutralizing residue acid by base in the following base-catalyzed transesterification step would lead to an extra requirement for catalysts (both acid and base) (Shiu et al., 2010). In contrast, acidic heterogeneous catalysts can be easily retrieved after the pre-esterification and therefore no extra base is required for neutralization. Hence, environmentally friendly acidic heterogeneous catalyst might be specifically advantageous for the pre-esterification in the two-step *in situ* process and could potentially lead to even lower production costs by reducing catalyst consumption. Ion-exchange resins have been widely used to replace homogeneous catalysts in biodiesel production due to the high FFA conversion ratio, easy downstream processing, easy recycling and less corrosion (Ozbay et al., 2008). Among commercial resin catalysts, Amberlyst-15, an acidic styrene-divinyl benzene sulfonated ion-exchange resin, is promising in terms of its significant esterification efficiency and notable durability (Ozbay et al., 2008; Talukder et al., 2009). However, there has been no report on the conversion of FAME from microalgae biomass via a two-step *in situ* process using ion-exchange resin such as Amberlyst-15 as a catalyst.

The purpose of this work was to develop an improved two-step *in situ* process that directly produces FAME from microalgae biomass with high efficiency using Amberlyst-15 and to also explore the potential of recycling the catalyst in the *in situ* pre-esterification step to reduce its requirement as well as the environmental impact.

2. Methods

In this work the microalgae biomass was first cultured in the Biomass Processing and Bioproduct Engineering Laboratory at Washington State University and then lyophilized before use. The *in situ* pre-esterification was performed by using Amberlyst-15, which was retrieved later from the reactant mixture before base-catalyzed *in situ* transesterification. The effect of catalyst loading, methanol to biomass ratio, reaction temperature and time upon FFA reduction and FAME yield, as well as the activity of recycled Amberlyst-15 was studied. The FAME product was characterized using thermogravimetric analysis (TGA) and gas chromatography–mass spectrometry (GC–MS).

2.1. Materials

The green microalgae *Chlorella sorokiniana* (UTEX 1602) was obtained from the Culture Collection of Alga at the University of Texas (Austin, TX, USA). Agilent Bond Elut NH_2 cartridge (100 mg) from Agilent (Santa Clara, CA, USA) was used to fractionate lipids. Thin layer chromatograph (TLC) aluminum plates (20 cm × 20 cm × 250 μm) from Merck (Darmstadt, Germany) were used to identify the fractionated lipids. Standard fatty acids such as tridecanoic acid, myristic acid, palmitic acid, hexadecenoic acid, heptadecanoic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, eicosanoic acid and their methyl esters from Sigma Chemicals Company (St. Louis, MO, USA) were used as GC standards. Amberlyst-15 was obtained from Acros Organics (New Jersey, USA). All solvents and reagents were either of HPLC grade or analytical reagent grade and were obtained from commercial sources.

2.2. Microalgae biomass preparation and lipid composition analysis

The microalgae were inoculated in a 5 L fermentor (New Brunswick Scientific, CT, USA) growing heterotrophically by feeding on glucose for 2 days at 37 °C. The medium consisted of (per L) 20 g glucose, 1 g KNO_3, 621 mg $NaH_2PO_4{\cdot}H_2O$, 89 mg $Na_2HPO_4{\cdot}2H_2O$, 246.5 mg $MgSO_4{\cdot}7H_2O$, 9.3 mg EDTA, 0.061 mg H_3BO_3, 14.7 mg $CaCl_2{\cdot}2H_2O$, 6.95 mg $FeSO_4{\cdot}7H_2O$, 0.287 mg $ZnSO_4{\cdot}7H_2O$, 0.01235 mg $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 0.169 mg $MnSO_4{\cdot}H_2O$, and 0.00249 mg $CuSO_4{\cdot}5H_2O$. The pH value was maintained at 7.0 by feeding with 2 M H_2SO_4 solution. The biomass was harvested by centrifugation followed by lyophilization. The microalgae powder was ground in a mortar to obtain a homogenous feedstock for the experiment. The water content in the microalgae powder was measured by drying in the oven at 90 °C for 6 h.

To analyze the lipids composition of *C. Sorokiniana*, the total lipids were extracted from the microalgae biomass with modified Folch method (Folch et al., 1957) after bead beating (Biospec) with 0.5 mm glass beads 2 min twice. In short, methanol and chloroform was sequentially added to ruptured biomass to give one phase (Chloroform:Methanol:Water = 1:2:0.8, v/v/v). The lipids were extracted in room temperature for 1 h with periodical vortexing. Additional chloroform and 0.2 M KCl was added for the phase separation (Chloroform:Methanol:Water = 2:1:0.75, v/v/v). The lower phase was recovered and lipids were obtained by vacuum evaporation.

Fractionation and analysis of the FFAs and acylglycerols were performed on the solid phase extraction (SPE) cartridge followed by gas chromatography (GC) analysis. Crude lipid (10 mg) was dis-

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