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In situ ethyl ester production from wet algal biomass under microwave-mediated supercritical ethanol conditions

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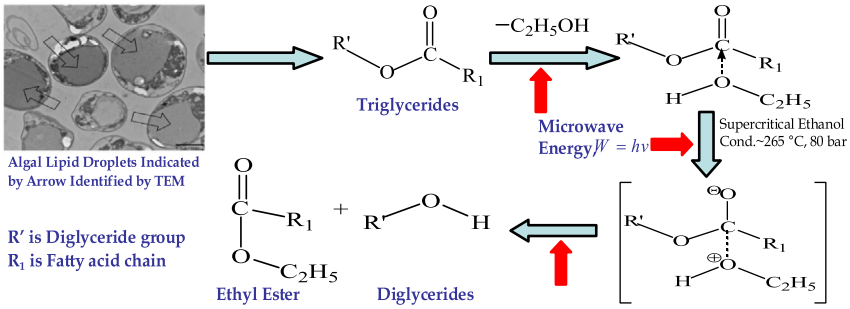
HIGHLIGHTS

- Direct conversion of wet algae to biodiesel under supercritical ethanol conditions.
- Study the effects of algae to ethanol ratio and reaction time on algal biodiesel yield.
- Controlled microwave power conditions with passive heating elements (SiC).
- No expensive and extensive harvesting and drying steps for algal biodiesel production.
- *In situ* transesterification using a green solvent and catalyst-free approach.

GRAPHICAL ABSTRACT



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ABSTRACT

An *in situ* transesterification approach was demonstrated for converting lipid-rich wet algae (*Nannochloropsis salina*) into fatty acid ethyl esters (FAEE) under microwave-mediated supercritical ethanol conditions, while preserving the nutrients and other valuable components in the algae. This single-step process can simultaneously and effectively extract the lipids from wet algae and transesterify them into crude biodiesel. Experimental runs were designed to optimize the process parameters and to evaluate their effects on algal biodiesel yield. The algal biomass characterization and algal biodiesel analysis were carried out by using various analytical instruments such as FTIR, SEM-EDS, TLC, GC–MS and transmission electron microscopy (TEM). The thermogravimetric analysis (TGA) under nitrogen and oxygen environments was also performed to examine the thermal and oxidative stability of ethyl esters produced from wet algae. This simple *in situ* transesterification process using a green solvent and catalyst-free approach can be a potentially efficient route for algal biodiesel production.

1. Introduction

Global demand for energy has been projected to increase by 49% by the year 2035 (EIA, 2012). As energy demand around the world increases, there is an increasingly intense competition for

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diminishing petroleum reserves. The current fossil fuel-based economy is unsustainable due to the negative environmental impacts, economic dependence, and energy security issues, and there is an urgent need to find a sustainable solution for this serious energy crisis (Demirbas, 2009). Biomass is one of the most suitable renewable energy sources, provided there are developments in effective new technologies for the generation of this bio-energy. This approach offers a great potential for the long-term storage of carbon and would contribute to a closed carbon cycle as well as reduce the greenhouse gas emissions compared with fossil fuels. The efficient utilization of biomass is an extremely important area for sustainable energy development (Klass, 1998).

Many pathways are currently under consideration for producing liquid fuels from biomass to supplement the fossil-based liquid transportation fuels. The most promising among these are algae-based advanced biofuels as high energy density fungible fuels for aviation, nautic and ground transport. Culturing microalgae as an alternative feedstock for biodiesel has drawn a special attention for many reasons including fast growth rate, potential for high lipid content, ability to capture carbon dioxide (CO_2) emissions, utilizing a wide variety of water sources, compatible with integrated production of fuels and co-products within biorefineries, removing pollutants from wastewater streams, effective land utilization and eliminating the dilemma in the food versus fuel debate (Hossain and Salleh, 2008; Meng et al., 2009). Three major components can be extracted from algal biomass: lipids (including triglycerides and fatty acids), carbohydrates, and proteins. While lipids and carbohydrates are fuel precursors (e.g. gasoline, biodiesel, ethanol, and jet fuel), proteins can be used for co-products (e.g. animal/fish feeds). An ideal algal biodiesel production process consist of a few key steps including algae cultivation, algae harvesting, lipid extraction, lipid to biodiesel fuel conversion and utilization of co-products from extracted algal oils and lipid extracted algae (Chisti, 2007). The extensive upstream and downstream processing makes algal biodiesel production an expensive and tedious process. In addition, there are certain techno-economical challenges in extractive-conversion process that prevent the successful commercialization of algal biodiesel. The major challenges are: (a) lack of effective and efficient harvesting technique; (b) high energy consumption in algae drying; (c) consumption of large amounts of hazardous chemicals in lipid extraction; (d) excessive lipid separation and purification; (e) expensive conversion processes. Therefore, it is critical to develop an easy and environmentally benign conversion or one-step method that reduces the chemical and energy consumption, and duration of the overall algal biodiesel production process.

There are a few potential studies that have reported the direct conversion of algal biomass to alkyl esters. These investigations using a one-pot approach are: (1) biodiesel production from wet algal biomass through *in situ* lipid hydrolysis and supercritical transesterification (Levine et al., 2010); (2) direct transesterification of a microalgae biomass using conventional heating with sulfuric acid as a catalyst (Johnson and Wen, 2009); (3) direct conversion (a one-stage method) of dry algal biomass to biodiesel production using microwave and ultrasound radiation with the aid of a SrO catalyst (Koberg et al., 2011); (4) alkali-catalyzed *in situ* transesterification of *Spirulina* sp. by methanol in reactions containing various solvents (Xu and Mi, 2011); (5) producing fatty acid alkyl esters directly from a biomass using an alkylation reagent (Hatcher and Liu, 2009). All these conversion steps including extraction, transesterification, and purification are all energy-and cost-intensive and strictly limited by nature of feedstock input, purity of reaction product, nutritional value of lipid extracted algae (LEA) and scale-up difficulties. Other significant problems in the direct algal biodiesel conversion process are long reaction time, controlling the process parameters such as temperature and pressure, processing feedstocks with high free fatty acid (FFA) contents, use of toxic solvents and optimization of process parameters for maximum yield. Herein, we report a novel integrated approach for direct conversion of wet algal biomass to biodiesel under microwave-mediated supercritical ethanol conditions. This process promotes a faster reaction mechanism, reduces energy consumption and extractive-transesterification time, and produces a significant yield of biodiesel. In addition, the application of catalyst-free synthesis with a green solvent, chemically safer reaction using microwaves and less contaminated by-product formation makes this biodiesel process 'eco-friendly' sustainable. The unique advantage of this process is that it also avoids expensive and extensive harvesting and drying steps for the production of biodiesel.

Microwave irradiation has been used to extract oils from biomass, soils and vegetable feedstock (Kiss et al., 2000; Pan et al., 2002). The main advantage of using microwave accelerated organic synthesis is the shorter reaction time due to rate enhancement. The rate of reaction can be described by the Arrhenius equation as: $K = Ae^{-\Delta G/RT}$, where 'A' is a pre-exponential factor, 'ΔG' is free energy of activation. The rate of chemical reaction can be increased through the pre-exponential factor A, which is the molecular mobility that depends on the frequency of the vibrations of the molecules at the reaction interface or the pre-exponential factor can be altered by affecting the free energy of activation (Lidstrom et al., 2001). Microwave-assisted heating is substantially more rapid than conventional heating as heat is delivered via radiation rather than convection and conduction.

In this report, several experiments were carried out to identify and optimize the effect of the process parameters involved in the extraction and transesterification of algal biomass under microwave-mediated supercritical ethanol condition. When heated up to the near- or supercritical stage, organic solvents become more and more transparent to microwave irradiation and the energy transfer is less effective (Kremsner and Kappe, 2005). Therefore, we depict the use of a passive heating element made of silicon carbide (SiC) to augment the microwave-mediated heating process at high temperatures. The supercritical conditions for ethanol are above 63 bar and 241 °C, which can be reached easily under microwave irradiation. Analytical results for algal biodiesel obtained from gas chromatography–mass spectrometry (GC–MS), thermogravimetric analysis (TGA), thin layer chromatography (TLC) and Fourier transform infrared spectroscopy (FT-IR) are also presented.

2. Methods

Wet algal paste (*Nannochloropsis salina* sp.) provided by the Solix Biofuels Inc was used in this study. For GC–MS analysis, C4–C24 even carbon saturated FAEEs mixture (1000 mg/mL in hexane, 49454U) and ethyl heptadecanoate, internal standard were purchased from Supelco®. Extra pure ethanol, hexane, sodium sulfate and activated carbon were procured from Acros Organics. For TLC analysis, acetic acid, diethyl ether, sodium sulfate and sulfuric acid were produced from Acros Organics, NJ, USA. All chemicals were at least of A.C.S. grade or better. The experiments were performed in an Anton Paar Synthos 3000 microwave reactor, utilizing four vessels in the Rotor 8SXQ80 (80 mL quartz vessels, 0–80 bar, 25–300 °C, 0–1400 W) with silicon carbide (SiC) as a passive heating element.

2.1. Characteristics of N. salina algal cells

Qualitative elemental analysis of algal biomass was determined by scanning electron microscopy (model S-3400N, Hitachi High Technologies, Pleasanton, CA, USA) equipped with an energy-dispersive X-ray spectrometer (Noran System Six 300, Thermo