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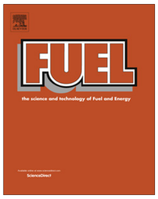

Single-step conversion of wet *Nannochloropsis gaditana* to biodiesel under subcritical methanol conditions

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HIGHLIGHTS

- One-step transesterification of wet algae under subcritical methanol condition.
- Fatty acid methyl esters analyzed with GC–MS, ^{1}H NMR, and TGA.
- Optimization of the one-step esterification under subcritical methanol.
- No need for drying the algae and a conventional catalyst.

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ABSTRACT

A single-step process for a direct conversion of wet algal biomass containing about 80% of water into biodiesel under subcritical methanol conditions is developed and presented in this work. This process may have energetic advantages with high free fatty acid (FFA) and water contents as the feedstock. At elevated temperatures, water hydrolysis and FFA esterification can simultaneously occur in a subcritical state. The influences of process parameters including reaction temperature (150–225 °C), reaction time (15–120 min) and methanol to wet biomass (vol./wt.) ratio (3:1–8:1) were investigated. The optimal conditions for this process are reported as: methanol to wet biomass (vol./wt.) ratio of around 6:1, temperature and time of about 225 °C, and reaction time of 90 min. The fatty acid methyl esters (FAMEs) were analyzed with GC–MS, FT-IR and thermogravimetric (TGA). This process does not require a catalyst and any drying pre-treatment steps. Thus, the process is cost-saving and environmental friendly for renewable biodiesel production.

1. Introduction

Biodiesel, as a renewable, economically viable alternative to petroleum-derived diesel, has received much attention as the world seeks to prevent the future oil crisis and the unpredictable consequences of climate change [1]. It is generally produced from the oils of palm, soybeans, canola, jatropha, etc. [2]. However, the great requirement of unsustainable large cultivation area of these oil crops has limited the wide application of biodiesel in supplementing petroleum derived diesel [3].

In recent years, microalgae have been suggested as a potential feed stock for biodiesel production. They have numerous advantages, including higher photosynthetic efficiency, higher biomass production, and higher grow rates, as compared to other food crops [4]. In addition, microalgae can grow in fresh water, marine non-potable water, or wastelands where nothing else grows without using arable land and competing with food production [5].

The conventional biodiesel production from microalgae usually requires dry algal biomass with water content no more than 10%. Microalgae have high moisture content after harvesting by centrifugal dewatering more than 60% of water [6]. Algal oil is extracted with organic solvent and then converted into biodiesel using a catalyst. The energy consumption in drying and solvent extraction processes accounted for up to 90% of the total process energy [7].

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Moreover, the conventional production uses organic solvent is not environmentally friendly. Direct transesterification is promising technique that generates fatty acid methyl esters (FAMEs) from wet algal biomass. It eliminates the need to isolate and purify lipid before converting it to biodiesel, which could be reduced the cost of biodiesel production [8]. However, this method has a problem that moisture content is a limiting factor for conversion efficiency of triglyceride [9,10].

Acid catalysts are less sensitive to the presence of free fatty acids (FFA) and can simultaneously conduct esterification and transesterification [11]. The esterification of free fatty acid is more resistant to the inhibition by water and enabled the higher FAME yield. Thus, acid hydrolysis of lipid from microalgae followed by esterification was carried out by Takisawa et al. [12]. In their report, wet algal biomass reacted with sulfuric acid to hydrolyzed intracellular lipid and subsequently FFA underwent esterification with methanol to produce FAME. The excess sulfuric acid in a hydrolysis process causes the degradation of FFA. Therefore, time, temperature and acid concentration must be controlled more carefully. Hence, supercritical alcohol reaction is of great interest to carry out such as no catalyst is required and a high conversion can be obtained in a short time [13,14]. A single-step extraction and conversion of wet algae to fatty acid methyl esters under supercritical methanol (SCM) has been demonstrated [15]. This process was performed at a high ratio of wet algae/methanol (1:9 wt./vol.), a high reaction temperature (255 °C) and a high reaction pressure (1200 psi) within 25 min. Under the supercritical condition, methanol acts as both an acid catalyst and a reactant to accelerate the reaction [16,17]. An excessive amount of methanol is still required to suppress the backward reaction of FAME to TAG and acts as an acid catalyst [18]. In addition, the reaction requires temperatures and pressures are much higher than the critical point of the reaction mixture led to high production costs and energy consumption. The addition of co-solvent such as hexane, propane, with supercritical conditions seems to be an efficient means to reduce can decrease the operating temperature, pressure and the amount of alcohol required [19,20]. However, the use of co-solvent has negative effects on environment and the purity of biodiesel produced.

Subcritical water (SCW) is a considered as a cost-saving and environmentally friendly. At high temperature, SCW act as nonpolar solvent like organic solvent. Moreover, SCW can also act as an effective catalyst for a hydrolysis [21]. In a previous work, it reported that triglyceride (TAG) was hydrolyzed to FA under SCW without adding catalyst [22,23]. H^+ (from dissociation of water and FA) and FA serve as a catalyst for hydrolysis. Additionally, phospholipid is known to be polar lipid was also hydrolyzed to FA and phosphorus containing products [24]. Thus biodiesel can be produced from phospholipids, free fatty acids, and triglycerides under subcritical condition. Hydrolysis of dewatered algae (80–90% water) under SCW followed by esterification with no added catalyst was also investigated [25]. They suggested a two-step non-catalyst biodiesel production process through intracellular lipid hydrolysis and supercritical esterification. First, cellular lipids were converted to fatty acids under subcritical water conditions. Second, fatty acids were esterified with supercritical ethanol to produce biodiesel in the form of fatty acid ethyl esters (FAEEs). They reported a maximum FAEE yield 66% (w/w). It indicated that esterification was inhibited from the biomass with high water content. Tsigie and co-workers have developed a single-step non-catalytic conversion process for producing fatty acid methyl esters (FAMEs) from wet *Chlorella vulgaris* under subcritical water and methanol conditions, and reported a FAME conversion yield of 89.71% at 175 °C after 4 h of reaction time [26].

The objective of this study is to investigate the direct biodiesel production of wet algal biomass under subcritical water and methanol in the presence of nitrogen. The influence parameters on process including, reaction temperature, reaction time and ratio of wet biomass to methanol was investigated. Gas Chromatography–Mass Spectroscopy (GC–MS) was used to determine the FAME yield.

2. Experimental

2.1. Materials and methods

Nannochloropsis gaditana (CCMP – 1775) culture used in this study was obtained from the Provasoli-Guillard National Center for Culture of Marine Phytoplankton (CCMP). The *N. gaditana* was grown in the f/2 growth medium [27]. Methyl tricosanoate (C23:0) from Sigma Aldrich was used as an internal standard for the GC–MS analysis. Hexane and methanol was purchased from PHARMCO-AAPER (Shelbyville, KY) were used in this study. The $CDCl_3$ [99.8% D with 0.03% (v/v) tetramethylsilane (TMS)] used as the NMR solvent was purchased from Aldrich Chemical Co. (Milwaukee, WI). SPE silica columns for the purification of crude FAME's were purchased from Thermo Scientific (Waltham, MA). The subcritical methanol esterification was performed in a PARR 4593 stainless steel bench top reactor accompanied by a 4843 controller unit and were manufactured by Parr Instrument Company (Moline, Illinois, USA). Thermogravimetric analysis (TGA) of wet algal biomass and biodiesel were performed using Perkin Elmer Pyris 1 TGA (Perkin Elmer Inc., USA) instrument. A VARIAN^{unity} INOVA, nuclear magnetic resonance spectrometer and Attenuated total reflection–Fourier transform-infrared Instrument (ATR–FTIR) (Bruker, Equinox 55, Germany) was used to determine the chemical structure of algae biodiesel.

2.2. Properties of N. gaditana algal biomass

Composition of algal biomass samples were characterized with crude carbohydrate −56.97%, crude protein −14.26%, lipid content −21.76% and ash content −7.0%. The high heating value was determined to be 25.0 MJ/kg. Analyzes of algal biomass with TGA were also performed.

2.3. Reaction of wet N. gaditana with methanol under subcritical condition

Five grams of wet algae containing 80% water and methanol were loaded in a 100 mL PARR micro-reactor. To analyze the effects of conversion process parameters, experiments were conducted in three batches by varying one of the parameters and keeping the remaining two parameters constant. The reaction was carried out at reaction temperature from 150 to 225 °C, reaction times from 15 to 120 min, methanol to wet biomass (vol./wt.) ratio was 3:1–8:1 and the pressure was maintained (600–900 psi) in all experiments. At the end of the reaction, the reactor was cooled to room temperature before collecting the product mixture. This mixture was processed under a vacuum in a rotary evaporator to separate the unreacted methanol from the product mixture. About 10 mL of *n*-hexane was added to the remaining product to separate the biodiesel and then centrifuged (3200 rpm) for 5 min. The hexane layer containing biodiesel was purified in a short SPE silica column to elute only neutral components that were analyzed in GC–MS.

2.4. FAME analysis

Analysis of FAME content was performed using gas chromatography–mass spectrometry (GC–MS) system composed of an Agilent 5975 C MSD and an Agilent 7890 A GC equipped with a capillary