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Subcritical water extraction of lipids from wet algae for biodiesel production

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HIGHLIGHTS

- Extraction of lipids/oil from wet algal biomass.
- Water was used as solvent for extraction.
- Complete extraction of lipids using microwave assisted heating.
- 2–8 Times reduction in extraction energy.
- Observed potential byproducts (proteins, omega-3 fatty acids, sugars).

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ABSTRACT

An energy efficient extraction of algal lipids from wet algal biomass was performed at subcritical conditions of water. This was achieved using microwave assisted heating as well as conventional heating. The conventional heating subcritical water (C-SCW) extraction and microwave assisted subcritical water (MW-SCW) experiments were designed and conducted to study the effects of extraction temperature, time, and biomass loading on lipid extraction. The Response surface methodology was used to optimize the parameters for maximum extraction of lipids. The influence of extraction temperature is more when compared to other experimental parameters in both processes. The maximum extraction efficiencies were achieved at 220 °C using conventional heating and 205 °C using microwave heating. Complete extraction of lipids was observed with microwave assisted heating and 70% extraction efficiency was achieved using conventional heating. The energy required for extraction is greatly reduced (2–8 folds) when compared to the conventional solvent extraction. The potential by-products like protein rich residual algae, omega-3 fatty acids, and sugars in residual water phase were identified. The biomass and the crude extracts were characterized using GC–MS, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), and thermogravimetric analysis (TGA).

1. Introduction

The need for alternative energy sources to replace fossil fuels has motivated many researchers and policymakers to develop innovative research programs around the world. Development of biofuels for the transportation sector is one of those programs directed towards production of sustainable renewable fuels and significant progress has been achieved in development of some renewable biofuels. Biodiesel is best known among renewable fuels and is currently being produced from a wide variety of vegetable and plant oils. The implication of the utilization of vegetable oils to produce biodiesel has increased demand on the domestic markets and in some instances the production is often reduced

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due to scarcity of the oil [1]. Algae have long had the attention of biofuel investigators as a new source of oil for biofuel production as it can produce more oil compared to other biofuel feed stocks in shorter periods of time and in smaller areas. Algae are photosynthetic organisms which utilize solar energy to grow and convert water and carbon dioxide into lipids and other metabolites. They also can be grown on waste water generated by the agricultural, food industry [2]. Some researchers also identified the possibility of using waste water generated from coal seam gas industry to grow algae [3]. Algae have been used as a source to produce a wide variety of natural products for pharmaceutical, biomedical, and nutraceutical industries. Carbohydrates, polyunsaturated fatty acids (PUFAs), vitamins, minerals, and dietary fibers are some of the commercial products derived from algae other than oils. Development and marketing of these byproducts are crucial for sustainable production of algae biodiesel and this strategy is widely known as 'algal bio refinery' [4,5].

Different methods have been demonstrated to produce biodiesel from microalgae. These processes involve drying of algal biomass and extracting oils with expeller press, solvent extraction, etc., [6,7] and some researchers have used supercritical CO_2 extraction of lipids to produce biofuels [8]. The extraction of oils is the most energy intensive step among the four steps; it consumes nearly 85% of production energy in the dry extraction method [9]. To eliminate the energy consumption involved in drying, wet processing methods have been explored to produce biofuels. Direct conversion of wet algal biomass to biodiesel was demonstrated using a supercritical ethanol transesterification method [10]. But due to limitations in scalability of this process, a large scale production is very difficult.

Subcritical water (SCW) extraction or hydrothermal liquefaction (HTL) is another way of isolating or producing necessary feedstock for biofuels. Water is identified as an environmentally benign, non-toxic medium, with selective extraction or reaction capabilities and is a readily available green solvent. The process of converting biomass in HTL will be performed at medium-temperatures (200–370 °C) and high pressure. The characteristics of bio-crude or crude extract produced during this process vary with process temperature and pressure. The solubility of organic matter begins to increase rapidly at about 200 °C, and this enhanced solubility for organic compounds is provided by a homogeneous single-phase medium for organic synthesis in subcritical water [11]. The reduction of the dielectric constant makes water a suitable solvent for small organic compounds, as its dielectric constant drops from 80 at 25 °C to 40 at 200 °C. Subcritical water extraction has been demonstrated for the extraction of mannitol from olive leaves [12], and essential oils from coriander seeds [13].

In hydrothermal liquefaction and at elevated temperatures, biochemical compounds present in the biomass undergo reactions like hydrolysis, repolymerization to form energy dense biocrude oil, bio-char, water soluble compounds and gaseous products. During this process, the oxygen present in the biomass will be removed by dehydration in the form of water, and by decarboxylation in the form of carbon dioxide [14,15]. Successful liquefaction of whole algae was demonstrated by Biller et al [16,17], Brown et al. [18] and Toor et al. [19] at temperatures of 300 °C or higher to produce an energy dense bio-crude oil. The major obstacle to refine the bio-crude oil in regular refineries is its higher nitrogen content, which requires special catalysts or processing strategies [19,20]. As discussed earlier, the commercialization of algal biofuels requires co-production of high value by-products from algae along with fuels. With whole algae conversion in HTL, the option of by-product has to be sacrificed in order to produce bio-crude oil.

To demonstrate algae bio-refinery and produce fuel, subcritical water extraction was chosen. This is the first study of this kind where lipids/oils can be extracted directly from wet algal biomass while preserving the valuable by-products. In this study along with conventional heating SCW extraction, microwave assisted SCW method for the extraction of lipids was performed. The heat transfer mechanism in conventional heating depends on the thermal conductivity of the solvent, and sample. The convective currents make it a slow process in conventional heating, where in microwave heating the volumetric heating makes the heat transfer process is fast and rapid [21]. Microwave-assisted extraction is a fairly new technology which has greater selectivity towards desired compounds and a faster and better recovering capacity than traditional methods [22]. In this novel process, the resistance offered by the solution to the passing electrophoretic migration of ions of electromagnetic field causes friction between molecules resulting in the generation of heat [23]. Along with external heat, the water inside the cell body evaporates and bursts cell walls making extraction of cellular contents much easier [24,25]. There have been successful demonstrations of the extraction of essential oils from the leaves of murraya koenigii [26], and plant materials [27].

In this study, extraction of lipids/oil was demonstrated through conventional heating subcritical water extraction (C-SCW) and microwave-assisted subcritical water extraction (MW-SCW). Both the processes are more selective towards lipids/oils. Preliminary observations provided the basis for central composite design, which was employed to study the effects of extraction temperature, extraction time, and biomass loading on crude extract yield. When optimum parameters were established for each method, extraction efficiency was determined and compared to a conventional solvent extraction method. Produced crude extracts were also analyzed by FT-ICR MS for qualitative compositional description. Lipid extracted algae (LEA) was analyzed for nutrient value and calorific value. The thermal behavior of algae, crude extract and pure algal oil samples was determined using a thermogravimetric analyzer (Perkin Elmer Pyris 1 TGA).

2. Experimental section

2.1. Materials and methods

Nannochloropsis salina algal biomass was received from Solix biofuels (Fort Collins, Colorado, USA) and NMSU Energy Research Laboratory. Moisture content was 62% and 63% for respective biomasses in above stated order and both were harvested by centrifugation. All solvents used in this study were analytical grade reagents.

PARR 4593 stainless steel bench top reactor accompanied by a 4843 controller unit manufactured by Parr Instrument Company (Moline, Illinois, USA) was used for conventional heating extraction experiments. The microwave-assisted subcritical water extraction experiments were performed in an Anton Paar multiwave 3000 microwave reactor (operating parameters: 0–60 bar, 25–220 °C, 0–1400 W, 10–60 mL/Teflon tube reactor with 16 tubes) enclosed with a specially designed rotor (Graz, Austria). Both reactors are equipped with pressure gauges. Imaging of thin sections of algae was carried out with a model H-7650 transmission electron microscope (Hitachi High-Technologies America, Pleasanton, CA). Thermo gravimetric analysis (TGA) of wet algal biomass was performed using Perkin Elmer Pyris 1 TGA (Perkin Elmer Inc., USA) instrument. A Hewlett Packard 5890 gas chromatograph with a 5972a mass selective detector equipped with a capillary column DB-23, 30 m × .25 mm diam. × .25 μm film was used for fatty acid methyl ester analysis. Compositional analysis of intact lipids was performed for lipid extracts by direct infusion into a hybrid linear ion trap FT-ICR mass spectrometer (LTQ FT, Thermo, San Jose, CA) equipped with an Advion Triversa NanoMate (Advion, Ithaca, NY).