



A route to produce renewable diesel from algae: Synthesis and characterization of biodiesel via in situ transesterification of *Chlorella* alga and its catalytic deoxygenation to renewable diesel



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HIGHLIGHTS

- In situ transesterification of *Chlorella* algae with sulfuric acid as a catalyst.
- FAME yield is 96–98% from the theoretical one.
- Characterization of purified biodiesel.
- Residual biomass after transesterification contained sugars and proteins.
- Successful hydrodeoxygenation of *Chlorella* based biodiesel over Ni–H–Y–80 zeolite catalyst.

ARTICLE INFO

Article history:

Received 23 June 2014

Received in revised form 23 December 2014

Accepted 25 March 2015

Available online 14 April 2015

Keywords:

Algae
Biodiesel
Transesterification
Deoxygenation
Fuel quality

ABSTRACT

In situ transesterification of *Chlorella* alga was performed using 5–20 wt% sulfuric acid as a catalyst at either 60 or 100 °C. The maximum ester yield in the range of 96–98% is comparative to the specification of ester content in biodiesel, 96%. A high excess of methanol was used in transesterification ensured also a high ester yield. The FAME was purified via adsorption of chlorophyll and carotenoids onto a clay. Properties of the purified biodiesel were investigated with several methods. The results showed that the *Chlorella* based biodiesel exhibits slightly lower oxidative and thermal stability compared to soybean based biodiesel due to the presence of polyunsaturated FAMES. In addition to biodiesel, also the residual biomass was characterized showing that it contained sugars and proteins. An additional hydrogenation would increase the oxidative stability. Hydrodeoxygenation of *Chlorella* based biodiesel was also demonstrated over 5 wt% Ni–HY-80 zeolite with SiO₂/Al₂O₃ ratio of 80 and with 5 wt% Pd/C at 300 °C and 30 bar in dodecane as a solvent. Ni–HY-80 was superior to Pd/C catalyst giving more than 95% yield of hydrocarbons.

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1. Introduction

Energy demand in the world is expected to increase by 59% by the year 2035 [1]. In addition, liquid transportation fuels from renewable resources are urgently needed due to the depletion of fossil resources. During the last 10 years intensive research efforts have been devoted for production of liquid biofuels, such as ethanol, butanol, biodiesel and green diesel. Among these biofuels only the green diesel, which has been synthesized either via catalytic

hydrodeoxygenation or deoxygenation of triglycerides and fats, exhibits the same fuel properties as conventional diesel, since it has a similar composition. On the other hand, ethanol and butanol exhibit lower heating values and can suffer from incomplete burning thus forming oxygenated, harmful, gaseous byproducts. Chemically biodiesel is methyl ester mixture of fatty acid containing oxygen. Thus it does not have the same composition as fossil diesel and it causes also corrosion of engines [2].

The raw materials for production of green diesel have traditionally been triglycerides from vegetable oils. This approach faces, however, the ethical challenges, such as competition in the raw material supply with the food supply, thus alternative resources

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should be found. Algae have beneficial properties, such as high growth rate and lipid content [1]. Furthermore, their lipid content is possible to tune via a proper nutrient supply. The biggest challenge in the commercial utilization of algae as a lipid source for fuel is its costly drying step.

The next step after drying is extraction of lipids from algae. Algae extraction has already been investigated for more than two decades by applying several methods and different solvents. Mechanical or chemical rupture of hydrophilic cell walls in order to enhance the extraction capacity was also applied utilizing ultrasound [3], microwaves, or supercritical CO₂ [4,5]. The algae oil extracted from dry algae can be used for synthesis of biodiesel. This process is not, however, economically very feasible [6]. Furthermore, lipid extraction is not very selective, especially with polar solvents [7–9], since polar phospho- and glycolipids are also then extracted, whereas higher extraction selectivities toward triacylglycerides have been obtained with non-polar solvents, such as hexane [3]. On the other hand, hexane has difficulties to open the cell wall and typically low extraction yields have been achieved.

Algae oil transesterification has been recently demonstrated already by a few authors [10,11]. For example in [10] alkali catalyzed transesterification resulted in over 95% FAME yields within 60 min using KOH as a catalyst. In addition, three different algae oils, originating *Chlorella*, *Nannochloropsis* and from a third one, which name was not revealed, were transesterified with the alkaline catalyst, NaOH [11]. In [11] the main aim was to characterize the algae oil based FAME.

In several methods the utilization of wet algae has been proposed, for example hydrothermal treatment and transesterification of wet algae. The results showed that in the two step process composed of a hydrolysis step followed by in situ supercritical water transesterification, maximally 79 wt% FAME was achieved with the crude biodiesel yield of 68.3% at 275 °C during 120 min. It has also been reported that the transesterification of wet algal biomass is not very efficient resulting in 20% less FAME yields compared to the process starting from dry biomass [4].

For process intensification in algae extraction and transesterification, a few different approaches have been described, for example in situ transesterification [12–16], in situ transesterification under supercritical ethanol [17] or methanol [18,19], a two-step method comprising in situ hydrolysis of wet algae followed by supercritical transesterification of wet fatty acid rich solid fraction [6] and thermo-chemical conversion of algae to biofuels [20]. One-step in situ transesterification of dry algae over acidic [11–14] and basic catalysts [15] has been also proposed. Already after 4 h transesterification a nearly equilibrium conversion was achieved at 60 °C and at 90 °C with *Chlorella* algae using 0.04 mol sulfuric acid as a catalyst with the molar ratio of methanol to oil 315:1 [14] indicating that 60 °C is already an adequate temperature for this reaction. In addition the effect of water was studied in [14] and the results revealed that water has a detrimental effect on conversion, since already with the water level of 0.7 wt% only 81.7% of the equilibrium conversion was achieved. On the other hand, in base catalyzed transesterification of algae the highest yield of FAME from *Chlorella vulgaris* was 77.6 wt% after 75 min reaction time using the molar ratio of methanol to oil of 600:1 at 60 °C [15]. In addition, product characterization was done for biodiesel from *Chlorella* alga synthesized via in situ transesterification using 90:1:3.8M ratio of methanol, oil and sulfuric acid [21]. In that work the main emphasis was on studying the effect of growing conditions on the lipid yield and on biodiesel quality. Transesterification of marine microalga, *Schizochytrium mangrovei* PQ6 was also demonstrated using HCl as a catalyst, a co-solvent, dichloromethane together with methanol at 60 °C during 3 h [22]. The FAME yield based on algal oil was 88%. Thermochemical conversion of *Chlorella pyrenoidosa* at 350 °C

during more than 30 min in the presence of ethanol resulted in the production of solid residue, bio-oil with the heating capacity of 36.45 MJ/kg and gas showing also the potential of this thermochemical approach [20].

Biodiesel has also been synthesized under supercritical ethanol [17] or methanol [18,19]. In the former work [17] the FAME yield achieved during 30 min was 67% at 275 °C starting from wet alga *Nannochloropsis Salina* and using 1:9 dry algae to ethanol (wt%/vol) ratio [17]. In the in situ supercritical methanolysis of algae, *N. Salina*, under microwave heating maximally about 22 % FAME was obtained at 130 °C and 4 MPa using the algae to MeOH ratio of 15 wt%/vol during 10 min with 3 wt% KOH as a catalyst.

In the two step method, in situ hydrolysis of wet algae followed by transesterification of wet acid rich residue has been demonstrated by Levine et al. [7].

Recently catalytic hydrotreatment of crude algal oil has been studied either over Ni–H-Beta catalysts [23–25], Pd/C [26] or using supercritical water at 430 °C over Pt/C, Mo₂C and H-ZSM-5 catalysts [27]. The results showed that about 78% of liquid alkanes were achieved with mildly acidic Ni–H-Beta catalyst at 260 °C under 40 bar hydrogen. The theoretical liquid hydrocarbon yield was calculated to be 84%. Noteworthy is that these alkanes were mainly octadecane (59%) together with 19% heptadecane [24]. In the work of Robota et al. [26] hydrotreatment of algal oil in a continuous mode at 350 °C under 5.5 MPa producing 85% of alkanes was performed. The ratio between C18 to the sum of C18 and C17 together with the ratio C16 to C16 + C15 increased from 0.3 to 0.6 during time on stream. In addition, 76 wt% of carbon was retained in the feedstock after algal bio-oil treatment at 430 °C in supercritical water using Mo₂C as a catalyst [27].

Biodiesel contains oxygen and thus it is not directly compatible with diesel motors causing corrosion and incomplete burning. Catalytic deoxygenation of biodiesel is thus an efficient method to transfer biodiesel to so-called green or renewable diesel. Catalytic deoxygenation of fatty acids and triglycerides has been already demonstrated both in semibatch [28,29] and continuous mode [30] over Pd/C catalysts. Catalytic deoxygenation of biodiesel has been earlier demonstrated using Pd/SBA-15 [31] and Pt/Al₂O₃ [32] as catalysts. In the former work [30] 70% conversion of technical methyl oleate was achieved at 270 °C, 60 bar hydrogen during 6 h over Pd/SBA-15, whereas deoxygenation of methyl stearate resulted in 40% yield of heptadecane over 1 wt% Pt/Al₂O₃ in 6.8 bar helium at 325 °C within 6 h at 44% conversion [32]. The above mentioned short summary of the state-of-the art in algae extraction and biofuel production shows that the algae process technology is not yet fully established and more research is required.

The aim of this work was to synthesize biodiesel from *Chlorella* algae using sulfuric acid as a catalyst, to determine the composition of biodiesel and its fuel properties. In addition, catalytic hydrodeoxygenation of algae-derived biodiesel was demonstrated both over Pd/C and Ni–HY-80 zeolite catalysts. Since lipid fraction is not the main part in alga, the residual fraction after transesterification has been analyzed and its utilization has been emphasized.

2. Experimental

2.1. Raw material

Dry *Chlorella* powder from Fuqing King, Dramsa Spirulina Co., Ltd., China was used as a feedstock in the current work. According to manufacturer it contains 57.3 wt% protein, 17.3 wt% carbohydrates, 2.3 wt% of chlorophyll and maximally 7 wt% moisture and ash based on dry weight. The particle size of the spray-dried powder was 125 µm.

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