Ethyl esters biodiesel production from *Spirulina sp.* and *Nannochloropsis oculata* microalgal lipids over alumina-calcium oxide catalyst

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ABSTRACT

In this study, we present the ethyl esters biodiesel production from *Nannochloropsis oculata* and *Spirulina sp.* microalgal lipids on 60 wt% CaO on Al_2O_3 catalyst at 50 °C and 1.0 atm. The activity of the catalyst was studied as a function of ethanol:lipid molar ratios, catalyst amounts and reaction times. It was found that 6 wt% of the lipids as catalyst amount resulted in 59% biodiesel yield in 30 min at 12 of ethanol:lipid molar ratio whereas 90—99% biodiesel yield was obtained at 24 and 48 of ethanol:lipid molar ratios. In order to achieve 90—99% yields, the basic strength was found to be weak and to be in the form of bi-carbonate, whereas high basicity was not necessary. Besides, pure CaO and Al_2O_3 were not active under the same reaction conditions. We found that the glycerolysis of triacylglyceride occurred in series with the reverse of the transesterification of the triacylglyceride when the catalyst amount was 6 wt% of the lipids and the ethanol:lipid molar ratio was 24 and 48 and the reaction time was 60 min.

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1. Introduction

The fossils fuels and their derivatives have been the main energy sources in transportation, industrial and residential operations. Unfortunately, their usages have increased air pollutant emissions, such as greenhouse gases, for decades [1,2]. The major contributor is the transportation sector; for instance 28% of total CO_2 emission and ~84% of the transportation related CO_2 emission comes from the road transportation [3]. On the other hand, biofuels, which are CO_2 neutral fuels, are viable choices to replace fossil fuels but their most significant drawback was the operating cost of their production. For instance, ~80% of the total cost in the biodiesel production using oil crops was related to its operating cost. Besides, the usage of the oil crops for fuels production was not desirable due to increasing demand of oil crops for human consumptions [4]. Therefore, an alternative oil source could be lipid containing aqua-biomass, such as microalgae or macroalgae.

The usage of microalgae as compared to macroalgae has many advantages. For instance, microalgae have high growth rates; e.g. doubling in 24 h [5]; 15—300 times more oil production using microalgae than traditional oil crops on an area basis could be possible [6]; microalgal lipid contents could be adjusted with the change of growth medium composition [7]; multiple times harvesting a year are possible [8]; salty or waste water and atmospheric carbon dioxide as the carbon source are used in growing microalgae; and they are non-toxic and highly biodegradable [8].

Biodiesel can be produced with the transesterification and/or esterification of variety of microalgal/macroalgal lipids and an alcohol in the presence of a catalyst. In general, methanol as the alcohol and sulfuric acid or sodium hydroxide as the homogeneous catalyst has been used because of their high activities at low temperatures and 1.0 atm. For instance, Miao and Wu [9] reported the production of methyl esters biodiesel from heterotrophically grown *Chlorella protothecoides* microalgae using sulfuric acid and methanol at 30 °C whereas Li et al. [10] showed that 98.2% of *Chlorella protothecoides* microalgae could be converted to biodiesel using an immobilized lipase in 12 h. In addition, Hossain et al. [11] showed that biodiesel could be produced from the lipids of macroalgae species, *Oedigonium* and *Spirogyra,* and methanol using sodium hydroxide as the catalyst. In contrast, there are few studies and some patents on the methyl ester biodiesel production from microalgal lipids and methanol over heterogeneous catalysts in the literature. For instance, Umdu et al. [12] was the first to report highly active alumina supported calcium oxide and magnesium oxide catalysts made with a sol-gel method in the

transesterification of *Nannochloropsis oculata* at 50 °C and 1.0 atm. Carrero et al. [13] showed that 25% of the highest biodiesel yield was obtained in the esterification of *N. gaditana* microalgal lipid with methanol over H-Beta zeolite, ZSM-5, Beta, and H-ZSM-5 zeolites at 115 °C in 4.0 h. Teo et al. [14] reported that 92% of biodiesel yield was achieved using calcium methoxide catalyst and methanol in the transesterification of *Nannochloropsis oculata* microalgal oil at 60 °C in 30–240 min. Similarly, Carrero et al. [15] observed 94% of the highest biodiesel yield at 100 °C in 4.0 h from *N. gaditana* microalga in the esterification/transesterification using methanol over Amberlyst-15, CT-269, CT- 275, KSF clay and silica-alumina catalysts. But they reported very low reusability of the ion-exchanged resin catalysts. Recently, Guldhe et al. [16] reported that ~98% of *Scenedesmus obliquus* microalgal lipid was converted to methyl ester biodiesel over chromium-aluminum mixed oxide catalyst, prepared with a precipitation method, in the presence of methanol in 4.0 h at 80 °C.

The use of ethanol instead of methanol in the production of biodiesel seems to be a better alternative because ethanol is produced from biological sources and also, improves cold temperature issues, such as cloud point, of the biodiesel [17]. There are few studies on the use of ethanol and vegetable oils over homogeneous and heterogeneous catalysts in the production of ethyl esters biodiesel [18–20]. However, to the best of our knowledge, there are no studies on the production of ethyl esters biodiesel from microalgal lipids and ethanol over heterogeneous catalysts at 50 °C and 1.0 atm in the literature.

In this study, ethyl esters biodiesel production from *Spirulina sp.* (preferred due to commercial availability in large quantities, [4]) and *Nannochloropsis oculata* (*N.oculata*) marine microalgae (preferred due to its high fatty acid content, [4–6]) over an alumina-calcium oxide catalyst was studied as a function of ethanol:lipid molar ratios, the amount of the catalyst and the reaction time at 50 °C and 1.0 atm.

2. Material and methods

2.1. Catalyst preparation

Alumina-calcium oxide catalyst, 60 wt% CaO on Al_2O_3, was synthesized using a modified single step sol–gel method [12,21,22]. The single step sol-gel preparation method and the drying procedure were the same as the procedures given by Yalman [22] but the calcination temperature and the calcination time used in this study was 700 °C and 6.0 h, respectively. Finally, the calcined catalyst was ground and sieved to less than 325 mesh sizes prior to be used in the activity measurements.

2.2. Algal lipid extraction and ethyl ester biodiesel production

Freeze dried *Spirulina sp.* marine microalgae powder, grown organically and free of additives and irradiation, was purchased from Optimally Organic Inc. Also, *N. oculata* marine microalgal paste, grown in a growth medium and harvested with the method given in the literature [23], was obtained from Prof. Dr. Durmaz of Ege University. The paste was dried at 60 °C under vacuum of 100 mbar for 12 h. Then, microalgal lipids from dried *Spirulina sp.* and *N. oculata* marine microalgae powders were extracted with hexane in a Soxhlet extractor operated at 80 °C for 10–24 h using a similar procedure given by Miao and Wu [9]. The extraction procedure used in this study was the partial extraction because hexane was non-polar solvent; thus, eliminating the extraction of non-lipid and polar-lipid compounds [24–26]. After the extraction, the excess hexane was evaporated using a rotary evaporator at 50 °C and 100 mbar to obtain the microalgal lipid.

2.3. Catalyst activity and characterization

In our recent study [22], similar 60 wt% CaO on Al_2O_3 catalyst whose the calcination temperature was different was used in the transesterification of canola oil with ethanol and we found that ~100% ethyl ester biodiesel yield was obtained in less than 1.0 h under the reaction condition of 9:1 ethanol:canola oil molar ratio and 6.0 wt% of the oil as the catalyst amount at 50 °C. Therefore, 60 wt% CaO on Al_2O_3 catalyst calcined at 700 °C was used in the production of the ethyl esters biodiesel from *Spirulina sp.* and *N. oculata* microalgal lipids and ethanol in a batch reactor at 50 °C and 1.0 atm under the following reaction conditions: 12:1.0, 24:1.0 and 48:1.0 of ethanol:lipid molar ratios; 6.0 wt%, 12 wt% and 18 wt% of the lipid as the catalyst amounts; and 30 min, 60 min and 120 min of the reaction times.

All the reaction conditions in the production of ethyl esters biodiesel from microalgal lipids over the catalyst resulted in a single liquid phase formation since ethanol:oil molar ratios were in excess of the stoichiometric molar ratio. In our previous studies [21, 22], we developed a procedure in our lab to separate the single liquid phase into biodiesel and glycerol rich phases (details are given in Supplementary Materials). This separation procedure resulted in the biodiesel rich phase, containing biodiesel amount greater than 98 wt% as determined by GC analyses (a GC chromatogram is also given in Supplementary Material). The analyses were done using Agilent 6890 N Ga Chromatograph equipped with a FID detector and a DB-WAX 122–7032 column with a 60 m of column length, 0.25 mm of column diameter and 0.25 μm of film thickness. The separation in the column was achieved using an isothermal analysis method: The column was at 225 °C and for injection port and detector, 250 °C was used. Helium flow and split ratio were set at 32 cm/s and 150, respectively. Biodiesel yield was calculated using the following equation:

$$\text{Biodiesel yield (wt\%)} = \frac{\text{amount of ethyl ester biodiesel (g) in upper phase}}{\text{initial amount of microalgal lipid (g)}} \times 100$$

Crystalline phases present in the catalysts were determined by X-ray diffraction technique (Philips X'pert Pro XRD, operated at 40 kV and 45 mA) and also average crystallite sizes were calculated from the peak broadening of the diffraction peaks using Scherrer equation given below.

$$d = \frac{K\,\lambda}{(B\,Cos\theta)}$$

where d was the average crystallite size, K was Scherrer constant (~0.9), λ was the wavelength of the X-ray (λ = 0.15406 nm), B was the peak broadening of a diffraction peak found using the full width at half maximum (given in radian) of the peak and θ was the main diffraction angle of the peak given in degree [27].

The basicity and basic strength of all the catalysts were determined using FTIR with carbon dioxide as the probe molecule. The amount of irreversibly adsorbed CO_2 gave the total amount of basic sites on solid surfaces and also, its absorption band wavenumber was the strength of the basic site [28].

3. Results and discussion

3.1. Crystalline phases and basicities of the catalysts

As seen in Fig. 1, the analysis of XRD pattern of 60 wt% CaO/Al_2O_3 catalyst using standard diffraction reference patterns on X'Pert HighScore Plus software (PANalytic B.V.) showed that the