Eco-friendly Biodiesel Production from Waste Olive Oil by Transesterification using Nano-tube TiO_2

Nader Ghaffari Khaligh, Sharifah Bee Abd Hamid, and Taraneh Mihankhah

***Abstract*—** It has become necessary to find alternative clean and renewable energy sources due to the limited oil and natural gas reservoirs, the rise in greenhouse gas emissions and environmental pollution. Biodiesel is known as a nontoxic, renewable and environmental friendly biodegradable fuel that is free from sulfur and aromatic compounds. Also the combustion performance properties of biodiesel have been considered to be better than conventional fossil fuel. Due to a higher flashpoint; storage, transportation, and handling of these fuels are simpler than diesel fuel. Biodiesel is considered as a renewable, sustainable and environmental friendly fuel that is mainly produced by transesterification reaction between vegetable oil and methanol. Herein nano-tube TiO_2 is considered as suitable heterogeneous catalyst for eco-friendly biodiesel production from waste olive oil at 120 ºC. This method has the advantages of high yield, clean reaction, and simple methodology. The catalyst can be recycled without significant loss of activity.

***Keywords*—**Biodiesel, Nano-tube TiO_2, Recyclable catalyst

I. Introduction

BIODIESEL is normally produced as fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE) by the transesterification of triglycerides (present in vegetable oil, algal oil or animal fat) and methanol or ethanol, respectively [1,2]. Due to the high viscosity and low volatility of pure vegetable oil the fuel lines and fuel injectors would clog and the piston heads would experience increased fouling [3]. Blending of oil with petroleum diesel, pyrolysis (Thermal Cracking), emulsification and transesterification have been found as the different procedures to reduce the viscosity of triglycerides [4].

Nano-tube TiO_2 have attracted extensive research because of its novel properties such as chemical stability, large surface area, non-toxicity, and low production cost [5]. It have been found a large number of diverse applications that include solar dyesensitized solar cells [6], photocatalysts [7], orthopedic and bioimplant applications [8], solid-phase extraction adsorbents [9], solar energy applications [10], and photo-electrochemical cells for the solar generation of hydrogen [11].

For the transesterification reaction, heterogeneous catalysis offers three main advantages over homogeneous catalysis: (1) the catalyst can be recycled, (2) the separation and purification of the biodiesel and glycerol products is easier due to the absence of salts and diminished soaps formation, and (3) significant reduction in the water required to wash the product phases [12].

In pursuit of our recent studies to develop environmentally friendly synthetic methodologies [13], herein, we report the application of nano tube TiO_2 as a reusable catalyst in the promotion of the biodiesel production from olive oil.

II. Experimental

The transesterification reactions were carried out in a 250 mL stainless steel high pressure Parr reactor. Each reaction was performed with a 4:1 volume ratio (30:1 molar ratio) of methanol to oil and a catalyst concentration of 4.4 wt% of oil. The feedstock for the transesterification reaction was waste cooking or frying olive oil. The anhydrous methanol purchased from Sigma-Aldrich (99.8% purity) and was used without further processing. Nano tube TiO_2 with defined shape and size was easily synthesized by a literature reported method [14].

Nano tube TiO_2 (200 mg), waste cooking or frying olive oil (5 mL) and methanol (20 mL) were placed in the stainless steel reactor. The reactor was then pressurized to 5 bar with argon gas to create an inert atmosphere. The resulting mixture was continuously stirred at 120 °C for 4 h. When the reaction was completed, the reactor was cooled using an ice bath.

The reactor effluent was centrifuged for 5 min at 4,000 rpm in an Eppendorf centrifuge. The supernatant was collected and placed in an oven to remove the excess methanol. After the excess methanol evaporates two phases remain: the top phase is rich in biodiesel while the denser bottom layer is rich in glycerol. Nano tube TiO_2 catalyst was washed with acetone and dried in the oven overnight. The catalyst was characterized using the same methods and equipment used to characterize the fresh nano tube TiO_2.

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III. Results and Discussion

In a typical reaction nano tube TiO_2, waste cooking or frying olive oil, and methanol were placed in the stainless steel reactor and an inert atmosphere. The resulting mixture was then continuously stirred and heated to 100, 120 or 150 °C. The reaction time ranged between 1-4 h and was begun as soon as the thermocouple registered the desired reaction temperature. The highest conversion, 91.2 %, was obtained at 120 ºC and 4 h of reaction time. This demonstrates that nano tube TiO_2 can serve as an effective catalyst for biodiesel synthesis.

The biodiesel conversion was quantified using ^{1}H NMR. Samples from biodiesel, placed in $CDCl_3$ (Sigma-Aldrich 99.8 atom % D) and then analyzed in a Bruker Avance 400 MHz. Composition of FAME mixture was estimated using an Agilent GC-Mass-6890 instrument.

The ^{1}H NMR provides a spectrum of chemical shifts belonging to the protons present in the sample. Two peaks were used to quantify the reaction progress, the peak belonging to the α-methylene protons adjacent to carbonyl group (-C$\underline{H_2}$-COOCH$_3$) in triglycerides and the methoxy group (-COOC$\underline{H_3}$) in FAMEs at 2.30 and 3.66 ppm, respectively [15]. The conversion can be calculated by determining the area of the peaks generated by these protons.

Initially the reaction takes place slowly with low conversions due to the strong mass transfer limitations [16]. When the reaction time reached approximately 2.0 hours, the reaction rate and conversion incremented quickly [17].

The four FAMEs were identified in the biodiesel from waste olive oil and methyl oleate is the major FAME (68.46 wt.%) followed by methyl linoleate (15.71 wt.%) and methyl palmitate (13.96 wt.%). Methyl stearate is present as minor constituent (1.77 wt.%).

The reusability of the nano tube TiO_2 was exemplified by production of biodiesel from waste olive oil in presence of recycled catalyst. Biodiesel was obtained in 90% and 88% conversion after three runs within 4 h (monitored by GC-MS) which clearly demonstrates the practical recyclability of this catalyst.

IV. Conclusion

The production of biodiesel was described in presence of nano tube TiO_2. The effect of temperature and reaction time was studied on the conversion. In spite of the mass transfer limitations between the two liquid phases and solid catalyst, it was possible to achieve a conversion of 91.2 % within 4 h at 120 ºC. It was confirmed that higher conversion was achieved with increasing temperature and longer reaction time.

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