Nano-MgO catalyzed production of biodiesel from Non-edible Colza oil

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Abstract: Biodiesel is a fuel consisting of long chain fatty acid alkyl esters made from renewable vegetable oils such as colza, used cooking oils, alga or animal fats. Biodiesel is a well known alternative, renewable fuel which provides less emission when compared with the conventional fossil-based diesel fuel. In this study, biodiesel was produced from non-edible Colza oil and methanol, using MgO nanoparticles as catalyst. Nono-MgO powder was santhesized and analyzed with X-Ray diffraction prior to use as catalyst. Average crystalline size of MgO was 16 nm. Optimum conditions for these reactions were 3.3 % MgO as catalyst, MeOH/oil of molar ratio 15:1 and reaction temperature 62 °C, for a period of 3 h. The yield of methyl ester was 85% in 1.5 h and 91% in 3 h.

Keywords: *Biodiesel, Colza oil, Transesterification, MgO, Nano-catalyst*

Nomenclature

B10 .... Mixed fuel containing 10 % Biodiesel
B20 .... Mixed fuel containing 20 % Biodiesel
B100 ... Mixed fuel containing 100 % Biodiesel
FAMEs ………………Fatty Acid Methyl Esters
XRD …………………………….X-Ray Diffraction

1. Introduction

The synthesis of biodiesel (fatty acid methyl esters, FAMEs) from various sources including animal fats and plant-based oils has attracted considerable attention [1, 2]. The main reaction in biodiesel production is transesterification of fatty acids that leads to fatty acids methyl esters. The transesterification reaction requires an alcohol as a reactant (almost methanol) and a catalyst (acid, base or nano-catalyst) [3, 4, 5].
Biodiesel has the potential to replace a fraction of the petroleum diesel because it can be mixed with petroleum diesel fuel in various ratios and can be used in any impression ignition engine without the need for motor modification [6]. Producing and using biofuels for transportation offers alternatives to fossil fuels that can help provide solutions to many environmental problems. Using biofuels in motor vehicles helps reduce greenhouse gases emissions. Full cycle analysis indicates that, on average, biofuels emit less CO_2 than conventional fuels [7]. Scientists believe CO_2 is one of the main greenhouse gases contributing to global warming. Neat biodiesel (100 % biodiesel) reduces CO_2 emissions by more than 75 % over petroleum diesel. Using a blend of 20 % biodiesel reduces CO_2 emissions by 15 % [8]. Due to the low or zero content of pollutants such as sulfur in biofuels, the pollutant (SO_2, etc.) emission of biofuels is much lower than the emission of conventional fuels. Using biodiesel in a conventional diesel engine substantially reduces emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter. These reductions increase as the amount of biodiesel blended into diesel fuel increases. The best emissions reductions are seen with B100 [2, 6].
The use of biodiesel decreases the solid carbon fraction of particulate matter (since the oxygen in biodiesel enables more complete combustion to CO_2) and reduces the sulfate fraction (biodiesel contains less than 24 ppm sulfur). Emissions of nitrogen oxides (NOx) increase with the concentration of biodiesel in the fuel. Some biodiesel produces more NOx than others, and some additives have shown promise in modifying the increases [7].

In addition, a number of other technical advantages of biodiesel fuel are: it prolongs engine life and reduces the need for maintenance (biodiesel has better lubricating qualities than fossil diesel), it is safer to handle, being less toxic, biodiesel is an efficient, clean, 100 % natural energy alternative to petroleum fuels and biodiesel is better than diesel fuel in terms of sulfur content, flash point, considerable reduction in carbon monoxide (CO), smoke, particulate matter, polyaromatic hydrocarbons content and high biodegradability [9].
Currently, the most common way to produce biodiesel is by liquid-phase reaction involving a homogenous basic metal Oxide, Hydroxide or Methoxide such as Magnesium Oxide (MgO) catalyst. Solid base catalysts have many advantages, such as simple preparation, mild reaction conditions, high activity, fine selectivity, easy separation, less contamination and so on. A solid base catalyst in nanoscale (nano-solid-base-catalyst) is more excellent in catalytic reaction. The tremendous surface area on nano materials increases the reaction area and the active center extraordinarily, and leads to catalytic reactions, which is a highly efficient and timesaving process [10].
Some studies have been conducted via non-catalytic transesterification with supercritical methanol [11, 12, 13]. As a result, the reaction was found to be completed in a very short time. Compared with the catalytic processes under normal pressure, purification of products is much simpler and more environmentally friendly. However, the reaction requires temperatures of 350 – 400 °C and pressures of 43 – 65 MPa, which are not available in practice in industry. Furthermore, such high temperatures and pressures lead to high production costs and energy consumptions. However, present study focused on biodiesel production from colza oil in atmospheric pressure and room temperature.
Non-edible colza oil is an economical feedstock for the production of biodiesel in Iran. In general, it contains large amounts of free fatty acids and the production process using this feedstock is usually less complicated than that using other oils such as used cooking oils.

2. Methodology

In this study, at first, nano-MgO catalyst prepared and characterized with XRD (X-Ray Diffraction) instrument. The XRD powder diffraction was carried out by Philips – pw 3710 instrument using Cu Kα radiation at 50 kv and 250 mA. Then the transesterification reaction was done and effects of methanol/oil ratio, catalyst ratio and temperature, on the biodiesel conversion from (non-edible) colza oil are investigated.
Figure 1 shows the reaction between triglycerides and alcohol in the presence of catalyst to produce mono-esters that are termed as biodiesel. This figure depicts the transesterification reaction.

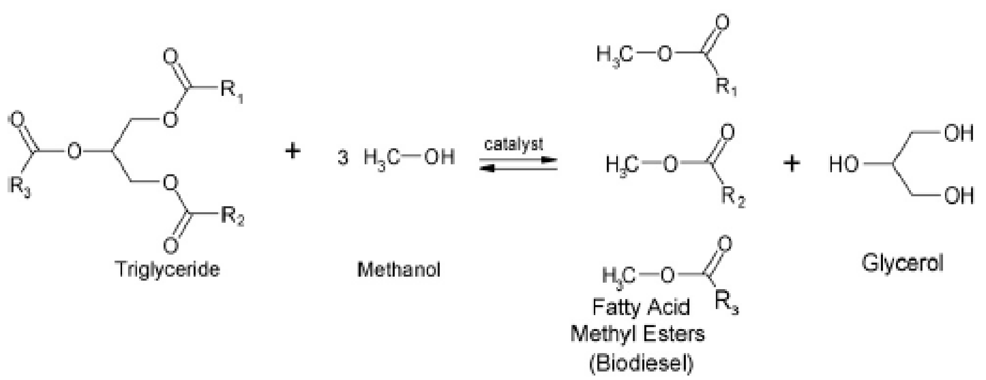

Fig. 1. Transesterification reaction.

An ideal transesterification reaction differs on the basis of variables such as fatty acid composition and the free fatty acid content of the oil. Other variables include the type of catalyst, alcohol, water content in oil and the rate of stirring [4, 14]. Sharma and Singh [15] emphasized that mode of stirring is equally important, where better yield was obtained with mechanical stirring than with magnetic stirring.
Raw materials contribute to a major portion in the cost of biodiesel production. The choice of raw materials depends mainly on its availability and cost. Firstly, the colza oil was boiled at temperatures between 100-120 °C for a period of 20 min to eliminate the water and other waste materials. Prepared biodiesel samples were analyzed by an Agilent 6890N GC-Mass instrument.

3. Results and Discussion

For synthesis of nano-size MgO, Magnesium Nitrate [$Mg(NO_3)_2.6H_2O$] and Oxalic Acid [$(COOH)_2.2H_2O$] were used in a 1:1 molar ratios. These materials were dissolved separately in ethyl alcohol and stirred to obtain two clear solutions. These two solutions were then mixed together to yield a thick white gel. The gel product was digested for 12 hour and dried subsequently at 120 °C for 2 hour, ground, sieved through 200 mesh. Finally, produced powder was calcined at 550 °C for 4 hour, and cooled slowly (2 °C/min) to room temperature. Synthesized nono-MgO was analyzed with XRD prior to use as catalyst.
The XRD peaks showed formation of periklase MgO nanopowders. The crystallite size estimated by Sherer`s method resulted in average crystalline size of about 16 nm.

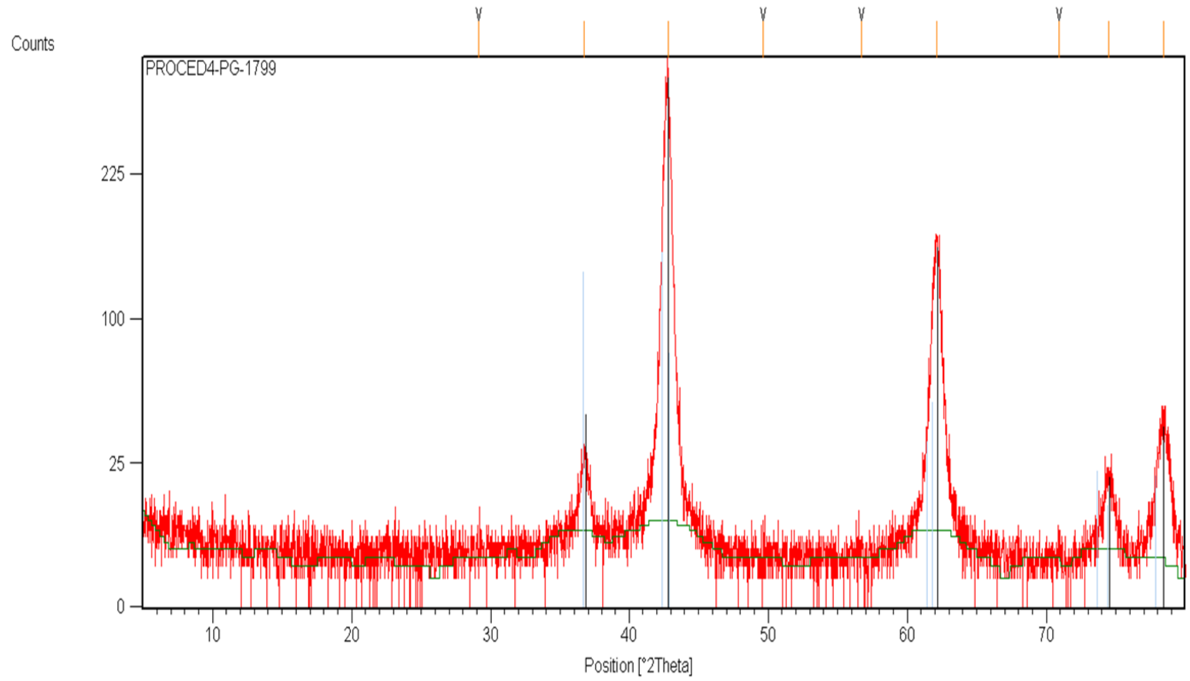

Fig. 2. XRD pattern of MgO nanopowder.

The transesterification reaction conditions were optimized during the experiments. The best result was obtained under the following experimental conditions: oil/ methanol molar ratio of 1:15; temperature of 62 ˚C and catalyst percentage of 3.3 % (W/W) to the oil.

Non-edible Colza is for production of biodiesel and also lower the cost of biodiesel. It consists of 90 - 95 W % of FFA (Oleic, Linoleic, Palmitic) and the rest are sitosterol and traces impurities. The catalytic transesterification of free fatty acids and water always produce negative effects, since the presence of free fatty acids and water causes soap formation, consumes catalyst, and reduces catalyst effectiveness.

4. Conclusions

In this study, at first, nano-size MgO with an average crystalline size of about 16 nm, was prepared and characterized with XRD instrument. For synthesis of nano-size MgO, Magnesium Nitrate and Oxalic Acid were used. Fatty Acid Methyl Esters (biodiesel) was produced from transesterification of non-edible Colza oil with methanol, using synthesized MgO nanoparticles as catalyst. Then the reaction conditions were optimized. The yield of 91% could be achieved when the reaction was carried out at a catalyst content of 3.3%, with a molar ratio of methanol to oil of 15:1, a reaction temperature of 62 °C, and a reaction time of 3h.

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