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Heterogeneous Catalyzed Synthesis of Biodiesel from Crude Sunflower Oil

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Abstract

Biodiesel is the fatty acid alkyl esters that are used as the substitute for petro-diesel. The aim of the present work is to optimize biodiesel production from plant based non-edible crude oils with methanol using heterogeneous catalyst by transesterification for its commercialization. The factors affecting the biodiesel production from plant oils are volume of feedstock (oil), volume of alcohol (excess reactant), quantity of calcium hydroxide (catalyst), reaction time, temperature, and agitation speed. Transesterification is the reaction between acid and alcohol to produce ester in the presence of alkali catalyst. In this work, transesterification was carried out between crude sunflower oil and methanol in the presence of calcium hydroxide as catalyst. Finally, the maximum conversion of 85.6% was achieved at the optimum process parameters of 2 L of crude sunflower oil, 0.3 L methanol, 23 g of calcium hydroxide, reaction time of 24 h, temperature of 65 °C, and agitation speed of 100 rpm. The results showed that crude sunflower oil could serve as potential renewable substrate for biodiesel commercialization.

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Keywords: Crude sunflower oil, Calcium hydroxide, Transesterification, Biodiesel

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1. Introduction

Biodiesel is an alternative fuel for clean combustion from domestic and renewable resources. The fuel is a mixture of alkyl esters of fatty acids made from pure edible vegetable oils, pure non-edible vegetable oils, waste vegetable oils, crude vegetable oils, algal oils, animal fats or recycled fats [1]. Biodiesel can be used in its pure form with little or no modification in existing diesel engines, wherever applicable.

Biodiesel is easy to use, biodegradable, non-toxic and essentially free of Sulphur and aromatics. It is generally used as a petro-diesel additive to reduce particulate, carbon monoxide, hydrocarbon and pollutant concentrations in diesel vehicles [2]. When used as an additive, the resulting diesel fuel may be referred to as B5, B10 or B20. This is the percentage of biodiesel that is mixed with petro-diesel. For example, B5 means that biodiesel and petro-diesel are mixed in the ratio of 5:95 [3].

Biodiesel is produced by the process in which oils are combined with alcohol (ethanol or methanol) in the presence of a catalyst (alkali or heterogeneous) to form ethyl or methyl esters. Ethyl or methyl esters of biomass can be mixed with conventional diesel fuel or used as a pure fuel (100% biodiesel) [4]. Biodiesel can be made from vegetable oil, animal fat, or microalgae oil. The three basic ways of producing biodiesel

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from oils and fats are as follows [5]:

1. Direct transesterification of oils or fats catalyzed by alkali or heterogeneous catalyst (If free fatty acid (FFA) < 2.5%)
2. Esterification of oils or fats by acid catalysis and then by transesterification (If FFA > 2.5%)
3. Conversion of oils and fats to its fatty acids and then to biodiesel

The most common feedstock of edible oils used to produce biodiesel are soybean oil [6], rapeseed oil [7] and palm oil [8], which accounts for the bulk production of global biodiesel. Other raw materials may come from non-edible sources such as Jatropha [9], mustard [10], flax [11], and hemp [12]. Animal fats, including sebum [13], lard [14], yellow fat [15], chicken fat [16] and fish oil [17] derivatives, may contribute to a small percentage of biodiesel production in the future, but their supply is limited and inefficient to raise animals for their fat.

Biodiesel can be mixed with petro-diesel in any proportion to produce a biodiesel blend, or it can be used in a pure form. Like petro-diesel, biodiesel works with the diesel engine with auto-ignition and essentially requires little or no engine modification, as biodiesel has similar properties to diesel [18]. It can be stored as a petro-diesel and therefore does not require a separate infrastructure. The use of biodiesel in conventional diesel engines results in a significant reduction in the emission of unburnt hydrocarbons, carbon monoxide and particulates. Currently, a large number of biodiesel production plants around the world are functioning to full capacity, and a large number are under construction or designed to meet growing global demand [19].

Literature studies show that abundant scientific reports are available on production of biodiesel from pure edible vegetable oils [6-8], pure non-edible vegetable oils [9-12], waste vegetable oils [20-22], algal oils [23-25], and animal fats [13-17]. But, only limited literature is available on biodiesel production from crude vegetable oils [26-27], and recycled fats [28-29]. Hence, the present work focuses on the optimization of process parameters for production of biodiesel from plant based non-edible crude oils with methanol using heterogeneous catalyst by transesterification for its commercialization.

2. Materials and Methods

2.1. Materials

Crude sunflower oil was generously provided by Omani Vegetable Oils & Derivatives Company (LLC), Raysut, Oman. All the chemicals used in the work are of analytical grade and the products of VWR International. Double distilled water was used in this study.

2.2. Methods

A known volume of crude sunflower oil (2 L) was mixed with known volume of methanol and known quantity of calcium hydroxide and mixed well for certain time and temperature with mixing. After the time is completed, the mixture was allowed to settle for 8 h and the bottom glycerol layer was removed and acidulated with phosphoric acid to separate glycerol, sodium phosphate and methanol. Sodium phosphate is reacted with water to produce phosphoric acid and recycled back. From the top layer, the mixture of biodiesel and water with little quantity of methanol was washed to remove excess methanol present, and dried to remove moisture from biodiesel. Finally, FFA of oil and biodiesel were measured and the percentage conversion was calculated using the equation as given below:

$$\% \; conversion = \frac{(FFA \; in \; oil - FFA \; in \; biodiesel)}{FFA \; in \; oil} x100$$

FFA was estimated following the procedure as follows [30]: Standard solvent was prepared by mixing 25 mL diethyl ether and 25 mL 95% ethanol, and titrated against 0.1 N KOH using 1 mL of 1% phenolphthalein solution as an indicator. 5 g of oil was dissolved in 50 mL of standard solvent in a 250 mL Erlenmeyer flask. The contents are titrated against 0.1 N KOH using few drops of phenolphthalein as an indicator. The end point is the appearance of pink color that lasts for 15 s. Then, FFA was calculated using the equation as below:

$$Free \; fatty \; acid \; value \; (mg \; KOH/g \; oil) = \frac{Titre \; value \; x \; Normality \; of \; KOH \; x \; 28.05}{Mass \; of \; oil \; in \; g}$$

The effect of methanol (0.1-0.5 L) was studied by fixing volume of oil, mass of calcium hydroxide, time, temperature and agitation speed at 2 L, 23 g, 24 h, 65 °C and 100 rpm respectively. The effect of catalyst (13.8-32.2 g) was studied by fixing volume of oil, volume of methanol, time, temperature and agitation speed at 2 L, 0.3 L, 24 h, 65 °C and 100 rpm respectively. The effect of time (16-32 h) was studied by fixing volume of oil, volume of methanol, mass of calcium hydroxide, temperature and agitation speed at 2 L, 0.3 L, 23 g, 65 °C and 100 rpm respectively. The effect of temperature (55-75 °C) was studied by fixing volume of oil, volume of methanol, mass of calcium hydroxide, time and agitation speed at 2 L, 0.3 L, 23 g, 24 h and 100 rpm respectively. The effect of agitation speed (50-150 rpm) was studied by fixing volume of oil, volume of methanol, mass of calcium hydroxide, time and temperature at 2 L, 0.3 L, 23 g, 24 h and 65 °C respectively.

3. Results and Discussion

Figure 1(a) shows the effect of volume of methanol on percentage conversion at constant values of volume of oil of 2 L, mass of calcium hydroxide of 23 g, reaction time of 24 h, temperature of 65 °C and agitation speed of 100 rpm. Volume of methanol varied from 0.1 to 0.5 L. Volume of methanol was selected based on the molar ratio of oil to methanol. From the literature, molecular weight of oil is 292 g/mol. In transesterification reaction, oil is the limiting reactant and methanol is the excess reactant.

According to the reaction stoichiometry, 1 mole of oil reacts with 3 moles of methanol to produce biodiesel and glycerol. But, in practice, moles of methanol required to produce

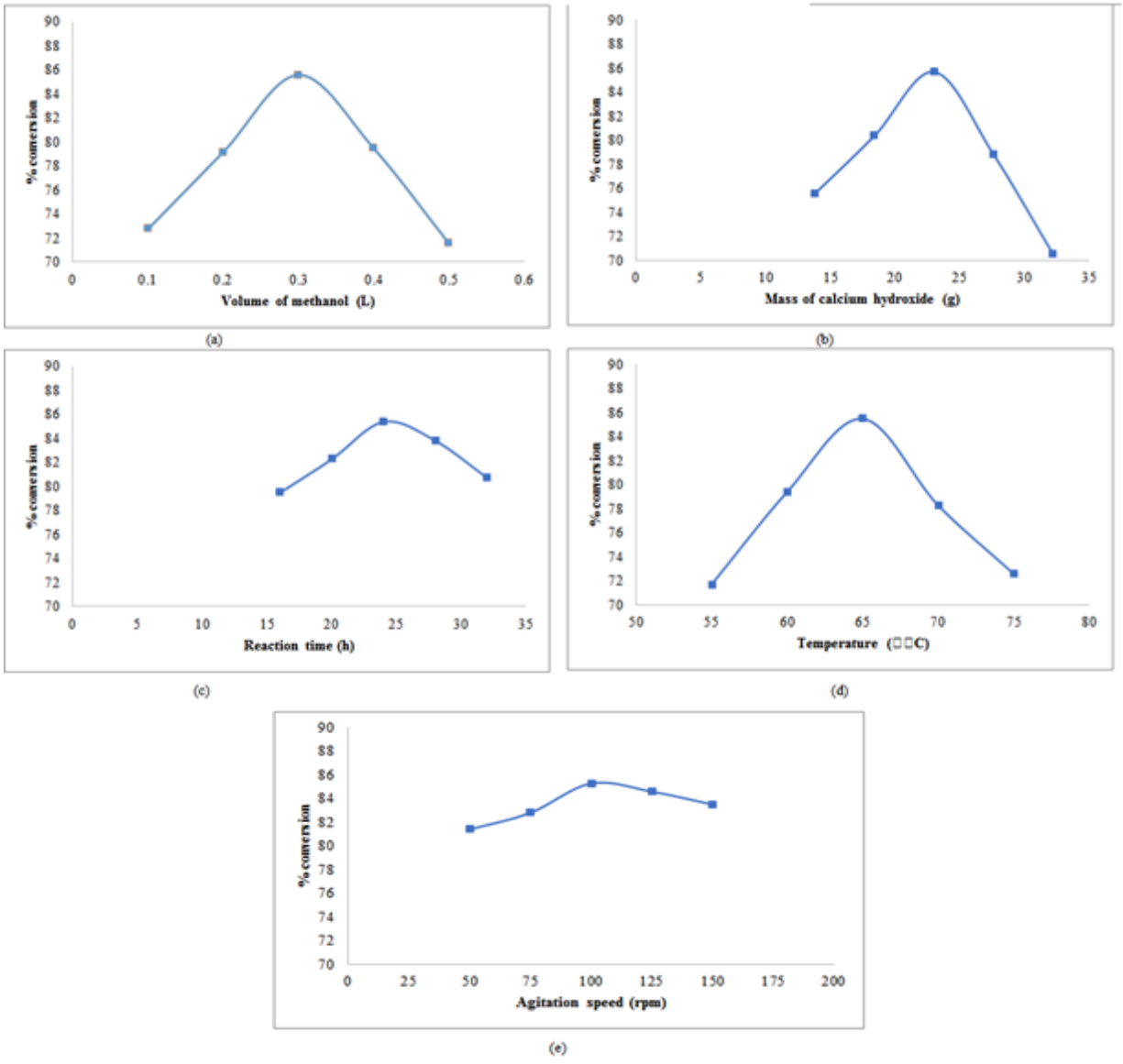

Figure 1. Effect of (a) volume of methanol (b) mass of calcium hydroxide (c) reaction time (d) temperature and (e) agitation speed on percentage conversion

biodiesel is more than the stoichiometric requirement. Percentage conversion initially increased with increase in volume of methanol. After 0.3 L of methanol, conversion decreased. This is due to the fact that high content of methanol reduces the quality of biodiesel and hence, decrease in conversion was observed [31].

Figure 1(b) shows the effect of mass of calcium hydroxide on percentage conversion at constant values of volume of oil of 2 L, volume of methanol of 0.3 L, reaction time of 24 h, temperature of 65 °C and agitation speed of 100 rpm. Mass of calcium hydroxide varied from 13.8 to 32.2 g. Mass of calcium hydroxide was selected based on the mass ratio of catalyst to oil. In transesterification reaction, oil is the limiting reactant and methanol is the excess reactant and alkali or heterogeneous materials as catalyst. According to the standard operating procedure, mass ratio between catalyst and oil should be between 0.5 and 2% (w/w). Percentage conversion initially increased with increase in mass of calcium hydroxide. After 23 g of calcium hydroxide, conversion decreased. This is due to the fact that catalytic poisoning occurs at higher concentration of catalyst [32].

Figure 1(c) shows the effect of reaction time on percentage conversion at constant values of volume of oil of 2 L, volume of methanol of 0.3 L, mass of calcium hydroxide of 23 g, temperature of 65 °C and agitation speed of 100 rpm. Reaction time varied from 16 to 32 h. Reaction time was selected based on the literature. In transesterification, reaction should be carried out between oil, methanol and catalyst for certain period of time. Percentage conversion initially increased with increase in time. After 24 h, conversion decreased [33].

Figure 1(d) shows the effect of temperature on percentage conversion at constant values of volume of oil of 2 L, volume of methanol of 0.3 L, mass of calcium hydroxide of 23 g, time of 24 h, and agitation speed of 100 rpm. Reaction temperature var-

ied from 55 to 75 °C. Reaction temperature was selected based on the boiling point of alcohol. In transesterification, reaction should be carried out between oil, methanol and catalyst at certain temperature. Percentage conversion initially increased with increase in temperature. After 65 °C, conversion decreased. This is due to the fact that above 65 °C, loss of methanol is more which leads to the decrease in conversion [34].

Figure 1(e) shows the effect of agitation speed on percentage conversion at constant values of volume of oil of 2 L, volume of methanol of 0.3 L, mass of calcium hydroxide of 23 g, time of 24 h, and temperature of 65 °C. Agitation speed varied from 50 to 150 rpm. The effect of agitation speed on percentage conversion is not significant [35].

4. Conclusion

The aim of the present work was to optimize biodiesel production from plant based non-edible crude oils with methanol using heterogeneous catalyst by transesterification for its commercialization. Finally, the maximum conversion of 85.6% was achieved at the optimum process parameters of 2 L of crude sunflower oil, 0.3 L methanol, 23 g of calcium hydroxide, reaction time of 24 h, temperature of 65 °C, and agitation speed of 100 rpm. The results showed that crude sunflower oil could serve as potential renewable substrate for biodiesel commercialization.

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