

Optimizing of Biodiesel Production: A Review

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Abstract: *The world is confronted with the clone crises of fossil fuel depletion and ecological deprivation. The random extraction and utilization of fossil fuels have led to a drop in petroleum reserves. Petroleum based fuels are obtained from restricted reserves. These limited reserves are highly concentrated in definite region of the world. Biodiesel, which is considered to be a potential alternate of straight diesel, is biodegradable, non-toxic, and renewable. The production of biodiesel from edible and non-edible oil can be optimized by using various parameters such as catalyst concentration, amount of methanol required for reaction, reaction time and reaction temperature.*

Keywords: methanol, transesterification, catalyst, reaction time

1. Introduction

The increased use of diesel fuel resulted in depletion of its fossil reserves. This triggers for many initiatives to search for alternate fuel, which can supplement or replace such fossil fuel. In recent years, research has been directed to explore plant-based fuels and plant oils and fats as fuels have bright future [1]. Biodiesel, which is considered to be a potential alternate of straight diesel, is biodegradable, non-toxic, renewable, and has reduced emissions of CO, SO₂, particulates, and hydrocarbons as compared to conventional diesel [2]. The environmental, operational and economic benefits associated with the utilization of biodiesel as an alternative fuel for diesel engines have been demonstrated by numerous independent studies and have been well accepted [3–9].

The most common way to produce biodiesel is transesterification. In this reaction, triglycerides, as the main components of vegetable oils, react with an alcohol to produce fatty acid mono-alkyl esters and glycerol as a by-product. Methanol is the most commonly used alcohol because of its low price compared to other alcohols. In this case, the reaction is referred to as methanolysis. Generally, this reaction is catalyzed by a basic or an acid catalyst. The alkali catalysts are the most commonly used, because they make the process faster and the reaction conditions are more moderated. The stoichiometry of methanolysis reaction requires 3 mol of methanol and 1 mol of triglyceride to give 3 mol of fatty acid methyl ester (FAME) and 1 mol of glycerol. This is the general transesterification reaction, because it consists of a number of consecutive reversible reactions. The first step is the conversion of triglycerides to diglycerides, which is followed by the conversion of diglycerides to monoglycerides and of monoglycerides to glycerol, yielding one methyl ester molecule from each glyceride at each step [10,11].

Like other vegetable oils, castor oil is constituted mainly by triglycerides which consist of three fatty acids and one molecule of glycerol. The fatty acids of this oil consist of approximately 80–90% ricinoleic, 3–6% linoleic, 2–4% oleic, and 1–5% saturated fatty acids. Castor oil is a viscous,

pale yellow nonvolatile and non-dry oil. Due to this particular chemical composition castor oil is a raw material in great demand by the pharmaceutical and chemical industry. Its use as fuel for internal combustion engines, however, can become complicated because of its extremely high viscosity and high water content. Thus a better method to use castor oil in engines as fuel is its transesterification [12].

2. Materials and Methods

All the oils were first filtered by cloth mainly to remove the dirt and other inert materials from the oil and then placed in a conical flask equipped with magnetic stirrer, thermometer and condenser. Under agitation the raw oil was heated up to nearer to the boiling point to remove the water contaminant present in the oil. After that oil is allowed to cool down under room temperature, and the treated oil alone was taken for biodiesel production purpose. Again, under agitation, the above treated oil was heated up to a desired temperature on a hot plate. A fixed amount of freshly prepared sodium hydroxide–methanol solution was added into the oils, taking this moment as the starting time of the reaction. When the reaction reached the preset reaction time, heating and stirring were stopped. The products of reaction were allowed to settle overnight. During settling two distinct liquid phases were formed: crude ester phase at the top and glycerol phase at the bottom. The crude ester phase separated from the bottom glycerol phase was then washed by cold or warm de-ionized water several times until the washed water became clear. The excess methanol and water in ester phase were then removed by evaporation under atmospheric condition.

3. Biodiesel production

K. Noiroj et al [13] was done the transesterification of palm oil to methyl esters (biodiesel) was studied using KOH loaded on Al₂O₃ and NaY zeolite supports as heterogeneous catalysts. Reaction parameters such as reaction time, wt% KOH loading, molar ratio of oil to methanol, and amount of catalyst were optimized for the production of biodiesel. The 25 wt% KOH/Al₂O₃ and 10 wt% KOH/NaY catalysts are suggested here to be the best formula due to their biodiesel

yield of 91.07% at temperatures below 70°C within 2–3 h at a 1:15 molar ratio of palm oil to methanol and a catalyst amount of 3–6 wt%. The leaching of potassium species in both spent catalysts was observed. The amount of leached potassium species of the KOH/Al₂O₃ was somewhat higher compared to that of the KOH/NaY catalyst. The prepared catalysts were characterized by using several techniques such as XRD, BET, TPD, and XRF.

T. Eevera et al [14] studied, both edible (coconut oil, palm oil, groundnut oil, and rice bran oil) and non-edible oils (pongamia, neem and cotton seed oil) were used to optimize the biodiesel production process variables like catalyst concentration, amount of methanol required for reaction, reaction time and reaction temperature. The fuel properties like specific gravity, moisture content, refractive index, acid value, iodine number, saponification value and peroxide value were estimated. Based on the cetane number and iodine value, the methyl esters obtained from palm and coconut oils were not suitable to use as biodiesel in cold weather conditions, but for hot climate condition biodiesel obtained from the remaining oil sources is suitable.

N.U. Soriano et al. [15] used Lewis acids (AlCl₃ or ZnCl₂) were used to catalyze the transesterification of canola oil with methanol in the presence of tetrahydrofuran (THF) as co-solvent. The conversion of canola oil into fatty acid methyl esters was monitored by ¹H NMR. NMR analysis demonstrated that AlCl₃ catalyzes both the esterification of long chain fatty acid and the transesterification of vegetable oil with methanol suggesting that the catalyst is suitable for the preparation of biodiesel from vegetable oil containing high amounts of free fatty acids. Optimization by statistical analysis showed that the conversion of triglycerides into fatty acid methyl esters using AlCl₃ as catalyst was affected by reaction time, methanol to oil molar ratio, temperature and the presence of THF as co-solvent. The optimum conditions with AlCl₃ that achieved 98% conversion were 24:1 molar ratio at 110°C and 18 h reaction time with THF as co-solvent. The presence of THF minimized the mass transfer problem normally encountered in heterogeneous systems. ZnCl₂ was far less effective as a catalyst compared to AlCl₃, which was attributed to its lesser acidity. Nevertheless, statistical analysis showed that the conversion with the use of ZnCl₂ differs only with reaction time but not with molar ratio.

A.C. Carmo et al. [16] prepared Biodiesel has been obtained by esterification of palmitic acid with methanol, ethanol and isopropanol in the presence of Al-MCM-41 mesoporous molecular sieves with Si/Al ratios of 8, 16 and 32. The catalytic acids were synthesized at room temperature and characterized by atomic absorption spectrometry (AAS), thermal analysis (TG/DTA), X-ray diffraction (XRD), nitrogen absorption (BET/BJH), infrared spectroscopy (IR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The reaction was carried out at 130°C whilst stirring at 500 rpm, with an alcohol/acid molar ratio of 60 and 0.6 wt% catalyst for 2 h. The alcohol reactivity follows the order methanol > ethanol > isopropanol. The catalyst Al-MCM-41 with ratio Si/Al = 8 produced the largest conversion values for the alcohols

studied. The data followed a rather satisfactory approximation to first-order kinetics.

J.K. Rodríguez-Guerrero et al. [17] obtained biodiesel by the reaction of castor oil with ethanol under sub and supercritical condition (200–350°C at endogenous pressure) using small amounts of sodium hydroxide (NaOH) as catalyst was studied. The influence of the operating variables such as temperature, reaction time, ethanol:oil molar ratio and catalyst concentration (when used) on the reaction yield was evaluated using a statistical design of experiments along with the surface response methodology for both the catalytic and non-catalytic processes. It was observed that using only 0.1% wt of NaOH for the catalytic process, amount smaller than the necessary to neutralize the castor oil, it was possible to obtain high yields. The maximum ethyl ester yield reached was 98.9% for the catalytic process and 56.2% for the non-catalytic process. Additionally, the reaction kinetic was determined and it was found that a pseudo first order model represents the overall reaction. Activation energies were calculated from the Arrhenius equation for both processes.

Z.J. Predojevic [18] discussed about characterize biodiesel produced by two-step alkali transesterification of waste sunflower oils (WFOs) using methanol and KOH as catalyst and at the same time to investigate the influence of different purification methods on the properties and yields of the obtained products. Three different methods have been chosen for the purification of the product mixture after the transesterification reaction: washing the mixture with (a) silica gel, (b) 5% phosphoric acid, and (c) hot distilled water. The physical and chemical properties of the used feedstocks and the obtained biodiesel were determined and compared in order to investigate the effects of WFO properties and purification methods on the product characteristics and yields. In general, it could be said that properties of biodiesel reflected the ones of the feedstocks. The produced biodiesel met the criteria required to be a diesel substitute with respect to the density at 15°C, kinematic viscosity at 40°C, acid values (except in the case of biodiesel obtained from WFO with acid value higher than 3 mg KOH/g), iodine values, the content of methyl ester of linolenic acid, and the purity. The biodiesel yields were inversely linked to the acid value and viscosity of the feedstocks. Results showed that silica gel and phosphoric acid treatments gave the highest (approx 92%), while the hot water treatment the lowest yields (approx 89%), recommending the silica gel and phosphoric acid treatments as more suitable for the purification of crude methyl esters obtained after the conversion of waste frying oils by two-step alkali transesterification reaction.

H. Imahara et al. [19] used Non-catalytic biodiesel production technologies from oils/fats in plants and animals have been developed in our laboratory employing supercritical methanol. Due to conditions in high temperature and high pressure of the supercritical fluid, thermal stability of fatty acid methyl esters and actual biodiesel prepared from various plant oils was studied in supercritical methanol over a range of its condition between 270 °C/17 MPa and 380 °C/56 MPa. In addition, the effect of thermal degradation on cold flow properties was studied. As a result, it was found that all fatty acid methyl esters including poly-unsaturated ones were

stable at 270 °C/17 MPa, but at 350°C/ 43 MPa, they were partly decomposed to reduce the yield with isomerization from cis-type to trans-type. These behaviors were also observed for actual biodiesel prepared from linseed oil, safflower oil, which are high in poly-unsaturated fatty acids. Cold flow properties of actual biodiesel, however, remained almost unchanged after supercritical methanol exposure at 270°C/17 MPa and 350°C/43 MPa. For the latter condition, however, poly-unsaturated fatty acids were sacrificed to be decomposed and reduced in yield. From these results, it was clarified that reaction temperature in supercritical methanol process should be lower than 300°C, preferably 270°C with a supercritical pressure higher than 8.09 MPa, in terms of thermal stabilization for high-quality biodiesel production.

A. Bouaid et al. [20] was used samples of biodiesel prepared by the process of transesterification from different vegetable oils: high oleic sunflower oil (HOSO), high and low erucic Brassica carinata oil (HEBO and LEBO) respectively and used frying oil (UFO). These biodiesels, produced from different sources, were used to determine the effects of long storage under different conditions on oxidation stability. Samples were stored in white (exposed) and amber (not exposed) glass containers at room temperature. The study was conducted for a period of 30-months. At regular intervals, samples were taken to measure the following physicochemical quality parameters: acid value (AV), peroxide value (PV), viscosity (η), iodine value (IV) and insoluble impurities (II). Results showed that AV, PV, η and II increased, while IV decreased with increasing storage time of biodiesel samples. However, slight differences were found between biodiesel samples exposed and not exposed to daylight before a storage time of 12 months. But after this period the differences were significant.

J. Xin et al [21] was studied Oxidation stability of safflower biodiesel stabilized with propyl gallate whose concentration spreads from 0 to 5000 ppm was studied by Rancimat method at temperatures from 100°C to 120°C. It was consequently demonstrated that the induction period of biodiesel increases with the increase of antioxidant concentration and decreases with increase of temperature. Kinetics on its oxidation was described by the first order rate law with an accuracy higher than 0.98. The reaction rate of propyl gallate consumed in safflower biodiesel obtained from the experiment fits well with Arrhenius equation and the activation energy obtained from Arrhenius equation was 97.02 kJ/mol. Logarithm of induction periods determined by Rancimat method with various antioxidant concentrations shows a linear relation with temperatures. It was, consequently, found that the Rancimat method for the oxidation stability determination shows an approximate correlation between storage stability and Rancimat induction period. The Rancimat method cannot directly measure the overall storage stability of fuels, since other conditions such as presence of water, microbial contamination and storage conditions would affect fuel quality during storage.

R.A. Candeia et al [22] was evaluated the influence of biodiesel concentration on such blends when mixed to diesel in 5, 15, 25 and 50 volume percentages. For each blend, both methanol and ethanol biodiesels were investigated. The

biodiesel samples were physicochemically characterized. Their rheological behavior was analyzed. It was observed that the biodiesel enrichment leads to an acceptable increase in the viscosity and to a decrease in the volatilization of the binary blends. The viscosity was also shown to be temperature-dependent, as well as the fatty acids chain length and unsaturation.

O.J. Alamu et al. [23] studied the effect of ethanol–PKO ratio on PKO biodiesel yield with a view to obtaining optimal feedstock ratio. Experiments were conducted for ethanol–PKO ratios 0.1, 0.125, 0.15, 0.175, 0.2, 0.225 and 0.25 under transesterification conditions of 60°C temperature, 120 min reaction time and 1.0% KOH catalyst concentration. Results obtained gave 29.5%, 54%, 75%, 89%, 96%, 93.5% and 87.2% average PKO biodiesel yield for the respective feedstock ratios. This shows increase in biodiesel yield with ethanol–PKO ratio up to 0.2. Standard fuel test results of the PKO biodiesel are within biodiesel specifications.

E. Alptekin, M. Canakci [24] in this study, methyl esters were produced from five edible vegetable oils (sunflower, soybean, canola, corn and cottonseed) and blended with two different diesel fuels at 2%, 5%, 10%, 20%, 50% and 75% on a volume basis to characterize the key fuel properties of the blends such as density, viscosity, pour point, distillation temperatures and flash point. The results showed that the fuel properties of the blends were very close to those of diesel fuels at low concentrations upto 20% of methyl esters.

K. Ramezani et al. [25] in this paper, parameters affecting castor oil transesterification reaction were investigated. Applying four basic catalysts including NaOCH₃, NaOH, KOCH₃ and KOH the best one with maximum biodiesel yield was identified. Using Taguchi method consisting four parameters and three levels, the best experimental conditions were determined. Reaction temperature (25, 65 and 80°C), mixing intensity (250, 400 and 600 rpm), alcohol/oil ratio (4:1, 6:1 and 8:1) and catalyst concentration (0.25, 0.35 and 0.5%) were selected as experimental parameters. It was concluded that reaction temperature and mixing intensity can be optimized. Using the optimum results, we proposed a kinetic model which resulted in establishing an equation for the beginning rate of transesterification reaction. Furthermore, applying ASTM D 976 correlation, minimum cetane number of produced biodiesel was determined as 37.1.

M. Kouzu et al [26] was studied solid base catalyst for biodiesel production with environmental benignity, transesterification of edible soybean oil with refluxing methanol was carried out in the presence of calcium oxide (CaO), -hydroxide (Ca(OH)₂), or -carbonate (CaCO₃). At 1 h of reaction time, yield of FAME was 93% for CaO, 12% for Ca(OH)₂, and 0% for CaCO₃. Under the same reacting condition, sodium hydroxide with the homogeneous catalysis brought about the complete conversion into FAME. Also, CaO was used for the further tests transesterifying waste cooking oil (WCO) with acid value of 5.1 mg-KOH/g. The yield of FAME was above 99% at 2 h of reaction time, but a portion of catalyst changed into calcium soap by reacting with free fatty acids included in WCO at initial stage of the transesterification. Owing to the neutralizing reaction of the

catalyst, concentration of calcium in FAME increased from 187 ppm to 3065 ppm. By processing WCO at reflux of methanol in the presence of cation-exchange resin, only the free fatty acids could be converted into FAME. The transesterification of the processed WCO with acid value of 0.3 mg-KOH/g resulted in the production of FAME including calcium of 565 ppm.

X. Liu et al [27] studied physical and chemical characterizations of calcium methoxide were investigated to assess its performance as an excellent solid base catalyst using some instrumental methods, such as BET surface area measurement, scanning electron micrographs and particle size distribution. Then, it was used to catalyze transesterification of soybean oil to biodiesel with methanol. The effects of various factors such as mass ratio of catalyst to oil, reaction temperature and volume ratio of methanol to oil were studied to optimize the reaction conditions. The results showed that calcium methoxide has strong basicity and high catalytic activity as a heterogeneous solid base catalyst and it was obtained a 98% biodiesel yield within 2 h in this reaction. Besides, the recycling experiment results showed it had a long catalyst lifetime and could maintain activity even after being reused for 20 cycles.

4. Conclusions

Various biodiesel preparation methods were discussed in this paper.

- The production of biodiesel from edible and non-edible oil can be optimized by using various parameters such as catalyst concentration, amount of methanol required for reaction, reaction time and reaction temperature.
- The influence of the working variables such as temperature, reaction time, ethanol:oil molar ratio and catalyst concentration on the reaction yield was evaluated using a statistical design of experiments along with the surface response methodology for both the catalytic and non-catalytic processes.
- The biodiesel yields were inversely linked to the acid value and viscosity of the feedstocks
- The induction period of biodiesel increases with the increase of antioxidant concentration and decreases with increase of temperature.
- It was observed that the biodiesel enrichment leads to an acceptable increase in the viscosity and to a decrease in the volatilization of the binary blends.

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