

Original Research Article

Optimization study of biodiesel used frying oil

K.Dhanasekaran^{1*} and M.Dharmendirakumar²

¹Department of Chemical Engineering, Arulmigu Meenakshi Amman College of Engineering, Vadamavandal-604 410, India

²Department of Applied Science and Technology, Alagappa College of Technology, Anna University, Chennai-600 025, India

*Corresponding author e-mail:

A B S T R A C T

Keywords

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With the usage evidence shows the fossil fuel generated higher pollution problems than renewable energies and this is time to change into renewable energies such as Biodiesel, bioethanol and biogas. In that, biodiesel is very easy to process in to useful product and used frying oils such as sunflower oil (UFSO), Palm oil (UFPO) are used to convert biodiesel with KOH catalyst. The Characterization and optimization parameters are: methanol to oil molar ratio (3:1, 5:1, 7:1 and 9:1), Catalyst concentration (0.5, 1.0, 1.5 and 2.0 wt. %), temperature (50, 55, 60 and 65°C), time (30, 60, 90 and 120 min) and methanol. The optimized biodiesel parameters of sunflower (UFSO), Palm oil (UFPO) are: molar ratio of alcohol to oil is 7:1, 1.0 wt % of catalyst concentration, 60°C temperature, and 90 min reaction time.

Introduction

Transesterification of used frying oils and fats is the main source to make biodiesel. Transesterification is a three-step consecutive reversible reaction of oils or fats with alcohol to form Biodiesel and glycerol. The presence of a catalyst is needed. So, used frying oil can be used as a biodiesel sources and partially improve the global problems. In addition, the utilization of used frying oils diminishes the problems of contamination, because the reusing of these waste greases can reduce the burden of the government in disposing of the waste, maintaining public

sewers, and treating the oil wastewater (Encinar *et al.*, 2007). The use of waste cooking oil as biodiesel feedstock reduces the cost of biodiesel production (Canakci *et al.*, 2007). Hence, the use of waste cooking oils and non-edible oils should be given higher priority over the edible oils as biodiesel feedstock (Connemann *et al.*, 1988). Considerable research has been conducted to investigate the production of biodiesel from waste oil under acid (Zheng *et al.*, 2006), alkaline (Encinar *et al.*, 2005; Felizardo *et al.*, 2006) and enzyme catalysis (Watanabe *et al.*, 2001; Chen *et*

al., 2006). Acid catalysis is more efficient when the amount of FFA in the oil exceeds 1% (Freedman *et al.*, 1984). Though, acid-catalyzed transesterification is insensitive to FFA in the feedstock; it requires longer reaction time and higher temperature. Many researchers recommend using acid-catalysis as pretreatment step followed by alkaline catalyzed step (Zheng *et al.*, 2006). Wang *et al.*, (2007) were adopted this kind of two-step catalyzed process to prepare biodiesel from used frying oil. In the first step, FFAs of used frying oil were esterified with methanol catalyzed by ferric sulfate. In the second step, the triglycerides in the used frying oil were transesterified with methanol (methanol/oil molar ratio=6) catalyzed by 1.0 wt% potassium hydroxide at 65°C for an hour. After this two-step catalysis process, the final product with 97.02% conversion of biodiesel was obtained. Nevertheless, some researchers (Meher *et al.*, 2006; Gerpen *et al.*, 2005 and Tiwari *et al.*, 2007) have pointed out that the Alkali-catalyzed transesterification could be completed as long as the FFA content in the oil is not greater than 1% and all materials should be substantially anhydrous. Basic catalysts lead to higher conversion of methyl esters at low temperature, atmospheric pressure and minimum response time, which reduces the cost of the process considerably (Ghadge *et al.*, 2005). Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides (CH₃OK, CH₃ONa), but less active. In this sense, the reactions that used sodium or potassium hydroxides were faster than the reactions with the sodium or potassium methoxides. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1

or 2 mole%. However, even if a water-free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide with the alcohol (Wang *et al.*, 2007).

In this paper, two used frying oil is source used and is one of the most premises choices of biodiesel process. One of the major concerns on biodiesel production is the price of feedstock; utilization of used frying oil significantly enhances the economic viability of biodiesel production with using KOH Catalyst.

Materials and Methods

Materials

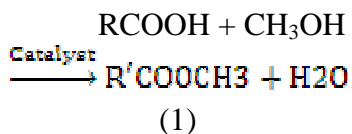
The material sources were: used frying oils such sunflower and palm oils are collected from local restaurants with high FFA content. The chemicals are Methyl alcohol of 99.9 % purity was purchased from SD Fine Chemicals; Mumbai and KOH pellets of 98.2 % purity were purchased from Nice Chemicals, Kerala.

Experimental procedure

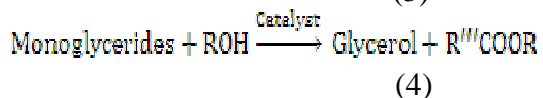
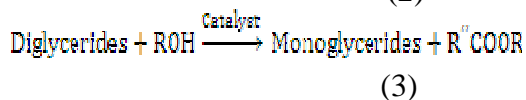
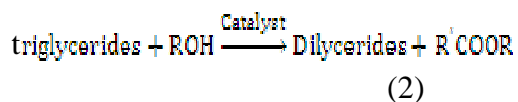
Used frying oil is collected from local restaurants and heated to 110°C and removes the water molecules then filter by 10µm cloth to separate all food waste and suspended materials. Generally, biodiesel production is strongly influenced by FFA content of the used frying oil and the amount of catalyst had impact of conversion of esters during the transesterification process. Owing to its high FFAs, the transesterification of used frying oil to biodiesel catalyzed directly used longer reaction time and obtained only lower biodiesel yield can be achieved. So, a two-stage process is followed to convert the biodiesel from

used frying oil. First stage, an acid-catalyst (sulfuric acid) was used to esterify (pretreatment) the used frying oil. For that, a three-neck flask with a water-cooled condenser was filled with 200 ml of used frying oil, 40 ml of anhydrous methanol and 4 ml of sulfuric acid (H₂SO₄). The mixture was vigorously stirred for 1.5 h at 50°C. After reaction, the mixture was filtered and the unreacted methanol was separated from the liquid phase via distillation. The pretreated oil is washed three times with sodium chloride solution and then dried using anhydrous sodium sulfate. After the pretreatment, the FFA value of the pretreated oil was lesser than that of freshly used cooking oil.

This esterification reaction was described as below:



The second stage, a homogeneous catalyst (NaOH, KOH, CH₃ONa, and CH₃OK) is used to transesterify the pretreated oil:



The reaction procedure was as follows: first, the catalyst was dispersed in methanol using stirring system was connected to it. Then, the pretreated oil was added into the Striring mixture and heated to 50°C for three hours. After thorough mixing and kept it overnight; two layers were formed. In that, the upper layer consists of biodiesel whereas the

lower layer consists of Glycerin and this layer consist of excess methanol, unreacted catalyst and soap. This unreacted methanol was distilled off under a vacuum condition while biodiesel layer was separated with the help of separating system and finally remaining glycerin layer is separated and then distilled to get 98 % purified glycerin. The separated biodiesel is purified with hot water until the P^H gets neutral.

Results and Discussion

Effect of Catalyst

Free fatty acids (FFAs) content after acid esterification should be minimal or otherwise less than 2% FFAs. These FFAs react with the alkaline catalyst to produce soaps instead of esters. It depicts the effect of FFAs on the yield of methyl ester during alkali catalyzed transesterification. There is a significant drop in the ester conversion when the free fatty acids are beyond 2% (Naik *et al.*, 2008). The acid value of UFSO is 3.54% and UFPO is 4.25%. Due to High FFA, if this oil would have been used directly with base catalysts it would give only lower Biodiesel yield. After pretreatment process, the acid value of UFSO is 1.65% and UFPO is 1.84%. Now, this pretreated oil used with 7:1 molar ratio of alcohol to oil, 1 wt % of KOH catalysts and 90min reaction time at 60°C. In that, Fig 3.1 describes UFSO shows better biodiesel yield behavior than UFPO. Naturally, KOH is frequently soluble in solvent and easily promote the reaction. Generally, catalyst concentration can affect the rate of biodiesel reaction and beyond the limitation of catalyst additions it represented in Fig 3.1. So, KOH catalyst used with 0.5, 1.0, 1.5 and 2.0 wt. % concentration for both UFSO and UFPO in that, 0.5 wt.% shows only 74% and 65%

biodiesel yield for UFSO and UFPO and also 1.5 wt.% shows only 86% and 72% biodiesel yield for UFSO and UFPO. For, 2.0 wt.% catalyst shows biodiesel yield to 74% and 56% decreases due to its higher concentration of catalyst addition gives negative effect of biodiesel production. Whereas describes 1.0 wt. % of catalyst shows 95% and 88% biodiesel yield for UFSO and UFPO higher biodiesel yield than other concentrations. In general, as the catalyst concentration increased, the conversion of triglycerides also increased. This is because an insufficient amount of catalyst results in an incomplete conversion of triglycerides into fatty acid esters (Nye *et al.*, 1983). In basic catalyst, a slight decrease in ester content was observed in the experiments with 1.5 wt % of catalyst with regard to the experiments with 1 wt %. This is because the addition of excess alkaline catalysts caused more triglycerides participation in the saponification reaction, resulting in increased production of soap and mentioned reduction of the esters yield (Krishnangura *et al.*, 1992). So, any increase in concentration of catalyst beyond the neutralization limit results in decrease in biodiesel conversion. These results are very similar to those found in the literature in transesterification processes of used frying oil with methanol and other alcohols that also concluded that potassium hydroxide was the best catalyst (Fangrui *et al.*, 1999; Allen 1998).

Effect of Temperature

The primary advantage of higher temperatures influences to shorter reaction time. However, higher reaction temperatures causes methanol to vaporize resulting in decreased yield. In this process, the temperature ranges used 50, 55, 60 and 65°C and in order to optimize

biodiesel yield with using the constant parameters are: alcohols to oil molar ratio of 7:1 with KOH concentration of 1 wt. % for UFSO and UFPO at 90 min reaction time. Figure 3.2 describes biodiesel yield with respect to temperature ranges of 50, 55, 60°C for both UFSO and UFPO. 50°C shows, biodiesel yield were 73% for UFSO and 60% for UFPO again increases the temperature to 55°C and biodiesel yield also increases. Further the temperature increases to 60°C, the biodiesel yield were 94% for UFSO and 85% for UFPO. When the temperature decreases, the rate of reaction also decreases. Therefore, the equilibrium concentration was strongly conditioned by the temperature and favored for the same; that is, the equilibrium concentration increased as the temperature increased. Therefore the optimum temperature is 60°C for UFSO and UFPO biodiesel process. Encinar *et al.*, (2007) explained three temperatures like 35, 60, 78°C for used frying oil in 12:1 molar ratio of methanol-oil condition with 1 wt. %. But in that 60, 78°C temperatures show almost same curve, whereas in the present case three temperatures show different curve with 6:1 ratio and 1 wt % of KOH used. Encinar *et al.*, (2010) explained about castor oil with temperatures (25, 35, 45, 55, 65°C) and methanol/oil ratio (3:1, 6:1, 9:1, 12:1) with different catalyst concentrations.

Effect of Reaction Time

According to many researchers, the biodiesel yields are directly proportional to the reaction times used. This experiment was conducted from the reaction time of 30, 60, 90 and 120 min with the constant parameters: 60°C of reaction temperature for 1 wt % of KOH catalyst used in 7:1 molar ratio of UFSO and UFPO. Figure

3.3 show that effect longer mixing gives higher yield than using shorter time. So, 90 min of reaction time gave a good result than other reaction times used here. In other words, the biodiesel yields increases with increasing the reaction time. However, based on the results, it shows that the biodiesel yields were lower when reaction time of 120 min was used. This undesirable result may be due to the higher soap formation when longer reaction time was used. Thus, the rate of soap formation was also increased.

Effect of molar ratio

Generally, the stoichiometry of the reaction requires 3 moles of methanol per mole of triglycerides to yield 3 moles of biodiesel and 1 mole of glycerol. Methanol is a commonly used alcohol for transesterification because of its low price and highly reactive nature (Zhou *et al.*, 2003). For example, the molar ratio of 1:6 moles of soybean oil to methanol has been found to be the most suitable in the case of alkali-catalyzed transesterification because an excess of alcohol is required to drive the reaction (Lang *et al.*, 2001). For acid-catalyzed transesterification, a 1:30 vegetable oil to alcohol ratio is generally used (Wang *et al.*, 2007). In this experiment, UFSO and UFPO were used with varying molar ratios of methanol and oil (3:1, 5:1, 7:1 and 9:1) and 1.0 wt% KOH at 60°C with 90 min reaction time as represented in Figure 3.4. As mentioned, the transesterification activity also depends on the molar concentrations of methanol to oil and also associated with the type of catalyst used. If the molar ratio increased from 3:1 to 7:1 and then biodiesel yield content also increased for UFSO as well as UFPO. Now, molar ratio increases from 7:1 to 9:1, methyl esters content decreased biodiesel yield and

excess of molar ratio increases much then biodiesel yield also increases. Excess of methanol is required to shift the equilibrium favorably during transesterification for better yields of biodiesel. Therefore, 6:1 molar ratio gives a better result than other molar ratios and also repeated same procedure done for UFSO and UFPO. The higher alcohol molar ratio interferes with the separation of glycerol because there is an increase of solubility. In addition, an excess of alcohol was able increase the conversion of di-monoglycerides, but there is possibility of recombination of esters and glycerol to form monoglycerides because their concentration and also increasing during the course of the reaction, in other words the reactions conducted with low molar ratios. Many researchers have reported an alcohol to oil molar ratio of 6:1 to be the optimal ratio, while (Freedman *et al.*, 1986) reported that the maximum biodiesel production was obtained at a molar ratio of 7:1 in transesterification of used frying oil. In base catalysis, this effect can be observed quickly because the reaction is fast, whereas in acid catalysis requires with high concentration of the reaction. These results are similar that where obtained in the ethanolysis of peanut oil (Lang *et al.*, 2001; Leung *et al.*, 2006 and Feuge *et al.*, 1949) described about the ethanolysis of sunflower oil. In general, an acid catalyst requires a higher molar ratio of methanol/oil than basic catalysts (Schwad *et al.*, 1987). In consequence, the alcohol/oil molar ratio is one of the most important variables affecting the esters yield and although the stoichiometry ratio for transesterification required 3 moles of alcohol and 1 mole of triglyceride, excess of alcohol was used in practice. Hence, the alcohol molar/oil ratio is an important factor that must be always optimized (Encinar *et al.*, 2010).

Fig 3.1 Biodiesel yield with KOH concentration

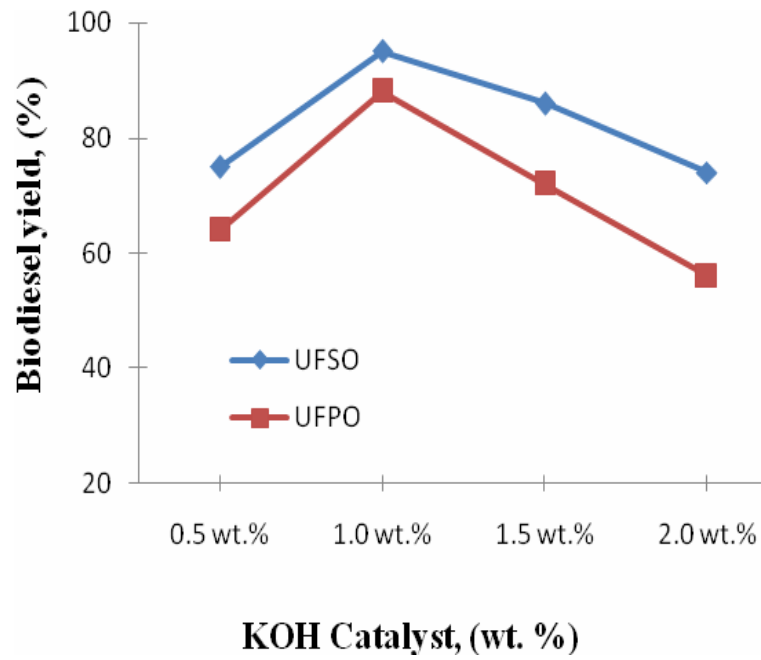


Fig 3.2 Biodiesel yield with Temperature

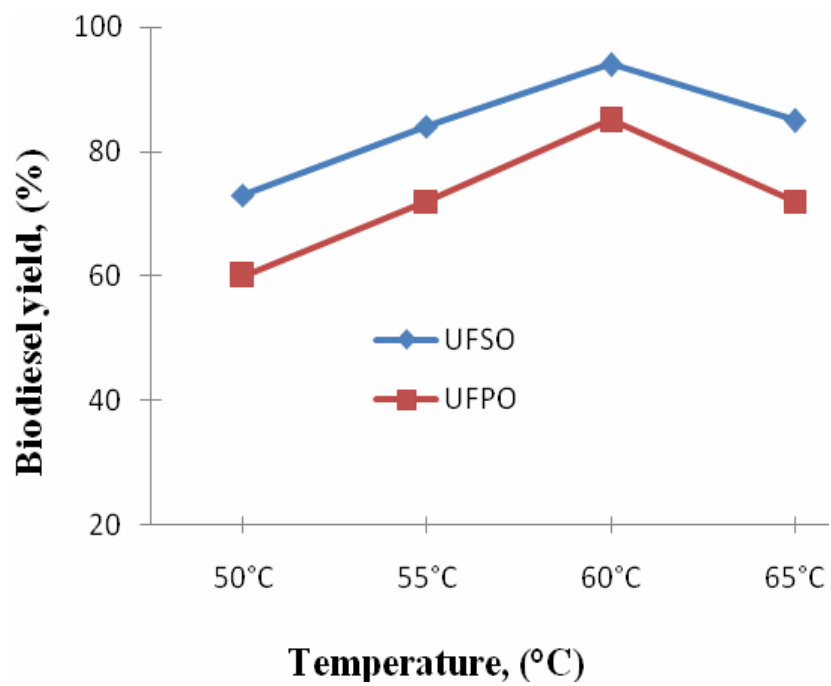


Fig 3.3 Biodiesel yield with reaction time

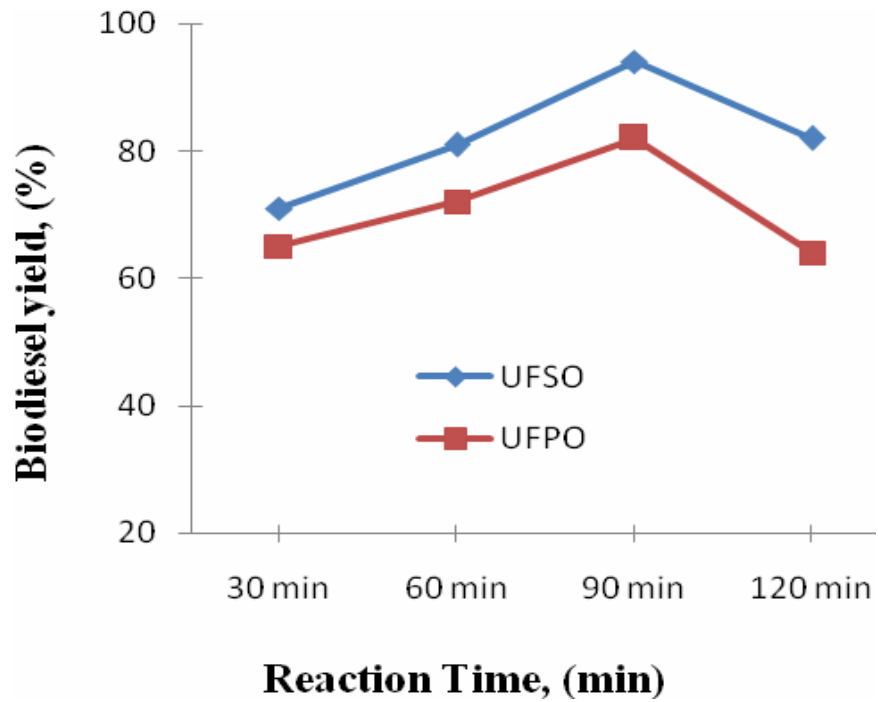
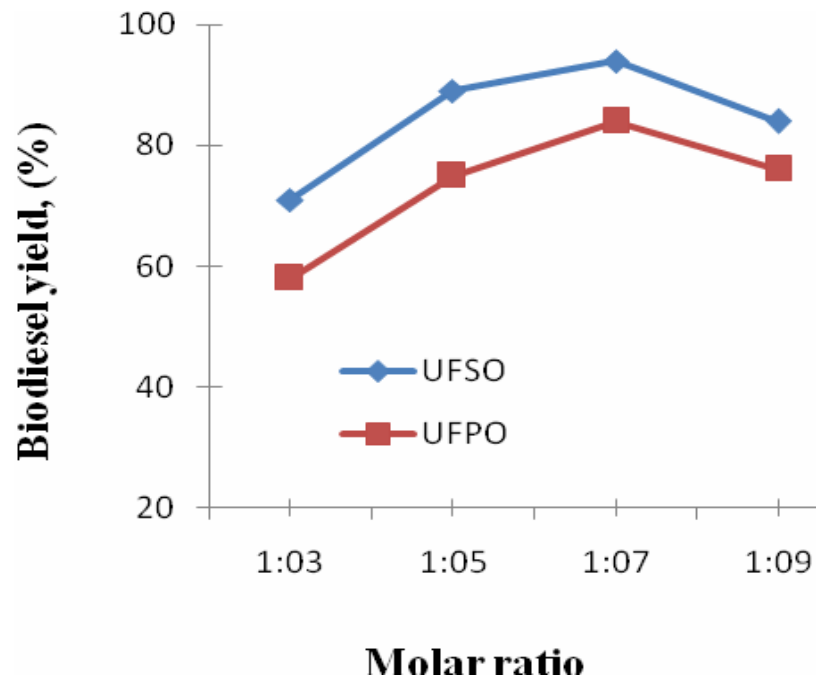


Figure 3.4 Biodiesel yield with molar ratio



Biodiesel are eco-friendly sources to reduce the green house effect and incomplete combustion due to its green fuel nature. Used frying oil is an effect source for transesterification of biodiesel why because it reduces the total production cost into half and also UFSO and UFPO are easily available sources are being used today and also most of the time used frying oils are being used by two stage processes. Based on the above results, UFSO gave higher biodiesel yield than UFPO by using KOH catalyst and biodiesel yield results also near to EN standards. The characterized and optimized parameters are: catalyst concentrations are 0.5, 1.0, 1.5 and 2.0 wt % were employed and the optimum catalyst concentration of 1.0 wt. %. The temperature ranges of 50, 55, 60 and 65°C used for biodiesel production and the optimum temperature is 60°C. The methanol/oil molar ratio was one of the variables that influence on the process with the range of molar ratios employed (3:1, 5:1, 7:1 and 9:1) and the best results is obtained at 7:1. Therefore, usage of fresh oil than used frying oil have highly profitable.

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