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Improving the Yield of Biodiesel from Karanja Oil Transesterification using Nano Catalyst

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Abstract : Biodiesel is a promising alternating environmentally benign fuel to mineral diesel. Stable and active heterogeneous mixed metal oxide of $KTiO_2$ nanocatalyst was synthesized and exploited using karanja oil transesterification processfor the development ofeasier transesterification process. The synthesized catalyst was characterized by XRD, and HRTEM studies for their structural characteristics. It was found that $KTiO_2$ nanocatalyst exhibits good catalytic activity. Also its was noticed that the catalytic performance was greatly depends on (i) Catalyst concentration (ii) Methanol to oil molar ratio (iii) Reaction temperature and (iv) Reaction time. A highest 84.5% of conversion was obtained at the optimum reaction parameters with 4% of catalyst loading and 7% potassium loading. The $KTiO_2$ nanocatalyst shows good catalytic performance, which could be a potential candidate for the large-scale biodiesel production from Karanja oil at the reduced temperature and time.

1. Introduction

Biodiesel fuel (BDF) is well known as a renewable, nontoxic, biodegradable, and environment-friendly that can substitute petro-diesel perfectly which can be used directly or as diesel mixture in engines with little changes. Biodiesel can be produced through transesterification of vegetable oils and fats with methanol in the presence of a suitable catalyst[1]. Any type of feedstock that contains free fatty acids and/or triglycerides such as vegetable oil, waste oil, animal fats, and waste greases could be converted into biodiesel [2,7]. In conventional method of transesterification reaction (homogeneous catalysts) number of purification steps are involved to meet the stipulated qualities thereby increase the capital and operating costs. Therefore, for the development of an environmentally benign process and the reduction of the production cost, a new process using heterogeneous catalyst is introduced[3,5].

Numerous investigations have been made on the BDF production using heterogeneous base catalysts as they offer higher catalytic activity than solid acid catalysts. Metal oxides CaO, SrO, MgO, etc., mixed metal oxides Ca/Zn, Ca/Mg, etc., alkali-doped metal oxides CaO/Al2O3, MgO/ Al2O3, Li/CaO, etc., Al2O3-supported alkali metal oxide catalysts Na/NaOH/c-Al2O3, K2CO3/Al2O3 hydrotalcites and K/Ca/Al/Fe3O4 magnetic composites are used as solid base catalysts[5,6]. Although these heterogeneous catalysts have some advantages such as easier catalyst separation and pollution reduction, most of them have few limitations such as high reaction temperature (>120ºC), long reaction time (>24 h) and low catalytic stability with significant leaching of catalyst components to the deactivation of the catalyst. The use of nanocatalyst provides higher catalytic activity, easier to separate and reusable, simple operational procedures, and regenerates of less pollution[6,9].

Therefore, the heterogeneous catalyst was prepared by impregnation method and the catalytic activity towards the transesterification of karanja oil (conversion of the methyl esters) was examined. X-ray diffraction (XRD) and HRTEM analysis were used for catalysts characterization. The effect of reaction variables such as methanol to oil molar ratio, reaction time, reaction temperature, and catalyst loading on the conversion of methyl esters were investigated and optimized for higher yield.

2. Preparation and Characterizaion of Nano Catalyst

2.1. Preparation

Refined karanja oil was purchased from local market. Methanol (>99% purity) was of analytical grade purchased from E-Merck, India and was used as received without purification. Initially the Titanium oxide (anatase) was mixed with required amount of water andKNO_3 (Merck) at 3, 5, 7 w/w% as the potassium precursor. Then the solution was heated slowly to evaporate the excess amount of water. The magnetic stirrer speed was maintained 500 rpm and the mixture was stirred continuously at 100˚C to achieve the homogeneity until the mixture becomes paste-like precursor. The precursor was kept oven at 120˚C to remove the water particles. After, this the $KTiO_2$ was milled to produce fine particles. Finally the powder was calcinated in a furnace at 500 ˚C for 2hrs and cooled for 8 hours to remove NO_x content.

2.2 Characterization

The powder X-ray diffraction (XRD) pattern for the synthesized nanocatalyst samples were recorded using a diffractometer and the obtained peaks are shown in figure 1, which is compared with the standard curve of anatase, shown in figure 2. The phases present in the samples were identified with the help of JCPDS (Joint Committee of the Powder Diffraction Standard) database files. The XRD patterns of TiO2–K nanocatalysts show the formation of hexagonal KNO_3 (JCPDS No.: 89-1397) and Tetragonal TiO2 (JCPDS No.: 89-6975) phases clearly indicating that KNO_3 and TiO2 were partially present in the form of hexagonal and tetragonal crystallites. The XRD patterns exhibits the formed metal oxide- nitrate catalyst was possibly the mixed oxide and nitrate of a Ti and K and did not form any specific structures but they were present as separate oxides and nitrates respectively. On the other hand the characteristic peak of KNO_3 was almost changed with respect to Ti substitution

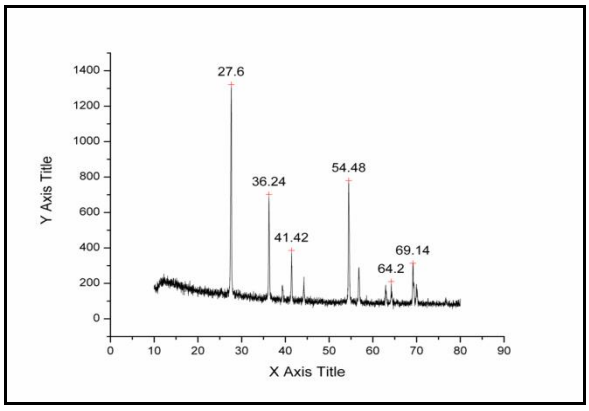

Figure 1: XRD analysis of prepared K-TiO_2

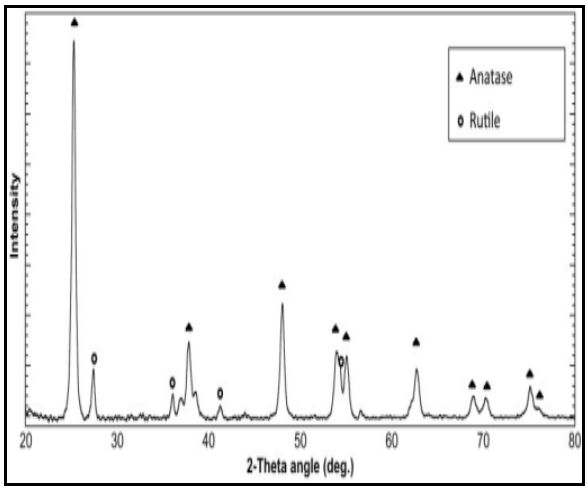

Figure 2: XRD analysis of standard TiO_2 anatase

High-resolution transmission electron microscopy (HRTEM) is an imaging mode of the transmission electron microscope (TEM) that allows for direct imaging of the atomic structure of the sample. The prepared sample was analyzed using HRTEM technique and the electrons were focused on the catalyst at 50nm scale and the result is shown in figure 3. The potassium particles were adsorbed on the surface of Titania, which is evident from the distinct colouration at the outer periphery. The particles were found to be spherical in shape and from the scaling, average particle size were found to be 200nm

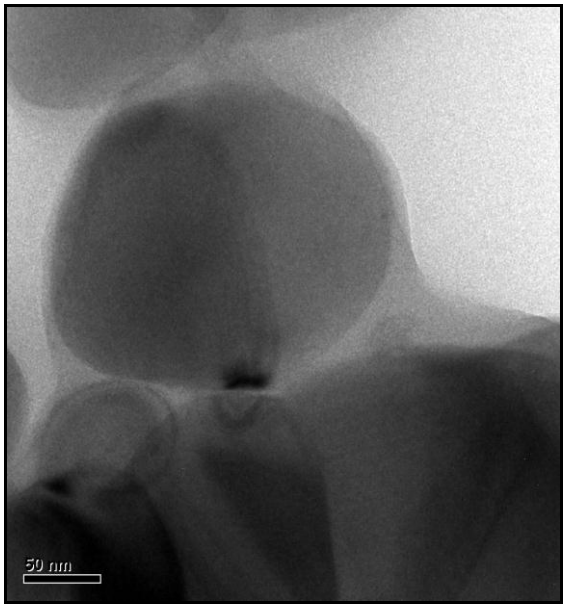

Figure 3: HRTEM analysis of prepared K-TiO_2 at 50nm

3. Experimental Setup and Procedure

3.1 Transesterification Experimental Setup

The experimental setup consists of a round bottom flask, connected to a condenser. The condenser is inturn connected to a water bath with a motor, for forced water circulation. Water circulation is required to condense the evaporating gases and to readmit them into the round bottom flask. The round bottom flask and condenser is placed over an oil bath, filled with silicon oil for better heat transfer and stability. The entire setup is placed over a magnetic stirrer with heater arrangement. Magnetic pellet was used to achieve the stirring action. Constant stirring at 500 rpm was achieved using the magnetic pellet and stirrer. The experimental setup is shown in figure 4.

Figure 4: Experimental setup

3.2 Optimization Procedure

Four parameters have to be optimized in the present workto achieve maximum yield. The parameters to be optimized are as follows

1. Percentage of catalyst loading
2. Reaction time
3. Methanol to oil ratio
4. Percentage of potassium loading

The first three parameters were first optimized by conducting 3^3= 27 experiments and a numerical search technique. The most optimal conditions were found out. Using this fourth parameter was optimized. The experiments were conducted with 3 variables, namely catalyst weight %, methanol: oil molar ratio and reaction time as shown in table 1.

From the below set of experiments, the yield of biodiesel was calculated in each case and the reaction resulting in the highest yield was taken as optimality for reaction time and methanol: oil molar ratio.

The optimized time and molar ratios were later used to optimize the percentage catalyst loading, among 2, 3, 4, 5, and 7%. Finally the three parameters that were optimized so far were used to optimize the percentage potassium loading among 2, 5, 7, 10, and 12%.

Table 1: combination parameters

weight of catalyst in (w/w) % of oil	Methanol to oil molar ratio	Time in hrs	yield in %
3	6	3	79.4
3	6	5	81.8
3	6	7	80.2
3	9	3	81.4
3	9	5	83.3
3	9	7	79.8
3	18	3	79.4

3	18	5	81.2
3	18	7	77.4
5	6	3	77.2
5	6	5	79.8
5	6	7	78.1
5	9	3	78.3
5	9	5	81.5
5	9	7	77.9
5	18	3	73
5	18	5	75.2
5	18	7	70.8
7	6	3	72.5
7	6	5	75.8
7	6	7	73.2
7	9	3	64.8
7	9	5	62.3
7	9	7	61.2
7	18	3	74.5
7	18	5	80.2
7	18	7	74.1

4. Results and Discussions

4.1 Optimization of reaction time and methanol : oil molar ratio

Initially transesterification was done with KOH base catalyst with 1% catalyst weight, molar ratio 9, reaction temperature 60°C and reaction time of 1.5 hours, to obtain the maximum yield on weight basis was 77.6%.Totally 27 experiments were conducted and the yield of biodiesel was calculated by weight method, given by the equation (1).

$$\text{Yield } \textit{percentage } (\%) = \frac{\text{Mass of biodiesel produced}}{\text{Mass of oil}} * 100 \quad (1)$$

The results showed a maximum yield at a reaction time of 5 hours and a molar ratio of 9. As the results were consistent in all cases, these values might be helpful to suggest an optimum value. The results of the above experiments are shown in figure 4.1, 4.2, 4.3.

In each case the molar ratio 9 and reaction time 5 hours, showed the highest peak. Yield was the highest in molar ratio 9 and lowest in molar ratio 18. Similarly yield was highest in 5 hours and lowest in 7 hours. The maximum yield obtained from the experiments was 83.3% at 3% catalyst weight, 9 molar ratio and reaction time of 5 hours. The conclusion here is that the optimal value of molar ratio is 9 and optimal reaction time is 5 hours.

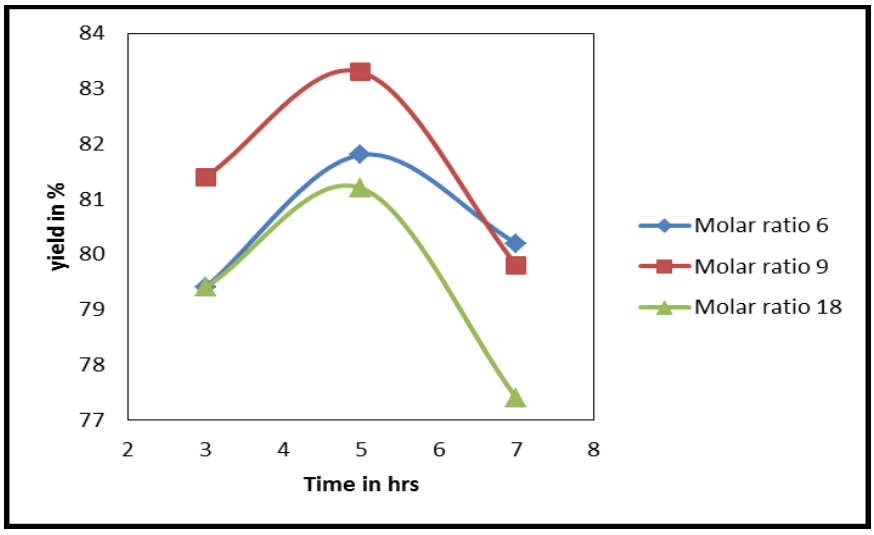

Figure 4.1 Results for 3% weight

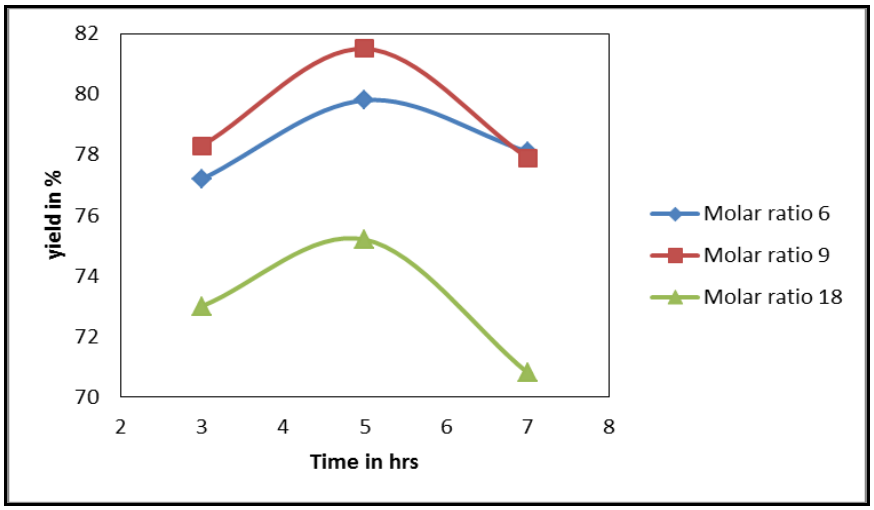

Figure 4.2 Results for 5% weight

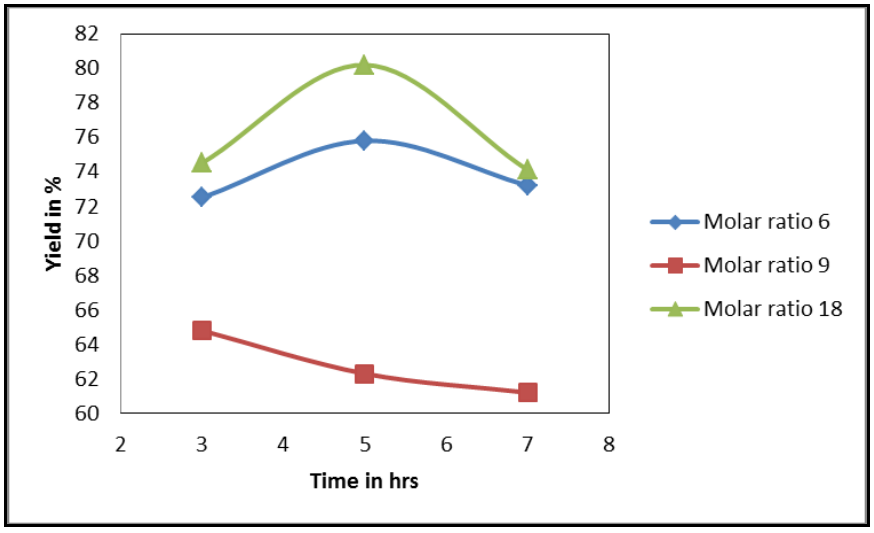

Figure 4.3 Results for 7% weight

4.2 Effect of Methanol : Oil Molar Ratio

The methanol/oil molar ratio is known to be one of the most important variables affecting the biodiesel yield. In order to evaluate the effect of methanol/oil molar ratio on biodiesel yield, transesterification was conducted at different methanol/oil molar ratios (1:6, 1:9, and 1:18) at 60°C temperature. The relationship between different Molar ratios and the biodiesel yield was when the yield increases with increasing molar ratio from 1:3 to 1:9. The biodiesel yield was 83.23% could be achieved. However, when the molar ratio increases, the yield apparently decreased.

Since, transesterification is an equilibrium process lower methanol/oil molar ratio may result in an incomplete transesterification. Increasing the methanol/oil molar ratio will shift the reaction to the ester formation direction[8]. However when the methanol/oil molar ratio is set too high, the excessive alcohol may favor conversion of diglycerides to monoglycerides, and a slight recombination of esters and glycerol to monoglycerides because their concentrations keep increasing during the course of the reaction [9].

4.3 Optimization of Catalyst Weight

The reactions were conducted with catalyst weight percentages of 3%, 5% and 7%. Of the three the maximum yield was obtained at 3% weight. To obtain the optimal value, numerical search method was used. Since the yield was lower at 5% than 3%, the next trials were conducted at 2 and 4%. The maximum yield of 83.36% was obtained at 4% weight of catalyst and hence 4 % catalyst weight was concluded as the optimal value. The results of catalyst weight % vs. yield % are shown in figure 4.4.

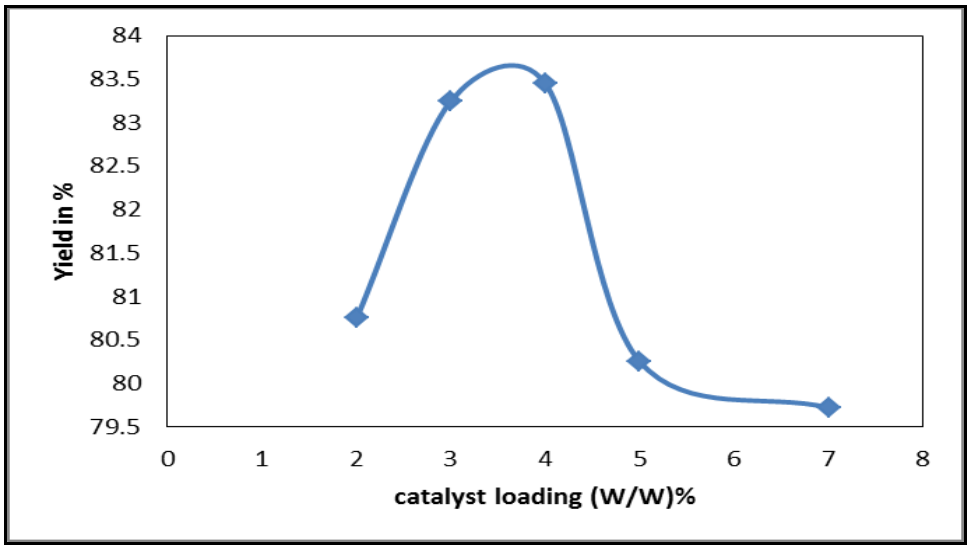

Figure 4.4 Catalyst weight % vs. yield

4.4 Effect of Catalyst Type

Figure 4.3 shows the influence of catalyst type on the biodiesel yield. As can be seen, $KTiO_2$ catalyst presented the best behavior. Moreover, the hydroxide catalysts showed better results than the counterpart methoxide catalysts. This observation was in agreement to evaluate the effect of catalyst types on methyl and ethyl ester yields. The different effects exhibited by these four kinds of catalysts could be explained by the fact that their chemical molecular weights were different[6]. At the same weight concentration, the amount of methoxides available for each mole of triglyceride will differ. The effectiveness of catalysts might be correlated with the molar concentration of the catalyst formulation. Since $KTiO_2$ in 4% potassium loaded catalyst has the lowest molecular weight, it has the best performance in the biodiesel production.

4.5 Optimization of Potassium Loading

All the above experiments were conducted with 4 % potassium loading on the catalyst. To optimize the percentage loading of potassium, search method was used. From the above cases it was concluded that the most optimal parameters are 4% catalyst weight, methanol: oil molar ratio 9, reaction time 5 hours. Now with these

optimized conditions, experiments were carried out with various potassium loadings, such as 2%, 5%, 7% and 12%. The results obtained are shown in figure 4.5. It can be seen that a maximum yield of 83.36% was obtained at 7% potassium loading.

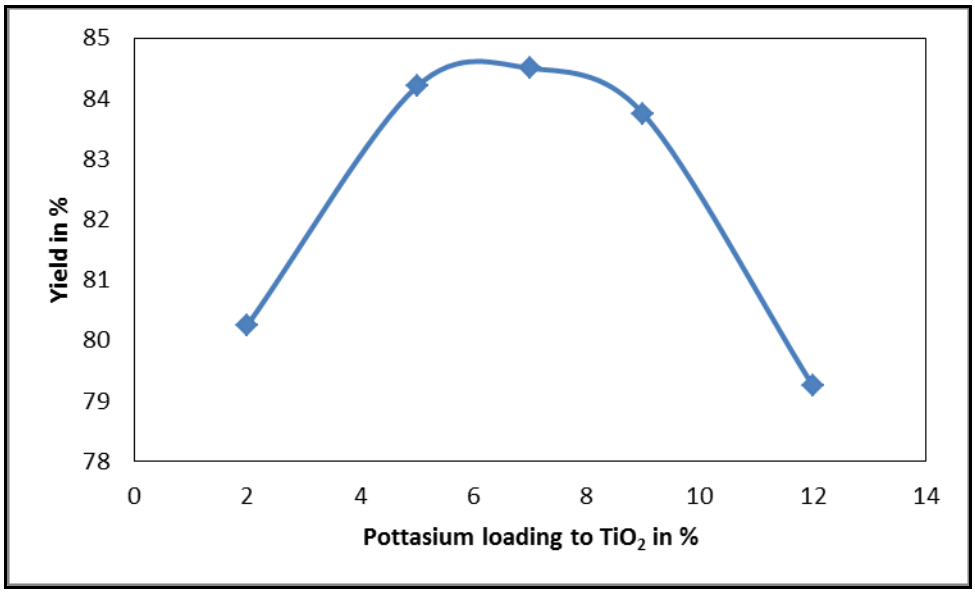

Figure 4.5 Potassium loading % vs. yield

4.6 Effect of Potassium Concentration

The effect of catalyst concentration on the biodiesel yield is shown in Figure 4.4. When the concentration of potassium was below 10 wt.% (by weight of karanja oil), the lowest yields were obtained because the added catalyst was insufficient to catalyze the reaction for completion. In contrast, the best results were achieved at the concentration of 7 wt%. Further addition of excessive amount of catalyst (10 wt%) not only made the separation more complicated, but reduced the biodiesel yield. These results agreed with that discovered the parameters also obtained similar results that there was a decrease in the yield with the increase in the catalyst concentration[6,8,9]. This phenomenon can be attributed to the fact that at higher catalyst concentration, emulsion was formed and the dissolved soap can increase the methyl ester solubility in the glycerol, causing additional yield loss.

5 .Conclusion

The present study explore the variation in yield of biodiesel using potassium loaded TiO_2. A maximum yield of 83.36% was obtained at 4% catalyst weight, methanol to oil molar ratio of 9, reaction time of 5 hours and potassium loading of 7%. The catalyst was characterized using XRD and HRTEM techniques and was found to have an average size of 200nm. The effect of the catalyst after optimization was that it resulted in 7% higher biodiesel yield compared to the base catalyst KOH. The catalyst promises to be potential candidate for large scale biodiesel production at reduced cost and energy usage.

References

1. Madhuvilakku R, Piraman S. Biodiesel synthesis by TiO 2–ZnO mixed oxide nanocatalyst catalyzed palm oil transesterification process. Bioresource technology, 2013, 150:55-9.
2. Mamilla, Venkata Ramesh, M. V. Mallikarjun, and G. Lakshmi Narayana Rao. "Preparation of biodiesel from Karanja oil." *Int. J. Energy Eng* 1 (2011): 94-100.
3. Rengasamy, Mookan, et al. "Transesterification of castor oil using nano-sized iron catalyst for the production of biodiesel." *Journal of Chemical and Pharmaceutical Sciences ISSN* 974 (2014): 2115.
4. El-Shimi, H. I., et al. "Biodiesel production from Spirulina-platensis microalgae by in-situ transesterification process." *Journal of Sustainable Bioenergy Systems* 3.03 (2013): 224.

5. Salinas, Daniela, Sichem Guerrero, and Paulo Araya. "Transesterification of canola oil on potassium-supported TiO 2 catalysts." *Catalysis Communications* 11.8 (2010): 773-777.
6. Mutreja, Vishal, et al. "Nanocrystalline potassium impregnated SiO 2 as heterogeneous catalysts for the transesterification of karanja and jatropha oil." *RSC Advances* 5.58 (2015): 46890-46896.
7. Canakci, Mustafa. "The potential of restaurant waste lipids as biodiesel feedstocks." *Bioresource technology* 98.1 (2007): 183-190.
8. Chen, Yi-Hung, et al. "Biodiesel production from tung (Vernicia montana) oil and its blending properties in different fatty acid compositions." *Bioresource Technology* 101.24 (2010): 9521-9526.
9. Hu, Shengyang, et al. "Gas–liquid countercurrent integration process for continuous biodiesel production using a microporous solid base KF/CaO as catalyst." *Bioresource technology* 123 (2012): 413-418.

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