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Optimization of Process Parameters to Enhance the Yield of Biodiesel by using Heterogeneous Catalyst

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Abstract : Depletion of fossil fuel resources and raising demand for fuels are the major drives for the research on alternative fuels. Biodiesel produced from vegetable oils is one of renewable fuel which fulfils most of the requirements. Conventionally, biodiesel is produced by transesterification of vegetable oil with methanol in the presence of alkali catalyst. Homogeneous base catalyst processes suffer from several drawbacks and disadvantages. The problem can be overcome by the use of heterogeneous catalyst. Washing process is not required using heterogeneous catalyst during biodiesel production which deducts the use of wash water and also the catalyst can be regenerated and so has very low wastage. The glycerine obtained from heterogeneous catalyst is also of very high purity. So in this work the biodiesel produced by homogenous catalyst was compared with the heterogeneous catalyst such as TiO2, CaO and CaO nano particle impregnated on zeolite. The percentage conversion is similar for CaO nano partice and KOH homogeneous catalyst.
Keywords: Biodiesel, transesterification, Nanoparticle, Catalyst.

Introduction

Today we are living in a world which is facing an acute energy crisis[1]. To meet the demand and supply deficit we have to switch from non-renewable energy sources to alternative and renewable energy resources [2]. The major advantages of the biomass-derived fuels are their renewability, biodegradability, non-toxicity and low emissions. Due to this, synthesis of biofuels and biochemicals from non-food crops and non-edible oils is getting more attention especially in the developing countries. Biodiesel is alternative energy source for petroleum diesel due to its nontoxicity, environmentally safe, and biodegradability[3,4]. Biodiesel is a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. The use of biodiesel in conventional diesel engines results in substantial reduction in emission of unburnt hydrocarbons, carbon monoxide, and particulate[5, 6]. Fatty acid methyl/ethyl esters, commonly referred to as biodiesel, are promising candidate as alternative diesel fuel. The name biodiesel has been given to transesterified vegetable oil to describe its use as a diesel fuel and renewable nature. Biodiesel can be produced from a variety of sources such as vegetable oils and animal fats as well as waste cooking oil[7-9]. It can be produced either by transesterification of triglycerides or by esterification of fatty acids with low molecular weight alcohols. Biodiesel possess viscosity much closer to that of petrodiesel and can be used in diesel engine without any modification in the engine[10 - 12]**.** Esters of higher alcohols with fatty acids can be used as biolubricants [13]. This fuel is biodegradable and non-toxic and has low emission profiles than petroleum diesel. Biodiesel is miscible with petrodiesel in all proportions and can be used as such or mixed with petroleum diesel for direct application in diesel engines[14]. In the case, when biodiesel is blended with petroleum diesel, it is represented as BX, where X is the percentage of biodiesel[15].

Materials and Methods

Materials

Waste cooking oil obtained from local restaurant as a source of triglycerides for transesterification reaction. Oil sample was characterized to measure the physical and chemical characteristics that affect the ability of feedstock to be used for biodiesel production such as acid value, free fatty acid content, saponification value, flash point, fire point and viscosity based on ASTM methods[16]. All catalysts and chemicals are of analytical grade and are of high purity.

Catalyst

The heterogeneous catalyst used for the study was calcium oxide, Titanium dioxide and calcium oxide nano-particle. The Nano catalyst was prepared by using sodium hydroxide, ethyl glycol and hydrated calcium nitrate[17-19]. 1g of sodium hydroxide is dissolved in ethyl glycol and hydrated calcium nitrate. The mixture is stirred at room temperature then the mixture is left in static condition for the time period of 5 hours. The solution is washed with water and the particles are separated by using Grade 1 Whattman filter paper. The obtained particles are dried until the moisture is removed then it is calcinated at the temperature of 700°C. The calcium nano particle is then impregnated on the surface of zeolite. Both zeolite and calcium nano particle is mixed together using ethanol and the impregnation is done by using ultrasonification[20, 21].

Transesterification

Transesterification is one of the methods for the production of biodiesel[22]. In this reaction, a fat or triglyceride reacts with three moles of alcohol to give three moles fatty acid alkyl ester (biodiesel) and one mole of glycerol as the by-product. The most common alcohol used for biodiesel preparation is methanol as it is the least expensive alcohol. As base catalyst is used for transesterification reaction, fats and oil used for it must be free from fatty acids. Transesterification reaction was carried out at 60-70°C and at the atmospheric pressure. As the boiling point of methanol is 65^{0}C, therefore, to avoid evaporation losses of methanol by addition to the heated oil, preheating of oil was done upto 60°C[23]. The reaction time was considered from the point of addition of alcoholic solution of catalyst to the heated oil. After the completion of the reaction time, the reaction mixture was allowed to cool down and transferred to the separating funnel for separation of phases**.** The upper phase consisted of methyl esters, and the lower phase consists of the glycerol, excess alcohol, and the catalyst. The upper methyl esters layer was washed with the warm water in order to remove excess alcohol and catalyst [24]. For heterogeneous catalyst the fixed amount of catalyst (15% by wt) is added to requisite amount of methanol (**Figure 1**).

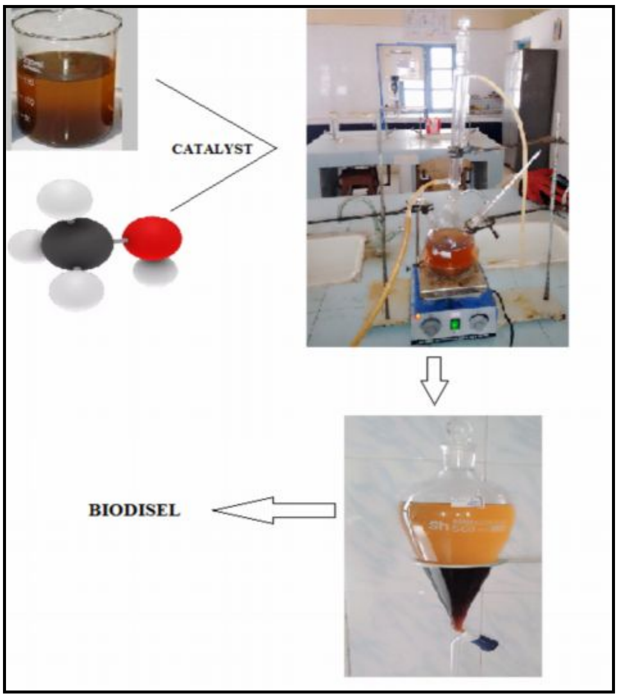

Figure 1 Experimental setup for transesterification reaction.

Results and Discussion

The variation of yield was depending on temperature. At lower temperature the yield is not much higher but with increase in temperature the yield was increases [25, 26]. Further rise in temperature beyond 70°C the yield decreases due to evaporation loss of alcohol.

Three different heterogeneous catalyst has been used for transesterification are titanium dioxide (TiO_2), calcium oxide (CaO), calcium oxide nano particle impregnated on zeolite. While using titanium dioxide as heterogeneous catalyst the transesterification reaction was carried out but the result was not satisfactory. The product obtained using titanium dioxide is not pure form and difficult for separation. So the other two heterogeneous catalysts were used for further studies. After the reaction time was completed the reaction mixture is allowed to cool and separated into two phases. After separation of the phases the glycerol and heterogeneous catalyst is taken and catalyst can be regenerated and reuse for further process. There are several advantages of using heterogeneous catalyst, it does not require the washing steps and also the heterogeneous catalyst can be regenerated and it can be reused[27 - 29].

Firstly the reaction was carried out by taking 6:1 methanol to oil ratio for the reaction time of 2 hours, similarly the transesterification was performed with the same methanol to oil ratio for 4 hours and 6 hours. The results obtained by all the three reactions were not satisfactory. In the second set of the experiment the methanol to oil ratio is taken as 9:1. The transesterification was performed for 2 hours, 4 hours and 6 hours. In this set of experiment the yield increased with increase in time. The maximum yield was obtained at the reaction time of 6 hours. **Table 1** shows the %conversion of the biodiesel at different reaction time and 9:1 methanol to oil ratio by using CaO and CaO nano particle impregnated on zeolite. In the third set of experiment the oil to methanol ratio was 10:1 and the transesterification reaction was performed for the reaction time of 2 hours, 4 hours and 6 hours. Out of the three reaction time and methanol to oil ratio, the maximum conversion was obtained by reaction time of 6 hours and 9:1 methanol to oil ratio.

Table 1 Percentage Conversion for various process conditions

Catalyst	Volume of Waste Cooking Oil (mL)	Time (h)	Weight percentage of Catalyst (%)	Methanol to oil ratio	Volume of Biodiesel obtained (mL)	Conversion (%)
CaO	500	2	15	9:1	225	45
	500	4	15	9:1	285	57
	500	6	15	9:1	375	75
CaO-NP impregenated on Zeolite	500	2	15	9:1	275	55
	500	4	15	9:1	380	76
	500	6	15	9:1	485	97

Kinetic Studies

Due to complex composition of feedstocks, only a few non-catalytic transesterification kinetics studies have been investigated[30-33]. The reaction rate constants were determined, and the effect of other reaction parameters was investigated such as molar ratio of alcohol to oil, temperature, catalyst type and concentration (21). The biodiesel extraction by transesterification using various base catalysts followed the first order reaction and the relationship between rate constant and concentration has been obtained by plotting graph between $\ln C_{A0}/C_A$ versus time (22 - 25). From the slope rate constant can be calculated as $0.230h^{-1}$ for CaO catalyst and $0.503h^{-1}$ for CaO nanoparticle catalyst impregnated on zeolite (**Figure 2**). The SEM image confirm the CaO nanoparticle was impregnated on zeolite (**Figure 3**)

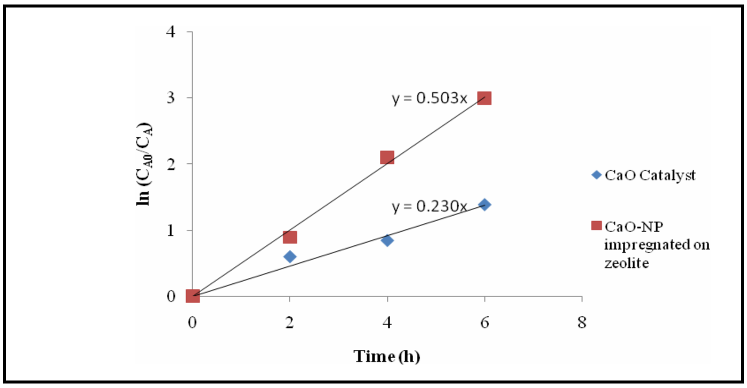

Figure 2 First order reaction kinetics.

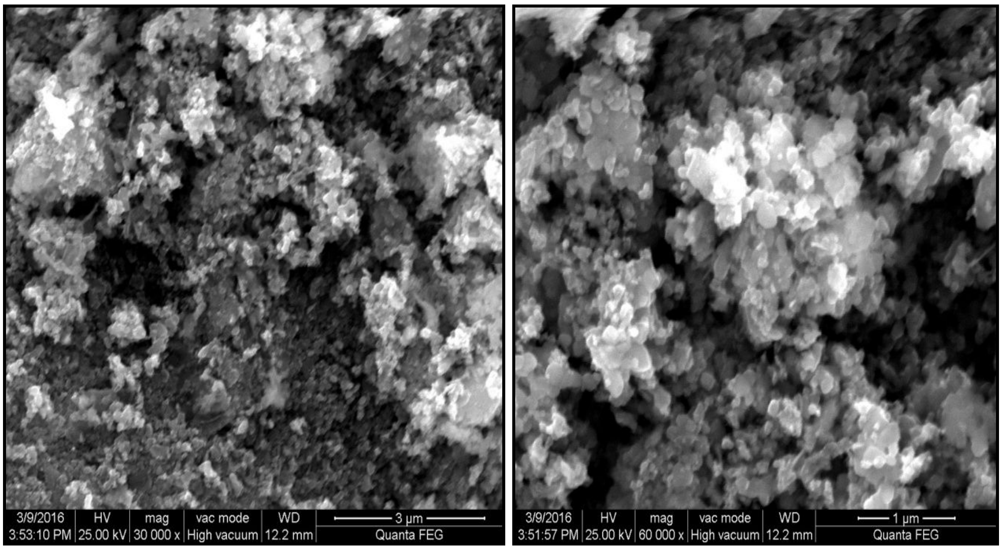

Figure 3 SEM image of CaO nanoparticle catalyst impregnated on zeolite.

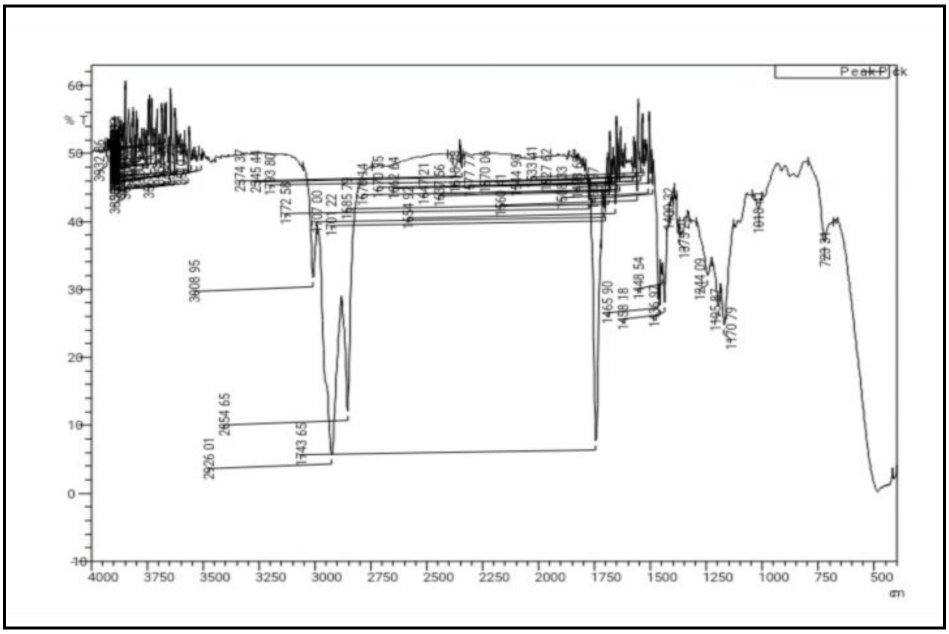

Figure 4 FTIR spectra of biodiesel obtained by using CaO nano particle impregnated on zeolite.

Ftir Analysis

The presence of esters in the biodiesel was confirmed with the help of FTIR analysis which was shown in **Figure 4**. An ester with the characteristic absorptions at 1743 cm^{-1} for C=O stretch and 2926 cm^{-1} for $–CH_2$ stretch and 1119 cm^{-1}, 1249 cm^{-1} for –C–O– stretch. The characteristic of biodiesel obtained from CaO nanoparticle catalyst impregnated on zeolite was compared with KOH homogeneous catalyst (**Table 2**).

Table 2 Characteristics of biodiesel

Catalyst	Density	Kinematic Viscosity	Flash point	Fire point	Calorific Value
	kg/m^3	cm^2/s	°C	°C	kJ/kg
KOH	918.68	0.139	142	146	41345
CaO-NP	946.73	0.149	153	158	40879

Conclusion

The transesterification reaction using heterogeneous catalyst was carried out and optimization has been carried out at different reaction time and methanol to oil ratio. The maximum conversion was obtained by reaction time of 6 hours and 9:1 methanol to oil ratio. Among the heterogeneous catalyst titanium dioxide (TiO_2), calcium oxide (CaO), calcium oxide nano particle impregnated on zeolite the result obtained for TiO2 was not satisfactory. The percentage conversion of biodiesel using CaO catalyst was 75% & that of CaO nano particle impregnated on zeolite is found out to be 97.1%. Advantage of the heterogeneous catalyst over homogeneous catalyst was virtually no waste is generated; the process setup is simple as there are no purification steps. In the heterogeneous process glycerin is directly produced with high purity, the operating costs and environmental impacts associated with the investment in the distillation unit and refining process are reduced. These results show that the heterogeneous catalyst is the effective catalyst for the manufacture of biodiesel.

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