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Optimization of transesterification process for biodiesel production from waste oil

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Abstract

Biodiesel, which is considered as a possible substitute of conventional diesel fuel, is vegetable oils by transesterification with methanol. The resulting Biodiesel is quite similar to conventional diesel fuel in its main characteristics. Direct usage of these triglyceric esters (oils) is unsatisfactory and impractical for long term usages in the available diesel engines due to high viscosity, acid contamination, and free fatty acid formation resulting in gum formation by oxidation and polymerization and carbon deposition. In the transesterification of different types of oils, triglycerides react with an alcohol, generally methanol or ethanol to produce esters and glycerol. To make it possible a catalyst is added to the reaction**.** The present investigation was carried out to study the waste oil transesterification by using alkali (NaOH) as a catalyst and 85% esters (biodiesel) conversion was obtained.

Key-Words: Biodiesel, Transesterification, Alkali, Waste oil

Introduction

Majority of the worlds energy needs are supplied through petrochemical sources, coal and natural gases, with the exception of hydroelectricity and nuclear energy, of all, these sources are finite and at current usage rates will be consumed shortly[1]. The high energy demand in the industrialized world as well as in the domestic sector and pollution problems caused due to the widespread use of fossil fuels make it increasingly necessary to develop the renewable energy sources of limitless duration and smaller environmental impact than the traditional one. This has stimulated recent interest in alternative sources for petroleum-based fuels. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available. One possible alternative to fossil fuel is the use of oils of plant origin like vegetable oils and tree borne oil seeds. This alternative diesel fuel can be termed as biodiesel[2].

Biodiesel is a biodegradable, nontoxic, and clean renewable fuel with properties similar to conventional diesel. It is produced from renewable resources, and has low emission profiles. So it is environmentally beneficial. However the cost of biodiesel is high due to the high cost of raw material (about 70–75% of the total cost).

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So biodiesel is still not commonly used in daily life mostly due to the high production cost involved, though this fuel has been developed for about three decades[3, 4]. A cheaper raw material for biodiesel production could be a solution. The raw materials for biodiesel production now mainly include biological sources such as vegetable seed oil, soybean oil and some recovered animal fats [5, 6].

Vegetable oil methyl esters, commonly referred to as ''biodiesel,'' are prominent candidates as alternative diesel fuels. The name biodiesel has been given to transesterified vegetable oil to describe its use as a diesel fuel[7, 8]. There has been renewed interest in use of vegetable oils for making biodiesel due to its less polluting and renewable nature as against the conventional diesel, which is a fossil fuel leading to a potential exhaustion[9]. Biodiesel is technically competitive with or offer technical advantages compared to conventional petroleum diesel fuel. The vegetable oils can be converted to their methyl esters via transesterification process in the presence of catalyst. Methyl, ethyl, 2-propyl and butyl esters were prepared from vegetable oils through transesterification using potassium and/or sodium alkoxides as catalysts. The purpose of the transesterification process is to lower the viscosity of the oil. Ideally, transesterification is potentially a less expensive way of transforming the large, branched molecular structure of the bio-oils into smaller, straight chain molecules of the type required in regular diesel combustion engines[10].

The most important variables affecting the methyl ester yield during the transesterification reaction are molar ratio of alcohol to vegetable oil and reaction temperature. Biodiesel has become more attractive recently because of its environmental benefits. The viscosity values of vegetable oils are between 27.2 and 53.6mm2/s whereas those of vegetable oil methyl esters are between 3.59 and 4.63mm2/s [11, 12]. The flash point values of vegetable oil methyl esters are highly lower than those of vegetable oils. Biodiesel is an environmentally friendly fuel that can be used in any diesel engine without modification.

Waste refining oil, which is a by-product in vegetable oil refining, mainly contains free fatty acids (FFAs) and acylglycerols, and is a candidate of material for Biodiesel fuel. In order to provide Fatty Acid Methyl Esters (FAMEs) at a reasonable price, production of FAMEs not only from refined vegetable oils, but also from crude or waste material and from by-products of oil processing has been attempted; one of the materials is acid oil. It is reproduced currently as industrial FFAs, although their demand is almost in saturation. Conversion of the acid oil to Biodiesel fuel is thus expected to avoid oversupply of the industrial FFAs and their price down [13, 14].

Material and Methods

Vegetable oil primarily contains triglycerides and their chemical structure is significantly different from that of mineral diesel. Transesterification is an efficient method to convert high viscosity vegetable oil into a fuel with chemical properties similar to those of mineral diesel. Waste (by-product of oil processing) oil was procured for the present investigation and base catalyzed transesterification (NaOH) was used to prepare Biodiesel from waste oil. Methanol (Merck) of 99.5% purity was used. Washing of the biodiesel was also performed to remove impurities.

Washing of oil

Firstly the pretreatment of the waste oil was performed by washing. 1 litre of waste oil was mixed with 1 litre of water, shaken properly and mixture was allowed in separating funnel. Impurities dissolved with water, settled down in the lower layer or bottom of the separating funnel and oil sample must be in the upper layer of separating funnel. Little quantity of calcium carbonate was added to separate left water and other impurities from waste oil.

Filtration and heating of oil

Waste oil is filtered to remove dirt, charred food and other non-oil material often found. Water is removed because its presence causes the triglycerides to hydrolyze to give salts of the fatty acids instead of undergoing transesterification to Biodiesel. This is often accomplished by heating the filtered oil to approximately 120^0C.

Neutralization of the free fatty acids (Titration)

A sample of the cleaned oil is titrated against a standard solution of base in order to determine the concentration of free fatty acids (RCOOH) present in the waste oil.

Transesterification process

One-step alkali base catalyzed transesterification

Firstly, in the transesterification process, different catalyst NaOH-to-oil ratios (0.5%-10% w/v) and different waste oil-methanol ratios (1:1, 1:2, 1:3, 1:4, 1:5 and 1:6 v/v) were used to investigate their influence on the methyl ester yields of the oils. All the reactions were carried out in the reaction glass tubes, which were immersed in a glass water bath placed on the plate of magnetic stirrer of 400 rpm. The temperature and the reaction time for all process were maintained at 55 ± 1^0C and for 2 h., respectively. After the reaction, the mixture was allowed to settle for 2 h.-overnight before separating the glycerol layer and the top layer including methyl ester fraction was removed in a separated bottles. The same procedure was conducted for the investigation of optimum reaction temperature and reaction time.

Two-step acid-base catalyzed transesterification

Acid pretreatment: On this step, the waste vegetable oil was poured into the reaction glass tubes and heated. The solution of concentration H_2SO_4 acid (1.0% based on the oil weight) in methanol was heated at 55 ± 1^OC and then added into the reaction glass tubes. Different methanol to oil ratios by weight were used, namely at 1:1, 2:1, 3:1, 4:1, 5:1, 6:1 were investigate their/influence on the acid value of waste vegetable oil. After one hour of reaction, the mixture was allowed to settle for 2 h and the methanol–water fraction at the top layer was removed. The optimum condition having the lowest acid value was used for the main transesterification reaction.

Base catalyzed transesterification: In the second step, optimum condition for NaOH to oil ratio and methanol to oil ratio were investigated. Firstly, the oil product that has been pretreated from the first step was poured into the reaction glass tubes and heated at 55 ± 1^OC. The solution of NaOH in methanol at 0.5%-10% v/v of the oil were heated to 55 ± 1^OC prior to addition and then added to the heated oil. The reaction mixture was heated and stirred again at 55 ± 1^OC and 400 rpm for 2 h. The mixture was allowed to settle 2 h or overnight before separate the glycerol layer to get the methyl ester layer of fatty acids on the top.The same procedure was conducted for the investigation of optimum methanol to oil ratio, reaction temperature and reaction time.

Results and Discussion

Transesterification process

For the maximum conversion of oil to methyl esters by transesterification from waste oil optimum methanol to waste oil ratio (v/v) 4:1, 8% of NaOH concentration, 55 ± 1^0C reaction temperature and 8 hours reaction time were selected and 80/20% (Biodiesel/glycerol) conversion was obtained. After gravity separation of the glycerol water washing of Biodiesel was performed in order to remove the impurities present in the product. If they are not removed, it may cause problem during storage and can damage the fuel system and other components of the engine.

Variables Affecting Transesterification reactions There are various parameters, which affected the transesterification reaction:

Catalyst Concentration

The effect of NaOH concentration was studied in the range of 0.5%-10% (weight of NaOH/Volume of oil). The reaction temperature and reaction time were kept constant. The results for different catalyst concentration are shown in table-1. It was found that the ester yield decreases as the amount of catalyst increased from 8% for Waste oil and reduces the almost 50% of yields of methyl esters. This lesser yield at high NaOH concentration may possibly be due to soap formation. These viscosities first decrease up to 2.5% NaOH concentrations and after that it is almost constant. Excess NaOH reduces the yield and leads to undesirable extra processing cost because it is necessary to remove it from the reaction products at the end.

Molar ratio of Methanol to waste oil

One of the most parameter affecting the yield of esters is the molar ratio of Methanol to oil. Methanol was used in the range of 1:1 to 5:1 (molar ratio of methanol to oil), keeping other parameters fixed. The reaction temperature was kept constant at 55 ± 1^0C, and reaction was performed with for 6-8h. The reaction was performed with different concentrations of NaOH. The results are shown in table-2. The max. conversion was obtained at the ratio of 4:1, methanol to oil ratio for base catalyzed transesterification oil of waste oil. The reason behind using 4:1 ratio of methanol to oil rather than 3:1 for max. conversion, was that excess quantity of alcohol or methanol is required to 'drives' the reaction closer to the 99.7% yield, we need to meet the total glycerol standard for fuel grade biodiesel. In the range of 1:1 and 2:1 ratio of methanol to oil, no conversion was obtained because transesterification requires 3 mol of methanol per mole of triglyceride to give 3 moles of fatty esters and 1 mole of glycerol. It was observed that the ester yield increases with increase in molar ratio of methanol to waste oil, and for low values of molar ratio the ester yield was sensitive to the concentration of NaOH.

Reaction Temperature

Reaction temperature is also an important variable that affected the transesterification reaction. For studding the effect of reaction temperature on the transesterification reaction, the reaction temperature was varied as 35, 40, 50, 55, and 60^oC, while the other parameters such as molar ratio of methanol and NaOH concentration were kept constant. It was found that the ester yield increases as the reaction temperature increases till the 55 ± 1^0C and then ester yield decrease as the reaction temperature increases above 55 ± 1^0C. The optimum conversion was obtained at 55 ± 1^0C. The reason behind the maximum conversion obtained at 55 ± 1^0C reaction temperature was that the transesterification reaction be a positive manner decrease in ester yield above 55 ± 1^0C is due to a negative interaction between the temperature and catalyst concentration due to the side reaction of Saponification. The results are shown in table 3.

Reaction Time

Reaction time is also an important variable that affect the reaction very much. It was observed that the ester yield increases as the reaction time increases. Reaction starts very fast and almost $80^{\%}$ of the conversion takes place in first 5 minute and after 1 hour almost 90- 93% conversion of triglycerides into esters takes place but it take 6-8 hours in finishing. The results are shown in table-4.

For Biodiesel production from waste oil by alkali catalyzed reaction it was found that this is a very good process of production with relatively high conversion. Under optimum conditions Fatty acid methyl esters yield from waste oil was 80% in one-step alkali-base catalyzed reaction. And for two-step acid–base catalyzed reaction 85% Biodiesel conversion was obtained. Transesterification reaction parameters control the yield of ester while catalyst removal is required for purification of the ester to make it suitable fuel for diesel engines. Pyrolysis and Microemulsion process are not satisfactory and hence only the transesterification process is accepted for large scale production of biodiesel from waste oil.

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Table 1: Estimation of NaOH Concentration for Transesterification reaction

Types of sample	**Biodiesel conversion at different concentration of NaOH**														
	0.5 %	1 %	1.5 %	2 %	2.5%	3%	3.5 %	4%	4.5 %	5%	6.0 %	7.0 %	8.0 %	9%	10 %
Waste oil-(One step)	0%	0 %	0%	0 %	0%	25 %	30%	35 %	40%	45 %	55%	70%	80%	70 %	65 %
Waste oil-(Two step)	0%	0 %	0%	0 %	0%	30 %	35%	40 %	45%	50 %	60%	75%	85%	75 %	60 %

Table 2: Effect of Molar ratio of methanol to waste oil on Transesterification

S. No.	**Sample**	**Biodiesel conversion at different Methanol-oil ratio (MEAN±SEM)**					
		1:1	**2:1**	**3:1**	**4:1**	**5:1**	**6:1**
1.	Waste Oil (One- step)	0±0.0	0±0.0	40%±0.52	75%±43	75%±0.42	75%±0.49
2.	Waste Oil (Two- step)	0±0.0	0±0.0	50%±0.56	80%±32	80%±0.46	80%±0.53

Table 3: Effect of Reaction Temperature on Transesterification

S.No.	**Sample**	**Biodiesel conversion at different temperature (MEAN±SEM)**					
		35 °C	**40 °C**	**45 °C**	**50 °C**	**55 °C**	**60 °C**
1.	Waste Oil (One- step)	0±0.0%	45%±0.24	50%±0.15	70%±0.25	80%±0.18	70%±0.41
2.	Waste Oil (Two- step)	0±0.0%	50%±0.42	60%±0.14	75%±0.15	85%±0.24	75%±0.21

Table 4: Effect of Reaction Time on Transesterification

S.No.	**Sample**	**Biodiesel conversion at different reaction time (MEAN±SEM)**				
		1h.	**2h.**	**4h.**	**6h.**	**8h.**
1.	Waste Oil (One- step)	25%±0.24	45%±0.25	75%±0.43	100%±0.16	100%±0.24
2.	Waste Oil (Two- step)	28%±0.14	48%±0.35	77%±0.36	100%±0.62	100%±0.18