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Prospects of Biodiesel production by Alkali-based transesterification from *Jatropha curcas* and waste oil

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Abstract

The increasing industrialization and motorization of the world has led to step rise for the demand of petroleum based fuels. Petroleum based fuels are obtained from limited reserves. These finite reserves are highly concentrated in certain regions of the world. So the scarity of known petroleum reserves will make renewable energy resources more attractive. The most feasible way to meet this growing demand is by utilizing alternative fuels. Biodiesel is defined as the monoalkyl esters of vegetable oils or animals fats. Biodiesel is the best candidates for diesel fuels in diesel engines. The biggest advantage that biodiesel has over gasoline and petroleum diesel is its environmental friendliness. Biodiesel probably has better efficiency than gasoline. Biodiesel is now mainly being produced from oils like soybean, rapeseed, palm oils and also from non edible oils obtained from plant species such as *Jatropha curcas* (Ratanjot), *Pangamia pinnat*a (Karanj), *Chlorophytum inophyllum* (Nagchampta) etc. Vegetable oils have to undergo the process of transesterification to be usable in internal combustion engines. Transesterification is the reaction of a fat or oil with an alcohol to form esters and glycerols.

Key-Words: Biodiesel, Oils, Transesterification, Fuels

Introduction

Biodiesel is an eco-friendly, alternative diesel fuel prepared from domestic renewable resources i.e. vegetable oils (edible or non- edible oil) and animal fats. These natural oils and fats are made up mainly of triglycerides. These triglycerides when reacted chemically with lower alcohols in presence of a catalyst result in fatty acid esters. These esters show striking similarity to petroleum derived diesel and are called "Biodiesel". As India is deficient in edible oils, non-edible oil may be material of choice for producing bio diesel. For this purpose Jatropha curcas considered as most potential source for it. Bio diesel is produced by transesterification of oil obtains from the plant[1]. Biodiesel production is a very modern and technological area for researchers due to the relevance that it is winning everyday because of increase in the petroleum price and the environmental advantages[2]. The idea of biodiesel is not new. Infact Rudolf Diesel investigated the significance of bio -fuels back in the 19th century stating, "The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in the course of time, as important as petroleum and the coal for products of the present time"[3]. 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[4]. 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[5].

Biodiesel is a biodegradable, nontoxic, and clean renewable fuel with properties similar to conventional diesel. It is produced from renewable resources, and

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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). 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[6, 7]. 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 [8, 9].

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[10, 11]. 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[12]. 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[13].

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 [14]. 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[15].

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 [16].

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.

In the present research, base catalyzed transesterification (NaOH) is used to prepare Biodiesel from *Jatropha curcas* oil (JCO) and 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: For one-step transesterification 1 litre of JCO was heated to 65^0C in a round bottom flask. Catalyst (NaOH- 0.5 to 10% w/w) was dissolved in methanol (1:1 to 6:1 v/v- methanol to oil ratio) and was poured into the round bottom flask containing the heated JCO while stirring the mixture continuously. A temperature of 55 ± 1^0 was maintained for 1 hour and reaction products were allowed to settle under gravity for 6-8 hour in a separating funnel. The product of the transesterification process i.e. waste oil methyl ester

was present in the upper layer and glycerol was in the lower layer of separating funnel respectively. The bottom layer of glycerol was removed and upper layer was mixed with distilled water to remove impurities like unreacted methanol, unreacted oil and catalyst. The mixture was again allowed to settle under gravity for 6h and lower layer of water containing impurities was drained out. This process investigation was conducted for the optimization of reaction temperature, reaction time, molar ratio of alcohol to oil and catalyst on the ester yield as well as conversion process. Reaction temperature was varied from 35-60^{0}C, catalyst concentration was studied in the range of 0.5-10%, reaction time was observed for 1 h to 8h.

Two-step: For two-step acid-base catalyzed transesterification we performed Acid pretreatment firstly then also performed 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^{O}C 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^{O}C. The solution of NaOH in methanol at 0.5%-10% v/v of the oil were heated to 55±1^{O}C prior to addition and then added to the heated oil. The reaction mixture was heated and stirred again at 55±1^{O}C 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. Similar methods were performed to obtain Biodiesel from waste oil. Combine results are shown in tables.

Results and Discussion

For the maximum conversion of oil to methyl esters by transesterification from JCO/waste oil, optimum methanol to waste oil ratio (v/v) 4:1/4:1, 4/8% of NaOH concentration, 55±1^{0}C reaction temperature and 6/8 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 reaction

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 graph-1. It was found that the ester yield decreases as the amount of catalyst increased from 4% for JCO and 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 JCO and 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^{0}C, and reaction was performed with for 6-8h. The reaction was performed with different concentrations of NaOH. The results are shown in graph-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^{o}C, 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^{0}C and then ester yield decrease as the reaction temperature increases above 55±1^{0}C. The optimum conversion was obtained at 55±1^{0}C. The reason behind the maximum conversion obtained at 55±1^{0}C reaction temperature was that the transesterification reaction be a positive manner decrease in ester yield above 55±1^{0}C is due to a negative interaction between the temperature and catalyst concentration due to the side reaction of Saponification. The results are shown in graphs-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 graph-4.

Conclusion

The focus of the investigation carried during this work was oriented towards the conversion of high viscous oils to Biodiesel or Fatty acid methyl esters. Oils can be used as diesel fuel but due to high viscosity they cause many problems like poor atomization, incomplete combustion, leading to heavy smoke emissions and high flash point of oil attributes to lower volatility characteristics. For Biodiesel production from JCO and 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 JCO was 85% in one-step alkali-base catalyzed reaction. For two-step acid–base catalyzed reaction 90% Biodiesel conversion was obtained. Likely 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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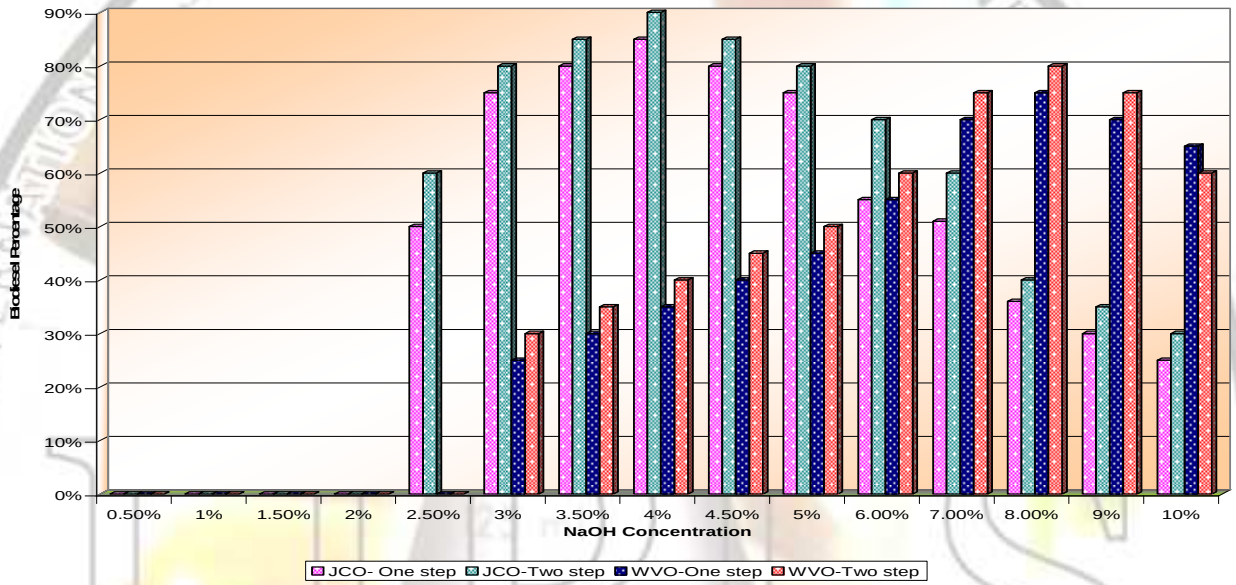
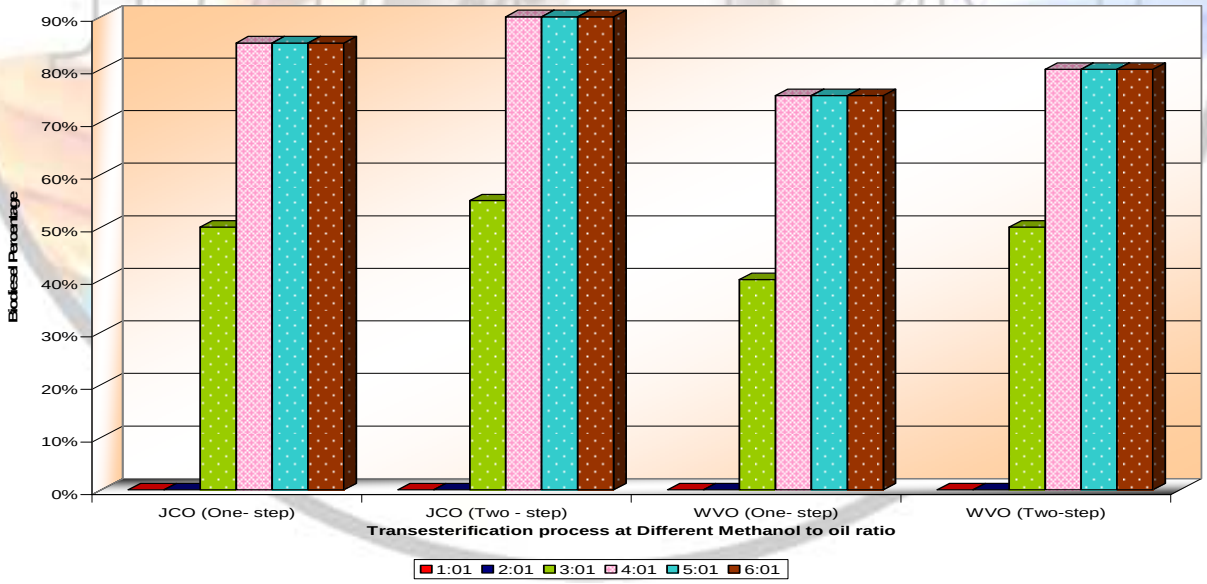
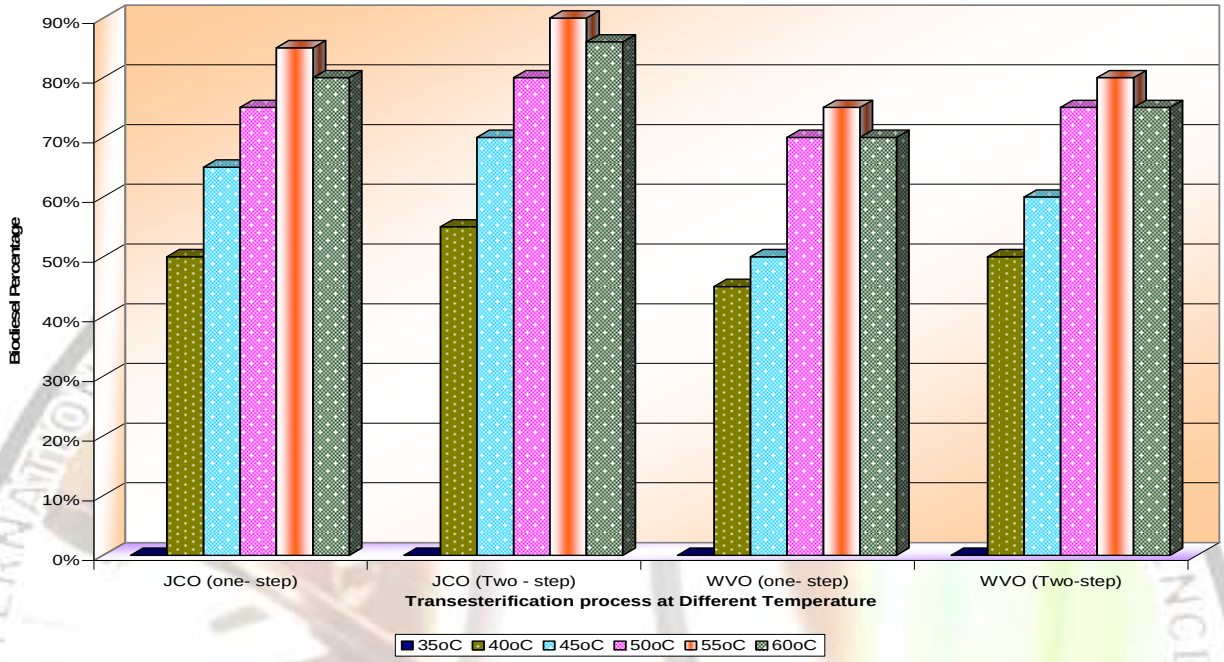


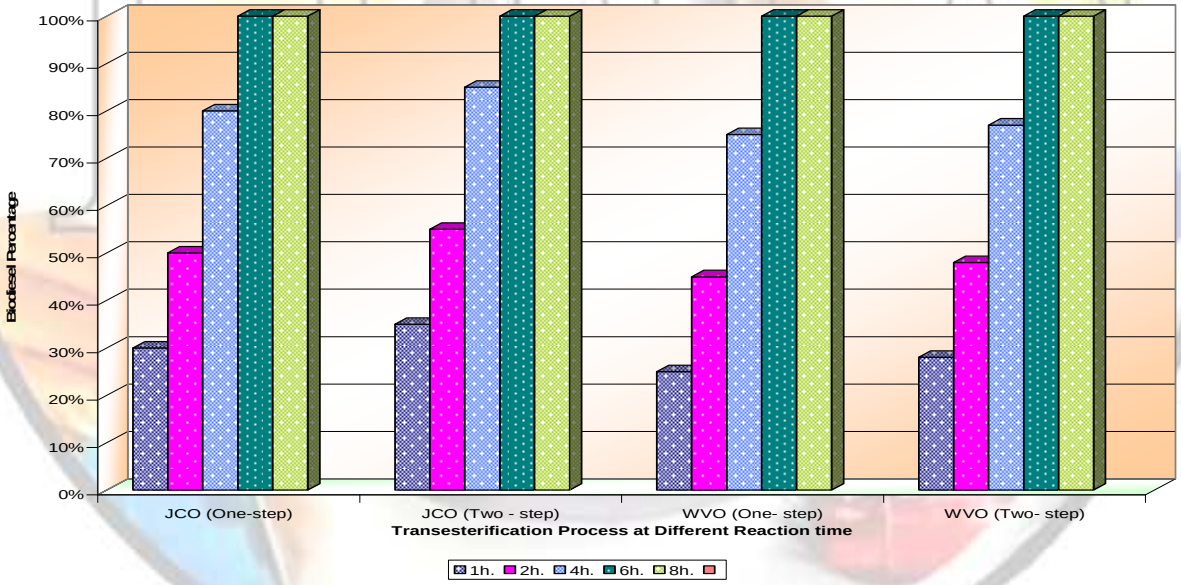
Graph 1: Estimation of NaOH Concentration for Transesterification reaction



Graph 2: Effect of Molar ratio of methanol to oil on Transesterification



Graph 3: Effect of Reaction Temperature on Transesterification



Graph 4: Effect of Reaction Time on Transesterification