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Review Article

# Optimization of Biodiesel Production Methods: A Review

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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, petroleum, engines etc.

## Introduction

Biodiesel as an alternative fuel for diesel engines is becoming increasingly important due to diminishing petroleum reserves and the environmental consequences of exhaust gases from petroleum-fuelled engines. Biodiesel, is made from renewable sources, consists of the simple esters of fatty acids. As a future prospective fuel, biodiesel has to compete economically with petroleum diesel. One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids such as inedible oils, animal fats, waste food oil and byproducts of the refining vegetables oils [1

Biodiesel is appreciated as a future alternative of diesel fuel also due to its advantages in reducing the exhaust emission. The production costs are high, thus biodiesel receives government subsidiaries in order to compete on the markets with the petroleum-based fuel [2, 3].

Biodiesel production has received considerable attention in the recent past as a biodegradable and nonpolluting fuel. The production of Biodiesel by transesterification process employing catalyst has been industrially accepted for high compression and reaction rates [4].

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Biodiesel is made from the oils of various types of oilseed crops like sunflower, palm, cottonseed, rapeseed, soybean and peanut etc. [5]. The use of Biodiesel is almost as old as diesel engine. Rodulf Diesel patented his engine in 1982 and introduced the first diesel engine intended to run on vegetable oil. In 1900 he ran the engine on peanut oil for several hours successfully. In 1912 he predicted that in future the vegetable oil will be a fuel like diesel oil [6].

Microbial oils, otherwise referred to as single cell oils (SCO) produced by various microorganisms, are now believed as a potential feedstock for biodiesel production due to their specific characteristics such as they are not affected neither by seasons nor by climates, they own high lipid content, can be produced from a wide variety of sources with short period of production especially from the residues with abundant nutrition, and so on [7, 8]. The microbial oils, however, are mainly used as commercial sources of arachidonic acid (ARA) and docosahexaenoic acid (DHA) [9-11]. The research on microbial oils was focused on these polyunsaturated fatty acids (PUFAs) and related report that whether it could be used for biodiesel production was few. In addition, microbial oils must be absolutely safe if used as dietary supplements while microbial oils needed not when used for biodiesel production.

## METHODOLOGY FOR BIODIESEL PRODUCTION

There are atleast four ways in which oils and fats can be converted into Biodiesel, namely:

1. Blending.
2. Micro emulsion.
3. Pyrolysis and
4. Transesterification.

Transesterification being the most commonly used method [12, 13].

### 1. Blending:

The direct usage of vegetable oils as biodiesel is possible by blending is with conventional diesel fuels in a suitable ratio and these ester blends are stable for short-term usages. The blending process is simple which involves mixing alone and hence the equipment cost is low [12].

*Bio-fuels blending:*

"Utilizing the current petroleum distribution infrastructure, blending is typically carried out at the storage or loading terminal," reports Jon Denis of Enraf Fluid Technology. "The most common locations for blending are the storage tank, the load rack headers or most effectively at the load arm. The most important requirement for this process is the accurate volume measurement of each product. This can be done through sequential blending or ratio blending, but most beneficially utilizing the side-stream blending technique." Ethanol blended fuel contains properties that make this difficult. Ethanol, by nature, will attract any $H_2O$ encountered on route or found in storage tanks. If this were to happen in a 10% blend and the concentration of $H_2O$ in the blended fuel reaches 0.4%, the combined Ethanol and $H_2O$ drops out of the blend. The exact point of drop out depends on the Ethanol percentage, make-up and temperature. If this drop out occurs the Ethanol combines with the $H_2O$ and separates from the fuel, dropping to the bottom of the storage tank. The resulting blend goes out of specification and getting back to the correct specification requires sending the contaminated Ethanol back to the production plant.

**Disadvantages:**

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, free fatty acid formation resulting in gum formation by oxidation and polymerization and carbon deposition [13].

**2. Pyrolysis**

Pyrolysis refers to chemical change caused by application of heat to get simpler compounds from a complex compound. The process is also known as cracking. Vegetable oils can be cracked to reduce viscosity and improve cetane number. The products of cracking include alkanes, alkenes, and carboxylic acids. Soyabean oil, cottonseed oil, rapeseed oil and other oils are successfully cracked with appropriate catalysts to get biodiesel. By using this technique good flow characteristics were achieved due to reduction in viscosity.

**Disadvantages:**

Disadvantages of this process include:

I. High equipment cost and need for separate distillation equipment for separation of various fractions.
II. Another disadvantage is that also the product obtained was similar to gasoline containing sulfur, which makes it less eco-friendly [14].

**3. Microemulsion:**

Micro emulsification is another technique that has been reported to produce biodiesel and the components of a biodiesel microemulsion include diesel fuel, vegetable oil, alcohol, and surfactant and cetane improver in suitable proportions. Alcohols such as methanol, ethanol and propanol are used as viscosity lowering additives, higher alcohols are used as surfactants and alkyl nitrates are used as cetane improvers. Viscosity reduction, increase in cetane number and good spray characters encourage the usage of micro emulsions but prolong usage causes problems like injector needle sticking, carbon deposit formation and incomplete combustion ([15].

**Disadvantages:**

Alcohols such as methanol, ethanol and propanol, and alkyl nitrates are used in this process. Viscosity reduction increase in cetane number and good spray characters encourage the usage of Microemulsion but disadvantage of this is that prolong usage causes problems like- Injector needle sticking, carbon deposit formation and incomplete combustion [15].

**4. Transesterification:**

The most popular method of producing biodiesel is the transesterification of vegetable oils. Biodiesel obtained by transesterification process is a mixture of mono-alkyl esters of higher fatty acids. Transesterification is the alcoholysis of triglyceric esters resulting in a mixture of mono-alkyl esters and glycerol.

*Transesterification Process:*

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**.**

**$CH_2$ – OCOR1 | CH – OCOR2 | $CH_2$ – OCOR3 (Triglyceride) + 3 $CH_3OH$ (Methanol) → 3 $RCOOCH_3$ (Methyl ester) + $CH_2$ - OH | CH - OH | $CH_2$ - OH (Glycerol)**

The overall process is normally a sequence of three consecutive steps, which are reversible reactions. In the first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and of monoglycerides to glycerol, yielding one methyl ester molecule per mole of glyceride at each step [16].

Triglyceride + R'OH ⟶ Diglyceride + $R'COOR_1$

Diglyceride + R'OH ⟶ Monoglyceride + $R'COOR_2$

Monoglyceride + R'OH ⟶ Glycerol + $R'COOR_3$

**Base catalyzed Transesterification:**

For a basic catalyst, either sodium hydroxide (NaOH) or potassium hydroxide (KOH) should be used with methanol or ethanol as well as any kind of oils, refined, crude or frying. In this process, Alcoxy is formed by reaction of the catalyst with alcohol and then alcoxy is reacted with any vegetable oil to form Biodiesel and glycerol. The alcoxy reaction is given below:

$$R\text{-}CH_2OH + NaOH \longrightarrow H_2O + R\text{-}CH_2ONa$$

The alcohol-oil molar ratio that should be used varies from N=1:1- 6:1. However N= 6:1 is the most used ratio giving an important conversion for the alkali catalyst without using great amount of alcohol are usually methanol or ethanol. The oils used come from any vegetable, e.g. corn, canola, peanut, sunflower, soybean, olive, palm etc. The amount of catalyst that should be added to the reactor varies from 0.5% to 1% w/w [17]. The standard value for the reaction to take place is 60$^o$C, but depending on the type of catalyst different temperature s will give different degrees of conversion, and for that reason the temperature range should be from 25 to 120$^0$C [18, 19]. There may be risk of free acid or water contamination and soap formation is likely to take place, which makes the separation process difficult [20].

In the alkali catalytic methanol transesterification method, the catalyst (KOH or NaOH) is dissolved in methanol by vigorous stirring in a small reactor. The oil is transferred into the biodiesel reactor, and then, the catalyst/alcohol mixture is pumped into the oil. The final mixture is stirred vigorously for 2 h at 340 K in ambient pressure. A successful transesterification reaction produces two liquid phases: ester and crude glycerin. Crude glycerin, the heavier liquid, will collect at the bottom after several hours of settling. Phase separation can be observed within 10 min and can be complete within 2 h of settling. Complete settling can take as long as 20 h. After settling is complete, water is added at the rate of 5.5% by volume of the methyl ester of oil and then stirred for 5 min, and the glycerin is allowed to settle again. After that washing is done to get the clear ester layer [21].

The base catalyzed transesterification of vegetable oils proceeds faster than the acid catalyzed reaction. The first step is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic generates a tetrahedral intermediate from which the alkyl ester and the corresponding anion of the diglyceride are formed. The latter deprotonates the catalyst, thus regenerating the active species, which is now able to react with a second molecule of the alcohol, start another catalytic Cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol. Alkaline metal alkoxides (as $CH_3ONa$ for the methanolysis) are the most active catalysts, since they give very high yields (>98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol [22].

**Mechanism:**

Mechanism of alkali-catalyzed transesterification is given below –

- The first step involves the attack of the alkoxide ion to the carbonyl carbon of the triglyceride molecule, which results in the formation of a tetrahedral intermediate.
- The reaction of this intermediate with an alcohol produces the alkoxide ion in the second step.
- In the last step the rearrangement of the tetrahedral intermediate give rise to an esters.

**PRE STEP: -**

$$OH^- + ROH \rightleftharpoons RO^- + OH^- + H^+$$

OR

$$NaOR \rightleftharpoons RO^- + Na^+$$

***Acid catalyzed Transesterification:***

This way of production is second conventional way of making the Biodiesel. The idea is to use the triglycerides with alcohol and instead of a base to use an acid, the most commonly used is Sulfuric acid [23] and some authors prefer sulfonic acid this type of catalyst gives very high yield in esters but the reaction is very slow, requiring almost always more than one day to finish [24]. Freedman and Pryde get the desirable product with 1% of sulfuric acid with a molar ratio of 30:1 at 65$^0$C and they get 99% conversion in 50, while the Butanolysis will need 117$^o$C but the time should be 3 and 18 hours, respectively, As in alkali catalyst if an excess of alcohol is used in the experiment then better conversion of triglyceride is obtained, but recovery of glycerol become more difficult [25].The temperature range varies from 55 to 80$^o$C **.**The acid transesterification is a great way to make biodiesel if the sample has relatively high free fatty acids content. A kinetic modeling for soybean oil has been made by Freedman. He makes the kinetic with BuOH using a molar ratio of 30:1 with 1% $H_2SO_4$ at five different temperatures.

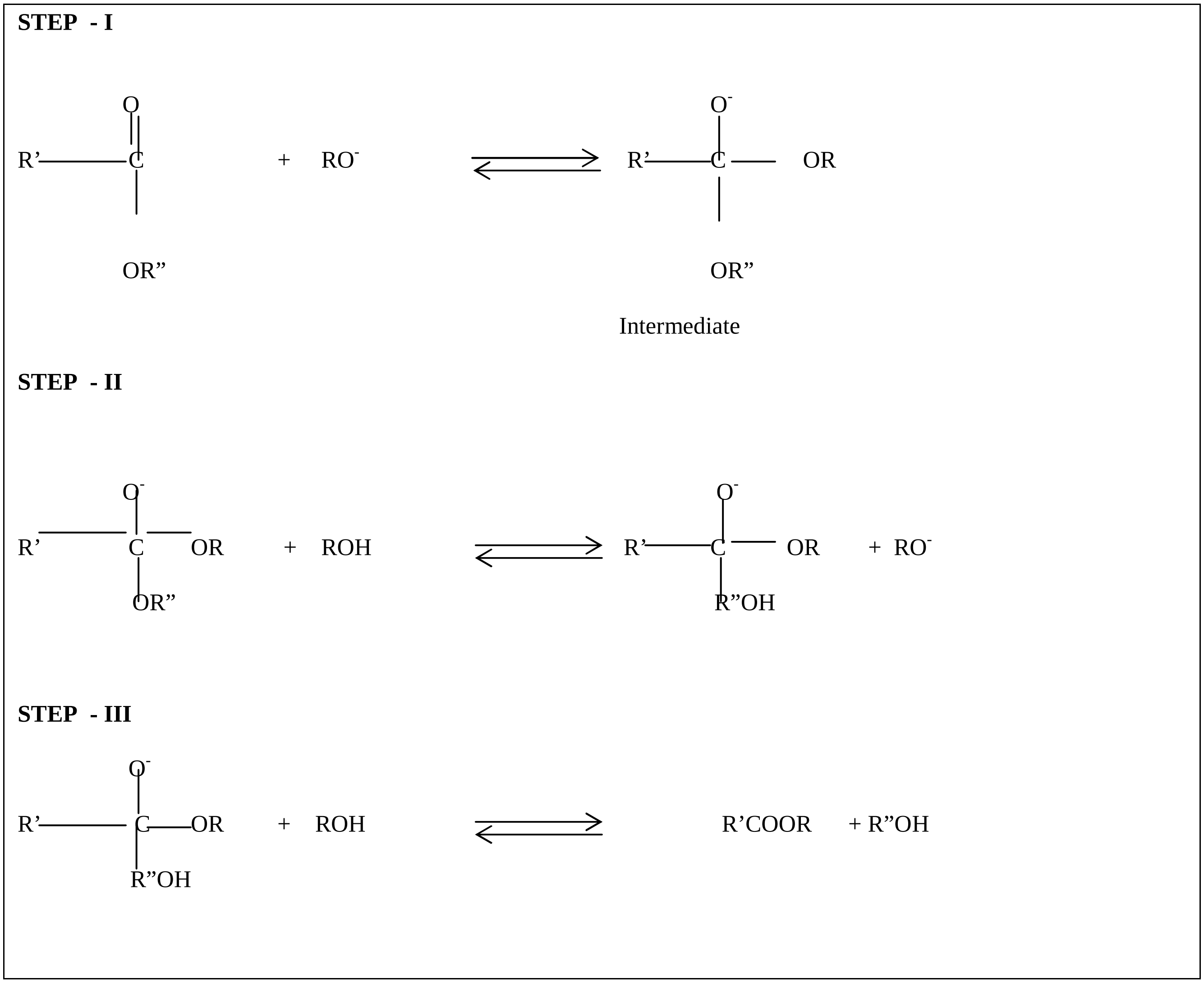
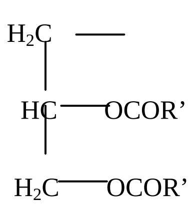



***Fig. 1: Mechanism of base catalyzed transesterification***

Where R” =

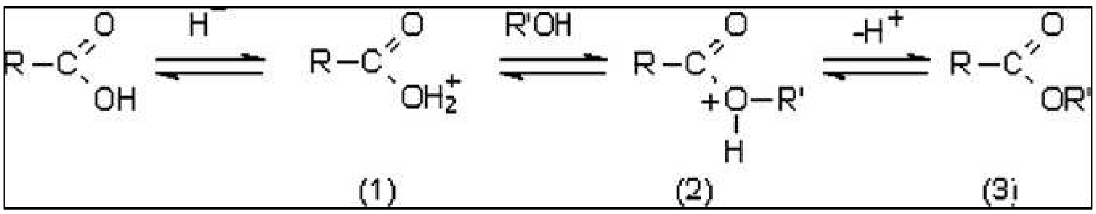



R’ = Carban Chain of fatty acids. R = Alkyl group of alcohol.

Bronsted acids catalyze the transesterification process, preferably by sulfon and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow. The alcohol/vegetable oil molar ratio is one of the main factors that influence the transesterification. An excess of the alcohol favors the formation of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so the ideal alcohol/oil ratio has to be established empirically, considering each individual process. Fig 2. Shows the mechanism of acid catalyzed esterification of fatty acids.

- The initial step is protonation of the acid to give an oxonium ion (1)
- Which can undergo an exchange reaction with an alcohol to give the intermediate (2)
- And this, in turn, can lose a proton to become an ester (3)

**Fig. 2: Mechanism of acid catalyzed esterification of fatty acids.**



Each step in the process is reversible, But in the presence of a large excess of the alcohol, the equilibrium point of the reaction is displaced so that esterification proceeds virtually to completion.

Next Fig 3 shows the transesterification of vegetable oils. In this instance, initial protonation of the ester is followed by

- Addition of the exchanging alcohol to give the intermediate (4),
- Which can be dissociated via the transitions state (5)
- To give the ester (6) [26].

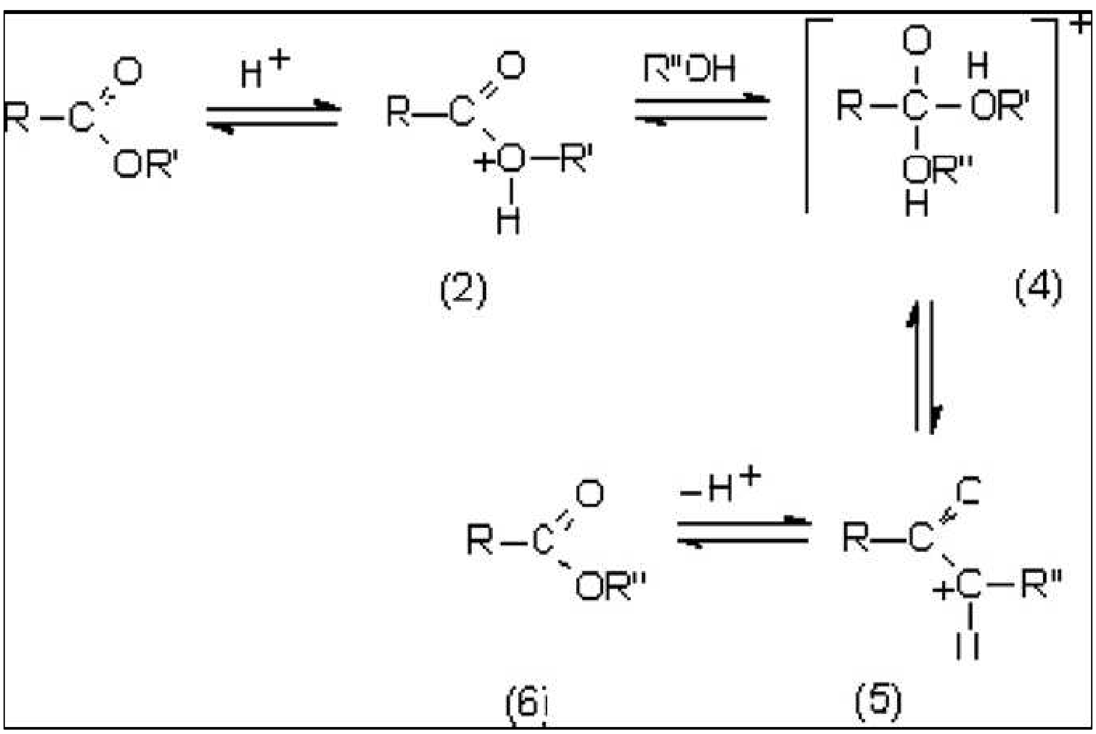


**Fig. 3: Mechanism of acid catalyzed transesterification of vegetable oils.**

**Disadvantages of using acid catalyst:**

- The disadvantages using acid, as a catalyst like sulfuric acid and sulfonic acid, is that this type of catalyst gives very high yield in esters but the reaction is very slow, requiring always more than one day to finish .
- In the acid catalyst transesterification, if an excess of alcohol is used then better conversion of triglycerides is obtained, but recovering glycerol become more difficult and that is why optimal relation between alcohol and raw material has should be determined experimentally considering each process as a new problem [19, 23].

**Lipase catalyzed Transesterification:**

It has been recently found that enzymes such as lipase can be used to catalyze transesterification process by immobilizing them in a suitable support. The advantages of immobilization are that the enzyme can be reused without separation. Also the operating temperature of the process is low ($50^0$C) compared to other techniques. Disadvantages include inhibition effect, which was observed when methanol was used and the fact that enzymes are expensive [27]. Shimadha worked on production of Biodiesel using lipase but waste oil as raw material. They started the enzymatic production using normal oil and methanol and the first interesting result was that if the amount of the molecular relationship is larger than 0.5%, the product becomes insoluble of alcohol. This fact reduces the activation with lipase [28].

**Advantages of using lipase catalyst:**

There are many advantages of using lipase as a catalyst

- Possibility of regeneration and reuse of the immobilized residue, because it can be left in the reactor if you keep the reactive flow.
- Use of enzymes in reactors allows use of high concentrations of them and that makes for a longer activation of the lipase.
- A bigger thermal stability of the enzyme due to the native state.
- Immobilization of lipase could protect it from the solvent that could be used in the reaction that will prevent all the enzyme particles getting together.
- Separation of product will be easier using this catalyst [16].

*Disadvantages of using lipase catalyst:*

There are some disadvantages of using lipase as a catalyst:

- You can lose some initial activity due to volume of the oil.
- Number of support enzyme is not uniform.
- Biocatalyst is more expensive that the natural enzyme
- Enzyme may be inhibited by methanol
- Exhaustions of enzyme activity may occur
- High cost of enzyme
- Limitation of number of microorganism, which produce lipase.
- Physical factors affect the enzymatic activity [4].

*Supercritical methanol transesterification:*

The simple transesterification process discussed above is confronted with two problems i.e. the process is relatively time consuming and it needs separation of the catalyst and saponified impurities from the biodiesel. These problems are not faced in the supercritical methanol transesterification. This is perhaps due to the fact that the tendency of two-phase formation of vegetable oil. Methanol mixture is not encountered and a single phase is formed. As a result the reaction was found to be complete in a very short time within 2-4 min. Further since no catalyst is used, the purification of biodiesel is much easier, trouble free and environmental friendly. The result of transesterification of rapeseed oil in the supercritical methanol method indicates that at temperature of $239^o$ C and pressure of 8.09 mia, glycerol and methyl esters is obtain as the principal products [29].

**The non-catalytic supercritical methanol transesterification:**

The non-catalytic supercritical methanol transesterification is performed in a stainless steel cylindrical reactor (autoclave) at 520 K. In the transesterification process, the vegetable oil should have an acid value less than 1, and all materials should be substantially anhydrous. If the acid value were greater than 1, more NaOH or KOH would be spent to neutralize the free fatty acids. Water also causes soap formation and frothing. The stoichiometric ratio for the transesterification reaction requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid ester and one mole of glycerol. Higher molar ratios result in greater ester production in a shorter time. The vegetable oils were transesterified 1:6–1:40 vegetable oil-alcohol molar ratios in catalytic and supercritical alcohol conditions [30].

*Disadvantages:*

In the non-catalytic supercritical methanol vegetable oil transesterification, the value less than 1 and all materials should be substantially anhydrous. If the acid value were greater than 1, more NaOH and more KOH would be spent to neutralize the fatty acids and water also causes soap formation and frothing [26].

**Catalytic supercritical methanol transesterification:**

Catalytic supercritical methanol transesterification is performed in the autoclave in the presence of 1–5% NaOH as catalyst at 520 K. In the catalytic supercritical methanol Transesterification method, the yield of conversion rises to 60–90% for the first 1 min. [30].

## CONCLUSION

The world is confronted with the twin crisis of fossil fuel depletion and environmental degradation. The indiscriminate extraction and consumption of fossil fuels have led to a reduction in petroleum reserves, so alternative fuels, energy conservation and management, energy efficiency and environmental protection have become very important in recent years. The increasing impact bill has necessitated the search for liquid fuels as an alternative to diesel, which is being used in large quantities on transport, agriculture, industrial, commercial and domestic sectors. So Biodiesel obtained from oils has been considered a promising option. There are four ways in which oils and fuels can be converted into Biodiesel, namely Blending, Pyrolysis, Micro emulsion and Transesterification. Alkali or Base catalyzed transesterification is the promising area of research for production. Base catalyzed transesterification has been found to be an effective technique to prevent some long term problems associated with utilization of vegetable oils such as fuel filter plugging, injector cooking, and formation of carbon deposit in combustion chamber, ring sticking and contamination of lubricating oils. So Biodiesel has become more attractive to replace petroleum fuel.

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