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# A Review on Recent Strategy of Biodiesel Production from Waste Cooking Oil and Influencing Parameters

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#### **Abstract:**

To minimize the biofuel cost, in recent day's waste cooking oil was used as feedstock. Catalysts used in this process are usually acids, base, and lipase. Since lipase catalysts are much expensive, the usage of lipase in biodiesel production is limited. In most cases, NaOH is used as alkaline catalyst, because of its low cost and higher reaction rate. In the case of waste cooking oil containing high percentage of free fatty acid, alkaline catalyst reacts with free fatty acid and forms soap by saponification reaction. Also, it reduces the biodiesel conversions. In order to reduce the level of fatty acid content, waste cooking oil is pretreated with acid catalyst to undergo etherification reaction, which also requires high operating conditions. In this review paper, various parameters influencing the process of biofuel production such as reaction rate, catalyst concentration, temperature, stirrer speed, catalyst type, alcohol used, alcohol to oil ratio, free fatty acid content, and water content have been summarized.

### 1. INTRODUCTION

Fuels, generated from biological feed stocks, are termed as "biofuels." In general, biofuels can be broadly classified into first-generation fuels and second-generation fuels. First generation fuels or conventional biofuels are generally derived from sugar, starch, and vegetable oil source. Whereas, secondgeneration biofuels are generated from sustainable feedstocks. Because of high viscous nature, direct application of vegetable oil as a fuel in compression ignition engines has been limited. It is possible to reduce its viscosity by converting vegetable oil into alkyl esters using transesterification reaction. Nowadays, biodiesel production has been increased enormously to compete with fossil fuels. Biofuels are mostly derived from edible oil, nonedible oil, fats, waste cooking oil, and algae. Advantage of using virgin vegetable oil (edible oil) as raw material for production of biodiesel is their low free fatty acid content. Similarly, the main advantage of biodiesel synthesis over nonedible oil source is due to their high free fatty acid content. Instead of using virgin vegetable oil, waste cooking oil can be used as raw material for biodiesel production. In most of hotels, restaurants, and in other food industries, the waste cooking oil is either simply discharged into the river or dumped into the land. Inspite of this, the waste cooking oil can be used effectively for the biodiesel synthesis. Biodiesel production from waste cooking oil is found to be economically feasible method.. The property of biodiesel depends on the type of fresh cooking oil used. Biodiesel can also be blended with mineral oil. Even the wastes (byproducts) generated from biodiesel production can be used for power production.

# 2. BASIC REACTION MECHANISM INVOLVED IN THE PRODUCTION OF BIODIESEL

## 2.1 Transesterification

The major component of vegetable oil is triglycerides. When the triglycerides react with alcohol in the presence of base catalyst,

this is called "transesterification." In this reaction, triglycerides are converted to diglyceride, monoglyceride, and finally converted to glycerol.

#### 2.2 Side Reaction (saponification Reaction)

If vegetable oil contains free fatty acid, it will react with homogenous base catalyst to form soap and water. The main drawback in this reaction is the consumption of catalyst and increased difficulty in separation process, which leads to high production cost. In addition to that, formation of water in the product will also inhibit the reaction.

# 2.3 Side Reaction (Hydrolysis Reaction)

Water generated either from vegetable oil or formed during saponification reaction will hydrolyze triglyceride to form more free fatty acid.

#### 2.4 Esterification

In order to eliminate saponification reaction (formation of soap when FFA reacts with homogenous base catalyst) vegetable oil can be pretreated with acid catalyst, which esterifies free fatty acid to form esters of free fatty acid (biodiesel). This reaction is very much useful when raw material contains high percentage of free fatty acid (esterification of free fatty acid to form free acid esters). But this reaction is slower than base catalyzed transesterification reaction.

# 3. FACTORS AFFECTING THE PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL

#### 3.1 Water Content

Water content in waste cooking oil will accelerate the hydrolysis reaction and simultaneously reduce the amount of ester formation. Water content should not always exceed 0.5% to obtain 90% yield of biodiesel and it is more critical for an acid-catalyzed reaction than base-catalyzed reaction. When acid

catalysts are used for esterification of free fatty acid to form esters, water is obtained as by-product. Water will naturally inhibit acid-catalyzed reaction and also its presence in the product will decrease the efficiency of engines. In most cases waste cooking oil is preheated to 120°C to evaporate water molecules and those water molecules present in the product can be removed by using anhydrous sodium sulfate or magnesium sulfate anhydrous. Some enzymes require certain amount of water to be active, which is lesser than monolayer amount of water molecules around the enzyme molecules; if water present in raw material exceeds this limit, it will decrease the conversion by deactivating the lipase.

## 3.2 Free Fatty Acid

Waste cooking oil contains high free fatty acid content than the fresh cooking oils. Hence, it is know that higher free fatty acid contents will lead to formation of soap and water. Similarly, if free fatty acid content exceeds 3%, transesterification reaction will not proceed even with homogenous base catalyst. Hence this problem could be solved by using heterogeneous catalyst and also on pretreatment with acid homogenous catalyst or heterogeneous catalyst to esterify the free fatty acid to form free fatty acid ester. Usually, the acid-catalyzed reaction rate is low and high reaction conditions are required. Soaps formed while neutralizing free fatty acid using homogenous base catalyst can be converted back to free fatty acid by adding phosphoric acid to decanted glycerol and soap mixture obtained from final product.

#### 3.3 Type of Alcohol

In most cases, methanol is used for the production of biodiesel, because recovery of methanol from the final product is much easier. Yield of biodiesel obtained from waste cooking oil using methanol is higher than other alcohols (ethanol, butanol) and viscosity of biodiesel obtained using methanol is lesser than that of biofuel obtained from other alcohols. The cost of methanol is lesser than that of other alcohols, but ethanol is less toxic than methanol. Ethanol can be obtained from renewable source. When ethanol or isopropanol is used it will form azeotrope with water, which inturn makes difficulty in separation of water from alcohol during distillation process. In some cases, i-butanol or t-butanol is added as solvent to the reaction mixture to avoid the inhibition of lipase by methanol or glycerol. But in most of enzymatic reactions, ethanol is being used instead of methanol.

#### 3.4 Catalyst Type

In recent years, various catalysts (homogenous, heterogeneous, and enzyme catalyst) had been tested for the production of alkyl esters. Vicente et al. [14] studied using various base catalysts for production of alkyl esters and concluded that NaOH is the fastest catalysts among the catalysts used (NaOH, KOH, sodium methoxide, the potassium methoxide). Refaat et al. reported that KOH gives the highest yield for feedstock he had used. Some of the researchers used concentrated sulfuric acid as acid catalyst, but it requires high reaction time and high reaction condition. Even 1% (mole) can give up to 99% conversion. In the case of raw material having higher free fatty acid content, acid catalyst (homogenous/heterogeneous) are used for esterification reaction. Acid catalyst can be used simultaneously for both esterification and transesterification reactions. One of the main disadvantages in using homogenous catalyst is the recovery of catalyst from the final product and formation of soap. To overcome this issue

most of researchers used heterogeneous catalyst because heterogeneous catalyst is not affected by free fatty acid and moisture present in the raw material. Enzyme catalytic reaction is the slowest reaction among all other catalytic reactions. They can be used for both esterification and transesterification processes. Though the separation of product is easier while using enzyme catalyst, preparation of enzyme catalyst is most critica.

#### 3.5 Catalyst Concentration

In the absence of catalyst, conversion of waste cooking oil into biofuel requires high temperature conditions. When catalyst concentration is increased, the yield of the product will also increase. This is due to enhancement in rate of reaction. However, the conversion decreases with excess catalyst concentration, which may be due to increased viscosity of the reaction mixture. Many researchers studied by varying the catalyst concentration and also optimized the concentration of catalyst based on product yield and catalyst recovery. Chen et al. used CuVOP and reported that 1.5% of catalyst concentration is most effective for the production of biodiesel from soya bean oil. Increase of enzyme concentration will increase the percentage conversion. But beyond the certain limit, agglomeration of enzyme will take place. It will decrease the active site available on substrate. Dehkordi and Ghasem studied with heterogeneous solid catalysts comprising CaO- and ZrO2-mixed oxides, with different molar ratios of Ca and Zr. It was reported that by increasing Ca/Zr ratio, biodiesel yield was increased. But the stability of catalyst was decreased. Hence the optimum catalyst concentration would vary depending upon the type of raw material and catalyst.

#### 3.6 Temperature

Temperature has significant influence on transesterification reaction. If the reaction temperature is increased, then the rate of reaction and yield of product will also tend to increase. The temperature should not exceed the boiling point of alcohol. This will avoid vaporization of alcohol. But if the reaction temperature is maintained below 50°C, then the viscosity of biodiesel will increase. In some cases, waste cooking oil is preheated to 120°C to remove water particles present in the raw material and then cooled to 60°C. For an enzymatic reaction, conversion increases over a temperature range of 30-55°C. In case of lipase as catalyst, Jatropha oil reported maximum conversion at 55°C and for cotton seed oil maximum conversion was obtained at 50°C. Freedman et al. Found that there was no difference in conversion for temperatures 45°C and 60°C. But at 32°C, conversion was much lower than conversion obtained at 45°C and 60°C. After 4 hours, conversion at 32°C was slightly higher than conversion obtained at other temperatures. Refaat et al. Studied fresh and waste cooking oil from both domestic and commercial sources and reported highest yield at 65°C for all the feed stocks using KOH catalyst. Chen et al.found that the reaction time was reduced significantly to get maximum yield of biodiesel by using of microwave heating.

#### 3.7 Reaction Time

When the reaction was carried out for a longer time, even 99% of yield could be obtained, but it depends on the availability of reactants in the reaction mixture. If the reaction parameters are not properly adjusted, there are possibilities for the backward reaction, which will decrease the yield of product. For lipase-

catalyzed reaction, time required varies over a range of 7–48 hours. Kapilakarn and Peugtong found that reaction time also affects the product cost. Al-Widyan and Al-Shyoukh reported that when the reaction time increases, specific gravity of the product decreases in an exponential manner and ends with an asymptotic value with respect to time. Refaat et al. obtained a yield of 96.10% for 1 h duration and for reaction time  $> 1 \, h < 3 \, h$ , it was reported that there was no significant increase in biodiesel yield (96.350%). Hence, reaction time should be optimized to reduce the production cost.

#### 3.8 pH

pH is not a major factor, when base/acid catalyst are used in the reaction. When lipase was used as catalyst, pH needs to be considered, because at lower or higher pH value, enzymes may decompose. Devanesan et al. studied biodiesel production from Jatropha oil using immobilized Pseudomonas fluorescence and studied the effect of pH and concluded that pH value of 7 is optimum for production for biodiesel.

#### 4. PROCESS DESCRIPTION

If the acid value of waste cooking oil exceeds 1-2 mg KOH/mg of feed stock then pretreatment of waste cooking oil is required before it gets reacted with alkaline base catalyst.

#### 4.1. Process I

Waste cooking oil may contain particulate matter and other impurities. Such impurities are removed by allowing the waste cooking oil through the filter. Feed stock oils are usually preheated to 60°C by heat exchangers. Alcohol and acid catalysts are properly mixed in mixer before they were allowed into the esterification reactor. The mixing temperature is usually maintained at 60°C [68]. Catalyst mixture and preheated feedstock are allowed into the esterification reactor. Esterification reaction was carried out between 80 and 90°C and at 1 atmospheric pressure. Products from esterification reactor were cooled to 45°C, and catalyses are removed or neutralized before allowing into the settling tank to remove the methanol and water mixture. From the top of the settling tank, methanol and water mixture is removed and taken to distillation column to separate methanol from methanol water mixture and methanol is reused. The bottom product of separating vessel is taken to process II for transesterification reaction. Schematic representation of the process I is shown in Figure

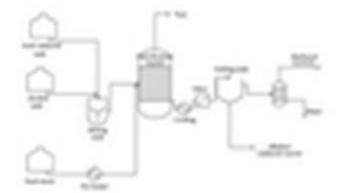


Figure.4. Pretreatment of high free fatty acid feed-stock with acid-catalyzed reactor—process I.
4.2 Process II

Catalyst and alcohol are mixed in the mixer and products obtained from process are taken into the transesterification reaction column along with catalyst and alcohol mixture. Reactor temperature is usually maintained at 65°C, 1 atmospheric pressure, and 1:6 molar ratio of oil to alcohol. Products of transesterification reactor are feed into separator 2. From the separation tank, biodiesel and alcohol mixture is distilled to separate methanol and biodiesel. Methanol from distillation column is recycled and reused. Biodiesel is washed with hot water and sent to separator to remove water and biodiesel. From the third separator tank, biodiesel is sent to storage tank. Bottoms of second separator section are moved to the alcohol and glycerol distillation column. From the top of distillation column methanol is recycled. Bottom product of distillation column is taken as byproduct. Schematic representation of the process II is shown in Figure 5.

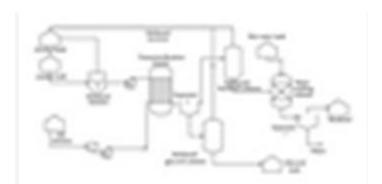
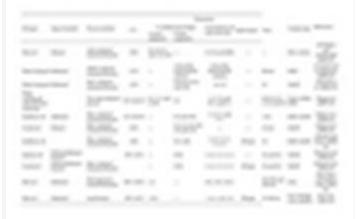


Figure.5. Alkali-catalyzed treatment of pretreated waste cooking oil—process II.

The recent research works on various waste cooking oils under different operating parameters as shown in Table 2.

Table.2. Recent research on waste cooking oil and operating parameters.



#### 5. CONCLUSION

Cost of biodiesel can be reduced by using waste cooking oil as feed stock. High fatty acid content in waste cooking oil could be reduced by pretreating waste cooking oil with acid catalyst. Water produced during the esterification process can inhibit acid catalyst, and this can be eliminated by stepwise reaction mechanism. Methanol is the most suitable alcohol because of its low cost and easy separation from biofuel. Methanol to oil ratio for the acid-catalyzed reaction depends on amount of free fatty

acid. For base-catalyzed reaction, 6:1 is optimum ratio for transesterification reaction. Concentration of catalyst depends on nature of catalyst used: either heterogeneous or homogenous. Stirrer speed helps to enhance rate of reaction. In most cases, optimum speed of stirrer was maintained in the range of 200–250 rpm.

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