ABSTRACT

Waste cooking oil as feedstock to produce biodiesel & Saponification reaction as by product

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Biodiesel produced cost from virgin vegetable oil is higher than that of fossil fuel, because of high raw material cost. To minimize the bio-fuel cost, the alternate is found to be waste cooking oil used as feedstock. Food against fuel conflict will not arise if this is used for biodiesel production. Catalysts used in WCO bio-fuel are usually acids, base, and lipase. But lipase catalysts are more 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 esterification 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.

Keywords: Waste cooking oil, lipase, saponification, esterification & catalyst

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, second-generation biofuels are generated from sustainable feedstocks. The major classification of biofuels is shown in Figure 1. Because of high viscous nature, direct application of vegetable oil as a fuel in compression ignition engines has been limited [1]. It is possible to reduce its viscosity by converting vegetable oil into alkyl esters using transesterification reaction [2–4]. Nowadays, biodiesel production has been increased enormously to compete with fossil fuels. The production of biodiesel in recent years around the world is shown in Figure 2. Biofuels are mostly derived from edible oil, non edible 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 [5]. Similarly, the main advantage of biodiesel synthesis over non edible oil source is due to their high free fatty acid content [6]. Instead of using virgin vegetable oil, waste cooking oil can be used as raw material for biodiesel production [8]. 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 [9]. Different sources of raw material used for the production of biodiesel are shown in Figure 3. The property of biodiesel depends on the type of fresh cooking oil used [10]. Biodiesel can also be blended with mineral oil [11].

Even the wastes (byproducts) generated from biodiesel production can be used for power production [12].

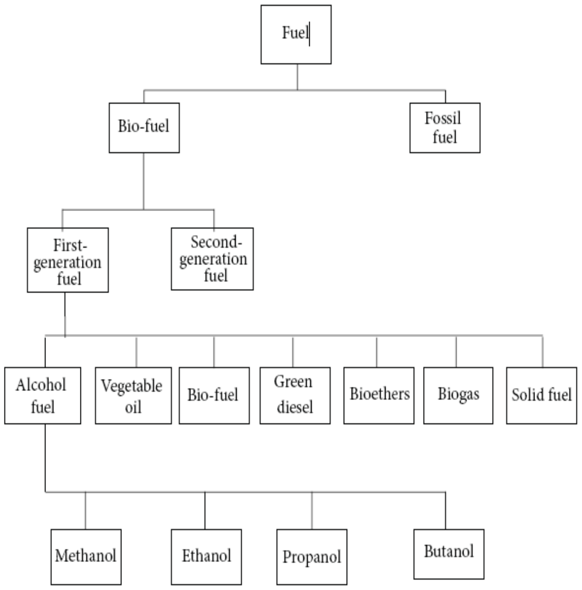


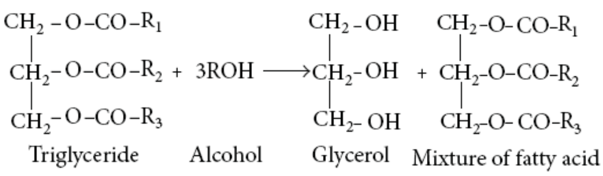
FIGURE 1: Classification of biofuels.

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. The reaction mechanism is shown in Scheme 1.

Side Reaction 1(Saponification Reaction)

If vegetable oil contains free fatty acid, it will react with homogenous base catalyst to form soap and water. The saponification reaction is represented as shown in Scheme 2.



SCHEME 1

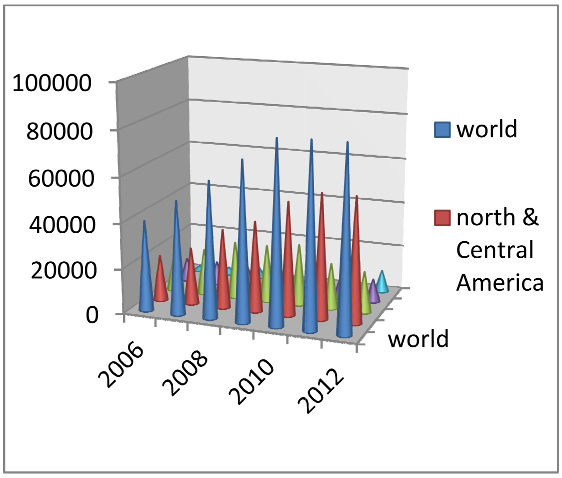


Figure 2: Production of biodiesel in recent years [7].

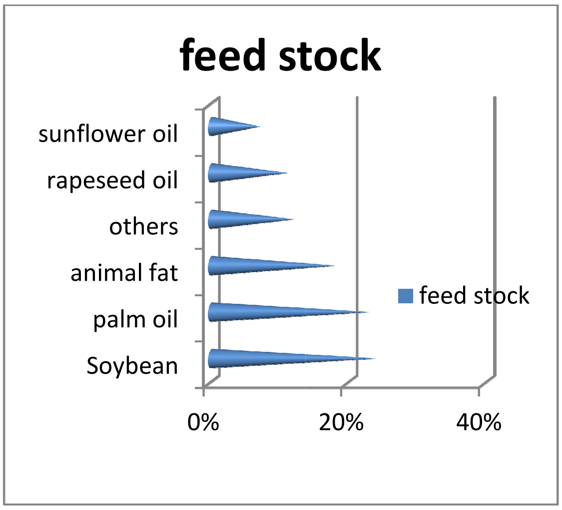


Figure 3: Production of biodiesel from different feed stock [13].

$$R_1\text{-}COOH + NaOH \longrightarrow R_1COONa + H_2O$$

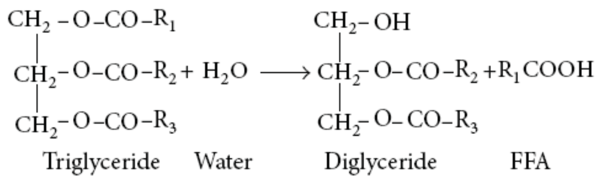
FFA Sodium hydroxide Soap Water

SCHEME 2

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.

Side Reaction 2(Hydrolysis Reaction)

Water generated either from vegetable oil or formed during *saponification* reaction will hydrolyze triglyceride to form more free fatty acid. The hydrolysis reaction is given as shown in Scheme 3.



SCHEME 3

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. The esterification reaction is given as shown in Scheme 4.

$$R_1\text{–}COOH + ROH \longrightarrow R\text{–}O\text{–}CO\text{–}R_1 + H_2O$$

FFA (alcohol) Fatty acid ester (water)

SCHEME 4

Factors affecting the production of biodiesel from waste cooking oil

Water Content

Water content in waste cooking oil will accelerate the hydrolysis reaction and simultaneously reduce the amount of ester formation [14]. Water content should not always exceed 0.5% to obtain 90% yield of biodiesel.

Free Fatty Acid

Waste cooking oil contains high free fatty acid content than the fresh cooking oils [15]. 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 [16]. Hence this problem could be solved by using heterogeneous catalyst [12, 17, and 18] and also on pretreatment with acid homogenous catalyst [19, 20–22] or heterogeneous catalyst [11] 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 [10]. 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 [6].

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) [24] and viscosity of biodiesel obtained using methanol is lesser than that of biofuel obtained from other alcohols [24].

Alcohol to Oil Ratio

To produce three moles of alkyl esters, three moles of alcohol and one mole of triglyceride are required [25].Alcohol tooil ratio always haspositive, effecton biofuel conversion.

Catalyst Type

In recent years, various catalysts (homogenous, heterogeneous, and enzyme catalyst) had been tested for the production of alkyl esters. Vicente et al. [26] 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. [27] reported that KOH gives the highest yield for feedstock he had used. Some of the researchers used concentrated sulfuric acid as acid, but it requires high reaction time and high reaction condition. Even 1% (mole) can give up to 99% conversion .

Catalyst Concentration

In the absence of catalyst, conversion of waste cooking oil into biofuel requires high temperature conditions [28].

Stirrer Speed

The mixing of reactants is very important to achieve completion of transesterification reaction and also it increases the yield of product [29].

Temperature

Temperature has significant influence on transesterification reaction [30]. If the reaction temperature is increased, then the rate of reaction and yield of product will also tend to increase.

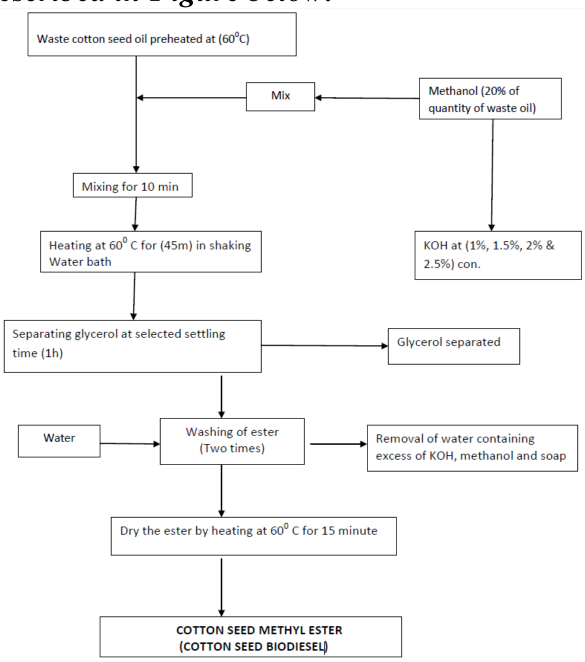
Reaction Time

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 [24, 30]. For lipase-catalyzed reaction, time required varies over a range of 7–48 hours [31].

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. [32] 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.

The methyl transesterification of waste cotton seed were carried out as per the steps described in Figure below.



Conclusions

The recovery of esters by transesterification of waste cotton seed oil with methanol is affected by varying the composition of catalyst.

- The blends B10, B15, B20 of cotton seed have higher flash and fire point as compare to diesel.
- The blends B10, B15, B20 of cotton seed have higher cloud and pour point as compare to diesel.
- Ash content increases as we increase the amount of biodiesel in petro diesel. The blends B10, B15 and B20 of cotton seed have higher ash content as compared to diesel.
- The esters of cotton seed are found to have carbon residue content lower than that of diesel which is better for engine performance and it also prevents carbon deposition inside the combustion chamber.
- The calorific values of diesel and cotton seed methyl ester were found as 43,000 & 40,000KJ/Kg respectively.
- Use of 10% blend of CSME as partial diesel substitutes can go a long way in conservation measure, boosting economy, reducing uncertainty of fuel availability and making more self-reliant.

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