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Biodiesel Production from High Free Fatty Acid Feed Stocks through Transesterification

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Abstract

Transesterification is one of the most popular methods to decrease the viscosity of vegetable oils to produce biodiesel. It is the reaction of vegetable oil/ fats with an alcohol to give fatty acid alkyl esters in the presence of a catalyst with glycerol as by product. A catalyst is used to increase the rate of reaction and yield. The reaction is very much affected by the free fatty acids content in the feedstock. This paper discusses the appropriate method to produce biodiesel from the high High Free Fatty Acid (FFA) feed-stocks.

1. Introduction

There is a realization throughout the world that the petroleum resources which are non-renewable are being rapidly depleted. The growing demand for energy and gradual disappearance of fossil fuels may lead to severe energy crisis. World over researchers are looking for the renewable alternatives which is vegetable oil [1].The high viscosity of vegetable oils are the main hurdles to use it as fuel in diesel engine which causes poor fuel atomization resulting in poor combustion, ring sticking, injector coking, injector deposits, injector pump failure and lubrication oil dilution by crank case polymerization. [2-3] Biodiesel is produced as fatty acid methyl esters (FAME) from transesterification process in vegetable oils and animal fats with methanol. [4]

Feedstocks which contain triglyceride such as vegetable oils, waste oils, animal fats and waste greases can be converted into biodiesel by transesterification process. According to National Biofuel policy of India, biodiesel shall be obtained from non-edible oil seeds produced from waste, degraded and marginal lands. Biodiesel will be permitted to produce from indigenous feed-stocks [5]

2. Biodiesel Feedstocks

In developing countries, edible oils can not be used as fuel because it may cause food scarcity and other environmental problems by utilizing arable land. Therefore, non-edible vegetable oils are become more attractive for biodiesel production. Non-edible oilseed crops include Jatropha curcus, Madhuca indica (mahua), Pongamia pinnata (Karanja), Camelina sativa (Camelina),Cotton seed (Gossypium hirsutum), Cumaru, Cynara cardunculus, Abutilon muticum, neem (Azadirachta indica), jojoba (Simmondsia chinensis), Passion seed (passiflora edulis), Moringa (Moringa oleifera), Tobacco seed, rubber seed tree (Hevca brasiliensis), Salmon oil, Tall (Carnegiea gigantean), Coffee Ground (Coffea arabica), Nagchampa (Calophyllum inophyllum) , Croton megalocarpus, Pachira glabra, Aleurites moluccana, Terminalia belerica.[6]

3. Biodiesel Production Processes

Low FFA or edible feedstock can be converted to biodiesel by homogeneous basic catalytic process using sodium hydroxide or potassium hydroxide as catalyst. High yield can be obtained at normal room temperature and pressure due to low mass transfer resistance since the catalysts exist in the same liquid phase as the reactants. However, this process cannot be used for feedstocks containing high FFA content. Side reactions take place to deactivate the basic catalyst by the impurities resulting saponification with the formation of soaps and thus reducing the biodiesel yield. [7]

3.1 Transesterification Process

First step is the process of purification; any foreign materials in the oil are filtered out. Filtered oil is then heated to about 1100C to remove any moisture present in the oil. Presence of moisture will convert fatty acids into salts instead of having fatty acids of triglyceride molecule undergo transesterification. [8]

Ethanol and methanol are commonly used as alcohol in transesterification process. Methanol is more preferred over ethanol due to its high reaction rate but later one is renewable and derived from agricultural sources. Transesterification of vegetable oils produce fatty acid alkyl esters and glycerol. Glycerol is heavier than esters, its layer settle down at the bottom of reaction vessel. Monoglycerides and Diglycerides are the intermediate product in this process. [9]

3.2 Single Step Transesterification

Transesterification is one of the most popular methods to reduce viscosity of oils to produce biodiesel. For low FFA feedstock, single step transesterification is sufficient to convert the whole oil in to biodiesel. The reaction is reversible and therefore, excess alcohol is used to complete the reaction. [10] Most of the non-edible vegetable oils have

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high level of free fatty acid and if free fatty acid content in the oil is more than 3% then alkali catalyzed transesterification will not be feasible. If the free fatty acid content is below 2%, alkaline transesterification is preferred. It is reported that alkaline transesterification is 4000 times faster than acid transestrification. [11]

3.3 Two Step Transesterification:

Non-edible oil feedstocks contain higher amount of impurities in the form of moisture & free fatty acids. Therefore, alkali catalyzed transesterification process is not suitable for the production of biodiesel [12]

Two step transesterification process method is used for the production of biodiesel from feedstocks containing high free fatty acids. Two step transesterification process can be used to produce biodiesel from high FFA oils. In this process, the first step is the esterification of FFA to FAME followed by a second step, alkali catalyzed transesterificaton. This technique gives high yield of biodiesel. [13]

In case of high FFA content feedstock, biodiesel is produced using two step processes. The first step consists of acid pretreatment of feedstock to bring down the FFA content followed by tranesterification with homogeneous base catalyst. [14]

Two step transesterfication processes also reduces high level of FFA to less than 1% for Mahua oil. Pretreatment of Mahua oil was carried out with 0.30-0.35 v/v methanol to oil ratio in the presence of 1% v/v H2SO4 as an acid catalyst in 1 hour reaction at 333 K. After this, biodiesel was produced by transesterification reaction using 0.25v/v methanol to oil ratio (6:1 molar ratio) and 0.7% w/v KOH as an alkaline catalyst resulting in the yield of 98% biodiesel from mahua oil. [15]

Two step processes was carried out to reduce acid value of karanja oil. The production method was studied for karanja oil containing FFA upto 20%.First step consists of acid catalyzed esterification by using 0.5% H2SO4, molar ratio 6:1 to produce methyl ester by reducing acid value and then alkali catalyzed transesterification have been carried out. The yield obtained during this two step transesterification process was 96.6-97%. [16]

Two step pretreatment process (acid esterification) was carried out to reduce acid value from 48 to 1.72 mg KOH/g with 0.40 and 0.35 v/v methanol-oil ratio and 1.0% v/v H2SO4 as catalyst at a temperature of 63(+ - 2) 0C with 1 hour reaction time for high FFA content rubber seed oil followed by transesterification using methanol oil ratio of 0.30 v/v, 0.5 w/v KOH as alkaline catalyst at 55(+-2)0C with 40 min reaction time to yield 98-99% methyl ester. [17]

4. Factors Affecting The Yield:

The Factors which affect transesterification process are the quantity and type of alcohol and catalyst, reaction temperature, pressure and time of reaction, amount of free fatty acids and water in oils. In case of presence of large quantity of free fatty acids (> 1%) in oils, the conversion is difficult since it forms soap with alkaline catalyst. The soap may prevent separation of biodiesel from glycerine. Some researchers used alternative double stage transesterification process for feedstock having higher acid value. [18-19]

4.1 Impact of Free Fatty Acids Content On Yield

Free fatty acid content in oil is one of the important factors which affect tranesterification process. [20] Sufficient yield of biodiesel can be produced with homogeneous base catalyst if the FFA content of feedstock is 0.5 wt% or less. However, the biodiesel yield reduces sharply to 6% with an increase in FFA content to 5.3 wt%. [16]

The efficiency to produce biodiesel may be determined by an important property of biodiesel feedstock i.e. fatty acid composition. The percentage and type of fatty acids composition depend upon type of plant species and their growth conditions. Non-edible oils have fatty acid composition of aliphatic compounds with a carboxyl group at the end of a straight chain.C16 and C18 fatty acids are generally present. [21]Non-edible oils generally contain high amount of free fatty acids which increase the cost of production and decrease the yield of biodiesel. [22]

Oils containing higher amount of fatty acids and water, forms large amount of soap. In case of high amount of free fatty acids, fatty acid will produce soap with reaction with base catalyst which reduces the separation of glycerin and biodiesel. There will be increase in viscosity and formation of gel due to presence of soap which decreases ester yield and inhibit the separation of glycerol. [23-24]

4.2 Effect of Catalyst Concentration and Types of Catalyst Used

Selection of the type of catalyst is one of the important parameter in transesterification reaction. It depends on the type of quality of feedstock. In general, homogeneous base catalysts are used for biodiesel production due to high yield conversion, short reaction time, lower reaction temperature and economical use. However, acid catalysts are incorporated in the production process for feedstock of high FFA content. [25]

The catalysts used for the transesterification of vegetable oils are classified as alkali, acid, enzyme or heterogeneous. Alkali catalysts like sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide are more effective. [26]

4.3 Effect of Molar Ratio

Methanol to oil molar ratio varied in the range of 3:1 to 12:1 for Jatropha oil and waste cooking oil and found the maximum ester conversions at molar ratio of 9:1. It was reported that further increase in molar ratio could not affect the yield amount and therefore, it was concluded that yield increased with increase in molar ratio upto 9:1. [27]

4.4 Effect of Reaction Time and Temperature

Rate of reaction is affected by reaction temperature. Transesterification reaction will be completed at room temperature, if enough time is provided. At atmospheric pressure, the reaction is conducted at 60-700C which is closer to boiling point of methanol. Removal of free fatty acids from oils is required for these reaction conditions by refining or pre-esterification. Degummed & de-acidified feedstock is used at these conditions for biodiesel production. Negative effect on the conversion is reported if the temperature exceeds beyond this limit.[28].

85% transesterification reaction was completed in 15 minutes & 97% in 3 hours using 1% KOH as catalyst. It was observed that transesterification reaction proceeded rapidly at catalytic concentration of 1% KOH while 87% conversion was observed in 3 hours using 1.2% KOH as catalyst. It was observed that the best yield was obtained using 1% catalytic concentration of KOH [29]

5. Conclusion

Transesterification is the reaction of vegetable oil fats with an alcohol to give fatty acid alkyl esters in the presence of a catalyst with glycerol as by product. A catalyst is used to increase the rate of reaction and yield. However for high FFA vegetable oils two step transterification process seems to be more efficient and gives higher conversion yield.

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