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Wet and Dry Washing Purification Method for Biodiesel

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Abstract

Decreasing petroleum reserves have led to an increased demand for an alternate and renewable source of fuel. Biodiesel, being biodegradable, cleaner burning alternative, has emerged as a successful option and has been formed using trans-esterification processes or using chemical or enzyme catalysis, using readily available sources such as Jatropha, soybean oil, rapeseed oil. But it still is not pure to use commercially. This article focuses on purification of biodiesel via wet washing and dry washing methods so as to reduce the concentration of methanol, glycerol and other impurities.

1. Introduction

Biodiesel is a renewable fuel that can be synthesized from edible, non-edible and waste oils [1]. The research on the production of biodiesel has increased [2] significantly in recent years due to diminishing petroleum reserves.

As such there is the need for an alternative fuel which endows with biodegradability, low toxicity and renewability. This article focuses on purification of biodiesel via wet washing and dry washing methods so as to reduce the concentration of methanol, glycerol and other impurities.

A number of processes have been developed for biodiesel production involving chemical or enzyme catalysis or supercritical alcohol treatment. Plant oils, animal fats, microalgae oils and waste products such as animal rendering, fish processing waste and cooking oils have been employed as feedstock for biodiesel production.

2. Characteristics Of Biodiesel

- Biodiesel is a cleaner burning alternative to petroleum-based diesel fuel. The use of biodiesel as diesel fuel is advantageous due to its easy availability, portability, renewability, higher combustion efficiency [3], lower sulphur and aromatic content, higher cetane number [3] and higher biodegradability. It is much less combustible, with a flash point greater than 423 K compared to 350 K for petroleum-based diesel fuel. Biodiesel has a higher cetane number (around 50) than diesel fuel, no aromatics, no sulphur, and contains 10–11% oxygen by weight. Biodiesel has a viscosity close to that of diesel fuels.[4]
- The combustion of petroleum-based diesel fuel is a major source of air pollution including contaminants carbon monoxide (CO), nitrogen oxides (NOx), sulphur oxides (SOx), particulate matter (PM), and volatile organic compounds (VOCs).Biodiesel being a renewable fuel made from vegetable oils, animal fats, plants like jatropha seeds may reduce air pollutant(green house) emissions [5].

  It is biodegradable; its combustion products have reduced levels of particulates, sulphur oxides, carbon oxides, nitrogen oxides, and therefore, significantly reduces pollution.
- Only alternative fuel that runs in any conventional, unmodified diesel engine. It doesn't require any changes in storage facilities.
- Can be used alone or mixed in any ratio with petroleum diesel fuel, most common being a mix of 20% biodiesel with 80% petroleum diesel, or "B20".
- The main disadvantages of biodiesel(from vegetable oil) as diesel fuel are its higher viscosity, lower energy content,[6] higher cloud point and pour point, higher nitrogen oxide emission, lower engine speed and power, injector coking, engine compatibility, high price ,and higher engine wear.

3. Production Method

The process of biodiesel production is usually carried out by catalysed transesterification [7, 8, 9] with alcohol, most likely methanol. A catalyst is usually involved to improve the reaction rate and yield by promoting an increase in the solubility of

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alcohol which is otherwise sparingly soluble in oil phase. [10]

Alkalies (sodium hydroxide, potassium hydroxide, carbonates, and corresponding sodium and potassium alkoxides), acids (sulphuric acid, sulfonic acid or hydrochloric acid), or enzymes can be used to catalyse the reaction. Base-catalysed trans-esterification is much faster than the acid-catalysed one (base catalysed transesterification is basically finished within one hour) and is most often used commercially. There are several methods for carrying out this transesterification reaction including the supercritical processes [11], Common batch reactor, ultrasonic methods, and even microwave methods. Trans-esterified biodiesel comprises a mix of mono-alkyl esters of long chain fatty acids.

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CH2 -COO -R1                                   R1-COO-R'      CH2-OH
     I                                                    +     I
CH-COO –R2        + 3 R'OH   catalyst          R2-COO-R'      CH-OH
     I                       ------------>                      I
CH2-COO–R3                                     R3-COO-R'      CH2-OH
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Triglyceride Alcohol Fatty acid esters Glycerol

Researchers have successfully produced biodiesel from oil derived from used coffee grounds, Or from Jatropha curcas [12][13][14], a poisonous shrub-like tree that produces seeds considered by many to be a viable source of biodiesel feedstock oil, algae. Large amounts of lipids have been isolated from single-celled fungi and turned it into biodiesel in an economically efficient manner. Recently, alligator fat was identified as a source to produce biodiesel [15]

4. Purification Of Biodiesel

The biodiesel produced has impurities that settle out into the glycerol layer, including unfiltered particulates, methanol and glycerine. The impurities left in the crude biodiesel after the reaction are dangerous to any combustion system and must be removed. They may remain in biodiesel either as by product, free Fatty Acids during trans-esterification process or coming from any other sources due to contamination also have an effect on its stability. Feedstock should be dried to control water content which causes hydrolysis of fats and oils to FFAs.

Table [16]:

Impurity Effect

- Free Fatty Acid (FFA) Corrosion, low oxidative stability
- Water Formation of FFA, corrosion, bacterial growth
- Methanol Low density and viscosity, low flash point, corrosion
- Glycerides High viscosity, injector deposits, Crystallization
- Metals (soap, catalyst) Injector deposits, high sulphated ash (filter lockage), abrasive engine deposits.
- Free Glycerine Settling problems, Increases in aldehydes and acrolein exhaust emissions

There are two generally accepted methods to filter and purify biodiesel: wet and dry washing.

5. Wet Washing

The more traditional wet washing method is widely used to remove excess contaminants and leftover production chemicals from biodiesel.

Its techniques involve water wash (with distilled or tap water), bubble wash etc.. In this process a fine water mist is sprayed over the fuel. The fuel's impurities are removed as the water settles to the bottom of the tank [17].

This process is used to remove impurities such as soap, catalyst, glycerol and residual alcohol from biodiesel. It involves addition of certain amount of water to crude biodiesel and agitating it gently to avoid formation of emulsion. The process is repeated until colourless wash water is obtained, indicating complete removal of impurities. However, the inclusion of additional water to the process offers many disadvantages, including increased cost and production time. Consumption of water and Na2SO4, high biodiesel products drying cost long time for water washing and the process is less ecologically viable. There is considerable loss in product due to formation of soap and emulsion, and treatment could incur high energy cost. until recently the commonest effective technique to remove glycerol and methanol from biodiesel product mixture is by water washing, since both glycerol and methanol are highly soluble in water.

6. Dry Washing

As such newer purifying techniques were found. One that is intensively used is Dry Washing. The dry washing technique commonly employed to purify crude biodiesel is usually achieved through the use of silicates (Magnesol or Trisyl), ion exchange resins (Amberlite or purolite), cellulosic, activated clay,

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activated carbon, and activated fibre, etc. These Adsorbents consist of acidic and basic adsorption (binding) sites and have strong affinity for polar compounds such as methanol, glycerine, glycerides, metals and soap. Dry washing is usually carried out at a temperature of 65*C and the process is mostly completed within 20–30 min. It was found that soap and glycerine can be removed by a combination of four modes. These modes are filtration, physical adsorption, ion exchange and soap removal by glycerine affinity.

The benefits of dry washing over the conventional wet washing method are as follows:--

1. The dry wash process decreases production time. Dry washed biodiesel can be ready for use in a few hours and is significantly quicker to produce than wet-washed fuel.
2. The dry wash process can lower costs. [18] In addition to the ever-increasing cost of water and the significant expense of water removal equipment, disposal of effluent water is often the single largest cost during production. Environmental agencies are vigorously pursuing illegal disposal of effluent waste. Hefty fines and imminent closure await those found breaking the law.
3. Less space is required to conduct the dry wash process. Settling is the key to effective water removal. Numerous large wash tanks and additional water settling tanks are usually required in the wet wash process.
4. The dry wash process creates high-quality fuel. Since water isn't added in the dry wash process, it's possible to achieve less than 500 parts per million (ppm) water content in accordance with ASTM D 6751. In wet washing, the fuel's water content is usually more than 1,000 ppm, making it expensive, difficult and time-consuming to effectively remove.
5. Total surface area coverage of wash tank is minimized; solid waste has alternate uses, saves space, and improves fuel quality.

7. Various Dry Washing Techniques:--

Magnesol

The adsorbent used -magnesium silicate can be reused. Magnesol used in the dry wash process has commercial use as compost and an animal feed additive. It also holds fuel source potential. It was found that there was no significant change in density, kinematic viscosity, iodine number, water content, saponification number or cetane index due to purification. Adsorption can be used to remove both soluble soap and glycerine. The soap and glycerine adsorption capacity of ion exchange resins can be regenerated using a methanol wash.[19]

8. Glycerine/Soap Interaction:

Soap has a stronger affinity for the glycerine portion of the biodiesel, therefore glycerine can aid in the removal of soap. As glycerine becomes adsorbed on the surface of the purification media, soap is entrapped in the glycerine layer and removed from the biodiesel stream.

9. Sawdust

Sawdust from a lumber mill was tested for its soap reduction properties. [20] They tested the sawdust with raw biodiesel containing 4% methanol and 2000 ppm of soap. They found through several tests that if less than 14.9g of biodiesel was purified per gram of sawdust; it would effectively remove the soap and glycerine. Wood soaks up the crud from unwashed biodiesel. Specifically, it reduces the soap and glycerine. One advantage of using sawdust is that there is no need to remove the methanol before sending the biodiesel to the sawdust. Biodiesel achieved complete absorption of the soap with 4% methanol.

10. Ion Exchange Resin

As the Biodiesel passes through the resin, the Ion Exchange process takes place whereby an atom of hydrogen is strongly attracted to the contaminants in the Biodiesel, but not the Biodiesel itself. This strong attraction usually results in an atom of hydrogen being replaced (exchanged) with an atom of a contaminant. The contaminant is now attached to the resin in place of the hydrogen and the hydrogen molecule is left in the Biodiesel. This all happens on a molecular basis and is a very efficient method of cleaning the fuel. it was found that ion exchange resin has little effect on methanol concentration after the bed has reached equilibrium. Purification with the ion exchange resin [21] caused the acid value of the purified biodiesel to increase slightly. Oxidative stability did not seem to be affected. Soap and glycerine were reduced significantly. Ion exchange resins offers good performance and provide cost benefits in the removal of glycerine and water, removal of salts, soap, and catalyst and also eradicate water washing [17].

11. Bentonites

Bentonites have had a positive effect on acid value and the removal of soap, methanol and glycerol in the 0.50–1.00 wt. % range [22] [23].Methanol was the most highly retained impurity with a 98% removal rate. Soap was reduced by 24–40% and glycerol by 15–20%. Although the results obtained with bentonites were slightly lower than with Magnesol _, FFA retention (16–30%) can be useful in samples from high FFA feedstock.

Dry washing however has some disadvantages. Information regarding the chemical composition of the resin is difficult and little effects on methanol. Involve highly consumable incurring expensive, require significant resources, larger size of powder grains making them exceedingly difficult to remove, and this caused an abrasive contaminated fuel.

12. Other Techniques

Dry washing agent such as activated carbon is commonly used to remove biodiesel excess colour. Glycerine was also used as a solvent to wash impurities. The clay; especially acid clay treated with sulphuric acid is a preferable, which is superior in the aspects of dealkaline effect, deodorant effect and decolouring effect.

Membranes- Contrary to both wet and dry washing techniques, membrane biodiesel purification process does not require both water and absorbent. Membrane processes [17]

Are usually based on the theory that higher permeates fluxes are followed by lower selectivity and higher selectivity is followed with lower permeates fluxes.

Advantages of this method are that it provides good yield, high purity and quality finished products that are comparable to the conventional diesel fuels, simple, with less energy consumption, provides enormous environmental benefits and energy savings. Reduction in separation and purification costs, improved fuel quality, and high recovery of valuable products. Zero waster washing with no waste discharges, and provide biodiesel with less glycerol content. However organic membranes are less stable and get easily swollen in organic solvent.

13. Conclusion

Biodiesel offers a wide range of benefits that makes it a highly viable alternative fuel source for the foreseeable future. The fuel's quality rests in large part on the purity and cleanliness of the final product. achievement of high quality biodiesel fuel could provide the following benefits: reduction in elastomeric seal failures, decrease in fuel injector blockages and corrosion due absence of glycerol, catalysts and soaps, reduces degradation of engine oil thereby providing high engine performance, better lubricant properties and better quality exhaust emissions

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