Production, Characterization and Process Variables of Biodiesel from Non-Edible Plant Oil (Neem & Soapnut): A Review

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Abstract: Owing to higher fossil fuel prices in the coming few years it becomes necessary to search for an alternative fuel which must be clean, green and economical. The 2nd Generation biofuels challenges a sustainable relaxation for whole world and for upcoming generations, if explored efficiently. Biodiesel is a more attractive alternative fuel source for diesel engines as they were well known in their renewability and non-polluted emissions. But the major problem arises for the commercial use of biodiesel is cost. In effect of searching alternative sources and based on experimental data, this review carries a better explanation on Neem (Azhadirachta indica) and Soapnut (Sapindus mukorossi) oil a cheaply available non edible sources, stepping towards the reduction of cost during the production and making as economically feasible model. As non-edible oils were enriched in higher levels of free fatty acid content hence, a two-step catalyzed methods is used in trans esterification process for biodiesel production. The comparison between the biodiesel produced from neem oil and soapnut oil taken place on the basis of their physicochemical characteristics, economic feasibility and eco friendly nature. The efficiency of the biodiesel is further examined in vehicle engine and an overview of gases emissions was noted. The physicochemical properties from obtained biodiesel were under lined based on ASTM values. The observed values of the biodiesel can be compared with the other oil. This review paper mainly focus on extraction of oil, biodiesel processing, physio chemical characteristics and effect of different parameter on production of biodiesel.

Keywords: Non-edible oils (Neem & Soapnut), Biodiesel, Free Fatty Acid (FFA), Trans esterification, Two-step catalyzed method.

1. Introduction

The world energy consumption highlights that a major portion of the total energy consumed are derived from combustion of fossil fuels. Among all the fossil fuels, the liquid petroleum based fuels contributes a maximum because of their inherent physicochemical and combustion properties. The reserves of fossil fuels, mainly the liquid fuels are not unlimited and it may exhaust, if not utilize economically, within few decades. The efforts are being make throughout the World to reduce the consumption of liquid petroleum fuels wherever is possible. There are two general approaches in use, first is to switch over the energy consumption machines on alternative energy source which are either reproducible or they are abundant and the second is to enhance the efficiency of combustion machines. This could be achieved by understanding the physicochemical processes involved during the combustion. Such knowledge is also beneficial in view of propulsion; mitigation of combustion generated the pollution and control of fire hazard in the handling of combustibles.

Recently, the developing countries like India and China have experience of significant increase in energy demand. The world's largest oil producer's countries have suffered from much warfare, political and social instability. Diminishing the fossil fuel resources and coupled with the steady increase in energy consumption. It has spurred research interest in the alternative and other renewable energy sources.

Biodiesel is among the most promising fossil fuel alternatives in this time. The use of animal fats and edible

oils for the biodiesel production has been a great concern because they compete with the food materials. The major problem for commercialization of biodiesel is its cost around 70-90% of biodiesel cost is arises from the cost of feed stocks [25]. Because, the most of biodiesel was prepared from the edible oils like soyabean, rapeseed, sunflower, safflower, canola, palm and fish oil. World annual petroleum consumption and vegetable oil production is about 4.018 and 0.107 billion tons [1]. The cost of edible oils is very higher than Petroleum Diesel and if we use edible oils for biodiesel production then it will leads to food oil crisis. In the recent years, due to increase in demand of vegetable oils for food, it is very difficult to justify the use of vegetable oils for biodiesel production and these oils could be more costly to use as fuel and due to continue increase in price and no renewability of petroleum products, which are obtain from natural sources, It has been generated that 98% of carbon emissions result from petroleum products via combustion. The continued and increasing use of petroleum diesel cause air pollution and increases the global warming problem caused by CO2 and other particulate matters.

The growing demand for fuel and the increasing concern for the environment due to the use of petroleum products have led to the increasing popularity of biodiesel as a useful alternative and environmentally friendly energy resource. Most of the biodiesel was prepared from edible oils like soyabean, rapeseed, sunflower, safflower, canola, palm and fish oil. Cost of edible oils is very higher than Petroleum Diesel and we use edible oils for biodiesel production leads food oil crisis. The above problem can solved by using cheapest, low cost non edible plant oils such as Neem

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(*Azhadirachta indica*) and Soapnut (*Sapindus* mukorossi) as feed stocks for biodiesel production.

The direct use of vegetable oils as a fuel for engine can cause numerous engine problems like incomplete combustion, poor fuel atomization, engine fouling and carbon deposition on fuel injector. Hence viscosity of vegetable oils is reduced by Transesterification method. The Trans esterification process is widely used for industrial biodiesel production because it gives high yield with low temperature, pressure and short reaction time. The biodiesel is 100% based on vegetable oil. Biodiesel made up of about 10% of oxygen, that makes biodiesel is a "natural oxygenated fuel". It produced by a reaction of vegetable oil with the alcohol in presence of a catalyst. The use of vegetable oils is too much beneficial to the environment, economy and to the atmosphere [25].

2. Non-Edible Oil Seeds:

NEEM (AZHADIRACHTA INDICA)

Neem (Azadirachta indica) is a tree in the family Meliaceae which is grown in varied parts of India. The other names of neem are Veppam, Nimba, Margosa and Vepa. The Neem grows on almost all types of soils including clayey, saline and alkaline conditions etc. Neem can reach up to a height of 15 - 20 to 35 - 40 m and it bears an ovoid fruits which is 2cm by 1cm and each seed contains one kernel. Neem seed obtained from this tree are collected, de-pulped, sun dried and crushed for the oil extraction. The seeds have 45% oil which has great potential for the biodiesel production. Neem oil is generally light to dark brown, bitter in taste and has a rather strong odor that is said to combine the odors of peanut and garlic. It contains mainly of triglycerides and large amounts of triterpenoid compounds and they are responsible for the bitter taste. It is hydrophobic in nature and in order to emulsify it in water for application purposes, it has to be formulated with appropriate surfactants. The major component fatty acids of Neem oil are Palmitic acid (19.4%), Stearic acid (21.2%), Oleic acid (42.1%), Linoleic acid (14.9%) and Arachidic acid (1.4%) [18].

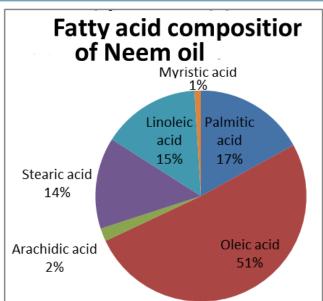


Chart 1: Fatty acid composition of Neem oil [21]



Figure 1: Neem Tree



Figure 2: Neem fruit, seed

SOAPNUT (SAPINDUS MUKOROSSI)

The soapnut fruit is produced from Sapindus Mukorossi, family of Sapindaceae and it is also known as soap-nut tree which is found in the tropical and sub-tropical region of the world including America, Asia and Europe. The soapnut oil has been considered as non-edible oil which is having a significant potential for the biodiesel production [37]. The Sapindus Mukorossi tree is a bear fruits that are commonly known as soapnuts and are of higher potential in saponin content. The saponin is a natural washing detergent, which is commonly used for cleaning purpose among all other things [11]. Soapnut plant has gentle insecticidal properties. Soapnut containing following acids like arachidic acid, palmitic acid, stearic acid, linoleic acid, oleic acid, eicosenoic acid, linolenic acid, lgnocerc acid, patmtolec acid, behenc acid, erucic acid and other.

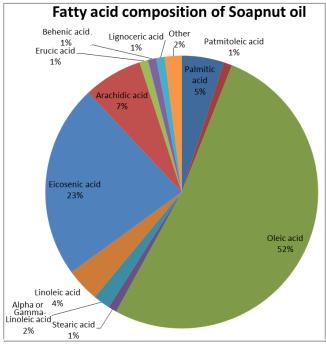


Chart 2: Fatty acid composition of Soapnut oil [11]



Figure 3: Soapnut tree



Figure 4: Soapnut fruit, seed

3. Materials and Methods

3.1 Oil Processing Technology of Neem & Soapnut Oil Seeds

1. <u>Oil extraction</u>: - 50g of seed of each sample is placed in a filter paper. The sample with filter paper was placed into a soxhlet apparatus and an extraction flask was fitted with 250ml of petroleum ether by using an electric heating mantle. The petroleum ether was gently heated and this continued for four hours after that the extraction process was stopped by noticing how oil comes with the petroleum ether. With the help of evaporation technique, the oil was separated from the solvent and the filter paper was removed and dried. Calculate the weight of the filter paper and its content and the change in mass determined. The experiment was repeated by using the same amount of the sample.

2. Degumming and Purification: - The oil is heated to 60° C, and activated carbon is added, which decolorize the oil. The bleached oil is then mixed with water thoroughly and heated again to 60° C, stirred vigorously for 15 min, filtered, and cooled. The sludge on the filter paper is discarded. The extracted oil (purified) is transferred into a glass bottle and stored in a refrigerator until all analyses will completed.

3.2 Effect of Different Process Variables on Production of Biodiesel

The most important process variables which effect the Trans esterification reaction are as follows:

Reaction Temperature:

The reaction temperatures strongly influence the rate of reaction. However, given enough time, the reaction will proceed to close completion stage even at the room temperature. Normally, the reaction is conducted very close to the boiling point of alcohol at atmospheric pressure. These reaction conditions require the oil which is free from free fatty acids by refining or pre esterification. Any other increment in temperature is reported to have a negative effect on the conversion rate. Trans esterification process can proceed satisfactorily at ambient temperatures in the case of the alkaline catalyst and it was observed that the biodiesel recovery was affected at very low temperature but conversion rate was almost unaffected [13].

Ratio of Alcohol to Oil:

The molar ratios of alcohol to oil affect the yield of ester. According to stoichiometry, the Trans esterification requires only 3 moles of alcohol per mole of triglyceride to yield 3 moles of fatty esters and 1 mole of glycerol. When alcohol is used 100% then the rate of reaction is at its highest. The higher molar ratio of alcohol to oil, conversion increased but recovery decreased because of poor separation of glycerol. It was found that optimum molar ratio of alcohol to oil depends upon type and quality of oil [22].

Catalyst Type and Concentration:

Alkali catalysts are the most effective Trans esterification catalyst compared to the acidic catalyst. The Trans methylations process occurs 4000 times faster in case of an alkaline catalyst than those catalyzed by the same amount of acidic catalyst because alkaline catalysts are less corrosive than acidic catalysts for industrial equipment's. The Trans esterification is mainly conducted with alkaline catalysts. The increased concentration of catalyst does not increase the conversion and it increases the extra costs because it is necessary to remove it from the reaction medium at the end [40].

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Purity of Reactants:

The impurities of oil also affect conversion levels. Under these conditions, about 67 to 84% conversion into esters by using crude oils compared with 94 to 97% when using the refined oils. The free fatty acids in the original oils also interfere with the catalyst; under the conditions of high temperature and pressure. The oils should be properly filtered and oil quality is very important in this regard [17].

Mixing Intensity:

To understand of the effect of mixing on the kinetics of the Trans esterification process is a valuable tool in the process scale-up and design. It was observed that after adding alcohol and catalyst to the oil, 5 to 10 minutes stirring helps in higher rate of conversion and recovery [17].

Effect of Alcohol Type:

Methanol gave the best biodiesel yield as comparison to butanol and ethanol. Methanol is simple in chemical structure so the Trans esterification reaction is more likely to occur but butanol and ethanol are more complex in terms of chemical structures, therefore Trans esterification is difficult to occur. The base catalyzed formation of methyl esters is easy to the formation of ethyl ester. In case of ethanolysis, the formation of emulsions is more stable and very complicates in the separation and purification of esters but in the case of methanolysis, formation of emulsions easily and quickly breaks down to form a lower glycerol rich layer and upper methyl ester rich layer [24].

Effect of Reaction Time:

The rate of conversion of oil to biodiesel approaches to equilibrium conversions with the increased reaction time. The maximum ester conversion is achieved at 2 hour reaction time; the reaction is very slow during the first minute due to dispersion of methanol into catalyst and mixing. From 1 to 5 minute, the reaction proceeded very fast [31].

Effect of Moisture and Water Content on the Yield of Biodiesel:

The water could pose a greater negative effect on the yield of biodiesel hence the feedstock should be free from water even a small amount of water (0.1%) would decrease the ester conversion from vegetable oil in the trans esterification reaction. The yield of biodiesel decreases due to presence of water and FFA because they cause soap formation, consume the catalyst and reduce the effectiveness of the catalyst. The moisture content of oil is removed by heating in oven for 1 h at 383 K. The water in the vegetable oil had negligible effect on the conversion while using lipase as a catalyst [33].

Effect of Free Fatty Acids:

After the acid esterification, free fatty acids content should be low or blow than 2% FFAs. These free fatty acids react with the alkaline catalyst to produce soaps instead of esters and there is a significant drop in the ester conversion when the free fatty acids are beyond 2% [30].

Effect of Stirring:

Stirring plays very important role in the yield of biodiesel production. The Trans esterification process was carried out with 180, 360 and 600rpm (revolutions per minute) and the

yield of methyl ester was same with 360 and 600 rpm. The yield of biodiesel production increased from 85% to 89.5% when magnetic stirrer (1000 rpm) was replaced with mechanical stirrer (1100 rpm) [26].

Effect of Specific Gravity:

The minimum value of the specific gravity of the final product is a symbol of completion of reaction and removal of heavy glycerine. The specific gravity of the final product decreased up to 2 hours of reaction time by using 30:1 molar ratio and up to 4 hours of reaction time using 45:1 and 56:1 molar ratio after which it was almost constant. The best combination of process reduced the product specific gravity from 0.912 to 0.864 with 100% catalyst, by 56:1 molar ratio at 303 K in 4 hours of reaction time [28].

4. Conclusion

The global human population is going to increase very fastly, so the more land may be needed to produce food for human consumption (indirectly via animal feed) and this problem already exists in Asia. Vegetable oil prices are relatively high there. The same thing will eventually happen in the rest of the world and this is the potential challenge to biodiesel. Due to the high consumption of diesel fuels and other limited sources of the energy are reasons for an enormous rise in price of petroleum fuels. The Vegetable oils are clean burning, non-toxic, renewable, biodegradable and environmental friendly transportation fuels which can be used in neat or in blend form with petroleum derived. Today, the biodiesel production from edible oil is much more expensive than diesel fuels due to relatively high cost of edible oil. There is a necessary need to explore non-edible oils as alternative feed stock for the biodiesel production from non-edible oils like Neem, Jatropha & Soapnut etc. owing to big climatic diversity. The extraction of oil from these non-edible plants and its conversion to biodiesel involves energy consumption at various stages which is starting from the plantation to the end use in the compression ignition engine due to some process variables. So, by analysis of these process variables, we can get maximum yield of biodiesel production from non-edible plant (Neem & Soapnut) oils and with the help of different physicochemical properties of Neem oil and Soapnut oil, we can differentiate that the quality, purity and efficiency of biodiesel to fuel.

The world annual petroleum consumption is about 4.018 and the vegetable oil production is about 0.107 billion tons, respectively. There is a large variety of plants available which produce non-edible oils and which can be considered for biodiesel production. The non-edible oils are quickly and easily available in many parts of the world and they are very cheap in cost as compared to edible oils. The demand of vegetable oils and the cost of biodiesel can be reduced by non-edible oils instead of vegetable oils. Biodiesel can be produced from non-edible vegetable oil and it has great potential as an alternative diesel fuel. Non-edible oils are a boon for developing and petroleum-poor countries.

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