INTRODUCTION

The term "waste vegetable oil" (WVO) refers to vegetable oil which has been used in food production and which is no longer viable for its intended use. Waste vegetable oil arises from many different sources, including domestic, commercial and industrial. Waste vegetable oil is a potentially problematic waste stream which requires to be properly managed. The disposal of waste vegetable oil can be problematic when disposed, incorrectly, down kitchen sinks, where it can quickly cause blockages of sewer pipes when the oil solidifies. Properties of degraded used frying oil after it gets into sewage system are conductive to corrosion of metal and concrete elements. It also affects installations in waste water treatment plants. Thus, it adds to the cost of treating effluent or pollutes waterways (Szmigielski et al., 2008).

Biodiesel refers to a vegetable oil or animal-based fuel consisting of long chain alkyl (methyl, ethyl or propyl) esters. It is a renewable, biodegradable, environmentally benign energy efficient, substitution fuel which can fulfill energy needs without sacrificing engine's operational performance. Thus, it provides a feasible solution to the twin crises of fossil fuel depletion and environmental degradation. Any fatty acid source may be used to prepare biodiesel. Thus, any animal or plant lipid should be a ready substrate for the production of biodiesel. The use of edible vegetable oils and animal fats for biodiesel production has recently been of great concern because they compete with food materials - the food versus fuel dispute (Pimentel et al., 2009; Srinivasan, 2009).

There are concerns that biodiesel feedstock may compete with food supply in the long-term (Lam et al.,2009; Metzger, 2009). Hence, the recent focus is the use of non-edible plant oil source and waste products of edible oil industry as the feedstock for biodiesel production meeting the international standards.

The world is currently challenged with global warming, depletion of non-renewable fossil fuel and environmental pollution. The major sources of greenhouse gas emissions are fossil fuels (Endalew et al., 2011). To overcome these challenges, there is a need to find alternative energy sources that are renewable, economically feasible and environmentally friendly. Biodiesel has a great potential as an alternative fuel.

The process used to convert these oils to Biodiesel is called transesterification. Transesterification involves stripping the glycerin from the fatty acids with a catalyst such as sodium or potassium hydroxide and replacing it with an anhydrous alcohol, that is, usually methanol. Any fatty acid source may be used to prepare biodiesel, but in the scientific articles reviewed, transesterification reactions have been studied for many vegetable oils such as soybean, rapeseed, sunflower, safflower, canola, palm and fish oil. Since the prices of edible vegetable oils, e.g. soybean oil, are higher than that of diesel fuel, waste vegetable oils and non-edible crude vegetable oils as Jatropha are used. Methyl, rather than ethyl, ester production was modeled because methyl esters are the predominant commercial products, methanol is considerably cheaper than ethanol and the downstream recovery of unreacted alcohol is much easier. Among the most commonly used alkaline catalysts in the biodiesel industry are potassium hydroxide (KOH) and sodium hydroxide.

Table 1. Difference Between Biodiesel and Petrodiesel.

BIODIESEL	PETRODIESEL
It manages global warming.	It emits greenhouse gases and it is therefore responsible for global warming.
It serves as a super lubrication agent and as such cleans deposits of petroleum diesel from pipes and tanks.	Possesses no such property.
Higher cetane number which makes engines start very smoothly and run better with clear emissions.	It has a lower cetane number.
It is environment friendly and highly economical as well since it does not incur import cost.	It is an imported product for most nations and it is less economical.
It has a high flashpoint of 300 – 400°F.	It has a lower flashpoint of 125°F.

Plate 1: Difference Between Biodiesel and Petro-diesel

DISCUSSION

The process of transesterification is similar to saponification. Saponification is soap making. To make biodiesel fuel efficiently from waste vegetable oils and animal fats we have to avoid one major problem: soap formation. Soap making requires a trans fatty acid or triglyceride (oil, fat, or kitchen grease) and then blending it with a solution of sodium hydroxide ($NaOH$, caustic soda) and water. This reaction causes the ester chains to separate from the glycerin. These ester chains are what the soap becomes. They are also called lipids. Their unique characteristics of being attracted to polar molecules such as water on one end and to non-polar molecules like oil on the other end is what makes them effective as soap. In transesterification, KOH and ethanol are mixed to create sodium methoxide ($Na+CH3O$). When mixed in with the WVO/fat this strong polar bonded chemical break the trans fatty acid into glycerin and also ester chains (biodiesel).

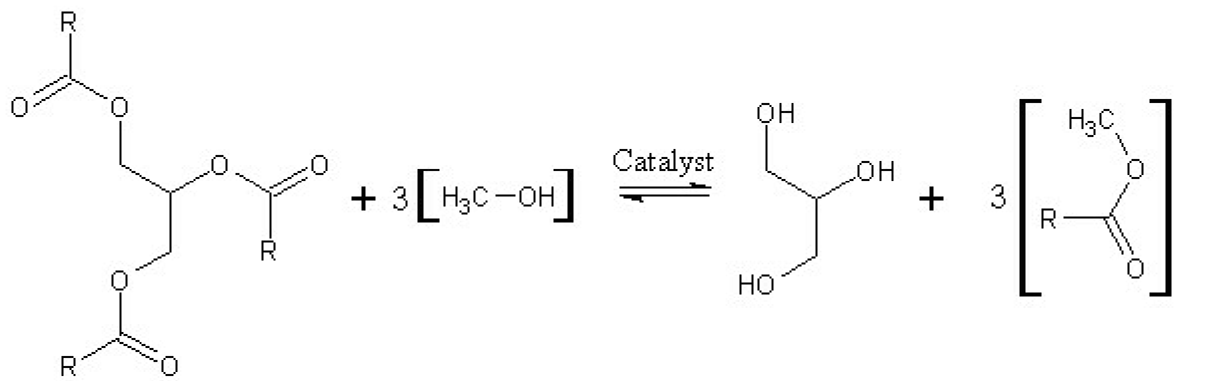
The major steps required to synthesize biodiesel from waste vegetable oil are as follows:

1. **Purification:** If waste vegetable oil is used, it is filtered to remove dirt, charred food and other non-oil material often found. Water is removed because its presence causes the triglycerides to hydrolyze to give salts of the fatty acids instead of undergoing transesterification to give biodiesel. At home, this is often accomplished by heating the filtered oil to approximately 120°C. At this point, dissolved or suspended water will boil off. When the water boils, it spatters (chemists refer to it as "bumping"). To prevent injury, this operation should be done in a sufficiently large container (at most two thirds full) which is closed but not sealed. In the

laboratory, the crude oil may be stirred with a drying agent such as magnesium sulphate to remove the water in the form of water of crystallization. The drying agent can be separated by decanting or by filtration. However, the viscosity of the oil may not allow the drying agent to mix thoroughly.

2. **Neutralization of free fatty acids:** A Sample of the cleaned oil titrated against a standard solution of base in order to determine the concentration of free fatty acids (RCOOH) present in the waste vegetable oil sample. The quantity (in moles) of base required to neutralize the acid is then calculated.

3. **Transesterification:** While adding the base, a slight excess is factored in to provide the catalyst for the transesterification. The calculated quantity of base (usually sodium hydroxide) is added slowly to the alcohol and it is stirred until dissolves. Sufficient alcohol is added to make up three full equivalents of the triglyceride and an excess is added to drive the reaction to completion. The solution of sodium hydroxide in the alcohol is then added to a warm solution of the waste oil and the mixture is heated (typically 50°C) for several hours (4 or 8 typically) to allow the transesterification to proceed. A condenser may be used to prevent the evaporative losses of the alcohol. Care must be taken not to create a closed system which can explode. An example of the transesterification reaction equation is shown in skeletal formula below:



Triglyceride Methanol (3) Glycerol Methyl Esters (3)

Since natural oils are typically used in this process, the alkyl groups of the triglyceride are not necessarily the same. Therefore, distinguishing these different alkyl groups, we have a more accurate depiction of the reaction: R1, R2, R3: Alkyl group.

During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkali (NaOH, KOH, or Alkoxides). The main reason for doing a titration to produce biodiesel, is to find out how much alkaline is needed to completely neutralize any free fatty acids present, thus ensuring a complete transesterification. Empirically 6.25g / L NaOH produces a very usable fuel. One uses about 6g NaOH when the WVO is light in color and about 7g NaOH when it is dark in color. The alcohol reacts with the fatty acids to form the mono-alkyl ester (or biodiesel) and crude glycerol. The reaction between the bio-lipid (fat or oil) and the alcohol is a reversible reaction so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion.

4. **Workup:** Once the reaction is complete, the glycerol should sink. When ethanol is used, it is reported that an emulsion often forms. This emulsion

can be broken by standing, centrifugation or the addition of a low boiling (easily removed) non-polar solvent, decanting and distilling. The top layer, a mixture of biodiesel and alcohol, is decanted. The excess alcohol can be distilled off or it can be extracted with water. If the latter, the biodiesel should be dried by distillation or with a drying agent.

5. **Quality Testing:** Diesel engines requires fuel of a certain quality. You just can't pour poor-quality biodiesel into the tank and expect the engine to go on and on without problems. You have three very dangerous enemies: free glycerin, poorly converted oils/fats and lye catalyst. Free glycerin and mono-, di- and triglycerides (poor ester conversion) will form gum-like deposits around injector tips and valve heads, lye can damage the injector pump. The key to good fuel is to just do it right and finish it. Use pure chemicals (sulfuric acid, lye and methanol) and measure them accurately. A proper wash will get rid of any glycerin and remaining lye.

    i. **Wash Test:** This is the most useful all-round test, and it's very simple: Put 150 ml of unwashed biodiesel (settled for 12 hours or more, with the glycerin layer removed) in a half-liter glass jar or PET bottle. Add 150 ml of water (at room temperature), screw the lid on tight and shake it up and down violently for 10 seconds. Then let it settle. The biodiesel should separate from the water in half an hour or less, with amber (and cloudy) biodiesel on top and milky water below, and no more than a paper-thin white interface layer between the oil and water. This is quality fuel, a completed product with minimal contaminants. Wash it and use it with confidence. But if it turns into something that looks like mayonnaise and won't separate, or if it only separates very slowly, with a thick, creamy white layer sandwiched between the water and the biodiesel, it's not quality fuel and your process needs improvement.

- Either you've used too much catalyst and made excess soap. Or,
- An incomplete reaction with poor conversion has left you with half-processed monoglycerides and diglycerides, fuel contaminants that also act as emulsifiers. Emulsifiers are used to make stable mixtures of oil and water, such as, indeed, mayonnaise. Or,
- Both: that is, too much catalyst as well as poor conversion.

ii. **Reprocessing Test:** The barnyard tests for your fuel are to take a liter of finished fuel, process it again as if it were new vegetable oil. If any more glycerin drops out, then you know it wasn't as good as it could have been. Also, look at your wash water. The second wash should be almost completely clear. The third wash should be nearly crystal clear. After settling 24 hours after a third wash, the fuel should be transparent when held up to light in a glass jar. If slightly hazy, simply heating the fuel to 9°F (32°C) should clarify it. If it clarifies with minimal application of heat, it is then fit for use. If all the above 'tests' turn out well, you probably have a fuel that would analytically beat fuel produced using continuous process (i.e. commercial) methods.

iii. **Methanol Test:** Take exactly 25ml of biodiesel and dissolve it in exactly 225ml of methanol in a measuring glass. The biodiesel should be fully soluble in the methanol, forming a clear bright phase.

If not, there is pollution in the biodiesel. Each ml of undissolved material corresponds to 4% by volume. If there any undissolved material at the bottom of the measuring glass, it means there is, your reaction is not complete. This method does not cover every aspect of quality, but it gives a hint. It is valid only for biodiesel made from vegetable and animal oils. It is not valid for biodiesel made from oils with a very wide fatty acid pattern, such as fish oils.

iv. **Viscosity Test:** Viscosity levels are a comparative indicator of biodiesel quality. Even at the laboratory or industrial level, viscosity testing alone cannot tell you if the process has gone far enough before reaching equilibrium and that there are not unacceptably high levels of harmful unreacted and partly reacted materials in your fuel. Unconverted monoglycerides (MGs) and diglycerides (DGs) are fuel contaminants that can cause injector coking and engine damage. MGs and DGs are very similar in viscosity to biodiesel and stay in solution with it after an incomplete reaction, they cannot be washed out. The allowed maximums are low: less than 1% for DGs and less than half that for MGs. Viscosity tests might get you within 5% accuracy, not nearly close enough for a useful quality check. Viscosity is that property of a fluid by virtue of it resistance to shear. Kinematic and Dynamic viscosities are very important properties of oil. The viscosity of Biodiesel is determined using Saybolt Universal Viscometer.

v. More quality checks

AleksKac has provided some useful quality checks:

There is a rule of thumb: the brighter yellow in color, the better the crack. As a standard you should take virgin sunflower oil yellow color in see-through sunlight. (It's a sort of colorimetry). Then take a glass jar of your fuel and place it in front of a white wall in the evening. When seen in the reflected light of a tungsten bulb it should not change to orange (a very simple case of absorption spectrometry).

- Nicely cracked biodiesel: very pale yellow (less than virgin sunflower oil) and no change in color with artificial lighting;
- Acceptable biodiesel: yellow like virgin sunflower oil or straw, but will get orangey undertone in reflected tungsten light;
- Deeper color biodiesel has a lot of glycerin in it in the form of various glycerides. Not good for standard engines.

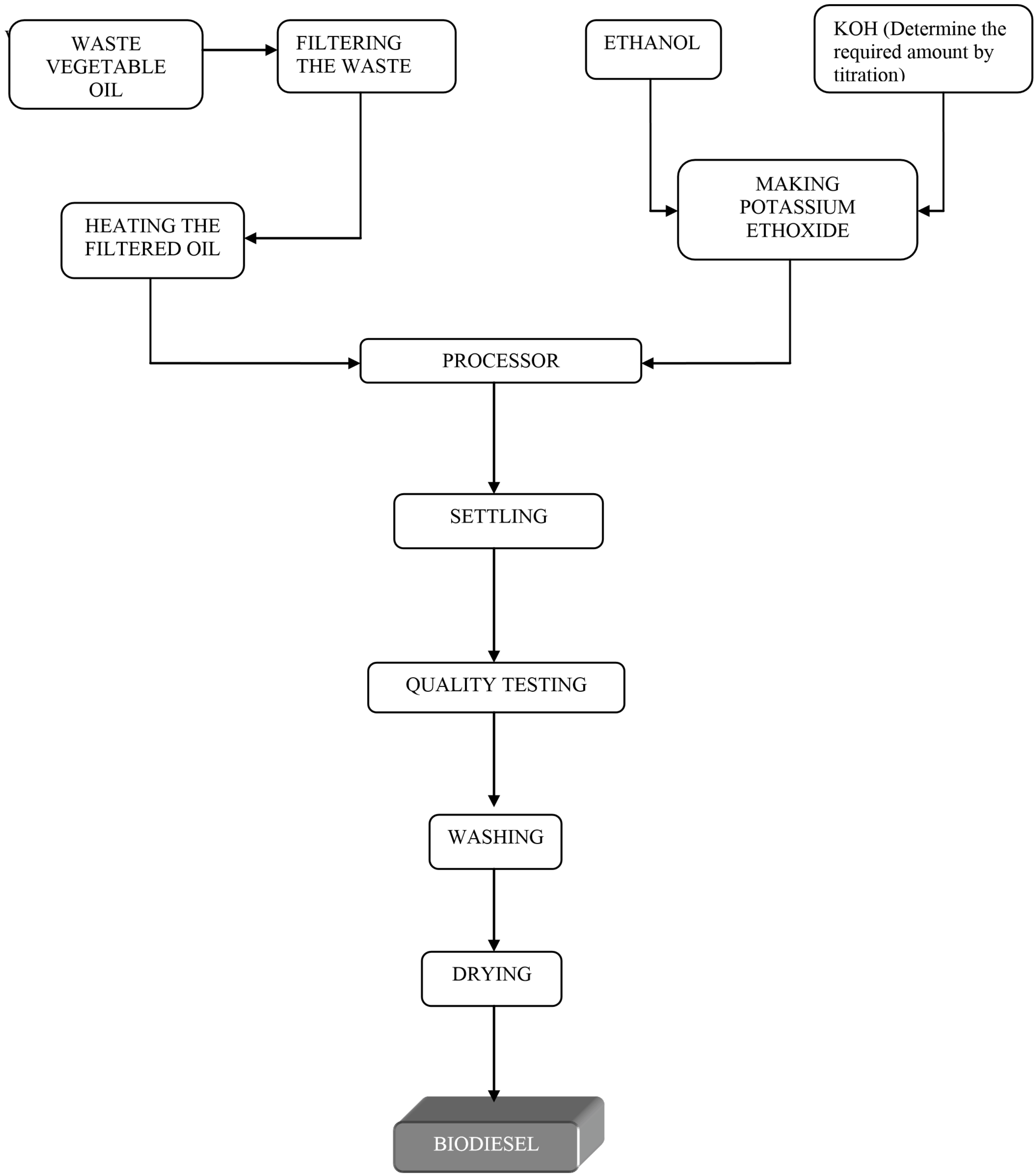


Fig. 1: Flow Chart of the Production Process

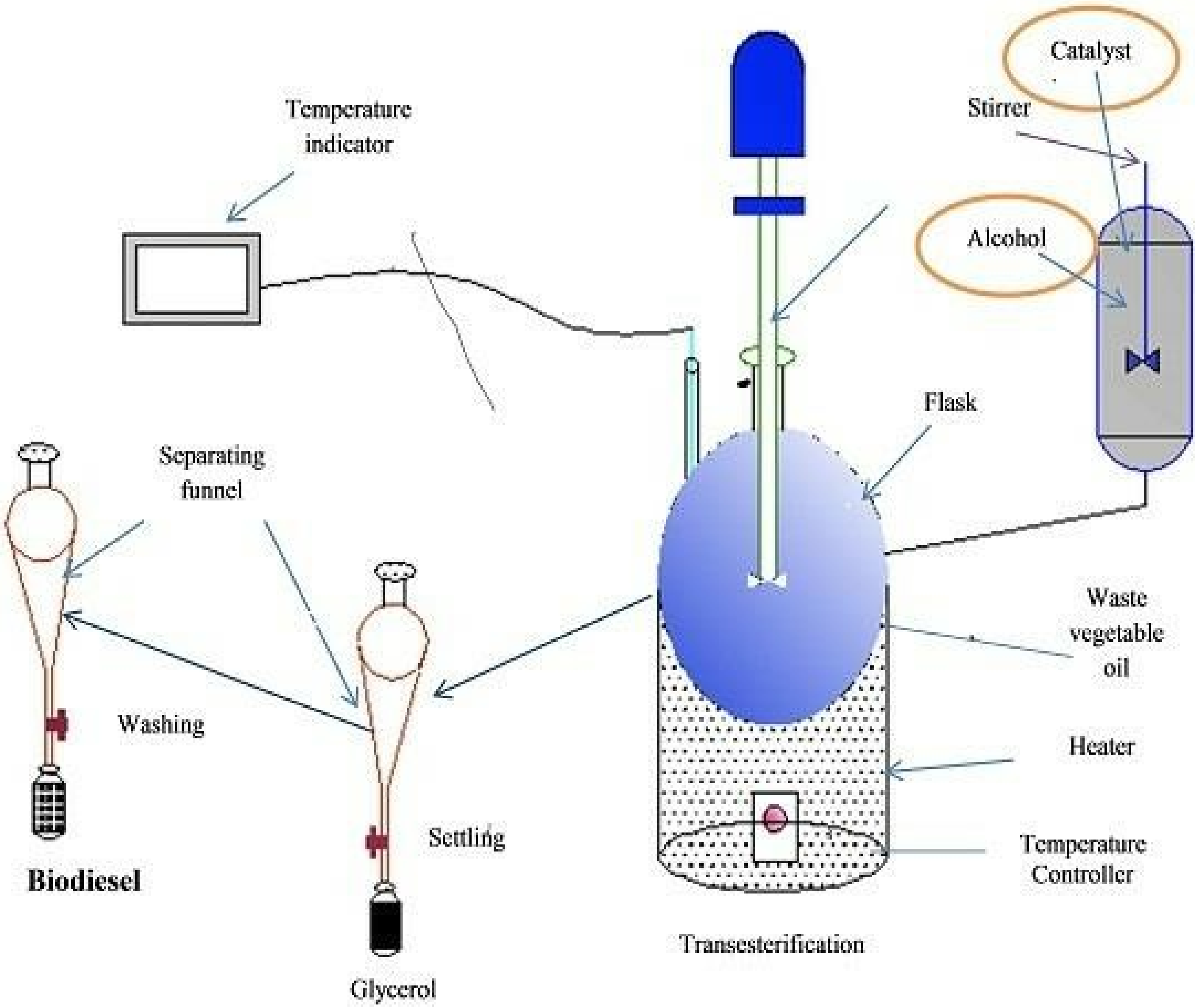


Plate 2: Experimental Setup for Biodiesel Production

Storage Conditions for Biodiesel

Biodiesel can be stored for long periods of time in closed containers with little headspace. The containers should be protected from weather, direct sunlight and low temperatures. Avoid long term storage in partially filled containers, particularly in damp locations like dock boxes. Condensation in the container can contribute to the long-term deterioration of the petroleum diesel or biodiesel. Low temperature can cause the Biodiesel to get, but the Biodiesel will quickly liquefy again as it warms up. In cold weather, additives can be used to prevent gelation.

Fuel tanks should be kept as filled as possible (regardless of whether they contain Biodiesel), particularly during rainy winter months or periods in inactivity, to minimize the condensation of moisture. Condensed moisture accumulates as water in the bottom of the storage tank and can contribute to the corrosion of metal fuel tanks, especially with petroleum diesel that contains sulfur. The condensed water in the fuel tank can also support the growth of bacteria and mold that use the diesel and Biodiesel hydrocarbons as a food source. These hydrocarbon- degrading bacteria and molds will grow as a film or slim in the tank and accumulate. They are frequently referred to incorrectly as 'algae' in advertisements for fuel treatments, perhaps because the colonies often have a reddish orange color and tend to form mats.

Biodiesel should be stored in clean dry tanks. Though the flash point of biodiesel is high, still some storage precautions are needed to be taken. It can be stored for long periods in closed containers with little head room but the container must be protected from direct sun light, low temperature, and weather. Underground storage is preferred in cold climates, but low temperature can cause biodiesel to gel.

The biodiesel or its blends should be stored at temperature of at least 15°C higher than the pour point of the fuel. While blending the biodiesel care should be taken to avoid very low temperatures as the saturated compounds can crystallize and separate out to cause plugging of fuel lines and filters.

Plate 3: Fuels at Different Stages

CONCLUSION

Biodiesel is gaining more importance as an attractive fuel due to the depleting fossil fuel resources. It will be helpful for decreasing the global warming. If we use unused and less fertile land for cultivating vegetable oil or jatropha in a large scale, then it does not make any hamper in the food production for the mankind. Above all, Biodiesel is a safe, clean and environment friendly fuel which can be used in the automobile without a change in the configuration of the engine.

RECOMMENDATION

Further study should be done on the production of biodiesel. As the price of crude oil is touching sky high, we need more alternative energy solutions to reduce our dependence on fossil fuels. The environmental benefits cannot be overlooked either since it is renewable, readily available and sustainable even as they reduce greenhouse gas (GHG) emissions unlike petroleum-based fuels.

REFERENCES:

Arjun, B., Chhetri, K., Chris,W., & Islam, M.R (2008). Waste Cooking Oil as An Alternate Feedstock for Biodiesel Production. *Energies.* 1(1), pp. 3-18; Doi:10.3390/en1010003.

Devarukhkar, S.D., Pardesi, A., & Yerunkar, S. (2015). Production of Biodiesel from Waste Vegetable Oil. *Weekly Science Research Journal,* 2(42). Doi: 10.9780/2321-7871/1202013/53.

Fragkou, I.A., & Martin, W. (2014). *Production of Biodiesel from Waste Cooking Oil.* Canada.

Mangesh, G.K., & Ajay, K.D. (2006). *Waste Cooking Oil – An Economical Source for Biodiesel.* Chittagong, Bangladesh.

Matt, G. (2009). *Biodiesel Production.* USA, New York.

Refaat, A.A. (2010). Different Techniques for the Production of Biodiesel from Waste Vegetable Oil. *International Journal of Environmental Science* and *Technology.* 7(1), pp. 183-213.

Refaat, A.A., Attia, N.K., Sibak, H.A., ElSheltawy, S.T., & ElDiwani, G.I. (2007). Production, Optimization & Quality Assessment of Biodiesel from Waste Vegetable Oil. *International Journal of Environmental Science* and *Technology.* 5(1), pp. 75-82.

Roshid, M.M., Ahamed, J.U., & Chowdhury, U.S. (2012). *Production of Biodiesel from Waste Vegetable Oil.* Paper Presented at the 5th BSME International Conference on Thermal Engineering. Retrieved April 17, 2018 from Researchgate.net.