

# Ethanol-Based Biodiesel from Waste Vegetable Oil

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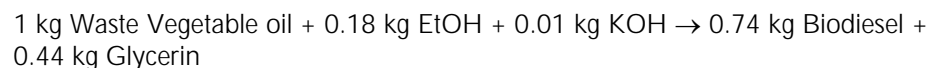
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Waste vegetable oil, mainly coming from frying residues, can be used as raw material to obtain a diesel fuel (biodiesel). Biodiesel, a nontoxic, biodegradable, diesel-like fuel, is an important energy alternative capable of decreasing environmental problems caused by the consumption of fossil fuels. The utilization of waste vegetable oils as raw material in biodiesel production was studied. Research was undertaken to establish the availability of used vegetable oil to supply a biodiesel process. It is intended that this work forms an academic study combined with an environmental and technological analysis of the merits of biodiesel as a sustainable fuel.

Laboratory experimentation investigated the possibility of using waste vegetable oil from the local fast food chains, and potassium hydroxide as catalyst for the transesterification process. The cleaned waste vegetable oil undergoes transesterification for 4 hours, after which, the biodiesel is separated from the glycerin by gravity. Washing is necessary to remove residual catalyst or soap. Overall material balance for the process gives:



The biodiesel, in pure form (B100) and in 50% proportion (B50) with petroleum diesel, was run in an essentially unmodified Toyota 2C diesel engine. Smoke density (opacity) and CO exhaust emission both decreased with B50. However, Nox increased with B50. Fuel consumption during engine power testing is significantly greater using the biodiesel, but is also significantly reduced with B50.

**Keywords:** Biodiesel, waste vegetable oil

## INTRODUCTION

Biodiesel is a domestic renewable diesel fuel that can be used alone or in a blend with

conventional diesel fuel. There are several benefits to using biodiesel as a blended fuel in diesel engines: Biodiesel has a lower flash point than petroleum diesel and thus helps prevent

damaging fires; biodiesel burns cleaner than petroleum diesel and thus reduces particulate matter thus lowering emissions of nitrogen, carbon monoxide and unburned hydrocarbons; the odor of burned biodiesel fuel is considered by many to be less offensive than petroleum diesel; there are only limited or no needed modifications to current engines to use biodiesel; there would be no need to change the transportation and storage systems to handle biodiesel; biodiesel behaves similarly to petroleum for engine performance and mileage; and biodiesel dissipates engine heat better than petroleum diesel.

Waste vegetable oils used for cooking are an attractive source of biodiesel, but are more difficult to convert because they contain 2-10% free fatty acids (the cause of the rancid taste). However, there is a hierarchy of preference for waste vegetable oil. Oils that stay liquid at lower temperatures are preferred. Light oils such as canola (rapeseed), soy or sunflower are the best. Heavier oils such as peanut and corn are slightly less desirable because they can thicken more easily. Palm oil, coconut oil and vegetable shortening are least desirable because they are often solid at room temperature.

Oils that have been used for cooking only vegetables, such as fries and tempura, are ideal. After that, fried fish followed by fried chicken are acceptable foods to cook in. The most problematic are oils used in frying animal fat laden foods such as beef and pork. While you *could* turn this grease into biodiesel, it contains a very high amount of free fatty acids and will tend to gel more at higher temperatures.

The study was aimed at evaluating the use of waste vegetable oil for biodiesel production. The most commonly used and most economical process is called the *base catalyzed esterification with methanol*, typically referred to as "the methyl ester process". Methanol however is highly toxic, does not produce a visible flame when burning, can be absorbed through the skin, and is 100% miscible with water, so any kind of spill presents a serious problem. Ethanol, on the other hand, provides the advantage of making a biodiesel fuel produced entirely from renewable resources.

The use of ethanol in biodiesel production has not been studied as extensively as has methanol. Sodium hydroxide is not a suitable catalyst because it was not sufficiently soluble in ethanol and it tends to promote undesirable gel and emulsion formation during transesterification.

Experiments in the laboratory made use of a homogeneous blend of the waste vegetable oil, mainly coming from frying residues from five major food chains in the city (Jollibee, McDonald's, Chowking, Greenwich, and KFC). The collected waste vegetable oils included palm, coconut, and corn feedstock. The free fatty acid content, and the fatty acid composition of the waste oils were not evaluated. Moreover, qualification of the ester product as biodiesel (American Society of Testing and Materials (ASTM) specifications designated in ASTM D-6751) was not established.

## **LABORATORY-SCALE ETHANOL-BASED BIODIESEL PRODUCTION**

### **Methodology**

The waste vegetable oils were collected from the warehouses of each of the 5 food establishments. Equal volumetric fractions of the waste oils were obtained, and cleaned, and blended. To avoid negatively impacting the subsequent production costs, the clean-up process of the waste oils was minimized as much as possible. The clean up included filtering the oil through double-layer cheesecloth to remove large particles and debris. After the particles were removed, the oil was heated to approximately 130 °C for an hour to reduce moisture levels to below 0.7%.

To determine the amount of KOH needed to titrate the fatty acid in the oil blend, the following procedure was followed: One milliliter of the cleaned oil was mixed with 10 milliliters of propanol, and the mixture added with 2 drops of phenolphthalein solution. KOH solution (1.044 g KOH in 1 L water) was added drop wise to the resulting mixture with vigorous stirring until the solution stays pink. For each liter of waste

vegetable oil, 1.044 gram of granular KOH will be needed for each milliliter of KOH solution used to titrate the free fatty acids, plus the amount required to form the potassium ethoxide catalyst.

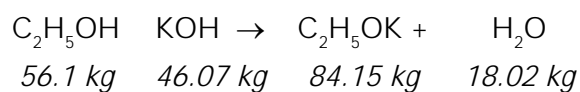
Laboratory esterification was carried out using a predetermined amount of potassium hydroxide dissolved in 0.18 kg ethanol added to 1 kg vigorously stirred cleaned oil. Stirring was continued at room temperature, the mixture was transferred to a separatory funnel and the glycerol was allowed to separate. After draining off the glycerol, the ethyl ester was transferred into a clean separatory funnel. It was washed with agitation with a volume of water, and was left over a second volume of water until most of the ethanol was removed.

The ethyl ester was allowed to settle and separate after each addition of water. Water from the ester was removed by slowly heating it to 120°C (while stirring) for an hour.

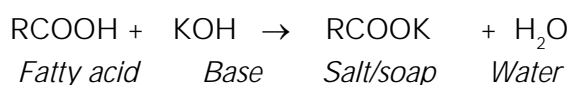
## RESULTS AND DISCUSSION

### Determination of Amount of KOH Catalyst

The fatty acid contained in the waste oil can be neutralized by the basic KOH to produce an undesired substance (a soap, which is an emulsifying agent). The amount of KOH needed, therefore, should allow for the amount needed in the production of the potassium ethoxide catalyst,



in addition to that which is necessary for the neutralization of the fatty acid in the oil.



Titration data for the cleaned oil show that around 0.004 kg of the granular KOH is needed to neutralize the fatty acid content of 1 liter of oil.

### Ethyl Ester Process (Transesterification)

The KOH used reacted with the ethanol to produce the potassium ethoxide catalyst. The reaction mixture then contained 0.18 kg of free ethanol available for the production of the biodiesel and 0.01 kg of ethanol as potassium ethoxide catalyst, for every kilogram of the cleaned waste vegetable oil. The KOH is added at 1.3 per cent of the weight of cleaned oil.

The reaction mixture changed to a turbid orange-brown color within the first few minutes; then it changed to a clear transparent brown color; finally, the mixture again became somewhat turbid and orange-brown colored due to the emulsified free glycerol which was formed.

Any water added to the entire system will reverse the reaction and will quench a proportional amount of the potassium ethoxide catalyst (4.67 part of catalyst per part of water).

Studies on the reaction time show that the yield was optimum at 4 hours. Low ester yields of about 63.6 per cent were obtained.

Soaps, at least in trace amounts, may have been formed during or subsequent to the transesterification process. These reactions have a tendency to occur during the transesterification because of the small amount of water in the system. However, even small quantities of water (less than 1%) can decrease the extent of the conversion reaction. The source of the interfering water for this reaction may be the use of water-containing ethanol, or water in the other reactants at the beginning (from atmospheric exposure). In any case, only a trace of soap needs be formed to promote emulsification of the ester with the wash water.

### Washing of Ester Product

Washing the ester product is necessary in order to improve its fuel properties, largely by removing residual free glycerol and small amounts of potassium remaining from the catalyst. Many of the impurities in the ester have a greater affinity for the water, and they are transferred

by diffusion across the phase boundary into the water, which is greatly hastened by agitation. Agitation can increase the area of phase contact by emulsion formation, or can promote transfer by maintaining the most effective concentration gradient for transfer across the interface.

Some observations that indicated washing was completed included a clear water layer, or the same amount of water was removed as was added in the solution, or the water layer reached approximately pH 7. Completeness of the washing was also determined by noting the emulsion-forming tendency. A sample was stirred vigorously, which formed an emulsion of large, clear, shiny droplets that should quickly separate, settle, and disappear upon cessation of stirring.

The method for washing can be devised, as follows. It will consist of a series of 4 washings, starting with the addition of about 0.18 unit weight of water per unit weight of the biodiesel layer. A second washing will require about 0.14 unit weight of water per unit weight of the resulting biodiesel separated from the water/glycerol layer. The third and fourth washing will require, respectively, 0.09 and 0.04 unit weight of water per unit weight of the resulting biodiesel separated from the water/glycerol layer in each wash. The mixtures are allowed to settle in each of the 4 washes, and the water/glycerol layer drained off every time.

Overall material balance for the process gives:

1 kg Cleaned Waste Vegetable oil + 0.18 kg EtOH + 0.006 kg  $C_2H_5OK$  + 0.01 kg KOH  $\rightarrow$  0.74 kg Biodiesel + 0.44 kg Glycerin + 0.016 soap/ $H_2O$

## FUEL SPECIFIC PROPERTIES

The average density of the biodiesel was 0.905 kg/L, and absolute viscosity was from 98.4 to 110.9 Pa-s. Heating value was estimated to be 44,431.54 KJ/kg.

### Vehicle Test

The biodiesel, in pure form (B100) and in 50% proportion (B50) with petroleum diesel,

was run in an essentially unmodified Toyota 2C indirect injection diesel engine.

The fuel consumptions by the vehicle per unit time in unreplicated comparisons were compared with those for 3 different petroleum diesel brands. Fuel consumption during engine power testing was significantly greater using the B100 as compared with those using the 3 petroleum diesel brands, but is also significantly reduced with B50 (San Miguel *et. al.* 2004). In all cases, fuel consumption was considerably greater with the B100 and the B50 than with the petroleum diesel, the differences ranging from 10.6 to 52.8 per cent. Differences between the B100 and B50 were about 41 per cent. This may be due to the lower viscosity of the biodiesel produced compared with that of the commercially available petroleum fuel, resulting to greater amount of the biodiesel fuel injected to the combustion chamber.

Smoke density (opacity) was not measured, but the smoke generated from the use of B100 has an irritating barbeque-like smell that causes smarting when it comes in contact with the eyes. This greatly reduced when the B50 was used.

CO exhaust emission was considerably greater with the B100 than with all 3 brands of petroleum diesel, the differences ranging from 0.037 to 0.046 per cent. Differences between the B100 and B50 were about 0.037 per cent. CO exhaust emission both decreased with B50. However, NOx increased with the use of B50. NOx emission was considerably less with the B100 than with all 3 brands of petroleum diesel, the differences ranging from 0.0006 to 0.0008 per cent. Differences between the B100 and B50 were about 0.0006 per cent.

## FEEDSTOCK AVAILABILITY

An opportunity for economic growth may reside in the processing of the waste vegetable oil generated from food service establishments in the city into biodiesel. No estimate is available of the amount of waste cooking oil that is potentially collectible for recycling, but survey data show that

about 291 kg per day can be collected at present from the 5 fast food service establishments in the city (Baiting, A.B., *et al.* 2004). The price available from these establishments ranged from ₱10 to 11 per kg of waste vegetable oil.

The new fuel can be used by vehicles thus reduce air pollution, while creating a value added market for spent vegetable oils. Biodiesel will help create a market for these feedstock and help reduce the amount of waste oil being dumped into landfills and sewers. It is likely that the uncollected waste oil is being dumped into sewage systems or landfill sites, thereby generating additional waste disposal problems.

The quality of this waste oil is expected to vary, depending on the vegetable oil used, and variations in cooking practices and waste oil storage and collection systems.

## CONCLUSIONS

The experimental work carried out in this project shows that biodiesel can be produced on a small scale from the waste vegetable oil generated from food service establishments.

However, more research on the esterification of blends of waste vegetable oils is needed, to establish process requirements for higher yield and quality, and to find ways of improving its properties. Ester yields obtained from the oil used in these trials have been low in comparison with those obtained from established methanol-based processes. Raising of yields has a significant effect on the economics of biodiesel production.

More studies should also be conducted to reduce the possibility of forming an emulsion during the water washing process. The wash

methodology could be improved, possibly with the use of mechanical stirring, the mechanism for which should be included. Washing with aeration mixing might also improve the washing process.

More information is required on alternative uses for small amounts of glycerol. When a use for the glycerol has been decided, the removal of methanol and any further processing of the glycerol can be specified.

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