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# ECOLOGICAL FUEL PRODUCED FROM WASTE VEGETABLE OILS AND AGRICULTURAL SEED OILS

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## Abstract

*Biodiesel is a crop-derived liquid fuel that is made from a wide range of renewable locally grown plant resources and can even be made from recycled cooking oils and animal fats. We produced Biodiesel by converting the triglyceride oils to methyl (or ethyl) esters with a process known as transesterification. The reaction requires heat and a strong base catalyst (hydroxide), to achieve complete conversion of the vegetable oil into the separated esters and glycerin. The quality of biodiesel is also dependent on the relative amounts of the used reactants and catalyst, the degree of agitation and the reaction time as well as the quality of the used frying oil. Better yield was obtained when rapeseed oil was used.*

***Key Words**: transesterification, biodiesel, rapeseed oil, used frying oil*

## Introduction

Biodiesel is a crop-derived liquid fuel that is made from a wide range of renewable locally grown plant resources, as well as from recycled cooking oils and animal fats. The simple technology involved in making the fuel and its clean-burning properties make it very viable as both a vehicle fuel and source for residential and commercial heating. Biodiesel is nearly carbon-neutral, meaning it contributes almost zero emissions to global warming. Since biodiesel comes from plants and plants breathe carbon dioxide, there is no net gain in carbon dioxide from using biodiesel. Biodiesel also dramatically reduces other emissions fairly dramatically. Plus, the exhaust smells like popcorn or French fries. Biodiesel is safe to handle because it is biodegradable and non-toxic. According to the National Biodiesel Board, "neat biodiesel is as biodegradable as sugar and less toxic than salt." The one emission that goes up slightly with biodiesel is NOx (up to 15%). NOx contributes to smog. Engine modifications can reduce NOx emissions.

Vegetable oil contains negligible levels of sulfur and reduces emissions of sulfur dioxide responsible for acid rain. Since Biodiesel is made entirely from vegetable oil, it does not contain any sulfur, aromatic hydrocarbons, metals or crude oil residues. The absence of sulfur means a reduction in the formation of acid rain by sulfate emissions, which generate sulfuric acid in our atmosphere. The reduced sulfur in the blend will also decrease the levels of corrosive sulfuric acid accumulating in the engine crankcase oil over time.

The lack of toxic and carcinogenic aromatics (benzene, toluene and xylene) in Biodiesel means the fuel mixture combustion gases will have reduced impact on human health and the environment. The high cetane rating of Biodiesel (ranges from 49 to 62) is another measure of the additive's ability to improve combustion efficiency. In addition, Biodiesel blends have reduced emissions of polyaromatic hydrocarbons, another group of potentially carcinogenic substances found in petroleum.

Biodiesel is comprised of vegetable oil methyl esters. These are hydrocarbon chains of the original vegetable oil that have been chemically split off from the naturally occurring "triglycerides". The hydrocarbon chains are generally 16 to 20 carbons in length, and they are all oxygenated at one end, making the product an excellent fuel. Each ester chain retains two oxygen atoms forming the "ester" and giving the product its unique combustion qualities as an oxygenated vegetable based fuel. Biodiesel is nearly 10% oxygen by weight.

Petroleum diesel, in contrast, is made up of hundreds of different hydrocarbon chains (roughly in the range of 14-18 carbons in length), with residues of sulfur and crude oil remaining. Diesel fuel sold today, even "low sulfur, low aromatic" diesel, contains 20-24% aromatics (benzene, toluene, xylenes etc.), which are toxic, volatile compounds responsible for the fire/health hazards and pollution associated with petroleum diesel. Vegetable oils are also more environmentally friendly in the case of a spill. The fuel is biodegradable, and will quickly break down, preventing long-term damage to soil or water. In some European countries like Norway, Sweden, Poland, Slovakia, and Czech Republic legislation for tax exemption has been passed to encourage the gradual replacement of fossil with less polluting fuels such as Biodiesel. Transesterification is necessary before vegetable oil can be used in most diesel engines.

## Experimental

Biodiesel is produced from vegetable oils by converting the triglyceride oils to methyl (or ethyl) esters with a process known as transesterification. The transesterification process reacts alcohol with the oil to release three "ester chains" from the glycerin backbone of each triglyceride. The reaction requires heat and a strong base catalyst (NaOH or KOH), to achieve complete conversion of the vegetable oil into the separated esters and glycerin. The glycerin can be further purified for sale to the pharmaceutical and cosmetic industries. The mono-alkyl esters become the Biodiesel, with one-ninth the viscosity of the vegetable oil. The amount of free fatty acids in the frying oil sample was determined by means of titration with 0.1M NaOH in the presence of bromthymol blue as indicator.

The specific gravity of the oils and of biodiesel was determined with the density meter. The density of a liquid is usually expressed as specific gravity (the density of the liquid relative to water). The commercial unit of measurement for the specific gravity of diesel fuels is API (American Petroleum Institute) Gravity. The relation between API Gravity and specific gravity (SG) is:

$$\text{API Gravity} = \frac{141.5}{\text{SG}} - 131.5$$

Viscosities at 40°C were measured by means of a U-tube viscometer. The viscosimeter was filled with sample to a level marked on the viscometer tube and was thereafter placed in a water bath at 40°C for half an hour to allow the viscometer and its content to reach 40°C.

In our experiments we produced Biodiesel from rapeseed oil and from used frying oil.

## Results and Discussion

To make biodiesel fuel efficiently from used vegetable oils and rapeseed oil we had to avoid one major problem: soap formation. Soap is formed during base-catalyzed transesterification (using lye) when sodium ions combine with free fatty acids present in used (and some virgin) vegetable oils. The soaps diminish the yield because they bond the methyl esters to water.

The quality of biodiesel attained is also dependent on the relative amounts of reactants and catalyst that are used, degree of agitation and reaction time as well as the quality of the frying oil used as reactant. It is therefore important that the quality of the used frying oil be described before it is used in the transesterification process. We performed a titration to determine the amount of excess catalyst required to neutralize the free fatty acids in the used oil. The sample was titrated with 0.1M NaOH in water solution, in the presence of bromthymol blue. The amount of free fatty acids (FFA) was expressed as acid value (AV = mg NaOH/g sample). FFA content is related to AV through the relation:

$$\text{FFA (wt\%)} = \frac{1}{10} \cdot \frac{\text{AV}}{\text{MW}_{\text{NaOH}}} \cdot \text{MW}_{\text{FFA}}$$

where: $MW_{NaOH}$ = 40 g/mol, $MW_{FFA}$ = 274 g/mol

The conversion is given by (Nye, 1983): FA (wt%) = 0.685 AV

The quality parameters of the oils are presented in Table 1. The density of used frying oils did not differ significantly from that of rapeseed oil.

**Table 1**. Quality parameters of the rapeseed oil and the used frying oil

| Oil | AV mg NaOH/g | FFA % | Viscosity at 40°C, $mm^2/s$ | Specific gravity at 20°C |
|---|---|---|---|---|
| Rapeseed oil | 0.5 | 0.342 | 43.9 | 0.921 |
| Used frying oil | 3.80 | 2.603 | 46.3 | 0.924 |

The molar ratio of alcohol to triglycerides is one of the most important variables affecting the yield of biodiesel. The accepted molar ratio of alcohol to triglycerides is 6:1.

Water in the frying oil feedstock affects the transesterification reaction. Methanol is less sensitive to water than ethanol as a reactant in the transesterification reaction. Water present in the frying oil will also result in a greater extent of saponification, reducing the yield of Biodiesel. Therefore, water was removed by heating the oil to 110°C. After boiling the water off, the oil was filtered.

The type and quantity of the catalyst is also very important for the transesterification reaction. A catalyst is used in the transesterification reaction to break the chemical bonds between the glycerine molecule and each of the three esters attached to it. The reaction can be acid-or-base catalysed, however base catalysis is more favorable since the vegetable oil is acidic. If the vegetable oil has a high fatty acid and water content, then an acid-catalysed transesterification is more suitable. Common bases used in the reaction include NaOH and KOH and common acids include $H_2SO_4$ and HCl (Pelley, 2001).

When used frying oil is a reactant in the base catalyzed transesterification reaction, the base serves as a reactant as well as a catalyst. Firstly, the base neutralizes the free fatty acids present in the oil, and secondly, the base catalyses the transesterification reaction.

We used base catalysis in the first experiment, with rapeseed oil. In the second experiment, with used frying oil, we performed a two-step transesterification reaction (in table 2, the reaction conditions). The first-stage process is not transesterification, but pure and simple esterification. Esterification is followed by transesterification. The first step uses a one-phase acid-catalyzed process to convert the free fatty acids into methyl esters, before using base catalysis to convert the triglycerides, in the second step. The fatty acids are converted at close to the boiling temperature of the methanol (60°C). Methanol-NaOH solution (sodium methoxide) was prepared freshly during experiments in order to maintain the catalyst activity.

**Table 2**. The reaction conditions in the experiments

| | Experiment 1 | Experiment 2 |
|---|---|---|
| Rapeseed oil (ml) | 300 | |
| Used frying oil (ml) | | 300 |
| $H_2SO_4$ 96% (ml) | - | 0.3 |
| NaOH (g) | 1.05 | 1 |
| Methanol (ml) | 60 | 60 |
| Reacting time (h) | 2 | 2.5 |
| Molar ratio methanol: raw oils | 6:1 | 6:1 |
| Reaction temperature (°C) | 60 | 55 |
| Washing | Deionized water | Deionized water |

The methyl esters were separated from glycerine with a funnel. Glycerin settles at the bottom of the funnel. The yield in Biodiesel was greater and the reaction time was shorter in the first experiment, when rapeseed oil was used, as compared with the second experiment (Figure 1). The quality parameters of Biodiesel are presented in Table 3. Viscosity of a fuel will indicate its ability to flow through the fuel system, as well as the ability of the fuel to lubricate the fuel pump and injector.

The kinematic viscosity of the obtained biodiesel met the German Biodiesel Standard (3.5-5 cSt) and US National Biodiesel Standard (1.9-6.0 cSt) (Martin, 1996). The viscosity was an important quality parameter of the Biodiesel since the aim of the transesterification reaction was to reduce the viscosity of the used frying oil. The AV also met the German (0.5max) and US standard (0.8max) (Martin, 1996).

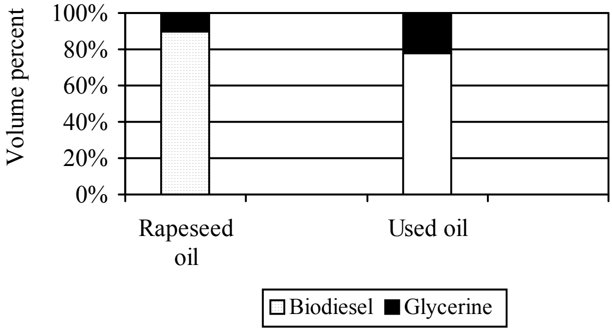


**Fig. 1**. Volume percentage yields of reaction products

**Table 3**. Quality parameters of Biodiesel

| Biodiesel | AV mg KOH/g | Viscosity 25°C, cSt | Viscosity 40°C, cSt | Specific gravity, 15 °C |
|---|---|---|---|---|
| Rapeseed | 0.08 | 5.9 | 4.8 | 0.89 |
| Used frying oil | 0.15 | 6.30 | 5.13 | 0.89 |

## Conclusions

The transesterification of recycled oils with methanol was successfully performed with a maximum biodiesel yield of 78.04%. A greater yield in Biodiesel was obtained when rapeseed oil was used (90%). The used frying oil contains free fatty acids and water, which might reduce the yield in Biodiesel by forming by-products (soaps).

## References

Martin M. (1996). Diesel Fuel Derived from Vegetable Oils, VI: Specifications and Quality Control of Biodiesel. *Bioresource Technology,* 56, 7-11.

Nye, M.J. et al. (1983). Conversion of Used Frying Oil to Diesel Fuel by Transesterification: Preliminary Test. *J. Am. Oil Chem. Soc.,* 60, 1598-1601.

Pelley M. (2001). Mike Pelly's biodiesel method. http://www.journeyto forever.org/biodiesel_mike.htlm.