Emission characteristics of biodiesel fuels produced from Rapeseed Oil

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Abstract. This present research is focused on emission characteristic of biodiesel fuels produced from rapeseed oil. Biodiesel fuels are produced through an optimization of transesterification conditions based on the variation of the molar ratio of alcohol /oil using methanol and ethanol. Best samples are obtained after a transesterification reaction involving an alcohol/oil molar ratio of 18:1, 1% of potassium hydroxide as catalyst, 60 minutes of reaction time, a reaction temperature at 60°C and a stirring speed of 650rpm. The biodiesel fuels show a higher fuel consumption rate and exhaust gas temperature when the engine speed is increased. They also exhibit lower NOx emission with a slight rise in CO and CO₂ emission compared to mineral diesel fuel tested in same conditions.

1. Introduction
Diesel engine constitutes the most effective internal combustion engine used in engineering machinery for power generation (Klaus Mollenhauer and Helmut Tschoeke, 2010). A vast majority of these engines is engaged in transportation (road, railway, naval etc.) and electricity generation, giving rise to their important role in the global economy moving (John, 2007). Fossil fuels are commonly used to run diesel engine due to its high thermal efficiency. The energy generated from the combustion of these fuels leads to an excellent engine performance. However, it simultaneously generates harmful emission gas such as CO₂ (carbon dioxide), CO (carbon oxide), NOx (nitrogen oxides), and PM (particular matters) which threat the sustainability of our ecosystem by contributing to the environmental pollution and global warming (Bentley, 2002). Additionally, the high energy demand combined with the limited petroleum is also major issues which lead to their fast depletion with expectation about 40 years (Gerling, 2007).

These are key factors that motivate research and development for alternative diesel fuel with maximum efficiency and minimum environmental pollutions. In this context, biodiesel can be considered as the most feasible options correspond to its renewability and compliance with fuel standard (Rafael and Juan, 2012).

Biodiesel can be obtained from biological sources such as vegetable oil, animal fat, algae and recycling cooking oil. These raw materials content triglycerides molecules which are converted into fatty acid alkyl ester (biodiesel) by using a specific reaction called transesterification. This is a chemical reaction involving triglycerides with an alcohol in the presence of a catalyst to yield biodiesel and glycerol as by-product (Mushtaq, 2013). The properties of the biodiesel depend strongly on this reaction and are strictly checked before its use in diesel engine. Nevertheless, the incomplete combustion of biodiesel in diesel engine releases harmful gas through the atmosphere. Among them,
carbon monoxide (CO), carbon dioxide (CO₂), Oxides of Nitrogen (NOx) are widely emitted. In fact, many researches considered that CO emissions are reduced when diesel engine is fueled by pure biodiesel (Ozsezen et al., 2009). Experiments are carried out by Kalligeros et al. (2003) and Usta (2005) to estimate the emission characteristic of biodiesel fuels produced from sunflower oil and Tabaco seed oil, respectively. They report a lower CO emission of produced fuels. Alcohol type used in the biodiesel production can influence CO emission. In particular, Bajju et al. (2009) disclosed that biodiesel fuel based methyl esters emits less CO than those based on ethyl esters. In fact, biodiesel is a lower-carbon fuel, so it has a lower elemental carbon-to-hydrogen ratio than diesel (Ozsezen et al., 2009). On the contrary, Ramadhas et al. (2005) pointed out that CO₂ emissions from biodiesel are raised or are similar to diesel one, due to more efficient combustion from diesel fuels.

As for NOx emission, many researchers understand that the oxygen content in biodiesel is responsible of an increase tendency for NOx emission (for example, Hansen et al., 2006). However, Lapuerta et al. (2008) found that the oxygen content in biodiesel has no influence in NOx emission. In order to produce higher quality biodiesel fuel for better estimation, the corresponding fuel properties can be controlled by the transesterification process. The purpose of the present study is performed to optimize the transesterification reaction conditions in order to obtain a quality biodiesel with good engine performance and low toxic gas emission. Best biodiesel samples from the optimum reaction conditions are tested in diesel engine in order to evaluate and compare their performance and emission characteristics with mineral diesel.

2. Experimental Method

2.1. Raw material and chemicals
Rapeseed oil namely Brassica Napus is selected as a raw material because it is widely available around the world and belongs to the preferred oil feedstock for large scale production of biodiesel (Hoekman et al., 2012). Methanol (CH₃OH; 99.8%) and Ethanol (C₂H₅OH; 99.5%) are used in transesterification reaction catalyzed by potassium Hydroxide KOH pellets (85.0%). Acetic Acid is used during the washing process performed after reaction.

2.2. Transesterification process
As a first step, 100g of rapeseed oil is poured in a glass flask of 500ml and preheated in thermal batch to eliminate moistures. Then, the required amount of alcohol (methanol or ethanol) and catalysts (potassium hydroxide), for each sample, is measured and mixed in an Erlenmeyer flask. The solution is stirred on magnetic plate to dissolve the KOH pellets to make methoxide/ethoxide solution which is then added into the preheated oil. The reaction is then started and is run for the required time under stirring condition at ambient pressure. Here, alcohol concentration is varied by making samples with 6:1; 9:1; 12:1; 15:1; 18:1 and 21:1 of molar ratio. Consequently, better transesterification parameters, for each experiment, are 1% of potassium hydroxide as catalyst; 60°C of reaction temperature; 30 min of reaction time and 650 rpm of stirring. After completion of reaction, samples are set to decantation for phase separation by gravity. In other words, the biodiesel floats on the top of the reaction vessel while the glycerol sinks in the bottom.

The crude biodiesel fuel produced is removed and treated with acetic acid to neutralize any unreacted hydroxide, methoxide or ethoxide. It is also washed with water to remove soluble salts (from potassium hydroxide), unreacted alcohols and partial glycerides. Any water that might have mixed with the biodiesel is removed by heating process.

2.3. Fuel Characterization
In general, the biodiesel fuel is characterized by its relative density, viscosity and high heating value. The density is measured at 15°C according to EN ISO 12185 test method (Mert and Atilla, 2015). Dynamic viscosity is measured by using a Brookfield digital viscometer (DV-II+ Pro) connected to a water bath with circulating pump (Brush less DC Pump, model DC 40-2470). Measurement is done at
40°C for three different share rate set at 7.4s-1, 15s-1 and 37s-1 based on the standard test method ATSM D445.

The calorific value is measured using the Shimadzu Auto-Calculating Bomb calorimeter CA-4AJ and according to ASTMD240-14 standard test method (Demirbas, 1998). It is calibrated for 26456 J/g at 20°C with standard benzoic acid. Here, measurement is repeated three times and its average is employed as the final value.

2.4. Engine Test

After analyzing the fuel properties of biodiesel produced here, best samples are tested in diesel engine to evaluate their performance and emission characteristic. Related engine characteristic of mineral diesel is measured under the same conditions to compare with that of produced biodiesel.

Engine test is performed by using Yanmar diesel engine (TF70V-E model). Its specification is given in Table 1.

| Measurement item | Measurement range       | Resolution   |
|------------------|-------------------------|--------------|
| CO₂              | 0…25Vol.%               |             |
| CO, H₂-compensated | 0…10000ppm              | 1ppm         |
| NO               | 0…4000ppm               | 1ppm         |
| NO₂              | 0…500ppm                | 0.1ppm       |
| SO₂              | 0…5000ppm               | 1ppm         |
| H₂S              | 0…300ppm                | 0.1ppm       |
| CO₂-(IR)         | 0…50Vol.%               | 0.01 Vol. %  |
|                  | (0~25Vol. %)            | (0~25Vol. %) |
|                  |                         | (>25Vol. %)  |
| HC               | Natural gas:             |             |
|                  | 100…40000ppm            | 10ppm        |
|                  | Propane:                | 10ppm        |
|                  | 100…21000ppm            | 10ppm        |
|                  | Butane:                 | 10ppm        |
|                  | 100…18000ppm            | 10ppm        |
| K-type (NCr-N)   | -200~1370°C             | 0.1°C        |
| S-type (Pt10Rh-Pt) | 0~1760°C               | 1°C          |

Table 1. Specification of Diesel Engine Model TF70V-E

Measurement is carried out at three different engine speeds, i.e., 1000, 1500 and 2000rpm. Each experiment is repeated three time to calculate the mean values and all data are obtained under steady operation. Fuel consumption rate is measured by observing the volumetric rate from the fuel tank supported by stopwatch.

The exhaust gas temperature and emission characteristic from the biodiesel are analyzed simultaneously by using a Testo 350 Flue Gas Analyzer (TESTO, Inc.). Flue gas analyzer port is set at the end of engine’s chimney as show in the experimental set up (Figure 1). Note that the cetane number for the biodiesel fuel was not measured in the present study.
Table 2. Thermal properties for ROME and ROEE.

| Samples | Relative density (15°C; g/ml) | Kinematic viscosity (40°C; mm²/s; 15⁻¹) | High heating value (MJ/kg) |
|---------|-------------------------------|--------------------------------------|--------------------------|
| ROME    | 0.865                         | 3.49                                 | 40.81                    |
| ROEE    | 0.853                         | 4.50                                 | 39.94                    |
| Diesel  | 0.806                         | 2.50                                 | 45.44                    |

Nitrogen oxides (NOx) are the most significant environmental pollutants emitted from a diesel engine. NOx emission under different engine speeds, form three fuels, is depicted in Figure 2. One observes that NOx decreases with the increase in engine speed. This is generally explained by the shorter residence time available for NOx formation, which may be the result of an increase both in the volumetric efficiency and flow velocity of the reactant mixture specifically at higher engine speed (Amit, 2012). At low and medium engine speed, diesel fuel produces maximum NOx compared to the two fuels, while at high engine speed (2000rpm), NOx emission from ROEE fuel
becomes slightly higher than the other tested fuels. The variation of NOx is proportional to the flue gas temperature and can also depend on the nature of the fuel. Generally, NOx emission includes nitric oxide (NO) and nitrogen dioxide (NO$_2$). NO is the predominant oxide of nitrogen generated from the engine combustion and contributes to ozone formation and is considered as non-toxic gas by itself.

![Figure 2. NOx emission from diesel engine under different speed.](image)

Emission characteristic of CO, for biodiesel and diesel fuels, is depicted in Figure 3. CO emission from ROEE is continuously higher than other fuels and remains practically constant for any engine speed. This confirms that biodiesel based methyl esters emit less CO compared to those based on ethyl esters (Baiju et al., 2009). Meanwhile, the trends of CO emission from ROME and diesel are constantly unstable with the variation of engine speed. In fact, when substituting diesel fuel with biodiesel many factors may influence significantly the variation of CO emission. Generally a decrease trend in CO emission is more evident even though some studies have found that CO emission from biodiesel is higher than that of pure diesel fuel (Cardone et al., 2002; Krahl et al., 2009). At low engine speed, CO emission from biodiesel fuels is higher compared to diesel fuel. This is partly due to the poor atomization conditions influenced by the higher viscosity of biodiesel and the low flue gas temperature which lead to high CO emission (Fontaras et al., 2009). At medium engine speed, CO emission from ROME decreases and becomes the lowest compared to other fuels, as shown in Figure 3.

Figure 4 illustrates CO$_2$ emission for biodiesel and diesel fuels. Emission from ROEE is linearly increased with an increase in engine speed. One observes that there is no significant variation of CO$_2$ emission from ROME under varied speed. In contrast, diesel fuel emits more CO$_2$ compared to ROME at medium speed before its emission decreases and reaches the same level as ROME at high speed. The few carbon dioxide (CO) emission from ROME can be explained by its lower elemental carbon-to-hydrogen ratio than diesel.
4. Conclusion
This study has been performed on the production of biodiesel fuel by transesterification reaction and emission characteristics by engine test. From the results, the optimum reaction conditions for the transesterification of rapeseed oil i.e., alcohol/oil molar ratio 18:1, 1% of potassium hydroxide as catalyst, reaction time 30 minutes, reaction temperature 60°C and stirring speed of 650rpm gave the best results. Fuel properties of normal diesel tested in the same condition is closed to the biodiesel and particularly for those produced by using methanol in the transesterification. Results from engine test discloses that that exhaust emission gas such as nitrogen oxides (NOx) and nitric oxide (NO) are reduced with the increase in engine speed in contrary to carbon oxides CO and carbon dioxide CO$_2$ which are slightly increased. In comparison with diesel fuel, the two biodiesel types (ROME and ROEE) have higher fuel consumption rate because of their lower heating value and their oxygen content. ROME exhibited low emission gas compared to ROEE and mineral diesel as well.

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