

## Effect of mixture of alcohols on biodiesel properties which produced from waste cooking oils and compare combustion performance and emissions of biodiesels with petrodiesel

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**Abstract.** Increasing the petroleum price and environmental problems have been driving forces to find alternative and renewable energy resources. Biodiesel has attracted the attention of many researchers due to various advantages associated with its usages. Several aspects including the type of catalyst, molar ratio of alcohol to oil, temperature, purity of reactants and free fatty acid content have mainly influence on transesterification. In this work, waste cooking oils and two types of alcohols with different molar ratio of methanol to ethanol and potassium hydroxide as catalyst were used as materials. Effect of alcohol on the physical properties, combustion efficiency and emitted gases of biodiesels were studied and compared with petrodiesel. Mixture of methanol and ethanol were used for transesterification in order to optimize solvent property of methanol and rapid equilibrium using methanol. Waste cooking oil is considered as the most suitable material due to its availability and cost-effectiveness. To examine the performance and emissions of biodiesels, a wet base semi-industrial boiler was used for combustion and a flue-gas analyzer has measured the emitted gases. Finally, physical properties of biodiesels were measured in Abadan's Oil Refinery Laboratory.

**Key Words:** biodiesel; combustion efficiency; emission; renewable energy; waste cooking oil.

**Abbreviations:** FFA-Free Fatty Acid; ASTM-American Society for Testing and Materials; cSt.-CentiStoke; CN-Cetane Number; PPM-Part Per Million; N/A-Not Available; RPM-Revolution per Minute; WCO- Waste Cooking Oil.

**Introduction.** The exponential growth of world population would be ultimately led to increasing the energy demand in the world. Petroleum is a non-renewable energy resource; which means that the resources of this type of fossil fuel are finite and would be run out upon continuously usage. Both of the shortages of resources and increasing the petrol price have been led to finding new alternative and renewable energy resources. Apart from these situations, environmental issues also have driving force for development of alternative energy resources, since burning of fossil fuels would be cause various environmental problems including global warming, air pollution, acid precipitation, ozone depletion, forest destruction, and emission of radioactive substances (Dincer 2000). The alternative energy resources include hydro, wind, solar, geothermal, hydrogen, nuclear, and biomass (Demirbas 2005). Biofuels derived from biomass are considered as the most promising alternative fuel resources because they are renewable and environmental friendly. Biofuels can be defined as any liquid or gaseous fuels that can be produced from biomass, including biodiesel, alcohol and biogas (Launhardt & Thoma 2000). Biodiesel can be produced from methanol, ethanol and vegetable oils which are agriculturally derived products. Compared to petrodiesel, biodiesel has many advantages such as lower engine emissions, biodegradable, renewable, and superior lubricating property (Alcantara et al 2000) but it slightly increases fuel consumption, whereas engine power is slightly reduced or remains constant compared to petrodiesel (Pischinger et al 1982).

Currently, the cost of this fuel is a primary factor that limits its use. One way to reduce the cost of biodiesel is to use a less expensive form of vegetable oil such as waste oils. Many reports are available on the use of waste cooking oil for biodiesel production (Cvengroš & Cvengrošová 2004; Dorado et al 2002, Tomasevic & Siler-Marinkovic 2003). The reason that waste cooking oil (WCO) cannot be directly used in diesel engines is back to high viscosity of these materials that it makes many problems for fuel injector. There are a number of ways for reduction of waste cooking oils' viscosity. Dilution, micro-emulsification, pyrolysis, and transesterification are four techniques applied to solve the problems encountered with the high fuel viscosity. One of the most common methods that used to reduce oil viscosity in the biodiesel industry is called transesterification (Demirbas 2008). Mixed methanol-ethanol system was used in order to use better solvent properties of ethanol and equilibrium conversion using methanol. In general, physical and chemical properties and also performance of ethanol were comparable to those of the methanol. Ethanol has higher viscosity, lower cloud and pour points, lower smoke opacity and almost same heat content relative to methanol.

Many researchers investigated about important reaction conditions and parameters on alcoholysis of triglycerides. They also prepared methyl and ethyl esters from palm and sunflower oils using NaOH as the catalyst and using 100% excess alcohol and applied heat in the reaction. Lago et al (1985) proposed the use of ethanol for both oil extraction and esterification process. Clark et al (1984) transesterified soybean oils into ethyl and methyl esters, and compared the performances of the fuels with petrodiesel (University of Idaho 1994).

The optimum conditions developed for production of good quality biodiesel from used sunflower oil were: molar ratio of methanol to oil 6:1, with 1% of KOH, at 25°C and reaction time of 30 min (Dmytryshyn et al 2004). The alkali-catalyzed transesterification can be completed at low temperatures and pressures with high conversion rates, which mean lower operating cost of alkali-base method compared with other methods (Leung & Guo 2006). Excess catalyst was used to neutralize free fatty acids (FFA) present in waste cooking oil. A process was developed by Canakci & Gerpen (2001) where the high FFA feedstock was initially treated using acidic catalyst to reduce FFA level below 1%. Pre-treated feedstock with FFA less than 1% was then transesterified with methanol using alkaline catalyst. It was observed that two-step acid catalyzed esterification followed by alkaline catalyzed reaction improved ester yield.

The objective of this study is to produce biodiesel from waste oil which collected from restaurant of Ahvaz Faculty of Petroleum Engineering. Waste oil used for two deals: (1) it has lower price relative to pure oils, and (2) avoid from environmental problems. At first, waste oil esterifies to reduce FFA to lower than 1% and then transesterification perform by mixtures of methanol-ethanol and KOH as catalyst. When biodiesel was produced, physical properties were measured in Abadan's Oil Refinery laboratory. Combustion tests of biodiesels and petrodiesel carry out in heat transfer's laboratory of Petroleum University to find out: (1) effect of mixture of alcohol on biodiesel's performance and their emissions, and (2) compare the overall performance of biodiesels and petrodiesel. Addition to the performance, gas emissions and percent reduction of emissions relative to diesel are compared.

**Material and Method.** Experimental procedure comprised of three sections: (1) biodiesel production, (2) ASTM tests, and (3) combustion. Tests were carried out in two separate laboratories in the Ahvaz Faculty of Petroleum Engineering, in April 2012. Transesterification reactions were accomplished in the gas research laboratory. The combustion test was carried out in the heat transfer laboratory.

**Raw material.** In this study, waste cooking oils which were collected from restaurant of Ahvaz Faculty of Petroleum Engineering, have been used as feedstock. Methanol and ethanol with a purity of 99.5% were purchased from Merck and used without any treatment. Potassium hydroxide, sulphuric acid and silica gel were purchased from local shop.

**Apparatus.** LR 2000P modularly expandable laboratory reactor was used for transesterification. The reactor was double-walled jacketed with 2 liters vessels available



Figure 1. LR 2000 P Laboratory Reactor.

made of stainless steel, with bottom discharge valve. Figure 1 shows the LR 2000p reactor. An Eurostar power control-visc P7 overhead stirrer for mixing with 8 to 290 rpm was used. The combustion study was accomplished on a fully instrumented water jacketed combustion chamber equipped with a sterling 90UK Spec liquid fuel burner. This combustion chamber is a stainless steel horizontal cylinder which has one meter long and 45 cm inner diameter and outer diameter of 50 cm. A KANE QUINTOX 9106 flue-gas analyzer which equipped with electrochemical cells allows investigation of CO, NO and SO<sub>2</sub> in exhaust stack in addition to the standard analysis.

### ***Biodiesel production***

***Pre-treatment of WCO.*** The WCO collected from restaurant of Ahvaz Faculty of Petroleum Engineering was contaminated with water, solid particles, FFA and many other impurities. Water creates a problem such as foaming during transesterification; since, WCO was pre-treated before the reaction. Solid particles of waste oil were filtered by a No. 40 Quantitative. WCO was mixed with silica gel (10 weight percent, 50

meshes) to remove water content by stirring the mixture and vacuum filtration for the removal of silica gel.

***Esterification.*** For reducing the FFA of WCO, it should be esterified before the transesterification by one acidic catalyst to avoid saponification problems. Two liter of WCO was poured into the batch reactor. Two weight percent of sulphuric acid as a catalyst was mixed with 3:1 molar ratios of alcohol to oil and mixed vigorously. The solution then poured into the WCO and reacts at 60°C for 2h with 290 rpm. When the reaction was completed, thick layer of soap was formed which interfered with the glycerol separation.

***Transesterification.*** Waste oils were converted into biodiesel by alkali-catalyzed transesterification reaction at the same operating conditions. In alkali catalytic transesterification method, catalyst is dissolved in mixture of methanol/ethanol by vigorous stirring in a batch reactor. Transesterification reactions were carried out at optimum conditions - 6:1 molar ratios of alcohol to oil, 60°C reaction temperature and 1 wt% of alkali catalyst concentration - which already reported for alkali-based approach (Barnwal & Sharma 2005; Houri Jafari & Baratimalayeri 2008; Gui et al 2008; Maa & Hanna 1999; Kandedo et al 2009; Keera & El Sabagh 2011). The anhydrous waste oil which esterifies one stage was poured into the reactor and allowed to equilibrate to the temperature of reaction (heated to 60°C) at 290 rpm. Hot water circulated in the jacket of reactor provided necessary heat for reaction. Catalyst was dissolved in various amount of methanol/ethanol and then was added to the waste oil. Various mixture of methanol/ethanol include 5:1, 4.5:1.5, 4:2, 3.5:2.5, 3:3 and catalyst with concentration of 1 Wt% to oil were used. The final mixture is stirred vigorously for 2h at 60°C in atmospheric pressure.

A successful transesterification reaction produces two liquid phases. Glycerin has higher density relative to biodiesel and goes to bottom of funnel separator after hours.

Phase separation can be observed within 15 min and can be complete within 4h of settling. After drain of the glycerin, biodiesel was washed out from impurities and unreacted agents by warm water. Finally biodiesel dried by silica gel (10 weight percent, 50 meshes) to remove water content by stirring the mixture and vacuum filtration for the removal of silica gel.

**Operating conditions.** Combustion tests were carried out at different operating conditions into the semi industrial boiler at a steady state condition that permitted good repeatability. All fuels were tested at the same operating conditions which are defined by setting fuel pressure, fan damper setting and choosing a nozzle. Air/fuel ratio and fuel pressure can be varied by the user.

**Results and Discussion.** Transesterification of WCO with alcohols was carried out in LR2000P reactor, using KOH as catalyst. Table 1 presents operating conditions and yield of various methyl-ethyl esters that were produced.

Table 1

Operating conditions and yield of esters

Sample	Operating conditions					Yield (%)
	Methanol (ml)	Ethanol (ml)	KOH (gr)	Oil (lit)	T (°C)	
5:1	410	120	17.5	2	60	85.4
4.5:1.5	364	174	17.5	2	60	84.8
4:2	324	232	17.5	2	60	82.6
3.5:2.5	284	292	17.5	2	60	80.1
3:3	238	352	17.5	2	60	78.3

Operating conditions were the same except for the molar ratio of methanol/ethanol. The amount of ester is depicted in this table as the product of reaction. It was observed that with decreasing the molar ratio of methanol/ethanol, yield of biodiesel was decreased, since methoxide radicals has a higher reactivity relative to ethoxide radicals and with decreasing the methanol and increasing of ethanol, reactivity was decreased.

**Physical properties.** Physical properties of biodiesel such as flash point, cetane index, heating value, viscosity, etc. were determined with the methods given in Table 2.

Table 2

Standard methods applied for biodiesel properties

Physical property	Test method
Flash Point	ASTM D 93
Cetane Index	ASTM D 976
Heating Value	ASTM D 240
Viscosity	ASTM D 445
Specific Gravity	ASTM D 1298
Copper Strip Corrosion	ASTM D 130
Cloud Point	ASTM D 2500
Pour Point	ASTM D 97
Acid Number	ASTM D 974
Water and Sediment	ASTM D 2709
Carbon Residues	ASTM D 198
Total Sulfur	UOP 357

Physical properties of biodiesel that has been produced at the laboratory were measured in Abadan's oil refinery laboratory and depicted in Table 3. It was observed that by decreasing the molar ratio of methanol/ethanol, viscosity was increased from 4.7 to 6.1

cSt, total sulphur was increased from 1.4 to 2.6 ppm, cloud point was increased from -2 to 0°C and heating value increased from 39.62 to 40.40 MJ/Kg.

Table 3

Physical properties of biodiesel

Test	Product					Reference	
	5:1	4.5:1.5	4:2	3.5:2.5	3:3	Petrodiesel	ASTM
Flash Point (°C)	190	170	154	160	163	55	min 130
Cetane Index	56.2	57.4	57.8	58.0	58.6	min 50	min 51
Heating Value (MJ/Kg)	39.62	39.87	40.03	40.20	40.40	45.4	37.6-40.5
Viscosity @ 40°C (cSt.)	4.7	5.0	5.4	5.7	6.1	2-4	1.9-6.0
Specific Gravity	0.886	0.886	0.887	0.889	0.888	0.857	0.880
Copper Strip Corrosion	1a	1a	1a	1a	1a	1a	No. 3 max
Cloud Point (°C)	0	-1	-1	-2	-2	-6	N/A
Pour Point (°C)	-4	-5	-6	-7	-7	-19	N/A
Acid Number (mg KOH/g)	0.255	0.247	0.241	0.236	0.209	0.002	0.800
Water and Sediment	0.002	0.004	Trace	0.001	0.001	Trace	0.005
Carbon Residues (Wt %)	0.004	0.002	0.002	0.003	0.002	max 0.01	max 0.05
Total Sulfur (ppm)	1.4	2.1	2.3	2.5	2.6	50-500	15

**Boiler performance.** To examine the performance and emissions of all the fuels, a wet base semi-industrial boiler was used. Figure 2 presents the combustion laboratory unit.



Figure 2. Combustion Laboratory Unit.

The flame burns within a stainless steel combustion chamber which is water cooled and of sufficient size to prevent flame impingement under normal conditions. Observation windows on the side of the chamber allow the flame to be observed. The burner has different air settings that can be set to give different air to fuel ratios. Cooling water inlet and outlet temperature, air inlet temperature, exhaust temperature, flame temperature, cooling water flow rate, fuel flow rate, and mass flow rates of air and fuel were read from control panel. All fuels were burned at two fuel pressure of 120 and 160 psi. Average of fuel consumption at 120 psi is 5.6 L h<sup>-1</sup> for biodiesels and 5.4 L h<sup>-1</sup> for petrodiesel. At 160 psi, 6.12 L h<sup>-1</sup> petrodiesel and 6.42 L h<sup>-1</sup> biodiesel were consumed. Combustion efficiency of boiler was calculated by using the inlet and outlet water temperatures, heating value of fuel, and flow rates. In this study, combustion efficiency and emissions of biodiesels were compared to those of petrodiesel. For every set of experimental test, temperature and emissions readings were recorded after steady-state combustion was achieved as indicated by stable exhaust gas and water outlet temperature values. For better reliability, all tests repeats at 5 times.

**Exhaust temperature.** Figures 3a and 3b depict the variation of exhaust temperature ( $T_{exh}$ ) with Air/Fuel (A/F) ratio. The  $T_{exh}$  for biodiesels varied between 563 to 629°C at 120 psi and 613 to 688°C at 160 psi. Exhaust temperature of petrodiesel varied from 596 to 637°C at 120 psi and 657 to 703°C at 160 psi. With increasing the fuel pressure, flue gas temperature of biodiesels and petrodiesel were increased. Petrodiesel have higher exhaust temperatures relative to biodiesels because of lower mass flow rates and higher heating value of petrodiesel. Tashtoush et al (2003) also reported the higher exhaust temperature of petrodiesel than biodiesels if the fuels had been injected at the equal fuel pressure to the boiler. Variation of  $T_{exh}$  with A/F was different from variation of  $T_{exh}$  with fuel pressure. At the lower A/F ratios,  $T_{exh}$  of biodiesels and petrodiesel were closer than higher A/F. It is seen that in Figures 3a and 3b the exhaust temperature decreases as A/F ratios increases. Decrease of exhaust temperature with increasing A/F ratios is related to two effects. The first is the entering excess air to boiler which is colder than the gases in it and the second is that the heat generation in system is constant while it is distributed as sensible heat between circulating water in boiler and gases which leave boiler. Despite these results, Batey (2003) reported no significant difference in the exhaust temperature of biodiesel compared with petrodiesel.

It can be seen that in Figures 3a and 3b,  $T_{exh}$  was increased by decreasing the methanol/ethanol ratio. This might be due to the higher heating value of biodiesels at lower methanol/ethanol ratios. Biodiesel which produced from lower ratio of methanol/ethanol has exhaust temperature closer to that of petrodiesel. In this study, biodiesel which produced from molar ratio of 3:3 has a highest exhaust temperature between other.

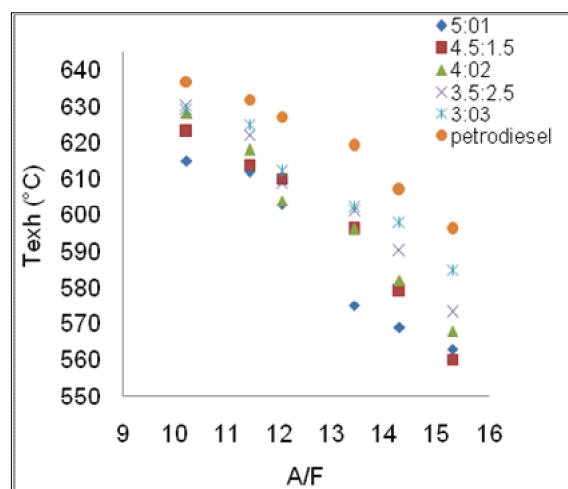


Figure 3a. Variation of  $T_{exh}$  (°C) vs. A/F ratio at 120 psi.

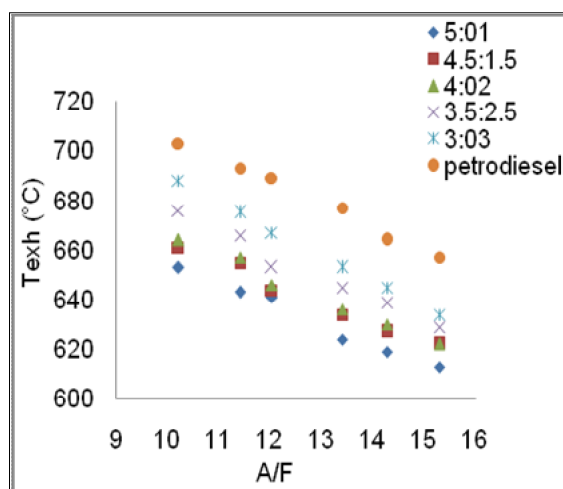


Figure 3b. Variation of  $T_{exh}$  (°C) vs. A/F ratio at 160 psi.

**Combustion efficiency.** The combustion efficiency,  $\eta_c$ , is the ratio of heat which transferred to water in jacket of boiler,  $Q_w$ , to the amount of heat input to boiler,  $Q_{in}$ . Figures 4a and 4b presents the variation of combustion efficiency in relation to A/F ratio at two fuel pressure. By increasing the A/F ratio, temperature of flame was decreased; hence, difference between cooling water temperature and flame temperature results to a reduction of  $Q_w$  which consequently leads to a lower efficiency of system. The combustion efficiencies increased as the fuel pressure increased. This trend was observed due to this fact that rising fuel pressure enhanced the spray characteristics of the fuels.

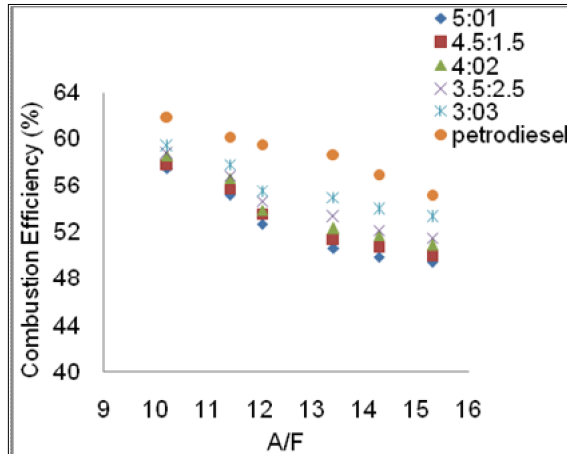


Figure 4a. Variation of combustion efficiency (%) vs. A/F ratio at 120 psi.

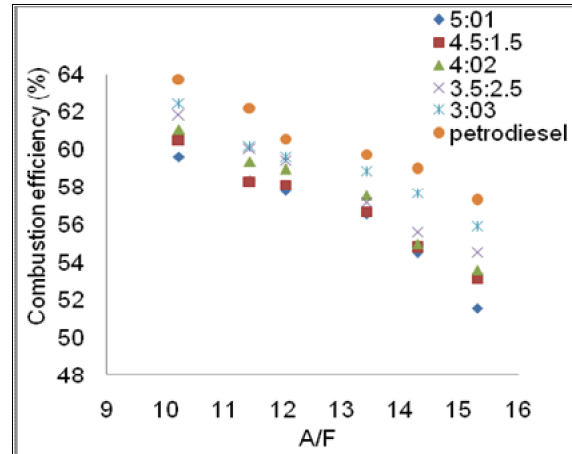


Figure 4b. Variation of combustion efficiency (%) vs. A/F ratio at 160 psi.

Figures 4a and 4b indicate that petrodiesel has performed a little better but only to 2 to 6%. This reason may be due to the lower density and viscosity of petrodiesel compared to biodiesel which in turn may have better mixability and uniform distribution in flame. Biodiesel, produced from lower molar ratio of methanol/ethanol, has a better efficiency. This effect was related to the increasing the boiler's temperature with decreasing the methanol/ethanol ratio.

### Emissions

**Nitrogen oxides ( $NO_x$ ).** Figures 5a and 5b show the measured emissions of nitrogen oxides ( $NO_x$ ) for all fuels at 120 and 160 psi of the fuel pressure.

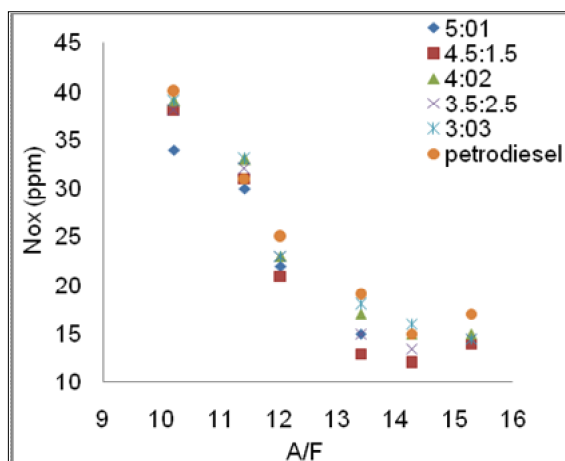


Figure 5a. Variation of  $NO_x$  (ppm) vs. A/F ratio at 120 psi

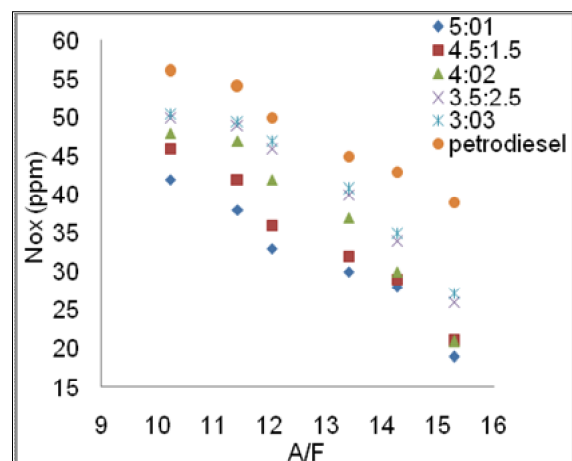


Figure 5b. Variation of  $NO_x$  (ppm) vs. A/F ratio at 160 psi

The utilization of biodiesels in the diesel engines often led to an increase in  $NO_x$  emissions (Heywood 1988; Walker 1994; Szybist & Kirby 2005; McCormick et al 2001; Cheng et al 2006; Hess et al 2005), while various results were obtained in boilers (Batey

2003; Krishna et al 2001; Krishna et al 2002; Krishna 2003; Krishna 2004; Kiat Ng & Gan 2010; Win Lee et al 2004; Vanlaningham et al 2004). When biodiesel is burnt in boilers,  $\text{NO}_x$  tends to decrease because combustion process is different than in engines (open flame for the boilers, enclosed cylinder with high-pressure spray combustion for engines). The formation of  $\text{NO}_x$  depends mainly on the percentage of oxygen and exhaust temperatures. By increasing the exhaust temperature and the oxygen on boiler, the  $\text{NO}_x$  was increased. By increasing the A/F ratio, since higher amount of air entered in boiler and entrance heat was constant, the exhaust temperature was reduced and hence  $\text{NO}_x$  was reduced at the flue gases. Many researchers reported a reduction in  $\text{NO}_x$  emissions by using biodiesels compared with petrodiesel over a wide range of A/F at two different energy rates of a boiler (Tashtoush et al 2003; Bahamin Bazooyar et al 2011; Afshin Ghorbani et al 2011).

By decreasing the molar ratio of methanol/ethanol, flame temperature was increased; hence, the amount of  $\text{NO}_x$  was increased. Therefore, temperature has a more effect on amount of  $\text{NO}_x$ . Petrodiesel have higher  $\text{NO}_x$  relative to biodiesels at 160 psi but if the fuels had been injected at 120 psi, this amount almost is equal for petrodiesel and biodiesels.

*Carbon monoxide (CO)*. Figures 6a and 6b show the measured emissions of carbon monoxide (CO) with A/F ratio for all fuels at 120 and 160 psi. It was seen that biodiesels emits less pollutants than petrodiesel. The higher concentration of CO for petrodiesel is due to the higher carbon content by weight of petrodiesel relative to the biodiesel (Goering et al 1987; Vera et al 2007; Szybist & Kirby 2005). The high flow rate of entrance air extinguished the flame and led to poor distribution of the fuel in the chamber. Furthermore, the high ratio of air relative to fuel caused a decreased temperature and led to incomplete and unstable combustion of fuels. Consequently, the high fuel pressures and low A/F led to improvement in combustion of biodiesels and petrodiesel in the boiler. At constant A/F, amount of CO reduces by decreasing molar ratio of methanol/ethanol. Biodiesel with molar ratio of 3:3 emitted about 47.3 to 51.2% at 160 psi and 42.5 to 57.1% at 120 psi less CO relative to petrodiesel.

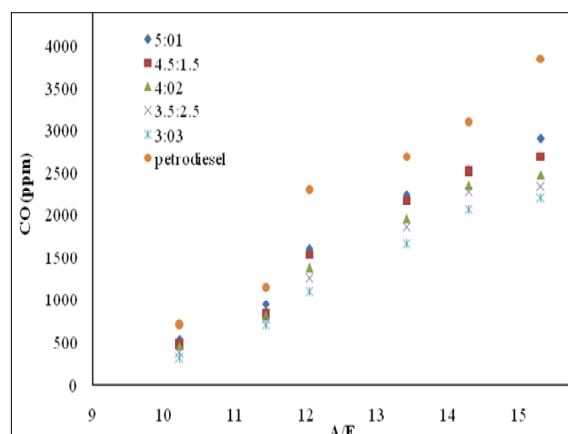


Figure 6a. Variation of CO (ppm) vs. A/F ratio at 120 psi

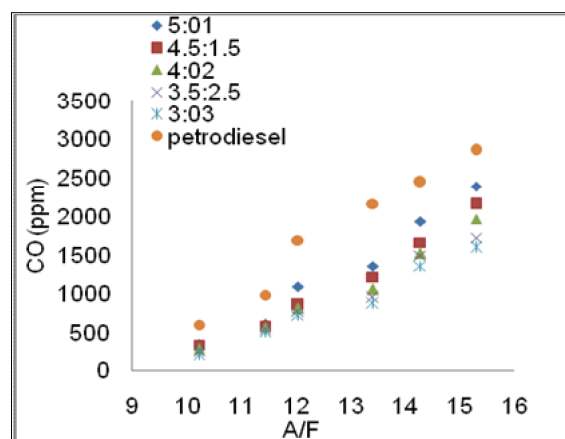


Figure 6b. Variation of CO (ppm) vs. A/F ratio at 160 psi

*Carbon dioxide (CO<sub>2</sub>)*. Figures 7a and 7b show variation of CO<sub>2</sub> with A/F ratio for all fuels at 120 and 160 psi and they also show that 63 to 74.4% at 120 psi and 54.67 to 64.12% at 160 psi reduction in CO<sub>2</sub> is attainable if biodiesel with 3:3 mole ratio of methanol/ethanol is burnt instead of petrodiesel at the same condition. Petrodiesel emitted higher amounts of CO<sub>2</sub> in contrast to five different types of biodiesels at six different A/F ratios and two fuel pressure of the boiler which make biodiesels more suitable for using in boilers than petrodiesel. Higher CO<sub>2</sub> of petrodiesel's combustion is due to the higher carbon content of petrodiesel relative to the biodiesel. Biodiesel releases only the CO<sub>2</sub> that was absorbed by the plants as they were growing and making



oil. With increasing A/F ratios, the percent of CO<sub>2</sub> in flue gas of all fuels decreased, because the flue gas diluted with increasing air. With decreasing molar ratios of methanol/ethanol, percent of CO<sub>2</sub> in the flue gas was decreased.

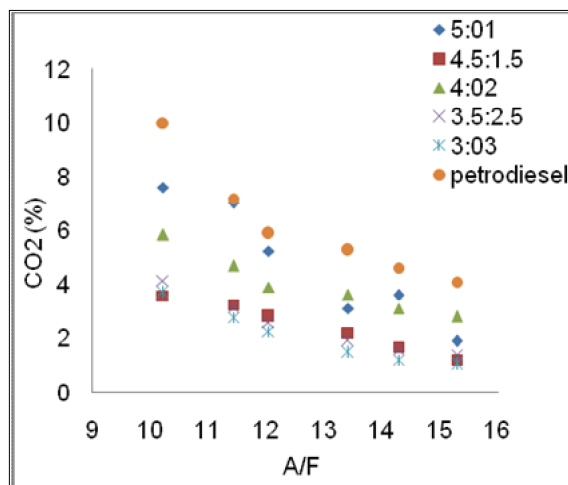


Figure 7a. Variation of CO<sub>2</sub> (%) vs. A/F ratio at 120 psi

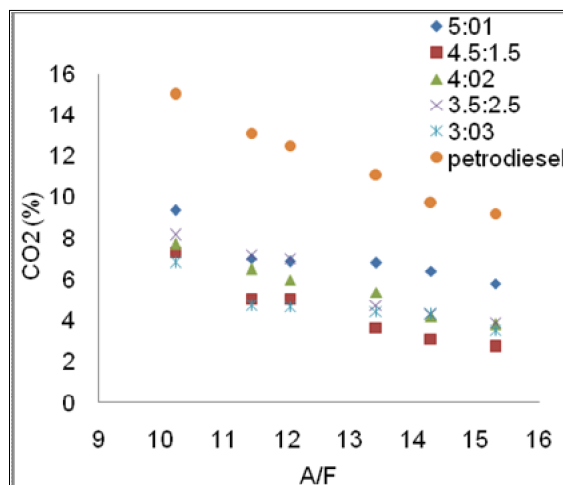


Figure 7b. Variation of CO<sub>2</sub> (%) vs. A/F ratio at 160 psi

If biodiesel with 3:3 molar ratios of alcohols burnt instead of 5:1 molar ratio, CO<sub>2</sub> was decreased from 44.74 to 66.11% at 120 psi and 27.12 to 39.14% at 160 psi.

*Sulphur dioxide (SO<sub>2</sub>)*. Figures 8a and 8b show variation of the emissions of sulphur dioxide (SO<sub>2</sub>) with A/F ratios. As it is shown, the SO<sub>2</sub> emission of biodiesel is almost negligible compared to petrodiesel since it contains much less sulfur than typical petrodiesel. Base of sulphur in the biodiesel was return to methanol. Methanol was produced from corn and corn has sulphur. When methanol was used for producing of biodiesel, this sulphur was observed in the biodiesel.

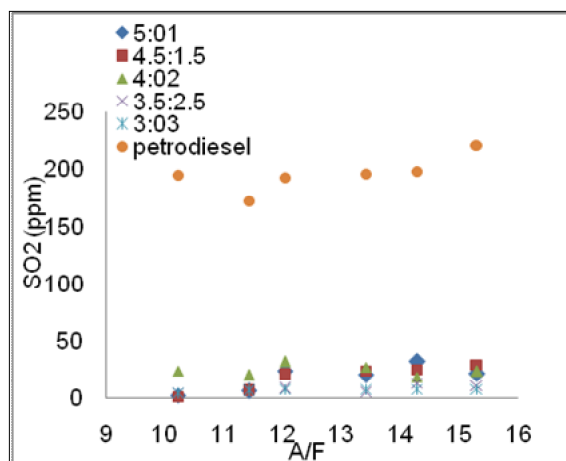


Figure 8a. Variation of SO<sub>2</sub> (ppm) vs. A/F ratio at 120 psi

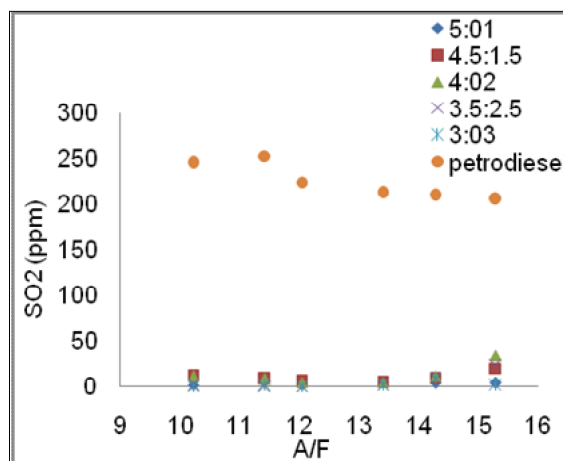


Figure 8b. Variation of SO<sub>2</sub> (ppm) vs. A/F ratio at 160 psi

**Conclusion.** This experimental study compares the physical properties, emissions and combustion efficiencies of biodiesels based on WCO and various mixture of methanol-ethanol in a semi industrial boiler. The investigations were carried out at steady state conditions of the boiler, and results were obtained after five frequent experiments which have good repeatability. The effect of fuel pressure and A/F ratio upon combustion performance and emissions of the biodiesels and petrodiesel were studied in order to find out the probable advantages or disadvantages of mixture of methanol-ethanol on biodiesel and compared to that of petrodiesel.

Cloud and pour point of all methyl ethyl esters were in the range of ASTM. Type of alcohol used in transesterification has an insignificant effect on cetane index, flash point, heating value, and other physical properties of esters except for cloud point and pour point. Biodiesel which produced from lower molar ratio of methanol/ethanol has a higher yield than other esters. This effect was related to the increasing the boiler's temperature with decreasing the methanol/ethanol ratio. Biodiesel has a high flash point, therefore for a good combustion it should be blend with petrodiesel. Combustion efficiency of esters was lower than that of petrodiesel but only 2 to 6 percent. With increasing molar ratio of methanol/ethanol, NO<sub>x</sub> emissions were decreased in the boiler. Ester with 5:1 molar ratio of methanol/ethanol emitted the lowest NO<sub>x</sub> in biodiesels.

Esters which were produced from lower molar ratio of methanol/ethanol have a higher efficiency and lower emitted gases except NO<sub>x</sub> relative to other; hence, by decreasing the molar ratio of methanol/ethanol, the produced biodiesel has a better property, combustion efficiency and lower emitted gases.

Finally, the proposed alternatives to petrodiesel significantly decrease the amount of waste oil residues as well as subsidies spent for agricultural over-production, whilst becoming less dependent on fossil oil.

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