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Quaternary Blends of Diesel, Biodiesel, Higher Alcohols and Vegetable Oil for CI Engine: A Review

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***Abstract*- Biofuel production is seen in many countries around the world as an alternative fuel with less carbon footprint and GHG emission compared to the fossil fuels. Vegetable oils, biodiesel and alcohols are important alternative fuel resources for diesel engines. Prominent fuels of the three types include: soybean oil which has efficient amount of productivity, biodiesel made of waste oils which do not affect food security and alcohols with high number of carbons. There is potential to use quaternary blends of diesel fuel, waste oil methyl ester, soybean oil and higher alcohols, such as propanol and pentanol, in diesel engines for the purpose of increasing the use of biofuels and decreasing fossil fuel consumption. In this work, diesel fuel (D) was mixed with biodiesel (B), and biodiesel-vegetable oil (VO)-alcohol blends using the higher alcohols of propanol (Pro) and pentanol (Pen). Test fuel blends of DB (50 vol% D-50 vol% B), DBVO Pro (40 vol% D-40 vol% B-10 vol% VO-10 vol% Pro), DBVO Pen (40 vol% D-40 vol% B-10 vol% VO-10 vol% Pen) were prepared through the splash blending method and tested in a diesel engine.**

***Index Terms*- Bio Fuel, hydrocarbon (HC) emissions, carbon monoxide (CO)**

I. INTRODUCTION

A country's economic progress majorly depends upon its energy resources. Highly developed countries like the USA and China have a high energy consumption rate compared to other developing nations of the world. It has been reported that India's absolute primary energy consumption is only $1/29^{th}$ of that of the world, $1/7^{th}$ of USA and 1/1.6 time of Japan. However, with the increasing danger posed by pollution, there is an urgent need to shun the excessive use of pollution releasing conventional sources of energy and switch over to environment friendly options like the renewable energy resources.

Reliance on fossil fuel power faces critical limits and the first limit to fossil fuels is that they are finite in nature.

The second critical limit for fossil fuel use, is the associated global warming. Fossil fuels cannot be used until their complete depletion without causing catastrophic damage to the earth. Studies show that if we burn all recoverable fossil fuels, it would be sufficient to destroy the Atlantic Ice Sheet, which would lead to dramatic climate change and sea level increase.

Therefore, there is need to develop sustainable alternative fuels, which can gradually decrease the demand of fossil fuel. That is why the phenomenon of renewable energy come in contact.

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Renewable energy comes from replenishable energy sources such as sunlight, wind, etc. It has been estimated that India's renewable energy production amounts to a total of over 100,000 MW. There is a fully dedicated ministry of New and Renewable Energy, assisted by several state nodal agencies that work to enhance India's position in use of renewable energy sources. The ministry works in coordination with various NGOs and village development societies to outstretch the renewable energy programmes to every corner of the country. Moreover, there is a separate agency named Indian Renewable Energy Development Agency Limited (IREDA) which works to provide term loans for various renewable energy projects.

As the number of vehicles around the world increases, use of alternative fuels in internal combustion engines has become as a necessity. Both the European Union (EU) and the US have adopted new initiatives for the use of biofuels in vehicles, to reduce emissions and decrease the dependency on fossil fuels.

There are two main alternative fuels which are used in internal combustion engine, bio-oils and biodiesel made of various vegetable oils as well as animal fat and bio-alcohols. Vegetable oils and biodiesel are compatible with diesel engines while bio-alcohols can be used in both spark ignition and compression ignition engines.

Diesel engine is most popular engine because of their higher efficiency and less fuel consumption. It means a diesel engine is generally 20% more efficient then an equivalent petrol engine. Thus, it is important to focus on all three alternative fuel resources of bio-oils, biodiesel, and bio-alcohols for new opportunities. Vegetable oils and biodiesel are compatible with diesel engines while bio-alcohols can be used in both spark ignition and compression ignition engines.

Vegetable oils has been tested in diesel engines for many years. Soybean oil (also known as soy-oil) is the most widely used oil in the US and throughout the world. Soybeans are the dominant oilseed in the US, accounting for about 90% of US oilseed production. Straight use of neat vegetable oils is limited in internal combustion engines because of their high viscosities and densities, and this limitation has led to the use of biodiesel which has relatively better fuel properties. However, the high production cost of biodiesel, its relatively high viscosity as compared to diesel, poor cold flow properties and high NOx emissions are important parameters to limit the use of biodiesel.

Generally, alcohol not used directly in diesel engine, some properties of alcohol fuel are suitable additive for diesel & biodiesel. So, to reduce the disadvantages of biodiesel, diesel-biodiesel or vegetable oil mixtures are blended with alcohols or similar additives. There is initiative by EU to increase the use of biofuels in diesel engines as much as 20% by the year 2020. To achieve this purpose, bio-alcohols have become important alternatives and additives.

Recent studies have developed novel pathways to use jojoba oil to produce biodiesel and high value alcohols for pharmaceuticals and cosmetics applications. However, there is little data on the emissions of jojoba, algae, and chocolate waste fuels on engines. This study aims to build upon existing literature on diesel engine performance using chocolate waste methyl ester, jojoba methyl ester and algae methyl ester as alternative fuels, adding emissions data under varying loads and injection timing. Alcohols are clean fuels due to hydroxyl (OH) in their molecular structures. The solubility of alcohol in diesel fuel depends on following factors-

- Water content,
- Temperature,
- Additives,
- Hydrocarbon composition of the diesel fuel

In addition, low viscosity and density of alcohols allow vegetable oils to be used in diesel engines and have increased the use of microemulsion over transesterification because of easiness and lower cost. Especially methanol (CH3OH) and ethanol (C2H5OH), are not good alternative fuels because of their low cetane numbers. However, the number of carbons in alcohols affects overall fuel properties. As the number of carbons increases (higher alcohols), alcohols can be mixed with organic molecules more easily and reach higher cetane no. and heat of combustion. Thus, higher alcohols have better potential to mix with diesel than lower alcohols.

One of the higher alcohols, n-butanol (C4H9OH) & 1-pentanol has frequently been used and tested in diesel engines in recent years and evaluated as a blend with diesel-biodiesel mixtures. Due to higher latent heat of evaporation (LHE) of n-butanol and 1-pentanol had multiple disadvantageous outcomes such as a cooling effect in-cylinder, lower combustion efficiency and slightly higher carbon monoxide (CO) and hydrocarbon (HC) emissions as compared. Yilmaz et al. used a two-cylinder diesel engine and evaluated diesel-biodiesel vegetable oil-alcohol blends to investigate engine performance and emission characteristics. Blends consisted of 5% alcohol (ethanol, methanol, butanol), 5% vegetable oil, 20% biodiesel and 70% diesel. Vegetable oil-biodiesel-alcohol-diesel blends increased HC and CO emissions while decreasing NOx emissions as compared to diesel, and it was noted that vegetable oil improved the lubricity. Rakopoulos et al. used cotton oil and its methyl ester in the same study because of the high volume of cotton oil in Greece. Studies included the performance and emission characteristics of a 4-cylinder diesel engine running diesel-cotton oil, diesel-alcohol, and diesel-biodiesel blends.

Results based on the limited number of studies with regards to vegetable oils, biodiesel and bio-alcohols show that vegetable oils of high production and potential depending on local conditions can be alternative resources such as soybean oil to be used with diesel and to makebiodiesel which would increase the percentage of bio-fuel input in diesel engines. Engine emission should indicate positive impact on environment by showing less GHG emission. The purpose of this work is to investigate and compare the engine performance and emission characteristics of a diesel engine running on various quaternary blends of diesel, biodiesel, vegetable oil and higher alcohols which could potentially serve as a future generation alternative fuel. With that purpose in mind, 40% diesel, 40% waste oil methyl ester, 10% soybean oil and 10% higher alcohol of propanol orpentanol by volume were blended, and the fuels of DBVO Pro and DBVO Pen were prepared. Engine emission and performance results of these fuels were compared to those of diesel and diesel-waste oil methyl ester blends.

II. EXPERIMENTAL METHOD

The experiments were performed using an Onan DJC type, indirect injected, four-cylinder diesel engine generator (Fig. 1). Further general information for this generator can be found in Table 1. AN EMS 5002exhaust gas analyser was used to measure the emissions. The analyser provided a CO2 range of 0–20% by volume with a resolution of 0.1% by volume, an O2range of 0–25% by volume with a resolution of 0.01% by volume, a NO range of0–5000 ppm with a resolution of 1 ppm, a CO range of 0–10% by volume with are solution of 0.01 % by volume, and an HC measurement range of 0–2000 ppm with a resolution of 1 ppm. BAR 97 Low gas was used during the calibration procedure of the EMS 5002.While testing, the calibration procedure was repeated regularly. The engine ran on neat diesel for at least 10 minutes prior to switching to an auxiliary fuel tank containing the binary and quaternary blends to prevent cold-start effects. The test fuel mass was measured before and after each trial at each load and the fuel mass consumption was determined. A K thermocouple was used to measure the exhaust gas temperature. Performance and exhaust gas emission tests were conducted at four electrical loads (0, 3, 6, 9) kW.

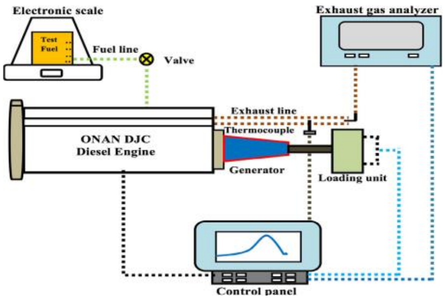

Fig. 1 Schematic layout of the experimental set-up

Table 1. General specifications of the test engine

Engine type	**General specifications of the test engine.**	
Onan DJC	Bore	82.55 mm
	Stroke	92.28 mm
	Fuel injection	Indirect
	Maximum power	12 kW
	Speed	1800 rpm
	Compression ratio	19:1
	Number of cylinders	4
	Number of cycles	4
	Intake system	Natural aspirated
	Cooling system	Air-Cooled

III. TEST FUELS

A commercially waste oil biodiesel (ASTM D6751) was used in this study. To measure the fatty acid compositions of the waste oil bio-diesel Agilent technologies 6890 Network GC system is used. DB-225 column (30m long, 0.25mm diameter and 0.2 µm film thickness) was used. Waste oil biodiesel and neat soybean oil consisted of 12.99%, 14.64%saturated and 82.87%, 84.76% unsaturated fatty acid methyl esters (FAME) and fatty acid (FA), respectively. The measured FAME compositions (%) of biodiesel and neat soybean oil are given in Table 2 and Table 3 respectively.

Table 2 Fatty acid composition of waste oil methyl ester.

S.N.	Fatty acid ester	Composition (wt. %)
1.	Methyl Palmitate	9.12
2.	Methyl Stearate	3.45
3.	Methyl Arachidate	0.20
4.	Methyl Behenate	0.22
5.	Saturation	12.99
6.	Methyl Palmitoleate	0.13
7.	Methyl Oleate	25.68
8.	Methyl Linoleate	50.74
9.	Methyl Linolenate	6.32
10.	Unsaturation	82.87
11.	Others	4.14

Table 3 Fatty acid composition of neat soybean oil

S.N.	Fatty acid	Composition (wt.%)
1.	Myristic (C14:0)	0.10
2.	Palmitic (C16:0)	10.26
3.	Stearic (C18:0)	3.52
4.	Arachidic (C20:0)	0.23
5.	Behenic (C22:0)	0.26
6.	Lignoceric (C24:0)	0.27
7.	Saturation	14.64
8.	Palmitoleic (C16:1)	0.11
9.	Oleic (C18:1)	26.55
10.	Linoleic (C18:2)	51.04
11.	Linolenic (C18:3)	7.06
12.	Unsaturation	84.76
13.	Others	0.6

Test blends were prepared by the splash-blending method, which is the most common and cheapest process and kept at the room temperature for 15 days and no separation was observed. All fuel blends were miscible and stable for the duration of the tests.The basic properties of the test fuels are listed in the table 4.

Table 4 Basic properties of the test fuels

S. N.	Test Fuel	Density (g/ml) at 25o C	Kinematic viscosity (mm2/s) at 40oC	Cetane Number	Lower Heating value (MJ/kg)	Flash point (o C)	Latent Heating (kJ/kg) at 25o C
1.	ASTM D6751	0.880	1.9–6.0	≥47	–	100–170	–
2.	Diesel	0.818	2.95	54	44.8	70	270
3.	Biodiesel	0.855	4.57	52	40.5	126	–
4.	Soybean Oil	0.920	33.1	38	37.3	315	–
5.	Propanol	0.804	2.41	12	29.82	22	779
6.	Pentanola	0.815	2.89	20	34.94	49	308
7.	DB	0.836	3.67	53.1	42.62	-	-
8.	DBVO Pro	0.841	4.4	47.3	40.90	-	-
9.	DBVO Pen	0.843	4.36	48.1	41.34	-	-

IV. RESULTS AND DISCUSSION

The results of the engine performance and emission characteristics are presented and discussed for quaternary blends of diesel, waste oil methyl ester, soybean oil and propanol or pentanol. The detailed discussion of followings is also presented

1. Measurement of tested fuel property
2. Brake specific fuel consumption
3. Brake thermal efficiency
4. Exhaust gas temperature
5. CO emission
6. HC emission
7. NOX emission

Measurement of tested fuel property

When the basic fuel properties are examined in Table 4, it is seen that soybean oil, a component of the quaternary blends, has higher density and kinematic viscosity as compared to the other fuels. Thus, the quaternary blends have higher density and kinematic viscosity than diesel, because of large molecular weight and complex chemical structure. Cetane number is one of the most important parameters affecting combustion performance in diesel engines. Because alcohols have low cetane numbers, they cannot be used in diesel engines directly. On the other hand, soybean oil and biodiesel cetane numbers are higher than alcohols but lower than diesel. As a result, cetane numbers of quaternary blends were determined to be lower than diesel.

DB >DBVO Pen>DBVO Pro

Similarly, soybean oil, biodiesel and alcohols have lower heating values due to the oxygen content in their chemical structures, which lead the quaternary blends to have lower heating value than diesel

DB >DBVO Pen>DBVO Pro

It was determined that the fuel properties of the quaternary blends met the ASTM D6751standards, and that a cetane improver or an additive was not necessary.

Brake specific fuel consumption

In Fig. 2, it was indicated that BSFC decreased with increasing engine loads. BSFCs of the DB, DBVO Pro and DBVO Pen show similar behaviour at 9 kW engine load, as can be seen in Fig. 2. Minimum BSFCs of diesel fuel, biodiesel, DB, DBVO Pro and DBVO Pen were obtained at 9 kW as (344.33, 377.00, 363.33, 366.67, and 362.67) g/kWh, respectively. Because of lower heating contents of biodiesel and DB (see Table 4), obtained BSFCs of biodiesel and DB were higher than diesel fuel at all engine loads. Mean BSFCs of biodiesel and DB increased by 7.23% and 4.53% compared to that of diesel fuel. The presence of pentanol in the blend has little decreasing effect on BSFCs. DBVO Pen decreased BSFC values an average of 0.6%, while DBVO Pro increased by 5.02%. Mean BSFCs of diesel fuel, biodiesel, DB, DBVO Pro and DBVO Pen were calculated as (443.78, 475.50, 461.28, 489.22, and 460.22) g/kWh, respectively. The high BSFC of DBVO Pro is caused by the high oxygen mass fraction of 26.7% in the propanol molecule. The low cetane number of propanol increases the ignition delay time, resulting in more heat transfer to the cylinder wall and piston head. As a result, energy that could be converted to brake power inside the cylinder decreased, leading to higher BSFCs.

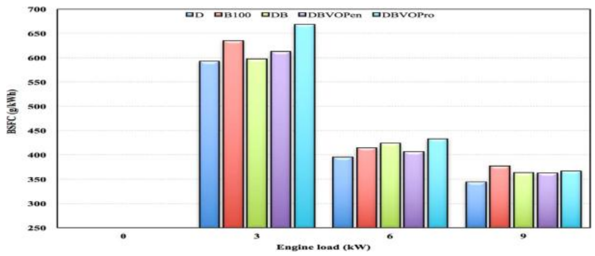

Fig. 2. The variation of BSFCs in relation to the engine load.

Brake Thermal Efficiency

BTE is inversely proportional to the lower heating value and BSFC. Thus, it decreases with respect to load as BSFC increases. The variation in BTE between the test blends, diesel fuel, and biodiesel with respect to engine load is shown in Fig. 3. For the test fuels, the Be increased with engine load. DB decreased the BTE by 2.44% while B100increased the BTE by an average of 3.19% compared to diesel fuel. BTE values of the test fuels for diesel fuel, B100, DB, DBVO Pro and DBVO Pen are in the range of (13.57–23.34) %, (14.00–23.58) %, (14.15–23.25) %, (13.18–24.01) % and (14.23–24.01) %, respectively. Mean BTE values of DBVO Pro is like that of DB, while DBVO Pen increased by 4.51% compared to DB. DBVO Pen exhibit better BTE than DBVO Pro because DBVO Pen shows lower BSFC (see Fig. 2). This may be attributed to the higher oxygen contents of higher alcohols.

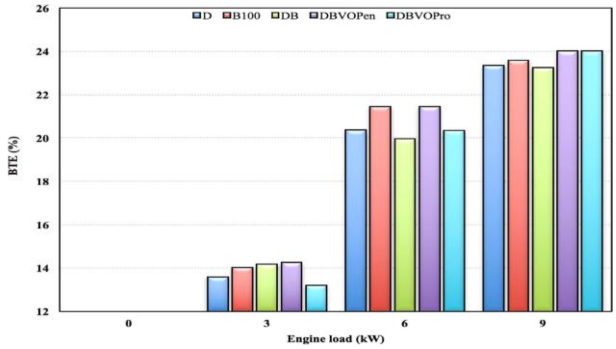

Fig. 3. The variation of BTEs in relation to the engine load.

Exhaust Gas Temperature:

From Fig. 4 it is observed that exhaust gas temperatures of test fuels increased with increasing engine load, which leads to higher in-cylinder temperatures due to higher injected fuels in the combustion chamber. Exhaust gas temperatures of diesel fuel, B100and DB show similar behaviour and magnitude at (0, 3, and 6) kW engine loads, as can be seen in Fig. 4. Compared to diesel fuel, the exhaust gas temperatures of B100 and DB at 9 kW engine load increased by 18.05%and 11.07%, respectively. The addition of higher alcohols to ternary blends has an increasing effect on exhaust gas temperatures at all engine loads. Exhaust gas temperatures of DBVO Pro and DBVO Pen increased by 33.66% and31.94% compared with DB, which can be attributed to the higher oxygen content of chemical structures of higher alcohols.

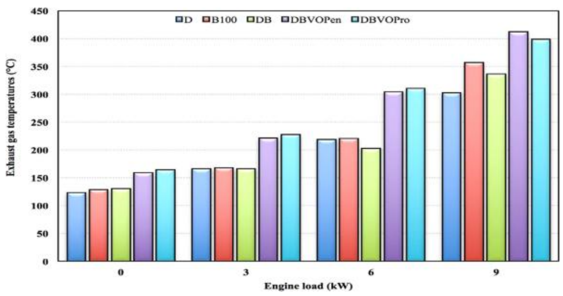

Fig. 4. The variation of EGTs in relation to the engine load.

CO emission

Fig. 5 shows the variation of CO emission for diesel fuel, biodiesel, and test blends as a function of engine load. Main reasons for an increase in the formation of CO emission are the lack of oxygen in the combustion chamber and the rich fuel/air ratio. Mean reduction in CO emission for B100 was 7.58% compared to that of diesel fuel, which can be attributed to its higher kinematic viscosity and density. Ignition delay increased with increasing diameter of fuel droplets, which results in a lower evaporation rate and thus, leads to higher CO formation. Quaternary blends increased CO emission compared to that of DB at all engine loads. Among the quaternary blends, DBVO Pro produced min. CO value (0.11%) at 0 kW load and DBVO Pen produced max. CO value (0.03%) at 3 kW load condition. CO emissions of DBVO Pro and DBVO Pen increased by 29.87% and 19.61% compared with DB. These increases are mainly due to the higher latent heat of evaporation of higher alcohols (see Table 4). In the recent work of Sharon et al. conducted on a stationary constant speed direct-injection diesel engine emissions were also found to be higher at low loads and lower at high loads for diesel-used palm oil-butanol blends comparing to the those of diesel fuel. They indicate that the high viscosity of used palm oil and high latent heat of evaporation of butanol was the main cause for increasing CO emissions at low loads. Also, they stated that the oxygen content of butanol blends, which helps increasing in-cylinder temperature, result in lower CO emissions at high loads.

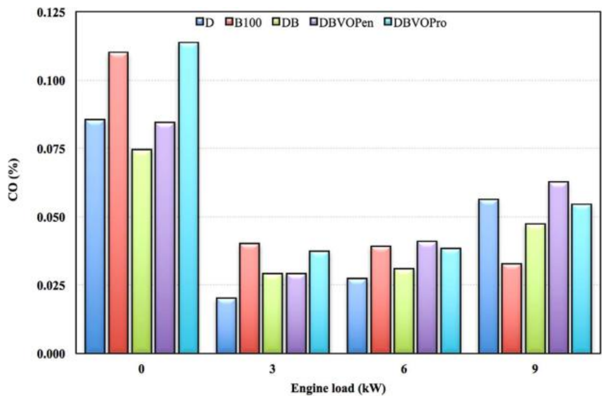

Fig. 5. The variation of CO emissions in relation to the engine load.

HC Emission

The variation of HC emission of diesel fuel, biodiesel, and test blends with respect to engine load are given in Fig. 6. Hydrocarbons in the exhaust emission are due to non-homogeneous combustion conditions within the combustion chamber and cause incomplete combustion. Hydrocarbons are produced due to a) Misfires and partial burns, b) Flame quenching in crevice volumes, c) Wall quenching and deposits, d) Oil absorption. Like CO emissions, HC emissions of B100 were higher than those of diesel at all loads except at the 9-kW load. When all engine loads are considered, B100 emitted higher HC emissions by77.16% compared to that of diesel fuel and the biggest and smallest difference between diesel and B100 occurred at 3 kW and 9 kW loads, respectively. As compared to diesel fuel, HC emission of B100 increased three-fold at the 3-kW load, with corresponding values of 1.73 for diesel fuel and 5.82 for B100.The average values of HC emissions of DBVO Pro and DBVO Pen were higher than that of DB at 12.52% and 22.01%, respectively. Similar results were observed in the literatures [49] for diesel-used palm oil butanol blends. This can be attributed to the lower cetane number of pentanol, which leads to deep fuel penetration across to the cylinder wall during the long ignition delay period causing a quenching effect, which results in higher HC emissions.

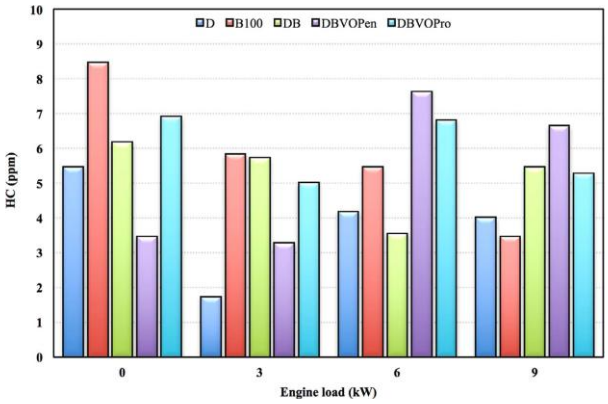

Fig. 6. The variation of HC emissions in relation to the engine load.

NO_x Emission

Fig. 7 shows the variation of NOx emission for diesel fuel, biodiesel, and test blends as a function of engine load. Oxides of nitrogen (N2) are composed of 90 vol% nitric oxide (NO), 5 vol% nitrogen dioxide (NO2), and 5 vol% nitric oxide (N2O, N2O3, and N2O5). Using the equation given in Refs. [47,50], NO emission is a function of residence time related to oxygen concentration and combustion temperature. NO formation rates increase with increasing in combustion temperatures and oxygen concentrations. As can be seen in Fig. 7 NOx emissions increase with increasing engine load, which led to higher combustion temperatures, resulting in higher NOx emissions. B100 and DB emitted lower NOx emission than diesel fuel by 1.26% and 9.3%, respectively. The main reason for this can be attributed to the low cetane numbers ofB100 and DB. Low cetane number leads to injection of more fuel into the combustion chamber and because the concentration of NOX is dependent on the availability of O2, NOX declines when the mixture is rich. Compared with diesel fuel, NOx emissions of DBVO Pro and DBVO Pen show no noticeable difference at whole engine loads. NOx emissions were found to be slightly lower with DBVO Pro (min. NOx value is 48.18 ppm at 0 kW load) and DBVO Pen (max. NOx value is503.09 ppm at 9 kW load) at low and medium engine loads. However, as engine load increased, only a slight increase can be observed for propanol and pentanol blends, seen in Fig. 7. Higher alcohols have allowed heating value and high latent heat of vaporization which means that more heat will be absorbed during vaporization of propanol and pentanol. Thus, exhaust gas temperatures decreased, which led to a decrease in NOx emission of DBVO Pro and DBVO Pen. The reduction of NOx emissions for DBVO Pro and DBVO Pen were 11.9% and 7.7%, respectively, \compared to that of DB. As a result, propanol and pentanol addition to ternary blend has the advantage of a decrease in NOx emissions because of their fuel properties.

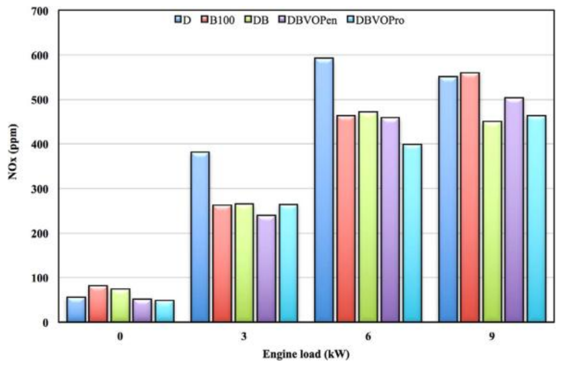

Fig. 7. The variation of NOx emissions in relation to the engine load.

V. CONCLUSION

The study revealed that the diesel bio-fuel blends could be successfully used as a source of alternate fuel in the diesel engine. By high percentage of biofuel blend is valuable from environmental and economic point of views. To increase the use of biofuels in diesel engines Quaternary blends of vegetable oils, biodiesel and alcohols with diesel used in diesel engines. Thus, in this work, effects of the addition of higher alcohols (propanol and pentanol) to diesel–biodiesel vegetable oil blends were investigated on the engine performance and exhaust emissions, without any engine modification. Pentanol has several advantages over lower alcohols as an alternative fuel for diesel engines since many of the fuel properties of pentanol are more like those of diesel than are those of lower alcohols. Moreover, it can be produced from cellulosic biomass on a large scale. Having this motivation in mind, pentanol can produce more effective results than lower alcohols in diesel engines. Main conclusions from this study are as follows:

- The addition of propanol and pentanol to ternary blends prevented the higher density and kinematic viscosity of vegetable oil in quaternary blends and improved basic fuel properties.
- The most important advantage of pentanol blends is that it can be safely used in diesel engines without any engine modification or any additive.
- Presence of 5% and 10% pentanol in the blends decreased exhaust gas temperatures as compared to that of diesel. However, 20%, 25% and 35% pentanol blends showed 3.58, 14.65 and 12.54% increased exhaust gas temperatures from that of diesel, on average, which can be attributed to higher combustion efficiency due to higher oxygen content of pentanol.
- The diesel engine operated smoothly and safety with DBVO Pro and DBVO Pen, and no negative effects were noticed during the engine tests.
- BSFCs slightly decreased for DBVO Pen, while they increased for DBVO Pro by 5.02% compared to that of DB.
- The higher oxygen content within the chemical structures of propanol and pentanol led to higher exhaust gas temperatures than the DB blend at whole test loads.
- The addition of propanol and pentanol to ternary blends increased CO and HC emissions because of their higher latent heat of evaporation and lower cetane numbers.
- NOx emissions of the quaternary blends containing propanol and pentanol were found to be lower than the blend of DB.

Based on the findings of this study, it seems reasonable to assume that DBVO Pen and DBVO Pro can be used as alternatives to diesel fuel at the expense of their insufficient fuel economy. And future research should focus on a comprehensive assessment of engine durability.

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