JOURNAL OF ENGINEERING annals OF FACULTY OF ENGINEERING HUNEDOARA

EMISSION AND PROPERTIES CHARACTERISTICS USING ADDITIVE–ETHANOL–DIESEL FUEL BLENDS ON A DIESEL ENGINE

1.Fathollah OMMI, 2.Kouros NEKOFAR, 3.Vahid PIROZFAR

1Mechanical Engineering Department, Tarbiat Modares University, Tehran, IRAN
2Islamic Azad University of Tafresh, Tafresh, IRAN
3Chemical Engineering Department, Tarbiat Modares University, Tehran, IRAN

ABSTRACT
In this study, exhaust smoke, other emission, physical and chemical properties of ethanol–diesel fuel with and without additives are studied. The fuel additives selected in the formulations were 2–Methoxy ethyl ether (MXEE), nitro Methane and nitro Ethan. The properties tests included density, viscosity, cetane index, flash point, boiling point, volatility and distillation. An additive used to keep the blends homogenous and stable, and an Ignition improver, which can enhance cetane number in blends. Fuel formulations comprising 2–5%v/v additives and 5–10%v/v ethanol and diesel 90–95%v/v were prepared. The performance of the new fuel formulations were studied on a MB–OM 457 LA diesel engine in Idle and cut off speed position. The results showed that soot formation can be reduced by more than 50%, 30% and 27% with the diesel formulations; E–NE5–10, E-NM5–10 and E-MX5–10, respectively.

Keywords:
Diesel fuel additive-soot reduction–emission–Emulsification characteristics–physicochemical properties

1. INTRODUCTION

Diesel fuel is a fuel consists mainly of aliphatic hydrocarbons containing 8–28 carbon atoms with boiling points varying from 130 to 370˚*C*. [Braun, 2003] In diesel engines, finding new formulations and optimization of fuel properties, such as oxygen content, sulfur content, aromatic content, volatility, have been required to break through the trade-off relation for reducing both soot and NOx emissions, and improve the diesel combustion processes and exhaust emissions [Fujimoto, 1995; Senda, 2000]. The reduction of emissions through addition of oxygenated compounds depends on the molecular structure of the diesel fuel and the fuel's oxygen content [Kitamura, 2001] Therefore, the diesel's composition and the use of additives directly affect the properties of density, viscosity, volatility, behavior at low temperatures, and Cetane number (CN) [Guibet, 1999; Gu.Ru, 2002; Ladommatos, 1996]. Ethanol is an enable additive for adding to diesel fuel that can be made from many raw materials such as sugar cane, molasses, potato, corn, barley, etc. by using already improved and demonstrated technologies [De Caro, 2001; Kremer, 2000]. The objective of this work was to find the optimum replacement of diesel fuel by additive-ethanol–diesel blended fuels and compare the performance of diesel engine fueled with new fuel [Schuetzle, 2002]. Towards this end, an experimental study was carried out to test the performance of various additive-ethanol–diesel fuel mixtures; the content of ethanol is 5, 7.5 and 10% by volume, respectively.

2. EXPERIMENTAL

2.1. Materials

The ethanol used in the tests was limited to essentially anhydrous ethanol because other kinds of ethanol are not soluble or have very limited solubility in the vast majority of diesel fuels. This solubility is dependent on the water content of the blend fuels. To overcome this problem, a solubilizer or is indispensable in ethanol–diesel blended fuel. Physical and chemical property of diesel fuel Used in the formulation are given in Table 1. Commercial diesel fuel and analysis-grade anhydrous ethanol (99.7% purity) were used in this test. The compound of ethanol–diesel blends involves solubilizer or improver's dosage, ethanol, and diesel fuel. The blending protocol was to first mix the improver (0.25% v/v for all ethanol–diesel blends except for pure diesel fuel) with ethanol, and then blend this mixture into the diesel fuel. For example, 5% ethanol–diesel blend (E5) consists of 0.25% solubilizer, 4.75% ethanol, and 95% diesel.

Many types of oxygenated blends with different fractions of ethanol–additive in diesel fuel are selected for the study. In our experiment, the blend of 5% ethanol and 95% diesel is called E5. Blend of 7.5% ethanol and 92.5%diesel is called E7.5. Blend of 10% ethanol and 90% diesel is called E10. The oxygenated compounds selected in the formulations were 2–Methoxy ethyl ether (MXEE), nitro Methane and nitro Ethan. Physicochemical characteristics of the base diesel and oxygenated compounds Used in the formulation are given in Table2.

Table 1. Physical and chemical property of diesel fuel (Research Institute Petroleum Iran, 2007)

Specifications	**Tehran1**	**Tehran2**
Specific Gravity @ 15.56 ºC /15.56 ºC	0.8413	0.8424
Density @ 15 ºC g/cc	0.8405	0.8415
Cetane Index	54.74	56
Flash Point ºC	65	72
Sulphur Content wt%	0.68	0.7
Kinematics Viscosity @ 40º C cSt	4.87	3.48
Cold Filter Plugging Point ºC	+3	+1
Pour Point ºC	0	-5
Carbon Residue On 10% bott. wt%	0.14	0.29
Ash Content wt%	Trace<0.001	Trace<0.001
Water Content vol%	Trace<0.05	0.05
Copper Corrosion,3hrs @ 100ºC	1a	1a
Acidity mgKOH/gr	Trace<0.05	0.05
Distillation :		
Initial Boiling Point ºC	165	181
10% Vol. Recovery ºC	206	219
50% Vol. Recovery ºC	294	306
90% Vol. Recovery ºC	361	372.5
Final Boiling Point ºC	386	382
Recovery Vol%	98	99

Table 2. Physicochemical characteristics of the base diesel and oxygenated compounds used in the formulations

*Improvers (e.g. Isooctyl nitrate)	Molecular Formula	Molecular Weight	Cetane Number	Density, Kg/m3	Lower Heating Value, MJ/Kg	C%	H%	O%
TAEE (Tertiary amyl ethyl ether)	$C_7H_{16}O$	116		763.64				13.8
Nitro-Methane	$C_1H_3N_1O_2$	61.04		1138		19.6	4.9	52.4
Nitro-Ethane	$C_2H_5N_1O_2$	75.067		1054		32	6.6	42.6
Nitro-Propane (2NITROPROPANE)	$C_3H_7N_1O_2$	89.09				40.0	7.88	36
EXEE (2-ethoxy ethyl ether)	$C_8H_{18}O_3$	162.227	113 -136	910	33.2	59	11	30
MXEE (2-Methoxy ethyl ether)	$C_6H_{14}O_3$	134.174	112-130	937	30	54	10	36

*Improvers (e.g. Isooctyl nitrate)	Autoignation Temperature , C	Boiling point ,C	Vapor pressure, Kpa	Flash point, C	Specific Gravity	Boiling point ,C
TAEE (Tertiary amyl ethyl ether)	–	102	13.45	–	–	102
Nitro-Methane	418	100–103	27.8	35	1.138	100–103
Nitro–Ethane	414	114–116	–	30	1.045	114–116
Nitro–Propane (2NITROPROPANE)	428	118–121	–	28	0.990–0.995	118–121
MXEE (2–ethoxy ethyl ether)	–	189	–	71	–	189

2.2. Test Procedure

Diesel fuel used in Tehran was employed in this work as baseline diesel fuel (Tehran1 and Tehran2). The Physical and chemical property of diesel fuel used in the formulation are given in Table 1. Emissions and combustion characteristics were studied on a MB–OM 457 LA diesel engine both in Idle Speed and in Cut off Speed position. Table 2 shows the engine specifications. The ways for gas exhaust analysis are full flow, partial flow and free flow in diesel. An exhaust gas analyzer (AVL 465 DYGAS and MRU 1600L type) was employed to measure emissions of NOx, THC, CO and CO2 on line in raw exhaust. The resolution of the gas analyzer, are 0.1%Vol. for NOx, 0.01%Vol. for CO, 1ppm for HC and 0.1%Vol. for CO2. At each measurement, the sampling duration was 10 min.

Table 3. Engine specifications

Rated power (hp)/speed (rpm)	240/2200
Maximum torque (Nm)/speed (rpm)	824/1500
Cylinder number	6
Compression ratio	16.1:1
Cylinder volume	11580

The Cetane Index (CN) can be calculated as follows:

ASTM D 976

$$CI = 454.74 - 1641.416\,D + 774.74D^2 - 0.554\,B + 97.803\,(\log B)^2$$

where: D = density at 15^oC [g/mL] determined by Test Method ASTM D 1298, B = mid–boiling temperature [^oC] determined by Test Method ASTM D 86 and corrected to standard barometric Pressure.

ASTM D 4737

$$CI_{4737} = 45.2 + 0.0892\,T_{10N} + [0.131 + 0.901B]\,T_{50N} + [0.0523 + 0.420\,B]\,T_{90N} + 0.00049\,[T^2_{10N} - T^2_{90N}] + 107\,B + 60\,B^2$$

where: D = density at 15^{o}C [g/mL] determined by Test Method ASTM D 1298, B = [exp {(–3.5) (D – 0.85)}] –1, T_{10} = 10% distillation temperature [^oC] determined by Test Method ASTM D 86 and corrected to standard barometric pressure, $T_{10N} = T_{10} - 215$, T_{50} = 50% distillation temperature [^oC] determined by Test Method ASTM D 86 and corrected to standard barometric pressure, $T_{50N} = T_{50} - 260$, T_{90} = 90% distillation temperature [^oC] determined by Test Method ASTM D 86 and corrected to standard barometric pressure, $T_{90N} = T_{90} - 310$.

3. RESULTS & DISCUSSION

3.1. Blend Stability and Phase Separation

Fuel instability is an obvious problem when phase separation occurs. Thus, water tolerance of the ethanol/diesel blends was determined by blending additional water into samples of the mixtures. Ethanol solubility in diesel is affected mainly by two factors, water content and temperature of the blend. Avoidance of this separation can be summarized in two ways: by adding a co–solvent or by adding an emulsifier [Letcher, 1983]. Because ethanol is soluble in diesel fuel in only small quantities (<12.5%Vol.), therefore either an emulsifier (Span 85, i.e. sorbitan trioleate) or a co-solvent (n-butanol) is required to prepare the ethanol in diesel blends. In present work, the ethanol used was 99.7% .The maximum amount of the ethanol in blends was below 12.5Vol%.

3.2. Cetane Number and Cetane Index

Cetane number is one of the most important properties of a diesel fuel, which is generally similar to the Many attempts have been made to improve the Cetane number of diesel engine fuels in order to reduce the emissions of smoke and soot. The cetane Index specified by ASTM Standard D 976 for Tehran1 diesel is 54.74 and for Tehran2 are 56. Since octane number and cetane number have inverse relationship, thus the addition of ethanol with high octane number exhibits a low cetane rating in the blend. Lower cetane numbers indicate longer ignition delays, allowing more time for fuel to vaporize before combustion begins. However, an ignition improver was used to increase the cetane number of blends. The three-ignition improver used was 2–Methoxy ethyl ether (MXEE), nitro Methane and nitro Ethan. The amount of ignition improver was 2,5% of the amount of ethanol in each blend. This provided similar ignition delay as diesel fuel. The Cetane index for blends with different fractions of additives and ethanol in volumetric proportions of 5, 7.5 and 10% v/v are presented in table 3 and figure 1.

Table 3 . Physicochemical properties of various fuels (additive–ethanol–diesel)

Vol. %	Type	Density @ 15 ºC g/cc	Distillation (T) 10% Vol. Recovery ºC	30%	50%	90%	Cetane Index (ASTM D 976)	Cetane Index (ASTM D 4737)	T10 N	T50 N	T90 N	B
5	E	0.8335	194	254	280	347	55.4302074	55.99554493	-21	20	37	0.0594501
7.5	E	0.8318	182	255	275.5	342.5	55.15697133	55.11627374	-33	15.5	32.5	0.065772619
10	E	0.8312	84	240	271.5	338.5	54.55701633	53.59651971	-131	11.5	28.5	0.068013093
5	E-NM2	0.8343	196	250	293.5	360.5	57.50168233	58.60086832	-19	33.5	50.5	0.056487789
7.5	E-NM2	0.8335	188	252	290	357	57.2079716	57.80820075	-27	30	47	0.0594501
10	E-NM2	0.8318	85	242	285	352	56.94261871	56.43122972	-130	25	42	0.065772619
5	E-NM5	0.8349	195.5	259	296	363	57.68707624	58.71061945	-19.5	36	53	0.054271493
7.5	E-NM5	0.8332	192	248.5	289.5	356.5	57.22910334	58.13741791	-23	29.5	46.5	0.060563107
10	E-NM5	0.8324	86	243	287	354	57.08259612	56.49732996	-129	27	44	0.063536845
5	E-MX2	0.8338	193.5	245	292	359	57.4336194	58.41591779	-21.5	32	49	0.058338261
7.5	E-MX2	0.8322	185	248	287	354	57.15295288	57.73231815	-30	27	44	0.064281581
10	E-MX2	0.8316	88	240	284	351	56.83438132	56.20629153	-127	24	41	0.066518921
5	E-MX5	0.834	197	252	293	360	57.5259945	58.75026504	-18	33	50	0.057597684
7.5	E-MX5	0.8335	189	251	290	357	57.2079716	57.87143075	-26	30	47	0.0594501
10	E-MX5	0.8321	90	242	286	353	57.01358772	56.30618489	-125	26	43	0.064654145
5	E-NE2	0.8348	194.5	258	295	362	57.56562091	58.49907645	-20.5	35	52	0.054640552
7.5	E-NE2	0.8343	188	249.5	292	359	57.25908329	57.75384027	-27	32	49	0.056487789
10	E-NE2	0.8316	88	240	285	352	57.0131614	56.43679302	-127	25	42	0.066518921
5	E-NE5	0.8351	195	258	296.5	363.5	57.69493412	58.65255334	-20	36.5	53.5	0.053533761
7.5	E-NE5	0.8336	9423	250	291	358	57.33928264	55.99554493	9208	31	48	0.059079357
10	E-NE5	0.8324	94	242.5	287.5	354.5	57.16909607	56.34286355	-121	27.5	44.5	0.063536845
	Diesel	0.8415	206		306	361	56.88132118	57.03984689	-9	46	51	0.030196953

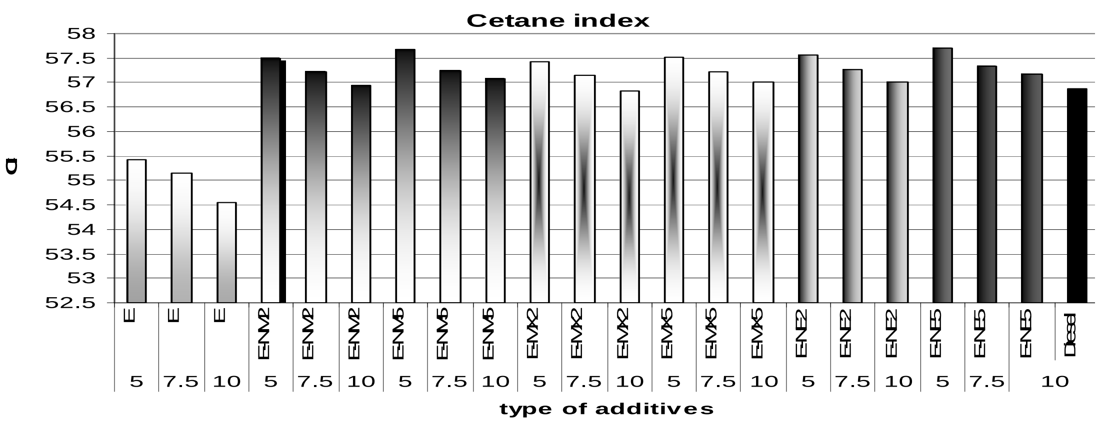

FIG.1. Cetane index of blend fuels and diesel fuel

As shown in Fig. 1, cetane Index of the blends decreases with ethanol content. The value of E10 reduces more significantly than that of E5. Both E5 and E10 are less than the minimum cetane Index of Tehran diesel fuel standards, 54.77. In order to enhance CN or CI, a fuel, which contains 0.1% Vol additives (e.g. 2% of ethanol-Nitro methane) and 4.9% vol ethanol fuel (E-NM2 in 5% Ethanol-additive), and a fuel with 0.25% vol additives (e.g. 5% of ethanol-Nitro methane) and 9.5% vol ethanol fuel (E-NM5 IN 10% Ethanol–additive) were prepared.

It is also seen that additive and ignition improver can slightly restore the viscosity of the blends (Fig.2), and increase the CI (e.g. of E–NM2 in 5% and E–NM5–10 to 57.5 and 57.08, respectively), which can improve combustion process, ensure good cold starting, reduced noise and long durability for diesel engines.

3.3. Viscosity

Fuel viscosity play important role in the lubrication of fuel injection systems. The addition of ethanol to diesel lowers fuel viscosity. Fig.2 shows the experimental results of blend fuels. As shown in Fig.2, the addition of ethanol to diesel lowers fuel viscosity. It is also seen that additive and ignition improver can restore the viscosity of the blends.

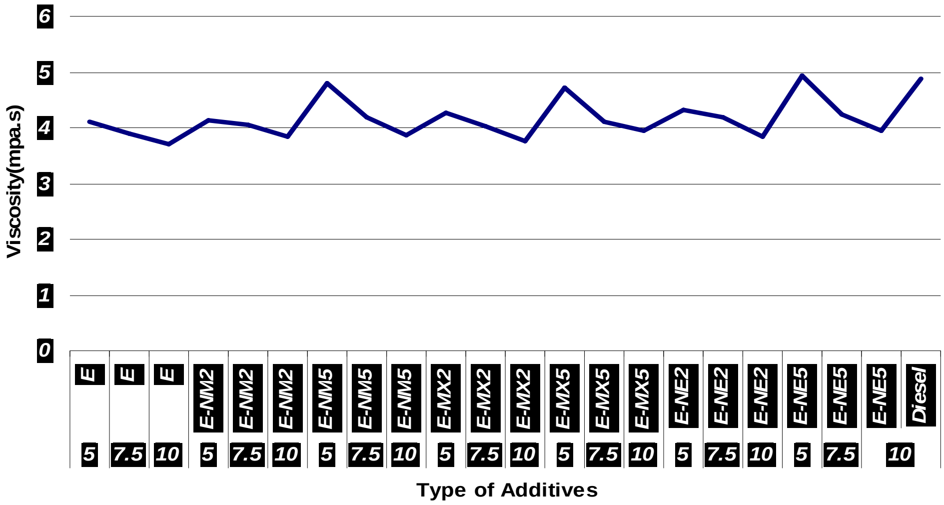

FIG.2. Viscosities of blend fuels and diesel fuel

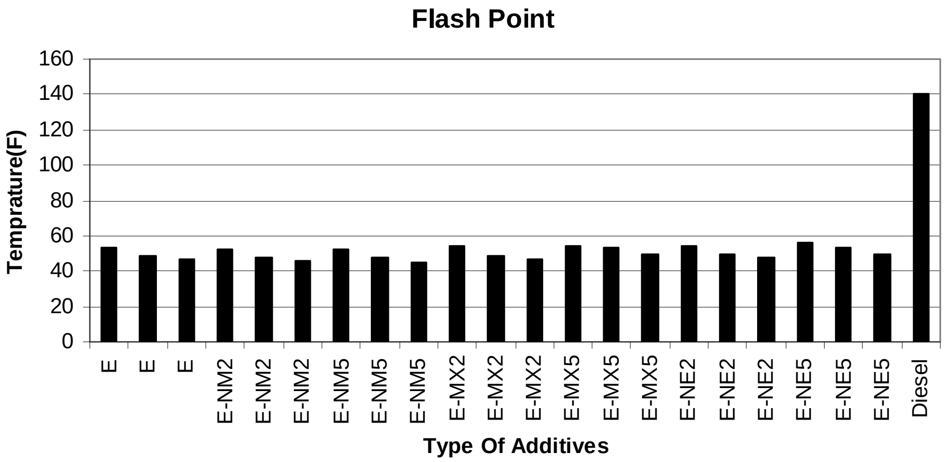

FIG.3. Flash points of blend fuels and diesel fuel

3.4. Flash point

The flash point is the lowest temperature at which a fuel will ignite when exposed to an ignition source. The flashpoint of the fuel affects the transporting and storage classification of fuels and the precautions that should be used in handling the fuel. In guidelines established by the National Fire Protection Agency (NFPA) in the US for safe storage and handling of flammable liquids, the discriminating fuel property was the flashpoint. Liquids such as gasoline and ethanol are Class A liquids as they have flashpoints below 37.8C, whereas diesel fuel is Class B with a flashpoint above 37.8C. Hence, the addition of ethanol to diesel would change the NFPA classification from Class B to Class A, thus requiring more stringent storage requirements such as greater distance in location of storage tanks from property lines, buildings and other tanks [Battele, 1998]. Fig.3 shows the experimental results and flash points of blend fuels. As shown in Fig.3, the addition of ethanol to diesel lowers flash point. It is also seen that additives and ignition improver can slightly restore the flash point of the blends.

3.5. Volatility and distillation

Fig. 4 shows the distillation curves of blend fuels. It can be seen from Fig. 4 that the addition of ethanol to diesel fuel modifies the shape of distillation curves at the temperatures below 200C. Increasing the ethanol content resulted in a higher volatility of the blends.

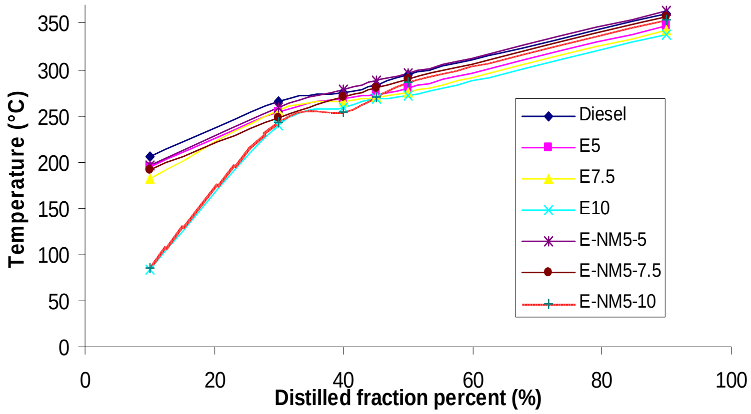

Fig.4. Distillation curves

The distillation curves of the blends with or without the additive and ignition improver only differ slightly at the same ethanol content.

3.6. Density

The addition of ethanol to diesel fuel changes the physicochemical properties of the blends. With the increase of ethanol, density of the blends decreases. This is shown in Fig. 5. It is also seen that additive and ignition improver can slightly restore the density of the blends.

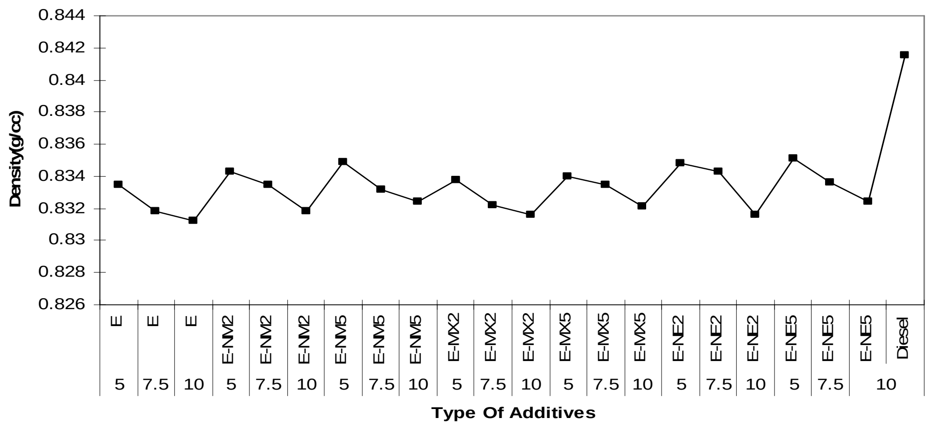

Fig.5. Density of blend fuels and diesel fuel

4. ENGINE TESTS AND RESULTS

The results of soot formation for five different samples are presented graphically in Fig. 6. Each sample was tested in an engine with the specification given in Table 2. Using the base diesel with different dosage of additives and producing many type of blend that showed in Table 3. For discussion about this case study, we selected five blends from all blends for analyzing and testing emission.

It can be seen from figure 5 that the addition of ethanol to diesel reduce soot ratio substantially. As this figure show the experimental results Of base diesel fuel, E, E–NM5, E–NE5, E–MX5 that present affect improvers and oxygenate components on ethanol-diesel fuel blend. In order to make a comparison between ethanol and additive-ethanol-diesel fuel for their relative soot suppression effects, combinations of Figure 4–9 and table 4. We can be seen that addition NM, MX, NE to ethanol-diesel blend highly lower concentration of soot than affect of ethanol on fuel. Following the same analyses as at K value (is indicating factor soot in principles of diagnostic methods). Table.4 contains the average of reduction ratios for different blends that it can be seen affect of addition E, NM5, MX5, NE5 on soot reduction that reduce 23%, 30%, 27% and 51% of soot, respectively. In addition, NE5 is more effective than other blends

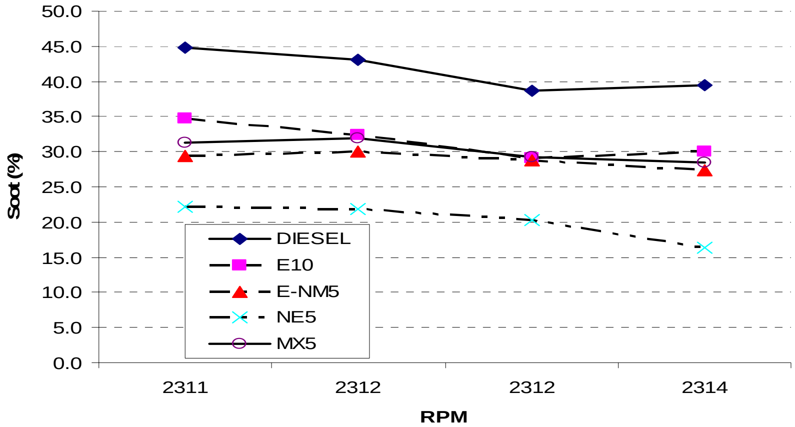

Fig.6. Comparison of soot volume fraction measurement results

Table 4 . The soot reduction ratios by the addition of ethanol and other additives

	Average Exhaust Soot (%)	K value	Reduction of soot By additive
diesel	41.5	1.24	0
E	31.6	0.88	-23.85542169
E–NM5	28.9	0.78	-30.36144578
E–NE5	20.1	0.52	-51.56626506
E–MX5	30.2	0.84	-27.22891566

Table.5 shows the total emission results obtained from the blend fuels at the Free Acceleration Test, at the Idle Speed. Comparison of the emission results shows a slight increase on NOx and slight reduction on CO emission when moving from pure diesel fuel–to–fuel blends.

The increase of the NOx emissions can be explained by the decrease of the CI and CN with the addition of the ethanol. In addition, the E–NM5 and E–NE5 highly increased NOx emission cause NO content in material's structure of NM and NE. According to table5, NOx emission related to T–GAS that it could be seen T–GAS reduction at E–NE5 cause NOx reduction in emission.

Table 5. Emission ratios by the addition of ethanol and other additives

Type	HC (ppm Hexan	CO (%)	CO2 (%)	O2 (%)	Lambda	NO (ppm)	NO2 (ppm)	T-GAS (˚C)	T-Amb (˚C)
Ambient	1	0	0	20.94		0	0	30	27.7
Cold	15	0.04	2.1	17.64	6.757	258	250	92.1	28
Before	19	0.09	2.2	18.03	7.072	272	168	139.9	30.3
E	20	0.08	2.2	18.16	6.629	294	199	137.1	31.9
E–NM5	27	0.05	1.9	17.96	7.401	317	223	131.4	31.9
E–NE5	19	0.06	1.9	18.54	7.592	256	168	126.1	31.4
E–MX5	19	0.07	2.0	18.66	7.301	274	174	132.7	31.8

Engine test reports by different investigators show a unanimous agreement on the significant reduction of soot due to the presents of ethanol in the diesel fuel blend. However, the reported results on the emission of other species are different.

5. CONCLUSIONS

The addition of ethanol to diesel fuel changes the physicochemical properties of the blends. This work was undertaken to study and compare the effects of different content of additive–ethanol–diesel blend fuels on physicochemical properties of the blends and the following conclusions can be obtained from the study:

1. Blending ethanol to the Tehran1 diesel fuel show a profound effect on soot reduction (25% soot reduction with 10% ethanol)
2. With the increase of ethanol, density, cetane number, kinematics viscosity, high heat value and aromatics fractions of the blends decrease. Distillation temperatures also change.
3. Additive can enhance the stability of ethanol blended diesel fuel, and partly restore their viscosity.
4. Ignition improver is needed to enhance their Cetane number.
5. Ethanol is soluble in diesel fuel in only small quantities (<12.5%Vol), either an emulsifier (Span 85, i.e. sorbitan trioleate) or a co-solvent (n–butanol) is use to prepare the ethanol–in–diesel blends.
6. The results show that the nitro Ethan restores the physicochemical properties of the diesel fuel is better than 2–Methoxy ethyl ether (MXEE) and nitro Methane.
7. The soot formation can be reduced by more than 50%, 30% and 27% with the diesel formulations E–NE5–10, E–NM5–10 and E–MX5–10, respectively.

REFERENCES

[1] Battelle. (1998). Flammability limits for ethanol/diesel blends. Final Report prepared by Battelle, Columbus, OH, USA.

[2] Braun, S., Appel, LG. (2003). A poluic¸a˜o gerada por ma´quinas de combusta˜o interna movidas a` diesel–A questa˜o dos particulados. Estrate´gias atuais para a reduc¸a˜o e controle das emisso˜es e tende^ncias futures, 27:472–82.

[3] De Caro, PS., Mouloungui, Z., Vaitilingom, G., Berge, JCh. (2001). Interest of combining an additive with diesel–ethanol blends for use in diesel engines. Fuel, 80(4):565–74.

[4] Fujimoto, H., Senda, J., Shibata, I. and Matsui, K. (1995). "New Concept on Lower Exhaust Emission of Diesel Engine", *SAE Paper*, 952062.

[5] Guibet, J., Faure–Birchem, E. (1999). Fuels and engines. Paris: Editions Technip.

[6] Gu¨ru¨, M,. Karakaya, U., Altiparmak, D., Alicilar, A. (2002). Improvement of diesel fuel properties by using additives. *Energy Convers Manage*, 43:1021–5.

[7] Kremer, FG., Fachetti, A. (2000). Alcohol as automotive fuel–Brazilian experience. *SAE Paper*, 01–1965.

[8] Kitamura, T., Ito, T., Senda, J., Fujiimoto, H. (2001). Extraction of the suppression effects of oxygenated fuels on soot formation using a detailed chemical kinetic model. *JSAE* Rev, 22:139–45

[9] Ladommatos, N., Parsi, M., Knowles, A. (1996). The effect of fuel cetane improver on diesel pollutant emissions, *Fuel*, 75:8–14.

[10] Letcher, T.M. (1983). Diesel blends for diesel engines. *S. Afr. J. Sci.* 79 (1), 4–7.

[11] Schuetzle, D., Han, W., Srithammavong, P., Akarapanjavit, N., Norbeck, JM., Corkwell, K. (November 2002). The evaluation of diesel/ethanol blends for diesel vehicles in Thailand: performance and emissions studies. *Proceedings of the 14th international symposium on alcohol (ISAF)*, Phuket, Thailand.

[12] Senda, J., Kawano, D., Hotta, I., Kawakami, K., and Fujimoto, H. (2000). "Fuel Design Concept for Low Emission in Engine Systems", *SAE Paper* 2000–01–1258