

چکیده فارسی

بررسی تاثیر افزودنی‌های اکسیژن دار و نیتروژن دار بر روی خصوصیات فیزیکی - شیمیایی و آلاینده‌های سوخت دیزلی

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در این مقاله تاثیر افزودنی‌ها بر روی دانسیته، ویسکوزیته، عدد ستان، نقطه اشتعال، دمای جوش، فراریت و تقطیر بررسی شده است. یک افزودنی می‌تواند هم به صورت یک پایدارکننده ترکیب و هم به صورت یک بهبود دهنده احتراق به کار برده شود که بدین وسیله می‌توان خواص سوخت (مخصوصاً عدد ستان) را به منظور بهبود فرایند احتراق بالا برد. فرمول‌بندی‌های جدیدی که برای سوخت پیشنهاد شده است، شامل ۲ و ۵ درصد حجمی افزودنی (نیترو متان، نیترو اتان، ۲- متوکسی اتیل اتر) در مخلوط اتانول-افزودنی و ۵، ۷/۵ و ۱۰ درصد حجمی از این ترکیب در سوخت دیزل است که این ترکیبات بر روی یک موتور دیزل MB-OM 457 LA آزمون شده‌اند. در این پروژه انواع گازها و دوده‌ی خروجی از این موتور آنالیز شده و تغییرات آن بررسی شده است. نتایج نشان داد که تشکیل دوده می‌تواند به اندازه‌ی ۵۰، ۳۰ و ۲۷ درصد به ترتیب با فرمول‌بندی‌های E-MX5-10، E-NM5-10 و E-NE5-10 کاهش یابد.

واژگان کلیدی: افزودنی سوخت دیزل، خواص فیزیکی و شیمیایی، کاهش دوده، بهبود دهنده‌ی عدد ستان، گازهای خروجی و آلاینده، احتراق

Conclusions

With the increase in the amount of ethanol in the fuel blends, cetane number, kinematics viscosity and flash point decrease. Distillation temperatures also change. To improve the cetane number of the fuel mixture, different additives: NM, NE and MXEE were used. The results showed that nitro ethane restores the cetane number of the diesel fuel more than 2-methoxy ethyl ether or nitro methane. Blending ethanol with Tehran 1 diesel fuel shows a profound impact on soot reduction (25% soot reduction with 10% ethanol). 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. The NO_x , CO, CO_2 and HC emissions resulting from additive-ethanol-diesel fuels were found to differ from pure diesel emissions. With the increase in additives-ethanol contained in diesel, CO_2 emissions decrease, while HC emissions increase. The change in the amount of CO and NO_x emissions depended on the type of additives. NO_x increases for higher fuel/air ratios. NO_x also increases at higher gas temperatures. The results also show that additives with nitrogen in their molecular structure produce higher NO_x in comparison to other additives.

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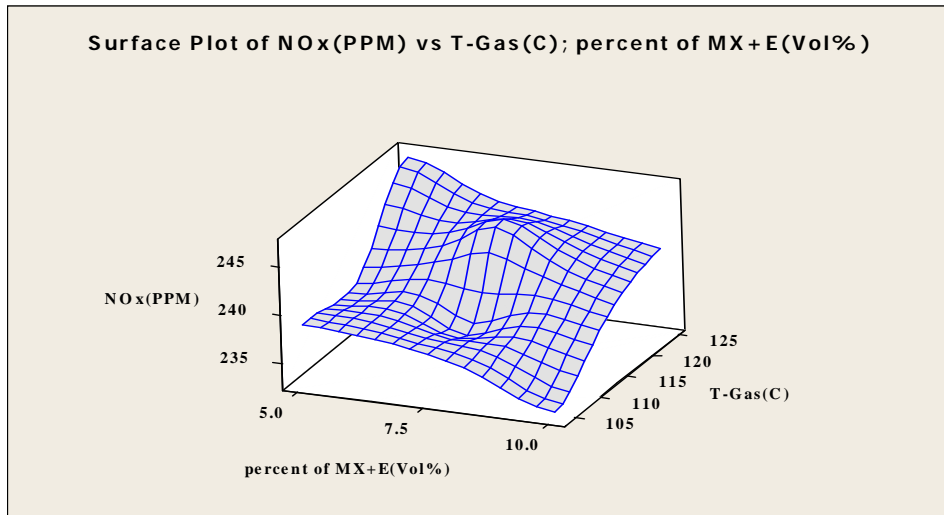


Figure 9. The effect of different factors on NO_x Emission in combustion of MXEE-ethanol-diesel fuel blends

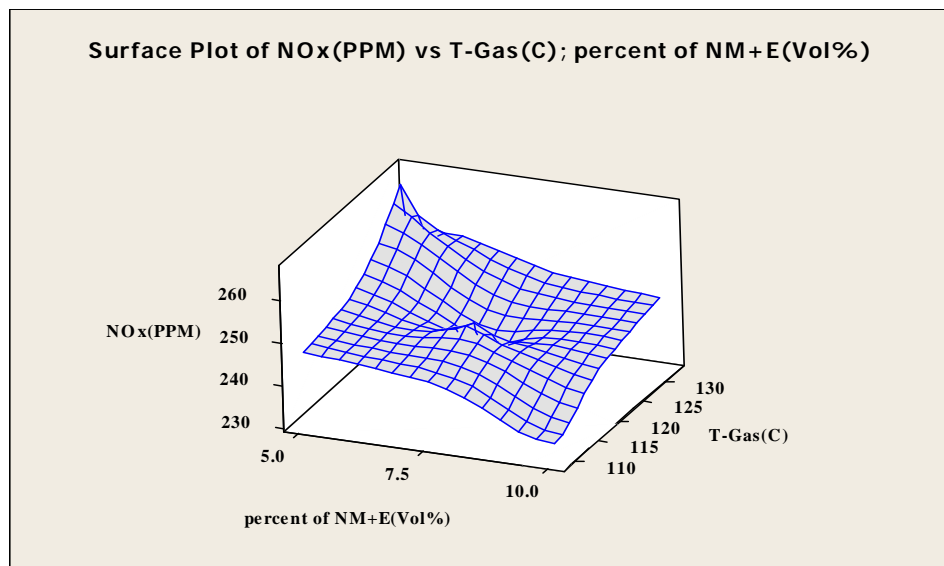


Figure 10. The effect of different factors on NO_x Emission in combustion of Nitro methane-ethanol-diesel fuel blends

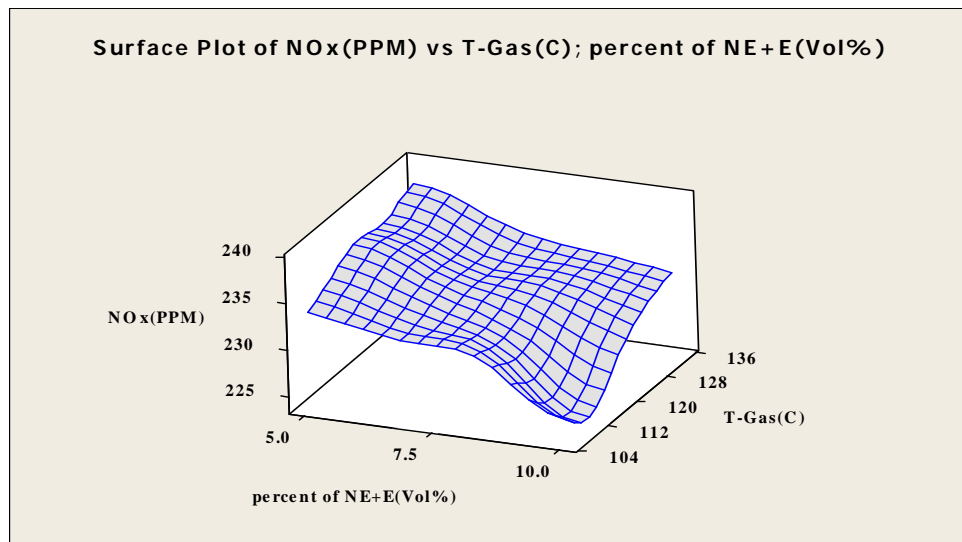


Figure 11. The effect of different factors on NO_x Emission in combustion of nitro ethane-ethanol-diesel fuel blends

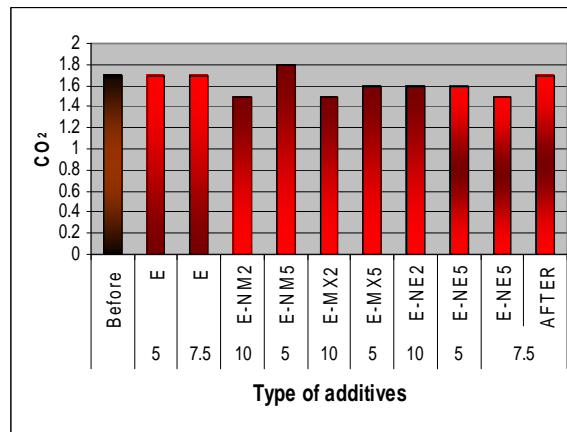


Figure 6. Comparison of CO₂ volume fraction measurement results

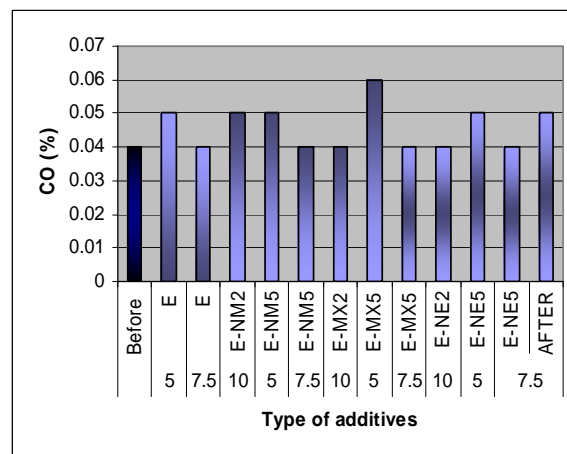


Figure 7. Comparison of CO volume fraction measurement results

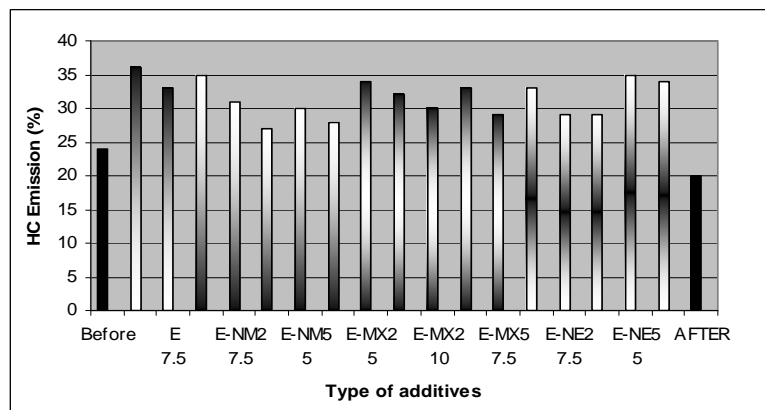


Figure 8. Comparison of HC volume fraction measurement results with different additives

According to Table 5, Fig.6 and Fig.7, the emission results show a slight reduction in CO₂ and a slight increase in CO emission when switching from pure diesel fuel to fuel blends. Moreover, as Fig. 8 demonstrates, HC emission is higher for all mixtures and conditions.

Gas temperature, pressure, fuel/air ratio are factors that influence the NO_x emission. NO_x production increases for high ratios of fuel to air, and at high gas temperatures.

The increase in the NO_x emissions can be accounted for by the decrease in the CI and CN when adding ethanol [4]. Comparison of the oxygenated additive (MXEE) with other oxygenated additives (NM, NE), which contain nitrogen in the molecular structure, shows that the latter increases NO_x formation when nitrogen is present in the chemical structure of such additives.

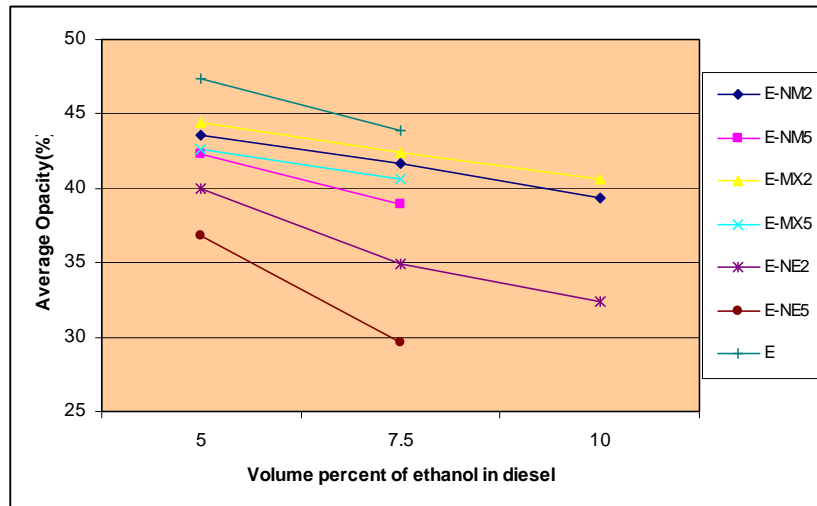


Figure 5. Comparison of soot volume fraction measurement results

Table 4- Soot reduction ratios by introduction of ethanol and other additives.

	Average Exhaust Soot (%)	K Value	Reduction of Soot by Additive
diesel	41.5	1.24	0
E10	31.6	0.88	-23.8
E-NM5-10	28.9	0.78	-30.4
E-NE5-10	20.1	0.52	-51.6
E-MX5-10	30.2	0.84	-27.2

In Table 4, the average soot reduction ratios after addition of E, NM5, MX5, and NE5 are presented. The results show that the NE5 is more effective than others in reducing soot formation.

Emission

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 in NO_x, and a slight decrease in CO emission when shifting from pure diesel to fuel blends.

Data in Table 5 shows the NO_x emission relation with T-GAS, with E-NE5 formulation as fuel both NO and NO₂ emissions are reduced with lower gas temperature.

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

Type	HC(ppm) Hexane	CO (%)	CO ₂ (%)	O ₂ (%)	Lambda	NO(ppm)	NO ₂ (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	21	0.06	1.9	18.54	7.592	256	168	126.1	31.4
E-MX5	22	0.08	2	18.66	7.301	274	174	132.7	31.8

Engine test reports from different investigators show good agreement on the significant reduction of soot due to the presence of ethanol in the diesel fuel blend. However, the reported results on the emission of other species are different. Lu et al. studied the effect of ethanol and cetane number improver on emissions in the diesel engine, and found that NO_x and smoke emissions decreased when diesel engine was fueled with blends. Moreover, CO emission significantly increased for lower and medium loads. HC emission was lower in overall engine operating conditions [6]. He and coworkers reported increased HC emission with addition of ethanol into diesel fuel. They also found that the NO_x emission did not change; however, they reported higher CO emission when ethanol was present in the fuel [2].

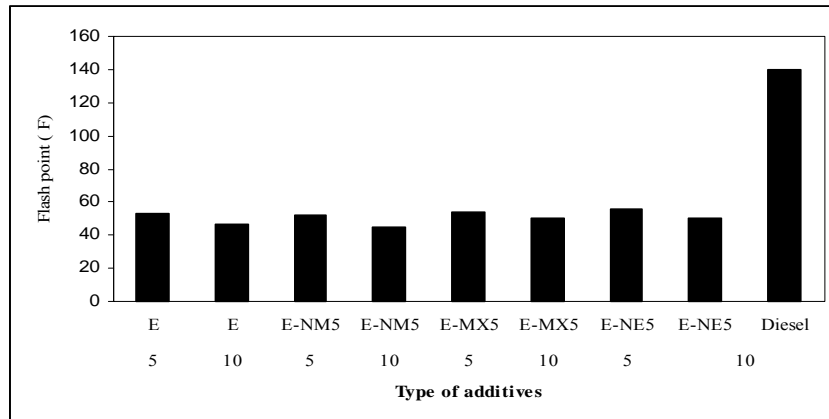


Figure 3. Flash points of the blend fuels and the diesel fuel.

Volatility and Distillation

The influence of the addition of ethanol on the volatility of diesel fuel was studied through the distillation method. In Fig. 4, the distillation curves of the diesel fuel and blends of ethanol are presented. As can be seen in Fig. 4, the addition of the ethanol to diesel fuel modifies the shape of distillation curves at the temperatures below 205°C. Increasing the ethanol content resulted in a higher volatility of the blends. The distillation curves of the blends with or without the additive and ignition improver only differ slightly for the same ethanol content. Based on Fig. 4, the volatility of the E10 and E-NM5-10 samples, both containing 10% ethanol, is significantly different from the others by about 30% distillation point. He et al. evaluated the distillation curves of the ethanol-blended diesel fuels, and found similar results, although their additives and fuel properties were different from those used in the present study [2].

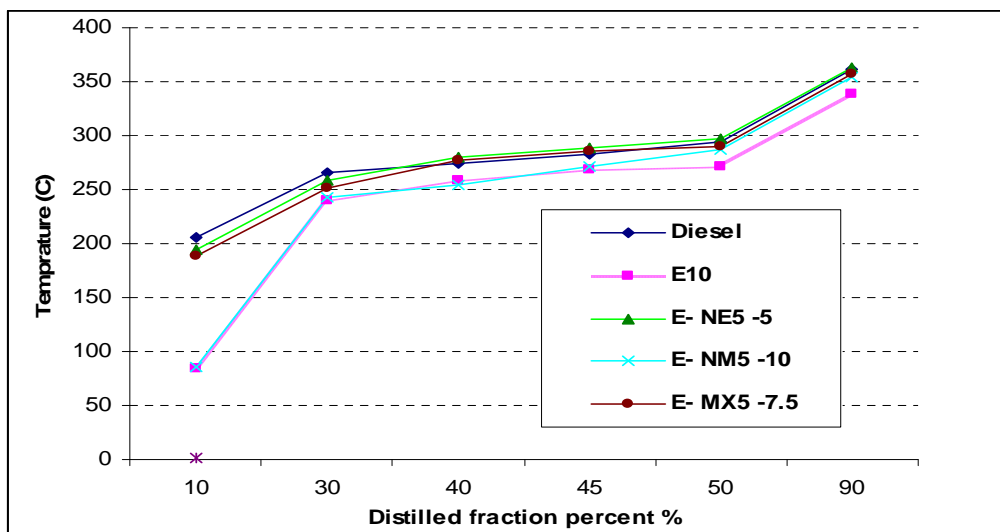


Figure 4. Distillation curves.

Results and Discussion

Soot reduction

Specifications of the test engine are provided in Table 2. The results of soot formation for different samples are presented graphically in Fig. 5, and in Table 4 the soot formation data for different blends are compared. The results show that addition of 10% ethanol in the absence of other additives reduces the soot formation by 23.8%. Ignition improvers can reduce soot formation even further. The maximum of 51% soot reduction was obtained with the blend containing 9.5% ethanol, 0.5% nitro ethane and 90% diesel fuel.

The experimental results of Kass et al. demonstrate a consistent reduction in PM of 20%-27% for an additional 10% ethanol blend [9]. Also in a study of the emissions from the combustion of ethanol blended diesel fuel, He et al. realized a reduction in the smoke emission from 6.3% to 43.8% when the ethanol content changed from 10% to 30% [2].

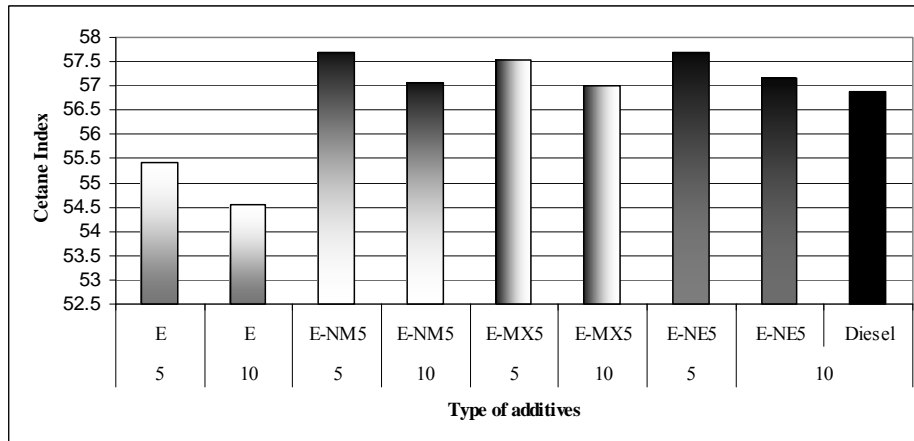


Figure 1. Cetane index of the blend fuels and the diesel fuel.

The ignition improvers can also slightly restore the viscosity of the blends (Fig. 2). Those can also improve the combustion process; ensure good cold starting, reduced noise and long durability for diesel engines [15].

Viscosity

Fig. 2 shows the experimental results relating to the viscosity of the diesel fuel and the blends. It can be understood from Fig. 2 that the addition of ethanol to diesel lowers fuel viscosity. Li and Zhen [3] studied physio-chemical properties of the ethanol-diesel blend fuel, and found that with ethanol contents of 10-20%, the viscosity does not reach the minimum requirements for diesel fuels. In the present experiments, the maximum amount of ethanol in the blends was 10%. It is also seen that the CI additives can slightly improve the viscosity of the blends.

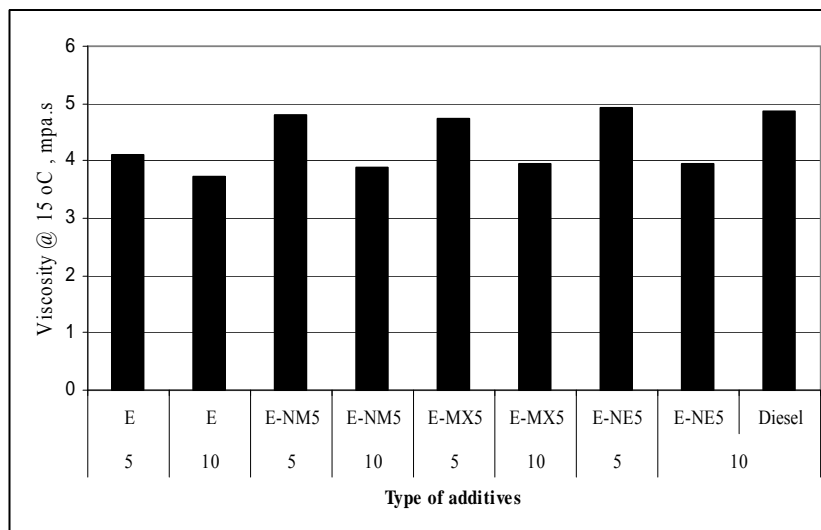


Figure 2. Viscosities of the blend fuels and the diesel fuel.

Flash point

The flash point is the lowest temperature at which a fuel ignites when exposed to an ignition source. 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 37.8°C, while diesel fuel is Class B with a flashpoint above 37.8°C. Hence, the addition of ethanol to diesel would change the NFPA classification from class B to class A, thereby requiring more stringent storage requirements like greater clearances between storage tanks and property lines, buildings and other tanks [14]. 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 improvers can slightly restore the flash point of the blends. Li et al. [3] reported similar variations on flash point with varying amounts of ethanol blended into the diesel fuel.

Fuel properties and results

Blend stability and phase separation

Ethanol solubility in diesel is affected mainly by two factors, water content and temperature of the blend. Avoidance of this separation can be achieved in two ways: by adding a co-solvent, or by adding an emulsifier [13,14].

Because ethanol is soluble in diesel fuel in only small quantities (<12.5% Vol.), either an emulsifier (span 85, i.e. sorbitan trifoliate) or a co-solvent (n-butanol) is required to prepare the ethanol in diesel blends. In the present work, the ethanol used was 99.7%. The maximum amount of the ethanol in blends was below 12.5 Vol%.

Cetane number and cetane index

Cetane number (CN) is one of the most important properties of a diesel fuel, which is generally similar to the octane number of gasoline. 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 Tehran 1, and Tehran 2 diesel is 54.74 and is 56 respectively. Since octane number and cetane number are inversely proportional, the addition of ethanol with a high octane number exhibits a low cetane rating in the blend. Therefore, a cetane improver was used to increase the CI of blends. The three cetane improvers used were 2-methoxy ethyl ether, nitro methane and nitro ethane. The amount of ignition improver was 2.5% of the amount of ethanol in each blend. This created a similar ignition delay as diesel fuel. In order to evaluate the cetane index for the blends, the ASTM D 976 and ASTM D 4737 methods were employed. The results are presented in Table 3.

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

Vol%	Type	Density@ 15°C, g/cc	10% Vol. Recovery °C	30%	50%	90%	Cetane Index ASTM D 976	Cetane Index ASTM D 4737	T10N	T50N	T90N
5	E	0.8335	194	254	280	347	55.4	56.0	-21	20	37
7.5	E	0.8318	182	255	275.5	342.5	55.1	55.1	-33	15.5	32.5
10	E	0.8312	84	240	271.5	338.5	54.6	53.6	-131	11.5	28.5
5	E-NM2	0.8343	196	250	293.5	360.5	57.5	58.6	-19	33.5	50.5
7.5	E-NM2	0.8335	188	252	290	357	57.2	57.8	-27	30	47
10	E-NM2	0.8318	85	242	285	352	56.9	56.4	-130	25	42
5	E-NM5	0.8349	195.5	259	296	363	57.7	58.7	-19.5	36	53
7.5	E-NM5	0.8332	192	248.5	289.5	356.5	57.2	58.1	-23	29.5	46.5
10	E-NM5	0.8324	86	243	287	354	57.1	56.5	-129	27	44
5	E-MX2	0.8338	193.5	245	292	359	57.4	58.4	-21.5	32	49
7.5	E-MX2	0.8322	185	248	287	354	57.1	57.7	-30	27	44
10	E-MX2	0.8316	88	240	284	351	56.8	56.2	-127	24	41
5	E-MX5	0.834	197	252	293	360	57.5	58.7	-18	33	50
7.5	E-MX5	0.8335	189	251	290	357	57.2	57.9	-26	30	47
10	E-MX5	0.8321	90	242	286	353	57.0	56.3	-125	26	43
5	E-NE2	0.8348	194.5	258	295	362	57.6	58.5	-20.5	35	52
7.5	E-NE2	0.8343	188	249.5	292	359	57.3	57.7	-27	32	49
10	E-NE2	0.8316	88	240	285	352	57.0	56.4	-127	25	42
5	E-NE5	0.8351	195	258	296.5	363.5	57.7	58.6	-20	36.5	53.5
7.5	E-NE5	0.8336	9423	250	291	358	57.3	56.0	9208	31	48
10	E-NE5	0.8324	94	242.5	287.5	354.5	57.2	56.3	-121	27.5	44.5
	Diesel	0.8415	206		306	361	56.9	57.0	-9	46	51

On Fig. 1 the CI of diesel fuel is compared with its blends with the ethanol present at 5% and 10%. The influence of the other present additives on the CI of the fuel blends is also demonstrated. As shown in Fig. 1, cetane index of the blends decreases with the 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 standard value at 54.77. In order to enhance CN or CI, of the fuel, the addition of 0.1% Vol. additives (e.g. 2% of ethanol-nitro methane) was needed. The CI improver additive was first mixed with ethanol at the required volume ratio; the mixture was then added to the 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.

Commercial diesel fuel and analysis-grade anhydrous ethanol (99.7% purity) were used in these experiments. Each formulation of ethanol-diesel blends contained improver, ethanol, and diesel fuel. Three different types of oxygenated blends with different fractions of ethanol-additives in diesel fuel were selected for this study.

In this work, a blend of 5% ethanol and 95% diesel is called E5. A blend of 7.5% ethanol and 92.5% diesel is called E7.5, and a blend of 10% ethanol and 90% diesel is referred to as E10. The specifications of the diesel fuels used in this report are given in Table 1. These diesel fuels are produced at Tehran refinery (Tehran 1 and Tehran 2) and are currently being used in all diesel applications in Tehran. The oxygenated compounds selected in the formulations were 2-methoxy ethyl ether, nitro methane and nitro ethane. The physical and chemical properties of the diesel fuels and oxygenated compounds used in the formulations are given in Table 1.

Table 1- Physical and chemical properties of diesel fuels and oxygenated materials (research institute petroleum Iran, 2007).

Specifications	Tehran1	Tehran2	Nitro Methane	Nitro Ethane	MXEE
Molecular Formula	C _x H _y	C _x H _y	C ₁ H ₃ N ₁ O ₂	C ₂ H ₅ N ₁ O ₂	C ₆ H ₁₄ O ₃
Molecular Weight			61.04	75.067	134.174
Copper Corrosion,3hrs @ 100 °C	1a	1a			
Specific Gravity @ 15.56°C/15.56°C	0.8413	0.8424	1.138	1.045	-
Density @ 15 °C g/cc	0.8405	0.8415	1.138	1.054	0.937
Cetane Index	54.74	56	-	-	112-130
Flash Point °C	65	72	35	30	67-70
Sulphur Content wt%	0.68	0.7			
Kinematics Viscosity @ 40 °C cSt	4.87	3.48			
Cold Filter Plugging Point °C	3	1			
Pour Point °C	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			
Autoignation Temperature , C	-	-	418	414	-
Acidity mgKOH/gr	Trace<0.05	0.05			
Distillation:					
Initial Boiling Point oC	165	181	100-103	114-116	162
10% Vol.Recovery °C	206	219			
50% Vol.Recovery °C	294	306			
90% Vol.Recovery °C	361	372.5			
Final Boiling Point °C	386	382			
Recovery Vol%	98	99			

Test procedure

Emissions and combustion characteristics were studied on a MB-OM 457 LA diesel engine both in idle speed and cut-off speed positions. Table 2 shows the engine specifications. Gas analyses were carried out at full flow, partial flow and free flow in diesel. Two exhaust gas analyzers (AVL 465 DY GAS and MRU 1600L type) were employed to measure emissions of NO_x, THC, CO, CO₂ and soot on line in raw exhaust. The resolutions of the gas analyzer are 0.1% Vol. for NO_x, 0.01% Vol. for CO and 1 ppm for HC. At each measurement, the sampling duration was 10 min. The cetane index (CI) can be calculated according to ASTM D 976, and ASTM D 4737.

Table 2- 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

Investigation of the Effects of Oxygenate and Nitrate Component Additives on Physico-Chemical Properties and Exhaust Emission of Diesel Fuel

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This study evaluates the effect of additives on diesel and of additive-ethanol-diesel fuel blends on the density, viscosity, cetane number, flash point, boiling point, distillation and performance in engine tests. An additive is used to keep the blends homogenous and stable, and an ignition improver, which can enhance cetane number in ethanol-diesel fuel blends. The formulations were carried out with 5, 7.5 and 10% v/v of additive-ethanol starting from a base diesel. The presence of MXEE (2-Methoxy Ethyl Ether), NM (Nitro Methane), NE (Nitro Ethane) and ethanol in the diesel fuel significantly alters the characteristics of volatility (flashpoint and distillation curve) and increases the cetane number, improving the fuel's performance in engine tests. The performance of the new fuel formulations were studied on a MB-OM 457 LA diesel engine in idle and cut-off speed positions. 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.

Key Words: Diesel fuel additive, Physicochemical properties, Soot reduction, Cetane number improvers, Emission, Combustion

Introduction

Diesel fuel consists mainly of aliphatic hydrocarbons C₈₋₂₈ with boiling points varying from 130 to 370 °C [1]. Exhaust emissions from diesel engines contain many types of air pollutants, total hydrocarbon (THC), oxides of nitrogen (NO_x), such as particulate matter (PM), carbon monoxide (CO) and acid rain [2,3].

The global increase in energy demands and simultaneous restrictions on air pollutant gas emissions has led researchers to new resources. Much attention has been given to ethanol as an alternative fuel because it is a renewable resource, and can be made from raw bio-materials and waste biomass materials [4,5]. Ethanol has been highly used as fuel, mainly in Brazil, or as a gasoline additive for octane improver and better combustion in USA and Canada [6]. Also, interest has shifted to using ethanol-diesel blends in diesel engines in many countries [6,7].

Introduction of ethanol as oxygenated component into diesel fuel reduces both soot and emission [8,9]. However, there are many technical restrictions to the direct use of ethanol in diesel fuel due to the properties of ethanol, such as the solubility issue of ethanol in diesel fuel at a wide range of temperature and the low cetane number of ethanol. In fact, diesel engines cannot operate normally on an ethanol-diesel blend without special additives [1]. Therefore, fuel additives should be added to the ethanol-diesel blend. In particular, He et al. [2], Shi et al. [8] and Satge de et al. [10] have produced an additive which improves physico-chemical properties of ethanol-diesel blend fuel, such as cetane number and stability of blends, and its effect on performance and emissions of diesel engines. A number of researches have investigated the effect of nitrogen component in the ethanol-diesel blend [11,12]. Based on this background, the key purpose of this work is to evaluate the effect of oxygenate and nitrate components on emissions and combustion characteristics.

In diesel engines, finding new formulations and optimization of fuel properties, such as oxygen content, volatility, requires breaking the trade-off between soot and NO_x emissions, and improving the diesel combustion processes and exhaust emissions. The objective of this study was to find new formulations of additive-ethanol-diesel to replace the diesel fuel with a better combustion performance fuel. Experimental studies were conducted to test the performance of various additive-ethanol-diesel fuel mixtures.

Materials and Method

The ethanol used in these tests was limited to essentially anhydrous ethanol because hydrous ethanol is insoluble or has very limited solubility in the vast majority of diesel fuels. If we used hydrous ethanol (96% purity) in blends, the blending method would use improver (0.25% v/v for all ethanol-diesel blends except for pure diesel

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