Effect of Adding Oxygen Containing Additives to Unleaded Gasoline on Exhaust Emission

Mr. Suryawanshi P.N.
Department of Automobile Engg. M. M. Polytechnic, Kalewadi, Pune. India
Mr. Shinde V.V.
Department of Automobile Engg. M. M. Polytechnic, Kalewadi, Pune. India
Mr. Kurhade A.S.
Department of Automobile Engg. M. M. Polytechnic, Kalewadi, Pune. India

Abstract-
As world population grew, power plants, factories and ever increasing automobiles began to pollute the air to the extent that it was no longer acceptable. During the late 1940s, air pollution as a problem was first recognized in the Los Angeles basin in California .Two causes of this were the large population density and the natural weather conditions of area. Smoke and other pollutants from many industries and automobiles combined with the fog that was common in this ocean area and smog resulted. By the 1960s emission standards were beginning to be enforced in California. Then various ways are investigated to reduce emissions from an IC engine. Oxygen containing additives are used to improve gasoline's performance and reduce exhaust emissions is one of them. The main objective of this work is to find can Dimethyl Carbonate is used to reduce emission? In view of the above, it is decided to investigate the effect of adding Dimethyl Carbonate to unleaded gasoline on exhaust emission. The experimental setup to test blended fuel is prepared with multi cylinder four stroke spark ignition engine. The results indicate that CO and HC exhaust emissions are lower with the use of Dimethyl carbonate gasoline blended fuels as compared to the use of unleaded gasoline. The effect of above additive on NOx is insignificant.

Keywords: Spark ignition engine, Compression ratio, Exhaust emissions, Alternative fuel, Dimethyl Carbonate

Introduction
Until the middle of the 20th century the number of IC engines in the world was so small that the pollution they caused was tolerable. During that period the environment, with the help of sunlight stay relatively clean. As world population grew, power plants, factories and ever increasing automobiles began to pollute the air to the extent that it was no longer acceptable. During the late 1940s, air pollution as a problem was first recognized in the Los Angeles basin in California .Two causes of this were the large population density and the natural weather conditions of area. Smoke and other pollutants from many industries and automobiles combined with the fog that was common in this ocean area and smog resulted. During the 1950s, the smog problem increased along with that the automobile was one of the major contributors to the problem. By the 1960s emission standards were beginning to be enforced in California. During the next decade, emission standards were adopted in the rest of the United States and Europe and Japan. By making engines more fuel efficient and with the exhaust after- treatment, emissions per vehicles of HC, CO, and NOx were reduced by about 95% during the 1970s and 1980s. Lead, one of the major air pollutants was phased out as fuel additives during the 1980s. More fuel efficient engines were developed and by the 1990s the average automobile consumed less than half the fuel used in 1970. However during this time the number of automobiles greatly increased, resulting in no overall decrease in fuel usage. Further reduction of emissions will be much more difficult and costly. As world population grows emission standards have become more stringent out of necessity. The strictest laws are generally initiated in California, with the rest of the United States and word following. Although air pollution is a global problem, some regions of the world still have no emission standards or laws. However, many countries have started following Euro I and Euro II and more up to Euro III and IV norms. The petrol engine has provided reliable small power units for personalized transport and in this way revolutionized the living habits of people to great extent. Petrol powered vehicles now became the symbol of modern society. However,

in recent days the internal combustion engine powered vehicle have come under heavy attack due to various problems created by them such as air pollution.

Sources of atmospheric pollution

There are four possible sources of atmospheric pollution from a petrol engine powered vehicle:

1. Evaporative losses from both fuel tank and carburetor: 15 to 25 % of unburnt HC
2. Crankcase blowby: 20 to 35 % of unburnt HC
3. Tail pipe exhaust: 50 to 60 % of unburnt HC and almost all CO and NOx

Harmful pollutants emitted by spark ignition engines

1. Unburnt hydrocarbons (HC)
2. Oxides of carbon (CO and CO2)
3. Oxides of Nitrogen (NO and NO2)
4. Oxides of sulphur (SO2 and SO3)

SI Engine Emission Control Systems

Exhaust emissions can be controlled at optimum cost by one or more of the following approaches, depending on the limits to meet:

1. Engine design modification
2. Exhaust gas treatment
3. Fuel modifications (Blending gasoline with oxygen containing additives)

Fuel modification **(Blending gasoline with oxygen containing additives i.e. Oxygenates)**

The current use of oxygenates began in the latter half of the 1970s when crude oil shortages developed and the search for alternative fuels began in earnest. Methanol, which could be produced from coal, and bio-ethanol from agricultural feed stocks were extensively evaluated as replacements for petroleum-based motor fuel blocked by the need for a separate fuel distribution system and specially designed vehicles, commercial blending of alcohols in gasoline began in 1979 in West Germany and in 1981 in the United States. Separately, Brazil embarked on a monumental program to convert all motor fuel to either neat ethanol or a 20% ethanol / gasoline blend. Today, oxygenates are used by refiners not so much as a crude oil supplement but as an important and much needed source of octane. Octane demand has increased dramatically due to removal of lead anti-knock compounds from gasoline. Allowed lead levels in leaded gasoline are being reduced as recent medical evidence shows that current automotive lead emissions are a serious and costly health hazard.
Some commonly used oxygenates are used to improve gasoline's performance.

1. Methanol
2. Ethanol
3. Methyl Tertiary Butyl Ether (MTBE)
4. Ethyl Tert-Butyl Ether (ETBE)
5. Dimethyl Carbonate (DMC)

In this experimental we use Dimethyl Carbonate to investigate the effect of adding this to unleaded gasoline on exhaust emission

Dimethyl Carbonate (DMC)

Dimethyl Carbonate is a versatile compound that is used as catalysts in the process of methylation and carbonylation of variety of nucleophiles. It as an attractive eco friendly alternative to methyl halides (dimethyl sulfate) and phosgene.It is termed as green reagent, since it is nontoxic, made by clean process and biodegradable and it reacts in the presence of a catalytic amount of base thereby avoiding the formation of undesirable inorganic salts as byproducts. Dimethyl carbonate is abbreviated as DMC. It is an oxygenated renewable fuel and usually used as an oxygenated additives to blend with fossil fuels. Its purpose is to improve combustion and reduce emission in engines.

a) General Properties of Dimethyl Carbonate

1. DMC is a nontoxic compound as it is not produced from phosgene; rather it is produced catalytic oxidative carbonylation of methanol with oxygen.

2. DMC is classified as flammable liquid smells like methanol and does not have irritating or mutagenic effects either by contact or inhalation, therefore, it can be handled safely without the special precautions required.

3. DMC exhibits a versatile and tunable chemical reactivity.

b) Physical and Chemical properties of Dimethyl Carbonate

1. Physical status and appearance: Liquid
2. Odour: Pleasant
3. Molecular weight: 90.08 gm/mole
4. Color: Colorless, pure
5. Boiling Point: 900C
6. Melting Point: 20C
7. Critical temperature: 274.850C
8. Chemical Formula: C3-H6-O3
9. Chemical Name: Carbonic acid, Dimethyl ester.

c) Fuel properties of gasoline and dimethyl carbonate (DMC)

Property	Gasoline	Dimethyl Carbonate
Chemical Formula	C8H18	C3H6O3
Molecular Weight	114	90
Oxygen (mass %)	0	53.3
Net Lower Heating Value (KJ/Kg)	44000	15780
Stochiometric Air-Fuel Ratio	14.7	3.5
Octane Number	92-98	101-116

Fig. 1 Properties of gasoline and DMC

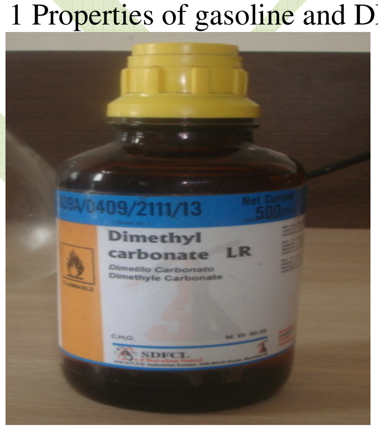

Fig2. Dimethyl Carbonate

Actual Experimental Set up

It consists of computerized Internal Combustion Engine Test Rig and NP Electronics five gas analyzer details of which are given below. A actual setup is shown in Fig. 3 The oxygen containing additives Dimethyl Carbonate was experimentally investigated in this study. The base fuel unleaded gasoline without any oxygenated containing additives, was used as reference fuel and base fuel for preparation of gasoline –DMC blend fuels. The unleaded gasoline was obtained from Bharane Petroleum franchisee of Hindustan Petroleum and DMC is obtained from Alpha Chemika, chemical Suppliers Andheri, and Mumbai

Fig 3 Four Cylinder Four stroke S.I. Engine Test Rig

The blended fuel was prepared on volumetric basis. Before using a new fuel blend, the engine was run sufficient time to consume the remaining fuel from the previous testing. The tests were conducted on a four stroke four cylinder spark ignition engine manufactured by Maruti Suzuki India for Wagonr cars. Its total stroke volume for one cylinder is 4932 mm^3. The major specifications are given in the Table 4.1.The maximum power of engine is 47.7 KW at 6200 rpm. The constant load of 3 N is added to engine for all testing. The various observations are taken for the speed of idle speed, 3500 rpm, 5000 rpm and 6500 rpm. Fuel consumption was measured with the help of calibrated burette and stopwatch.The concentrations of exhaust emission are measured with the help of gas analyzer. Under these condition experiment is carried out and emissions are analyzed and compared with reference fuel i.e. gasoline.

Engine Specifications

Sr. No.	Item	Specification
1	Make	Maruti Suzuki Wagon –R Engine
2	Type	Four stroke/ Water Cooled
3	Number of Cylinders	4
4	Cylinder bore X Stroke	68.5 X 72 mm
5	Maximum Power	47.7 KW at 6200 rpm
6	Fuel system	MPFI
7	Compression Ratio	9.2:1

Exhaust gas analyzer

Fig 4. Exhaust gas analyzer

Exhaust Gas Analyzer Specification

Sr. No.	Item	Specification
1	Make	NP Electronics

2	Type	Four gas analyser ECO GAS-4 with NOx and Engine oil temperature measurement.

Technical Specifications of Gas Analyzer

Measurement Parameters	Range	Resolution	Accuracy
CO (Carbon Monoxide)	0-9.99 %	0.01 %	± 0.06% Abs.
CO_2 (Carbon Dioxide)	0-19.9 %	0.10 %	± 0.04% Abs.
HC (Hydrocarbon)	0-15000 PPM	1 PPM	± 12 PPM Abs.
O_2 (Oxygen)	0-25%	0.01%	± 0.1% Abs.
NOX (Nitrogen Oxide)	0-5000 PPM	1 PPM	+ 20 PPM Abs.

Electrical Specifications

AC Power Supply : 100V to 265 V AC single Phase 50 Hz
DC Power Supply : 10.5V to 14V DC Battery
Power Consumption : 25 watts.

Experimental Procedure

First of all setup was made up ready as per block diagram. Then it was started with using 100% gasoline without any trace of DMC. Probe of gas analyzer was inserted in the exhaust pipe. When steady state was reached, observations were taken from the display of analyzer. Mean while with the help of stopwatch and calibrated burette the reading for fuel consumption is taken. The actual air fuel ratio readings were taken from the software attached to test rig from computer. After fist reading the speed of the engine was increased up to 3500 rpm and readings were taken. Same procedure was repeated for 5000 rpm and 6500 rpm. After the first set of experimentation engine was allowed to run so that it would consume all the fuel in the tank. After this, the first blend of fuel i.e. 95 % gasoline and 5% DMC was prepared on volumetric basis and similar procedure was repeated for different speed of idle speed ,3000 rpm, 5000 rpm and 6500 rpm with keeping load constant. Similarly another two sets of observations were obtained for 90% gasoline- 10 % DMC and 85% gasoline-15% DMC blended fuel. The observations were compared with reference fuel and consequently conclusions were drawn on the basis of them.

Results and Discussion

1) Emission of Carbon Monoxide (CO)

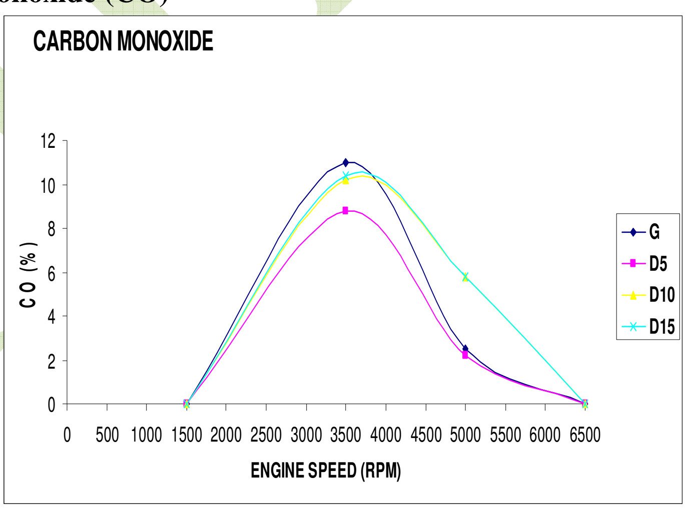

Fig. 5 Carbon Monoxide emissions at various speeds

Fig. 5 shows the CO emission under constant engine load (3 N m) and different engine speeds. Carbon monoxide's chemical formula is CO which is a colorless and tasteless gas. CO is formed in preference over the more usual carbon dioxide when there is a reduced availability of oxygen in the combustion process. As compared to unleaded gasoline, using the oxygen containing additives can obtain a significant reduction in CO emissions at 3500 rpm and 5000 rpm. This is because the properties of the blended fuels are changed because DMC is oxygen containing additive, and its oxygen content in the blended fuels can improve the combustion process. However, the change of CO emission was less observable at 6500 rpm, due to the shorter combustion time at a higher engine speed. The effect of different blended fuels on the reduction of CO emission that compared to unleaded gasoline at the engine speed of 5000 rpm. The CO emission of D5, D10 and D15 decreased approximately by about 65%, 61% and 2%, respectively.

2) Emission of Unburnt Hydrocarbon (HC)

Hydrocarbon (HC) emission is produced by gasoline engine that refers the air–fuel mixture, incomplete combustion during the combustion process. Fig. 6 shows HC emission under constant engine load (3 N m) and different engine speeds. As illustrated in Fig. 4b and c and compared to unleaded gasoline, using the oxygen containing additives can obtain a significant reduction in HC emissions at 5000 rpm. This result can be explained by the fact that the oxygenated characteristic of the added DMC is effective in enhancing the oxidation of hydrocarbons in the air. Nevertheless, the use of D10 and D15 blended fuels at engine speeds 6500 rpm, HC emission would increase. This is because at a higher engine speed, the combustion time is shorter, thereby reducing the heating value of the blended fuels and causing incomplete combustion during the combustion process. The effect of different blended fuels on the reduction of HC emission compared to unleaded gasoline at the engine speed of 5000 rpm. Compared unleaded gasoline, the HC emission of D5, D10 and D15 decreased by about 35%, 21.6% and 8.9%, respectively. These results indicates that DMC can be effective in reducing the HC emission of SI engine.

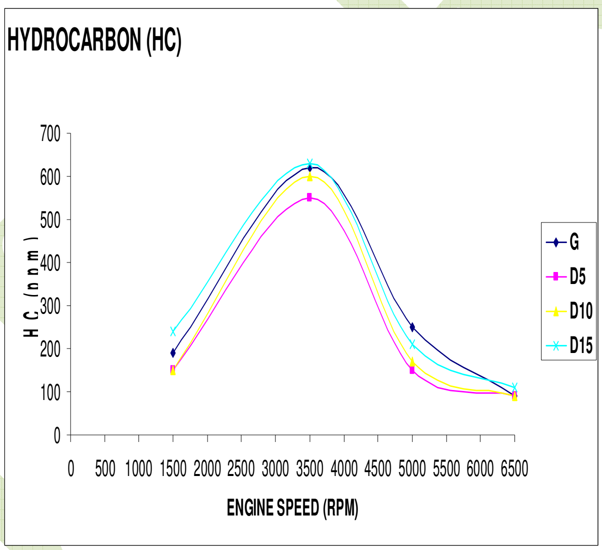

Fig. 6 Unburnt Hydrocarbon emissions at various speeds

3) Emission of Carbon dioxide (CO2)

Fig. 7 shows the CO2 emission under constant engine load (3 N m) and different engine speeds. As compared to unleaded gasoline, using the oxygen containing additives can obtain an increase of CO2 emissions at 5000 rpm. When blended fuels are used in the engine, the combustion reaction is more complete and the concentration of CO2 emission could get higher. It is because that DMC– gasoline are oxygen contain blended fuels, in addition, the blended fuels of D10 and D15 reduced the CO2 emission at 6500 rpm. This is because at higher engine speeds, the combustion reaction was incomplete as a result of the lower heating value of the blended fuels compared to unleaded gasoline. The effect of the different blended fuels on CO2 emission compared to unleaded gasoline at the engine speed of 5000 rpm. With D5 and D10, by 18% and 17%, respectively. However, for the D15 blended fuel the increase in CO2 emission was unobservable compared to other blended fuels, this is because the consumption of D15 blended fuel's heating value was more than other blended fuels. All in all, DMC can significantly increase the CO2 emission of the SI engine.

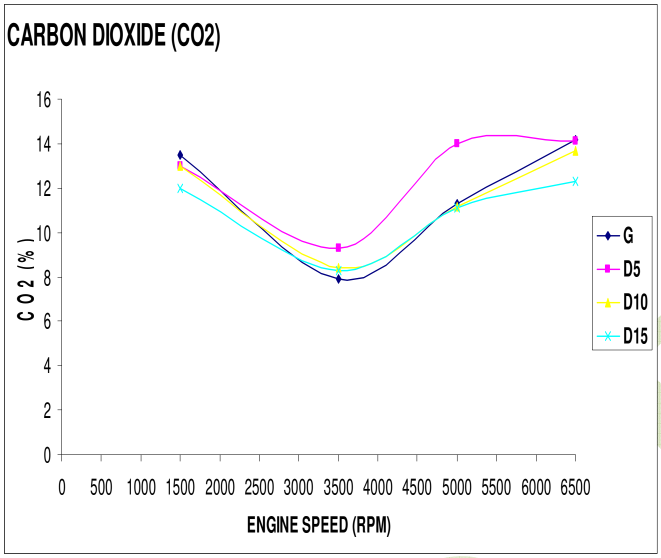

Fig. 7 Carbon dioxide emissions at various speeds

4) Emission of Nitrogen oxides (NOX)

Fig. 8 shows the NOx emission under constant engine load (3 N m) and different engine speeds. The NOX emission was highest at idle speed and 6500 rpm due to the equivalence air–fuel ratio approaching 1 (φ≈1). When the equivalence air–fuel ratio approaches 1, the flame temperature increases during the combustion process. As observed the influence of oxygen contain additives on NOX emission is insignificant .At idle speed and 6500 rpm, the oxygen containing blended fuels reduced the NOX emission probably due to their lower heating value resulting in the reduction of the flame temperature.

5) Exhaust temperature variations at various speeds

Fig. 9 shows that under constant engine load (3 N m) and different engine speeds, the exhaust temperature increases with engine speeds. When the engine speed is 6500 rpm, both the exhaust temperature and NOX emission were at the highest, thus proving that flame temperature can affect exhaust gas temperature and the emission of NOX pollutant during the combustion process in the cylinder. The exhaust temperature decreases with an increase in oxygen containing additives for all engine speeds. This is because compared to unleaded gasoline; the lower heating value of the blended fuels reduced the flame temperature during the combustion process.

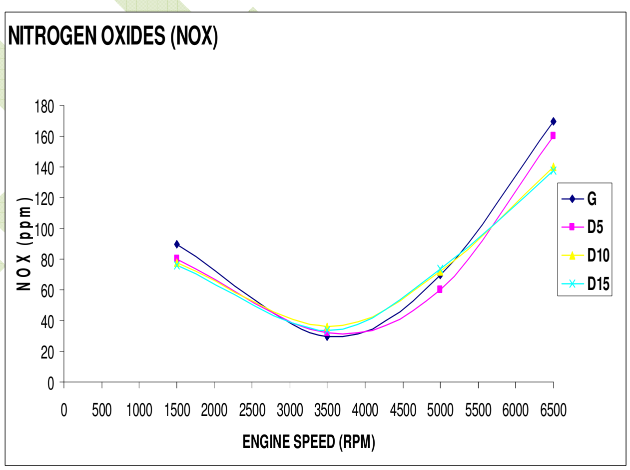

Fig. 8 Nitrogen oxides emissions at various speeds

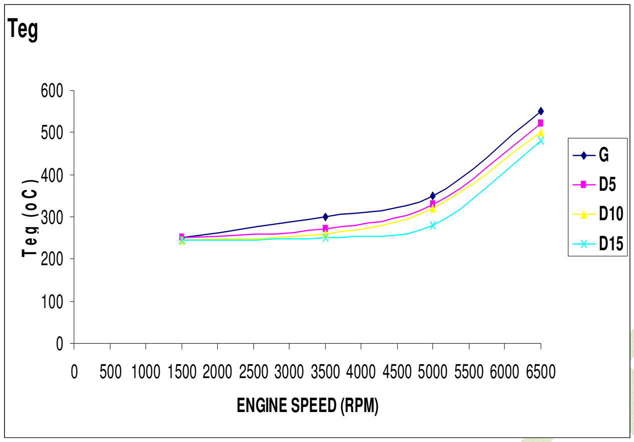

Fig. 9 Exhaust gas temperatures at various speeds

6) Fuel consumption variations at various speeds

In this study, the effect of blended fuels on fuel consumption was investigated. In the engine test, fuel injection was controlled by an electronic control unit (ECU).Under constant engine load (3 N m) and different engine speeds, fuel consumption increased as engine speeds increased. As observed, fuel consumption increased as the oxygen containing additives increased for all engine speeds. Ethanol and DMC have a lower heating value; therefore, in order to obtain the same power at the same operating conditions, the consumption of the blended fuels increased. The effect of different blended fuels on fuel consumption compared to unleaded gasoline at the engine speed of 5000 rpm. For D5, D10 and D15, by 22%, 42% and 56%, respectively. That proved that the heating value of blended fuels can affect the fuel consumption at the same operating conditions on the engine.

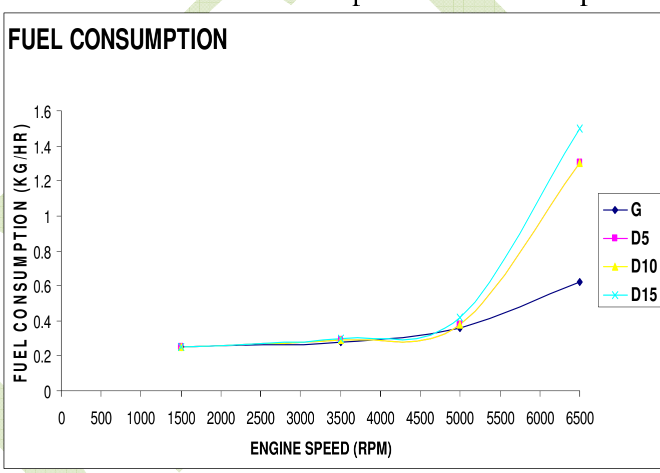

Fig. 10 Fuel consumption variations at various speeds

Conclusions

From this study, the main results can be summarized as below:

1) Using oxygen containing additives can effectively reduce exhaust emissions.
2) Compared to unleaded gasoline, D5 blended fuels produced the best results in engine emissions. The HC emission D5 are reduced about 24% and 35%, respectively, and the CO emission by about 65%. The effect of the oxygen containing additives on NOX emission was insignificant. This is because the effect of NOX emission on the equivalence air–fuel ratio was more than the oxygen containing additives.
3) Using oxygen containing additives increased fuel consumption. This is because the heating value of blended fuels being lower than unleaded gasoline. Using lower heating value of fuels changed the working conditions of the engine, such as compression ratio, ignition timing and so on.

4) In conclusion, as observed, fuel consumption increased as the oxygen containing additives increased for all engine speeds. Ethanol and DMC have a lower heating value; therefore, in order to obtain the same power at the same operating conditions, the consumption of the blended fuels increased.

References

[01] Kivi J., Niemi A, Nylund N.O, "Use of MTBE and ETBE as gasoline reformulation components. SAE technical paper, no. 922379; 1992.
[02] Noorman M.T. "The effect of MTBE, DLPE and TAME on vehicle emissions." SAE technical paper series, no. 932668; 1993.
[03] Li H.L, Prabhu S.K, et al. "The effect of methanol and ethanol on the oxidation of a primary reference fuel blend in a motored engine." SAE technical paper series, no. 50682; 1995.
[04] Kampbell D.H, An Y.J, Williams V.R. "Influence of methyl tert-butyl ether on lake water algae." Bull Environ Contam Toxicol 2001;67:574–9.
[05] Mennear J.H. "Carcinogenicity studies on MTBE: critical review and interpretation." Risk Anal 1997;17:673–81.
[06] Wen L.B., Xin C.Y., Yang S.C. "The effect of adding dimethyl carbonate and ethanol to unleaded gasoline on exhaust emission." Applied Energy (87) 2010 115-121
[07] Tundo Pietro, Selva Maurizio. "The chemistry of dimethyl carbonate." Acc Chem Res 2002;35(9):706–16.
[08] Palmer F.H. "Vehicle performance of gasoline containing oxygenates," paper C319/86.International conference on petroleum based fuels and automotive. London: I.Mech. E Conf. Publication 1986-11, MEP; 1986; p. 36–46.
[9] He BQ, Wang JX, Hao JM, et al. "A study on emission characteristics of an EFI engine with ethanol blended gasoline fuels." Atmos Environ 2003; 37:949–57.
[10] Huang ZH, Jiang DM, Zeng K, Liu B, Yang ZL. "Combustion characteristics and heat release analysis of a compression ignition engine fueled with diesel dimethyl carbonate blends." Proc Instit Mech Eng, J Automob Eng 2003;217(D7):595–606.