

INFLUENCE OF CeO₂ NANOPARTICLES ON METHYL TERTIARY BUTYL ETHER GASOLINE BLEND IN SPARK IGNITION ENGINE

by

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The search for suitable alternative for fossil fuel has been a challenge to the research community for the past two decades. So many alternatives have been identified and tested. However, a complete replacement cannot be provided without any penalties of cost, excess emission, poor operation, etc. The alcohols gave a new opportunity and a solution for that problem but had some setbacks of increased density and lower octane number. The present work focuses on striking a balance between advantages and disadvantages by using oxygenated additive with gasoline fuel. The additive CeO₂ along with methyl tertiary butyl ether (MTBE) offers many advantages. The seven samples, namely M10, M15, M20, M25, M20 + 50 mg/l, M20+100 mg/l, M20+150 mg/l have been prepared and tested on spark ignition engine. Here, 10, 15, 20, and 25 denote the MTBE volume in blends and 50 mg/l, 100 mg/l, and 150 mg/l indicate the CeO₂ in blends. The results have shown that only MTBE has caused an increase of 4% in brake thermal efficiency with M15 and then brake thermal efficiency has improved by 3% with M15 + 100 mg/l compared with pure gasoline. Fuel consumption has also been reduced upto 9% with M20 and 11% with M15+150 mg/l compared with pure gasoline. The maximum HC and CO reductions have also been observed from M20 and M20 + 150 mg/l. It was up to 19% and 22%, 23%, and 25% of HC and CO with M20, M20 + 150 mg/l. However, there has been an increase in CO₂ emission level because of excessive unburned HC reduction. The MTBE with CeO₂ has proved to be suited to all running conditions. The blends having more amounts of additive produce good combustion characteristics yet it should be restricted within 20 vol.% of MTBE and 150 mg/l of CeO₂.

Key words: MTBE, oxygenates, spark ignition engine, emission control

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Introduction

Additives are mixed with the gasoline for improving the performance and reducing the emission by enhancing the properties like octane rating, calorific value, *etc.* [1]. One of the special additives used is oxygenate, which facilitates complete combustion in the engines. Owing to the presence of oxygen molecules in the oxygenate additive, the fuel burns properly and produces maximum power output [2, 3]. Also there is a significant reduction in the emission of CO and HC particles [4]. The additive chosen for the present research work is MTBE, a colorless liquid at ambient conditions. However, the presence of excess oxygen in the combustion chamber improves the tendency of NO_x formation. The gasoline/ethanol fuel has been tested for cold start (at -7 °C) and warm start (at 22 °C) as per New European Driving Cycle and Artemis Driving Cycle. The engine has exhibited an increase in the average total emission factor while tested with the gasoline blended ethanol. The system has experienced a great increase in the emission during the cold start when oxygenated polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbons are added with the gasoline fuel. The results have highlighted the need for further study of commercial contemporary vehicles using the gasoline fuel [5].

Utilization of ethanol as substitute for gasoline in a spark ignition (SI) engine without any modification has been experimented. The engine ran at a constant speed for hours of testing fuelled by ethanol and its mixture with gasoline. The results have revealed an improved thermal efficiency with reduced brake specific fuel consumption (SFC). The alcohol nature of ethanol has greatly reduced the emission content and temperature. The results have depicted that gasoline mixture with 15% ethanol is best suited to the existing SI engine without any modification [6]. The oxygenated additives MTBE and di-isopropyl ether have been mixed with the sole gasoline and tested. The ASTM standard tests have been conducted for verifying the suitability of mixture fuel in the engine. The experiments have revealed a significant 6% reduction of HC, 13% reduction of CO, and 2% increase of brake thermal efficiency (BTE). However, the NO_x emission still has increased up to 33% compared to sole petrol [7].

Co-solvent like fuel oil should be used with alcohols during high compression ratio operation of SI engines because of the high octane number. The phase splitting problem will get reduced and eco-friendly fuel can be obtained. The modification in injection timing should be made to the engine while running on alcohol fuels [8, 9]. The utilization as neat alcohol or blended with regular fuels will improve the performance of engine. The addition of MTBE with the gasoline will reduce its density to the acceptable level with proper blending, whereas the alcohol will increase the density. Thus the vapour pressure of the gasoline blend will be increased [10]. The research octane number (RON) that increases by 1.9-11.8 on adding MTBE, however, is inferior to the lead alkyl compounds. The front end octane numbers (FEON) also gets improved which is directly proportional to the engine efficiency. No phase split up of the blend and formation of azeotrope will be exercised with MTBE in the gasoline [11]. To improve the BTE and reduce the NO_x further, a few of solid additives are suggested along with alcohol in gasoline or directly to the gasoline fuel. The Mn₂O₃ and CO₃O₄ have been used as nanoadditives along with ethanol and gasoline. Both improve the BTE up to 19.5% and 11.5%, respectively. Also it reduces the NO_x up to 20% compared with pure gasoline operation [12]. The additive (C₁₂H₂₅COO)₂Me that has been used with gasoline has reduced the SFC about 3.5% and has reduced the toxic emissions too. Also, it provides the smoother operations where vibrations and noise level of vehicle are minimal [13]. The CeO₂ nanoparticles with gasoline operations have produced better thermal efficiency about 30.98%, also have reduced the NO_x up to 60 ppm, and HC up to 10 ppm [14, 15].

From the aforementioned literature it can be concluded that the ethanol is a best alternative for gasoline engine, either as pure or additive mixed gasoline fuel [16]. Lower proportion of ethanol in gasoline blends can be utilized in gasoline engine without any modification, but pure ethanol requires major modifications in fuel system. Different forms of ethanol are mostly used to improve the engine performance and thermal efficiency. Also, the few nanoadditives such as Mn₂O₃, CO₃O₄, and (C₁₂H₂₅COO)₂Me have the tendency to improve the efficiency and reduce the harmful emissions in gasoline engine operation [17]. To the knowledge of the author, no work has so far been attempted using the CeO₂ nanoadditives with MTBE on gasoline engine. This research aims to analyze the influence of CeO₂ nanoparticles on different blends of MTBE and gasoline fuel in engine performance and emission formation [18, 19].

Materials and methods

The oxygenate MTBE has been chosen for this research from the previous literature. The additive exhibits good amount of improvement in the performance of the engines running with gasoline. Here the additive is mixed with sole gasoline in varying volumetric proportions from 10-25%. For this work, MTBE has been purchased from Validyn Engineering Solutions Pvt. Ltd., India and the diesel has been purchased from the Indian oil fuel station, India. The fuel properties for all the samples have been tested before starting engine testing and are given in tab. 1. The CeO₂ nanoparticles have been purchased from Nanoshel Company, India. The nanoparticle morphology has been determined by transmittance electron microscope (TEM) shown in fig. 1, Made: FEI from the Netherland, model: Tecnai 20 G2, Resolution: 1.8Å°, and Point: 2.40 Å°. The specifications of CeO₂ nanoparticles are given in tab. 2.

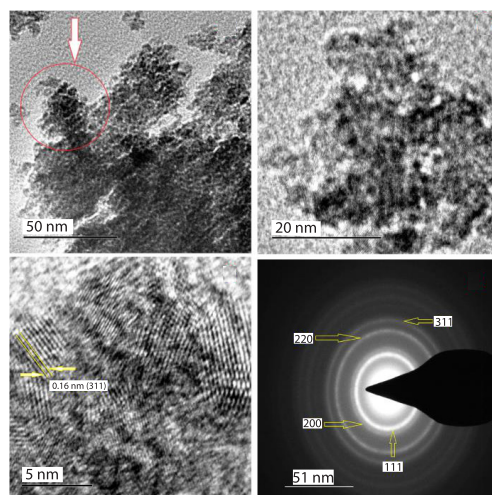


Figure 1. The TEM images of hybrid CeO₂ nanoparticles

Table 1. Property of fuel blends

Properties	Density at 15° C [gm/cc]	Flash point [°C]	Fire point [°C]	Kinematic viscosity at 40° C in cSt	Gross calorific value [MJkg ⁻¹]
Testing standards	IS 1448 P 32	IS 1448 P 69	IS 1448 P 69	IS1448P25	Bomb colorimeter
Gasoline	0.7432	43	38	0.6	47.09
M10	0.7429	44	40	0.58	42.83
M15	0.7427	44	42	0.57	42.15
M20	0.7423	45	42	0.57	41.63
M25	0.7421	46	43	0.55	41.48
M20 + 50 mg/l	0.748	49	50	0.57	41.5
M20 + 100 mg/l	0.751	52	53	0.58	41.52
M20 + 150 mg/l	0.755	54	55	0.58	41.53

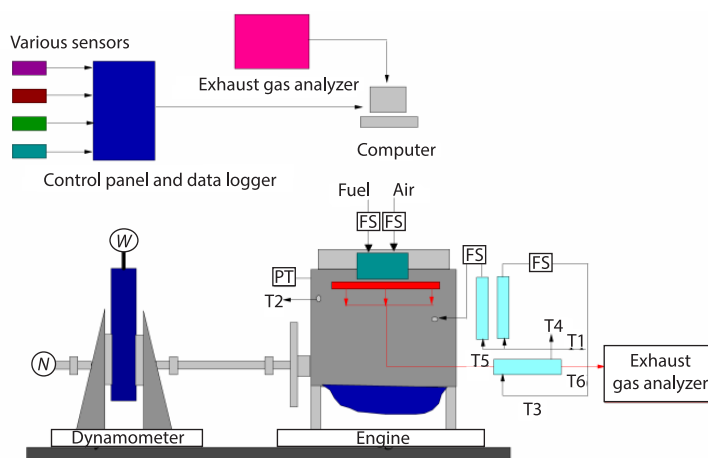
Table 2. Specification of CeO₂ nanoparticles

Particulars	Specifications
Particles	CeO ₂
Manufacturer	M/S Nanoshel Company, India
Chemical Abstracts Service (CAS) No	1306-38-3
Compound formula	CeO ₂
Molecular mass	172.11 g/mol
Average particle size diameter	Lesser than 80 nm
Density	7.15 g/cm ³
Appearance	Pale Yellow
Melting point	2340 °C

The CeO₂ can act as oxygen buffer to provoke the oxidation process further, especially the CeO₂ tends to reduce the NO_x in emission. The fuel blends have been prepared on systematic procedure which satisfies the stability criteria viz. dispersion stability, kinetic stability, and chemical stability [20, 21]. The nanoparticles have been dispersed by an ultrasonication for 50 minutes, to get the homogeneous mixture. To check the stability of nanoparticles, the fuel samples have been placed in a graduated scale glass test tube under static nature and it has been found that the particles have remained stable for 16 hours. To the best of authors' knowledge, this investigation has been done for the first time, and it provides new and significant information regarding performance enhancement and NO_x emission of gasoline engine with addition of MTBE and CeO₂ nanoparticles. The optimized blends of MTBE about 20 vol.% have tested with three different proportions of CeO₂ nanoparticles such as 50 mg/l, 100 mg/l, and 150 mg/l. All the experimental results are compared each other in order to BTE, cylinder pressure, CO, CO₂, unburned HC, and NO_x.

Experimental set-up

The experiments have been conducted on a computerized Maruthi make multi port fuel injection (MPFI) gasoline engine as shown in fig. 2 consisting of three cylinders, four stroke, multi-port fuel injection and eddy current type dynamometer for loading. The specifications of the engine are given in tab. 3. The specification of AVL DI gas analyzer shown in tab. 4.

**Figure 2. Schematic lay-out of the computerized MPFI gasoline engine set-up;**

T1 – $T_{\text{water inlet}}$
T2 – $T_{\text{water outlet}}$
T3 – $T_{\text{calorimeter water inlet}}$
T4 – $T_{\text{calorimeter water outlet}}$
T5 – $T_{\text{engine gas outlet}}$
T6 – $T_{\text{calorimeter gas outlet}}$
N – engine speed,
W – engine load,
FS – flow sensor,
PT – pressure transducer

Table 3. Specifications of MPFI gasoline engine

Make	Make maruti, type BS-VI, 3 cylinder, four-stroke, petrol (MPFI), water cooled
Description 7 rated speed	Computerized, power 50 Kw at 5500 rpm, type K10B, torque 90 Nm at 3500 rpm, bore, 998 cc
Dynamometer	Type eddy current, water cooled
Bore and stroke, CR	73 mm and 79.5 mm 11.0:1
Temperature sensor	Make radix, type RTD, PT100 and thermocouple, Type K
Rotameter	Engine cooling 100-1000 LPH; calorimeter 25-250 LPH
Data acquisition device	Make NI instrument USA, NI USB-6210, 16-bit, 250 kS/s

Table 4. Specifications of MPFI gasoline engine

Emission	Range	Resolution
HC	0-20 ppm vol.	1 ppm
CO	0-10 %vol.	0.01 vol.%
CO ₂	0-20 %vol.	0.1 vol.%
NO _x	0-5 ppm vol.	1 ppm

The experimental plan consists of testing the engine with gasoline blends containing MTBE in proportions of 10%, 15%, 20%, and 25% by volume. The 20% of blend has been mixed with CeO₂ nanoparticles in the proportions of 50 mg/l, 100 mg/l, and 150 mg/l. The fuel samples were prepared with high shear and ultrasonic mixer (Make Labman, 20 KHz, AC 220 V/50 Hz with probe diameter 9.5 mm) shown in fig. 3. The engine has been operated at a constant speed of 1500 rpm during the entire period of testing.



Figure 3. Photograph of ultrasonicator

Results and discussion

The influence of CeO₂ on MTBE blended gasoline fuel has been experimented on MPFI gasoline engine with constant speed. The performance, combustion and exhaust characteristics are discussed in this section.

Brake thermal efficiency

The variation of BTE for prepared fuel blends is shown in fig. 4. The BTE is higher for all the fuel blends than the pure gasoline. Among the samples, M20 + 150 mg/l have produced high BTE as compared to all other samples. It is mainly because of the enhancement of octane number and addition of CeO₂ nanoparticles in MTBE-gasoline blends, which causes the improvement in the BTE [22]. The maximum BTE has been found to be about 27.12% with M20 + 150 mg/l sample. Figure 3 shows BTE to be increasing with increasing the quantity of CeO₂ nanoparticles. Because CeO₂ provides the oxygen to facilitate more complete combustion and thus increases the BTE [23]. The improvement of BTE with M20+150 mg/l is 4.9% more than gasoline and 2% more than gasoline MTBE blends (M20).

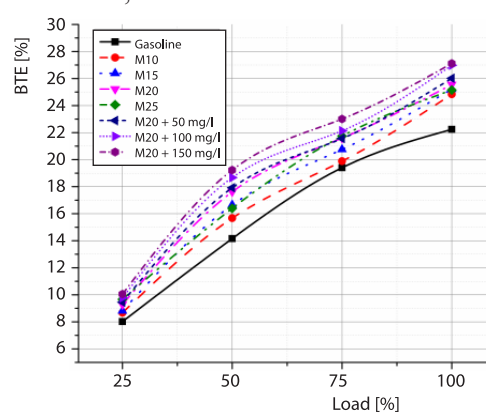


Figure 4. The BTE

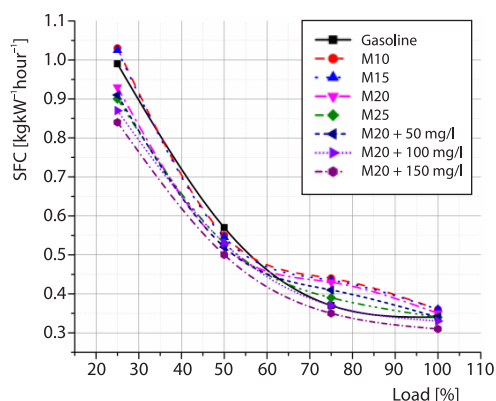


Figure 5. The SFC

been observed with M20 + 150 mg/l sample to be about 0.31 kg/kWh, whereas it is 0.34 kg/kWh for pure gasoline at higher engine loads.

Engine combustion

Generally, gasoline engine does not follow the stable running, the cyclic variation produces the inconsistencies in combustion process and it may lead to higher combustion [24].

Figure 6 represents the variations of cylinder pressure with crank angle. The cylinder pressure has been found to be lower in all the prepared fuel than the pure gasoline operation. Addition of MTBE and CeO₂ has resulted in the enhancement of the heating value which consequently has started burning at little lower cylinder pressure as shown in fig. 6.

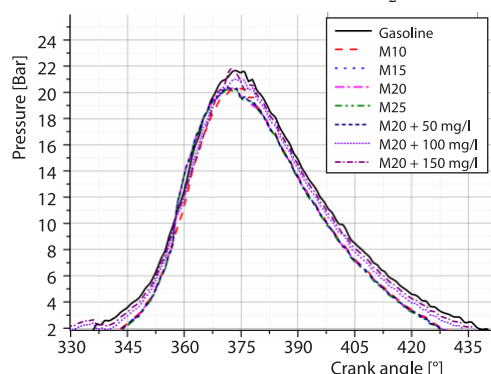


Figure 6. Cylinder pressure with crank angle

Specific fuel consumption

Figure 5 depicts the variation of the SFC of engine for prepared blends under different engine loads. Contrary to BTE, the SFC is reduced with all the blends of CeO₂ compared to gasoline operation. Here, the oxides in nanoparticles tend to oxidize the fuel effectively which leads to better BTE and lower fuel consumption. In addition, the vaporization of fuel mixture continues till the compression stroke when latent heat increases. If the fuel mixture absorbs more heat during vaporization, then work spent to the compression is reduced and thus increases the BTE and reduces the SFC. The lower SFC has

been observed with M20 + 150 mg/l sample, to be about 22.2 bar. The addition of MTBE increases the RON and FEON, which provides the better engine combustion. The CeO₂ nanoparticles in the fuel are having a very important role for increasing the pressure because the particles are exposed more in the fluid and allow to react more with the O₂ in the combustion chamber. Therefore, the improvements in increasing the pressure are observed with the addition of metal-based additives. The maximum cylinder pressure has been found with M20 + 150 mg/l sample, to be about 22.2 bar.

Emission analysis

The CO emission

Figure 7 shows the CO concentration in gasoline engine emission for various blends under different engine loads. The CO is found to be lower with gasoline and MTBE blends pure than gasoline and CeO₂ blends. The high CO emission is influenced by various parameters such as insufficient time for burning, chemical structure, non-homogeneity of the fuel. The MTBE induces the reduction of CO oxidization in expansion and exhaust stages and lean mixture due to fuel borne oxygen which causes more complete combustion [25]. The deficiency of oxygen may be the negative factor causes the higher CO emission in gasoline sole fuel and minimal MTBE blends. But it was reduced by adding of optimal CeO₂ and MTBE which shows in fig. 7.

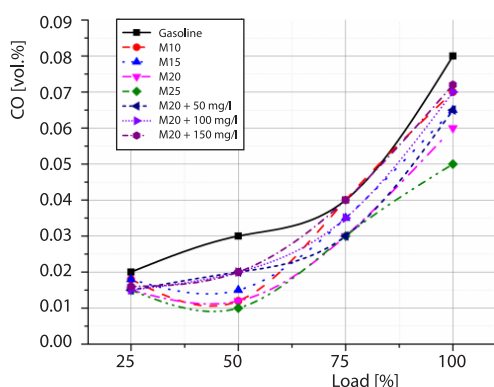


Figure 7. The CO with engine loads

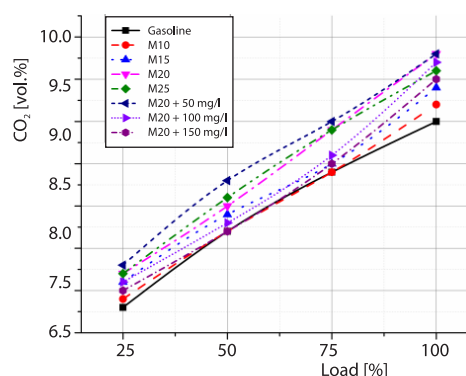


Figure 8. The CO₂ with engine loads

The CO₂ emission

Figure 8 depicts the CO₂ variations in different engine loads. The CO₂ is more in all the prepared blends than pure gasoline. Due to complete combustion with MTBE blend and CeO₂ addition, the combustion has occurred completely which has reduced the CO and increased the CO₂ in the emission. Providing more oxygen to the fuel mixture by MTBE and CeO₂, the CO is converted into CO₂ in later stages of gasoline cycle, which leads further enhancement of CO₂ in emission [26].

The unburned HC in the emission is shown in fig. 9 for various blends and gasoline under different loads. The HC is found to increase slightly with the increase of MTBE ratio in gasoline. This is due to reducing the heating value of the mixture, thereby facilitating the incomplete combustion and flame quenching effect near the chamber surfaces. But, HC is found to reduce with the addition of CeO₂ nanoparticles. This is because of oxygen supply by the nanoparticles. The maximum value has been found with the M25 sample and it is about 25 ppm.

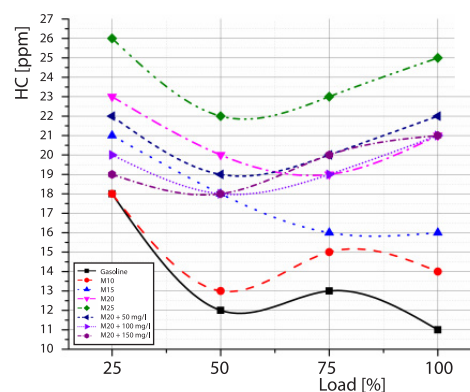


Figure 9. Unburned HC

The NO_x emission

The NO_x variation with different blends under various engine loads is shown in fig. 10. The NO_x reduces with the addition of MTBE. Here, the MTBE reduces the heating value which produces the lower heat during combustion, thus decreasing the level of NO_x in emission. The O₂ concentration and combustion temperature are the two main factors that influence the NO_x

Table 5. The NO_x (in ppm) emission with MTBE and CeO₂ blends

Load in [%]	Gasoline	M20 + 50 mg/l	M20 + 100 mg/l	M20 + 150 mg/l
25	243	235	245	265
50	445	432	447	478
75	652	635	649	682
100	964	942	958	987

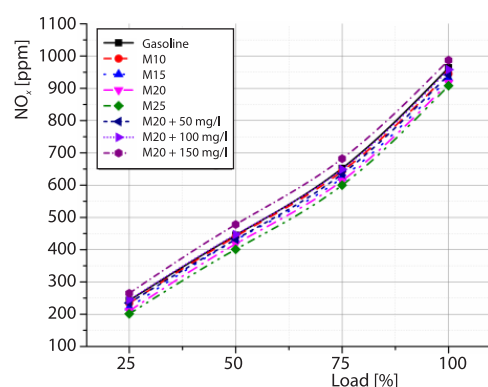


Figure 10. The NO_x with engine loads

formation. Here, adding of MTBE and CeO₂ nanoparticles increases the O₂ concentration in the mixture which reduces the NO_x formation in the emission. Table 5 indicates the NO_x emission with gasoline blended with CeO₂ and MTBE.

Conclusions

Addition of MTBE along with CeO₂ nanoparticles improves the engine performance and reduces the harmful emission, are as follows.

- The MTBE increases the BTE better than gasoline and further increment is caused by adding the CeO₂ nanoparticles due to O₂ concentration and improvement of octane number.
- The SFC has been found lower with MTBE and CeO₂ blended operations than pure gasoline operations, because of more complete oxidization of fuel mixture and more heat absorbing during compression.
- Minimal cylinder pressure has been found lower during the MTBE and CeO₂ blends operation than pure gasoline, which occurs because of the mixture having tendency to burn at lower pressure than gasoline.
- The CO has been found lower with MTBE blended fuel than pure gasoline and CeO₂ blended fuels. Sometimes, adding CeO₂ to gasoline takes more time for burning which causes the incomplete burning which increases the CO in emission.
- The unburned HC has been found higher slightly with MTBE blends, because of oxygen shortage. It started reducing by providing more oxygen with the addition CeO₂.
- The NO_x is reduced with MTBE and CeO₂ blends by providing enough oxygen and reduces heat release rate.

From this investigation, it has been found that Gasoline blended with 20 vol.% of MTBE along with 100 mg/l of CeO₂ produces better combustion as compared to other blends. The findings are BTE is about 27%, SFC is about 0.33 kg/Kwh at high load and the emissions such as 0.07 vol.% of CO, 19 ppm of HC, and 940 ppm of NO_x are observed at high loads.

Nomenclature

BTE – brake thermal efficiency
CeO₂ – cerium oxide
CO₃O₄ – cobalt (II, III) oxide
FEON – front end octane numbers
Mn₂O₃ – manganese (III) oxide
MPFI – multi port fuel Injection

MTBE – methyl tertiary butyl ether
RON – research octane number
SFC – specific fuel consumption
SI – spark Ignition
TEM – transmittance electron microscope

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