Ignition Delay and Soot Oxidative Reactivity of MTBE Blended Diesel Fuel

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Abstract

Methyl tert-butyl ether (MTBE) was added to diesel fuel to investigate the effect on ignition delay and soot oxidative reactivity.

An ignition quality tester (IQT) was used to study the ignition propensity of MTBE blended diesel fuels in a reactive spray environment. The IQT data showed that ignition delay increases linearly as the MTBE fraction increases in the fuel.

A four-stroke single cylinder diesel engine was used to generate soot samples for a soot oxidation study. Soot samples were pre-treated using a tube furnace in a nitrogen environment to remove any soluble organic fractions and moisture content. Non-isothermal oxidation of soot samples was conducted using a thermogravimetric analyzer (TGA).

It was observed that oxidation of 'MTBE soot' started began at a lower temperature and had higher reaction rate than 'diesel soot' across a range of temperatures. Several kinetic analyses including an isoconversional method and a combined model fitting method were carried out to evaluate kinetic parameters.

The results showed that Diesel and MTBE soot samples had similar activation energy but the pre-exponential factor of MTBE soot was much higher than that of the Diesel soot. This may explain why MTBE soot was more reactive than Diesel soot.

It is suggested that adding MTBE to diesel fuel is better for DPF regeneration since an MTBE blend can significantly influence the ignition characteristics and, consequently, the oxidative reactivity of soot.

Introduction

The reduction of soot and gaseous emissions remains a challenge if diesel engines are to continue to play a role in transportation applications into the future. Numerous efforts have been made to reduce soot formation and to enhance the oxidation characteristics of biodiesel. It has been reported that the use of oxygenated fuel additives not only inhibits soot formation but also enhances the soot oxidation rate [1]. Along with various oxygenated compounds such as dimethyl carbonate, dimethyl ether, methanol, ethanol, and ethyl tertiary butyl ether, methyl tert-butyl ether (MTBE) has also been used as a diesel additive to reduce smoke, NO_x , THC emissions, odor, and eye irritation in direct injection diesel engines [2, 3, 4].

While MTBE has been used as a gasoline additive replacing tetraethyl lead in order to increase octane rating and reduce engine knocking, it may also be a good candidate to optimize the fuel chemical composition and physical properties of diesel fuel. Mixing MTBE with diesel fuel is straightforward as there is no phase separation or any abnormal response from the engine. MTBE has a chain-branched compact-molecular structure, which leads to an enhanced resistance to decomposition during the ignition delay. As the MTBE increases the ignition delay there is a corresponding increase in the premixed combustion phase. As a consequence, the brake thermal efficiency improves and there is a considerable reduction in the generation of smoke [5]. Furthermore, the addition of a small amount of MTBE to diesel reduces soot and NO_x emissions simultaneously [6]. At higher temperatures, some fraction of MTBE may persist, decompose, and be used in oxidizing the soot before completing the combustion process inside the engine cylinder, which results in smaller amounts of soot [7]. MTBE has low viscosity and high volatility, characteristics which lead to enhanced mixing and production of a spray with droplets of small diameter [8].

Knowledge of the properties of MTBE is required for further understanding the combustion processes of MTBE-blended fuel in internal combustion engines. For example, fuel volatility will affect the rate of rise and height of the premixed burning spike. Increase in initial boiling point (or volatility) can lead to an increase in exhaust NO_x emissions [9, 10]. Ignition delay determines the nature of the premixed or mixing controlled combustion phase and has an impact on engine noise, emission characteristics, engine performance and efficiencies. For a longer ignition delay, the rate of the first stage of combustion increases dramatically, the engine noise also increases, as do usually NO_x, THC, and the soluble organic fraction (SOF). However, the higher local oxygen concentration in the MTBE-blended fuel mixture will have the opposite effect on exhaust gas emissions. In contrast to the MTBE-gasoline mixture, there is currently little experimental data for MTBE with diesel. In the present work, ignition propensities have been measured using an ignition quality tester (IQT) in a reactive spray environment of a range of MTBE-blended diesel fuels.

By comparison with other oxygenated fuel additives, the effect of MTBE in diesel has been much less studied, especially in terms of soot oxidation characteristics. As an after-treatment of diesel engine exhaust, diesel particulate filters (DPF) represent a good option. Soot particles are trapped on a filter in the DPF and then should be burned periodically. In normal diesel soot, the particles are fairly unreactive, this leading to blockage of the DPF and a higher back pressure on the engine which changes the engine performance. Improvement of fuel properties in terms of soot oxidative reactivity is essential for diesel exhaust gas after-treatment.

In the present work the effect of MTBE blends in diesel on the soot oxidative reactivity and, consequently, on DPF regeneration is investigated. Soot samples were collected directly from the exhaust of a single cylinder diesel engine running at a steady-state operation. Non-isothermal oxidation kinetics of the soot was studied using a thermogravimetric analyzer (TGA).

Table 1. Fuel properties

Fuel property	Value for the following test fuels	
	Diesel fuel	MTBE (C5H12O)
Specific gravity	0.84	0.746
Kinematic Viscosity (cSt) 20°C	4.7	0.47
Viscosity ~35°C (mm ² /s)	2.92	0.369
Lower calorific value (MJ/kg)	43	35.2
Cetane number	52	≈ 8.5
Boiling point (K)	452-639	328.2
IBP (°C)	178.9 min	50.5 min (55.2)
FBP (°C)	365.9 max	74.5 max
O ₂ content (%)	≤ 0.1	18.2
Ignition temperature (K)	523	698
Enthalpy of evaporation (kJ/kg)	250	340

Two test fuels were used: commercial diesel and a blend of 11 % MTBE by volume in diesel. The properties of the fuels are shown in Table 1.

Ignition Delay Characterization

Ignition delay times (ID) for MTBE blends in diesel fuel (0, 5, 10, 15, and 20 %) were measured in an IQT (Advanced Engine Technology, Ottawa) following the ASTM D 6890-12a protocol. A detailed description of the IQT apparatus and its operation can be found in the ASTM D 6890-12a. The experiments were performed at a charge air pressure of 21 atm, a temperature of 844 K, and nozzle opening pressure of 180 atm.

The ignition delay and derived cetane numbers for MTBE blend in diesel with increasing volume percentages of MTBE (increments of 5 %) are represented in Figure 1. Note that the base diesel fuel (0 % of MTBE) had a derived cetane number (DCN) of about 52, which conforms well with a standard for diesel fuel (45–55). As the MTBE proportion in the fuel increases, the ignition delay times increase. For example, an 11 vol% MTBE blend in diesel increased the ignition delay by 0.45 ms (with a corresponding decrease in DCN by 5).

Figure 1. Ignition delay and derived cetane numbers for MTBE-commercial diesel blends.

In general, a longer ignition delay leads to larger premixed burning part and less mixing controlled burning part. The ignition event in an IQT can be separated into the physical time delay required for formation of spray droplets and vaporization, plus a chemical time delay required for the evolution of low temperature oxidation chemistry. It was anticipated that the varying proportions of MTBE in the MTBE-blended diesel fuels would result in differing physical properties, with a consequent effect on the physical time delay associated with spray droplet formation and vaporization.

Figure 2 shows the variation in physical properties and chemical time delay resulting from differing proportions of MTBE in the test fuels. Physical time delay was measured as the delay between the beginning of the injector needle lift and the minimum point of the pressure curve inside the IQT combustion chamber. Note that the chemical delay time remained at around 1.5 ms regardless of the MTBE blend ratio. This means that differences in total ignition delay measured for the MTBE blend fuels can be attributed to differences in physical spray and mixing characteristics.

Figure 2. Variation of ignition delays with MTBE portion.

Due to its lower viscosity, the MTBE blend is expected physically to produce altered spray geometry with a short breakup length and this will result in enhanced mixing [4]. The high volatility of the MTBE in the blend will also help promote formation of the premixed gaseous mixture. On the other hand, evaporation of the diesel spray is considered to limit mixing: if so, the key parameter for the spray evaporation will be the enthalpy of vaporization rather than the fuel volatility. This factor will increase the physical ignition time delay. A relatively greater resistance to decomposition and the tendency for consumption of OH by MTBE are expected to affect both the physical and chemical aspects of ignition delay. The removal of OH radicals will provide more time for the other species to vaporize and to mix with air. Although of interest, there are no details currently available as to the chemical roles of eliminating OH and oxidizing the soot precursors.

Soot Sampling

Soot samples were collected using a four-stroke, single cylinder, air-cooled, direct injection diesel engine which was coupled to a Cressall TPR resistor AC6 load bank (6 kW at 110 V or 230 V AC) for load control. A commercial diesel fuel from a local gas station in Saudi Arabia was used as a base fuel. MTBE ($C_5H_{12}O$, Fisher Scientific) was selected as an oxygenated fuel (18.2 % of O_2 content). The MTBE was blended with the base diesel fuel with the proportion of 11 % by liquid volume, which is equivalent to about 2 % oxygen mass fraction in the blend. During the experiment, no phase separation of the blend was observed. Soot samples were collected while the engine operated at 2400 rpm and 66 % load. Prior to collecting soot samples, the engine was allowed to run for 45 min in order to ensure a steady-state operation. Soot samples were collected directly from the exhaust pipe after the steady-state condition had been reached. A 50 mm diameter Teflon filter paper was located in the exhaust bypass connected to a vacuum pump. The soot samples were scratched off the filter paper and pre-treated using a tube furnace up to 600 °C in a nitrogen environment to eliminate any soluble organic fractions and moisture. All soot samples were then stored in glass vials for subsequent non-isothermal kinetics analysis using a TGA. The detailed experimental setup

including the engine specification, properties of MTBE, and soot sample pre-treatment procedures are described in the literature [11].

Oxidation Kinetics Analysis of Soot Sample

There are several methods for calculation of the kinetic parameters from non-isothermal data. These methods are classified according to the mathematical approach into the isoconversional and model-fitting methods. The isoconversional methods have exceptional merits in that the activation energy can be unambiguously estimated without assumptions being made of the reaction model. The activation energy can be calculated as a function of conversion assuming that the reaction rate at constant conversion is only a function of temperature and is independent of the heating rate [12]. In this study, a simple linear integral isoconversional method proposed by Ortega [13] was adopted. This method leads to results which are consistent with those from the differential (Friedman method [14]) and integral non-linear procedure (Vyazovkin method [15]).

In a solid state reaction, the general kinetic equation that describes the reaction rate is usually written as follows:

$$d\alpha/dt = Ae^{-E/RT}f(\alpha) \quad (1)$$

where α is the reacted fraction, t is the time, $d\alpha/dt$ is the reaction rate, A is the Arrhenius pre-exponential factor, R is the gas constant, E is the activation energy, T is the process temperature and $f(\alpha)$ accounts for the reaction rate dependence on α . The kinetic model, $f(\alpha)$, is an algebraic expression which is usually associated with a physical model that describes the kinetics of the solid state reaction. Eq. (1) can be rearranged to obtain its integral form

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^t e^{-E/RT(t)} dt \quad (2)$$

According to the average linear integral method, for small segment ($\alpha - \Delta\alpha, \alpha$), E and A may be assumed constant, and from Eq. (2) one obtains:

$$g(\alpha - \Delta\alpha, \alpha) \approx A \Delta t e^{-E_\alpha/RT(t)} \quad (3)$$

For a linear heating program cases ($\beta = \Delta T / \Delta t = \text{const}$):

$$\ln g(\alpha - \Delta\alpha, \alpha) \approx \ln A - \ln(\beta/\Delta T) - E_\alpha/(RT) \quad (4)$$

Thus, for a given conversion and a set of experiments performed under different linear heating rates β_i ($i = 1, \dots, n$):

$$\ln(\beta_i/\Delta T_{\alpha,i}) \sim -E_\alpha/(RT_{\alpha,i}) \quad (5)$$

The activation energy for each α value is obtained from the slope of the plot of the left-hand side of Eq. (5) versus the reciprocal of the temperature.

On the other hand, model fitting methods are used to derive kinetic parameters associated with a particular reaction model. Some common reaction models are listed in the literature [16]. Unlike the isoconversional methods, the model-fitting methods are capable of identifying multi-step reaction models suitable for the description of complex kinetics. Recently, it has been reported that a modified Sestak-Berggren equation, i.e.

$f(\alpha) = c \times \alpha^m (1 - \alpha)^n$, with values for n and m in the range from 0.3 to 0.8 and -1 and 0.7 , respectively, not only fits every kinetic ideal model proposed for solid state reactions, but also the deviations of the ideal kinetic models [17]. Thus, Eq. (1) can be written as

$$d\alpha/dt = cA\alpha^m(1-\alpha)^n e^{-E/RT} \quad (6)$$

Writing Eq. (6) in the logarithmic form and rearranging, the following equation can be derived and this should fit every set of experimental data:

$$\ln(d\alpha/dt) - \ln[\alpha^m(1-\alpha)^n] = \ln cA - E/RT \quad (7)$$

To determine the proper n and m parameters, the square of the correlation coefficient of the linear regression between the left-hand side of Eq. (7) and the reciprocal of temperature was used for optimization. Optimization has been performed when the n and m parameters that yield the best linear correlation for the plot of the left-hand side of Eq. (7) versus the reciprocal of temperature are obtained. Then, the activation energy is obtained from the slope of the plot of the left-hand side of Eq. (7) versus the reciprocal of temperature and the pre-exponential factor multiplied by the factor c is obtained from the y-axis intercept.

Non-isothermal TGA tests were performed using a TGA analyzer (TA Instruments-Q5000IR) which allowed simultaneous measurements of weight loss as a function of time or temperature. A soot sample of about 3.0 mg was loaded into an alumina crucible and heated in high purity air (flow rate of 60 ml/min) from 25 to 700 °C at different heating rates of 2, 4, 6 and 8 K/min.

Figure 3 shows the reacted fraction of the soot samples as a function of temperature at different heating rates. Weight losses have been normalized, as is routine for the kinetic analysis of solid state reactions, and the process is described in terms of reacted fraction or α . It shows that the MTBE soot sample starts oxidation at a lower temperature and also ends at a lower one for all heating rates. This indicates that MTBE soot is more reactive than the diesel soot sample.

Figure 3. Reacted fractions corresponding to the thermal oxidation of (a) diesel soot, (b) MTBE soot sample.

Figure 4 shows the conversion rate of the two soot samples as a function of temperature for (a) diesel soot and (b) MTBE soot sample. From the beginning of the oxidation, the ascending parts of each curve combine together in a single line, which shows that there is no heat or mass transfer effect during oxidation. It is very clear from Figure 4 that MTBE soot has a higher maximum conversion rate at a lower temperature than that of diesel soot, this being consistent with the results for biodiesel and oxygenates reported in literature [18].

It is noteworthy that at none of the heating rates is there a shoulder shown by any of the curves, even though the soot sample was expected to yield a complex reaction mechanism. It is well known that rather than a single component, diesel soot is composed of multiple components each with different activation energy. In the case that a solid state reaction is described by two competitive processes with different kinetic parameters, the differential thermogravimetric curves at relatively lower heating rate would tend to show a shoulder [19]. Even though curves in Figure 4 show no shoulder, a number of possible complex mechanisms should be considered.

The activation energy of soot samples can be calculated at different reacted fractions (i.e. conversions) using the Ortega method (see Eq. (5)). Figure 5 shows that the dependences of activation energy on conversion are almost the same for both soot samples and any differences fall within experimental error. Two key points are revealed by Figure 5: first, both samples produce more than two reactions. Up to 20% conversion for

MTBE soot and 30% for diesel soot, the activation energy for both samples increases with conversion, then remains almost constant until the end of the oxidation process. Also of note is that the oxidations of the two soot samples can be described by the same activation energy dependence in spite of there being a complex mechanism. The only difference is that the oxidation of the MTBE soot shifts at an earlier stage of conversion due to the fact that it may be more reactive. However, this difference cannot explain the thermogravimetric results shown in Figures 3 and 4 which indicate that MTBE soot is more reactive than diesel soot. Quite how much faster the MTBE soot is oxidized is difficult to quantify.

Figure 4. Conversion rates corresponding to the thermal oxidation of (a) diesel soot, (b) MTBE soot sample.

Figure 5. Dependence of activation energy on conversion for diesel soot and MTBE soot sample, respectively.

The activation energy alone is not an indication of reactivity, but rather other kinetic parameters are needed in order to compare the reactivity of the two samples. Therefore, another method is required for calculation of these parameters. When carried out appropriately, the model fitting method has the ability to derive kinetic models that work over a wide range of temperatures and conversions, even for the more complicated reactions. The differential curves (i.e. reaction rates) shown in Figure 4, increase with progress to a maximum value and then immediately plummet to zero. This behaviour does not match the first-order reaction mechanism usually assumed in the Kissinger-Akahira-Sunose (KAS) method [20, 21]. Moreover, comparisons with several types of kinetic models outlined in the literature [22] reveal that not only an n -th order model with $n < 1$ but also a nucleation model is required to match the oxidation behaviour of the two soot samples. Consequently, a modified Sestak-Berggren equation should be adopted in this study rather than the n -th order mechanism usually used in other soot oxidation studies.

As shown in Figure 6, all thermogravimetric curves for the two soot samples obtained under different heating rates were analyzed by means of Eq. (7) for the n and m parameters. Each curve shown in Figure 6 yields a straight line for $n = 0.3$ and $m = 0.01$ with a correlation coefficient of $R^2 = 0.9971$ for diesel soot and $R^2 = 0.9975$ for MTBE soot, respectively. Possession of the same n and m parameters for the two soot samples suggests that they can be described by the same oxidation mechanism. On the other hand, the resulting activation energies, as obtained from the slopes are 160.8 and 161.7 kJ/mol for diesel soot and MTBE soot, respectively; and the values corresponding to cA as obtained from the intercept equal 2.82×10^8 and $1.06 \times 10^9 \text{ min}^{-1}$ for diesel soot and MTBE soot, respectively. The values of activation energy are very close and within experimental error but the value for the pre-exponential factor of MTBE soot is much higher than that of diesel soot (about 4 times greater). The increase in the pre-exponential factor of MTBE soot contributes to the increase in the rate of reaction (even for the same reaction mechanism) and, therefore, is indicative of its higher reactivity.

Figure 6. Combined analysis of diesel soot and MTBE soot oxidation by means of Eq. (7) for the n and m parameters obtained by the optimization procedure i.e. $n = 0.3$ and $m = 0.01$.

Figure 7. Comparisons of oxidation rate between reconstruction and experiment. Solid curves and dash curves indicate the reconstruction and the experimental data, respectively.

To check the validity of the kinetic parameters obtained (i.e. activation energies, pre-exponential factors, and the reaction orders in kinetic model), non-isothermal oxidation curves were reconstructed under the experimental conditions used and the results compared with the experimental data. As can be seen from Figure 7, there is a very good agreement between the reconstruction (solid lines) and the experimental data (dashed lines).

Conclusions

Methyl tert-butyl ether (MTBE) was added to diesel fuel in order to investigate the ignition propensity in a reactive spray environment using an ignition quality tester (IQT). The IQT data obtained using an MTBE blend in diesel showed that ignition delay increases linearly as the MTBE fraction increases. The increase of total ignition delay for the MTBE blend fuels was attributed mainly to physical delay.

The effects of an MTBE blend in diesel on the soot oxidative reactivity were also investigated through an oxidation kinetics analysis using a thermogravimetric analyzer. As shown by the results, MTBE soot is more reactive than the diesel soot generated from a stationary diesel engine and the oxidation rate of MTBE soot was found to be much higher than that for diesel soot over the temperature range considered in this study. The oxidation kinetic analysis revealed that the two types of soot have the same activation energy and possess the

same oxidation mechanism, but the pre-exponential factor of MTBE soot is significantly higher than that of diesel soot, this accounting for the higher reactivity of the MTBE soot.

For a better understanding of the soot oxidation characteristics of MTBE-blended diesel fuels, future studies using X-ray techniques, and elemental and surface analysis of the detailed nanostructure and physiochemical properties are planned.

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