Estimation of the Effects of Gasoline Additives on Exhaust Emissions

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Improvement in efficiency of CO₂ exhaust reduction and in reduction of harmful exhaust gas from automotives is now in demanded. For further reduction of NOₓ, fuel reformulation is necessary in addition to improving engine technology and improving after-treatment technology. Various additives are used in both gasoline and diesel fuel to meet environmental regulations and to improve performance. A change in the composition of the exhaust gases resulting from using fuel additives will change the impact of exhaust gases on atmospheric environment. In this study, a products model, which consists of the equilibrium calculation and the reaction calculation, was established to predict the change in the combustion products by addition of gasoline additives. As a result, the concentration of CO, CO₂, and NO were decreased by addition of oxygenates and increased by addition of a nitrous compound. However, because of the magnitude of the changes in the products due to the additives is small, effects of the oxygenates on the atmosphere would be also small since the products are removed with a three-way catalyst with an equivalence ratio of 1.0. The characteristics of the additives which affect the change in emissions were investigated by comparing the contribution of these factors to the emissions. It is shown that the C/H ratio and the enthalpy of formation of the additives affect the change in emissions. As the range of enthalpy of formation of the actual additives is restricted and limited, especially among the compounds with similar compositions, the C/H ratio would be effective and influential.

Keywords
Gasoline additive, Exhaust emission, Kinetic calculation, Octane improver, Oxygenate, Atmospheric environment

1. Introduction

Exhaust emissions from combustion systems such as automobiles have had a significant impact on the atmospheric environment. Carbon dioxide (CO₂), carbon monoxide (CO), hydrocarbon (HC), and nitrogen oxide (NOₓ) are directly emitted from their engines. HC and NOₓ produce secondary pollutants via photochemical reactions taking place in the atmosphere. Thus, improvement in efficiency of CO₂ exhaust reduction and reduction of harmful exhaust gas in such combustion system are now in demand. Especially, in large cities, the reduction of NOₓ emission is desired. For the further reduction of NOₓ, fuel reformulation is necessary in addition to the improvement of both engine and after-treatment technologies.

Various additives are used in gasoline and diesel fuel to meet environmental regulations and to improve performance. Changes in the composition of exhaust gases by fuel additives will change the impact of the gases on the atmospheric environment. To better understanding the effects of fuel additives on the exhaust gas, for developing an advanced combustion system, simulation technology of engine combustion is indispensable. In particular, as the addition of oxygenates, except for MTBE, to gasoline has become required in the US, an evaluation method for the impact of fuel additives on atmospheric environment is expected.

Many models of spark ignition (SI) engines are presented. Raine et al. established a model of NO formation in SI engines with a multizone burned gas. Schulz et al. compared the NO concentration profiles experimentally obtained in an SI engine by approaching with two different models. Goldaniga et al. investigated the chemical kinetics of oxidation of ethers under a high pressure oxidation conditions, both experimentally and numerically. Also, the effects of oxygenates on emissions have been studied. The generally acknowledged consequence of utilizing oxygenates, such as MTBE, as a gasoline component is known to lower the CO exhaust emissions, due to the leaning effect that inclusion of MTBE can provide. A small
decrease in HC is seen and the effect on NOx emissions is not usually beneficial. Graupner et al. investigated the effects of fuel oxygenates (notably MTBE) on regulated emissions for catalyst and non-catalyst car fleets and concluded that conventional emissions benefits of gasoline MTBE became less pronounced as engine/vehicle technology became more sophisticated. Miyawaki et al. evaluated MTBE as a motor fuel component for Japanese passenger cars. The results showed a decrease in CO and HC emissions by 19-37% and 25-44%, respectively. However, NOx emissions showed slight changes in the content of MTBE as it increased up to 15%. Furey and King evaluated evaporative and the exhaust emissions from cars fueled by gasoline containing ethanol or MTBE. Douthit et al. studied the performance features of 15% MTBE/gasoline blends, CO, and HC emissions that decreased but there was mostly a little to no change noted for the NOx emissions.

Though many studies are presented, the studies on the modeling of combustion in SI engines are limited to fuels of simple composition. Also, the characteristics of fuel additives which influence the atmospheric environment have not yet been theoretically clarified. Thus, it is important to establish a technique to predict the combustion products of a complex fuel containing fuel additives and to determine additive characteristics, which affect the emissions.

The purpose of this study is to estimate the CO, CO2, and NOx emissions from a gasoline engine, accompanied by changes in the fuel composition. In this study, the emission prediction model, which consists of both equilibrium reaction calculations, was established in order to investigate the effects of fuel additives on the emissions.

2. Calculation

2.1. Calculation Model and Procedure

The specifications of the gasoline engine used in this calculation are shown in Table 1. The model gaso-
i) The combustion chamber is filled with a fuel-air mixture at bottom dead center (BDC, 180°BTDC). Pressure and temperature at this point are 1 atm and 350 K, respectively. The fuel-air mixture is stoichiometric (equivalence ratio: 1.0).

ii) After adiabatic compression, the fuel-air mixture is ignited at top dead center (TDC). As the oxidation reactions of the hydrocarbon can be considered to proceed instantly, the concentrations of products at this time are calculated using the equilibrium calculation (CEC18) with constant-volume conditions.

iii) During the expansion process, NO is produced via the expanded Zeldovich mechanism, and the time-resolved profile of the NO concentration in this process is calculated by SENKIN9)-11). The results from the equilibrium calculation are considered as the initial data, and the change in the cylinder volume accompanied with motion of the piston is considered as the calculation conditions.

iv) The gas in the cylinder is exhausted at BDC (180°ATDC). The NO concentration at BDC is regarded as the NO emissions.

In this model, it is possible to estimate the effect of fuels of complex composition by utilization of the equilibrium calculation for fuel oxidation. As for NO simulation, by the consideration of the change in volume by motion of the piston in the expansion period and introduction of the function of volume to the kinetic calculation, it is possible to simulate the expansion period of the engine and the NO formation precisely.

2. 2. Gasoline Additives

Methyl-t-butyl ether (MTBE), ethyl-t-butyl ether (ETBE), methanol and ethanol were selected as the oxygenates. These are typical gasoline additives used as octane improvers. N,N-di-s-butyl-p-phenylenediamine (C14H24N2), which is a typical fuel oxidation inhibitor additive, was selected as the nitrous compound. The properties of these compounds are shown in Table 3. Table 3 Characteristics of Gasoline Additives Considered in This Study

<table>
<thead>
<tr>
<th>Additives</th>
<th>Formulation</th>
<th>Δ Hib [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTBE</td>
<td>C4H10O12</td>
<td>-2.99 × 10^3</td>
</tr>
<tr>
<td>ETBE</td>
<td>C4H10O12</td>
<td>-3.33 × 10^3</td>
</tr>
<tr>
<td>Methanol</td>
<td>C2H5OH</td>
<td>-2.04 × 10^3</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C2H5OH</td>
<td>-2.39 × 10^3</td>
</tr>
<tr>
<td>N,N-di-s-butyl-p-phenylenediamine</td>
<td>C14H24N2</td>
<td>-2.08 × 10^3</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3. 1. Effects of Fuel Additives on Emissions

Figure 2 shows the effects of the oxygenates on the emissions. Figure 2 indicates that the concentrations of CO, CO₂ and NO were decreased by addition of the oxygenates. As this tendency is qualitatively similar to the experimental data4)-7), the estimation of the com-
bustion products by this technique may be useful. However, the quantitative tendency is quite different. It was reported that CO emission decreased by 19-37% with MTBE addition up to 15 vol%5), but the prediction in this study showed a much smaller decrease in the CO emission. It is reported that the air-fuel ratio becomes lean accompanied with the addition of the oxygenates in actual gasoline engines, especially in classical engines, because the feedback control of air-fuel ratio is difficult, which results in the reduction of CO emission. However, as the prediction model in this study simulates the condition in which the feedback control of air-fuel ratio is completely performed, the air-fuel ratio is always fixed with its equivalence ratio as 1.0. Then the amount of reduction of CO predicted in this model would be smaller than that of experiment. Also, the prediction of emissions by this method can consider only the chemical characteristics of the fuel (composition and thermal property), and not the physical characteristics of the fuel (density and viscosity). Though the physical characteristics of the fuel influence the combustion conditions such as the flammability of the fuel, this prediction model cannot consider the change of the combustion conditions. As the quantity of change in the products with the addition is small, the effects of the oxygenates on the atmosphere would also be small because the products are removed by a three-way catalyst with an equivalence ratio of 1.0.

Figure 3 shows the effects of a nitrous compound on the emissions. Contrary to the results of the oxygenates, the concentrations of CO, CO₂ and NO increased with its addition. In this case, the change in the quantity is very small because the quantity of the nitrous compound added is very small. Thus the influence of the nitrous compound on the atmospheric environment is thought to be extremely small. However, the change in the products per amount of the nitrous compound added is larger than by the oxygenates. This difference in the tendency will be investigated in the next section.

### 3.2. Investigation of the Factors Contributing to the Emissions

The characteristics of the fuel additives which affect this calculation were the composition of the additives (oxygen or nitrogen contents ratio, C/H ratio) and enthalpy of formation. The characteristic of the additives which affect the change in the emissions was investigated by comparing the contribution of these factors to the emissions.

#### 3.2.1. Oxygen and Nitrogen Contents Ratio

To investigate the effect of oxygen and nitrogen contents ratio of the additives on the emissions, the calculation in which the oxygen and nitrogen contents ratio of additives were varied (C₈H₁₈NxOy; x, y = 0-3) was performed with the enthalpy of formation of the additives (~2.51 × 10² kJ/mol: equal to that of isoctane) and the quantity of addition to the model gasoline fuel (5.0 mol%) fixed. Figure 4 shows the effects of the oxygen and nitrogen contents ratio on the emissions. Figure 4 indicates that the effect of the oxygen and nitrogen contents ratio on the emissions is low.

#### 3.2.2. C/H Ratio

To investigate the effect of the C/H ratio of the additives on the emissions, the calculation in which the C/H
The ratio of the additives was varied was performed with the enthalpy of formation of the additives (−2.51 × 10^2 kJ/mol; equal to that of isooctane) and the quantity of addition to the model gasoline fuel (5.0 mol%) fixed. The additives considered in this calculation are ideal compounds, the compositions of which are C₅H₁₂, C₈H₁₈, C₁₄H₂₄, C₁₆H₂₂, and C₁₇H₁₈, respectively. The addition of C₈H₁₈ means that there is no addition.

Figure 5 indicates that the CO, CO₂, and NO emissions became higher with a higher C/H ratio. The increase in CO will originate from the higher adiabatic flame temperature, and the increase in CO₂ will originate from the increase in the contents ratio of carbon in the fuel-air mixture. Also, the increase in NO will originate from the increase in the initial temperature in the kinetic calculation, which attributed to the higher adiabatic flame temperature.

3.2.3. Enthalpy of Formation
To investigate the effect of the enthalpy of formation of the additives on the emissions, calculation in which the enthalpy of formation of the additives was varied was performed with the composition of the additives (MTBE; C₅H₁₂O) and the quantity of the addition to the

Additive: C₅H₁₂OₓNₙ (x, y = 0, 1, 2).

Fig. 4 Effect of Oxygen and Nitrogen Contents Ratio on Emissions

Additive: C₅H₁₂, C₈H₁₈, C₁₄H₂₄, C₁₆H₂₂, and C₁₇H₁₈.

Fig. 5 Effect of the C/H Ratio on Emissions

Additive: C₅H₁₂, C₆H₁₆, C₈H₁₈, C₁₀H₂₂, and C₁₇H₁₈.

Fig. 5 Effect of the C/H Ratio on Emissions
model gasoline fuel (5.0 mol%) fixed. The additives considered in this calculation are ideal compounds, with their enthalpy of formation varied from $-418 \text{kJ/mol}$ to $209 \text{kJ/mol}$. Figure 6 indicates that the CO and NO emissions became higher and the CO$_2$ emissions became lower with a higher enthalpy of formation. This result will originate from the higher adiabatic flame temperature due to the higher enthalpy of formation.

From these results, the characteristics of the gasoline additives affecting the change in the emissions would be the C/H ratio and enthalpy of formation. Considering that the range of the enthalpy of formation of the additives is narrow, the most effective property of the additives on the products would be the C/H ratio.

4. Conclusions

In this study, a products prediction model, which consists of the equilibrium calculation and the reaction calculation, was established in order to predict the change in the combustion products with the addition of gasoline additives. The results showed that the concentrations of CO, CO$_2$, and NO decreased with the addition of oxygenates and increased with the addition of the nitrous compound. However, as the quantity of change of the products due to the addition is small, especially for a small amount of additive, such as the nitrous compound, the effects of gasoline additives on the atmosphere would be small, because the products are removed by a three-way catalyst with an equivalence ratio of 1.0. The characteristics of the additives which affect the change in the emissions were investigated by comparing the contribution of these factors to the emissions. It was shown that the C/H ratio and the enthalpy of formation of the additives do affect the emissions. As the range of the enthalpy of formation of the actual additives involved is narrow, especially among the compounds with similar composition, the C/H ratio would be the most influential. Based on these results, it can be said that fuel additives with a smaller C/H ratio would reduce the CO, CO$_2$ and NO$_x$ emissions.

References

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要 旨

ガソリン添加剤による燃焼生成物の変化の予測

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現代社会において自動車エンジンからの排出ガスは大気環境に大きな影響を及ぼしている。そこで、地球温暖化への影響を低減するため、燃料の燃焼特性を改善する研究が行われている。自動車燃料は性能向上および環境規制への対応のために各種添加剤が添加されている。低環境負荷自動車燃料の開発を促進するためには、燃料添加剤による燃焼特性の変化を把握し、効果的なガソリンエンジンにおける燃焼生成物の予測モデルを構築し、燃焼生成物の変化に影響を及ぼすガソリン添加剤の特性を検証した。その結果、含硫化合物の添加により CO、NO 濃度が減少し、含窒素化合物の添加により増加する結果が得られた。しかしながら、添加剤による燃焼生成物の変化は小さいので、当量比 1 の条件で大気環境への影響の変化は極めて小さいと考えられる。また、計算に影響を及ぼす燃料添加剤の特性についてその寄与を検証した結果、添加剤の CH 比および生成エンタルピーが燃焼生成物の変化に影響を及ぼしていることが示唆された。

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