[Research Note]

Effects of Molecular Structures of Alkanes on Peroxide Formation and Cetane Number Improvement by Autoxidation

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(Received September 5, 2002)

Diesel fuels having poor ignition properties would induce problems such as diesel knock and engine starting problems in cold weather. Diesel fuels in such cases need to have improved ignition properties. The addition of cetane number improving agents to diesel fuels is one method to improve the ignition properties of diesel fuels. However, addition of cetane number improving agents is not always an economically practical solution to improve the ignition properties of diesel fuels. Our previous study showed that the cetane numbers of autoxidized fuels in which hydroperoxides were produced increased. It is important for the development of cetane number improving systems by autoxidation to investigate the effects of molecular structures of hydrocarbons on the formation of hydroperoxides and the cetane number improvement. In this study, effects of carbon numbers and branching of alkanes on the formation of hydroperoxides were investigated. As a result, smaller carbon numbers produced more hydroperoxides. Also, effects of the molecular structures of the hydrocarbons on cetane number improvement by produced hydroperoxides have been investigated. The result suggests that the hydroperoxide produced from alkanes having a lower carbon number increases cetane number more. Furthermore, polynuclear aromatic hydrocarbons such as naphthalene and 1-methyl naphthalene had inhibition effects on the hydroperoxide production by autoxidation. From above results, the autoxidation could be a good method for improving diesel fuels such as city diesel and kerosene having low aromatic compounds and low distillation ranges because these fuels have to add cetane number improving agents to increase its number.

Keywords
Cetane number, Diesel fuel, Hydroperoxide, Autoxidation, Polynuclear aromatic hydrocarbon

1. Introduction

Diesel fuels having poor ignition properties would induce problems such as diesel knock and engine starting problems in cold weather. Such diesel fuels need to have improved ignition properties. The ignition properties of diesel fuels can be rated in terms of their cetane number.

Addition of cetane number improving agents to diesel fuels is one method to improve the ignition properties of diesel fuels. In the 1940s and 1950s, organic peroxides were found to be effective cetane number improving agents as alkyl nitrates and other compounds were1). Li *et al.* examined the improvement in cetane number using some nitrates and organic peroxide and suggested that such improvement in cetane number correlated with the number of free radicals produced by thermal decomposition of the additive during preignition period2). Inomata *et al.* studied the effects of isopropyl nitrate and di-*t*-butyl peroxide on the spontaneous ignition of butane using a rapid compression machine and concluded that the most important factor is the heat release by the combustion of the additive during the preignition period3). Al-Rubaie *et al.* examined the effectiveness of some organic peroxides and nitrates in reducing the ignition delay period and concluded that the additives played a role in heat generation through rapid, exothermic, oxidative degradation following injection into the cylinder4). Clothier *et al.* made engine experiments with several additives at temperatures lower than in normally operating diesel engine5). Clothier *et al.* also reviewed how the cetane number improving agent worked6).

Our study suggests that free radicals in the preignition period should have an important role in improving their ignition properties7) and that azo compounds, which are known to be radical generating agents, improved the cetane number8). Also, our study suggested that 2,2-dinitropropane would improve the cetane number by producing 2-nitro-2-propyl radical9).

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The authors have attempted to calculate the pressure-temperature profile for the spontaneous ignition of butane in the presence of cetane number improving agents[10]. The authors applied the cetane number improving agents for LPG (Liquefied Petroleum Gas) in order to utilize the LPG as a diesel fuel[11)~14]. Furthermore, the authors investigated the effects of the cetane number improving agents on diesel exhaust emissions[15]. However, the addition of cetane number improving agents is not always an economically practical solution to improve the ignition properties of diesel fuels.

On the other hand, organic hydroperoxides are well known to be produced during autoxidation of hydrocarbons[16),17]. In our previous study, diesel fuels were autoxidized in the liquid phase under various conditions and the cetane numbers of the autoxidized fuels were investigated[18]. As a result, it was shown that the cetane numbers of autoxidized fuels increased. This result suggests that the autoxidation of diesel fuels is effective for cetane number improvement.

It is important for the development of cetane number improving systems by autoxidation to investigate the effect of the molecular structures of hydrocarbons on the formation of hydroperoxides and the cetane number improvement. Also, the effects of polynuclear aromatic hydrocarbons on hydroperoxide formation by autoxidation should be investigated because the inhibition of autoxidation by polynuclear aromatic hydrocarbons had been reported[19),20].

In this study, the effects of carbon number and branching of alkanes on the formation of hydroperoxides have been investigated. Also, the effects of molecular structures of hydrocarbons on cetane number improvement by the produced hydroperoxides have been investigated. Furthermore, the inhibiting effect of polynuclear aromatic hydrocarbons on hydroperoxide production had been investigated.

2. Experimental

2. 1. Samples

Decane, cetane (hexadecane), nonadecane, 2,2,4,4,6,8,8-heptamethylnonane, and 2,6,10,14-tetramethylpentadecane were used for investigating the effects of molecular structures. Samples, 10 vol% of 1-methylnaphthalene or naphthalene with 90% cetane was used for investigating the inhibiting effect of polynuclear aromatic hydrocarbons on the autoxidation of an alkane. These samples were used without purification.

2. 2. Autoxidation Method

One liter of a sample in a 1 *l* three-necked flask equipped with a reflux condenser, a gas inlet tube, and a thermometer, was heated using a mantle heater. Air was then introduced into the hot fuel to initiate autoxidation at 150°C for up to 6 h. The air flow rate was 200 m*l*/min.

2. 3. Hydroperoxides Measurement

The concentration of hydroperoxides was tested and measured by using the iodine method according to the test prescribed by the Japan Petroleum Institute (JPI-5S-46-96)[21].

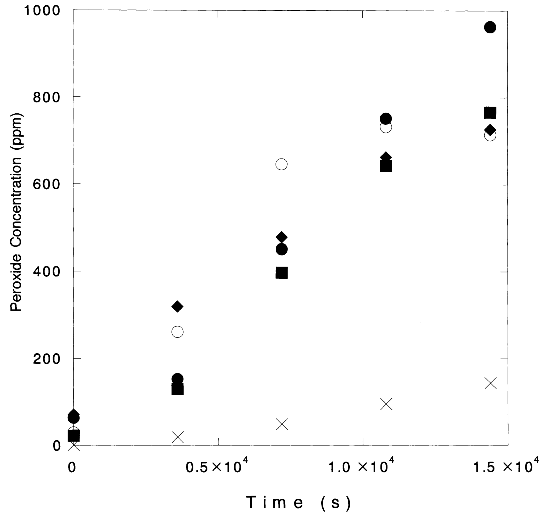
2. 4. Cetane Number Determination

The ignition properties of diesel fuel are rated in terms of their cetane number which was defined by reference to the ignition properties of standard mixtures of cetane (cetane number: 100) and 2,2,4,4,6,8,8-heptamethylnonane (cetane number: 15) under standard test conditions. The cetane number of fuel was determined by using a cooperative fuel research (CFR) engine prescribed by the American Society for Testing and Materials (ASTM-D613-84). Reference fuels having different (within 5 cetane) cetane numbers were used so that the test fuel could be determined by interpolation of the compression ratios of the two reference fuels.

Because the effectiveness of cetane number improvement of additives is dependent on the cetane number of the base fuel, it should be considered the same to investigate the effects of hydroperoxides produced by autoxidation of the alkanes on cetane number. Therefore, the effects of hydroperoxides on cetane number were estimated as follows. Mixtures of 40 vol% alkanes and 60% primary reference fuel (mixture of cetane and 2,2,4,4,6,8,8-heptamethylnonane) with 400 ppm or 800 ppm hydoroperoxide were prepared using the autoxidized hydrocarbons, non-autoxidized hydrocarbons, and reference fuels so that the cetane number of the mixture without hydroperoxide was 50. **Table 1** shows the mixture of the 40 vol% alkanes and 60% primary reference fuel used in this study. The data of Aoyama *et al.*[22] were used for cetane numbers of decane and 2,6,10,14-tetramethylpentadecane. The

Table 1 Composition of the Mixtures of 40 vol% Alkanes and 60% Primary Reference Fuel

Alkanes	Cetane number	Cetane [vol%]	2,2,4,4,6,8,8-Heptamethylnonane [vol%]
Decane	63	18	42
Cetane	100	1	59
Nonadecane	103	0	60
2,2,4,4,6,8,8-Heptamethylnonane	15	41	19
2,6,10,14-Tetramethylpentadecane	68	16	44



● Decane, ■ Cetane, ◆ Nonadecane, × 2,2,4,4,6,8,8-Heptamethylnonane, ○ 2,6,10,14-Trimethylpentadecane.

Fig. 1 Concentration of Hydroperoxides Produced by Autoxidation of Alkanes

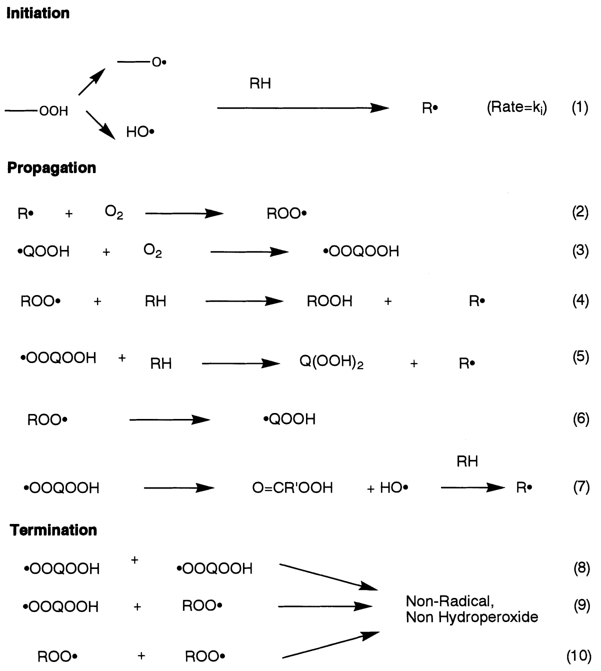


Fig. 2 Autoxidation Mechanism of Hydrocarbons

cetane number of nonadecane was measured using the same procedure used by Aoyama *et al.*[22].

3. Results and Discussion

3. 1. Effects of Molecular Structure of Alkanes on Hydroperoxide Formation

Figure 1 shows the concentrations of hydroperoxides produced by autoxidation of alkanes. The hydroperoxide concentration of the straight-chain alkane was decane > cetane > nonadecane, making it lower carbon number to produce more hydroperoxides. Though the hydroperoxide concentration of 2,6,10,14-tetramethylpentadecane was higher, the concentration was saturated by a longer autoxidation period. The hydroperoxide concentration of 2,2,4,4,6,8,8-heptamethylnonane was the lowest. It should be noted that the hydroperoxides were detected at the beginning of the autoxidation because no purification nor pretreatment of alkanes was carried out. This would affect the formation of the hydroperoxide.

Figure 2 shows the autoxidation mechanism of hydrocarbons that generalized the mechanisim of cetane[17],[18],[20]. Initially, an alkyl radical is produced by the hydrogen-abstraction reaction of radicals such as the hydroxy radical and alkoxy radical from the hydrocarbon molecule (1). The addition reaction of an oxygen molecule to the alkyl radical (2) and (3) follows to produce the alkylperoxy radical. Intermolecular (4), (5), and intramolecular (6) hydrogen abstraction by the alkyl peroxy radicals would produce the alkyl hydroperoxide. Thus hydroperoxides would be produced by autoxidation. Some hydroperoxy alkyl peroxy radicals decompose to produce alkoxy radicals and hydroxy radicals (7). The radical produced can also take part in the chain reactions. Radical-radical reactions to produce non-radical and non-hydroperoxy compounds terminate the chain-reaction (8)-(10). Using this scheme, the autoxidation rates of the hydrocarbons were calculated[20].

The rate of hydroperoxide formation was expressed as Eq. (1) using a steady-state approximation.

$$\frac{\mathrm{d}[-OOH]}{\mathrm{d}t} = k_4[ROO\bullet][RH] + \{2k_5[RH]+k_7\}[HOOQOO\bullet] \qquad (1)$$

where k_n is the rate of reaction (n) in **Fig. 2**. Assuming that $k_4 = k_5 = k_p$ and $k_8 = k_9 = k_{10} = k_t$, Eq. (2) can be obtained.

$$\frac{\mathrm{d}[-OOH]}{\mathrm{d}t} = k_p\left(\frac{k_i}{k_t}\right)^{1/2} \phi[RH][-OOH]^{1/2} \qquad (2)$$

where

$\phi = 1 + \psi(2 + \theta)/(1 + \psi)$,

$\psi = [HOOQOO\bullet]/[ROO\bullet]$ and

$\theta = k_7/k_p[RH]$

$k_i = k_1$

ϕ can be treated as a constant because $[RH]$ remains approximately constant.

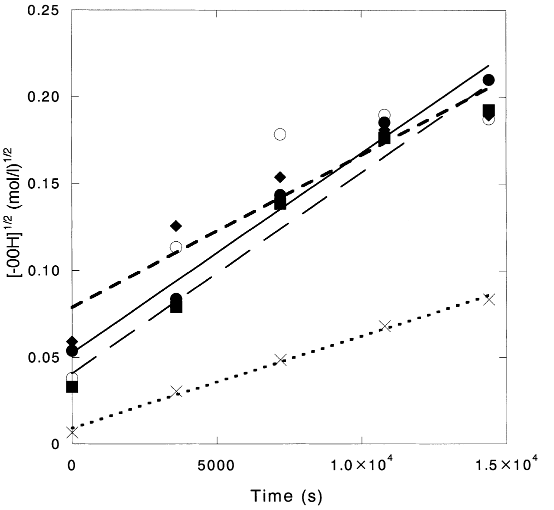
Equation (3) can be obtained from Eq. (2)

$$[-OOH]_t^{1/2} = K[RH]t \qquad (3)$$

where

$$K = \frac{1}{2}k_p\left(\frac{k_i}{k_t}\right)^{1/2} \phi$$

K is considered as the parameter of the hydroperoxide formation.



● Decane, ■ Cetane, ◆ Nonadecane, × 2,2,4,4,6,8,8-Heptamethylnonane, ○ 2,6,10,14-Tetramethylpentadecane.
——— Liner fitting of decane, — — Liner fitting of cetane, ▬ ▬ ▬ ▬ Liner fitting of nonadecane, ········ Liner fitting of 2,2,4,4,6,8,8-heptamethylnonane.

Fig. 3 Plot of $[-OOH]^{1/2}$ *vs.* Time

Table 2 *K* Factors of the Alkanes in This Experiment

Alkanes	K $[10^{-6}\ M^{-1/2}s^{-1/2}]$
Decane	2.234
Cetane	3.383
Nonadecane	3.715
2,2,4,4,6,8,8-Heptamethylnonane	1.544

Figure 3 shows the plot of the $[-OOH]^{1/2}$ *versus* time of our experiment. The $[-OOH]^{1/2}$ of all hydrocarbons except for 2,6,10,14-tetramethylpentadecane were propotional to the time. As the slope of the line was the $K[RH]$, the K factor of each hydrocarbon was calculated. **Table 2** shows the K factor. **Table 2** suggests that the K factor for a straight-chain alkane was nonadecane > cetane > decane. Thus, the alkanes having higher carbon number have a greater capabilty to produce hydroperoxide per one hydrocarbon molecule.

The hydroperoxide-production capability of the straight-chain alkane was considered to be dependent on its secondary hydrogen/primary hydrogen ratio because the secondary hydrogen atom can be more easily abstracted than the primary hydrogen atom. As the alkanes having higher carbon numbers have the greater secondary hydrogen/primary hydrogen ratio, these alkanes have the greater abilty to produce hydroperoxide per one hydrocarbon molecule. On the other hand, as the molecular weight of the alkane having higher carbon number is higher, its molarity is lower. Thus, alkanes having a lower carbon number would produce more hydroperoxides because the hydroperoxide concentration of the alkane is dependent on both its hydroperoxide-production ability and its molecular weight.

The *K* factor of 2,2,4,4,6,8,8-heptamethylnonane was the lowest because this compound is highly branched. With a lower chain-length and smaller secondary hydrogen/primary hydrogen ratio, this highly branched alkane would have less abilty to produce the hydroperoxide.

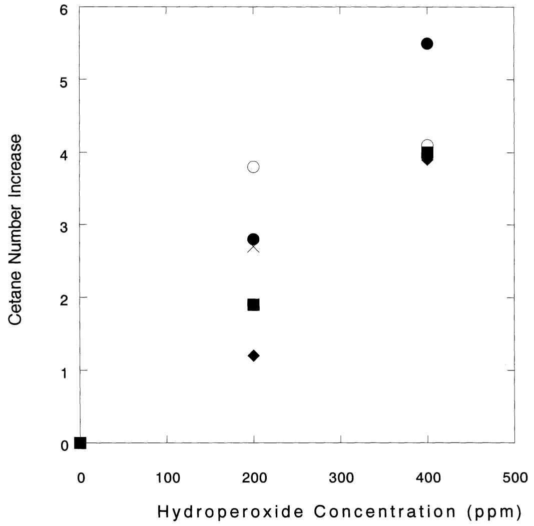
Figure 3 shows that the $[-OOH]^{1/2}$ of 2,6,10,14-tetramethylpentadecane was not proportional to time. As 2,6,10,14-tetramethylpentadecane has 4 tertially hydrogen atoms that can be abstracted more easily than secondary hydrogen atoms, its rates of hydrogen-abstraction reactions are higher than those of the straight-chain alkanes. On the other hand, 2,6,10,14-tetramethylpentadecane has steric hindrance due to its branched methyl group. These factors could produce the peculiar behavior related to the hydroperoxide-formation.

Note that the well-stirred conditions were not carried out in this experiment although sufficient oxygen was provided. This condition would affect the *K* factor. Also, this condition could be related to the peculiar behavior of the hydroperoxide-formation for 2,6,10,14-tetramethylpentadecane. Furtheremore, impurity of 2,6,10,14-tetramethylpentadecane and hydroperoxide existed before autoxidation could cause this peculiar behavior of the hydroperoxide-formation. In order to clarify this behavior, experiments using purified alkanes should be carried out.

3. 2. Effects of Hydroperoxides Produced by Autoxidation on Cetane Number Improvement

Figure 4 shows the effects of the hydroperoxides produced by autoxidation on the cetane number improvement. The cetane number increases for the hydroperoxide produced by autoxidation of straight-chain alkane was in the order: decane > cetane > nonadecane. Thus, the hydroperoxide produced from the lower carbon number alkanes increases the cetane number more.

Our previous study using the straight-chain alkyl nitrites had suggested that alkyl radicals having the higher carbon number would increase the cetane number more[7]. The result that the hydroperoxide produced from the alkanes having the lower carbon number increase cetane number more seems to contradict this earlier result. However, the chain-length of the alkyl radical produced from the hydroperoxide does not always correspond to their parent hydrocarbon because the chain-length depends on the position at which the -OOH is connected. Also, the cetane number increase of hydroperoxide produced by autoxidation of the 2,2,4,4,6,8,8-heptamethylnonane was no lower than the increase of those of the other alkanes used in this study.



● Decane, ■ Cetane, ◆ Nonadecane, × 2,2,4,4,6,8,8-Heptamethylnonane, ○ 2,6,10,14-Tetramethylpentadecane.

Fig. 4 Effects of Hydroperoxides Produced by Autoxidation on Cetane Number Improvement

These results suggest that the cetane number increase of hydroperoxide is not always correlated with the molecular structure of their parent hydrocarbon.

3. 3. Inhibiting Effect of Polynuclear Aromatic Hydrocarbons on Hydroperoxide Formation by Autoxidation

Both 10 vol% 1-methylnaphthalene and 10 vol% naphthalene with 90% cetane did not produce hydroperoxide by autoxidation. This result suggests that polynuclear aromatic hydrocarbons inhibit the hydroperoxide formation by autoxidation as was inhibited by a previous study that hydroperoxide was produced by autoxidation of kerosene containing single-nuclear aromatic compounds[18].

Igarashi *et al.* investigated very precisely the effects of naphtalene or alkylnaphthalene on autoxidation of cetane at 160°C[20]. They found that the naphthalene rings contribute to the inhibition of the autoxidation of cetane. Their finding supports our result. Also, our unpublished result showed that hydroperoxide was not produced by the autoxidation of commercial gas oil mixed with 20 vol% light cycle oil, which includes polynuclear aromatic hydrocarbons, supporting these phenomena.

From above results, kerosene could be a good candidate for autoxidized diesel fuel because of its lower concentration of polynuclear aromatic hydrocarbons due to its lighter distillate range than that of commercial diesel fuel. Also, the autoxidation could be a good method for improving diesel fuels such as city diesel, which have low aromatic compounds concentration and a low distillation range because these fuels have to add cetane number improving agents to increase the cetane number.

4. Conclusion

In this study, the effects of carbon number and branching of alkanes on the formation of hydroperoxides have been investigated. As a result, the lower carbon number produced more hydroperoxides. Also, the effects of the molecular structures of the hydrocarbons on the cetane number improvement by the produced hydroperoxides have been investigated. The result suggests that the hydroperoxide produced from alkanes having a lower carbon number increased the higher cetane number. Furthermore, polynuclear aromatic hydrocarbons such as naphthalene and 1-methyl naphthalene had an inhibition effect on the hydroperoxide production by autoxidation.

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要　　旨

飽和炭化水素の分子構造が自動酸化による過酸化物生成およびセタン価向上に及ぼす影響

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着火性の低い（低セタン価）ディーゼル燃料は低温始動性が悪く，ディーゼルノックを起こすなどの問題があるため，そのセタン価を向上させる必要がある。セタン価向上法としてはセタン価向上剤の添加が挙げられるが，セタン価向上剤の添加はコストがかかるため，新たなセタン価向上法の開発が期待されている。筆者らは，ディーゼル燃料を自動酸化することにより過酸化物を生成させ，その過酸化物によるセタン価向上法を提案した。炭化水素の分子構造が自動酸化による過酸化物生成に及ぼす影響および生成した過酸化物のセタン価向上効果に及ぼす影響を把握することは，自動酸化によるセタン価向上を実用化する上において重要である。そこで，本研究では，まず飽和炭化水素の炭素数，枝分かれが自動酸化による過酸化物生成量に及ぼす影響を調べた。その結果，直鎖の炭化水素においては，炭素数が小さいほど自動酸化による過酸化物濃度は高くなった。次に，生成した過酸化物のセタン価向上効果を測定した。その結果，直鎖の炭化水素においては，炭素数が小さいほど過酸化物のセタン価向上効果が大きくなる結果となった。さらに，ナフタレン類には自動酸化による過酸化物生成を抑制する効果が認められた。

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