

A Study on Applicability of Parameter Based on Molecular Structure to Combustion Characteristics

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ABSTRACT

A fundamental understanding of the relationship between chemical composition and combustion quality may provide an improved means of assessing fuel combustion characteristics. As such, a fuel parameter based on the average molecular structure of multi-component fuels, including petroleum-derived fuels and alternative fuels such as bio-fuel, is applied to predict both ignition and anti-knock quality. This parameter is derived from proton nuclear magnetic resonance (1H-NMR) analysis indicating hydrogen type distribution of fuel molecules. The predicted cetane number (PCN) calculated by the equation developed with 1H-NMR in this study shows a good correlation to the cetane number for a wide range of fuels. The appropriateness of the prediction model was confirmed with the following considerations. 1) A fundamental consideration on the effects of hydrocarbon types on cetane numbers. 2) The application of the model to other fuels, excluding those used in the development of the model. 3) The blending of cetane number behavior for typical diesel fuel components. The prediction models for both research octane number (RON) and motor octane number (MON) are also developed with 1H-NMR analysis and average molecular weight. Although the models give a good correlation, there seems to be room for improvement. Both of PCN and CN are highly correlated to the ignition delay measured with DI diesel engines operated under premixed charge compression ignition (PCI) conditions. The PCN can be applied to the ignition delay obtained by PCI operation. This study suggests that both the ignition and anti-knock qualities are highly controlled by the average molecular structure and molecular weight of fuels, regardless of fuel source and composition.

INTRODUCTION

In spite of intense worldwide research and development work on alternative drive trains, fossil fuel powered internal combustion engines (ICE) will still constitute the dominant powertrains in road transport and will prevail for at least the next few decades.

Therefore, their impact on global and local pollution and on the use of natural resources should be minimized. To this end, extensive fundamental and practical work was performed to evaluate the potential benefits of fuel property optimization on emissions and performances of ICEs [1,2,3,4]. This work indicated that the octane number (ON) is one of the most important properties for gasoline while the cetane number (CN) is one of the most important properties for diesel fuel.

Regarding the ON, for example, in modern knock sensor-equipped vehicles, increasing the ON can result in higher engine power output and better fuel consumption due to extending the spark knock limit [5]. However, it has been shown that increasing the motor octane number (MON) of gasoline can have unexpected effects on engine power output, with some vehicles showing almost no response or even a negative response to MON [6]. Hence, the octane index (OI) expressed by the following equation controls the anti-knock quality of gasoline evaluated with modern gasoline engines [6].

$$OI = RON - K(RON - MON)$$

K: Parameter estimated separately for each vehicle and driving cycle

It is well known that the sensitivity defined as RON minus MON, is highly affected by gasoline composition and hydrocarbon types [8]. Therefore, attention should also be

paid to the composition of the gasoline used when considering the anti-knock quality.

The compression ignition engine, conventional diesel engine and the advanced combustion concept, termed the premixed charge compression ignition (PCI) engine, all require the optimum ignition quality fuel. In particular, PCI engine performance and emissions are strongly controlled by the ignition quality[7,9]. Furthermore, the sensitivity of the quality in regards to engine conditions such as temperature and pressure, is highly affected by fuel composition and hydrocarbon types [10].

On the other hand, from the viewpoint of securing energy and reducing CO₂ emissions, the introduction of alternative fuels such as non-petroleum-derived fuels and bio-fuels for automotive fuels has been accelerated throughout the world. Thus, the study on ignition quality should cover a wide range of fuels.

So, in addition to practical use, to understand both the anti-knock and ignition quality of the fuel collectively, a correlation model based on fuel composition and/or hydrocarbon types for these qualities is considered to be useful. To develop the correlation equation for the CN and ON, some studies which used hydrogen and/or carbon types of fuels measured with a nuclear magnetic resonance (NMR) spectrometer, have been reported [11,12,13]. These models show a fairly good correlation for petroleum-derived fuels.

Accordingly, this study developed a new model to cover a wide range of fuels, including alternative fuels, by using hydrogen types specified with proton NMR. Also, the appropriateness of the models was discussed based on the fundamental relation between hydrocarbon types, the CN and ON, and several experiments. Furthermore, the relationship between the ignition delay (ID) measured under PCI engine conditions and the CN predicted by the new model was evaluated. The study is expected to help estimation of the anti-knock and ignition quality for a wide range of fuels in practical use and understanding the effect of average molecular structure on the auto-ignition processes fundamentally.

METHODOLOGY

The study consists of three steps of experiments and analysis as shown below.

1st step: The prediction equations for the CN and ON of a wide range of fuels are developed by using hydrogen type structural composition measured with a proton NMR spectrometer.

2nd step: The appropriateness of the prediction model for the CN is considered based on the following points and experiments. 1) The fundamental relationship between hydrocarbon types or molecular structure and ignition quality. 2) The application of the model to samples different from the 1st step test fuels. 3) The measurement of blending CN behavior using typical fuel components. Also, the appropriateness of the prediction model for the ON is considered.

3rd step: The relationship between the predicted CN and ID measured under premixed charge compression ignition (PCI) engine conditions is considered in order to understand the applicability of the model to PCI combustion.

EXPERIMENTAL SETUP AND PROCEDURES

TEST FUELS

The following four separate fuel groups were prepared for the study. The outline of test fuels is shown in [Table 1](#) and the distribution of fuels expressed with distillation temperature and ON or CN is shown in [Figure 1](#).

CN-Group: A wide variety of multi-component fuels including petroleum-derived fuels, non-petroleum fuels, and bio-fuels were prepared to develop the CN prediction equation. The fuels cover a wide range of physical properties, CN, and compositions.

ON-Group: A wide range of petroleum-derived gasoline base stocks and bio-fuels were prepared to develop the ON prediction equation. The fuels cover ON from 60 to 116, and 0 to 11.2 mass % in oxygen content.

ET-Group: The fuels were prepared to determine the ability of the resulting model to predict the CN. Also, this group covers a wide range of physical and chemical properties. However, CN-Group fuels are not included.

BCN-Fuel: To obtain blending cetane number behavior, typical diesel fuels in terms of composition were prepared and an outline of these fuels is shown in [Table 2](#).

Table 1. Outline of test fuels

	CN-Group	ON-Group	ET-Group
Test fuel number			
Total	74	22	53
Alternatives	10	6	5
Cetane number	11~95		3~100
RON		60~116	
MON		58~100	
T90(°C)	155~382	68.5~175	98~348
Elementary analysis (mass%)	H	9.8~15.9	10.2~15.9
	C	77.3~90.2	73.7~89.7
	O	0~10.5	0~11.2

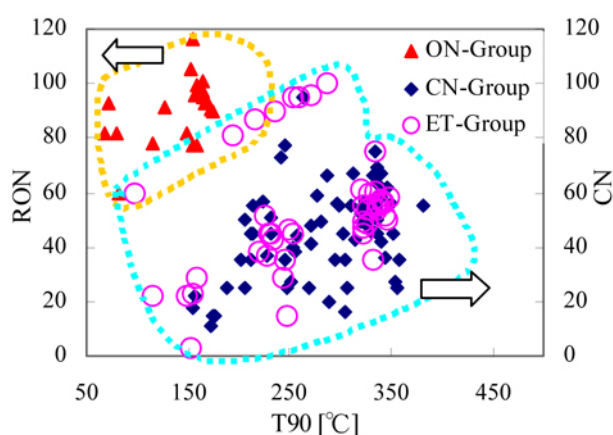


Figure 1. Distribution of test fuels expressed with distillation temperature (T90) and RON or CN

Table 2. Outline of BCN fuels

Sample	Component	CN	B P (°C)
N-Para	Normal paraffins	95	248~273
Iso-Para	Iso-paraffins	25	212~256
1R-Arom	Alkylbenzens	0	181~210
2R-Arom	Alkyl naphthalens	0	290~302
Olef.	Olefines	83	255
Naph	Decaline	40	190
RME	Rapeseed-methyl	53	327~352
Aleo.	Normal octanol	39	195

PROTON NMR

A technique to characterize the fuel chemistry, in terms of the specified hydrogen types of the fuel molecules by proton NMR spectroscopy, is used to predict the CN and ON for a wide range of fuels. The proton NMR measurements were carried out on a JEOL AL-400 spectrometer.

The proton resonance signals of samples were divided into five regions of chemical shift values and the signals in each

region were assigned to various types of hydrogen. The assignment used in the study and example of hydrogen type is shown in Figure 2.

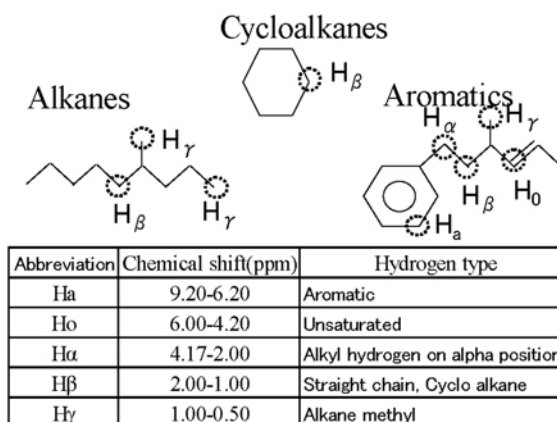


Figure 2. Assignment and example of hydrogen types on 1H-NMR spectra

CETANE NUMBER

The CN is measured according to ASTM D613. The CN of fuels with a CN of less than 30 were determined based on the CN of a mixture comprising 20% of the low CN sample and 80% of the high CN commercial type fuel.

OCTANE NUMBER

The research octane number (RON) and motor octane number (MON) were measured according to ASTM D2699 and D2700 respectively.

The ON of fuels with an ON of less than 70 was determined based on the ON of a mixture comprising 10% of the sample and 90% of iso-octane (primary reference fuel).

BLENDING CETANE NUMBER

The blending CN was obtained using a mixture blended with normal paraffinic fuel and each of the other types of components shown in Table 2. The procedure to obtain the blending CN is as follows: 1) The compression ratio required to give 13 deg. CA in ID (ID-LCR) for the mixture of the paraffinic fuel and each of the other fuels was measured with an engine operated under the CN measurement conditions. 2) The ID-LCR was measured for the primary reference fuel (PRF). The CN measurement was also measured with the engine. 3) The blending CN of the mixture was determined in comparison with the ID-LCR for PRF and the ID-LCR for the mixture.

IGNITION DELAY

The single cylinder direct injection diesel engine with a common rail system was used to obtain the ID. The engine