

Investigation of Autoignition of Propane and *n*-Butane Blends Using a Rapid Compression Machine

Hyunguk Kim, Yongseob Lim, Kyoungdoug Min*

School of Mechanical and Aerospace Engineering, Seoul National University, San 56-1, Shinlim-dong, Kwanak-gu, Seoul 151-742, Korea

Daeyup Lee

School of Mechanical Engineering, Inha University, 253 Yonghyun-dong, Incheon 402-751, Korea

The effects of pressure and temperature on the autoignition of propane and *n*-butane blends were investigated using a rapid compression machine (RCM), which is widely used to examine the autoignition characteristics. The RCM was designed to be capable of varying the compression ratio between 5 and 20 and minimize the vortex formation on the cylinder wall using a wedge-shaped crevice. The initial temperature and pressure of the compressed gas were varied in range of 720~900 K and 1.6~1.8 MPa, respectively, by adjusting the ratio of the specific heat of the mixture by altering the ratio of the non-reactive components (N₂, Ar) under a constant effective equivalence ratio ($\phi_f=1.0$). The gas temperature after the compression stroke could be obtained from the measured time-pressure record. The results showed a two-stage ignition delay and a Negative Temperature Coefficient (NTC) behavior which were the unique characteristic of the alkane series fuels. As the propane concentration in the blend were increased from 20 % and 40 % propane, the autoignition delay time increased by approximately 41 % and 55 % at 750 K. Numerical reduced kinetic modeling was performed using the Shell model, which introduced some important chemical ideas, represented by the generic species. Several rate coefficients were calibrated based on the experimental results to establish an autoignition model of the propane and *n*-butane blends. These coefficients can be used to predict the autoignition characteristics in LPG fueled SI engines.

Key Words : Autoignition, Rapid Compression Machine (RCM), Two-Stage Ignition Delay, Negative Temperature Coefficient (NTC), Shell Model, SI Engine

1. Introduction

Autoignition in an internal combustion engine is an important combustion phenomenon that affects an engine's performance. It is related to heat release, the pressure rise rate and emission formation such as hydrocarbons and nitrogen oxide. In order to meet stringent future emission

regulations, particularly, for heavy-duty vehicles, LPG fueled SI engines have been investigated (Kim *et al.*, 1997; Lee *et al.*, 2000). There have been numerous efforts to reduce NO_x emissions and develop the LPG fueled SI engines with increasing thermal efficiency at higher compression ratios.

While LPG fueled SI engines operate on a higher compression ratio to increase the thermal efficiency, they may face knocking due to the high end-gas temperature. Even though there have been several studies on the autoignition and knock modeling of the propane and *n*-butane (Pitz *et al.*, 1986; Griffiths *et al.*, 1993; Minetti *et al.*, 1994), they are inadequate for a 3-D

* Corresponding Author,

E-mail : kadmin@snu.ac.kr

TEL : +82-2-880-1661; FAX : +82-2-883-0179

School of Mechanical and Aerospace Engineering, Seoul National University, San 56-1, Shinlim-dong, Kwanak-gu, Seoul 151-742, Korea. (Manuscript Received April 12, 2001; Revised March 13, 2002)

simulation.

Rapid Compression Machines (RCM) are the most suitable device for investigating the autoignition and reaction characteristics of fuels at a high pressure, as they provide well controlled conditions (in terms of peak pressure and temperature), direct measurement of the ignition delay time, no disturbance in the residual gases, and high pressure measurements (Lee, 1993). Studies of autoignition chemistry in RCMs have been conducted in order to predict autoignition of various hydrocarbons such as propane, *n*-butane, *n*-pentane and *i*-octane (Griffiths *et al.*, 1993; Ranza *et al.*, 1994; Minetti *et al.*, 1995; Minetti *et al.*, 1996; Ho *et al.*, 1997, Westbrook *et al.*, 1998). Some results show the autoignition characteristics of propane and *n*-butane, but those of various blends of the two fuels are not available.

Previous studies using RCMs reported difficulty in determining the compressed temperature due to gas motion on the chamber wall as a result of the piston scraping the thermal boundary layer, which accelerates heat loss to the cylinder wall.

The reaction processes in RCMs are usually assumed to be uniform: this simplification was considered to be close to realistic conditions. However, it was revealed that the mixture conditions were far from uniformity (Lee, 1993). Therefore, the reaction in conventional RCMs occurs under non-uniform conditions, which results in an uncertainty in the core gas temperature. In this study, the piston head crevice was designed to minimize the uncertainty in the core gas temperature due to the piston corner vortex.

The reduced and detailed chemical mechanisms were also investigated (Pitz *et al.*, 1986; Minetti *et al.*, 1994). The detailed mechanism is usually too complex to apply 3-D simulations. Therefore, it is necessary to model a reduced mechanism, which considers only the more important reaction steps and radicals. The reduced mechanism of the Shell model needs to be validated by experimental results, before it can be applied to predicting the characteristics of the autoignition delay times over a wide range of conditions.

In this work, the autoignition delay time was measured for propane and *n*-butane blends in an

RCM. The core gas temperature was calculated with a thermodynamic equation based on the measured pressure. The Shell model was fitted to the measured autoignition delay time data for the blend. These modeling results may serve as a basis for engine cycle simulation and the autoignition characteristics in LPG fueled SI engines can be predicted.

2. Experiments and Modeling

2.1 Rapid compression machine

The RCM has been widely used to examine the in-cylinder flow, and the autoignition characteristics of the fuel and oxygen mixtures. Experimental research on the ignition delay is necessary for a better understanding of engine knock and to develop a chemical kinetic model that may be useful for a 3-D simulation. In particular, as the need for 3-D simulations increases with increasing computer performance, chemical kinetic modeling is essential for a wide range of problems. The development of a proper kinetic mechanism requires accurate experimental data, which are able to verify the mechanism. In order to study autoignition at high-pressures (1.6~1.8 MPa) and temperatures (720~900 K), a new rapid compression machine was developed. A schematic diagram of the RCM is shown in Fig. 1 and the basic dimensions are summarized in Table 1.

As shown in Fig. 1, the RCM consists of a driving air cylinder and a returning hydraulic

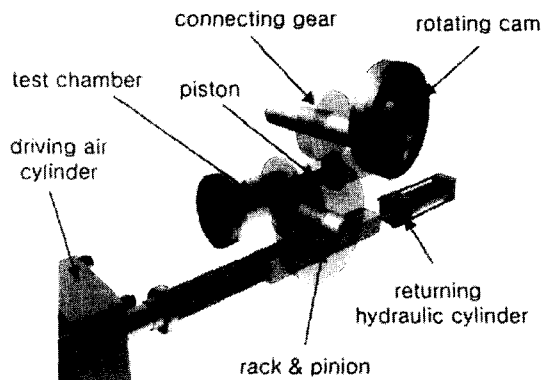
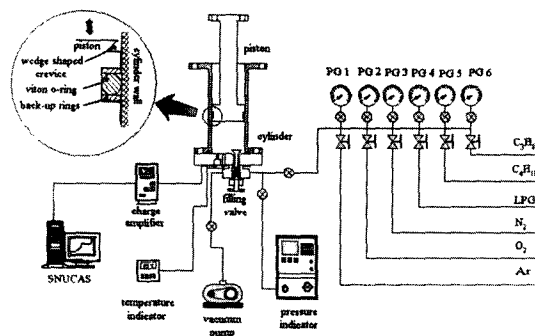


Fig. 1 Schematic diagram of the rapid compression machine

Table 1 Specifications of the rapid compression machine

Item	Specification
Test chamber bore (mm)	60
Maximum stroke (mm)	96
Compression Ratio	5.0~20
Clearance Height (mm)	5~20
Max. Peak Pressure (MPa)	0.9~6.2
Compression Time (ms)	20~45
Max. Peak Temperature (K)	980
Driving Air Pressure (bar)	2~4
Driving Chamber Diameter (mm)	250

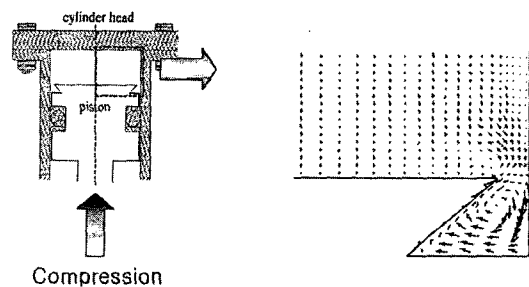
**Fig. 2** Schematic diagram of the autoignition measurements and the gas handling system

cylinder, a rack and pinion, gears, a piston, and a cam. The rack is driven by the air cylinder and rotates the connecting gear, which rotates the cam connected to the same stem. The cam is rotated by a connecting gear and induces rapid compression. In addition, it can be replaced to achieve a different stroke. The RCM was designed to be capable of varying the compression ratio between 5 and 20 by adjusting the connecting rod length.

A schematic diagram of the experimental apparatus is shown in Fig. 2. When the piston moves up, a rolled-up vortex is observed at the piston face and the cylinder-wall interface. This vortex enhances heat flux from the gas to the cylinder wall, which causes temperature non-uniformity within the combustion chamber. Therefore, the estimating the core gas temperature from the measured pressure is difficult. The piston crevice was designed to minimize the rolled-up

Table 2 Experimental conditions used

Item	Experimental conditions
Test Fuels	<i>n</i> -butane (100 %) propane (20 %) + <i>n</i> -butane (80 %) propane (40 %) + <i>n</i> -butane (60 %)
Temperature (K)	720~900
Pressure (MPa)	1.8
Equivalence ratio (ϕ_i)	1.0
Initial temperature (K)	298
Initial pressure (bar)	0.7~1.0
Sampling timing (kHz)	80

**Fig. 3** Simulation of the piston corner vortex by commercial CFD code (test gas: air, $P_1=101.1$ kPa, $T_1=293$ K)

vortex formation (Lee, 1993). In order to validate the effect of the wedge-shaped crevice, the fluid motion induced by the moving piston was simulated with commercial CFD code. As shown in Fig. 3, the scraped boundary layer is successfully captured by the piston crevice and a corner vortex is not observed at the interface between the piston and the cylinder wall.

The pressure-time data was measured by a piezoelectric transducer (Kistler 6061A) and recorded on a SNUCAS (a pressure measuring instrument) at a sampling frequency of 80 kHz. The fuels were filled into the test chamber through each fuel line and filling valves. In order to vary the core gas temperature at a given pressure, the heat capacity, γ was varied by altering the ratio of the non-reactive components (N_2 , Ar). The experimental conditions are given in Table 2.

The measured pressure-time records were reproducible within an acceptable range of approximately ± 0.01 MPa. It is very important to acquire an appropriate compression pressure for

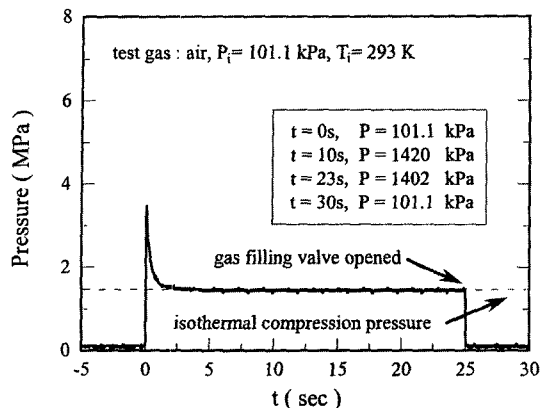


Fig. 4 Measured pressure showing the cooling of the test gas to the initial temperature

obtaining the right core gas temperature. Therefore, the test chamber seal was tested by acquiring sufficiently long time-pressure records, which were then compared with the autoignition delay time. Figure 4 shows the RCM parameters of the cooling time scale used to reach isothermal equilibrium. The compressed peak pressure fell rapidly to the isothermal compression pressure within two seconds, which is a sufficiently long time compared with the characteristic time of autoignition, and maintained this fixed isothermal compression pressure.

2.2 Determination of the core gas temperature (T_c)

It is important to determine the core gas temperature from the measured pressure data because the ignition delay time is quite sensitive to the temperature. The ideal adiabatic compression temperature (T_{ad}) is given by

$$T_{ad} = T_i (CR)^{\gamma-1} \quad (1)$$

where T_i is the initial temperature, CR is the mechanical compression ratio and γ is the ratio of the heat capacities of the mixture.

There are several uncertain factors for determining the core gas temperature during compression such as heat loss, a boundary layer effect and a vigorous corner vortex motion (Griffiths *et al.*, 1993; Lee, 1993; Minetti *et al.*, 1995). Griffiths suggested the core gas temperature for estimating

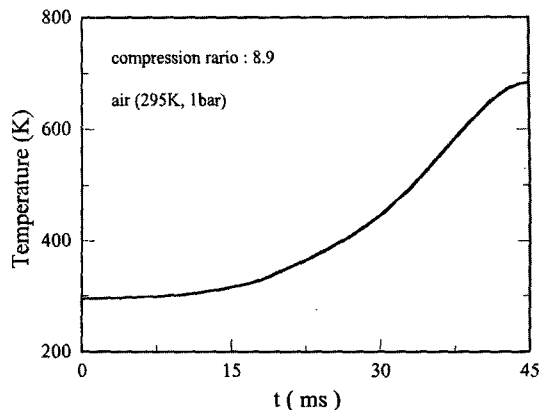


Fig. 5 Calculated temperature from the measured pressure data during compression

the compressed temperature since there is heat loss to the wall and a boundary layer effect during the compression stroke.

The core gas temperature T_c is given by

$$\ln \left(\frac{T_c}{T_i} \right) \int_{P_i}^{P_c} \frac{\gamma(T) - 1}{\gamma(T)} d \ln p \quad (2)$$

where T_i is the initial temperature, P_i is the initial pressure, P_c is the final pressure, and γ is the specific heat ratio which was obtained from the thermodynamic data. It can be said that the core gas temperature represents the adiabatic compression temperature because the core gas temperature is calculated based on the experimental pressure data during the compression stroke. The temperature-time record obtained from the measured pressure data is shown in Fig. 5.

Both the temperature history during the compression stroke and the core gas temperature can be obtained from the measured pressure records by Eq. (2).

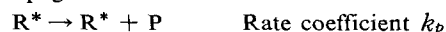
2.3 The shell model

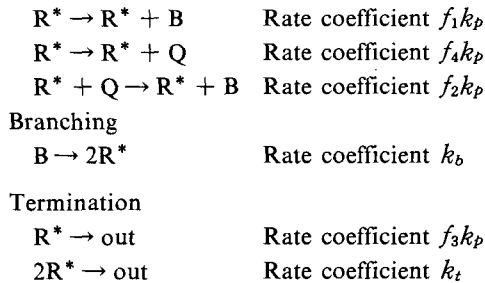
In the Shell model, autoignition chemistry is reduced to an eight-step chain branching reaction scheme, incorporated into four processes (Sazhin *et al.*, 1999).

Initiation



Propagation





Where RH represents the hydrocarbon fuel (C_nH_{2n}), R^* is the radical, B is the branching agent, Q is the intermediate agent, and P is the product consisting of CO, CO₂, and H₂O. The branching agent is related to hydroperoxide (RO₂H) at lower temperatures and hydrogen peroxide (H₂O₂) at higher temperatures. The intermediate species are related to aldehydes (RCHO). The main assumption of the Shell model is that the radical R^* entering into the scheme is treated as one type of radical using a steady-state hypothesis. In fact, it refers to different radicals.

The original Shell model uses the following equation to calculate the core gas temperature:

$$\frac{dT}{dt} = \frac{1}{C_v n_{tot}} \left(Q_k - Q_t - \frac{n_{tot} RT}{V} \frac{dV}{dt} \right) \quad (3)$$

Where C_v is the heat capacity for constant volume, n_{tot} is the total number of moles in the volume V and Q_k is the chemical heat release.

3. Results and Discussion

3.1 Two-stage ignition as feature of the pressure record

The pressure-time records for each blend of propane and *n*-butane are shown in Figs. 6 and 7 at the given values of T_c and an end-gas pressure in the range of 720~900 K and 1.6~1.8 MPa, respectively. The total ignition delay time, τ_d , was measured from the TDC to the moment in the post-compression process when the maximum pressure gradient was attained (Lee, 1993).

In Fig. 6, the ignition delay time of the blend is clearly lower as the core gas temperature is increased in the range of 720~800 K. However,

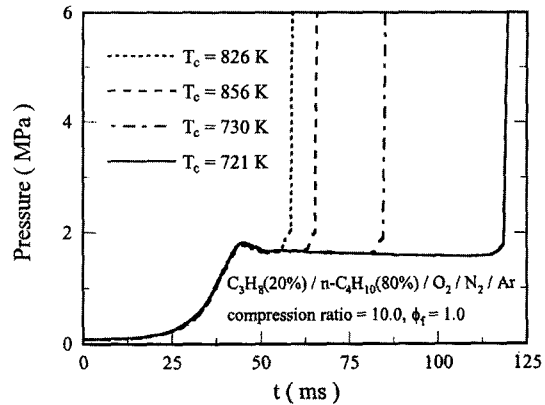


Fig. 6 Pressure-time profiles showing the compression stroke and subsequent autoignition according to the compressed gas temperature

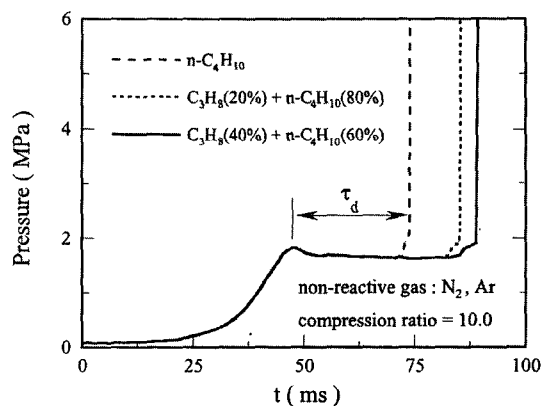


Fig. 7 Pressure-time profiles showing the compression stroke and subsequent autoignition according to the propane and *n*-butane blend ($T_c = 750 \pm 4$ K)

the ignition delay is increased as the temperature is further increased in the region of 800~870 K. This phenomenon of the ignition delay time increasing as the temperature increases is a unique characteristic of alkane hydrocarbon fuel oxidation, and it is referred to as Negative Temperature Coefficient (NTC) behavior.

Another remarkable phenomenon is the occurrence of a two-stage ignition delay. The reason for the occurrence of the two-stage ignition delay is as follows: The first stage ignition is interrupted by intermediate species such as aldehydes (RCHO) or hydrogen peroxide (H₂O₂), which are relatively stable radicals at low temperatures,

and a cool flame is generated as the propagation reaction stops. During the second stage ignition, the intermediate species concentration is increased considerably; more than that of the first stage ignition. After a short time, the temperature rises drastically as the intermediate species are rapidly decomposed into smaller radicals and the two-stage ignition is complete.

The pressure record associated with a 20 % of propane and 80 % of *n*-butane by volume blend is shown in Fig. 7 at the pressure of 1.8 MPa.

The propane in the blend contributes to lengthening the ignition delay time at the same core gas temperature. However, it is difficult to validate experimentally how the propane and *n*-butane work together during the combustion process after a compression stroke. As shown in Fig. 7, the propane fraction was increased two fold from 20 % to 40 %. The resulting ignition delay time was also increased by approximately 41 % and 55 %, respectively. The proportion of propane in the blend affects the ignition delay time considerably.

3.2 Ignition delay time as a function of core gas temperature

The ignition delay times measured for the propane and *n*-butane blend are represented according to the core gas temperature (T_c) for the blend in Figs. 8 and 9 for each fuel test and the Shell model at a pressure of 1.8 MPa.

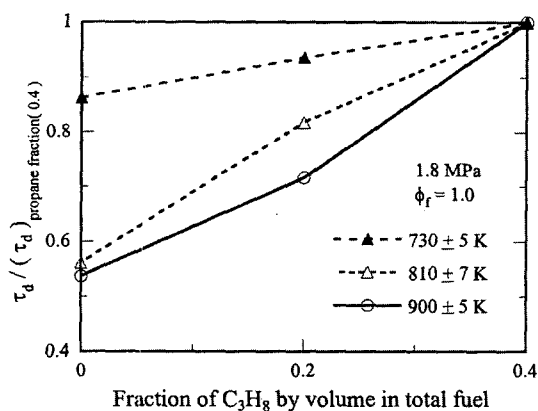


Fig. 8 The ignition delays measured for the propane and *n*-butane blend according to the compressed gas temperature

In Fig. 8, the normalized ignition delay time based on a 40 % propane blend for three core gas temperatures was compared. The ignition delay time in the low temperature region decreased linearly. As the temperature increased, the ignition delay time decreased more rapidly than what was observed in the low temperature region. However, in the high temperature region, its rate of decrease was slightly smaller as the propane fraction was decreased. At a core gas temperature of 730 K, the normalized ignition delay time for *n*-butane (0 % of propane fraction) was reduced by 12 % but for a propane 40 % blend at 900 K, it was reduced by 45 %.

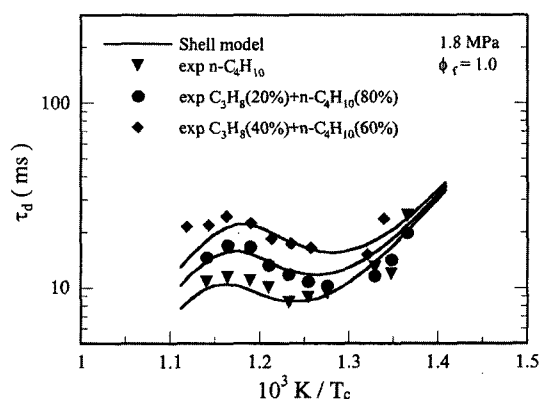
The Shell model predicted the time-dependence of both the temperature and the concentration of all generic species (Sazhin *et al.*, 1999). The Shell model parameters were determined by a sensitivity analysis with the experimental data in the ignition delays for the propane and *n*-butane blends. The parameters that changed according to the different fuels in the Shell model were also investigated. A_{F3} was varied to fit the Shell model to the experimental data. The pre-exponential factor, A_{F3} was determined according to the experimental data for the three test fuels. The predicted ignition delay time for the three fuel types, which were calculated using the kinetic rate parameters based on the original Shell model showed good agreement with the experimental results at a pressure of 1.8 MPa. A_{F3} was fitted into $(1.6 - 1.5(F-1))$ according to a function of the ratio of the *n*-butane fraction (F). The detailed kinetic rate parameters fitted to the blend are presented in Table 3 and the model prediction and the experimental data are shown in Fig. 9.

The dependence of the ignition delay time on the core gas temperature was clearly observed in the low and high temperature regions. As the propane concentration in the blend was increased (20 % and 40 %), the ignition delay time curves were shifted upward by approximately 40 % and 95 % in the NTC region.

The behaviors of the ignition delay time of the fuels are clearly divided into three distinct regions: a low temperature region (<750 K), the NTC region (750~850 K), and a high tempera

Table 3 Shell model constants for the different types of fuels

Parameter	Propane(1- <i>F</i>) + <i>n</i> -Butane(<i>F</i>)
<i>F</i>	0.6~1.0
<i>A</i> _{<i>p</i>1}	1.0 × 10 ¹²
<i>E</i> _{<i>p</i>1}	0.0
<i>A</i> _{<i>p</i>2}	1.0 × 10 ¹¹
<i>E</i> _{<i>p</i>2}	1.74 × 10 ⁴
<i>A</i> _{<i>p</i>3}	1.0 × 10 ¹³
<i>E</i> _{<i>p</i>3}	9.86 × 10 ²
<i>A</i> _{<i>q</i>}	3.96 × 10 ¹³
<i>E</i> _{<i>q</i>}	4.64 × 10 ⁴
<i>A</i> _{<i>b</i>}	6.51 × 10 ¹⁵
<i>E</i> _{<i>b</i>}	4.8 × 10 ⁴
<i>A</i> _{<i>t</i>}	3.51 × 10 ¹²
<i>E</i> _{<i>t</i>}	1.0 × 10 ³
<i>A</i> _{<i>f</i>1}	7.3 × 10 ⁻⁴
<i>E</i> _{<i>f</i>1}	-1.74 × 10 ⁴
<i>A</i> _{<i>f</i>2}	1.8 × 10 ²
<i>E</i> _{<i>f</i>2}	-8.12 × 10 ³
<i>A</i> _{<i>f</i>3}	1.6 - 1.5(<i>F</i> -1)
<i>E</i> _{<i>f</i>3}	1.16 × 10 ⁴
<i>A</i> _{<i>f</i>4}	1.7 × 10 ⁴
<i>E</i> _{<i>f</i>4}	3.48 × 10 ⁴
<i>x</i> ₁	1.0
<i>y</i> ₁	0.0
<i>x</i> ₃	-1.0
<i>y</i> ₃	0.0
<i>x</i> ₄	-1.0
<i>y</i> ₄	0.35

A*_{*i*}(cm, mole, s units) or *E*_{*i*}(cal/mole)Fig. 9** Ignition delay time for the propane and *n*-butane blend using the Shell model and the experimental results

ture region (>850 K). In the low temperature

region, the oxidation of the alkane hydrocarbon fuels is not sufficient to initiate the reaction because it requires a high activation energy. Similarly, in the temperature region below 700 K, longer ignition delay times are required. In the NTC region, as the initial temperature is gradually increased, the ignition delay time is decreased. In the high temperature region after the NTC region, the ignition delay time is further decreased due to drastic reactions.

4. Conclusions

The newly designed RCM was able to vary the compression ratio between 5 and 20 and minimize vortex formation on the cylinder wall by a wedge-shaped crevice. The temperature history during the compression stroke and the core gas temperature were obtained from the measured pressure record. At the same core gas temperature and pressure the autoignition delay time of propane is longer than that of *n*-butane. As the propane fraction is increased from 20 % to 40 %, the ignition delay time is also increased (41 % and 55 % at 750 K). The autoignition delay time measured for the propane and *n*-butane blends were successfully fitted into the Shell model as a function of the *n*-butane fraction. These modeling results provide a basis for engine cycle simulation to predict autoignition in LPG fueled SI engines.

Acknowledgment

This research was supported by the Combustion Engineering Research Center(CERC).

References

- Cox, A. and Cole, J. A., 1985, "Chemical Aspects of the Autoignition of Hydrocarbon-Air Mixtures", *Combustion and Flame*, Vol. 60, pp. 109~123.
- Griffiths, J. F., Halford-Maw, P. A. and Rose, D. J., 1993, "Fundamental Features of Hydrocarbon Autoignition in a Rapid Compression Machine", *Combustion and Flame*, Vol. 95, pp. 291~306.

- Ho, S. Y. and Kuo, T., 1997, "A Hydrocarbon Autoignition Model for Knocking Combustion in SI Engines", SAE Paper, 971672.
- Kim, I., Lee, D. and Goto, S., 1997, "Combustion Process Modeling Using a Mechanism in an LPG Lean Burn SI Engine", SAE Paper, 970899.
- Lee, D. and Goto, S. *et al.*, 2000, "Chemical Kinetic Study of a Cetane Number Enhancing Additive for an LPG DI Diesel Engine", SAE Paper, 2000-01-0193.
- Lee, D., 1993, "Autoignition Measurements and Modeling in a Rapid Compression Machine, Ph. D. Thesis, MIT.
- Minetti, R., Carlier, M., Ribaucour, M., Therssen, E. and Sochet, L. R., 1995, "A Rapid Compression Machine Investigation of Oxidation and Auto-Ignition of *n*-Heptane: Measurements and Modeling", *Combustion and Flame*, Vol. 102, pp. 298~309.
- Minetti, R., Carlier, M., Ribaucour, M., Therssen E. and Sochet, L. R., 1996, "Comparison of Oxidation and Autoignition of the Two Primary Reference Fuels by Rapid Compression," *The 26th Symposium International on Combustion*, pp. 747~753.
- Minetti, R., Ribaucour, M., Carlier, M., Fittschen, C. and Sochet, L. R., 1994, "Experimental and Modeling Study of Oxidation and Autoignition of Butane at High Pressure," *Combustion and Flame*, Vol. 96, pp. 201~211.
- Pitz, W. J. and Westbrook, C. K., 1986, "Chemical Kinetics of the High Pressure Oxidation of *n*-Butane and Its Relation to Engine Knock", *Combustion and Flame*, Vol. 63, pp. 113~133.
- Ranzi, E., Faravelli, T., Gaffuri, P., Pennati, G. C. and Sogaro, A., 1994, "A Wide Range Modeling Study of Propane and *n*-Butane Oxidation", *Combust. Sci. and Tech.*, Vol. 100, pp. 299~330.
- Sazhin, S. S., Sazhina, E. M. and Heikal, M. R., 1999, "The Shell Autoignition Model: A New Mathematical Formulation," *Combustion and Flame*, Vol. 117, pp. 529~540.
- Westbrook, C. K., Curran, H. J., Pitz, W. J., Griffiths, J. P., Mohamed, C. and Wo, S. K., 1998, "The Effects of Pressure, Temperature, and Concentration on the Reactivity of Alkanes: Experiments and Modeling in a Rapid Compression Machine", *The 27th Symposium International on Combustion*, pp. 371~378.