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Study on the Induction Period of Hydrocarbon for Alternative Rocket Fuel

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Abstract

Low and intermediate temperature ignition of n-butane is studied using a tailored condition behind a reflected shock wave. The tailored condition is established with long periods of constant pressure and temperature. The fluctuation of temperature is estemated from the results of the experiment and numerical calculation.

The ignition delay time for the stoichiometric mixture of n-butane and oxigen 80 % diluted by argon with a trace amount of carbon dioxide is obtained at a wide temperature between 785 and 1485 K and pressure between 1.5 and 6.0 atm. The ignition induction time at the high temperature agrees well with the data by Burcat et al. and becomes maximum at the low temperature , that is, it is close to the negative temperature coefficient region. The results promises the new era of the low temperature chemistry by the shock tube experiment.

1 Introduction

Extensive studies on low and medium temperature oxidation and ignition mechanism of hydrocarbons and other species have been performed recently since the importance of low and medium temperature chemistry (500 - 1200 K) is realized in many applications such as ignition and knocking in the internal combustion engine. However the method of study at low and medium temperature has not been established: the flash photolysis is applied at very low temperature; the rapid compression machine has a compression period where chemistry proceeds; the flow reactor is good at the temperature 1000 to 1300 K; the shock tube was used at the temperature higher than 1200 K.

The tailored condition technique behind the reflected shock wave gives an answer to the low temperature chemistry research. There are few reports on the shock tube study using the tailored condition. Just and colleagues performed the measurements using the tailored condition. The similar study on the induction period of n-heptane /oxygen mixture is recently performed by Ciezki and Admeit(Ref. 1).

The present study shows the establishment of the tailored condition behind the reflected shock wave, the optical measurement of the vibrational temperature using CO_2 emissions, the ignition induction period of n-butane /oxygen mixture at the pressure 1.5-6.0 atm using the developed technique of the tailored condition. Since some researchers showed that the chemical induction time can be very sensitive to temperature variations which occur due to non-uniformities behind shock wave(Ref. 2), the fluctuations of temperature during the tailored condition are estimated.

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2 Experiment

The present study is performed by a single-pulse stainless steel shock tube of 5.08 cm i.d. and 5.86 m length with a 0.1 m^3 dump tank (Fig. 1). A leak rate of 1.0 Pa/min or less and the initial vacuum condition of 0.1 Pa or less are attained. N-butane is a research grade 99.8 % pure, carbon dioxide, argon, helium, and oxygen are Nihon Oxigen Grade 99.99 % pure. The stoichiometric n-butane/oxygen/carbon dioxiside/argon (= 0.027/0.173/0.001/0.799) mixture is prepared for the ignition induction period experiment. The shock speed is obtained by a multi-channel time counter signaled from a piezoelectric transducer (Kistler 601H). The pressure and temperature behind a reflected shock wave is calculated from the shock relations taking into account of the temperature dependency of species enthalpy and the boundary layer effect based on the Mirels' theory. The time history of the temperature is obtained using the relation between the infrared emission intensity of CO_2 through a 4.2 μm wide band infrared filter and the computed temperature. The autoignition induction time is measured using the OH ultraviolet emission detected by the photo-multiplier after passing through a 10 cm monochromator (JASCO CT-10).

3 Numerical Calculation

In order to simulate the flow of the shock tube, one dimensinal Euler equation including two species Eq. 1 was solved with the following assumptions , (1)the flow field is one-dimensional; (2)the driver gas and the test gas are uniform mixture gas which can be considered as a single gas ; (3)the gas specific heat is a polynomial of temperature, but the equation of state for ideal gas is used; (4)the external forces such as gravity are neglected,

$$\frac{\partial U}{\partial t} + \frac{\partial F}{\partial x} = 0, \tag{1}$$

where the conservative vector U and the convective termes vector F are

$$U = \begin{bmatrix} \rho \\ \rho u \\ E \\ \rho Y_1 \end{bmatrix}, F = \begin{bmatrix} \rho u \\ \rho u^2 + P \\ (E+P)u \\ \rho Y_1 u \end{bmatrix}$$

The quantities ρ, T, P, u and Y_1 are density, temperature, pressure, velocity, and mass fraction of test gas, respectively. The driver gas and the test gas are assumed to be uniform, therefore each gas can be represented by one mass fraction. The quantity E is

$$E = \Sigma \rho_i h_i + \rho \frac{u^2}{2} - P$$

where

$$h_i = \int_{T^0}^{T} C_{pi} dT + h_i^0$$

is a specific enthalpy, and C_{pi} is a specific heat at constant volume of the i-th species which includes the real gas effect and is approximated by a polynomial so as to match with the data of JANAF table according to CHEMKIN method(Ref. 3):

$$C_{pi}/R_i = a_{1i} + a_{2i}T + a_{3i}T^2 + a_{4i}T^3 + a_{5i}T^4$$

These equation are solved using the second order accuracy Harten and Yee type TVD-upwind scheme. The boundary conditions at both end wall of the shock tube are reflective. Since the length of the shock tube used in the present study is 5860 mm, grid points are taken by 5861.

4 Results and Discussion

The tailored conditions in the wide temperature range are obtained for the several driver mixtures; He/Ar = 7/0, 5.5/1.5, 5/2, 4/3, in atmosphere. The test mixture to develop a calibration curve for tailored conditions contains 0.5 % CO_2 and 99.5 % Ar, which is mixed in a mixture tank at least for a day before the experiment. The tailored condition with a long duration time of the constant pressure and infrared emission intensity is obtained by changing the initial gas pressure several times at the fixed driver gas pressure and mixing ratio.

The 4.2μm infrared emission intensity from a trace amount of CO_2(< 0.05 %) behind reflected shock wave is measured and plotted for the computed temperature in Fig. 2. Generally the relation among the CO_2 μ_3 band emission intensity I, the initial CO_2 concentration N_{CO_2} and the temperature behind reflected shock wave T_5 is

$$\frac{I}{N_{CO_2}} \sim \frac{1}{e^{\frac{\theta_V}{T_5}} - 1} \qquad (2)$$

where θ_V is the vibrational characteristic temperature and about 3379.1 K. The characteristic temperature obtained from Fig. 2 is 3735.2 K which is very close to the theoretical one. The important point in Fig. 2 is that both tailored and non-tailored temperatures are determined from the relation in Fig. 2.

In order to estimate the fluctuation width of the temperature behind reflected shock wave, the method described by Stepanek(Ref. 5) has been chosen by differantiating the Eq. 2 as following:

$$\frac{dT}{T_5} = \frac{dI}{I} \frac{1 - e^{-\frac{\theta_V}{T_5}}}{\frac{\theta_V}{T_5}} \qquad (3)$$

From this method, the fluctuation width of temperature behind reflected shock wave in the case of Fig. 3 is estemated 36.9 K. This value can be permissible error of this type of experiment. On the other hand, the estimation from the computation is about 110 K. The latter value may become large because the temperature dependence of the enthalpy was neglected in this case. Therefore 110 K can be lowered by using the real gas effect.

The chemical induction time can be sensitive to temperature fluctuations due to the nonuniformities behind reflected shock waves. Fig. 4 shows the two types of ignition delay time for the stoichiometric n-butane/oxygen mixture; one is obtained in the tailored condition at the pressure 1.5 – 4.0 atm which has both constant temperature and pressure during the duration and another in the non-tailored condition at the pressure 4.0 – 7.0 atm which has only constant pressure duration and decreasing temperature. If the results in the non-tailored conditions would be obtained in the tailored conditions, their induction times would become shorter.

5 Conclusion

The usefulness and validity of tailored condition behind a reflected shock wave are shown and are applied for measuring the ignition induction period of the n-butane/oxygen mixture at the low and medium temperature. The temperature fluctuation widths behind reflected shock wave are estimated using the method of Stepanek and computing of one-dimensional Euler equation respectively. A rather high value from the latter method will decrease with the temperature dependency of the enthalpy.

Reference

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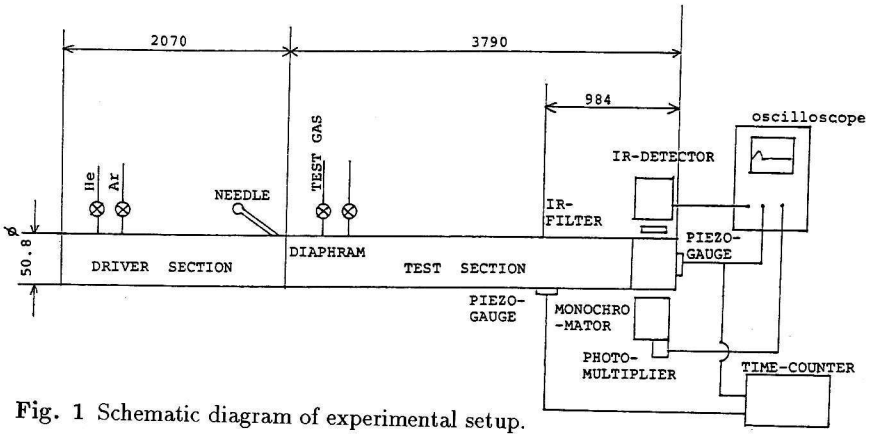


Fig. 1 Schematic diagram of experimental setup.

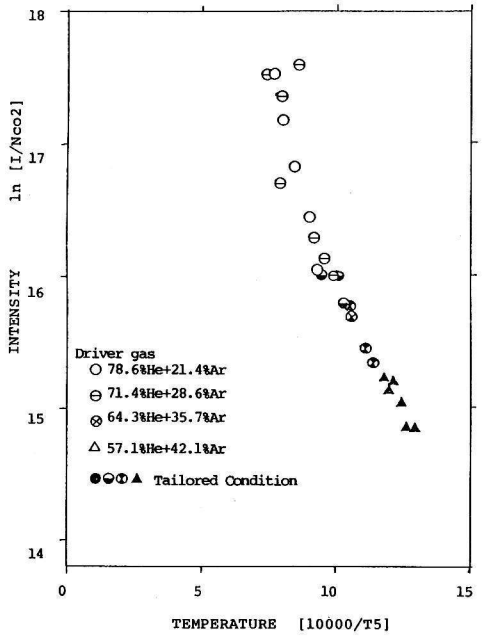
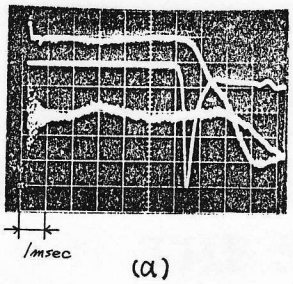
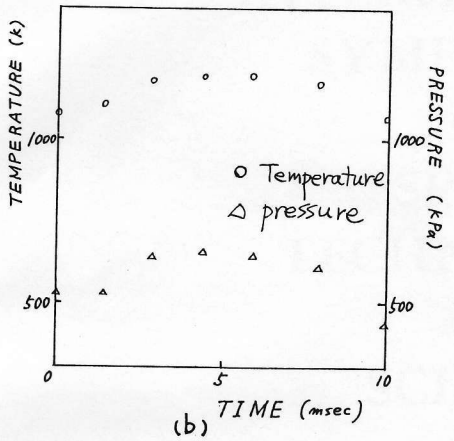


Fig. 2 The relation between the CO_2 emission intensity I and the computed tempersture in both tailored and non-tailored conditions.



(a)



(b)

Fig. 3 Comparison of temperature and pressure time history between calculation and experimental data.

(a) experiment
(b) calculation

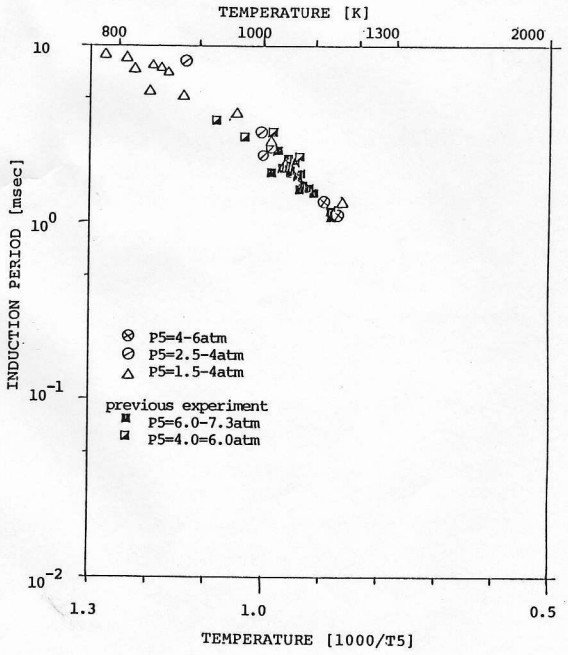


Fig. 4 The difference in ignition delay time between the non-tailored case($P_5 = 4 - 7$atm) and the tailored case ($P_5 = 1.5 - 4$atm).