

Reactivity Evaluation of Weak-Combustibility Fluids in Micro Flow Reactor with Streamwise Temperature Gradient

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ABSTRACT

A rapid combustibility evaluation method of weak-combustibility fluids has been proposed based on the micro flow reactor with a streamwise temperature gradient. The flame position was defined as the boundary between the rapid propagation stage and the following slow propagation due to local wall heating. The flame position was obtained through high-speed CH* chemiluminescence measurement. As the proof of concept, the combustibility of n-heptane/trans-1,2-dichloroethylene (TDCE) mixtures at different mixing ratios has been examined based on its flame position in the micro flow reactor. It was found that the wall temperature at the flame position is higher with the mole fraction of TDCE, which is in accordance with the previous finding that the flame speed reduces with TDCE addition.

KEYWORDS: Fluorocarbon, Combustibility, Micro flow reactor, Flame front

1. INTRODUCTION

Fluorocarbons are widely used in human life as the refrigerant, solvent and foaming agent. Since chlorofluorocarbons (CFCs) have high ozone depletion potential (ODP), their use was regulated by the Montreal Protocol in 1987¹. Hydrochlorofluorocarbons (HCFCs) and then hydrofluorocarbons (HFCs) were developed as their low-ODP alternatives. However, HCFCs and HFCs are greenhouse gases which have high global warming potential (GWP). It was agreed in the Kigali Amendment that developed countries should reduce 85% of HFC usage until 2036². In order to reduce the GWP, alternatives of HFCs shall have a molecular structure which decomposes easily in the air, such as Hydrofluoroolefins (HFOs) and hydrofluoroethers (HFEs). However, easy decomposition in the air generally means high reactivity with the oxygen also. It is of concern that they may become more combustible. For example, HFO-1234yf (GWP<1), a low-GWP substitute of HFC134a (GWP=1430), is classified as A2L (lower flammability refrigerants with a maximum burning velocity less than 10 cm/s) by the ASHRAE34 Designation and Safety Classification of Refrigerants³ in the USA and as combustible gas by the High-Pressure Gas Safety Act in Japan. Also, a discussion on necessary amendment of present refrigerants safety regulations in Japan is ongoing for such weak-combustibility fluids⁴. The evaluation of combustibility is important in the development of new low-GWP fluorocarbons.

Standard tests such as the ASTM E681⁵ and ISO 817⁶ are established for the evaluation of combustibility by measuring the flammability limits. In ASTM E681, the sample at different mixing ratios with air is filled in a 12L flask and ignited by an electric spark. Whether the mixture is flammable is evaluated according to the angle of flame propagation. Because the test is a batch process, it is time-consuming. The evaluation under various environmental conditions of temperature, pressure and humidity is difficult⁷. In order to select the weak-combustibility fluid out of a huge number of fluorocarbon candidates including their azeotropic and pseudo-azeotropic mixtures, it is necessary to perform an initial fast screening of them at various mixing ratios and conditions of pressure and humidity before moving onto the time-consuming evaluation through the conventional standard tests.

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The objective of the present study is to develop a fast screening method for weak-combustibility fluids based on the micro flow reactor approach proposed previously by Maruta et al.⁸⁻¹⁰. The approach, in which a normal or weak flame is formed in a small quartz tube with a given streamwise temperature distribution, was used for the investigation of the reaction mechanism of various fuels. Because the position of a normal flame formed in the micro flow reactor changes with the combustibility of the fuel, in the present study, the normal flame position is examined for various mixtures of n-heptane and weak-combustibility fluid as a measure of their relative combustibility.

2. EXPERIMENTAL SETUP

Figure 1 shows a schematic of the micro flow reactor in the present study. Through heating the downstream part of a small quartz tube, a temperature distribution of 300-1400K is formed in the streamwise direction. A normal flame of the fuel/air mixture is formed in the tube and its position is captured by CH* chemiluminescence imaging.

Figure 2 shows a schematic of the present experimental setup. Air is supplied by an air compressor and its flow rate is controlled by a mass flow controller (KOFLOC, MODEL 8500). The test fluid is injected through a needle of I.D. 0.18 mm into a T-junction tube connector where the fluid mixes with the air. The flow rate is kept constant by using a syringe pump (CMA, CMA-400). The T-junction tube connector is heated up to 100 °C by a silicone code heater (THREEHIGH, SC-100) in order to evaporate the test fluid. All the downstream section is kept at 120 °C by another silicone code heater to prevent the mixture from condensation. The quartz tube has an inner diameter of 2 mm and an outer diameter of 6 mm. A Kanthal A-1 wire electric heater is wrapped outside of 10 mm long downstream section of the quartz tube and this section is heated up to 1400 K by a voltage regulator (Sakaguchi E.H., VST-106). The streamwise temperature distribution on the inner wall surface of the quartz tube was measured using a thin R-type thermocouple with a wire diameter of 0.3 mm, when only an air flow of 40 cm/s is supplied. As shown in Fig. 3, a maximum temperature of approximately 1400 K and a streamwise temperature gradient of 56 K/mm are formed due to the heat conduction to the upstream side of the quartz tube and heat losses through the outer wall. In this report, the mixture of n-heptane and trans-1, 2-dichloroethylene is used while keeping the equivalent ratio of n-heptane and air at 1.0.

CH* chemiluminescence images of the flame are captured at 125 fps by a high speed ICCD camera (Photron, FASTCAM) with a CH bandpass filter (Asahi spectra, MZ0430, 430 nm/10 nm). Figure 4a shows a CH* chemiluminescence image and Figure 4b Shows the streamwise chemiluminescence intensity distribution at the radial position of peak intensity. Curve-fitting with Gaussian distribution is performed on the data above 20% of the measured peak. Finally, the peak position of the fitting curve is defined as the flame position.

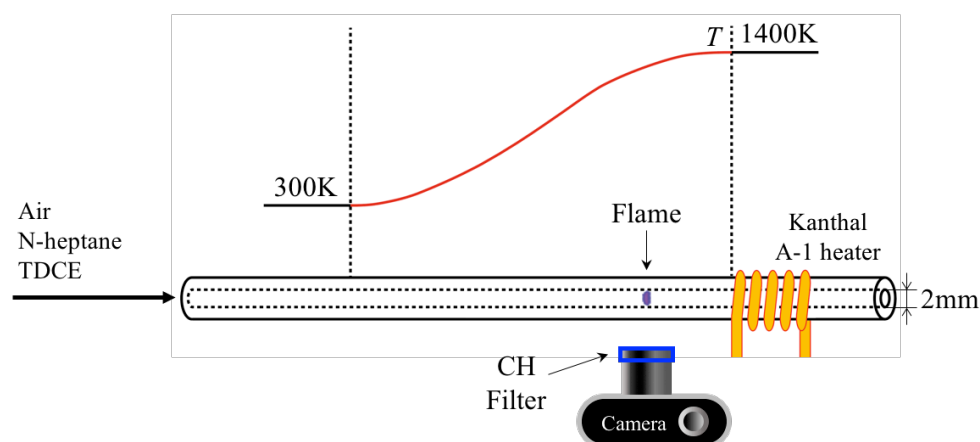


Fig. 1 Schematic of the micro flow reactor in the present study.

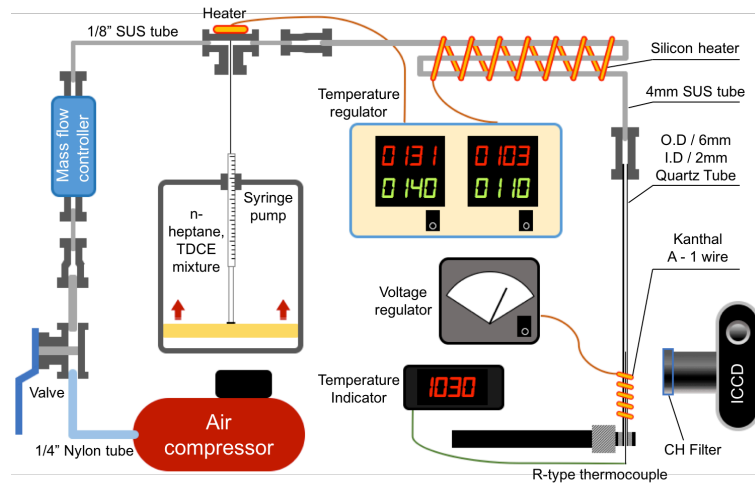


Fig. 2 Schematic of the present experimental setup.

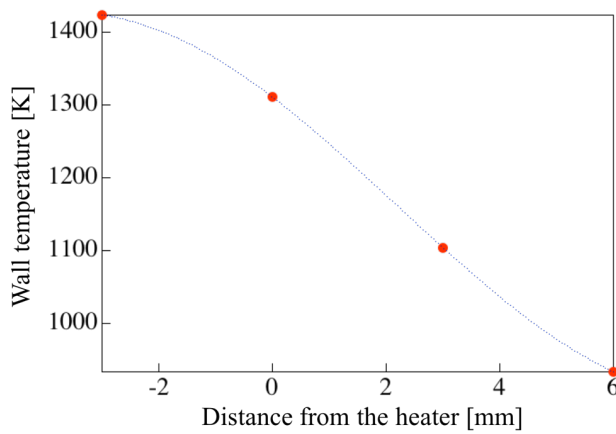


Fig. 3 Inner wall temperature distribution.

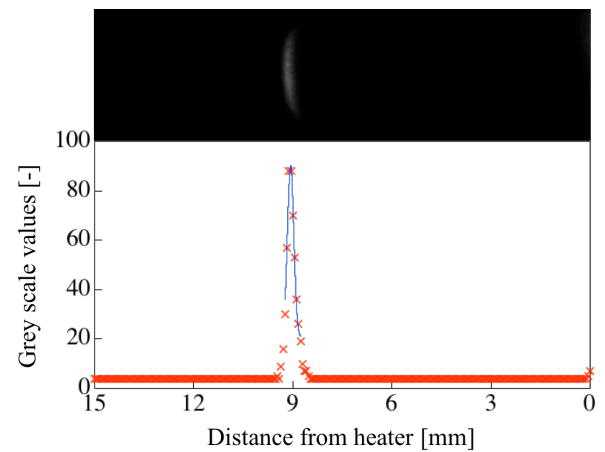


Fig. 4 (a) CH* chemiluminescence image of the n-heptane/air flame at 40 cm/s. (b) Streamwise intensity distribution.

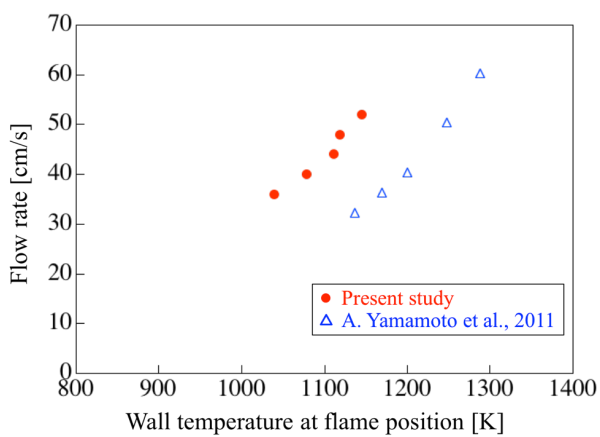


Fig. 5 Flow rate versus wall temperature at the flame position for n-heptane/air flames.

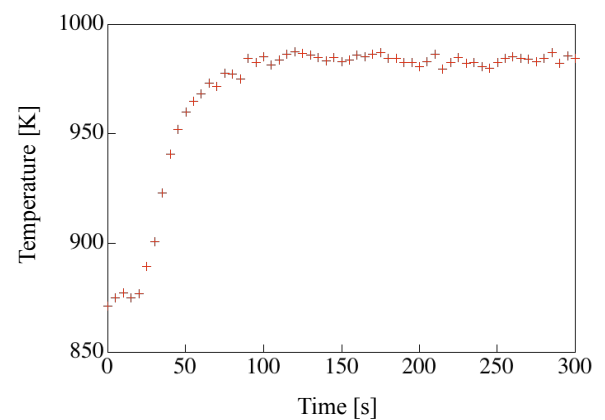


Fig. 6 Time history of outer wall temperature at 7.1 mm from the heater.

3. FLAME POSITION DEFINITION INDEPENDENT OF WALL TEMPERATURE CHANGE

It was reported previously that auto-ignition occurs at some high-temperature downstream position after the injection of the n-heptane/air mixture into the heated quartz tube, then the flame propagates upstream and stabilizes after a while¹¹. Figure 5 shows the wall temperature at the stabilized flame position at different flow rates. Note that the wall temperature in the horizontal axis is measured before flame is formed. It was found that the flame position moves gradually to the high-temperature downstream side with increasing the flow rate from 36cm/s to 52cm/s. This tendency is qualitatively in agreement with the result of Yamamoto et al.¹⁰, in which the flame position is defined as the initial position of the flame. The flame position measured in the present study shifts greatly to the low-temperature side. This is because the local wall temperature adjacent to the flame increases due to the heat generation of a normal flame¹⁰.

Figure 6 shows the time history of the outer wall temperature at 7.1mm from the heater (wall temperature of 870K in Fig. 5). The flow rate is 40 cm/s. Outer wall temperature was measured at 5 second intervals by a radiation thermometer (IMPAC, IN140/5-L). The measurement spot diameter is 0.9 mm, which is sufficiently small compared with the tube diameter. It was observed that the outer wall temperature rises due to the flame formation. The temperature rises for 90 seconds and finally stabilizes at a level over 100 K higher than the initial value.

Figure 7 shows the evolution of the flame position after the auto-ignition. Figure 8 shows the time history of the flame propagation speed. The propagation speed just after the auto-ignition is as high as approximately 7 mm/s, and then it decreases rapidly with time. On the other hand, as shown in Figure 7, the flame position after the rapid propagation still moves upstream gradually. At this stage, the propagation speed is as low as below 0.05 mm/s. The flame finally reaches a stable position after about 60 seconds as shown in Fig. 5. If fitting the two stages divided by $t = 2.5$ s in Fig. 8 with two exponential functions, the time constant of these two stages differs by over 100 times. It is obvious that the flame position is changed by two different physical phenomena in these two stages. During the first stage with a small time constant, flame propagates due to the ignition. During the subsequent stage with a large time constant, the wall temperature rises due to the heat generation of the flame and the flame moves upstream due to the wall temperature rise. Because the effect of wall temperature change on the flame position should be eliminated in the evaluation of combustibility, it is necessary to define the 'flame position' representing the combustibility as the final position of the first flame propagation stage (hereafter referred as flame position for simplicity). In order to determine this flame position mathematically, it is necessary to fit the two stages with functions reflecting their respective physical phenomena and to find the intersection of these two functions as the flame position. In the present report, curve fitting with the exponential function is performed to the data of flame propagation speed as shown in Fig. 8, and the flame position is determined as when the speed decreases to 5% of the maximum. An average of 12 trials is taken as the final value of flame position to reduce the uncertainty from the variation in flame speed.

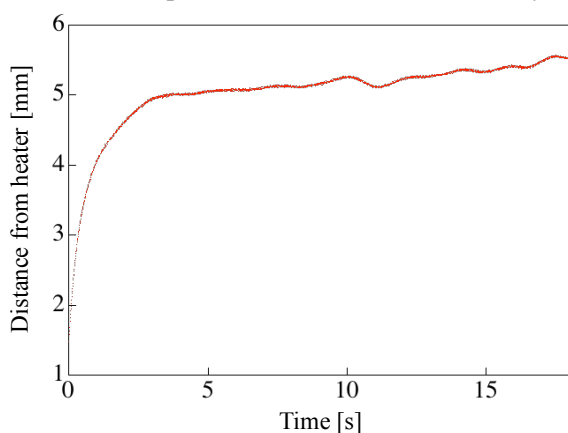


Fig. 7 Evolution of the flame position for the n-heptane/air flame at 40 cm/s.

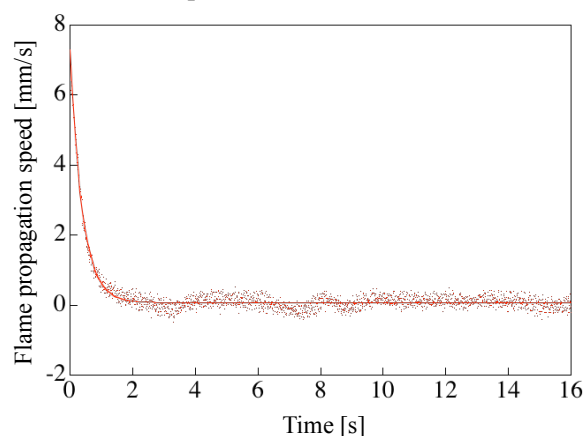


Fig. 8 Time history of the flame propagation speed for the n-heptane/air flame at 40 cm/s.

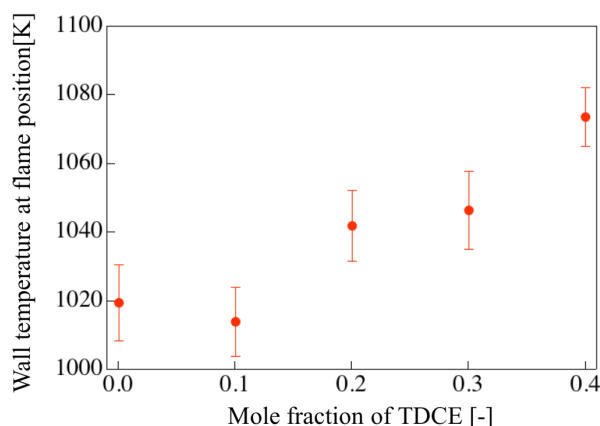


Fig. 9 Inner wall temperature at flame position versus the mole fraction of trans-1, 2-dichloroethylene.

4. EFFECT OF WEAK-COMBUSTIBILITY FLUID ADDITION

The effect of fluorinated and chlorinated hydrocarbons addition on the flammability limits has been investigated using the heptane cup burner method previously¹²⁻¹⁴. Their purpose is to find alternative to banned brominated hydrocarbon fire suppressants. Linteris et al. investigated the effect of trans-1, 2-dichloroethylene (TDCE) addition on the burning velocity of a methane/air Bunsen flame¹⁵. They found that the burning velocity decreases almost linearly with increasing the mole fraction of TDCE, and the velocity for a pure TDCE fuel decreases to approximately 10 cm/s, which is 1/4 of the methane flame. The combustion speed decreased almost linearly with increasing TDCE's mole fraction, and it decreased to 10 cm/s, which is 1/4 of pure methane.

In the present study, the combustibility of n-heptane/TDCE mixtures at different mixing ratios is evaluated according to their normal flame positions in the micro flow reactor. Figure 9 shows the wall temperature at the measured flame position for TDCE mole fraction of 0-0.4. The uncertainty of flame position is 0.2 mm, which is corresponding to an uncertainty of 10 K in the estimated wall temperature at the flame position. It is shown that the flame position moves to the high temperature side downstream with increasing the mole fraction of TDCE. The wall temperature at the flame position for a TDCE mole fraction of 0.4 is 54 K higher than that for the pure heptane case, which qualitatively agrees with the measured burning velocity data of Linteris et al.¹⁵ showing that the combustibility of the heptane flame is weakened by adding weak-combustibility fluid of TDCE. Although a quantitatively comparison with their result is difficult, this qualitative agreement proves that the suppression effect of weak-combustibility fluid addition can be successfully examined using the proposed approach in the present study.

5. CONCLUSIONS

A rapid screening method of the combustibility for weak-combustibility fluorocarbon fluids has been proposed based on the flame position of a normal flame formed in a micro flow reactor. As an initial trial, the flame position for mixtures of n-heptane and trans-1, 2-dichloroethylene was measured through the high-speed CH* chemiluminescence imaging. It was shown that the wall temperature at the flame position increases by 54 K with increasing the mole fraction of trans-1, 2-dichloroethylene from 0 to 0.4, which shows the feasibility of proposed combustibility evaluation method using the micro flow reactor.

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