Fire Safety Journal 71 (2015) 58–68

Contents lists available at ScienceDirect

Fire Safety Journal

journal homepage: www.elsevier.com/locate/firesaf

Quenching distance measurement of highly to mildly flammable compounds

Kenji Takizawa *, Naoharu Igarashi, Shizue Takagi, Kazuaki Tokuhashi, Shigeo Kondo

National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

ARTICLE INFO

Article history:
Received 20 April 2014
Received in revised form
19 November 2014
Accepted 23 November 2014
Available online 5 December 2014

Keywords:
Low GWP alternatives
Refrigerants
Quenching distance
Minimum flame radius
Minimum ignition energy
Burning velocity
Microgravity

ABSTRACT

Quenching distance measurements were carried out for 11 highly to only mildly flammable gases (which include alkanes, fluorinated alkanes and alkenes, and ammonia) to elucidate the ignition and quenching characteristics of low-GWP (global warming potential) alternative materials. For buoyant flames of mildly flammable compounds, conventional 25 mm diameter parallel plates in the vertical position provided significantly smaller quenching distance (d_q) than 100 mm diameter plates in the horizontal position. A good correlation was obtained between the quenching distance ($d_{q,h}$ in mm) measured by the latter test apparatus and the maximum burning velocity ($S_{u0,max}$ in cm s^{-1}) for these compounds: $d_{q,h} = 58.12(\rho_u S_{u0,\,max})^{-0.926}$, where ρ_u is the unburned gas density. The mildly flammable compounds that have $S_{u0,max}$ below 10 cm s^{-1} have a d_q more than three times larger than that of propane. Initial development of the schlieren flame radius was observed for mildly flammable CH_2F_2/air mixture using thin electrodes and a variety of spark energies. It was confirmed that the parallel plate quenching distance was essentially equal to the minimum flame diameter in a free space. By applying the measured $d_{q,h}$ and $S_{u0,max}$ in the simplified heat loss theory, the minimum ignition energy (E_{min} in mJ) was expressed by $E_{min}=0.0712 d_{q,h}^{2.97}$. The results showed that the mildly flammable compounds have E_{min} that is more than an order of magnitude greater than that of propane.

1. Introduction

In order to reduce environmental impacts, phase-out of high global warming potential (GWP) materials is currently a very important issue for the industries related to refrigerants, insulating foaming agents, and blowing agents. Regulations for the phase-out of R-134a (CH_2FCF_3) as a refrigerant of automotive air conditioning system has already come into effect in the EU and are anticipated to spread to other regions and applications. Because high-GWP compounds are stable in the atmosphere, the less stable compounds are now taken into consideration as lower-GWP alternatives. The properties that make the new compounds have higher reactivity in the atmosphere also make them more flammable. Considering this risk tradeoff, low-GWP compounds with mild flammability appear to be alternatives that provide the optimum balance of acceptable safety properties and environmental performance. Thus, risk assessments of mildly flammable compounds will need to be made before they are used in practical applications. (Hereafter, a compound whose maximum burning velocity ($S_{u0,\,max}$) is not higher than 10 cm s^{-1} is called "mildly flammable compound").

Considering the probability of fire hazard due to flammable gases, minimum ignition energy and quenching distance are some of the most important indices. Experimentally, minimum ignition energy (E_{min}) is the lowest spark discharge energy that can ignite a flammable gas mixture at the most ignitable concentration. Parallel plate quenching distance (d_q) is the minimum distance between two surfaces above which self-sustained propagation of a flame is achieved. A standard test method for determining E_{min} and d_q is specified in ASTM E582 [1]. These parameters, if obtained appropriately, are useful for designing the electrical equipment that may be deployed in areas with a potentially flammable gas atmosphere. Table 1 summarizes the published data of E_{min} and d_q for compounds relevant to this study [2–17]. For propane, the reported E_{min} range from 0.247 mJ [3] to 0.48 mJ [9]. For mildly flammable compounds, the reported E_{min} vary widely from <10 mJ to >10 J. This makes assessing the fire risk based on E_{min} very difficult. The difficulty in determining the reliable E_{min} is that it is very dependent on the electrode size, the gap between the electrodes, and the ignition spark density and duration [3,5,18–20].

Compared to measuring E_{min}, measuring d_q seems to be much easier, and provides reliable data on mildly flammable compounds. As listed in Table 1, the reported d_q of propane range from 1.7 to 1.9 mm; i.e., they are in good agreement. For mildly

* Corresponding author. Fax: +81 29 861 4770.
E-mail address: k.takizawa@aist.go.jp (K. Takizawa).

http://dx.doi.org/10.1016/j.firesaf.2014.11.013
0379-7112/

Table 1
Published E_{min} and d_q values for compounds relevant to the present study.

Compound	$S_{u0,max}$ (cm s^{-1})	E_{min} at $\phi=1$ (mJ)	E_{min} (mJ)	d_q at $\phi=1$ (mm)	d_q (mm)	Reference
Propane	38.7	0.39	0.25	1.75	–	2
(C_3H_8)		–	0.25	1.9	1.7	3
		–	0.3	–	1.7	4
		0.305	–	2.0	1.8	5
		–	0.33	–	–	6
		–	0.37	–	1.9	7
		–	0.46	–	–	8
		–	0.48	–	–	9
R-152a	23.6	–	0.38	–	–	10
(CH_3CHF_2)		–	0.89	–	3.2	4
R-143a (CH_3CF_3)	7.1	–	18,421	–	4.3	4
R-32	6.7	–	$30 < E < 100$	–	–	11
(CH_2F_2)		–	26,300	–	5.2	4
Ammonia	7.2	–	8	6.99	6.99	7
(NH_3)		–	14	–	–	12
		30	–	–	–	13
		–	> 90	–	–	14
		> 100	–	–	–	15
		–	170	–	–	14
		–	$100 < E < 300$	–	–	11
		300	–	–	–	13
		–	680	–	–	16
		–	> 1000	–	–	2
R-1234yf	1.5	–	< 300	–	–	17
($CH_2{=}CFCF_3$)		–	$5000 < E < 10000$	–	–	11
		–	> 250,000	–	–	11

flammable compounds, however, d_q is not readily available in the literature [4,7]. Verkamp et al. [7] measured d_q of ammonia as 0.275 in. (6.99 mm) at the stoichiometric concentration. Smith et al. [4] measured d_q and E_{min} for R-32 (CH_2F_2) and R-143a (CH_3CF_3) by a modified ASTM E582 method. In general, flames of mildly flammable compounds move upward due to buoyancy. However, previous studies used the same electrodes as have been commonly used for highly flammable hydrocarbons and did not consider the configuration of the electrodes for the buoyant flames.

As for the theoretical treatment of minimum ignition energy, there have been reported a few different expressions for calculating E_{min}. The minimum ignition energy is the energy that is just sufficient to establish the minimum flame sphere having the minimum radius necessary for self-sustained propagation. According to a simple heat loss theory [21,22], E_{min} is written by

$$E_{min} = (1/6)\pi d_{min}^3 \rho_b c_p (T_b - T_u). \quad (1)$$

Here d_{min} is the diameter of the minimum flame sphere in a free space, ρ_b is the burned gas density, c_p is the average isobaric heat capacity, and T_b and T_u are the burned and unburned gas temperatures.

Solving Eq. (1) requires T_b and d_{min} to be determined. Lewis and von Elbe [21] and Kondo et al. [23] postulated that the minimum flame has a diameter that is equal to the parallel plate quenching distance d_q and the same temperature as the adiabatic flame temperature T_{ad}. Their calculated E_{min} agreed qualitatively with the experimental values for various compounds but was quantitatively several times greater than the experimental E_{min}, on average. Turns [22] used Eq. (1) assuming that d_{min} is equal to the diameter of the flame kernel, which excludes the flame thickness from the flame diameter, and $T_b = T_{ad}$. The expression of the minimum flame in Eq. (1) is considered in a free space. If the flame quenching process in a free space is significantly different from that between the parallel plates, the minimum flame diameter, (below which a small flame cannot make transition to a self-sustained propagating flame) will be much different from d_q.

As for dynamic approaches to obtain the E_{min}, there have been reports of numerical calculation of E_{min}, which include an asymptotic analysis on activation energy [24], a set of chemical reactions [25], chemical reactions and configuration of electrodes [19,20], and flame growth rate [26]. Most of the calculated E_{min} agreed qualitatively with the experimental E_{min} (showing, for example, the concentration dependence), but quantitatively were from several times to more than an order of magnitude lower than the experimental E_{min}. Thus, even for small hydrocarbons there seems to be a difficulty in estimating the experimental E_{min}.

The objective of this study is to elucidate the ignition and quenching characteristics of mildly flammable compounds relative to highly flammable hydrocarbons. For this purpose we present comprehensively measured d_q of various flammable refrigerants and attempt to express E_{min} by using Eq. (1) and the experimental d_q or d_{min}. Finally, we discuss the possibility of estimating E_{min} in order to improve the current situation (where there is a wide variation in published E_{min} values for mildly flammable compounds).

2. Methods

2.1. General

Experiments were performed in a closed vessel with optical access at 298 ± 2 K and 101.3 kPa. Sample/air mixtures were directly prepared in the vessel by the partial pressure method. The sample/air mixture was fully mixed by a mixing fan in the vessel and left to settle for 1 min. Ignition was initiated with a DC electrical spark between a pair of electrodes place opposite each other. The spark energy was supplied by a combination of high-voltage short pulse discharge to break down the gap between the electrodes and constant power supply to sustain a long duration spark, producing constant voltage and current profiles. The duration of the first trigger spark was shorter than 500 ns and the subsequent main spark was adjustable (5 μs to 10 ms) via a timing circuit. The voltage was measured with a voltage meter (Tektronix, P6015A)