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Theoretical and experimental study of the inhibition and inert effect of HFC125, HFC227ea and HFC13I1 on the flammability of HFC32

*Zhao Yang**, *Huanwei Liu, Xi Wu*

Thermal Energy Research Institute, Tianjin University, 92 Weijin Road, Tianjin 300072, PR China

ABSTRACT

HFC32 is a potential alternative refrigerant with excellent thermal performance, but the flammability is a main obstacle for its applications. The group contribution method is utilized to analyze the inhibition efficiency of non-flammable refrigerants in binary mixtures. Furthermore, a novel equation of predicting the minimum inerting concentration of nonflammable refrigerants has been proposed by analyzing the variation of the flame propagation velocity and the flammable refrigerant concentration. Experimental studies of the explosion limits of HFC125/HFC32, HFC227ea/HFC32 and HFC13I1/HFC32 were carried out and the ranges of explosion limits were obtained. At the same time, the relationship between the maximum charge of the flammable refrigerants and lower flammability limit (*LFL*) was analyzed. The result demonstrates that the proposed novel theoretical equation can effectively predict the minimum inerting concentration of nonflammable refrigerants to flammable refrigerants, and the theoretical results have significance on the security application of the binary mixtures.

Keywords: Explosion limits; Group contribution method; Inhibition efficiency; Inerting concentration; Maximum charge; HFC32

1. Introduction

Recently, the problem of destroying environment by refrigerants is widely focused. CFCs and some HCFCs are gradually substituted by environment-friendly refrigerants according to the Montreal protocol. HCs such as HC290, HC600, and HC600a and HFCs such as HFC32 (CH_2F_2) and HFC152a (CH_3CHF_2) have been considered as alternative refrigerants for CFCs and HCFCs because of their zero ozone depletion potential (ODP), acceptable global warming potential (GWP) and high coefficient of performance (COP). HFC32 with advantages of thermo-physical properties, environmental characteristics, theoretic cycle performance and market availability has been a potential alternative refrigerant (Zhu and Shi, 2009). Han et al. (2007) proposed a new ternary non-azeotropic mixture of R32/R125/R161 as an alternative refrigerant to R407C. The performance of binary refrigerants R32/R290 and R32/R134a (Chen and Yu, 2008; Yu et al., 2010) was investigated as alternatives in heat pump systems. Thermodynamic properties and refrigerating performance of the alternative mixtures R32/R134a in water to water heat pumps have been analyzed by Yang et al. (2002), and its dynamic model and flammability during the leakage process have been investigated; but the possibility of burning and explosive accidents during the leakage process could not be excluded.

Although, HFC32 as an alternative refrigerant has been widely utilized in the heat pump system, its flammability and explosion limits should be investigated for further utilization. Many scholars have paid attention to the flammability of alternative refrigerants. Kondo et al. (2001, 2004) proposed an empirical method called *F*-number to predict flammability limit, the *F*-number is shown as follows:

$$F = 1 - \left(\frac{L}{U}\right)^{0.5} \quad (1)$$

where *L* is the lower flammability limit and *U* is the upper flammability limit. The *F*-number can be empirically

* *Corresponding author*. Tel.: +86 22 27890627; fax: +86 22 27890627.
E-mail address: zhaoyang@tju.edu.cn (Z. Yang).

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Nomenclature

Φ	inhibition coefficient
ΔX_i	the contribution value of the group i
A	constant coefficient
V_u	flame propagation velocity of mixture (m/s)
V_0	flame propagation velocity of flammable refrigerants (m/s)
n_i	the No. i group
n	number of groups
b	the dimensionless coefficient
C_{st}	stoichiometric concentration
C_{O_2}	the oxygen concentration in mixture (%)
C_{in}	the inerting concentration of nonflammable refrigerant (%)
$C_{in\,min}$	the minimum inerting concentration (%)
M_{max}	the refrigerant maximum refrigerant charge (kg)
LFL	lower flammability limit (kg/m^3)
A	house area (m^2)
h_0	the height of the indoor unit (m)
Q	cooling capacity (kW)

expressed by a simple linear combination of the terms which represent chemical groups in the molecule. At the same time, Kondo et al. (2009) investigated the flammability limits of five selected combustible gases (methane, propane, propylene, methyl formate and HFC-152a) each mixed with HFC-125, and analyzed the observed data using the extended Le Chatelier's formula. Blanco et al. (2007) have studied the effect of the temperature to the flammability limits, and found that an increase in temperature would result in an increase in the range of the explosion limits. Zhao et al. (2009) have measured the flammability limits of binary hydrocarbon mixtures in a combustion apparatus using an innovative method developed for this apparatus. Based on many experiment data and maximum R^2 values, a simple way was applied to modify Le Chatelier's law by powering the fuel percentage concentrations. This empirical modification significantly increased the prediction accuracy for industrial purposes. Van den Schoor et al. (2008) calculated the upper flammability limit of methane/hydrogen/air mixtures at elevated pressures and temperatures using three different numerical methods—(1) the calculation of planar flames with the inclusion of a heat loss term in the energy conservation equation, and the application of (2) a limiting flame propagation velocity and of (3) a limiting flame temperature. Pekalski et al. (2005a,b) and Pekalski and Pasman (2009) have tested two mixtures' explosion pressure rise, flame temperature and maximum rate of pressure. Additionally flame development was analyzed by flame emission spectroscopy and the post-oxidation mixture was analyzed by gas chromatography to characterize the oxidation mechanism of the flame. Furthermore, the influence of the ignition delay time on the explosion limits and explosion pressures of n-butane–oxygen mixture and a typical mixture for ethylene oxide production: methane–ethylene–oxygen has been studied by Pekalski et al. (2005a,b). Cammarota et al. (2010) have studied the gas explosions in 51 cylindrical tank reactor with stoichiometric methane–air mixtures at initial pressure and temperature up to 600 kPa and 400 K. Gharagheizi (2009) presented a quantitative structure–property relationship (QSPR) to predict the upper flammability limit of pure compounds from their molecular structures.

As for the inhibition and inert of nonflammable refrigerant, Noto et al. (1998) have investigated the inhibition effectiveness of halogenated compounds, and obtained the inhibition efficiency values of CF_3Br, CF_3I, CF_3H, C_2HF_5, C_2F_6 and CF_4. Hynes et al. (1998) studied the inhibition chemistry of CF_3CHFCF_3 using experimental and numerical modeling. Yang et al. (2004) have studied the inert effect of R134a and R227ea on the explosion limits of six flammable refrigerants, and proposed a model to calculate the explosion limits. Babushok et al. (1998) have dealt with the ultimate limits of chemical contributions to flame inhibition, and demonstrated that for such an inhibitor in a stoichiometric methane/air flame, additive levels in the 0.001–0.01 mole% would lead to decrease in flame velocity of approximately 30%. Moreover, Womeldore and Grosshandler (1999) have investigated the flame of HFC32/air, and the laminar flame speed for HFC32/air mixtures from stoichiometric to lean was also reported. Takizawa et al. (2008) have investigated the burning velocity of six types of fluoropropanes (HFC-281fa, HFC-281ea, HFC-272fa, HFC-272ca, HFC-263ea and HFC-263fb) by applying a spherical flame model to the pressure rise during combustion. Dastidar and Amyotte (2002) have studied the minimum inerting concentrations for combustible dusts in intermediate-scale (1 m^3) and laboratory-scale (20 L), and found that the laboratory-scale inerting levels were higher than intermediate-scale values.

In the present paper, inhibition efficiency of nonflammable refrigerants (HFC125 (CF_3CHF_2), HFC227ea (CF_3CHFCF_3) and HFC13I1 (CF_3I)) in binary mixtures was analyzed based upon the group contribution method, at the same time, a novel method of predicting minimum inerting concentration of nonflammable refrigerants was developed by analyzing the variation of the flame propagation velocity and the flammable refrigerant concentration. Furthermore, experimental studies of the explosion limits of HFC125/HFC32, HFC227ea/HFC32 and HFC13I1/HFC32 were carried out and the ranges of explosion limits were obtained, the relationship between the maximum charge of the flammable refrigerants and lower flammability limit was also analyzed.

2. Theoretical analysis of explosion limits

2.1. *Group contribution method*

Group contribution method has been widely used to predict many thermodynamic properties of substances because of its great generality and highly predictive nature. Comparing with other methods, the group contribution method has one main advantage: it does not require information about critical properties and acentric factor, which may not be available for all components in question, and it is applicable with only information on number of functional groups. Many refrigerants usually contain two or more functional groups, such as H, C, F, CL, Br, I, CH_2, CHF_2 and CF_3, whose contribution values usually keep invariant in different refrigerants.

The group contribution method can be expressed as follows:

$$\Phi = A\left(\sum_{i}^{n} n_i \cdot \Delta\phi_i\right) \qquad (2)$$