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Flammability of Trans-1, 3, 3, 3-tetrafluoroprop-1-ene and its binary blends

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ABSTRACT

R1234ze (E) is regarded as one of the competitive candidates of refrigerants. However its flammability has not been detected out completely. This paper contributed to the fundamental flammable characteristics and influences of R1234ze (E) as well as its blends by mixed with refrigerant R161 (fluoroethane) and R152a (1,1-difluoroethane) theoretically and experimentally. Firstly, the possibility of using R1234ze (E) as a refrigerant was analyzed by means of a technical review. Secondly, the flammability limits of pure R152a, R161 and R1234ze (E) were tested out respectively basing on a new built experimental rig. Continued, the flame image of R1234ze (E) was presented, and which was obtained under the testing condition of higher relative humidity of the surrounding air. In addition, the influence reasons of the relative humidity on the flammability limits of refrigerants were analyzed. Finally, the flammability limits of R1234ze (E)/R161 and R1234ze (E)/R152a were tested out under the different concentration ratios. The results showed that R1234ze (E) possessed a slight flame suppression effect on both R161 and R152a but could not make it unburnt completely under the experimental concentration range. And the flammability limits can be estimated by some a third order polynomial with acceptable accuracy.

1. Introduction

Nowadays, it is becoming urgent and vital to develop the new sustainable refrigerant alternatives which possess zero ODP (ozone depletion potentials), low GWP (global warming potential), non-hypertoxic, acceptable system energy efficiency, chemical stability, suitable operating pressures, safety, as well as the low cost [1–3]. However "no fluid is ideal in all regards" for the new generation refrigerants, as the NIST's (National Institute of Standards and Technology) scientists concluded [4]. Presently, the proposed available solutions of eliminating HCFCs (hydrochlorofluorocarbons) around the world can be addressed in three ways: first, taking the natural substances and their mixtures as refrigerants; secondly, developing the synthetic working fluids such as HFCs (hydrofluorocarbons), HFOs (hydrofluoro-olefins), or HFEs (hydrofluoroether) with low environment effecting features; thirdly, using the mixtures of the natural and artificial synthetic refrigerants [5]. Among these potential working fluids for the refrigeration systems, trans-1, 3, 3, 3-tetrafluoroprop-1-ene (CF_3CHCHF), in HFOs family, has been regarded as one of the most focused candidates.

1.1. Environmental properties of trans-1, 3, 3, 3-tetrafluoroprop-1-ene

Trans-1,3,3,3-tetrafluoroprop-1-ene, also named as R1234ze (E), consists of the carbons (C), hydrogens (H) and fluorine (F) elements, which has a C–C double bond. R1234ze (E) possesses zero ozone depletion potential since the lack of chlorine (Cl) element. The MIR (maximum incremental reactivity) of R1234ze (E) is determined to be 0.09 g O_3/g VOC [6], and its POCP (photochemical ozone creation potential), describing the potential of a molecule to contribute to O_3 formation relative to ethene, is 6.4 [7].

Orkin et al. [8] and Søndergaard et al. [9] concluded that the radiative efficiencies (RE) of R1234ze (E) was located in the range of 0.24–0.27 Wm^{-2} ppb^{-1} with a mean of 0.26 Wm^{-2} ppb^{-1}. While Hodnebrog et al. [10] calculated the RE value of R1234ze (E) was

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Nomenclature

K_i/K_j	Coefficients of the estimation equations
FL_{mix},	the flammability limits of mixtures,%
LFL_{mix}	lower flammability limits of mixtures,%
UFL_{mix}	upper flammability limits of mixtures,%
$f_{an\text{-}F}$	the concentration of anti-flammable refrigerant, %
$f_{ea\text{-}F}$	the concentration of easy-flammable refrigerants, %

Abbreviation

ASTM	American Society of Testing and Materials
COP	Coefficient of performance
DOT	Department of Transportation
LFL	Lower flammability limits, %
LGWP	low global warming potential
GWP	Global warming potential
HCFCs	hydrochlorofluorocarbons
HFCs	Hydrofluorocarbons
HFEs	Hydrofluoroether
HFOs	Hydrofluoro-olefins
HGWP	high global warming potential
MIR	Maximum incremental reactivity
NIST	National Institute of Standards and Technology
ODP	Ozone depletion potential
ORC	Organic Rankine Cycle
PLC	Programmable logic controller
POCP	Photochemical ozone creation potential
RE	Radiative efficiencies
POE	polyol ester
UFL	Upper flammability limit, %

Subscript

SL	the saturated liquid

0.04 Wm^{-2} ppb^{-1} by using absorption cross sections method, and modified the GWP of R1234ze (E) to be even "lower than 1" for 100 years (relative to that of CO_2), which was different from the previous value of about "6" as the UNEP (United Nations Environment Programme) ozone secretariat reported [11].

1.2. Thermophysical properties of trans-1, 3, 3, 3-tetrafluoroprop-1-ene

The molecular weight of R1234ze (E) is 114.0416 kg/mol [12], and its normal boiling point and freezing point are −18.95 °C and −156 °C at 101.3 kPa respectively [13]. The saturated liquid density of R1234ze (E) may be estimated by equations (1)–(2) as Grebenkov et al. proposed [14], and its isobaric specific heat capacity in the liquid phase was measured by Tanaka et al. by using a metal-bellows calorimeter [15]. Some other thermophysical and transport properties have been summarized in Table 1, which indicate its preliminary possibility of being used as a refrigerant in the heating or refrigerating systems.

$$\mathrm{Density}_{SL} = 129.73 \Big/ 0.26475^{(1+K_i)} \tag{1}$$

$$K_i = (1 - T/382.75)^{0.28571} \tag{2}$$

The superscript "SL" is the abbreviation of the saturated liquid; K_i is the connection coefficients of equation; and T is the temperature when calculated the density of R1234ze (E).

Table 1
Fundamental thermophysical properties of R1234ze (E).

Item	Data	References
Critical temperature	109.36 °C	[12]
Critical pressure	3634.9 kPa	[12]
Critical density	[1]486 kg/m^3; [2]4.29 mol/L	[1][13]; [2][12]
Vapour pressure at 25 °C	498.6 kPa	[13]
Heat of vaporisation at boiling point	195.4 kJ/kg	[13]
Vapour thermal conductivity at 25 °C	0.0136 W/m °K	[13]
Liquid viscosity at 25 °C	199.4 μPa s	[13]
Surface tension at −20 °C/20 °C	14.66/8.95 mN/m	[14]
Acentric factor	0.313	[12]
Dipole moment	[1]1.27; [2]1.44	[1][16]; [2][17]
Dielectric Strength (Vapor at 1 atm.)	0.12 kV/mil	[17]

1.3. Solubility of trans-1, 3, 3, 3-tetrafluoroprop-1-ene

R1234ze (E) is volatile, and its volatiles are 100% by volume [13]. The solubility of HFO-1234ze (E) in water is 373 ppm at 20 °C, and the solubility of water in R1234ze is 225 ppm at 20 °C [17].

Some commercial lubricating oils of POE (polyol ester) types were expected to be miscible with R1234ze (E). Motta et al. [18] found out that R1234ze (E) was soluble with the ISO 10 POE oil within the temperature range of −25 to 70 °C. R1234ze (E) possesses the better solubility than R1234yf and R1234yf/R32 blend, with fluoride ion concentrations less than 150 ppm, according to the experimental results of Rohatgi et al.[19] under the stability tests (a sealed tube method, under the condition of 175°Cfor 14 days) for three kinds of lubricants (mixed acid POE, branched acid POE, and PVE oil). Karnaz [20] tested out that the phase separation temperatures of R1234ze (E) with various lubricants (by 10% concentration) were less than −60 °C when mixing with polyol ester oil and 20 °C when mixing with the alkybenzene, polyalpha olefin and mineral oils.

1.4. Possible application of trans-1, 3, 3, 3-tetrafluoroprop-1-ene

R1234ze (E) may be used as a substitute for R113 in the heat transfer system, or as replacer for R11 in the aerosol propellant field, or as one of the new generation refrigerants for replacing HCFCs in refrigeration and replacing HGWP (higher global warming potential) HFCs in air-conditioning sectors [21]. Besides, R1234ze (E) was also considered as a substitute to R134a in the one-component foam applications, and the commercialization of R1234ze (E) for use as a blowing agent has been allowed in the European Union since September 2009 [22].

R1234ze (E) is also welcomed as the refrigerant of chillers, and the practical prototypes have been operated in Europe for about three years. Jribi et al. [23] studied a four bed adsorption chiller that employing highly porous activated carbon of type Maxsorb III as the adsorbent and R1234ze (E) as the refrigerant. Koyama et al. [24] studied the possibility of using R1234ze (E) and R1234ze (E)/R32 as the drop-in substitutes to R410A in heat pumps. After finishing the drop in tests to R134a, Babiloni et al. [25] resulted that the cooling capacity and discharge temperature of R1234ze (E)/R134a (also named R450A) were 6% and 2 °C lower than R134a as average respectively, while its COP (Coefficient of performance) is a little higher 1% approximately.