

Environmental risk assessment of hydrofluoroethers (HFEs)

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Abstract

Hydrofluoroethers (HFEs) are being used as third generation replacements to chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and perfluorocarbons (PFCs) because of their nearly zero stratospheric ozone depletion and relatively low global warming potential. HFEs have been developed under commercial uses as cleaning solvents (incl., HFE-7500, $C_7F_{15}OC_2H_5$; HFE-7200, $C_4F_9OC_2H_5$; HFE-7100, $C_4F_9CH_3$; HFE-7000, $n-C_3F_7OCH_3$), blowing agents (incl., HFE-245mc, $CF_3CF_2OCH_3$; HFC-356mec, $CF_3CHFCF_2OCH_3$), refrigerants (incl., HFE-143a, CF_3OCH_3 ; HFE-134, CHF_2OCHF_2 ; HFE-245mc, $CF_3CF_2OCH_3$), and dry etching agents in semiconductor manufacturing, (incl., HFE-227me, $CF_3OCHFCF_3$). From the environmental, ecological, and health points of view, it is important to understand their environmental risks for these HFEs from a diversity of commercial applications and industrial processes. This paper aims to introduce these HFEs with respect to physiochemical properties, commercial uses, and environmental hazards (i.e. global warming, photochemical potential, fire and explosion hazard, and environmental partition). Further, it addresses the updated data on the human toxicity, occupational exposure and potential health risk of commercial HFEs. It is concluded that there are few HFEs that still possess some environmental hazards, including global warming, flammability hazard and adverse effect of exposure. The partition coefficient for these HFEs has been estimated using the group contribution method; the values of $\log K_{ow}$ for commercial HFEs have been estimated to be below 3.5.

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1. Introduction

Scientists recognized as early as 1974 that the extensive use of chlorofluorocarbons (CFCs) will cause the adverse impact on the dynamic equilibrium of stratospheric ozone [1]. The depletion of the ozone layer, which shields the earth from the harmful effects of the sun's ultraviolet radiation, is caused by chlorine molecules in so-called ozone depleting substances (ODS) that have migrated to the stratosphere and then react catalytically with ozone, thus destroying it. Under a treaty known as the Montreal Protocol on Substances that Deplete the Ozone Layer, which was first established in 1987 and thereafter revised several times, CFCs which are mainly used as refrigerants, cleaning solvents, foam-blowing agents, aerosol propellants and fire-extinguishing agent, are

requested to be phased-out prior to the mid-1990s [2]. Besides participating in the destruction of stratospheric ozone, the release of CFCs may also contribute to global warming, which means that CFCs influence the reflection of infrared radiation from the surface of the earth and thus cause global climate change [3,4].

Hydrochlorofluorocarbons (HCFCs), because of their similarity to CFCs in physiochemical properties, have been used as interim replacements for CFCs [5]. However, it should be noted that HCFCs still contain chlorine, although the release of this chlorine to the stratosphere is expected to be small due to the attenuation processes in the troposphere [4]. According to the updated Montreal Protocol, a virtual phase-out of HCFCs is scheduled by 2020 [6]. On the other hand, perfluorocarbons (PFCs) and hydrofluorocarbons (HFCs) have been used as acceptable alternatives to halon and HCFCs because they possess several characteristics including near-zero ozone depletion potentials (ODP) and high

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thermal stability [7,8]. However, there are some environmental hazards (i.e. long atmospheric lifetime and high global warming potential), which may be still pointed out while using PFCs. Further, the third session of the United Nations Framework Convention on Climatic Change (UNFCCC) was held in Kyoto in December 1997, where PFCs were included into the set of the six major greenhouse gases (GHGs) for negotiation. According to the Kyoto Summit, a voluntary reduction goal of PFCs is scheduled in the 2008–2012 timeframe [8].

As described above, it is urgent to develop new alternatives having similar working properties to CFCs, HCFCs and PFCs. Since the early of 1990s, many applications have begun to use hydrofluorocarbons (HFCs) as friendly replacements. These working fluids contain no chlorine and are thus given ODP of essentially zero. However, some HFCs have relatively significant GWP [9,10]. For example, the GWP of HFC-134a (CF_3CFH_2), the most important HFCs from a commercial point of view (as refrigerant), is eight times less than that of CFC-12 (CF_2Cl_2) but 1300 times greater than that of CO_2 . Incorporating into their emissions to atmosphere from diverse sources such as air conditions, heat pumps and refrigeration devices, HFCs are thus considered as one of six target GHGs under the UNFCCC in 1997. For this reason, third-generation CFCs alternatives are currently considered to be the fluorinated ether series [11–14]. These species are analogous to HFCs with the addition of an ether linkage, reducing the atmospheric lifetimes, leading to lower GWP for these compounds compared to those of HFCs. For example, the atmospheric lifetimes and GWP of HFE-7100 ($\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$) versus HFC-43-10mee ($\text{CF}_3\text{CHFCHFCF}_2\text{CF}_3$), which are used as cleaning solvents in industry, are 0.77 years versus 15.9 years and 45 years versus 1610 years (on the 100-year time horizon relative to GWP of $\text{CO}_2 = 1$), respectively [10]. This paper aims to present the physiochemical properties, commercial uses, and environmental hazards (e.g. global warming, photochemical potential, flammability safety and environmental partition) for selected HFEs (Table 1). Further, the updated data on the toxicity, exposure and potential health risk of commercial HFEs are also summarized in this review paper. In addition, it should be mentioned that also hydrofluoro-

polyethers (HFPE) could be an alternative to CFC, HCFC, HFC and PFC.

2. Properties and uses of HFEs

2.1. Properties

It has been recognized that HFEs can be acceptably used as replacements to CFCs, HCFCs, PFCs and HFCs, because these chemicals possess many similar physical and thermochemical properties to these fluorocarbons, including high volatility, low thermal conductivity, low surface tension, and low or non-flammability. Common commercial/potential replacements mainly include HFE-7500 ($\text{C}_7\text{F}_{15}\text{OC}_2\text{H}_5$), HFE-7200 ($\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$), HFE-7100 ($\text{C}_4\text{F}_9\text{OCH}_3$), HFE-7000 ($\text{C}_3\text{F}_7\text{OCH}_3$), HFC-356mec ($\text{CF}_3\text{CHFCF}_2\text{OCH}_3$), HFE-143a (CF_3OCH_3), HFE-134 ($\text{CHF}_2\text{OCHF}_2$), HFE-245mc ($\text{CF}_3\text{CF}_2\text{OCH}_3$), HFE-227me ($\text{CF}_3\text{OCHFCF}_3$) and so on. The main physical properties of these compounds listed in Table 2 are mainly compiled from the manufacture's product Material Safety Data Sheet (MSDS), many available monographs or books [9,15,16], and references from multidisciplinary journals such as ASHRAE J. [17], ASHRAE Trans. [18], Chem. Tech. [12], Energy [19], Fluid Phase Equilib. [20–25], Int. J. Refrig. [11,13,26], J. Chem. Eng. Data [27–39], J. Chem. Thermodyn. [40,41], J. Fluorine Chem. [14,42,43].

2.2. Uses

Due to the production freezing of HCFCs for non-Article 5 Parties by the end of 2003 and the phase-out of HCFCs by the 2020 in the Montreal Protocol [5], several HFCs have been commercially used as refrigerants for replacing CFCs and HCFCs since the early of 1990s. These HFCs mainly include HFC-134a, HFC-152a, or azeotropic blends of HFCs (e.g. HFC-32/HFC-125) [44]. Thereafter, some HFEs have begun to be successfully developed in the mid of 1990s [12]. Table 1 also lists the principal uses of HFEs in the industrial and commercial purposes. Therefore, their commercial and

Table 1
Chemical identifications and principal/probable uses for selected HFEs

HFEs	Formula	CAS registry number	Principal/probable uses
HFE-125	$\text{CF}_3\text{OCF}_2\text{H}$	3822-68-2	Refrigerant
HFE-134	$\text{CHF}_2\text{OCHF}_2$	1691-17-4	Refrigerant, blowing agent
HFE-143a	CF_3OCH_3	421-14-7	Refrigerant
HFE-227me	$\text{CF}_3\text{OCFHCF}_3$	2356-62-9	Dry etching agent, refrigerant
HFE-245mf	$\text{CF}_3\text{CH}_2\text{OCF}_2\text{H}$	1885-48-9	Blowing agent, refrigerant
HFE-245mc	$\text{CF}_3\text{CF}_2\text{OCH}_3$	22410-44-2	Refrigerant, blowing agent
HFE-254pc	$\text{CHF}_2\text{CF}_2\text{OCH}_3$	425-88-7	Refrigerant, blowing agent
HFE-356mec	$\text{CF}_3\text{CHFCF}_2\text{OCH}_3$	382-34-3	Blowing agent, refrigerant
HFE-356mff	$\text{CF}_3\text{CH}_2\text{OCH}_2\text{CF}_3$	333-36-8	Refrigerant
HFE-7000 (HFE-347mcc)	$n\text{-C}_3\text{F}_7\text{OCH}_3$	375-03-1	Cleaning solvent, refrigerant
HFE-7100 (HFE-449mccc)	$\text{C}_4\text{F}_9\text{OCH}_3$	163702-08-7/163702-07-6	Cleaning solvent
HFE-7200 (HFE-569mccc)	$\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$	163702-05-4/163702-06-5	Cleaning solvent
HFE-7500	$\text{C}_7\text{F}_{15}\text{OC}_2\text{H}_5$	297730-93-9	Cleaning solvent

Table 2
Physical properties for selected HFEs

HFEs	Molecular weight	Boiling point (K)	Critical temperature (K)	Critical pressure (MPa)	Critical molar volume (cm ³ /mol)
HFE-125	136	235	354.4	3.631	236.1
HFE-134	118	279.4	420.3	4.228	212.9
HFE-143a	100	249.4	377.9	3.635	215.1
HFE-227me	186	263.0	372.4	2.333	319.6
HFE-245mf	150	302.2	444.0	3.420	291.0
HFE-245mc	150	278.4	406.8	2.887	294.7
HFE-254pc	132	310.4	463.7	3.560	276.2
HFE-356mec	182	327.5	474.2	2.944	357.6
HFE-356mff	182	336.9	476.3	2.783	364.0
HFE-7000 (HFE-347mcc)	200	307.2	437.7	2.481	377.4
HFE-7100 (HFE-449mccc)	250	334.2	468.5	2.228	450.5
HFE-7200 (HFE-569mccc)	264	349.2	482.0	1.976	509.7
HFE-7500	414	403.2	534.2	1.550	752.7

industrial uses such as refrigerant, cleaning solvent, foaming agent and dry etching agent are further described as follows.

2.2.1. Refrigerant

Prior to 1990, the majority of domestic refrigerators, freezers and air conditioners use CFC-12 and CFC-11 as the working fluids due to their thermodynamic properties, chemical stability, non-flammability and non-toxicity. With the recognition that the production of CFCs and HCFCs (as interim replacements for CFCs) will be totally banned and the existing appliances and equipments will ultimately need to be replaced, it is expected that HFCs will be more widely used as promising alternative refrigerants in the near future. However, it is again emphasized that a significant consideration in using HFCs is that they have been targeted as GHGs in the Kyoto Protocol. It is thus expected that some HFEs will gradually increase with its more extensive applications because of their lower cost than HFCs. As shown in Table 1, HFEs such as HFE-125, HFE-134, HFE-143a, HFE-227me, HFE-245mf and HFE-245mc can be used as potential refrigerants based on their excellent properties such as thermal stability, cycle performance, flammability, toxicity and tropospheric lifetime [12–14,45,46].

2.2.2. Cleaning solvent

In the past decade, the most common organic cleaning solvents applied in the electronic components, precision cleaning and metal finishing were chlorinated solvents (i.e. CFC-113 and 1,1,1-trichloroethane) and HCFCs (i.e. HCFC-141b and HCFC-225ca/cb). However, these substances were also phased-out in accordance with the Montreal Protocol [5]. Although there are many available methods or alternatives (incl., non-cleaning process, semi-aqueous cleaner, aqueous cleaner, supercritical fluid cleaner, plasma cleaning, mechanical cleaning etc.) for reducing or eliminating fluorocarbons in industry [44,47,48], it is necessary to use HFCs or HFEs as cleaning solvents in the some precision processes or equipments. Precision cleaning must be performed on

equipment that requires a high level of cleanliness to keep the working components operating effectively. Several electronic parts, aerospace military, medical, and analytical equipments/instruments use these solvents to ensure the extreme level of cleanliness and product integrity required. Currently, the only promising HFC in precision cleaning is HFC-43-10mee (1,1,1,2,3,4,4,5,5,5-decafluoropentane), which has being used for replacing HCFCs (i.e. HCFC-141b and HCFC-225ca/cb). However, the chemical material will be eventually phased-out under the Kyoto Protocol. HFEs were first introduced in 1996 as an environmentally acceptable alternative to CFCs, HCFCs and HFCs [49]. Currently, the most widely used HFEs series in industry include HFE-7500 (C₇F₁₅OC₂H₅), HFE-7200 (C₄F₉OC₂H₅), HFE-7100 (C₄F₉OCH₃) and HFE-7000 (*n*-C₃F₇OCH₃) because of their physical properties in similarity to HCFC-141b. Due to their physical properties (i.e. low solubility and heavy density), these cleaning solvents could be termed as dense non-aqueous phase liquid (DNAPL), examples of which include trichloroethylene and perchloroethylene, from a leakage or illegal dumping [50].

2.2.3. Blowing agent

Prior to 1996, CFCs (esp. CFC-11) were widely used as blowing agents in the production of flexible and rigid foam plastics that were applied to thermal insulation and packages [44,51]. With the implementation of the Montreal Protocol, alternatives to CFCs in the production of foam plastics are needed urgently. Presently, HCFCs are considered as interim replacements because they possess many properties similar to those of CFCs. HCFC-22 and HCFC-141b have, so far, been the primary substitutes for CFCs in industry. Although HCFCs have been used as blowing agents instead of CFCs to produce appliance (e.g. refrigerators and freezers) insulation, they are still phased-out due to the significant contribution to the greenhouse effect or global warming. On the other hand, HFC-245fa (1,1,1,3,3-pentafluoropropane) and HFC-365mfc (1,1,1,3,3-pentafluoro-*n*-butane) will be rapidly used as available alternatives to HCFCs in the near future [52].

According to the thermal conductivity, some HFEs are potential alternatives to the traditional blowing agents, including HFE-245mf, HFE-245mc, HFE-254pc and HFE-356mec [12,31,33,42,53].

2.2.4. Dry etching agent

Prior to mid-1990s, the most commonly used PFCs in semiconductor industry were CF_4 and C_2F_6 for the purpose of dry etching on the surface of wafer. Due to the goals for reduction by the Kyoto Protocol, several PFCs, including C_3F_8 and $c\text{-C}_4\text{F}_8$, have been used as substitutes for CF_4 and C_2F_6 because of their relatively smaller GWP [8]. It is well known that the etching either chemical solution (wet) or reactive gas plasma (dry) is the process of removing exposed SiO_2 thin-film in the pattern formed by photoresist exposure and development. Dry etching provides a higher resolution than wet etching and therefore is increasingly being employed as circuit elements become smaller [54]. Due to the same reasons as HCFCs and HFCs, the phase-out of production of these GHGs under the Kyoto Protocol and its amendments will be effective in the future. The regulation stimulated efforts to search for acceptable alternatives to dry etching agents. Currently, some HFEs have been proposed as for use as clean etching agents for semiconductor manufacture, including HFE-227me (CF_3OCHF_3) [55] and $\text{CF}(\text{CF}_3)\text{CF}_2\text{OCHF}_3$ [56].

2.2.5. Other applications

Some applications have been introduced or used as carrier solvents for coatings, and lubricants or friction-reduction agents on devices such as surgical knife blades [49].

3. Environmental hazards of HFEs

The fact that any organic chemical has the potential to impact the environments has been known for many years. HFEs, also considered as volatile organics, have extremely attractive properties, particularly high volatility and hydrophobicity compared to similar chemicals such as saturated fluorocarbons and ethers. It means that the atmosphere is the most likely fate for their emissions. The different environmental hazards, such as global warming, photochemical potential, flammability, and partition coefficient, between them, as summarized in Table 3. These issues are further discussed below.

3.1. Global warming

Several anthropogenic compounds including HFEs are once emitted into the atmosphere that may cause the earth's average temperature to rise, which is called global warming, or greenhouse effect. It means that these so-called greenhouse gases (GHGs) or radiatively-active gases influence the reflection of infrared (IR) radiation from the surface of the earth that they absorb strongly in the window region (8–12 μm) of the

IR spectrum. On the other hand, the atmospheric lifetimes of certain HFEs can be relatively long, resulting in a significant contribution of these compounds to global climatic changes on the time horizon. Therefore, the global warming potential of a compound is generally defined as a measure of its radiative forcing relative to a given reference compound integrated over a given time horizon [57].

As seen in Table 3, the global warming potentials (GWP) for selected HFEs are approximately linear with atmospheric lifetime. Basically, the atmospheric lifetimes and GWP of most HFEs are very similar to those of HFCs and HCFCs while they have relatively smaller values of these environmental properties compared to those of CFCs and PFCs because these replacements contain one or more C–H bonds, which are susceptible to attack by hydroxyl radicals and hence shorter atmospheric lifetimes in the troposphere [9,10,58,59]. For example, compared to HCFC-123 (GWP=90), HFC-134a (GWP=1300) and HFE-143a (GWP=660), the GWP values of CFC-113 ($\text{CCl}_2\text{FCClF}_2$) and PFC-116 (CF_3CF_3) are relatively high at about 5000 and 9200, respectively. It is noted that the GWP values of some HFEs (i.e. HFE-125, HFE-134 and HFE-227me) are substantially greater than CO_2 as seen in Table 3. Hence, though they are currently used in much smaller quantities than HFCs, PFCs and HCFCs, it is possible at this point to eliminate or reduce these HFEs emissions.

3.2. Photochemical potential

From the viewpoint of chemical structures and physical properties, HFEs belong to volatile organic compounds (VOCs), which have a high vapor pressure that allows them to evaporate quickly. Hence, these organic substances are volatile and insoluble in water. Following release into the environment, these compounds possibly reside in the lower atmosphere (i.e. troposphere) where they are photochemically oxidized into a variety of degradation products. As mentioned above, HFEs do not contain chlorine and are hence not ODS. Also, the presence of C–H bond in HFEs means that they can contribute to the formation of photochemical oxidants in the troposphere, in a similar manner to those of typical VOCs. It has been recognized that hydrocarbon compounds are readily liable to react with OH radical to convert them into carbonyl species, which are then removed by wet deposition via rainfall where hydrolysis will take place, and dry deposition to the surface [60,61]. However, the atmospheric concentration of these degradation products will be extremely small (order of ppb or ppt), indicative of no observable adverse environmental impacts associated with these compounds at such low concentration.

With respect to the gas-phase photochemistry of HFEs, it has been well established in the literature [62–72]. The gas-phase atmospheric oxidation products for selected HFEs are shown in Table 3. For example [70], HFE-7100 ($\text{C}_4\text{F}_9\text{OCH}_3$) is currently used as a cleaning agent in industry; its atmospheric oxidation mechanism is mainly initiated by re-

Table 3

Atmospheric lifetimes, global warming potentials and gas-phase atmospheric degradation products for selected HFEs

HFEs	Atmospheric lifetime (year) ^a	GWP ^b	Degradation products	Reference(s)
HFE-125	165, 165.2	15600, 14000	CF ₃ OC(O)F, CF ₂ O	[62–64]
HFE-134	24.8, 29.7	5800, 5720	CHF ₂ OC(O)F, CF ₂ O	[62–64]
HFE-143a	5.7	656	CF ₃ OC(O)H, CO ₂	[62,63]
HFE-227me	40, 8	4500	FC(O)OCF ₃ , CF ₃ C(O)F	[5,65,66]
HFE-245mf	2.6, 4.9	649	NA ^c	[10,12,67]
HFE-245mc	2.9, 5.1	697	NA ^c	[10,67]
HFE-254pc	1.4, 2.6	353	NA ^c	[10,67]
HFE-356mec	2.6, 0.94	99	NA ^c	[10,67]
HFE-356mff	0.294	39	CF ₃ CH ₂ OCHO	[63,68]
HFE-7000 (HFE-347mcc)	4.7	450	<i>n</i> -C ₃ F ₇ OC(O)H	[69]
HFE-7100 (HFE-449mccc)	5	410	C ₄ F ₉ OC(O)H	[70]
HFE-7200 (HFE-569mccc)	0.77	60	C ₄ F ₉ OC(O)CH ₃ , C ₄ F ₉ OC(O)H	[71]
HFE-7500	2.2	100	<i>n</i> -C ₃ F ₇ CF(OC(O)CH ₃)CF(CF ₃) ₂ , <i>n</i> -C ₃ F ₇ CF(OC(O)HCF)(CF ₃) ₂	[72]

^a Estimated values, which can be mainly calculated by the reciprocal of the pseudo-first order rate constant for its removal by OH radicals in the troposphere.^b Global warming potential with 100-year time horizon (relative to GWP of CO₂ = 1).^c Not available.

action with OH radicals. The fluorinated radical product, C₄F₉OCH₂, is rapidly oxidized with O₂ to give the corresponding peroxy radical C₄F₉OCH₂O₂. The peroxy radical rapidly reacts with trace species (e.g. NO) in the tropospheric atmosphere to give the alkoxy radical C₄F₉OCH₂O, which is probably reacted with O₂ to form the formate, C₄F₉OC(O)H. In contrast, the atmospheric lifetimes of the carbonyl products (i.e. esters) are rather unreactive toward Cl atoms and are likely to be similarly unreactive toward OH radicals. In view of the polar nature of these carbonyl products (e.g. esters, COF₂), the main atmospheric removal processes of these compounds can be possibly via wet deposition, dry deposition, photo-oxidation or hydrolysis in droplets to form degradation products COF₂, CO₂ and other species. Among these degradation products, it is noted that carbonyl fluoride (COF₂) is a powerful irritating gas which was set at 2 ppm as occupational exposure limit by the American Industrial Hygiene Association's time-weighted average (TWA) [73]. The carbonyl fluoride is easily hydrolyzed to form hydrogen fluoride, which is moderately toxic to human by inhalation due to the release of fluoride ions in contact with moist body tissues [74]. Unfortunately, there are no available

data on the atmospheric concentrations of these degradation products.

It has been shown that photochemical smog, which is a complex atmospheric pollutant mixture consisting of ozone, aldehydes, peroxyacyl nitrates, nitrogen dioxide and fine particulates, can cause burning eyes, throat irritation, and difficulty in breathing in many people, especially children and the elderly [60]. Although HFEs are chemically classified as VOCs, they are not legally regulated as VOCs. According to the U.S. EPA's definition in the Federal Register (FR), "VOC means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions" [75]. The regulation was then established based on the atmospheric lifetimes of organic compounds compared to reference compound (i.e. ethane), it would be regarded as a VOC-exempt compound. These compounds could be further announced to have negligible photochemical reactivity in FR and formally listed in the Code of Federal Register (CFR) (i.e. 40 CFR 51.100). Fortunately, most of commercial HFEs listed in Table 4 are on the VOC-exempt lists [75].

Table 4

Environmental hazards for commercial HFEs

HFEs	Flash point (°C)	Autoignition temperature (°C)	Flammability	VOC ^a	Log <i>P</i> _{ow} ^b
			LFL ^c UFL ^d		
HFE-134	NA ^e	NA ^e	3.3–21.3%	NA	−0.317
HFE-356mec	1 (closed cup)	NA	Nonflammable	NA	0.397
HFE-7000 (HFE-347mcc)	NA	415	Nonflammable	No	0.301
HFE-7100 (HFE-449mccc)	NA	405	Nonflammable	No	0.562
HFE-7200 (HFE-569mccc)	NA	375	2.4–12.4%	No	1.053
HFE-7500	NA	332	Nonflammable	No	1.837

^a Volatile organic compound, defined by the U.S. EPA in the Federal Register (FR).^b Octanol/water partition coefficient, estimated by the Meylan and Howard method [81].^c Lower flammability level in air.^d Upper flammability level in air.^e Not available/applicable.

3.3. Fire and explosion hazard

The flash point, autoignition temperature and flammability limits are often used to characterize the fire and explosion hazard of organic liquid and its vapor. However, the flammability limits of organic compounds are generally considered to be the most important safety property while using them in practice. They describe the well-specified range of compositions in which organic vapor–air mixtures will burn or combust with a flame or ignition in air at room temperature and atmospheric pressure [76]. From the view of occupational and environmental safety, this safety feature must be considered to be nonflammable or very low flammability nature while using these HFEs in industry. From the information on the manufacture's material safety data sheets, Table 4 also shows that most of commercial HFEs possesses nonflammable properties except HFE-7200 and HFE-134. However, it is noted that HFE-7200 having the lower flammability limit of 2.4% can be considered as one of the most flammable replacements to CFCs and HCFCs. Also, although most of HFEs possess low- and no-flammability potential at atmospheric pressure and room temperature, these substances can form high- or low-flammability potential with air at increased temperature and pressure [77].

3.4. Partition coefficient

Partition coefficient is empirically derived dimensionless property that describes how an organic substance distributes itself between hydrophobic (lipophilic) phase and aqueous phase. Hence, it is useful for describing and modeling the environmental fate of an organic compound. Because the octanol–water partition coefficient (K_{ow}) characterizes partitioning between aqueous and organic, lipid-like phases, it provides a significant indication of how much of an organic compound will be taken up by aquatic organisms. Due to values of K_{ow} ranging from 10^{-3} to 10^7 , values for K_{ow} are often reported as $\log K_{ow}$ [78]. Generally, organic compounds with high values of K_{ow} tend to be hydrophobic and partition to organic matter, lipids (fat) and soil. Thus, they are less mobile in the environment. Further, the coefficient can be applied in estimating other partition coefficients such as bioconcentration factor (BCF), organic carbon partition coefficient (K_{oc}) and water solubility [78,79].

The reported values of $\log K_{ow}$ for these HFEs were very scarce from the manufactures' material safety data sheets and available references [80]. It is well known that several methods are available for the estimation of K_{ow} for organic chemicals [78]. However, these approaches are somewhat complicated and not ease to use them. In the present paper, a simple group contribution method, or Meylan and Howard [81] method was used for estimating the partition coefficient as follows:

$$\log K_{ow} = 0.229 + \sum n_i f_i$$

where $\log K_{ow}$ is the base 10 logarithm of the ratio the chemical's concentration in octanol to the chemical's concentration in water, n_i the number of groups of type i in the molecule, f_i the contribution of each group to the partition coefficient, and the summation is taken over all groups. To validate the accuracy of the method in the estimation of partition coefficients for commercial HFEs, four common ethers (i.e. $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, diethyl ether; $\text{CH}_3\text{OC}(\text{CH}_3)_3$, *t*-butyl methyl ether; $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$, *n*-butyl ethyl ether; *bis*(2-chloroethyl)ether, $\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$) that are similar in chemical structure to these HFEs were estimated to obtain their partition coefficients, which were then compared to those that reported or measured in the literatures [78,82–84]. According to their molecular structures, the predicted values of $\log K_{ow}$ are given by:

$$\text{diethyl ether: } K_{ow} = 0.229 + 0.5473 \times 2 + 0.4911 \times 2 + (-1.2566) \doteq 1.05$$

$$t\text{-butyl methyl ether: } K_{ow} = 0.299 + 0.5473 \times 4 + 0.2676 \times 1 + (-1.2566) \doteq 1.43$$

$$n\text{-butyl ethyl ether: } K_{ow} = 0.299 + 0.5473 \times 2 + 0.4911 \times 4 + (-1.2566) \doteq 2.03$$

$$bis(2\text{-chloroethyl})\text{ether: } K_{ow} = 0.299 + 0.3102 \times 2 + 0.4911 \times 4 + (-1.2566) \doteq 1.57.$$

The experimental or reported values of diethyl ether, *t*-butyl methyl ether, *n*-butyl ethyl ether and *bis*(2-chloroethyl)ether are 0.89, 1.24, 2.03 and 1.50, respectively. Therefore, the predicted values of K_{ow} for four ethers are in errors within 15%, indicating that the Meylan and Howard method should be a practically useful approach for predicting the octanol–water partition coefficient for commercial HFEs.

Table 4 also lists the estimated values of $\log K_{ow}$ for commercial HFEs. For example, HFE-7500 has the molecular structure $\text{C}_7\text{F}_{15}\text{OC}_2\text{H}_5$. Referring to the contribution groups in the method, this compound can be represented by one $-\text{CH}_2-$ group, one $-\text{CH}_3$ (methyl) group, seven $>\text{C}<$ groups (no hydrogen, single bonds, three or more carbons attached), one $-\text{O}-$ (aliphatic attachment) group and fifteen $-\text{F}$ (aliphatic attachment) groups. The estimated value of $\log K_{ow}$ is thus given by:

$$\log K_{ow} = 0.299 + 0.5473 \times 1 + 0.4911 \times 1 + 0.2676 \times 7 + (-1.2566) + (-0.0031) \times 15 \doteq 1.84.$$

However, the reported $\log K_{ow}$ value for HFE-7500 is 4.9 [80], which is obviously larger than the calculated value (i.e. 1.84) from the Meylan and Howard method.

4. Human toxicity and exposure hazards

Due to their physiochemical properties in similarity to those of HFCs, it is expected that HFEs should have no significant health risk because of the low potential for human toxicity of HFCs from the results of mammalian (i.e. rat)

Table 5
Toxicological data for commercial HFEs

HFEs	Acute lethal concentration (ppm) ^a	Skin irritation	Mutagenicity	Acute oral toxicity (g/kg) ^b	Cardiac sensitization threshold (ppm)	Exposure limit (ppm)
HFE-356mec	NA ^c	Yes	NA	1.26	NA	NA
HFE-7000 (HFE-347mcc)	>30,000	No	Negative	>2	NA	75 ^e
HFE-7100 (HFE-449mccc)	>100,000	No	Negative	>5 ^d	>100,000	750 ^{e,f}
HFE-7200 (HFE-569mccc)	>92,000	No	Negative	>5	>20,000	200 ^e
HFE-7500	>100,000	No	Negative	>2	NA	750 ^e

^a The concentration lethal to 50% of a population (rat) by 4-h inhalation.

^b LD₅₀.

^c Not available.

^d Practically non-toxic.

^e 8-h Threshold limit value-time-weighted average, authorized by 3M Co.

^f American Industrial Hygiene Association (AIHA) Workplace Environmental Exposure Limits (WEEL) based on 8-h time-weighted average.

tests [3]. With respect to the toxicological profiles for commercial HFEs, there are no available data in the literature. According to the limited references [14,80,85], and material safety data sheet from the manufacturers, there are no significant evidences to support the assumption of carcinogenicity, mutagenicity, reproductive/developmental and other chronic effects for HFEs. As shown in Table 5, commercial HFEs briefly exhibit relatively low toxicity from the results of acute toxicity tests. For example [80], rat LD₅₀ values of HFE-7500 for dermal, inhalation and oral (5 days) exposure were >2000 mg/kg, 10,000 mg/L and >2000 mg/kg, respectively. Incorporating into both the concepts of biotransformation mechanism of HFCs [3], and atmospheric degradation mechanism of HFEs, it is possible to undergo cytochrome P450-catalyzed oxidation reactions as the occupational overexposure to HFEs. Evidently, some trace degradation toxics (e.g. hydrogen fluoride) may be formed in the body tissue. The situation is analogical with the formed trifluoroacetic acid (i.e. TFA) from HFC-134a, which has been detected both at various environmental water sources [86], and in urine [87].

The most significant response under the overexposure circumstances may be central nervous system (CNS) depression and/or cardiac sensitization related to the anesthetic properties of HFEs due to their relatively acute toxicity. On the other hand, the risk to HFEs from occupational exposure is generally discharges in high concentrations over short periods of time that occur infrequently. Accordingly, the acute inhalation toxicity data associated with exposure to HFEs are (1) no observed adverse effect level (NOAEL) or no observed effect level (NOEL), (2) lowest observed adverse effect level (LOAEL) or lowest observed effect level (LOEL), and (3) lethal concentration (LC₅₀) or approximate lethal concentration (ALC) [88]. Table 5 also summarizes cardiotoxicity values for commercial HFEs, which are also compiled from the manufactures' material safety data sheets and available references [80,85]. From the 28-day oral gavage study, it was reported that the NOEL and LOEL of HFE-7500 were estimated as 200 and 1000 mg/kg, respectively [80]. Thus, the exposure limits or approximate lethal concentrations of these HFEs could be set at high-level values. It is obvious from

Table 5 that the 750 ppm as an 8-h time-weighted average (TWA) for selected HFEs (e.g. HFE-7100) has recommended as exposure level or exposure guidance level by the American Industrial Hygiene Association's Workplace Environmental Exposure Level (WEEL) [85]. However, there is a noticeable feature in the cases of HFE-7000 and HFE-7200, that the manufacture has adopted 75 and 200 ppm as 8-h TWA exposure limit, respectively. However, there are to exist no available cases in the literature with respect to human risk hazards to overexposure of HFEs. In order to prevent the fluorocarbons from emitting to the workplace atmosphere and reduce the exposure risk, the blowing agent in the foaming insulation materials shall be recycled with the freezing system or adsorption equipment during the operation.

5. Conclusions

The Montreal Protocol and Kyoto Protocol have agreed to call for the phase-out and/or voluntary reduction on the production and emissions of HCFCs, PFCs and HFCs in the near future. Currently, hydrofluoroethers (HFEs) are being used as third generation replacements to them. Though HFEs discussed in this review paper have been exempted from the U.S. EPA's definition of volatile organic compounds (VOCs) due to their negligible effects on photochemical smog contribution, there are few HFEs to still possess some environmental hazards, including global warming, flammability hazard and adverse effect of exposure. For the protection of the environmental hazard and of human health, the emission of organic vapors containing HFEs in the workplace environment needs to be mitigated and even prevented. One of the most available control/prevention technologies employed for these purposes is to adopt new, environmentally friendly alternatives to HCFCs and HFCs. Some HFEs such as HFE-7500 (C₇H₁₅OC₂H₅) are being considered to replace HCFCs, HFCs and chlorinated solvents in applications in the cleaning of electronic components, and the heat transfer system due to their relatively low global warming potential and very low toxicity.

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