

Analysis and hazard evaluation of heat-transfer fluids for the direct contact cooling system

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Abstract : This paper discusses several low-temperature heat-transfer fluids, including water-based inorganic salt, organic salt, alcohol/glycol mixtures, silicones, and halogenated hydrocarbons in order to choose the best heat-transfer fluid for the newly designed direct contact refrigeration system. So, it contains a survey on commercial products such as propylene glycol and potassium formate as newly used in super market and food processing refrigeration. The stability of commercial fluids at the working temperature of -20°C was monitored as a function of time up to two months. And organic and inorganic compositions of candidate fluids were obtained by analytical instruments such as ES, XRF, AAS, ICP-AES, GC, and GC-MS. Analysis results indicate that commercial propylene glycol is very efficient and safe heat transfer fluids for the direct cooling system with liquid phase.

Key words : heat transfer fluid, propylene glycol, potassium formate, GC-MS

1. Introduction

There are many conventional heat transfer processes that act to transfer thermal energy from an object through the physical contact with a heat transfer fluid that is at a temperature colder than the object. A number of organic and inorganic fluids have been studied as heat transfer fluids for low temperature heat transfer processes.¹⁻⁹

Direct expansion systems commonly used in supermarket and food processing refrigeration are normally used with considerable amounts of chloro-fluorocarbons(CFCs) and hydrofluorocarbons(HFCs). However, those substances have given rise to

environmental concerns due to their ozone depletion and global warming potential.¹⁰ Compared to direct expansion systems, the content of refrigerant can be reduced significantly in secondary cooling systems. Secondary refrigeration is more efficient than direct refrigeration with liquidized gas (liquid nitrogen, ammonia, etc.) or mechanical refrigeration with a fluorocarbon-based refrigerant.¹¹⁻¹⁴

The advantages of secondary refrigeration are much less primary refrigerant use, fewer refrigerant leaks, fewer service requirements, and more stable process temperatures. However, the extra cost for pumps and heat exchangers of the secondary loop are required for secondary refrigeration as well as

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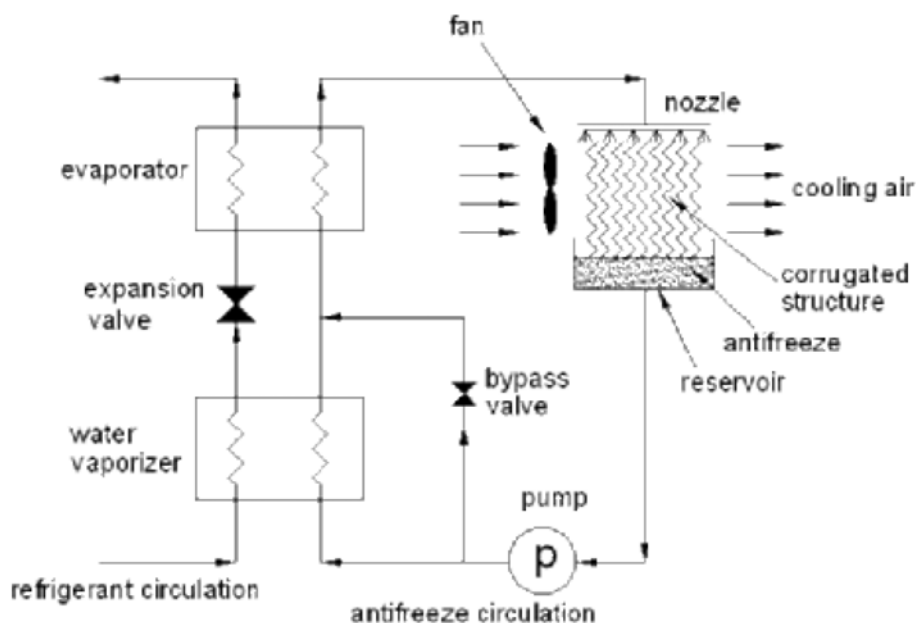


Fig. 1. Schematic diagram of the direct contact cooling system.

the additional cost of electric power. Another problem of secondary refrigeration system is the ice generation from the water vapour in the air around the system, especially evaporator area. This problem results in the reduction of heat transport properties, increase of electric power consumption, and damage of refrigerating goods.

Because those factors significantly affect economical efficiency, new refrigeration system was developed by our research group.¹⁵ The heat transfer fluid is directly used in the open system and is in contact with the air in order to cool down the environmental temperature. Our new process can solve the condensation problem of water vapour and also show good heat transfer efficiency.

This work contains a survey on the heat transfer fluids as presently used in supermarket and food processing refrigeration and an introduction to the refrigeration system using direct contact method with the heat transfer fluids. This refrigeration type achieves a good economical efficiency, which is due to removal of frost and saving of electric power. It combines the advantageous characteristics of the direct contact for the heat transfer fluid with secondary refrigeration technology. Chemical compositions of

selected heat transfer fluids were characterized by Emission spectrometer (ES), X-ray fluorometer (XRF), Atomic absorption spectrometer (AAS), Inductively coupled plasma atomic emission spectrometer (ICP-AES), and Gas chromatography/mass spectrometer (GC-MS).

2. Experimental

2.1. Design of the refrigeration system

The experiment was performed by using an in-house built refrigeration system. The schematic diagram of the designed refrigeration system is shown in Fig. 1. A detail description of this apparatus and the heat transfer fluid contact system characteristics was presented elsewhere.¹⁵

The refrigeration system is composed of cooling unit using liquid phase, equipment that needs to be cooled, and the transfer piping to that equipment, as well as evaporator, expansion valve, pumps, intermediate tanks, fans, and other components. Air from the outside passes through a fan and then is cooled down by the heat transfer fluid. The low temperature air is directed to the area that needs to be cooled. In a heat transfer fluid contact system, the heat transfer fluid

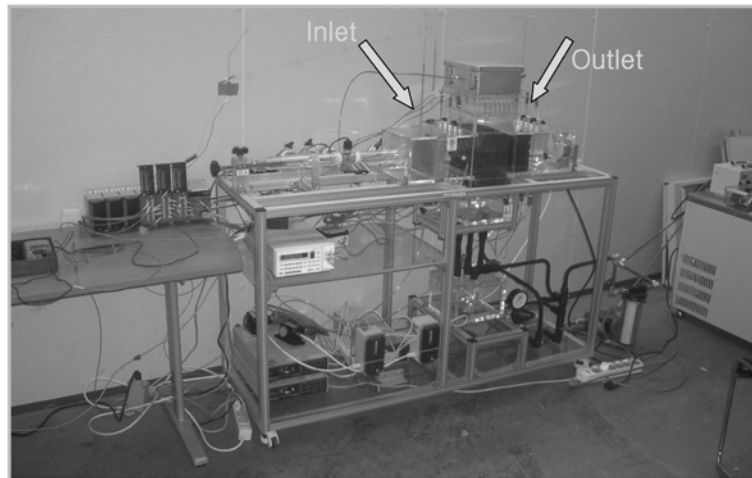


Fig. 2. Photograph of test rig for the direct contact cooling system with measuring devices.

falls down through the fill (corrugated structure) and is collected in the reservoir tank. (Fig. 2) The coolant flow through the fill removes heat from the air to the heat transfer fluid. The coolant leaving the reservoir tank is discharged at the evaporator, passes through flow meter, and goes back to the nozzle on the top of the fluid contact system.

Thermocouples and pressure gauges are mounted in the area to and from the heat transfer fluid contact system for air temperature and pressure measurement. One of the greatest features of this refrigeration system is the direct contact with the liquid-phase heat transfer media.

2.2. Heat transfer fluid analysis

Commercial propylene glycol (Solar P, SKC Korea) and potassium formate (TYFOXIT F30, TYFOROP GmbH, Germany) solutions were used as a heat transfer fluid. Their concentrations were measured by Brix refractometer (PR-32, ATAGO, Japan). Solutions were stored at -20°C to monitor the concentration change of fluids. Concentration and weight measurements were performed depending on the stored time.

The chemical compositions of heat transfer fluids were obtained by using Emission spectrometer (ES) (Emission Spectrograph, Jarrell Ash Co. USA), X-ray fluorometer (XRF) (RIX 2100, Rigaku, Japan),

Table 1. GC/MS Operating Condition

GC Condition			
Hardware	: Varian Star 3400CX		
Column	: J&W Scientific DB-1(60 m×0.32 mm ×1.00 μm)		
Carrier Gas	: He (99.9999%)		
Trapping Temp	: -150°C (5.5 min)		
Desorption Temp	: 170°C (11.30 min)		
	: 200°C (38.20 min)		
Injection volume	: 200 mL		
No	Rate ($^{\circ}\text{C}/\text{min}$)	Target Temp ($^{\circ}\text{C}$)	Duration (min)
1	Initial	-50	7
2	5	140	15
MS Condition			
Hardware	: Varian Saturn2000 GC/MS/MS		
Interface Temp	: 160°C		
Ionization mode	: Electron Impact (EI) Auto		
Scan Time	: 0.90 seconds/scan		
Detection mode	: Scan mode		

Atomic absorption spectrometer (AAS) (Solaar M, Unicam, UK), and Inductively coupled plasma atomic emission spectrometer (ICP-AES) (Polyscan-61E, Thermo Jarrell Ash, USA). Gas chromatography/mass spectrometry (GC-MS) and air GC-MS analyses were carried out by GC-MS (Finnigan Magnum, San Jose, CA USA) and GC/MS/MS (Saturn2000, Varian), respectively. The operating conditions of air GC-MS

Table 2. Properties of major heat transfer fluids

		Heat transfer	Viscosity	Corrosivity	Toxicity	Costs	Thermal stability	
Water-based	Inorganic Salts	CaCl ₂	excellent	very low	very high	non-toxic	low	poor
		K ₂ CO ₃	excellent	very low	very high	non-toxic	low	poor
	Alcohol/ Glycols	Methanol	moderate	low	Low	toxic	low	moderate
		Ethanol	moderate	low	Low	non-toxic	low	moderate
		EG	good	high	Low	toxic	low	good
		PG	good	high	Low	food safe	low	good
	Organic Salts	Potassium acetate	good	low	moderate	food safe	moderate	moderate
		Potassium formate	excellent	very low	moderate	food safe	moderate	moderate
	Hydrocarbon	Aliphatic	moderate	very high	Low	non-toxic	low	moderate
		Aromatic	good	low	Low	toxic	moderate	good
	Halogenated Hydrocarbon	TCE	good	low	Low	environmental concern	high	good
	Terpene		good	low	Low	food safe	very high	moderate
	Silicone		good	high	Low	food safe	very high	moderate

for analysis of volatile organic compounds in heat transfer fluid are listed in Table 1.

3. Results and Discussion

3.1. Selecting an appropriate fluid

Choosing the best heat transfer fluid is critical for the direct contact refrigeration system that is developed by our research group. Wrong selection of the heat transfer fluid for the process can result in additional cost, damage to equipment, and safety problem. Selecting a fluid is a complex task, based on a number of interrelated economic, technical, and environmental concerns. Low-temperature heat transfer fluids must have the following characteristics such as excellent thermophysical properties, compatibility with materials of construction, good stability, non-toxicity, and reasonable cost.

Because of thermophysical properties and numerous other favorable features, water is in general predestined for heat transfer in refrigerant loops. However, addition of a freezing-point depressing material is essential when water is applied to the system below 0°C. Water-based heat transfer fluids used currently belong to one of the following groups: inorganic salt solutions, organic salt solutions, and alcohol/glycol mixtures. There are also synthetic organic fluids

based on silicone oils, halogenated hydrocarbons, hydrocarbons, or terpene mixtures.¹⁶

Table 2 displays some main properties of commonly used low-temperature heat transfer fluids. Traditional inorganic heat transfer fluids containing calcium chloride or potassium carbonate are non-toxic and inexpensive coolants with excellent low-temperature thermophysical properties. However, one main disadvantage of inorganic solutions is its corrosive properties to metals.

Alcohols such as methanol and ethanol are much better compatible with the metals and alloys. However, methanol is very toxic and is excluded from application in food industry that is concerned in this study. Ethanol has very low boiling point so that it is not possible to use in this open system. Glycol-based fluids have several advantages including higher specific thermal conductivity and very low cost over synthetic organic fluids. Regardless higher viscosity at low temperature, non-toxic food grade propylene glycol can be used exclusively for food cooling instead of toxic-classified ethylene glycol.

Organic-salt solutions of potassium acetate or potassium formate can serve as highly efficient cooling fluid for food refrigeration as well as for modern wind tunnel systems. However, there is some limitation for construction metals due to corrosion

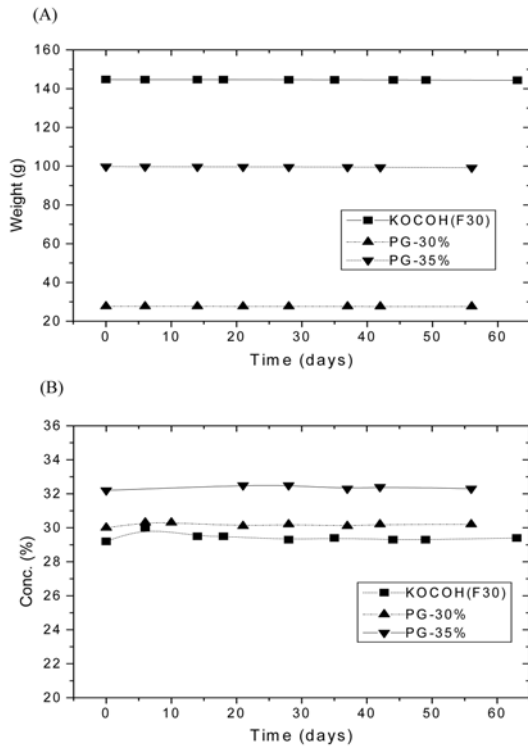


Fig. 3. Weights and concentrations of propylene glycol and potassium formate as a function of exposed time at -20°C.

problems.

Of the heat transfer fluids covered in this paper, propylene glycol and potassium formate aqueous solutions are more proper heat transfer fluids for the newly designed refrigeration apparatus containing the direct contact system with the fluid. One of important criteria for selecting a fluid in this system is non-toxic and environmentally friendly because the heat transfer fluids are used directly for food cooling applications.

3.2. Concentration measurement at operating temperature

Propylene glycol and potassium formate were chosen as a heat transfer fluid for the direct contact refrigeration system. In order to monitor their stability in the open system, the containers with propylene glycol or potassium formate were stored at -20°C and their weights and concentrations were measured.

Fig. 3(A) and Fig. 3(B) show the weight behavior and the concentration behavior for propylene glycol and potassium formate as a function of aging time at -20°C, respectively. The measurements were continued up to two months, at which point the weights and concentrations of propylene glycol and potassium formate still remained at the same value. Both of propylene glycol (30% and 35%) and potassium formate (30%) still have stable properties in the open atmosphere after long-time storage. This means that two candidates are very effective heat transfer fluids for newly designed cooling system.

3.3. Composition analysis

The chemical composition analysis results for commercial propylene glycol and potassium formate are summarized in Table 3. Elemental analyses for two heat transfer fluids were performed by ES and XRF. Small amounts of elements such as Na, Si, B, Al, etc. were observed in fluids. Any toxic composition was not found in the heat transfer fluids investigated in this work.

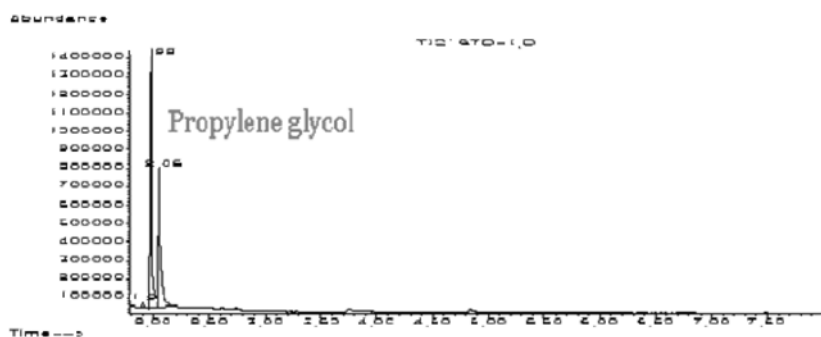
For quantitative analysis of fluids, GC, AAS, ICP-AES, and Karl-Fischer titration method were used (Table 4). The analytical result showed that com-

Table 3. Element information of propylene glycol and potassium formate by ES and XRF.

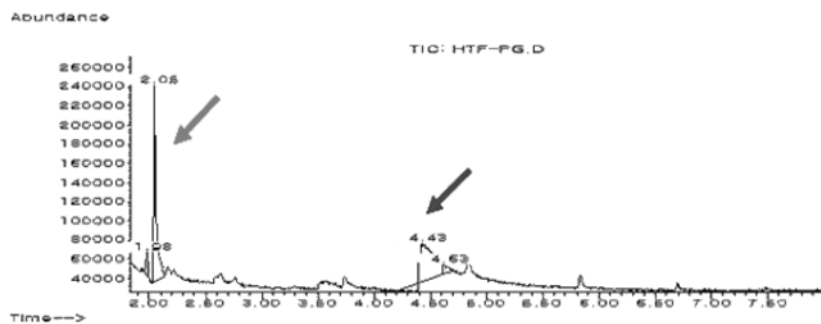
Composition											Analysis Method
Propylene Glycol											ES, XRF
Element (wt. %)	Fe	Si	Mg	B	Na	Ca	Al	S	Cl	Ni	
	$\leq 10^{-4}$	10^{-3}	10^{-4}	$\leq 10^{-3}$	10^{-2}	-	-	$\leq 10^{-3}$	$\leq 10^{-3}$	$\leq 10^{-3}$	$\leq 10^{-4}$
Potassium Formate											ES, XRF
Element (wt. %)	Fe	Si	Mg	B	Na	Ca	Al	S	Cl	Ni	
	$\leq 10^{-4}$	10^{-2}	10^{-3}	10^{-2}	10^{-1}	10^{-3}	10^{-2}	$\leq 10^{-3}$	$\leq 10^{-3}$	$\leq 10^{-3}$	$\leq 10^{-3}$

Table 4. Composition analysis of propylene glycol and potassium formate by GC, AAS, and ICP-AES

	Experimental Composition		Analysis Method
	Composition	(wt. %)	
Propylene Glycol	Propylene glycol	89.5%	GC
	K ₂ HPO ₄	K : 1.38% ⇒ 3.1%	AAS
	H ₂ O	P : 0.52% ⇒ 2.9%	ICP-AES
Total		7.7%	Karl-Fischer
Total		100.2%	
Potassium Formate	K	15.7% ⇒ 33.8% (KO ₂ CH)	AAS
	H ₂ O	66.7%	Karl-Fischer
Total		100.5%	



<Propylene glycol - SKY solar P>



<Standard - Benzotriazole>

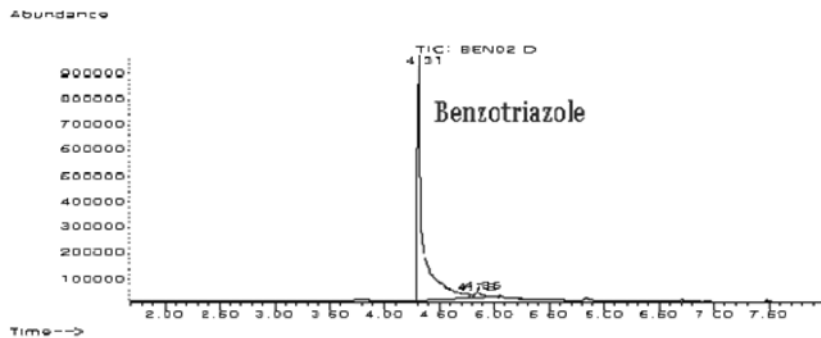


Fig. 4. Chromatogram of propylene glycol by GC/MSD.

Table 5. Quantitative analysis of volatile compositions in laboratory

No	Compound name	Conc.(ppb)	No	Compound name	Conc.(ppb)
1	Dichlorodifluoromethane	0.78	40	3M-1-butene	(-)
2	Chloromethane	0.68	41	Isopentane	0.93
3	1,2-Dichloro-1,1,2,2,-tetrafluoroethane	0	42	1-Pentene	0
4	Vinyl Chloride	0	43	Pentane	0.30
5	Bromomethane	0	44	Isoprene	1.33
6	Chloroethane	0	45	t-2Pentene c-2-pentene	0
7	Trichlorofluoromethane	1.94	46		
8	1,1-Dichloroethylene	0	47	2M-2-Butane	(-)
9	Dichloromethane	9.19	48	2,2-Dmbutane	0
10	1,1,2-Trichloro-1,2,2-trifluoroethane	0.10	49	Cyclopentene	(-)
11	1,1-Dichloroethane	0	50	4M-1-pentene	(-)
12	c-1,2-Dichloroethane	0	51	Cyclopentane	0
13	Chloroform	3.38	52	2M-pentane	0
14	1,2-Dichloroethane	0	53	3M-pentane	0.33
15	1,1,1-Trichloroethane	0	54	2,3-DMbutane	0.56
16	Benzene	0.23	55	2M-1-pentene	0
17	Carbon Tetrachloride	1.88	56	Hexane	4.07
18	1,2-Dichloropropane	0	57	c-2-Hexene	(-)
19	Trichloroethane	0.14	58	t-2-Hexene	(-)
20	c-1,3-Dichloropropene	0	59	Methylcyclopentane	0.45
21	t-1,3-Dichloropropene	0	60	2,4-Dmpentane	0
22	1,1,2-Trichloroethane	0	61	Cyclohexane	0.19
23	Toluene	6.16	62	2M-hexane 3M-hexane	0
24	1,2-Dibromoethane	0	63	2,3-Dmpentane	0
25	Tetrachloroethene	0	64	2,2,4-Tmpentane	0
26	Chlorobenzene	0	65	Heptane	0.27
27	Ethylbenzene	0.82	66	Methylcyclohexane	0
28	m,p-Xylene	1.73	67	2,3,4-Tmpentane	0
29	Styrene	0	68	2M-heptane	0
30	o-Xylene	1.09	69	3M-heptane	0
31	1,3,5-Trimethylbenzene	0	70	Octane	0.26
32	1,2,4-Trimethylbenzene	0	71	Nonane	0
33	m-Dichlorobenzene	0	72	Isopropylbenzene	0
34	p-Dichlorobenzene	0	73	α -Pinene	(-)
35	Isobutane	1.71	74	n-Propylbenzen	0
36	1-Butene	0.56	75	1,3,5-Tmbenzene	0
37	Butane	7.63	76	β -Pinene	(-)
38	t-2-Butene	0	77	1,2,4-Tmbenzene	0
39	c-2-Butene	0			

Table 6 Quantitative analysis of volatile compositions from outlet

No	Compound name	Conc.(ppb)	No	Compound name	Conc.(ppb)
1	Dichlorodifluoromethane	0.69	40	3M-1-butene	(-)
2	Chloromethane	0.75	41	Isopentane	0.69
3	1,2-Dichloro-1,1,2,2,-tetrafluoroethane	0	42	1-Pentene	0
4	Vinyl Chloride	0	43	Pentane	0
5	Bromomethane	0	44	Isoprene	1.23
6	Chloroethane	0	45	t-2Pentene c-2-pentene	0
7	Trichlorofluoromethane	1.88	46		
8	1,1-Dichloroethylene	0	47	2M-2-butane	(-)
9	Dichloromethane	83.73	48	2,2-Dmbutane	0
10	1,1,2-Trichloro-1,2,2-trifluoroethane	0	49	Cyclopentene	(-)
11	1,1-Dichloroethane	0	50	4M-1-pentene	(-)
12	c-1,2-Dichloroethane	0	51	Cyclopentane	0
13	Chloroform	20.45	52	2M-pentane	0
14	1,2-Dichloroethane	0	53	3M-pentane	0.25
15	1,1,1-Trichloroethane	0	54	2,3-DMbutane	0.22
16	Benzene	0.22	55	2M-1-pentene	0
17	Carbon Tetrachloride	0	56	Hexane	1.67
18	1,2-Dichloropropane	0	57	c-2-Hexene	(-)
19	Trichloroethane	0.11	58	t-2-Hexene	(-)
20	c-1,3-Dichloropropene	0	59	Methylcyclopentane	0.26
21	t-1,3-Dichloropropene	0	60	2,4-Dmpentane	0
22	1,1,2-Trichloroethane	0	61	Cyclohexane	0.18
23	Toluene	4.83	62	2M-hexane 3M-hexane	0
24	1,2-Dibromoethane	0	63	2,3-Dmpentane	0
25	Tetrachloroethene	0	64	2,2,4-Tmpentane	0
26	Chlorobenzene	0	65	Heptane	0
27	Ethylbenzene	0.66	66	Methylcyclohexane	0
28	m,p-Xylene	1.15	67	2,3,4-Tmpentane	0
29	Styrene	0	68	2M-heptane	0
30	o-Xylene	1.13	69	3M-heptane	0
31	1,3,5-Trimethylbenzene	0	70	Octane	0.13
32	1,2,4-Trimethylbenzene	0	71	Nonane	0
33	m-Dichlorobenzene	0	72	Isopropylbenzene	0
34	p-Dichlorobenzene	0	73	α -Pinene	(-)
35	Isobutane	1.74	74	n-Propylbenzen	0
36	1-Butene	0	75	1,3,5-Tmbenzene	0
37	Butane	7.54	76	β -Pinene	(-)
38	t-2-Butene	0	77	1,2,4-Tmbenzene	0
39	c-2-Butene	0			

mercial propylene glycol contained 89.5% of propylene glycol and about 3% of K_2HPO_4 . And AAS data for commercial potassium formate indicated 33.8% of CHO_2K . Hazardous materials were not found in these candidate heat transfer fluids.

Analysis for organic compounds in heat transfer fluid was conducted by GC-MS. As shown in Fig. 4, there was not observed any hazardous organic compounds in heat transfer fluid (propylene glycol) except one specific peak, even though there were several toxic materials found in potassium formate. This specific peak was identified as benzotriazole by MSD. In newly designed direct refrigeration system with liquid phase, safety is an essential requirement, so that the air GC-MS analyses of gas samples were revealed a complex mixture made up of organic compounds, which were identified by matching spectra with those in the Saturn library and were quantified by the VOC standards (Table 5 and 6). Canister is mounted in the area to and from the heat transfer fluid contact system for air GC-MS measurement. Fortunately, benzotriazole was not found in any air samples because it has high boiling point and is not volatile in this condition.

As shown in Tables, there was not any significant difference between two air samples before and after passing the heat transfer fluids. The amount of chloroform and dichloromethane in air sample after passing the cooling system increased up to 80 ppb and 20 ppb, respectively. However, those concentrations are much lower than the exposure limit in the workplace allowed by health hazard information of U.S. EPA. Therefore, propylene glycol is very suitable heat transfer fluids for the new refrigeration system.

4. Conclusions

The main advantages of the direct contact refrigeration system compared to the existing refrigeration system are preventing the frost near the evaporator (no need of the defrosting cycle), saving the electric power, and prevention of food and system damage.

In order to select the proper heat transfer fluids, several requirements such as thermal transport

properties, compatibility with other materials, long-term stability, economics, and safety were concerned. Therefore, provided specific requirements regarding new system design and fluid selection are taken into consideration, these fluids can serve as highly efficient heat transfer media for food cooling as well as for modern wind tunnel systems.

This paper described the composition analysis of selected fluids that appear to fill the need for a new heat transfer system. The atomic and organic composition of candidate fluids was obtained by analytical instruments such as ES, XRF, AAS, ICP-AES, GC, and GC-MS.

This study clearly demonstrated that commercial propylene glycol is very efficient and safe heat transfer fluids for the direct contact refrigeration system with liquid.

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References

1. ASHRAE. Secondary coolants (brines). In: Handbook of fundamentals. Atlanta: American Society of Heating, Air-Conditioning and Refrigerating Engineers, Inc., (ASHRAE), 1993 [chapter 18].
2. J. Cuthbert, *Chem. Eng. Progress*, **90**(7), 29 (1994).
3. S.C. Mohapatra, *Chem. Eng. Progress*, **97**, 47 (2001).
4. J.H. Hsu, D.J. Loikits, US Patent 5 847 246 (1998).
5. H.L. Febo, Jr., J.V. Valiulis, *Chem. Eng. Progress*, **92**, 52 (1996).
6. P.J. Bowen, *Combust. Sci. Technol.*, **130**, 25 (1997).
7. D. Ballard, W.P. Manning, *Chem. Eng. Progress*, **86**(11), 51 (1990).
8. P. Sukmarg, K. Krishna, W.J. Rogers, K. Kihm, M.S. Mannan, *J. Loss Preven. Process Ind.*, **15**(1), 19 (2002).
9. H.C.G. Fuchs, *Chem. Eng. Progress*, **93**, 39 (1997).
10. M.U. Rowland, *Nature*, **249**, 810 (1974).
11. R. Lugo, L. Fournaison, J.-M. Chourot, J. Guilpart, *Int.*

- J. Refrig.* **25**, 916 (2002).
12. A. Aittomaki, A. Lahti, *Int. J. Refrig.*, **20**(4), 276 (1997).
13. G.G. Maidment, X. Zhao, S.B. Riffat, G. Prosser, *Applied Energy*, **63**, 169 (1999).
14. S.G. Wang, R.Z. Wang, *Renewable Energy*, **30**, 589 (2005).
15. Y. Kim, Y. Shin, Y. Lee, S. Kim, Korea Patent, 2005-004656 (2005).
16. T.C. Marshall, C.R. Clark, D.W. Brewster, T.R. Henderson, *Toxicol. Applied Pharma.*, **58**(1), 31 (1981).

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