

H₂O REFRIGERANT: EXPLOITATION OF DISPERSED WATER

DROPLETS

KUO-MEI CHEN

Department of Chemistry, National Sun Yat-sen University, 70 Lien-hai Rd.

Kaohsiung, 804, Taiwan

Fax: 886-7-525-3912, e-mail: kmchen@mail.nsysu.edu.tw

ABSTRACT

To cope with the mandates imposed by the Montreal and the Kyoto Protocols, halogenated refrigerants will eventually be phased-out. H₂O, a natural working fluid which is environmental-friendly, chemically non-corrosive, non-flammable, and physiologically harmless, can be exploited as a high-performance refrigerant in the 4 ~ -25 °C temperature range. The successful operation of the water refrigeration system is based on the fact that the evaporation rate of the refrigerant is not controlled thermodynamically but kinetically. The refrigeration performance of micron-sized water droplets in a reduced pressure environment has been successfully demonstrated. A testing embodiment could be cooled down from room temperature to -20 °C within 6 minutes, where tap water at a flow rate of 80 mL/min was dispersed into micron-sized droplets by the liquid jet atomization technique. The exploitation of the water refrigerant in replacement of those with environmental and safety concerns is highly expected.

1. INTRODUCTION

Prior to the ratification of the Montreal and the Kyoto Protocols, compression technologies that utilize chlorofluorocarbon (CFC) refrigerants (Midgley and Henne, 1930) have dominated the domestic and the mobile air-conditioning markets for more than six decades. Under the control measures of the Montreal Protocol (UNEP, 2002), CFCs were phased-out on 1 January 1996 and hydrochlorofluorocarbons (HCFCs) will be phased-out on 1 January 2020 in developed countries. To comply with the first phase of the Kyoto Protocol, which has been effective since 1 January 2005, the amount of greenhouse gases emitted by developed countries should be reduced by 5.2% of the 1990 level during 2008–2012 (UNFCCC, 1997). As one of the six greenhouse gases specifically identified in the Kyoto Protocol, hydrofluorocarbon (HFC) refrigerants can no longer be considered as long-term substitutes of CFCs.

To support the sustaining demands on refrigerated products and air-conditioned living spaces of modern societies, entrepreneurs have advocated compression technologies that employ propane, carbon dioxide, and ammonia refrigerants in recent years (Lorentzen, 1995), in spite of the fact that these chemicals exhibit inherent limitations and hazards in safety. This transition stage can be overridden if a high-performance refrigerant which meets all the safety and environmental protection codes, can be identified in time, especially in the fields of domestic refrigeration and mobile air-conditioning systems.

2. ALTERNATIVE TECHNOLOGY

Even though water is an active ingredient in steam jet and absorption ($\text{NH}_3/\text{H}_2\text{O}$ and $\text{LiBr}/\text{H}_2\text{O}$) refrigeration systems (Althouse *et al.*, 1988), their state-of-the-art embodiments can only cool the water reservoir to 4 °C and their sole purpose is to air-condition large facilities. From past experiences, practitioners in the field are convinced that a refrigeration scheme based on a pure water refrigerant can never go beyond the standard freezing point of H_2O (0 °C) (Althouse *et al.*, 1988). On the contrary, a close examination on the temperature domain of metastability for liquid water at one atmospheric pressure reveals that supercooled water (still a liquid) can exist in the temperature range of 231–273 K (Angell, 1983 ; Debenedetti, 2003 ; Mishima and Stanley, 1998). Thermodynamically, the equilibrium vapor pressure differences between the supercooled water and ice are less than 20% in the temperature range of 0 ~ -25 °C (Kraus and Greer, 1984). Thus, the evaporative cooling is operative for both the liquid and solid micro-spheres so long as the external pressure is kept below 0.1 mbar (Kraus and Greer, 1984). In other words, the cooling effect is a kinetic process that relies on the surface area and the vapor pressure at a designated temperature of the refrigerant (Atkins, 1994). The refrigeration performance of the micron-sized water droplets in a vacuum environment (< 0.1 mbar) depends predominantly on the total surface areas of micro-spheres and partially on the relative abundances of these droplets in the supercooled and solid states. In the present work, an alternative technology which is based on dispersed water droplets in replacement of refrigerants with environmental and safety concerns is reported.

3. EXPERIMENT AND RESULTS

A schematic diagram of an experimental embodiment that measures the cooling rates of dispersed water droplets under a reduced pressure environment (< 0.1 mbar) is depicted in Fig. 1.

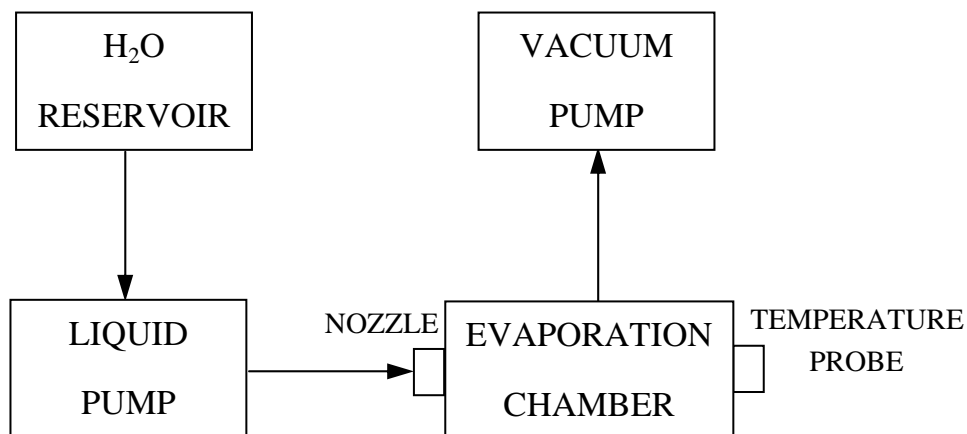


Figure 1: Schematic diagram of the experimental setup. A thermocouple temperature probe is attached to the outer surface of the evaporation chamber to measure its cooling rates.

The liquid pump (NP-CX-100, Nihon Seimitsu Kagaku, Japan) draws tap water from the refrigerant reservoir and forces liquid H_2O through a nozzle into the evaporation chamber. Six pinholes (diameters around 80 μm) are laser-drilled into the stainless steel nozzle plate. The instability of the liquid jets (Lin and Reitz, 1988) which is generated by forcing H_2O through these pinholes, disperses them into micron-sized water droplets. The liquid pump delivers a flow rate of 80 mL/min at a pressure of 30 bar. In the cooling rate measurements, the 1.5 L stainless steel evaporation chamber is pumped by a mechanical vacuum pump

(SD-450, Varian) to maintain an evaporative environment, with a pressure around 0.1 mbar or better. Typical results on the cooling rates of the water refrigerant are summarized in Fig. 2. The testing embodiment could be cooled down from room temperature to $-20\text{ }^{\circ}\text{C}$ within 6 minutes. The ultimate low temperature that utilizes the H_2O refrigerant is around $-25\text{ }^{\circ}\text{C}$, which extends the exploitation scope of the water refrigeration system from the air-conditioning into the sector of refrigerated products.

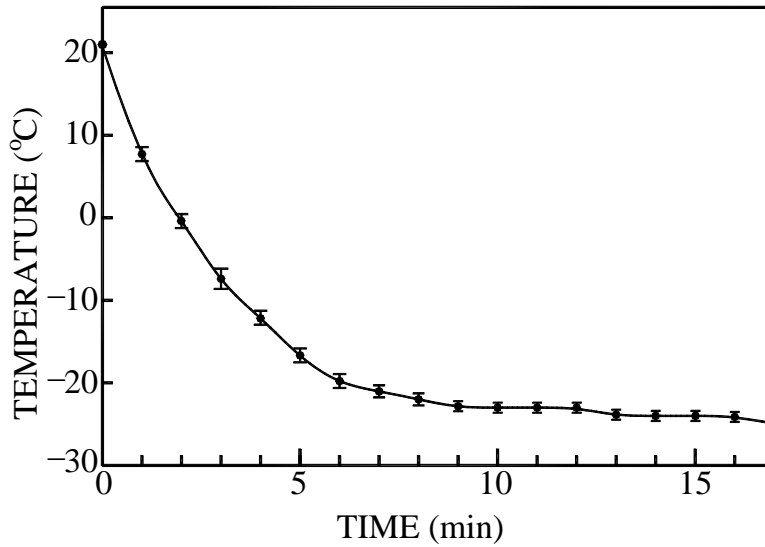


Figure 2: Cooling curve of the experimental embodiment. Error bars (1 standard deviation) are marked on the graph.

4. DISCUSSION AND CONCLUSIONS

The successful operation of the water refrigeration system is based on the fact that its evaporation rate is not controlled thermodynamically but kinetically. According to the kinetic theory of gases (Atkins, 1994), the

rate of evaporation $\frac{dN}{dt}$ is given by

$$\frac{dN}{dt} = \frac{-\Delta P N_A A}{(2\pi MRT)^{1/2}}, \quad (1)$$

where ΔP is the pressure difference between the equilibrium vapor pressure of the liquid at temperature T and the external pressure of the environment, N_A is the Avogadro's number, M is the molecular weight, R is the gas constant, and A is the surface area of the liquid phase. When a 1 cm^3 liquid droplet is dispersed into $1\text{ }\mu\text{m}$ micro-spheres, the surface area is increased by four orders of magnitude. Consequently, the rate of cooling is substantially enhanced by atomizing the liquid into micron-sized droplets. At a water flow rate of 80 mL/min , the cooling capacity of the testing embodiment is estimated to be 34 kJ/min . The essence of the water refrigeration system relies on the physical principle of the kinetic evaporation process. In addition to the environmental and safety advantages in comparison with those of the halogenated refrigerants and other

natural working fluids, the heat of vaporization of the hydrogen-bonded water (Atkins, 1994) ($\Delta H_{vap}^{\circ} = 40.6 \text{ kJ/mol}$) assures a satisfactory economy for every H_2O molecule pumped out of the embodiment, especially for an open-loop system in which H_2O can be expelled to the atmosphere. To improve the performance of the H_2O refrigeration technology, fundamental studies on the evaporation dynamics and reliable methods which can generate submicron-sized water droplets are indispensable (Krämer *et al.*, 1999 ; Smith *et al.* , 2002 ; Stöcket *et al.*, 2005 ; Wood *et al.*, 2002). A patent which describes the technical aspects of the hydrogen-bonded liquid refrigerants and the practical embodiments has been granted (Chen, 2007).

A refrigeration method that enhances the evaporation rate of liquid water by dispersing H_2O into micron-sized droplets is reported. The enclosure probabilities of impurities (nucleation centers) inside the individual H_2O micro-sphere are greatly reduced such that the onset of freezing from the heterogeneous nucleation mechanism is delayed. Combining these two characteristic properties with a reduced pressure environment, we can transform tap water at room temperatures into the supercooled state (down to $-25 \text{ }^{\circ}\text{C}$) in a compact embodiment. In summary, the environmental-friendly, chemically non-corrosive, non-flammable, and physiologically harmless water, in the form of dispersed droplets, can be exploited as a high-performance refrigerant in the $4 \sim -25 \text{ }^{\circ}\text{C}$ temperature range.

REFERENCES

- Althouse, A.D., Turnquist, C.H. and Bracciano, A.F., 1988, *Modern Refrigeration and Air Conditioning*, The Goodheart-Willcox Company, South Holland, Illinois.
- Angell, C.A., 1983, Supercooled water, *Annu. Rev. Phys. Chem.*, vol. 34: p. 593-630.
- Atkins, P.W., 1994, *Physical Chemistry*, Oxford University Press, Oxford, 5th Edition.
- Chen, K., 2007, Atomized liquid jet refrigeration system, US patent 7,159,407 B2.
- Debenedetti, P.G., 2003, Supercooled and glassy water, *J. Phys.: Condens. Matter*, vol. 15: p. R-1669-726.
- Krämer, B., Hübner, O., Vortisch, H., Wöste, L., Leisner, T., Schwell, M., Rühl, E. and Baumgärtel H., 1999, Homogeneous nucleation rates of supercooled water measured in single levitated microdroplets, *J. Chem. Phys.*, vol. 111: p. 6521-7.
- Kraus, G.F. and Greer, S.C., 1984, Vapor pressures of supercooled H_2O and D_2O , *J. Phys. Chem.*, vol. 88: p. 4781-5.
- Lin, S.P. and Reitz, R.D., 1988, Drop and spray formation from a liquid jet, *Annu. Rev. Fluid. Mech.*, vol. 30: p. 85-105.
- Lorentzen, G., 1995, The use of natural refrigerants: a complete solution to the CFC/HCFC predicament, *Int. J. Refrigeration*, vol. 18: p. 190-7.
- Midgley, T. Jr. and Henne, A. L., 1930, Organic fluorides as refrigerants, *Ind. Eng. Chem.*, vol. 22: p. 542-5.
- Mishima, O. and Stanley, H.E., 1998, The relationship between liquid, supercooled and glassy water, *Nature*, vol. 396: p. 329-35.

Smith, J.N., Flagan, R.C. and Beauchamp, J.L., 2002, Droplet evaporation and discharge dynamics in electrospray ionization, *J. Phys. Chem. A*, vol. 106: p. 9957-67.

Stöckel, P., Weidinger, I.M., Baumgärtel, H. and Leisner, T., 2005, Rates of homogeneous ice nucleation in levitated H₂O and D₂O droplets. *J. Phys. Chem. A*, vol. 109: p. 2540-6.

Wood, S.E., Baker, M.B. and Swanson, B.D., 2002, Instruments for studies of homogeneous and heterogeneous ice nucleation in free-falling supercooled water droplets, *Rev. Sci. Instrum.* vol. 73: p. 3988-96.

UNEP (United Nations Environment Programme), 2002, *Production and Consumption of Ozone-Depleting Substances under the Montreal Protocol: 1986-2000*, UNEP, Nairobi, Kenya.

UNFCCC, 1997, *Kyoto Protocol to the United Nations Framework Convention on Climate Change*.