Low-GWP Refrigerants: Options and Issues

Piotr A. Domanski*[(a)], Riccardo Brignoli[(a)],
J. Steven Brown[(b)], Andrei F. Kazakov[(c)], Mark O. McLinden[(c)]

[(a)]National Institute of Standards and Technology, 100 Bureau Dr., Gaithersburg, MD 20899, USA
[(b)]The Catholic University of America, 620 Michigan Ave, NE, Washington, DC 20064, USA
[(c)]National Institute of Standards and Technology, 325 Broadway, Boulder CO 80305, USA
*Corresponding author, Tel: 1-301-975-5877; Fax: 1-301-975-8973
E-mail: piotr.domanski@nist.gov

ABSTRACT

This research explored the possibilities for refrigerants having low global warming potential (GWP) with a particular focus on high-pressure applications. The search for suitable refrigerants relied on screening of a comprehensive database using filters of environmental acceptance, chemical stability in the system, low toxicity, coefficient of performance (COP), volumetric capacity (Q_{vol}), and flammability. Among different screening steps, the performance potential (COP and Q_{vol}) of the candidate fluids was assessed using a simulation model that included both thermodynamic and transport properties, and heat exchangers with optimized refrigerant circuitry. The study showed that the low-GWP refrigerant options are very limited, particularly for fluids with volumetric capacities similar to those of R-410A and R-404A. The identified fluids with good COP and low toxicity are at least mildly flammable. Accepting the thermodynamic argument that viable refrigerants are restricted to small molecules, it is our contention that the screened database contains all suitable candidates and our screening process yielded a list of the 'best' low-GWP fluids. Refrigerant blends allow for tradeoffs between COP, volumetric capacity, flammability and GWP. The probability of finding 'ideal', better-performing low-GWP fluids is minimal.

KEYWORDS: Air conditioning, coefficient of performance, refrigeration, thermophysical properties, working fluids

1. INTRODUCTION

An amendment to the Montreal Protocol adopted in October 2016 mandates a significant reduction of the weighted value of global warming potential (GWP) of fluids used in air-conditioning (AC) and refrigeration equipment. Consequently, hydrofluorocarbon (HFC) refrigerants having a high GWP will be replaced with low-GWP fluids. Earlier research demonstrated the availability of suitable hydrofluoroolefins (HFOs) for low-pressure applications (water chillers) and medium-pressure applications (e.g., automotive AC), with medium-pressure, low-toxicity HFOs that are mildly flammable. However, prior studies did not identify low-GWP, low-toxicity, nonflammable candidates that could replace the high-pressure refrigerants R-410A or R-404A. The goal of this research was to search for suitable low-GWP refrigerants for high-pressure applications.

2. DATABASE SCREENING

To search for the most suitable low-GWP refrigerants, we used the PubChem database listing over 60 million unique chemical molecules. Our study relied on establishing filters representing different refrigerant selection criteria and applying them to these molecules contained. We accepted the thermodynamic argument that viable refrigerants are restricted to small molecules, and we considered PubChem to be exhaustive for such molecules [1].

We limited our search to molecules with 18 or fewer atoms and comprising only the elements C, H, F, Cl, Br, O, N, or S, following the observation that only a small portion of the periodic table would form compounds volatile enough to serve as refrigerants. Despite their ability to deplete stratospheric ozone, we included Cl and Br since molecules including Cl or Br might have a negligible ODP and might be acceptable if they have a very short atmospheric lifetime. These restrictions reduced the pool of molecules for further consideration to 184 000. The next two filters were GWP_{100} and T_{crit}. The PubChem database does not contain these values for the vast majority of the compounds, so most had to be estimated using novel methods developed within this study based solely on the molecular structure. The prediction of GWP_{100} combined estimates of the radiative efficiency and atmospheric reactivity with hydroxyl radicals. The applied filters of $GWP_{100} < 1000$ and $320 K < T_{crit} < 420 K$ reduced the pool of candidates to 138 fluids. The next filters were for chemical stability and toxicity; both were applied manually. Compounds with generally unstable functional groups were dropped from further consideration [1].

3. PERFORMANCE EVALUATION

The filter of 320 K < T_{crit} < 420 K ensured that the accepted 138 low-GWP fluids had the COP and Q_{vol} in a general range of the current refrigerants used in small AC and refrigeration units. For accurate estimations of COP and Q_{vol}, we performed two rounds of thermodynamic cycle simulations at different levels of detail. The second simulation round used an advanced cycle model, which accounts for the effects related to transport properties and for the drop of saturation temperature with respect to pressure, dT_{sat}/dp. The model optimized the refrigerant circuitry in heat exchangers to maximize COP, i.e., it arrived at the optimized refrigerant mass flux that enhanced the refrigerant heat transfer coefficient at an acceptable penalty of pressure drop. This feature is important for a realistic representation of optimized heat exchangers relying on refrigerant forced-convection heat transfer.

Following cycle simulations, we generated a list of 28 single-component fluids deemed to be the best for consideration in small AC systems [2]. In this list, 21 fluids are a subset of the 138 fluids, i.e., those with 320 K < T_{crit} < 420 K after unstable or higher-toxicity fluids were removed along with those having low Q_{vol} or COP. With the intent to produce a complete list of refrigerant options, we added four fluids based on evidence of commercial interest, and an additional three fluids with T_{crit} < 320 K, including carbon dioxide (R-774). HFOs constitute the largest group in the final list. The other fluids are halogenated alkanes, halogenated oxygenates, hydrocarbons, halogenated nitrogen and sulfur compounds, and inorganic compounds. R-744 is the only low-toxicity and nonflammable fluid in the list, but it would operate in a transcritical cycle because of its low T_{crit}.

The identified fluids with good COP and low toxicity are at least mildly flammable. Most of the fluids are relatively large molecules with large molar heat capacities. As such, they experience greater throttling losses in the basic vapor-compression cycle than currently-used HFCs and markedly benefit from the economizer cycle (Figures 1a and 1b). The list includes six novel fluids. None of them are particularly compelling from a performance standpoint, particularly given that the hazards they may present are unknown.

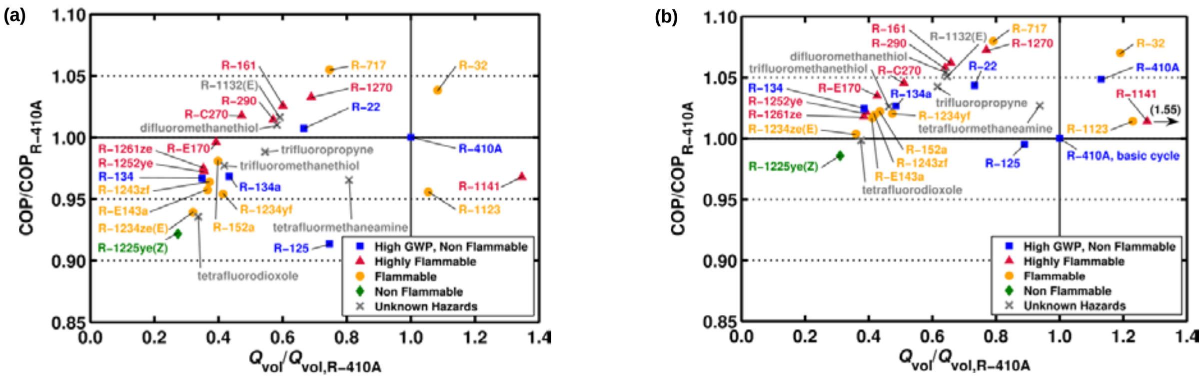

Figure 1: COP and Q_{vol} of selected fluids referenced to R-410A values; (a) basic cycle and (b) economizer cycle; (excludes fluids with low T_{crit}; includes R-22, R-134a, and R-125 for comparison purposes) [2].

4. CONCLUSIONS

Low-GWP refrigerant options are very limited, particularly for fluids with volumetric capacities similar to those of R-410A and R-404A. Fluids with good COP and low toxicity are at least mildly flammable. The probability of finding better-performing, low-GWP fluids is minimal. The limited refrigerant options and environmental concerns make it imperative to use refrigerants judiciously.

ACKNOWLEDGEMENT

This work was supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy under contract no. DE-EE002057 with A. Bouza and B. Habibzadeh serving as Project Managers.

REFERENCES

[1] McLinden, M. O., Brown, J. S., Kazakov, A. F., Brignoli, R., Domanski, P. A, 2017. Limited options for low-global-warming-potential refrigerants. *Nature Communications*, 8:14476, doi:10.1038/ncomms14476.

[2] Domanski, P.A., Brignoli, R., Brown, J.S., Kazakov, A.F., McLinden, M.O., 2017. Low-GWP Refrigerants for Medium and High-Pressure Applications, *Int. J. Refrig.*, 84:198-209, doi:10.1016/j.ijrefrig.2017.08.019.