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Sustainable recycling of refrigerants: Analysis of alternatives

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Abstract

The use of refrigerants has been continuously increasing in thermal control systems employed in residential premises, offices, storage, process operations and many more. Widely used refrigerants such as R-410A have become a target for regulations to prohibit their use because of environmental issues. R-410A is a blend of R-32 (Difluoromethane) and R-125 (Pentafluoroethane). Because of high global warming potential (GWP) of R-125, it has become a target for removal from R-410A and reuse. An additional issue is the recovery of the refrigerant from current and decommissioned thermal control units. This paper reports the results of an investigation related to the separation of refrigeration blend compounds, recycle and reuse of the refrigerant mixture compounds and alternative blend compositions, with emphasis on environmental, health and physical hazards as well as optimal refrigeration cycle operation. Two alternatives for feasibility of operating a continuous separation-recycling process are studied.

Keywords: Refrigerant blends, R-32, R-125, R-410A, recycling, global warming potential, safety-health-environmental hazards.

1. Introduction

Hydrofluorocarbons (HFCs) are known for their excellent performance as refrigeration fluids. Their durability, inertness and thermal stability have made them the selection of choice in air-conditioning (AC) units. Nevertheless, their stability makes their presence persistent when released to the atmosphere, with a lifetime between 15 and 29 years (Xu, 2013). Furthermore, their capacity to absorb infrared light make them potent greenhouse gases (Castro et al. 2021).

R-410A is an HFC-based refrigerant, initially invented and patented by Allied Signal (now Honeywell) in 1991, that became popular as a substitute for R-22 (Chlorodifluoromethane) after the Montreal Protocol (UNEP, 2021) took place. The commercial R-410A consists of 50 wt% of R-32 and R-125 whose individual global warming potential (GWP) values are 677 and 3170, respectively, and giving the blend GWP value of 1923. Note that the mixture of R-32 and R-125 forms an azeotrope at 91 mol% R-32 (Castro et al. 2021). The objective of this paper is checking the feasibility of removal of R-125 from R-410A as well as recycling and reuse of the separated compounds. Monjur et al. (2022) have reported the separation of R-32 and R-125 by a continuous extractive distillation process with ionic liquids as the solvent. The feasibility of this process is compared with a pressure-swing distillation process, which also generates various R-410A blend alternatives. The performance of the generated alternatives is compared in terms of coefficient of performance (COP) of the refrigerant within the refrigeration cycle. Also, the effect of hazardous properties (health, physical and environmental) is considered from the points of view of safe and optimal refrigeration cycle operation.

Because of limited space, calculation details, hazardous properties of chemicals, etc., are not given in this manuscript. They can be obtained from the corresponding author.

2. Data-based Analysis of Opportunities for Recycling of F-gases

According to EU F-Gas legislation, all HFC refrigerants from refrigeration systems and air-conditioning systems must be recovered (European Parliament and Council of European Union, 2014) and replaced. If recovered material is too contaminated for further recycling, it should be decomposed. According to the European Environmental Agency, by 2020, the refrigerant HFC-23 account for nearly 90% of F-gases destroyed in the EU. Considering limitations of resources as well as undesirable impacts, the recovery and reuse of refrigerants is an option worth considering (Castro et al. 2021), provided they satisfy the safety, health and environmental concerns as well as operability of the refrigerant cycles. For R-410A and its components (R-32, R-125) requirements mentioned below are applied:

- Vapor phase contaminants: Air and other non-condensables must be < 1.5% by volume at 25.0 °C
- Liquid phase contaminants: Water must be <10 ppm by weight; all other volatile impurities must be < 0.5 wt%; high boiling residue must be < 0.01 wt%

Note that the above requirements are not an issue as R-410A is considered to be a blend of only R-32 and R-125.

2.1. R-410A recycling capacity limitations

The main use for R-410A as a refrigerant is in air-conditioning and heat pumps. In 2013 around 86% of all R-410A produced was used for HVAC systems only. Therefore, this study has selected R-410A as a representative example for the study of recycling of refrigeration fluids.

The global production of R-410A increased from 193 kMT in 2012 to 238 kMT in 2016, and the estimated production in 2022 will be 292 kMT. China is the leading producer of R-410A, with about 45% of the global production in 2016, followed by North America, with a production share of around 30% (360 Research Reports, 2020). The share of R-410A produced in EU in the years 2009 and 2013 was around 12% (Makhnatch & Khodabandeh, 2019).

Analysis of the technical data on HVAC systems indicate a life cycle of an AC unit is in the range of 10-15 years. Therefore, in China, the USA and the EU, the total maximum capacity of R-410A available for recycling in the years 2022-2027 is expected to be around 12, 8, and 3 MT/h, respectively (assuming 8000 h/yr). To understand the amount of bulk material (AC units) to be recycled, the assumption made is that R-410A can be extracted only from small-scale AC units (less than 150 kg). Based on the available information on commercial AC units, the average unit weights of 70 kg and as a mass fraction of R-410A of 4 wt%. Therefore, to obtain 1 ton of refrigerant, recovery from 26 tons or 370 units of decommissioned cooling devices should be done. Considering an average recovery time from one unit of around 20 min, and costing USD 16 per hour as a median manufacturing operator salary in USA, together with the average mass of refrigerant mentioned above, recovery costs for R-410A in USA would be 2200 $/MT.

2.2. R-410A separation

In the case of R-410A, separation of the pure compounds is complex due to an azeotrope for a R-32 purity of 91% mol. Monjur et al. (2022) proposed separation via extractive distillation with an ionic liquid in a continuous process.

An alternative to solvent-based extractive distillation is pressure-swing distillation if the azeotrope composition changes when the pressure is changed. Figure 1 shows the process flowsheet for separation of R-32 from R-125, along with the changes in the Txy diagrams. In the first column, operation at 17 bara yields a distillate with a near azeotropic composition of 90 mol% R-32 (80 wt%) at a temperature of 25 °C, allowing the use of cooling water in the condenser. Then, pressure is lowered to 1 bara, shifting the system to the right side of the azeotrope and resulting in a bottom product which is 99.5 mol% R-32 (99 wt%). Details regarding the process and the comparative study can be obtained from the authors. Operational expenses derived from consumption of utilities are 18 times higher for distillation at pressure. Since distillation at pressure is more energy intensive than extractive distillation, this result was expected. Nonetheless, when considering the cost of replenishing the ionic liquid BMIN PF_6, processing costs for extractive distillation increase from 0.004 $/hr to 2.4 $/hr, while remaining at 0.07 $/kg for the proposed process. An additional advantage of not using an ionic liquid is that, as seen in section 3.2, the coefficient of performance of the recycled R-32 could be affected considering the low vapour pressures which characterize ionic liquids, even at small concentrations.

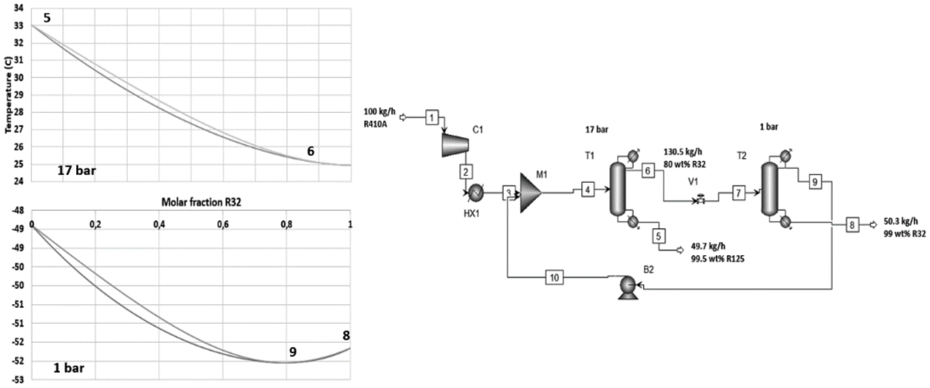


Figure 1: Flowsheet of pressure-swing distillation for separation of R-410A compounds, with Txy diagrams

Note, that the discussion in Section 2.1 indicates that reclaiming enough refrigerant to sustain a continuous process in a processing plant is not feasible, unless a periodic operational policy of collection followed by short periods of operation is applied. The design of the continuous process is sufficiently flexible to allow changes in production rates.

3. Evaluation of Alternatives: Recycle of F-gases

The high-pressure azeotropic distillation method provides opportunities for separation of R-32 and R-125 with individual purities of up to 95 and 99.5 wt%, respectively. In addition to the pure component product streams, the pressure swing distillation process allows intermediate product fractioning resulting in R-32 / R-125 mixtures of different compositions, which are investigated below

3.1. R-32 / R-125 mixture as a blend

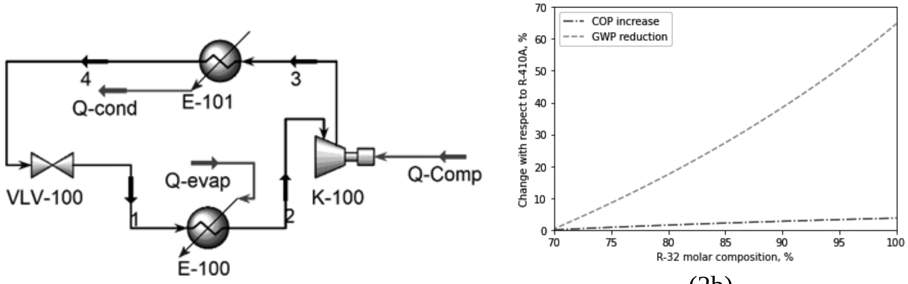
Recently, several options were proposed as a substitute for phasing-out of R-410A. Among the options are:

- Non-flammable (A1 rating) blends: R-448A, R-449A,B,C, R-458A, and R-407C,F with high GWP rating (>1000)
- A2L safety class blends such as R-447A (GWP = 572), R-447B (GWP = 714), R-452B (GWP = 674), with a fraction of R-32 and R-125 in the range of 89.5 – 95.1 and 4.9 – 10.5 wt% respectively

A1-rated refrigerants are available ranging from light commercial systems (0.15 – 5kW) to industrial solutions (up to 10MW). In contrast, A2L refrigerants due to safety concerns have limited use in low-power capacity units (Danfoss A/S, 2022). The full list of patented and approved blends can be obtained from the authors. Tailor-made blends can also be generated (Udomwong et al. 2021).

3.2. Evaluation of performance of R-32 / R-125 blend systems

To investigate the effect of the R-125 composition in the refrigerant mix on the mixture's GWP and coefficient of performance COP a refrigerant cycle (shown in Fig 2a) has been simulated with Aspen HYSYS using the Peng-Robinson equation of state as the thermodynamic model for phase equilibrium. The refrigerant cycle has four operations: compressor, evaporator, condenser, and valve. The ProREFD software (Udomwong et al. 2021) and ChemSub (Syeda et al. 2022) software also allows a detailed cycle simulation, hazardous effects analysis and refrigerant substitution.



(2b)

(2a)

Figure 2: Refrigeration cycle and effect of R-32 composition on COP of refrigeration cycle

At first, the standard composition of R-410A, which is 70 mol% of R-32, was simulated resulting in a GWP of 1924 and a COP of 7.5. It is shown that increasing the composition of R-32 results in a lower GWP but does not decrease the COP (see Fig 2b). A total replacement of R-125 with R-32 towards a pure compound product, results in a GWP reduction of 65% and a COP increase of 4%. Nevertheless, there is an inherent safety risk associated to R-32 as it is classified with a safety level of A2L, meaning that it does not pose a toxicity risk at concentrations of less than or equal to 400 parts per million, but it is a mildly flammable gas. Its flammability limits are between 14.4% to 29.3%, which poses a risk of explosion if leakage occurred in the AC system (Osuagwu, 2022) Conversely, R-410A is classified as an A1 refrigerant (highest rank in safety classification), meaning that it is non-toxic, non-flammable and relatively safe to store, use and distribute (Osuagwu, 2022).

3.3. Evaluation of second life of recycled R-125

R-125 has recently found limited application in other sectors rather than thermal control systems, even though 99% of R-125 produced worldwide by the reporting companies is used as a blend component for commercial refrigerants. It could also be used as a fire suppression agent because it is odorless, colorless, electrically non-conductive, non-corrosive, and leaves no residue. It was also reported to act as a foam-blowing agent (Yelisetty & Visco, 2009) for making polyurethane, as the polyurethane foams are made by reacting a di-isocyanate molecule with a polyol in the presence of a blowing agent. R-125 is to substitute chlorofluorocarbons and hydrochlorofluorocarbons, because of the ozone-depleting potential of the latter ones. It only works as an interim solution because of R125's GWP concerns. According to Karecki (2000), R-125 can also be used as a substitute for 1,1-difluoroethane for a Dielectric Etch Application in an Inductively Coupled Plasma Etch Tool. A comparison of the emissions from R-125/R-152a processes and a reference C_2F_6-based process showed that emissions reductions of 68 to 76% were attainable, in large part due to much higher feed gas conversion efficiency (Karecki, 2000).

4. Conclusions

It is found that, while the separation by ionic liquid based extractive distillation is theoretically feasible, its implementation is not practical as the amount of R-410A available for recovery would not sustain a continuous process. For a processing capacity of 100 kg/h of R-410A, the number of average-size units to be recovered per day is 900. This is equivalent to 270,000 average-size AC units per year, or 4% of the R-410A units that are estimated to go out of service in China in 2022. Considering the vast area for which the availability of refrigerant is calculated, the process capacity is deemed infeasible, while pressure swing distillation is found to give 34 times lower operating costs. Increasing the pressure shifts the azeotrope to 91 mol% of R-32 at 17 bara (from 80 mol% R-32, at 1 bara), making separation of both components possible by shifting between both sides of the azeotrope in two distillation columns operating at 1 and 17 bara. However, both continuous operations need to be operated in a periodic (or batch) mode with periods of collection and short separation operation. Additionally, the presence of ionic liquid in recycled R-32, even at small concentrations, presents a health hazard for humans. Regarding the use of R-32 as a stand-alone refrigerant, coefficient of Performance (COP) value is found to increase by up to 4% with respect to R-410A, while displaying a 65% reduction in GWP. However, the flammability and health hazard concerns for R-32 also need to be considered and a stricter monitoring of the safety issues would need to be implemented. As the ionic liquid does not vaporize, the batch operation mode for ionic liquid based extractive distillation may need new batch operations designs, unlike the organic solvent-based batch extraction operations.

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