Computer-Aided Molecular Design of Alternative Refrigerants

Aniket Chitre and Daniel Freake

1 Introduction and Aim

1,1,1,2-tetrafluoroethane (R134a) is a very commonly used refrigerant, however, as a hydrofluorocarbon (HFC), these are being phased out under the Kigali Amendment to the Montreal Protocol, signed in October 2016 (U.S. Department of State n.d.). HFCs are being phased out due to their high global warming potential (GWP). The aim of this project is to use computer-aided molecular design to propose alternative refrigerants meeting certain process conditions and performance specifications. This project presents a MINLP formulation using group contribution methods and imposing thermodynamical and structural constraints. This was solved using the global BARON solver in GAMS. An integer cut formulation is implemented to propose the 10 best alternative refrigerants, which should be investigated for further study.

2 Problem Formulation

It is assumed that the alternative refrigerant which this study aims to find will be used in a typical refrigeration cycle with an evaporating temperature (T_{evap}) of 272 K and condensing temperature (T_{cond}) of 316 K. Refrigerants are typically halogen derivatives of saturated aliphatic hydrocarbons. However, since this project is a study of potentially new refrigerants, all the groups listed in Table 1 are considered. In this table "r" is used to denote bonds that are to be part of a ring only. The formulation seeks to determine n_i, the number of groups of type i to be included in the synthesised molecule. Variables will be defined on an as-needed basis. A complete listing of variables is included in the appendix.

Acyclic	Cyclic	Halogens	Oxygen group	Nitrogen group	Sulphur group
$-CH_3$	$r-CH_2-r$	$-F$	$-OH$	$-NH_2$	$-SH$
$-CH_2-$	$>CH-r$	$-Cl$	$r-OH$	$>NH$	$-S-$
$>CH-$	$^r_r>C<^r_r$	$-Br$	$-O-$	$^r_r>NH$	$r-S-r$
$>C<$	$r=CH-r$	$-I$	$r-O-r$	$>N-$	
$=CH_2$	$r=C<^r_r$		$>C=O$	$-N=$	
$=CH-$			$^r_r>C=O$	$r-N=r$	
$=C<$			$O=CH-$	$=NH$	
$=C=$			$-COOH$	$-CN$	
$\equiv CH$			$-COO-$	$-NO_2$	
$\equiv C-$			$=O$		

Table 1: Functional groups considered

2.1 Objective Function

Considering the refrigeration cycle in Figure 1 and performing an energy balance on the evaporator, under the assumption that the compressor causes a negligible temperature increase, then we obtain the following equation:

$$Q \approx V_r \rho (T_{evap} - T_{cond})C_{pla} + V_r \rho \Delta H_{ve} \Rightarrow V_r \approx \frac{Q}{(\Delta H_{ve} - (T_{cond} - T_{evap})C_{pla})\rho} \tag{1}$$
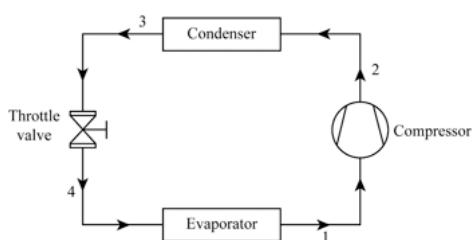

Figure 1: Refrigeration cycle

Where V_r is the volumetric flowrate of refrigerant. To minimise the size of the compressor, one needs to minimise V_r. ΔH_{ve} is the enthalpy of vaporisation at the process evaporating temperature (272 K) and C_{pla} is the liquid heat capacity at the mean process temperature ($T_{avg} = 294$ K). Therefore, according to the above equation, to maximise the efficiency of the refrigeration cycle one needs a high enthalpy of vaporisation (ΔH_{ve}) and low liquid heat capacity (C_{pla}) (Sahinidis et al. 2003). Hence, the proposed formulation of the objective function is:

$$min \; \frac{C_{pla}}{\Delta H_{ve}} \tag{2}$$

Several other formulations are possible for the objective function, however, the one above is followed in line with other papers which have previously studied this problem (Sahinidis et al. 2003). One may in particular wish to include environmental considerations into the objective function. Whilst this is not the approach taken in this project, additional constraints are suggested in section 4, which could be implemented to factor in the environmental impact of alternative refrigerants.

2.2 Constraints

2.2.1 Thermodynamic Constraints

The goal of this project is to identify refrigerants with a better thermodynamic performance than R134a. This translates to a higher ΔH_{ve} and lower C_{pla} than R134a. The properties of R134a are $\Delta H_{ve} = 20.322 \; kJ \; mol^{-1}$ and $C_{pla} = 143.915 \; J \; mol^{-1} \; K^{-1}$ (Rogers & Mayhew 2003). Additionally the project design specification states constraints for the vapour pressure at both evaporating and condensing temperatures, P_{vpe} and P_{vpc}.

2.2.1.1 Heat of Vaporisation

Equations 3 - 8 follow the group contribution method outlined by Joback and Reid to calculate the enthalpy of vaporisation at boiling temperature (ΔH_{vb}), boiling temperature (T_b) and critical temperature (T_c) (Joback & Reid 1987). The other equations define "reduced" properties (e.g. T_{br} is the reduced boiling temperature). These parameters are subsequently used in Watson's method in equation 9 to calculate ΔH_{ve} (Watson 1943).

$$\Delta H_{vb} = 15.3 + \sum_{i=1}^{N} n_i \Delta H_{vb,i} \tag{3} \qquad\qquad T_b = 198.2 + \sum_{i=1}^{N} n_i T_{b,i} \tag{4}$$

$$T_c = \frac{T_b}{0.584 + 0.965 \sum_{i=1}^{N} n_i T_{c,i} - (\sum_{i=1}^{N} n_i T_{c,i})^2} \tag{5}$$

$$T_{br} = \frac{T_b}{T_c} \tag{6} \qquad T_{evapr} = \frac{T_{evap}}{T_c} \tag{7} \qquad T_{condr} = \frac{T_{cond}}{T_c} \tag{8}$$

$$\Delta H_{ve} = \Delta H_{vb} \left(\frac{1 - T_{evapr}}{1 - T_{br}} \right) \geq 20.322 \frac{kJ}{mol} \; (H_{ve,R134a}) \tag{9}$$

Note all parameters with index i (except n_i), for example $T_{b,i}$, are constants taken from Joback and Reid's seminal paper. These are used to estimate the properties through the group contribution approach.

2.2.1.2 Heat Capacity

Equations 10 - 11 use Joback and Reid's group contribution method to estimate the critical pressure (P_c) and ideal gas heat capacity at average temperature (C_{poa}). Then as outlined by Rowlinson in a modification of Bondi's equation the acentric factor, ω, is calculated as an intermediate step to obtain the liquid heat capacity in equation 16 (Rowlinson 1982).

$$P_c = \frac{1}{(0.113 + 0.0032 \sum_{i=1}^{N} n_i a_i - \sum_{i=1}^{N} n_i P_{c,i})^2} \tag{10}$$

$$
\begin{aligned}
C_{poa} = &\sum_{i=1}^{N} n_i C_{po,ai} - 37.93 + \left(\sum_{i=1}^{N} n_i C_{po,bi} + 0.21 \right) T_{avg} \\
&+ \left(\sum_{i=1}^{N} n_i C_{po,ci} - 3.91 \times 10^{-4} \right) T_{avg}^2 + \left(\sum_{i=1}^{N} n_i C_{po,di} + 2.067 \times 10^{-7} \right) T_{avg}^3
\end{aligned} \tag{11}
$$

$$\alpha = -5.97274 - \ln \frac{P_c}{1.013} + \frac{6.09648}{T_{br}} + 1.28862 \ln(T_{br}) - 0.169347 T_{br}^6 \tag{12}$$

$$\beta = 15.2518 - \frac{15.6875}{T_{br}} - 13.4721 \ln(T_{br}) + 0.43577 T_{br}^6 \tag{13}$$

$$\omega = \frac{\alpha}{\beta} \qquad (14) \qquad\qquad T_{avgr} = \frac{T_{avg}}{T_c} \qquad (15)$$

$$C_{pla} = \frac{1}{4.1868}\left(C_{poa} + 8.314\left[1.45 + \frac{0.45}{1 - T_{avgr}} + 0.25\omega\left(17.11 + 25.2\frac{(1 - T_{avgr})^{\frac{1}{3}}}{T_{avgr}} + \frac{1.742}{1 - T_{avgr}}\right)\right]\right) \qquad (16)$$

$$\leq 143.915\frac{J}{mol\ K}\ (C_{pla,R134a})$$

Equations 9 and 16 outline the key thermodynamic constraints in order for the new refrigerant to be better than R134a. The entire set of equations needs to be implemented into GAMS, for the optimisation software to be able to calculate ΔH_{ve} and C_{pla} through these group contribution methods.

2.2.1.3 Vapour Pressure

The Riedel-Plank-Miller equation is used to obtain P_{vpc} and P_{vpe} as shown in equations 17 - 21 (Riedel 1954). Equations 22 and 23 outline the refrigerant vapour pressure design specifications as outlined in the projcet brief.

$$h = \frac{T_{br}\ln(\frac{P_c}{1.013})}{1 - T_{br}} \quad (17) \qquad G = 0.4835 + 0.4605h \quad (18) \qquad k = \frac{\frac{h}{G} - (1 + T_{br})}{(3 + T_{br})(1 - T_{br})^2} \quad (19)$$

$$\ln P_{vpcr} = \frac{-G}{T_{condr}}\left[1 - T_{condr}^2 + k(3 + T_{condr})(1 - T_{condr})^3\right] \qquad (20)$$

$$\ln P_{vper} = \frac{-G}{T_{evapr}}\left[1 - T_{evapr}^2 + k(3 + T_{evapr})(1 - T_{evapr})^3\right] \qquad (21)$$

$$P_{vpc} = P_{vper}P_c \leq 14\ bar \qquad (22) \qquad\qquad P_{vpe} = P_{vpcr}P_c \geq 1.1\ bar \qquad (23)$$

2.2.2 Structural Constraints

Structural constraints need to be imposed to eliminate combinations of groups which do not satisfy bonding requirements. The first of these constraint is that at least 2 groups are required to form a molecule, which defines the lower bound on the total number of groups. Group contribution methods are less accurate for larger molecules. Hence the upper bound for the total number of groups to be chosen was set as 7.

$$2 \leq \sum_{i=1}^{N} n_i \leq 7 \qquad (24)$$

If groups with only acyclic bonds are present and groups with only cyclic bonds are present then there must be groups with both acyclic and cyclic bonds present to link the both of these. $\underline{a}$, $\underline{c}$, $\underline{m}$ define the set of groups having acyclic bonds only, cyclic bonds only and both acyclic and cyclic bonds. The set of equations 25 - 29 defines this condition.

$$Y_A = \begin{cases} 1, & \text{if only acyclic bond group} \\ 0, & \text{otherwise} \end{cases} \qquad\qquad Y_A \leq \sum_{i\in\underline{a}} n_i \leq N_{max}Y_A||\underline{a}|| \qquad (25)$$

$$Y_C = \begin{cases} 1, & \text{if only cyclic bond groups} \\ 0, & \text{otherwise} \end{cases} \qquad\qquad Y_C \leq \sum_{i\in\underline{c}} n_i \leq N_{max}Y_C||\underline{c}|| \qquad (26)$$

$$Y_M = \begin{cases} 1, & \text{if both acyclic and cyclic bond groups} \\ 0, & \text{otherwise} \end{cases} \qquad Y_M \leq \sum_{i\in\underline{m}} n_i \leq N_{max}Y_M||\underline{m}|| \qquad (27)$$

$$Y_M \geq Y_A + Y_C - 1 \qquad (28) \qquad\qquad Y_M \leq Y_A + Y_C \qquad (29)$$

If groups containing cyclic bonds are present then at least three of them are needed. The binary variable Y_R is used to model this constraint (equation 30).

$$Y_R = \begin{cases} 1, & \text{if cyclic bond groups present} \\ 0, & \text{otherwise} \end{cases} \qquad 3Y_R \leq \sum_{i \in \underline{R}} n_i \leq N_{max} Y_R ||\underline{R}|| \qquad (30)$$

The number of groups that have an odd number of free bonds needs to be even.

$$\sum_{i \in \underline{B}} n_i = 2Z_B \qquad (31)$$

The number of bonds in the molecule needs to be greater or equal to the number of groups minus 1.

$$\sum_{i=1}^{N} n_i b_i \geq 2 \left(\sum_{i=1}^{N} n_i - 1 \right) \qquad (32)$$

The upper limit on the number of bonds in the molecule is the number of bonds in a complete molecule.

$$\sum_{i=1}^{N} n_i b_i \leq \left(\sum_{i=1}^{N} n_i \right) \left(\sum_{i=1}^{N} n_i - 1 \right) \qquad (33)$$

If groups containing single bonds only (S) and double bonds only (D) are present then there must be groups with both single and double bonds present to connect the two. The same can be said for the relationship between single and triple bonds (T). The set of equations 34 - 41 enforces this. Note: SD refers to groups with both single and double bonds; S/D refers to groups with single but not double bonds; D/S refers to groups with double bonds but not single bonds. (With a similar convention used for ST, S/T and T/S.)

$$Y_{SD_x} = \begin{cases} 1, & \text{if groups with S and D} \\ 0, & \text{otherwise} \end{cases} \qquad Y_{SD_x} \leq \sum_{i \in \underline{SD}} n_i \leq N_{max} Y_{SD_x} ||\underline{SD}|| \qquad (34)$$

$$Y_{SD_y} = \begin{cases} 1, & \text{if groups with S but no D} \\ 0, & \text{otherwise} \end{cases} \qquad Y_{SD_y} \leq \sum_{i \in \underline{S/D}} n_i \leq N_{max} Y_{SD_y} ||\underline{S/D}|| \qquad (35)$$

$$Y_{SD_z} = \begin{cases} 1, & \text{if groups with D but no S} \\ 0, & \text{otherwise} \end{cases} \qquad Y_{SD_z} \leq \sum_{i \in \underline{D/S}} n_i \leq N_{max} Y_{SD_z} ||\underline{D/S}|| \qquad (36)$$

$$Y_{ST_x} = \begin{cases} 1, & \text{if groups with S and T} \\ 0, & \text{otherwise} \end{cases} \qquad Y_{ST_x} \leq \sum_{i \in \underline{ST}} n_i \leq N_{max} Y_{ST_x} ||\underline{ST}|| \qquad (37)$$

$$Y_{ST_y} = \begin{cases} 1, & \text{if groups with S but no T} \\ 0, & \text{otherwise} \end{cases} \qquad Y_{ST_y} \leq \sum_{i \in \underline{S/T}} n_i \leq N_{max} Y_{ST_y} ||\underline{S/T}|| \qquad (38)$$

$$Y_{ST_z} = \begin{cases} 1, & \text{if groups with T but no S} \\ 0, & \text{otherwise} \end{cases} \qquad Y_{ST_z} \leq \sum_{i \in \underline{T/S}} n_i \leq N_{max} Y_{ST_z} ||\underline{T/S}|| \qquad (39)$$

$$Y_{SD_y} + Y_{SD_z} - 1 \leq Y_{SD_x} + Y_R \qquad (40) \qquad\qquad Y_{ST_y} + Y_{ST_z} - 1 \leq Y_{ST_x} \qquad (41)$$

The upper bound on the number of acyclic groups with single bonds is the number of free bonds of the other groups.

$$\sum_{i \in \underline{a}|b_i=1} n_i \leq \sum_{i \in \underline{m}} (b_i - 2)n_i + \sum_{i \in \underline{a}|b_i \geq 3} (b_i - 2)n_i + N_{max}(1 - Y_M)||\underline{a_1}|| \qquad (42)$$

Equations 43 - 45 ensure that acyclic groups with one, two and four bonds form viable molecules.

$$l = -N_{max}(||\underline{a_3}|| + 2||\underline{a_4}||) \qquad (43) \qquad\qquad u = N_{max}||\underline{a_1}|| \qquad (44)$$

$$lY_R \leq \sum_{i \in \underline{a}|b_i=1} n_i - \sum_{i \in \underline{a}|b_i=3} n_i - 2 \sum_{i \in \underline{a}|b_i=4} n_i - 2 \leq uY_R \qquad (45)$$

4

In equations 46 - 50 S refers to groups with acyclic single bonds, SR refers to groups with cyclic single bonds, (and with similar convention for D, DR, and T). These constraints ensure the number of available bonds need to be even for each type of bond so that bonds 'match', i.e. if a cyclic single bond is selected then another cyclic single bond must be chosen.

$$\sum_{i \in \underline{S}} n_i S_i = 2Z_S \qquad (46) \qquad \sum_{i \in \underline{SR}} n_i S_i^R = 2Z_{SR} \qquad (47) \qquad \sum_{i \in \underline{D}} n_i D_i = 2Z_D \qquad (48)$$

$$\sum_{i \in \underline{DR}} n_i D_i^R = 2Z_{DR} \qquad (49) \qquad \sum_{i \in \underline{T}} n_i T_i = 2Z_T \qquad (50)$$

The octet rule needs to be implemented to ensure that there are no free bonds.

$$m = \begin{cases} 1, & \text{for acyclic compounds} \\ 0, & \text{for monocyclic compounds} \end{cases} \qquad \sum_{i=1}^{N} n_i(2 - b_i) = 2m \qquad (51)$$

It should be noted that m can take a different form for bicyclic molecules, $m = -1$. This case was not taken into account due to its added complexity. Finally, one needs to include non-negativity and integrality requirements, as represented by the equations below.

$$C_{poa}, C_{pla}, \Delta H_{vb}, \Delta H_{ve} \geq 0 \qquad\qquad Y_i = 0 \ \text{ or } 1 \ for \ i \in \{M, A, C, R\}$$

$$P_c, P_{vpc}, P_{vpcr}, P_{vpe}, P_{vper} \geq 0$$
$$Y_i = 0 \ or \ 1 \ for \ i \in \{SD_x, SD_y, SD_z, ST_x, ST_y, ST_z\}$$

$$T_{avgr}, T_b, T_{br}, T_c, T_{condr}, T_{evapr} \geq 0$$
$$0 \leq n_i \leq N_{max}$$

$$h, G \geq 0 \qquad\qquad n_i : \ integer \ for \ i = 1, ..., N$$

$$\beta \leq 0 \qquad\qquad \alpha, \omega, k : \ unrestricted \ sign$$

$$Z_i : non - negative \ integer, \ for \ i \in \{B, S, SR, D, DR, T\}$$

2.3 Binary Reformulation and Integer Cuts

The integer variable n_i can be reformulated so that it is represented by binary variables only, $y_{i,k}$. The reformulation is represented by equation 52.

$$n_i = n_i^L + \sum_{k=1}^{K_i+1} 2^{k-1} y_{i,k} \ , \ \lor i \tag{52}$$

This goal of this project is to identify possible alternative refigerants. Instead of finding a single "best" solution, integer cuts were implemented in order to find the 10 best solutions. This gives a range of molecules which can then be further investigated for their suitability as refrigerants. Equation 53 was used to model this. Integer cuts work by excluding all previously found solutions. Ten integer cuts were implemented in order to find the 10 best refrigerants.

$$\sum_{i \in NZ^k} y_i - \sum_{i \in Z^k} y_i \leq |NZ^k| - 1 \tag{53}$$

2.4 GAMS Solver

The MINLP model was solved using the Branch-And-Reduce Optimisation Navigator (BARON) solver, as this guarantees global optimality of the solution. BARON implements algorithms of the branch-and-bound type enhanced with a variety of constraint propagation, and duality techniques to reduce the range of the variables during the course of the algorithm.

3 Results

3.1 Proposed Alternative Refrigerants

By running the integer cuts as discussed above GAMS identified ten alternative refrigerants as shown in Table 2. These results are presented in rank order as illustrated by increasing objective function values ($\Delta H_{ve}/C_{pla}$). From the C_{pla} and ΔH_{ve} values we can verify that the proposed refrigerants satisfy the constraints to have a higher enthalpy of vaporisation and lower liquid heat capacity than R134a.

Molecule	$\frac{C_{pla}}{\Delta H_{ve}}$ $[K^{-1}]$	C_{pla} $[J\ mol^{-1}K^{-1}]$	ΔH_{ve} $[KJ\ mol^{-1}]$
$Br - F$	8.350×10^{-4}	17.432	20.880
$F - SH$	8.550×10^{-4}	17.971	21.029
$CH_3 - Cl$	8.910×10^{-4}	19.229	21.584
$F - O - Cl$	1.018×10^{-3}	21.239	20.868
$F - S - F$	1.025×10^{-3}	21.052	20.534
$Cl - CH_2 - F$	1.086×10^{-3}	22.495	20.711
$CH_3 - O - CH_3$	1.188×10^{-3}	26.417	22.230
$CH_3 - CH_2 - CH_3$	1.255×10^{-3}	27.693	22.071
$CH_3 - O - F$	1.323×10^{-3}	28.483	21.524
$CH_3 - CH_2 - O - F$	1.391×10^{-3}	29.714	21.366

Table 2: GAMS solution for ten alternative refrigerants

These molecules were then checked for their stability and commercial availability online to decide whether they should be further studied as potential replacements for R134a.

Molecule	Name	Stability	Reaction	Availability	Remark
$Br - F$	Bromine monofluoride	Unstable	N/A	No	✗
$F - SH$	Sulfanyl fluoride	Unstable	N/A	No	✗
$CH_3 - Cl$	Chloromethane	Stable	N/A	Yes	✓
$F - O - Cl$	Chlorosyl fluoride	Unstable	Dissociates	No	✗
$F - S - F$	Sulfur difluoride	Unstable	Dissociates	No	✗
$Cl - CH_2 - F$	Chlorofluoromethane	Stable	N/A	Yes	✓
$CH_3 - O - CH_3$	Dimethyl ether	Stable	N/A	Yes	✓
$CH_3 - CH_2 - CH_3$	Propane	Stable	N/A	Yes	✓
$CH_3 - O - F$	Methyl hypofluorite	Unstable	N/A	No	✗
$CH_3 - CH_2 - O - F$	Ethyl hypofluorite	Unstable	N/A	No	✗

Table 3: Suitability of refrigerants for further study

Following this approach chloromethane, chlorofluoromethane, dimethyl ether, and propane have been identified as four potential refrigerants for further study. These are all in fact existing and known refrigerants under the names of R40, Freon 31, R-E170, and R290 respectively. However, R40 and Freon 31, as haloalkanes and HCFCs respectively, have already been phased out due to their ozone depletion potential (ODP). Therefore, dimethyl ether (R-E170) and propane (R290) are the only two viable replacements to R134a found from this study. Both are eco-friendly refrigerants with zero ODP and very low global warming potential (GWP) (Bolaji & Huan (2012), Linde (n.d.)). Both are commercially used, however, R290 is much more commonly used. From the results above it is clear that additional constraints need to be implemented in order to screen for the "environmental-friendliness" of suggested alternatives.

3.2 Evaluation of GAMS Solver Performance

A notable difference of our results compared to those published in other studies following a very similar methodology (Sahinidis et al. 2003) is that no solutions containing double bonds were found. This can be attributed to two factors. Firstly, during some of the integer cuts the solver timed out, which means it only reported back the best solution found within the given time. It can be assumed that within the solver time BARON only found single bonded solutions. Due to the complexity of the problem (both from the number of constraints implemented, along with the number of groups investigated) it appears that GAMS was not able to finish completely searching the solution space. The BARON solver uses a complete and rigorous global optimisation method, however, if the solver times out it may not have accessed the solution space containing double bonds. The solver time was set at 1000 seconds and could be increased further, however, it already reported back a sensible set of solutions with an increasing objective function value, therefore this was not carried out in this study. Secondly, the default solver tolerance on BARON is 0.1, i.e. even if there are double-bonded solutions with a better objective function value than the ones shown in Table 2, if these solutions were within 10% of our presented solutions, then BARON wouldn't necessarily find these solutions. The solver tolerance could have been altered, however, tightening it does make the problem increasingly computationally intensive.

4 Recommendations and Additional Constraints

Through the results it is evident that the model is not developed enough to determine the most suitable replacement for R134a. In order to increase the relevance of the findings more constraints need to be added to the model. Three possible constraints that could be implemented are detailed below.

4.1 Toxicity and Flammability

One wants to ensure that any alternative refrigerants proposed are non-toxic and non-flammable. Toxicity of a group can be measured through the effect it has on an organism. If there are any particular groups that display a high level of toxicity or make the eventual proposed molecule toxic then these groups should be excluded from the search. The flammability of the refrigerant is also important, as combustion can occur during its compression. For this reason molecules with poor combustion qualities are desired.

4.2 Ozone Depleting Potential

R134a is being phased out due to its ozone depleting potential (ODP). Hence, it only makes sense that a constraint should be enforced to ensure that the ODP of a selected molecule is lower than that of R134a (or even better - i.e. set to some internationally agreed level). The measurement of ODP is difficult but some groups, such as fluorocarbons, are known to have greater ODPs than others. The constraint would ensure that not too many ODP contributing groups are selected. A more sophisticated group contribution model for ODP would need to be developed to implement this constraint.

4.3 Economic Constraint

An important aspect of the refrigerant design that has been overlooked is cost. A refrigerant can fulfil all the model constraints but be expensive or rare. A maximum cost constraint could be implemented to ensure that the refrigerants found do not exceed a specific cost. The cost limit would have to be determined through an intricate balance between performance and economics.

4.4 Alternative Implementation of Constraints

Above, it has been suggested that toxicity, flammability, ODP and cost can be implemented through upper-bound constraints, however, an alternative approach would be to augment the objective function by adding a "cost" for each of the extra characteristics of the refrigerant. Each factor can have an individual weighting (α_i). In the equation below, CON_i represents the specific characteristic of the refrigerant being penalised for (e.g. toxicity, ODP etc.). A group contribution model or correlations of some type would be required for this to be implementable.

$$OF^{'} = OF + \sum_i \alpha_i \cdot CON_i$$

This sort of approach is transitioning towards multi-objective optimisation and a human decision maker would need to work out the weightings, α_i, to determine the relative importance of different characteristics of the refrigerant.

5 Conclusion

A computer-aided molecular design (CAMD) mixed-integer non-linear programme (MINLP) has been implemented in GAMS using the global BARON solver to search for alternative refrigerants to R134a. The MINLP was formulated as a combination of thermodynamic constraints (to provide better thermodynamic performance than R134a) and structural constraints (to ensure feasibility of the proposed molecules). Integer cuts were implemented to find ten possible alternatives. From this four were stable molecules: chloromethane, chlorofluoromethane, dimethyl ether, and propane. These are all existing and known refrigerants and of these only dimethyl ether (R-E170) and propane (R290) offer suitable replacements to R134a as eco-friendly refrigerants with zero ODPs and very low GWPs. Despite being structurally feasible molecules, chloromethane (R40) and chlorfluoromethane (Freon 31) are unsuitable solutions due to their high ODPs. These molecules have already been phased out by the Montreal Protocol. These results show that for this optimisation problem to find realistic refrigerant replacements additional constraints need to be considered. New constraints to factor into account toxicity & flammability, ODP, and refrigerant cost were proposed. To conclude, CAMD was effective at finding refrigerants but not necessarily novel refrigerants as the ones found had been previously used as refrigerants.

References

Bolaji, B. O. & Huan, Z. (2012), Energy performance of eco-friendly r-e170 and r510a refrigerants as alternatives to r134a in vapour compression refrigeration system, *in* '2012 Proceedings of the 9th Industrial and Commercial Use of Energy Conference', pp. 1–8.

Joback, K. & Reid, R. (1987), 'ESTIMATION OF PURE-COMPONENT PROPERTIES FROM GROUP-CONTRIBUTIONS', *Chemical Engineering Communications* **57**(1-6), 233–243.
URL: *https://www.tandfonline.com/doi/full/10.1080/00986448708960487*

Linde (n.d.), 'R290 (care 40) propane'.
URL: *https://bit.ly/2q9vpal*

Riedel, L. (1954), 'Kritischer Koeffizient, Dichte des gesättigten Dampfes und Verdampfungswärme. Untersuchungen über eine Erweiterung des Theorems der übereinstimmenden Zustände. Teil III: Kritischer Koeffizient, Dichte des gesättigten Dampfes und Verdampfungswärme. Untersuchungen über eine Erweiterung des Theorems der übereinstimmenden', *Chemie Ingenieur Technik* **26**(12), 679–683.
URL: *http://doi.wiley.com/10.1002/cite.330261208*

Rogers, G. F. C. & Mayhew, Y. R. (2003), *Thermodynamic and transport properties of fluids: SI units*, 5. ed., reprinted; si units edn, Blackwell, Oxford. OCLC: 249596641.

Rowlinson, J. S. (1982), *Liquids and liquid mixtures*, Butterworths monographs in chemistry, 3rd ed edn, Butterworth Scientific, London ; Boston.

Sahinidis, N. V., Tawarmalani, M. & Yu, M. (2003), 'Design of alternative refrigerants via global optimization', *AIChE Journal* **49**(7), 1761–1775.
URL: *http://doi.wiley.com/10.1002/aic.690490714*

U.S. Department of State (n.d.), 'The Montreal Protocol on Substances That Deplete the Ozone Layer'.
URL: *https://www.state.gov/key-topics-office-of-environmental-quality-and-transboundary-issues/the-montreal-protocol-on-substances-that-deplete-the-ozone-layer/*

Watson, K. M. (1943), 'Thermodynamics of the Liquid State', *Industrial & Engineering Chemistry* **35**(4), 398–406.
URL: *https://pubs.acs.org/doi/abs/10.1021/ie50400a004*

Appendices

A   Nomenclature

Symbol	Definition	Units
T_{evap}	Evaporating temperature	K
T_{cond}	Condensing temperature	K
P_{vpe}	Vapour pressure (at evaporating temperature)	bar
P_{vpc}	Vapour pressure (at condensing temperature)	bar
H_{ve}	Heat of vaporisation (at evaporating temperature)	$kJ\ mol^{-1}$
C_{pla}	Liquid heat capacity (at average operating temperature)	$J\ mol^{-1}K^{-1}$
H_{vb}	Heat of vaporisation (at boiling temperature)	$kJ\ mol^{-1}$
n_i	Number of groups	-
$H_{vb,i}$	Heat of vaporisation of group i (at boiling temperature)	$kJ\ mol^{-1}$
T_b	Boiling temperature	K
$T_{b,i}$	Boiling temperature of group i	K
T_c	Critical temperature	K
$T_{c,i}$	Criticial temperature of group i	K
T_{br}	Reduced boiling temperature	-
T_{evapr}	Reduced evaporating temperature	-
P_c	Critical pressure	bar
a_i	Number of atoms of group i	-
$P_{c,i}$	Critical pressure of group i	bar
C_{poa}	Ideal gas heat capacity (at average temperature)	$J\ mol^{-1}K^{-1}$
$C_{po,ai}$	Contribution -A- to heat capacity of group i (at average temperature)	$J\ mol^{-1}K^{-1}$
$C_{po,bi}$	Contribution -B- to heat capacity of group i (at average temperature)	$J\ mol^{-1}K^{-2}$
$C_{po,ci}$	Contribution -C- to heat capacity of group i (at average temperature)	$J\ mol^{-1}K^{-3}$
$C_{po,di}$	Contribution -D- to heat capacity of group i (at average temperature)	$J\ mol^{-1}K^{-4}$
α	Intermediate value to find the acentric factor	-
β	Intermediate variable to find acentric factor	-
ω	Acentric factor	-
T_{avgr}	Reduced average process temperature	-
T_{condr}	Reduced condensing temperature	-
h	Intermediate variable to find vapour pressure	-
G	Intermediate variable to find vapour pressure	-
k	Intermediate variable to find vapour pressure	-
P_{vper}	Reduced vapour pressure (at evaporating temperature)	-
P_{vpcr}	Reduced vapour pressure (at condensing temperature)	-
N_{max}	Maximum number of groups available	-
b_i	Number of available bonds of group i	-
l	Variable to define number of single bonded groups	-
u	Variable to define number of single bonded groups	-
Z_B	Non-negative integer variable	-
Z_S	Count of acyclic single bonds in the compound (non-negative)	-
Z_{SR}	Count of cyclic single bonds in the compound	-
Z_D	Count of acyclic double bonds in the compound	-
Z_{DR}	Count of cyclic double bonds in the compound	-
Z_T	Count of triple bonds in the compound	-
S_i	Number of available acyclic single bonds of group i	-
S_i^R	Number of available cyclic single bonds of group i	-
D_i	Number of acyclic double bonds of group i	-
D_i^R	Number of cyclic double bonds of group i	-
T_i	Number of available acyclic triple bonds of group i	-

Table 4: Nomenclature table

B Group Contribution Parameters

Groups	T_b [K]	ΔH_{ve} [kJ mol^{-1}]	T_c [K]	P_c [bar]
$-CH_3$	23.58	2.373	0.0141	-0.0012
$-CH_2-$	22.88	2.226	0.0189	0
$>CH-$	21.74	1.691	0.0164	0.002
$>C<$	18.25	0.636	0.0067	0.0043
$=CH_2$	18.18	1.724	0.0113	-0.0028
$=CH-$	24.96	2.205	0.0129	-0.0006
$=C<$	24.14	2.138	0.0117	0.0011
$=C=$	26.15	2.661	0.0026	0.0028
$\equiv CH$	9.2	1.155	0.0027	-0.0008
$\equiv C-$	27.38	3.302	0.002	0.0016
$r-CH_2-r$	27.15	2.398	0.01	0.0025
$>CH-r$	21.78	1.942	0.0122	0.0004
$_r^r>C<_r^r$	21.32	0.644	0.0042	0.0061
$r=CH-r$	26.73	2.544	0.0082	0.0011
$r=C<_r^r$	31.01	3.059	0.0143	0.0008
$-F$	-0.03	-0.67	0.0111	-0.0057
$-Cl$	38.13	4.532	0.0105	-0.0049
$-Br$	66.86	6.582	0.0133	0.0057
$-I$	93.84	9.52	0.0068	-0.0034
$-OH$	92.88	16.826	0.0741	0.0112
$r-OH$	76.34	12.499	0.024	0.0184
$-O-$	22.42	2.41	0.0168	0.0015
$r-O-r$	31.22	4.682	0.0098	0.0048
$>C=O$	76.75	8.972	0.038	0.0031
$_r^r>C=O$	94.97	6.645	0.0284	0.0028
$O=CH-$	72.24	9.093	0.0379	0.003
$-COOH$	169.09	19.537	0.0791	0.0077
$-COO-$	81.1	9.633	0.0481	0.0005
$=O$	-10.5	5.909	0.0143	0.0101
$-NH_2$	73.23	10.788	0.0243	0.0109
$>NH$	50.17	6.436	0.0295	0.0077
$_r^r>NH$	52.82	6.93	0.013	0.0114
$>N-$	11.74	1.896	0.0169	0.0074
$-N=$	74.6	3.335	0.0255	-0.0099
$r-N=r$	57.55	6.528	0.0085	0.0076
$=NH$	83.08	12.169		
$-CN$	125.66	12.851	0.0496	-0.0101
$-NO_2$	152.54	16.738	0.0437	0.0064
$-SH$	63.56	6.884	0.0031	0.0084
$-S-$	68.78	6.817	0.0119	0.0049
$r-S-r$	52.1	5.984	0.0019	0.0051

Table 5: Thermodynamic properties for groups (Joback & Reid 1987)

Groups	A	B	C	D
$-CH_3$	1.95E+01	-8.08E-03	1.53E-04	-9.67E-08
$-CH_2-$	-9.09E-1	9.50E-02	-5.44E-05	1.19E-08
$>CH-$	-2.30E+01	2.04E-01	-2.65E-04	1.20E-07
$>C<$	-6.62E+01	4.27E-01	-6.41E-04	3.01E-07
$=CH_2$	2.36E+01	-3.81E-02	1.72E-04	-1.03E-07
$=CH-$	-8	1.05E-01	-9.63E-05	3.56E-08
$=C<$	-2.81E+01	2.08E-01	-3.06E-04	1.46E-07
$=C=$	2.74E+01	-5.57E-02	1.01E-04	-5.02E-08
$\equiv CH$	2.45E+01	-2.71E-02	1.11E-04	-6.78E-08
$\equiv C-$	7.87	2.01E-02	-8.33E-06	1.39E-09
$r-CH_2-r$	-6.03	8.54E-02	-8.00E-06	-1.80E-08
$>CH-r$	-2.05E+01	1.62E-01	-1.60E-04	6.24E-08
$_r^r>C<_r^r$	-9.09E+01	5.57E-01	-9.00E-04	4.69E-07
$r=CH-r$	-2.14	5.74E-02	-1.64E-06	-1.59E-08
$r=C<_r^r$	-8.25	1.01E-01	-1.42E-04	6.78E-08
$-F$	2.65E+01	-9.13E-02	1.91E-04	-1.03E-07
$-Cl$	3.33E+01	-9.63E-02	1.87E-04	-9.96E-08
$-Br$	2.86E+01	-6.49E-02	1.36E-04	-7.45E-08
$-I$	3.21E+01	-6.41E-02	1.26E-04	-6.87E-08
$-OH$	2.57E+01	-6.91E-02	1.77E-04	-9.88E-08
$r-OH$	-2.81	1.11E-01	-1.16E-04	4.94E-08
$-O-$	2.55E+01	-6.32E-02	1.11E-04	-5.48E-08
$r-O-r$	1.22E+01	-1.26E-02	6.03E-05	-3.86E-08
$>C=O$	6.45	6.70E-02	-3.57E-05	2.86E-09
$_r^r>C=O$	3.04E+01	-8.29E-02	2.36E-04	-1.31E-07
$O=CH-$	3.09E+01	-3.36E-02	1.60E-04	-9.88E-08
$-COOH$	2.41E+01	4.27E-02	8.04E-05	-6.87E-08
$-COO-$	2.45E+01	4.02E-02	4.02E-05	-4.52E-08
$=O$	6.82	1.96E-02	1.27E-05	-1.78E-08
$-NH_2$	2.69E+01	-4.12E-02	1.64E-04	-9.76E-08
$>NH$	-1.21	7.62E-02	-4.86E-05	1.05E-08
$_r^r>NH$	1.18E+01	-2.30E-02	1.07E-04	-6.28E-08
$>N-$	-3.11E+01	2.27E-01	-3.20E-04	1.46E-07
$-N=$				
$r-N=r$	8.83	-3.84E-03	4.35E-05	-2.60E-08
$=NH$	5.69	-4.12E-03	1.28E-04	-8.88E-08
$-CN$	3.65E+01	-7.33E-02	1.84E-04	-1.03E-07
$-NO_2$	2.59E+01	-3.74E-03	1.29E-04	-8.88E-08
$-SH$	3.53E+01	-7.58E-02	1.85E-04	-1.03E-07
$-S-$	1.96E+01	-5.61E-03	4.02E-05	-2.76E-08
$r-S-r$	1.67E+01	4.81E-03	2.77E-05	-2.11E-08

Table 6: Gaseous phase heat capacity parameters for group contribution (Joback & Reid 1987)