

Molecular Design of Optimal Refrigerants

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1 Abstract

In this paper, we present a method to design an optimal refrigerant for industrial refrigeration. This is performed by selecting molecules from a certain subset of sub-groups. First, we find that the most optimal refrigerants are the ones that make the process thermodynamically efficient. We then formulate a mixed integer nonlinear program (MINLP) which calculates corresponding thermodynamic properties using the group contribution method and sets up appropriate operating condition bounds. Lastly, we solve the optimization problem using appropriate nonlinear, non-convex, mixed integer solvers to find that HN=O (nitroxyl) is the optimal refrigerant.

2 Introduction

Our primary objective is determining an optimal set of refrigerant molecules that can be produced using a common set of sub-groups. These molecules are then optimized with respect to typical operating, manufacturing, and process/safety conditions for industrial refrigeration. We begin by highlighting a set of assumptions and explore what makes an optimal refrigerant.

First, we assume we are using a single-stage vapor-compression refrigeration cycle as depicted in **Fig. 1**. This means that the vapor pressure at evaporation needs to be greater than atmospheric pressure (≈ 1.01325 bar) to prevent a leak into the compressor system. The vapor pressure at condensation should not exceed the maximum allowable working pressure (MAWP). A common value for the refrigerant system highlighted below is 10 bar. The condenser and evap-

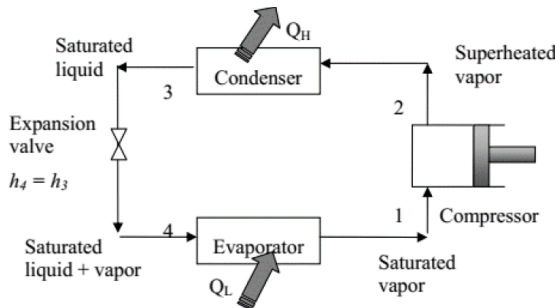


Figure 1: Typical single-stage vapor compression refrigeration cycle (Rachow, et. al 2017)

orator temperatures are taken to be common values (30 and 110 F, respectively).

Second, we assume that the process runs at steady state, avoiding thermodynamic property time dependence complications. This is a reasonable assumption because industrial processes only experience unsteadiness during startup and shutdown periods (Veret, et.al, 2020). Third, we assume that thermodynamic properties of the molecules can be calculated by relevant group contribution methods (Joback and Reid, 1987). In this method, molecular pure-component thermodynamic properties are assumed to be a summation of functional group contributions as shown in **Fig. 2**.

However, the Joback method is not very accurate as it neglects interactions between groups. In addition, deviating outside of its limited range can lead to large errors. For example, the enthalpy of formation (H_f) has an average absolute error (AARE) of 15.2% access to first-principles calculations such as Density Functional Theory (DFT) and methods that ac-

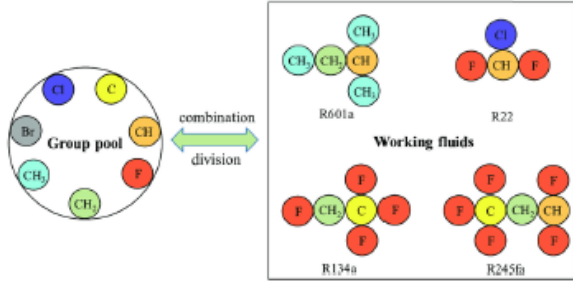


Figure 2: Diagram of group-contribution method (Shuozhuo, et.al, 2021)

count for group interactions like UNIFAC don't predict all of the properties which we are interested in, thus we stick to the Joback method. Lastly, we assume that the total molecule manufacturing cost is the sum of its functional groups. This is another poor assumption as the number and type of functional groups highly influence conditions such as the synthetic route, reaction conditions, and purification steps of the molecule. This means that cost can't be represented by a simple summation relationship. Even so, this assumption marks an important simplification for mathematical formulation.

The two main properties to account for optimal refrigerant molecules are enthalpy of vaporization, ΔH_{vap} , and liquid specific heat capacity, $C_{p,la}$. The enthalpy of vaporization should be maximized because it allows the refrigerant to absorb more heat, QL, during the evaporator phase (4- \dot{z} 1 in Fig. 1). This decreases the minimum required circulation rate in turn reducing pumping costs. $C_{p,la}$ should be minimized so that the liquid becomes easier to sub-cool (decreasing liquid temperature in the condenser phase, 2- \dot{z} 3 in Fig. 1). This is desired for typical refrigeration cycles because it ensures only liquid enters the evaporator and allows for a higher cooling capacity (Elliot and Lira, 1998). In addition, we summarize several thermodynamic, chemical, and process safety considerations as tradeoffs for selecting the optimal refrigerant are summarized in Table 1 below. We conduct a qualitative analysis of the optimal refrigerant to validate whether it is feasible for real-time

operation.

Property	What is Optimal?
Chemical Stability	Maximized
Toxicity	Minimized
Flammability	Minimized
Environmental Harm	Minimized
Refrigerant Production Cost	Minimized
Process Operating Cost	Minimized
Viscosity	Minimized
Thermal Conductivity	Maximized
Lubricant Miscibility	Maximized
Material Compatibility with Refrigerant	Maximized

Table 1: Summary of tradeoffs to be considered for refrigerant selection (Bhatia, 2020)

3 Problem Formulation

We previously mentioned that the most important consideration for the optimal refrigerants is the maximization of ΔH_{vap} and minimization of $C_{p,la}$. These optimality requirements can be combined into the following expression for the objective function (Sahindis, 2003).

$$\max \left(\frac{\Delta H_{vap,e}}{C_{p,la}} \right)$$

We can determine which molecule from a proposed group costs the least using the following objective function.

$$\min \sum_i y_i C_i$$

Where y_i is 1 if a functional group is chosen, 0 otherwise and C_i is the cost of the functional group. The following equations are used to calculate pure-component properties using the Joback method.

$$T_b = 198.2 + \sum_{i=1}^N n_i T_{bi}$$

$$T_c = \frac{T_b}{0.584 + 0.965 \sum_{i=1}^N n_i T_{ci} - \left(\sum_{i=1}^N n_i T_{ci} \right)^2}$$

$$C_{p0a} = \sum_{i=1}^N n_i C_{p0ai} - 37.93 + \left(\sum_{i=1}^N n_i C_{p0ai} + 0.21 \right) T_{avg} + \left(\sum_{i=1}^N n_i C_{p0ai} - 3.91 \times 10^{-4} \right) T_{avg}^2 + \left(\sum_{i=1}^N n_i C_{p0ai} - 2.06 \times 10^{-7} \right) T_{avg}^3$$

$$\Delta H_{vap,b} = 15.3 + \sum_{i=1}^N n_i \Delta H_{vap,bi}$$

$$\Delta H_{vap,e} = \Delta H_{vap,b} \left(\frac{1 - T_{evp}/T_c}{1 - T_b/T_c} \right)^{0.38}$$

Where T_b and T_c are the boiling and critical temperatures, P_c is the critical pressure, C_{p0a} is the ideal gas heat capacity at average temperature, n_i is the number of groups of type i , X_{yi} is the parameter y corresponding to the contribution of group i to the estimated pure-component property X , $\Delta H_{vap,b}$ is the enthalpy of vaporization at boiling temperature, and $\Delta H_{vap,e}$ is the enthalpy of vaporization at the evaporator temperature calculated using Watson's correction (Watson, 1943). Then, we calculate reduced temperatures.

$$T_{avg} = \frac{1}{2}(T_{cnd} + T_{evp})$$

$$T_{br} = \frac{T_b}{T_c}$$

$$T_{avgr} = \frac{T_{avg}}{T_c}$$

$$T_{cndr} = \frac{T_{cnd}}{T_c}$$

$$T_{evpr} = \frac{T_{evp}}{T_c}$$

Where T_{evp} , T_{cnd} are the evaporator and condenser temperatures. Then, we calculate the liquid heat capacity (C_{pla}) using Rowlinson's modification of Bondi's equation highlighted below (Rowlinson, 1969).

$$\alpha = -5.97214 - \ln\left(\frac{P_c}{1.013}\right) + \frac{6.09648}{T_{br}} + 1.28862 \ln(T_{br}) - 0.169347 T_{br}^6$$

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

$$\omega = \frac{\alpha}{\beta}$$

$$C_{pla} = \frac{1}{4.1868} \left\{ C_{p0a} + 8.314 \left[1.45 + \frac{0.45}{1 - T_{avgr}} + 0.25 \omega \left(17.11 + \frac{25.2}{(1 - T_{avgr})^{1/3} T_{avgr}} + \frac{1.742}{1 - T_{avgr}} \right) \right] \right\}$$

Where ω is the acentric factor calculated using Eqns 13-14. Lastly, we can calculate vapor pressure values at evaporating and condensing temperatures (P_{vpe} , P_{vpc}) using the Reidel-Plank-Miller equation highlighted below (Reidel, 1954).

$$h = \frac{T_{br} \ln\left(\frac{P_c}{1.013}\right)}{1 - T_{br}}$$

$$G = 0.4835 + 0.4605h$$

$$k = \frac{h/G - (1 + T_{br})}{(3 + T_{br})(1 - T_{br})^2}$$

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

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

$$P_{vpc} = P_{vpcr} P_c$$

$$P_{vpe} = P_{vper} P_c$$

Some reasonable operating conditions are that the refrigerant's vaporization and condensation pressure need to be within the bounds depicted below.

$$P_{vpe} \geq 1$$

$$P_{vpc} \leq 10$$

The relationships between all these constraints can be visually summarized by the following diagram.

The final constraints that we add will remove infeasible molecular structures:

1. The molecule should contain at least 2 functional groups.
2. The molecule should satisfy the octet rule.
3. There should be only one bond between adjacent functional groups.

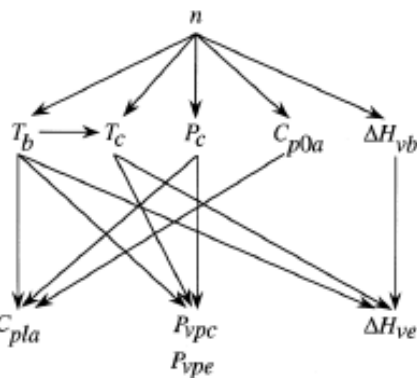


Figure 3: Relationship between estimated physical properties (Sahindis, 2003).

These are modeled below, respectively (Odele, et. al, 1993):

$$\sum_{i=1}^N n_i \geq 2$$

$$\sum_i n_i(2 - b_i) = 2m$$

$$\sum_{i=1}^N n_i \geq n_j(b_j - 1) + 2$$

Where $m = 1$ for acyclic compounds, $m = 0$ for monocyclic compounds, $m = -1$ for bicyclic compounds. Only the 2nd equation from above is implemented as a constraint because the others required more sets to be created and evaluated, adding unnecessary complication. This is a mixed integer nonlinear program (MINLP) because the correlations given by the group-contribution methods are non-linear and the decision parameter, y_i , is a discrete variable.

4 Solution Method

We used Excel's Solver Add-in to solve this MINLP. First, we entered the group contribution data for the Joback method into the spreadsheet (Joback, et. al,

Group#	GroupType	Tb	Tc	Cpa	Cpb	Cpc	Cpd	Pc	ΔHvap	#atoms	Legend
1	NR-CH3	23.58	0.0141	19.5	-0.00908	0.000123	-9.975-08	-0.0012	2.373	4	NR-norring
2	NR-CH2	23.86	0.0189	-0.907	0.095	-0.000044	1.191-08	0	2.726	3	R-ring
3	NR-CH	21.74	0.0161	-23	0.204	-0.000265	0.00000012	0.002	1.691	2	H-halogen
4	NR-C<	18.25	0.0067	-66.2	0.427	-0.000641	0.000000301	0.0483	0.636	1	OHA-alcohol
5	NR-CH2	18.18	0.0113	23.6	-0.0381	0.000172	-0.00000103	-0.0018	1.724	3	ONP-phenol
6	NR-CH	24.96	0.0129	8	0.105	-0.0000963	3.561-08	-0.0006	2.205	2	O-oxygen
7	NR-C<	24.14	0.0117	-28.1	0.208	-0.000306	0.000000146	0.0011	2.138	1	A-aldehyde
8	NR-C<	26.15	0.0076	27.4	-0.0557	0.000101	-5.072-08	0.0028	2.661	1	Ac-acid
9	NR-CH	9.2	0.0027	24.5	-0.0223	0.000111	-6.786-08	-0.0008	3.155	2	E-ester
10	NR-C<	27.38	0.002	7.87	0.0201	-0.0000833	1.391-09	0.0016	3.302	1	N-nitrogen
11	R-CH2	27.15	0.01	6.03	0.0854	-0.000008	0.000000018	0.0025	2.398	3	
12	R-CH	21.76	0.0102	-10.5	0.162	-0.00016	6.241-08	0.0004	1.942	2	
13	R-C<	21.32	0.0042	-90.9	0.557	-0.0009	0.000000569	0.0061	0.644	1	
14	R-CH	26.73	0.0082	-2.14	0.0574	-0.00000154	-1.595-08	0.0011	2.544	2	
15	R-C<	31.01	0.0143	-8.25	0.101	-0.000142	6.786-08	0.0008	3.059	1	
16	H-F	-0.03	0.0111	26.5	-0.0913	0.000191	-0.00000103	-0.0057	2.67	1	
17	H-Cl	38.13	0.0105	33.3	-0.0963	0.000187	-9.956-08	-0.0049	4.532	1	
18	H-Br	66.86	0.0133	28.6	-0.0649	0.000136	-7.541-08	0.0057	0.582	1	
19	H-I	95.84	0.0068	32.1	-0.0611	0.000126	-6.876-08	-0.0034	0.52	1	
20	O-OHA	92.88	0.0741	25.7	-0.0691	0.000177	-9.885-08	0.0012	16.826	2	
21	O-ONP	76.34	0.024	-2.81	0.111	-0.000116	4.945-08	0.0184	12.499	2	
22	O-ONR	22.42	0.0168	25.5	-0.0612	0.000111	-5.481-08	0.0015	2.41	1	
23	O-OR	31.22	0.0108	12.2	-0.0726	0.0000603	-3.866-08	0.0046	4.082	1	
24	O-C-ONR	76.75	0.038	6.45	0.067	-0.0000357	2.861-09	0.0031	8.972	2	
25	CH-CH2	94.97	0.0284	30.4	-0.0829	0.000236	-0.000000131	0.0028	6.645	2	
26	CH-CH2	72.24	0.0379	30.9	-0.0338	0.000016	-9.885-08	0.003	0.093	3	
27	CH-CH2	169.09	0.0791	24.1	0.0427	0.0000804	-6.876-08	0.0077	19.537	4	
28	O-CH2	81.1	0.0481	24.5	0.0402	-0.0000402	-4.521-08	0.0005	0.633	3	
29	CH2	-10.5	0.0143	6.82	0.0186	0.0000122	-1.786-08	0.0105	5.909	1	
30	N-CH2	73.23	0.0243	26.9	-0.0412	0.000164	-9.765-08	0.0109	10.788	3	
31	N-CH-NR	50.17	0.0295	-1.21	0.0762	-0.0000486	1.056-08	0.0077	6.436	2	
32	N-CH-NR	52.82	0.013	11.8	-0.023	0.000107	6.281-08	0.0114	0.93	2	
33	N-CH-NR	11.74	0.0168	-31.1	0.227	-0.00032	0.000000146	0.0074	1.896	1	
34	N-CH-NR	74.6	0.0255	0	0	0	0	-0.0099	3.335	1	
35	N-NR	57.55	0.0085	8.83	-0.00384	0.0000435	-0.000000226	0.0076	6.528	1	
36	N-NH	83.08	0	5.69	0.00412	0.000128	-8.885-08	0	12.169	2	
37	N-CH	125.68	0.0496	36.5	-0.0733	0.000184	-0.00000103	-0.0101	12.851	2	
38	N-CH2	152.54	0.0437	25.9	-0.00374	0.000129	-8.885-08	0.0064	16.738	3	
39	S-SH	63.56	0.0031	35.3	-0.0758	0.000185	-0.00000103	0.0084	6.884	2	
40	S-SR	68.78	0.0119	19.6	-0.00561	0.0000452	-2.766-08	0.0349	6.817	1	
41	S-SR	53.1	0.0019	16.7	0.00481	0.0000277	-2.116-08	0.0053	5.984	1	

Figure 4: Joback method group contribution data (Joback, et. al, 1987).

1987). This includes the boiling temperatures, critical temperatures, heat capacity factors (a, b, c and d), critical pressures, enthalpies of vaporization, and number of atoms as summarized below.

Then, we enter the model constraints, objective function, and decision parameters as summarized below.

In figure above, the leftmost table includes the discrete binary variable y_i that represents whether a functional group is selected. The upper right side

Group#	GroupType	y	Pure Component Properties									
1	NR-CH3	0	Tb	Tc	Pc	ΔHvap	ΔHfus	ΔHsub	ΔHvap	ΔHvap	ΔHvap	ΔHvap
2	NR-CH2	0	270.79	453.11023	79.01234068	11.2315931	0.59393001	0.60941301	0.09849	0.000001547		
3	NR-CH	0	A	B	C	D	E	F	G	H	I	J
4	NR-C<	0	-0.786184899	-0.50440584	0.1074028814	12.6702981	11.378	13.7770212	6.460507	1.62300599		
5	NR-CH2	0	A	B	C	D	E	F	G	H	I	J
6	NR-CH	0	0.46477781	0.00248058	0.00102109	4.50173717	1.06671546					
7	NR-C<	0	Molecular Weight									
8	NR-C<	0	Tb	Tc	Pc	ΔHvap	ΔHfus	ΔHsub	ΔHvap	ΔHvap	ΔHvap	ΔHvap
9	NR-CH	0	72.18	0.0164	13.55	0.01544	0.0001007	1.000007	0.0001	0.0001	0.0001	0.0001
10	NR-C<	0	270.79	453.11023	79.01234068	11.2315931	0.59393001	0.60941301	0.09849	0.000001547		
11	NR-CH2	0	Process Conditions									
12	NR-CH	0	Tb	Tc	Pc	ΔHvap	ΔHfus	ΔHsub	ΔHvap	ΔHvap	ΔHvap	ΔHvap
13	NR-C<	0	270.79	453.11023	79.01234068	11.2315931	0.59393001	0.60941301	0.09849	0.000001547		
14	NR-CH2	0	Objective Function									
15	NR-CH	0	Description	Units	Units	Units	Units	Units	Units	Units	Units	Units
16	NR-C<	0	Minimum vapor pressure	1.06671546	1.06671546	1.06671546	1.06671546	1.06671546	1.06671546	1.06671546	1.06671546	1.06671546
17	NR-CH2	0	Minimum vapor pressure	4.50173717	4.50173717	4.50173717	4.50173717	4.50173717	4.50173717	4.50173717	4.50173717	4.50173717
18	NR-CH	0	Capacities	11.378	11.378	11.378	11.378	11.378	11.378	11.378	11.378	11.378
19	NR-C<	0	Capacities	11.378	11.378	11.378	11.378	11.378	11.378	11.378	11.378	11.378
20	NR-CH2	0	Minimum vapor pressure	1.06671546	1.06671546	1.06671546	1.06671546	1.06671546	1.06671546	1.06671546	1.06671546	1.06671546
21	NR-CH	0	Minimum vapor pressure	4.50173717	4.50173717	4.50173717	4.50173717	4.50173717	4.50173717	4.50173717	4.50173717	4.50173717
22	NR-C<	0	Minimum number of atoms	2	2	2	2	2	2	2	2	2
23	NR-CH2	0										
24	NR-CH	0										
25	NR-C<	0										
26	NR-CH2	0										
27	NR-CH	0										
28	NR-C<	0										
29	NR-CH2	0										
30	NR-CH	0										
31	NR-C<	0										
32	NR-CH2	0										
33	NR-CH	0										
34	NR-C<	0										
35	NR-CH2	0										
36	NR-CH	0										
37	NR-C<	0										
38	NR-CH2	0										
39	NR-CH	0										
40	NR-C<	0										
41	NR-CH2	0										

Figure 5: Model constraints, objective function, and decision variables (Sahinidis, 2003).

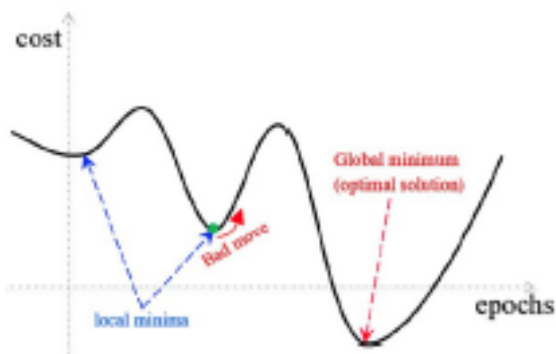


Figure 6: Local vs global minimum (Ahmed, et. al, 2020).

of the spreadsheet includes calculations for the pure-component properties with entered formulas corresponding to the constraints provided in the problem formulation section. Cells for the molecular sums and process conditions below the upper right hand corner were used for the calculations of pure component properties. The middle of the spreadsheet contains the final reduced constraints necessary for optimization. The constraints for minimum and maximum pressure/temperature were assumed based on typical refrigerant process conditions in the Introduction, while the remaining constraints are the non-negative constraints on intermediate pure component properties during group contribution method calculation. The cell for the final objective function value is also highlighted. With the setup in **Fig. 5**, we run the Solver tool with the Large Scale Generalized Reduced Gradient (LSGRG) Nonlinear engine to converge to a solution. We perform this for 3 sets of initial y_i values and generate answer reports to validate the robustness of the converged solution. In such a non-convex problem, it is easy for “converged solutions” which simply meet Karush-Kuhn-Tucker (KKT) optimality conditions (Ghojogh, et. al, 2021). Stationary, feasible points that satisfy force balances could in fact be local minima instead of global minima as suggested by the figure below. Thus various starting conditions need to be tested to find global minima and validate converged solutions.

5 Results and Discussion

The three answer reports produced by Solver, with different initial values of the discrete variable for each trial, are given below.

In Fig. 7-8, we enter a random set of zeroes and ones as a starting condition for the discrete variable y_i . In both cases, Solver converged on groups 29 and 36, which correspond to the functional groups =O and =NH with an objective function of 2.57. In Fig. 9, a greater degree of robustness was validated by entering initial values that resulted in an even higher objective function value but were infeasible. We found these values by first running the Solver tool without the condition of y_i being a discrete binary variable, in order to find infeasible decimal values that would result in an even higher value for the objective function. After finding these infeasible decimals, we entered as the initial values for the third trial to observe whether the tool would still converge at the identical feasible solution. Based on Fig. 9, it is clear that Solver was able to arrive at the identical solution of functional groups O=O and N=NH even for the infeasible starting point that was entered for a starting objective function value higher than 2.57 which removes some amount of uncertainty. This would mean that the optimal refrigerant molecule to build would be HN=O (nitroxyl). Nitroxyl is not currently used as a commercially available refrigerant, which has advantages and disadvantages. If nitroxyl is proven to be a superior refrigerant to industry standard, there are significant profits to be made. However, nitroxyl is likely not feasible as a refrigerant because it is highly reactive, unstable, and difficult to store (Gallego, et. al, 2021). Despite this, the molecule is very similar to those predicted by other models (Sahindis, 2003). Their model predicted nitrosyl fluoride (F-N=O) to be the best refrigerant. Even though they are quite similar, we get different answers because we likely reached a local minimum rather than a global minimum. This is because not enough initial conditions and iterations were done to sufficiently sample the highly, non-convex solution space.

Microsoft Excel Answer Report						
Worksheet: Model Constraints						
Report Created: Sun Apr 28 2024 17:06:36 GMT-0500 (Central Daylight Time)						
Result: Solver found a solution. All constraints and optimality conditions are satisfied.						
Engine: Standard LSGRG Nonlinear						
Solution Time: 739 milliseconds						
Iterations: 7						
Subproblems: 46						
Incumbent Solutions: 1						

Objective Cell (Max)			
Cell	Original Value	Final Value	
Model Constraints*	0.810901262	2.573296769	

Decision Variable Cells			
Cell	Original Value	Final Value	
\$C\$2	0	0	
\$C\$3	0	0	
\$C\$4	1	0	
\$C\$5	0	0	
\$C\$6	1	0	
\$C\$7	0	0	
\$C\$8	0	0	
\$C\$9	0	0	
\$C\$10	1	0	
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\$C\$36	0	0	
\$C\$37	1	1	
\$C\$38	0	0	
\$C\$39	1	0	
\$C\$40	0	0	
\$C\$41	0	0	
\$C\$42	0	0	

Constraints						
Cell	Original Value	Final Value	Lower Bound	Upper Bound	Slack	
\$B\$17	1.82926E-15	1.066871940	1	1E+30	-0.066871940	
\$B\$18	1.06545E-11	4.936737217	1	1E+30	-3.936737217	
\$B\$19	1.02.0316296	12.97092983	0	1E+30	-12.97092983	
\$B\$20	221.6659967	11.29158531	0	1E+30	-11.29158531	
\$B\$22	1.82926E-15	1.066871940	-1E+30	10	8.933128051	
\$B\$23	1.06545E-11	4.936737217	-1E+30	10	5.063262783	
\$B\$24	12	2	-1E+30	5	3	

Figure 7: Answer Report 1

Microsoft Excel Answer Report						
Worksheet: Model Constraints						
Report Created: Sun Apr 28 2024 17:09:23 GMT-0500 (Central Daylight Time)						
Result: Solver found a solution. All constraints and optimality conditions are satisfied.						
Engine: Standard LSGRG Nonlinear						
Solution Time: 636 milliseconds						
Iterations: 7						
Subproblems: 46						
Incumbent Solutions: 1						

Objective Cell (Max)			
Cell	Original Value	Final Value	
Model Constraints*	0.60265446	2.573296769	

Decision Variable Cells			
Cell	Original Value	Final Value	
\$C\$2	0	0	
\$C\$3	1	0	
\$C\$4	0	0	
\$C\$5	0	0	
\$C\$6	0	0	
\$C\$7	0	0	
\$C\$8	1	0	
\$C\$9	0	0	
\$C\$10	0	0	
\$C\$11	1	0	
\$C\$12	0	0	
\$C\$13	0	0	
\$C\$14	0	0	
\$C\$15	1	0	
\$C\$16	0	0	
\$C\$17	0	0	
\$C\$18	0	0	
\$C\$19	1	0	
\$C\$20	0	0	
\$C\$21	1	0	
\$C\$22	0	0	
\$C\$23	1	0	
\$C\$24	0	0	
\$C\$25	1	0	
\$C\$26	1	0	
\$C\$27	1	0	
\$C\$28	1	0	
\$C\$29	1	0	
\$C\$30	1	1	
\$C\$31	0	0	
\$C\$32	0	0	
\$C\$33	0	0	
\$C\$34	1	0	
\$C\$35	0	0	
\$C\$36	0	0	
\$C\$37	1	1	
\$C\$38	0	0	
\$C\$39	0	0	
\$C\$40	1	0	
\$C\$41	0	0	
\$C\$42	0	0	

Constraints						
Cell	Original Value	Final Value	Lower Bound	Upper Bound	Slack	
\$B\$17	2.1649E-03	1.066871949	1	1E+30	-0.066871949	
\$B\$18	8.31236E-50	4.936737217	1	1E+30	-3.936737217	
\$B\$19	219.2357287	12.97382983	0	1E+30	-12.97092983	
\$B\$20	321.4450475	11.29158531	0	1E+30	-11.29158531	
\$B\$22	2.1649E-03	1.066871949	-1E+30	10	8.933128051	
\$B\$23	8.31236E-50	4.936737217	-1E+30	10	5.063262783	
\$B\$24	16	2	-1E+30	5	3	

Figure 8: Answer Report 2

6 Conclusion

From solving a simplified formulation of a MINLP, we find that nitroxyl (H-N=O) is the optimal refrigerant. However, its electronic structure makes it unstable and derivatives like nitric acid (HNO_3) are known to be toxic. Nevertheless, this model is somewhat corroborated by similar ones like that proposed by Sahinidis claiming that nitrosyl fluoride (F-N=O) is the optimal refrigerant. We believe that there are a couple of improvements that we can make to our methods and model to reach a similar conclusion.

First, we could have made more specific assumptions about process conditions. In the model formulation we assume a specific temperature of condensation and evaporation based on typical refrigeration units. Having a range would allow the model more leeway in exploring the solution space for optimal solutions. If we were provided more accurate information describing an exact industrial refrigeration process in the problem statement, we could have narrowed down on a more precise refrigerant. Second, we could have used a more accurate group contribution method for determining thermodynamic properties which account for interactions between functional groups like the Nannodal method (Nannodal, et. al, 2004). We previously note that the Joback method is not very accurate as the data used to develop the model was limited and it doesn't account for these second order interactions. Third, we could have imposed more constraints to the model. We previously mentioned that some equations were neglected because they add too much complexity to the model from the creation/evaluation of multiple subsets. However, these equations along with other structural feasibility constraints described by Odele and coworkers are critical in determining molecular structures which obey common electronic structure rules. This would have made it somewhat easier to rule out infeasible molecules from being the global optimum. In addition, we could have added constraints on global warming potential (GWP) and calculated properties like viscosity and activity coefficients to determine whether the refrigerant was environmentally friendly and miscible with lubricants and process equipment as we highlight in Table 1. Lastly,

Microsoft Excel Answer Report
 Worksheet: Model Constraints
 Report Created: Sun Apr 28 2024 17:09:05 GMT-0500 (Central Daylight Time)
 Result: Solver found a solution. All constraints and optimality conditions are satisfied.
 Engine: Standard LSGRG Nonlinear
 Solution Time: 437 milliseconds
 Iterations: 7
 Subproblems: 48
 Incumbent Solutions: 1

Objective Cell (Max)			
Cell	Original Value	Final Value	
Model Constraints	3.25603083	2.57026769	

Decision Variable Cells			
Cell	Original Value	Final Value	
\$C\$2	0	0	
\$C\$3	0	0	
\$C\$4	0	0	
\$C\$5	0	0	
\$C\$6	0	0	
\$C\$7	0	0	
\$C\$8	0	0	
\$C\$9	0	0	
\$C\$10	0.112816676	0	
\$C\$11	0	0	
\$C\$12	0	0	
\$C\$13	0	0	
\$C\$14	0	0	
\$C\$15	0	0	
\$C\$16	0	0	
\$C\$17	0	0	
\$C\$18	0	0	
\$C\$19	0	0	
\$C\$20	0	0	
\$C\$21	0	0	
\$C\$22	0	0	
\$C\$23	0	0	
\$C\$24	0	0	
\$C\$25	0	0	
\$C\$26	0	0	
\$C\$27	0	0	
\$C\$28	0	0	
\$C\$29	0	0	
\$C\$30	0.052294963	1	
\$C\$31	0	0	
\$C\$32	0	0	
\$C\$33	0	0	
\$C\$34	0	0	
\$C\$35	0	0	
\$C\$36	0	0	
\$C\$37	0.886521508	1	
\$C\$38	0	0	
\$C\$39	0	0	
\$C\$40	0	0	
\$C\$41	0	0	
\$C\$42	0	0	

Constraints					
Cell	Original Value	Final Value	Lower Bound	Upper Bound	Slack
\$B\$17	1.000000906	1.086871949	1	1E+30	-0.086871949
\$B\$18	4.257247321	4.936737217	1	1E+30	-3.936737217
\$B\$19	8.149499997	12.97002083	0	1E+30	-12.97002083
\$B\$20	-2.86454E-15	11.29158531	0	1E+30	-11.29158531
\$B\$22	1.000000906	1.086871949	-1E+30	10	8.933128051
\$B\$23	4.257247321	4.936737217	-1E+30	10	5.063862769
\$B\$24	1.052033249	2	-1E+30	5	3

Figure 9: Answer Report 3

we could have considered the cost of producing the molecule to narrow down on a cost-effective refrigerant.

However, the biggest area to improve upon is the solution method. We previously mentioned that LS-GRG was used which is not specifically a global optimality engine. There is thus no guarantee that we found the best solution to the problem in the first place. OpenSolver’s NOMAD and BONMIN engines were utilized as well but they converge to the same solution as Solver’s LSGRG. The global optimizer, OpenSolver’s COUENNE engine, was also utilized but takes an unreasonable amount of time to solve the problem (241 seconds). For a greater degree of certainty, we need to devise a way to use the global optimizer effectively. Perhaps, adding more of the constraints we suggest (structural feasibility, GWP, narrower process conditions, etc.) will help the engine effectively navigate the non-convex solution space. Maybe if the extra constraints are too computationally expensive, we could implement a sequential pruning method which removes infeasible molecules from appearing in subsequent solutions via heuristics. Lastly, we can increase the constraint on the maximum number of functional groups once all of these improvements are implemented as this previously increased computational cost.

An interesting area to explore in the future are molecular trends and their effects on refrigerant properties. For example, why do chlorofluorocarbons (CFCs) exhibit excellent refrigerant efficiency? Are there periodic trends corresponding to molecular properties? How does molecular size impact refrigerant properties? How can we use this data to discover novel refrigerants that are environmentally friendly and safe with respect to a particular process? Although this proposed model and solution is promising, we are confident that we can improve upon our findings and elucidate meaningful results with the previous questions and proposed improvements in mind.

7 Sources

The link to the excel sheet which performs all calculations highlighted in this paper is available for download via this link.

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