Supplementary material for: High Performance HPs Using Tailored Refrigerants

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INITIAL VALUES

Table 1: The initial value for each decision variable.

Decision variable	Initial value	Type
P_c (Condenser pressure)	1.2 bar	Continuous
ΔT_{sub} (Condenser subcool)	0 K	Continuous
P_e (Evaporator pressure)	1.0 bar	Continuous
ΔT_{super} (Evaporator superheat)	0 K	Continuous
a (Number of double bonds)	0	Integer
y^e (Presence of more than two groups)	1	Binary
y^g (Presence of 2 or more geminal/aminal/hemi-aminal forming groups)	0	Binary
y^{cO} (Presence of cO groups)	0	Binary
$\boldsymbol{n}$ (Molecular/group vector)	Pentane	Integer vector

PROCESS CONSTRAINTS

Constraint 1

The condenser pressure must be at least 0.2 bar above the evaporator pressure.

$$P_c \geq P_e + 0.2 \tag{1}$$

Constraint 2

This constraint ensures that the minimum temperature in the condenser remains 5 K above the heat sink temperature to allow for heat exchange.

$$T_{c,out} \geq T_{sink} + 5\ K \tag{2}$$

Constraint 3

This constraint ensures that the maximum temperature in the evaporator remains 5 K below the heat source temperature to allow for heat exchange.

$$T_{e,out} \leq T_{source} - 5\ K \tag{3}$$

Constraint 4

The condenser outlet temperature must be greater than or equal to the evaporator inlet temperature. This is a redundant constraint that helps to guide the numerical solver.

$$T_{c,out} \geq T_{e,in} \tag{4}$$

Constraint 5

The evaporator inlet temperature must be greater than the normal boiling temperature ($T_{b,norm}$). This is a redundant constraint that helps to guide the numerical solver.

$$T_{e,in} \geq T_{b,norm} \tag{5}$$

Constraint 6

The compressor outlet temperature must be greater than the saturation temperature of the refrigerant at the condenser. This prevents two phase solutions in the compressor.

$$T_{com,out} \geq T_{c,vap} + \epsilon \tag{6}$$

Constraint 7

The reduced pressure (the pressure as a fraction of the critical pressure) in the condenser (P_c^r) must be less than or equal to 0.7.

$$P_c^r \leq 0.7 \quad (7)$$

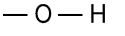
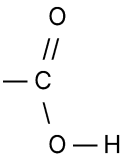
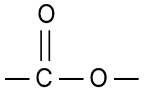
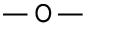
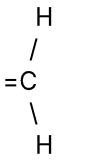
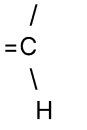
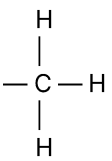
VARIABLE BOUNDS

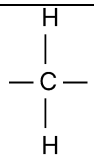
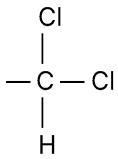
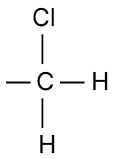
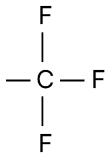
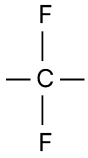
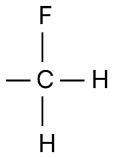
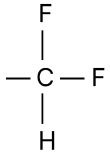
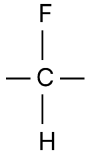
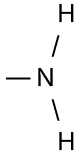
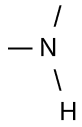
Table 2: The decision variable bounds.

Decision variable	Lower bound	Upper bound	Units
P_c (Condenser pressure)	1.2	145.0	bar
ΔT_{sub} (Condenser subcool)	0	100	K
P_e (Evaporator pressure)	1.0	80.0	bar
ΔT_{super} (Evaporator superheat)	0	100	K
a (Number of double bonds)	0	10	-
y^e (Presence of more than two groups)	0	1	-
y^g (Presence of 2 or more geminal/aminal/hemiaminal forming groups)	0	1	-
y^{cO} (Presence of cO groups)	0	1	-
$\boldsymbol{n}$ except for N (Molecular/group vector)	0	10	-
n_N (Molecular vector element for the tertiary amine group)	0	1	-

CHEMICAL STRUCTURES OF THE GROUPS

Table 3: The chemical structure of each group.

In-text symbol	Chemical structure	Description
OH		A generic hydroxyl or alcohol group. Can be for primary, secondary or tertiary alcohols.
COOH		A carboxylic acid group.
COO		An ester group.
C=O		A ketone group.
cO		A central (Located between two CH_2 groups) ether group.
eO		An end (Connected to a CH_3 group) ether group.
$=CH_2$		A methylidene group.
=CH		A methine group.
CH_3		A methyl group.

CH_2		A methylene bridge group.
$CHCl_2$		A dichloromethyl group.
CH_2Cl		A chloromethyl group.
CF_3		A trifluoromethyl group.
CF_2		A difluoromethylene bridge group.
CH_2F		A fluoromethyl group.
CHF_2		A difluoromethyl group.
CHF		A fluoromethylene bridge group.
NH_2		An amine group.
NH		An amine bridge group.
N		A tertiary amine group.

MOLECULAR CONSTRAINTS

Constraint 1

This constraint is the valency constraint (also known as the octet rule), which ensures there are no empty spaces on groups. $\boldsymbol{R}$ is the vector containing the valency value (i.e. the number of other groups a group can bond with) for each corresponding group in $\boldsymbol{n}$.

$$\sum_{i=0}^{19}[n_i(2-R_i)] = 2 \tag{8}$$

Constraint 2

This constraint enforces the maximum number of groups in the molecule.

$$\sum_{i=0}^{19} n_i \leq 35 \tag{9}$$

Constraint 3

This constraint ensures that for the selected groups, there is a possible molecular structure where each cO group is between two CH_2 groups. n_{cO}^{U} is the upper bound for the number of cO groups, i.e. 10.

$$n_{CH2} \geq n_{cO} + \frac{n_{cO}}{n_{cO}^{U}} \tag{10}$$

Constraint 4

This constraint ensures that for the selected groups, there is a possible molecular structure where each eO group can connect to a CH_3 group.

$$n_{CH3} \geq n_{eO} \tag{11}$$

Constraint 5

This constraint ensures that free double bonds always have another free double bond on a different group to attach to. This is achieved by ensuring that the total number of groups with a double bond is always equal to an even number. a is an integer decision variable.

$$n_{=CH2} + n_{=CH} = 2a \tag{12}$$

Constraint 6

This constraint ensures that there is always a =CH group for each $=CH_2$ group, to exclude structures with an even number of disconnected $=CH_2$ groups. For example, the combination $=CH_2$, CH_2, CH_2, $=CH_2$ satisfies all of the other molecular constraints but does not correspond

to a real molecule. This constraint excludes the small molecule ethylene.

$$n_{=CH} \geq n_{=CH2} \tag{13}$$

Constraint 7

Molecules with chains of nitrogens and/or oxygens such as peroxides and peracids are prevented as these are unstable. To prevent this, this constraint ensures that between every two groups that contain nitrogen and/or oxygen atoms, at least one group containing carbon atoms is present. Further, the group containing carbon atoms, referred to as a buffer group, must have (i) a valency of 2 or more (to be located between groups); and (ii) must not contain oxygen atoms. Condition (ii) excludes COO from the list of buffering groups as the oxygen atom in the group would form chains of nitrogen and/or oxygen atoms when attached to these. Condition (ii) also excludes the C=O group from the list of buffering groups, as the ketone group when attached to an oxygen or nitrogen containing group results in the formation of functional groups such as aldehydes, acids, and amides which are described with greater accuracy by their own group parameters. A CH=CH segment effectively acts as one group in the context of this constraint, therefore $n_{=CH}$ is multiplied by 0.5. The presence of a $=CH_2$ group makes one =CH group unavailable, it is for this reason that the $-0.5n_{=CH2}$ term is added.

$$n_{CH2} + n_{CHF} + n_{CF2} + 0.5n_{=CH} - 0.5n_{=CH2} \geq n_{C=O} + n_{COO} + n_{NH2} + n_{NH} + n_N + n_{cO} + n_{eO} + n_{OH} - 1 \tag{14}$$

Constraint 8

This constraint ensures that there are no geminal diols, aminals, or hemiaminals, because these make aliphatic molecules unstable. Geminal diols, aminals, and hemiaminals occur when a carbon atom bonds with two OH groups, two nitrogen groups, or one nitrogen group and one alcohol group, respectively. Let the set of alcohol and nitrogen containing groups be $\mathcal{G} = \{n_{OH}, n_{NH2}, n_{NH}, n_N\}$, and the sum of all groups in $\mathcal{G}$ be $\sigma_{\mathcal{G}}$. The binary variable y^g takes the value 1 only if $\sigma_{\mathcal{G}}$ is greater than or equal to 2.

When $\sigma_{\mathcal{G}}$ is less than 2, geminal diols/aminals/hemiaminals are not possible by definition and so no constraint is required to prevent them. When $\sigma_{\mathcal{G}}$ takes a value of 2 or more ($y^g = 1$), between each pair of groups g and g', where $g, g' \in \mathcal{G}$, there must be at least two buffering groups. Thus, it is guaranteed that there is a possible structure for the selected groups in the molecular vector where groups g and g' do not have to attach to the same carbon atom. It follows that for an acyclic molecule with 2 or more $\sigma_{\mathcal{G}}$ groups, there must be $2(\sigma_{\mathcal{G}} - 1)$ buffering groups. In molecules containing cO groups, all of the CH_2 groups forming the contiguous chain of cO and CH_2 groups are unavailable for bonding with $g \in \mathcal{G}$ as they are already being used by the ether groups. Thus, the number of available CH_2 groups for buffering in this context are:

$$\begin{cases} n_{CH2} & \text{If the number of cO groups is zero} \\ n_{CH2} - n_{cO} + 1 & \text{If the number of cO groups is non-zero} \end{cases}$$

To model both cases, we use binary variable y^{cO} that denotes the presence of cO groups. M is a sufficiently large number such that the effected side of the inequality is rendered active or inactive depending on the value of a binary variable.

$$-M(1 - y^g) \leq \sigma_{\mathcal{G}} - 2 + \epsilon \leq My^g \tag{15}$$

$$-M(1 - y^{cO}) \leq n_{\mathrm{cO}} - \epsilon \leq My^{cO} \tag{16}$$

$$[n_{CH2} - n_{cO} + y^{cO}] + n_{CF2} + n_{CHF} + n_{=CH} - n_{=CH2} \geq 2(\sigma_{\mathcal{G}} - 1) - M(1 - y^g) \tag{17}$$

Constraint 9

The function of this constraint is to prevent tautomers, i.e. molecules that will spontaneously rearrange to form a more stable isomer. Only two types of tautomerism are considered here: keto-enol and amine-imine. Aliphatic enols are in equilibrium with the much more predominant ketone tautomer:

$$\mathrm{R\text{-}CH{=}CH\text{-}OH} \rightleftharpoons \mathrm{R\text{-}CH2\text{-}CH{=}O}$$

Similarly, aliphatic enamines are in equilibrium with the usually much more predominant imine tautomer:

$$\mathrm{R\text{-}CH{=}CH\text{-}NH2} \rightleftharpoons \mathrm{R\text{-}CH2\text{-}CH{=}NH}$$

By preventing OH, NH, and NH_2 groups from joining to =CH groups, the unstable minority tautomer is excluded, ensuring useful designs. To enforce this, we ensure that for each occurrence of OH, NH, and NH_2 groups, carbon containing groups other than -CH are available. We note that this constraint still allows some tautomers such as CH_3-CH=CH-NH- or CH_3-CH=CH-OH. In its current form, it also excludes a few valid ether diols such as OH-CH_2-O-CH_2-OH. Reformulating a tautomerism constraint that excludes all or most tautomers and does not exclude any valid molecules is the subject of future work.

$$n_{CH3} + n_{CF3} + n_{CHF2} + n_{CH2F} + n_{CHCl2} + n_{CH2Cl} + n_{CH2} + n_{CF2} + n_{CHF} - n_{cO} \geq n_{OH} + n_{NH2} + n_{NH} \tag{18}$$

Constraints 10 & 11

These constraints prevent α-haloalcohols, molecules in which an alcohol group and a halogen are connected to the same carbon atom. For small molecules of size 2 groups, this means that an alcohol group may only connect to a CH_3 group. For larger molecules with more than 2 groups, the OH must connect to a CH_2 group. This is because these are the only remaining valid groups the alcohol group can connect to, given this new rule and given previous constraints. The binary variable y^e is

introduced to indicate if there are more than 2 groups selected.

$$-M(1-y^e) \leq \sum_{i=0}^{19} n_i - 2 - \epsilon \leq My^e \quad (19)$$

$$n_{CH2} \geq n_{OH} - M(1-y^e) \quad (20)$$

$$n_{CH3} \geq n_{OH} - My^e \quad (21)$$

VHC BENCHMARKS

VHC (MJ m^{-3})		T_{source} (K)				
		340	360	380	400	420
T_{sink} (K)	360	Ammonia **23.20**	–	–	–	–
	380	R-245fa **2.72**	R-245fa **4.93**	–	–	–
	400	Pentane **0.94**	Pentane **1.80**	Pentane **3.36**	–	–
	420	Pentane **0.67**	Pentane **1.29**	Pentane **2.43**	Pentane **4.51**	–
	440	No solutions **N/A**	Pentane **0.88**	Water **2.40**	Water **4.06**	Water **6.51**

Figure 1. The best benchmark for VHC at each source-sink temperature pair.