High Performance HPs Using Tailored Refrigerants - Supplementary Information, V2

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Chapter 1

Initial Conditions

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 2 groups)	1	Binary
y_g (Presence of 2 or more geminal/aminal/hemiaminal forming groups)	0	Binary
y_{cO} (Presence of cO groups)	0	Binary
$\boldsymbol{n}$ (Molecular group vector)	Pentane	Integer vector

Chapter 2

Process Constraints

2.1 Constraint 1

The condenser pressure must be at least 0.2 bar above evaporator pressure:

$$\begin{aligned} c_1^p &= P_c - [P_e + 0.2 \text{ bar}] \\ c_1^p &\geq 0 \end{aligned} \tag{2.1}$$

2.2 Constraints 2 & 3

These constraints ensure a minimum temperature difference to allow for heat exchange in the condenser and evaporator. This is fixed to 5 K.

The condenser outlet temperature must be at least 5 K above the sink temperature:

$$\begin{aligned} c_2^p &= T_{c,out} - [T_{sink} + 5 \text{ K}] \\ c_2^p &\geq 0 \end{aligned} \tag{2.2}$$

The evaporator outlet temperature must be at least 5K below the source temperature:

$$\begin{aligned} c_3^p &= T_{source} - [T_{e,out} + 5 \text{ K}] \\ c_3^p &\geq 0 \end{aligned} \tag{2.3}$$

2.3 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:

$$\begin{aligned} c_4^p &= T_{c,out} - T_{e,in} \\ c_4^p &\geq 0 \end{aligned} \tag{2.4}$$

2.4 Constraint 5

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

$$\begin{aligned} c_5^p &= T_{e,in} - T_{bnorm} \\ c_5^p &\geq 0 \end{aligned} \tag{2.5}$$

2.5 Constraint 6

The reduced pressure (the pressure as a fraction of the critical pressure) in the condenser ($P_{r,c}$) must be less than or equal to 0.7, in order to avoid the attempted evaluation of infeasible supercritical cycles, with a margin for error:

$$\begin{aligned} c_6^p &= 0.7 - P_{r,c} \\ c_6^p &\geq 0 \end{aligned} \tag{2.6}$$

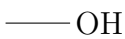
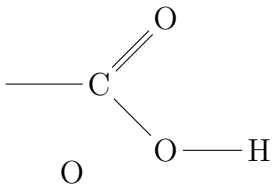
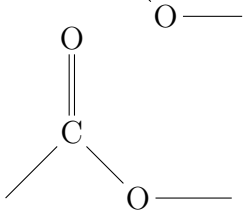
2.6 Variable Bounds

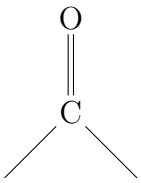
Variable	**Lower Bound**	**Upper Bound**	**Units**
P_c	1.2	145.0	bar
ΔT_{sub}	0	100	K
P_e	1.0	80.0	bar
ΔT_{super}	0	100	K

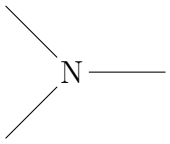
Chapter 3

Chemical Structures of the Groups

The chemical structures of the groups considered are given in Table 3.1. The lower limit for all groups is 0 and the upper limit for all groups other than the tertiary amine group is 10. The upper limit for tertiary amine is 1 to avoid complex branching structures. Complex branching structures will have decreased accuracy and produce less specific (and hence less useful) solutions due to the explosion in the number of possible isomers with each additional branch.

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	——O——	A central ether group. Must be located between two CH_2 groups.
eO	——O——	An end ether group. Must be connected to a CH_3 group.
$=CH_2$	$==CH_2$	A methylene group.
=CH	==CH——	A methine group.
CH_3	——CH_3	A methyl group.
CH_2	——CH_2——	A methylene bridge group.
$CHCl_2$	—$CHCl_2$	A dichloromethyl group.
CH_2Cl	—CH_2Cl	A chloromethyl group.
CF_3	——CF_3	A trifluoromethyl group.
CF_2	——CF_2——	A difluoromethylene bridge group.
CHF_2	—CHF_2	A difluoromethyl group.
CHF	——CHF——	A fluoromethyl group.
NH_2	——NH_2	An amine group.

NH		An amine bridge group.
N		A tertiary amine group.

Chapter 4

Molecular Constraints

4.1 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 is able to bond with) for each corresponding group in $\boldsymbol{n}$.

$$\begin{aligned} c_1^m &= \sum_{i=0}^{19} [n_i(2 - R_i)] - 2 \\ c_1^m &= 0 \end{aligned} \tag{4.1}$$

4.2 Constraint 2

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

$$\begin{aligned} c_2^m &= 35 - \sum_{i=0}^{19} n_i \\ c_2^m &\geq 0 \end{aligned} \tag{4.2}$$

4.3 Constraints 3 & 4

These constraints ensure correct behaviour of ether groups. Constraint 3 (Equation 4.3) ensures that cO groups are sandwiched between two CH_2 groups if cO is present and that the $CH_2-cO-CH_2$ groups always occur contiguously. The superscript 'U' refers to the upper limit for the number of that group, which in

the case of cO is 10. Please refer to Table 3.1 for the definition of the cO group.

$$\begin{aligned} c_3^m &= n_{\mathrm{CH_2}} - \left[n_{\mathrm{cO}} + \frac{n_{\mathrm{cO}}}{n_{\mathrm{cO}}^U} \right] \\ c_3^m &\geq 0 \end{aligned} \tag{4.3}$$

Constraint 4 (Equation 4.4) ensures that there is always at least one CH_3 group available that each eO group can bond with. Please refer to Table 3.1 for the definition of the eO group.

$$\begin{aligned} c_4^m &= n_{\mathrm{CH_3}} - n_{\mathrm{eO}} \\ c_4^m &\geq 0 \end{aligned} \tag{4.4}$$

4.4 Constraints 5 & 6

These constraints ensure that the groups containing double bonds bond to each other. To ensure this occurs, constraint 5 (Equation 4.5) enforces the selection of only an even number of double bond groups. a is an integer variable.

$$\begin{aligned} c_5^m &= \left[n_{=\mathrm{CH_2}} + n_{=\mathrm{CH}} \right] - 2a \\ c_5^m &= 0 \end{aligned} \tag{4.5}$$

Constraint 6 (Equation 4.6) excludes structures with an even number of disconnected $=CH_2$ groups such as below. To ensure this occurs, constraint 6 (Equation 4.6) ensures that the number of =CH groups equal or exceed the number of $=CH_2$ groups. For example, the combination =CH2, -CH2-, -CH2-, =CH2 which satisfies constraints 1 and 5 but does not have the double-bonded carbon groups connected to each other is excluded. Effectively, this constraint ensures that every =CH2 group is attached to a =CH- group. This prevents the small molecule ethylene, which must be assessed in the process separately.

$$\begin{aligned} c_6^m &= n_{=\mathrm{CH}} - n_{=\mathrm{CH_2}} \\ c_6^m &\geq 0 \end{aligned} \tag{4.6}$$

4.5 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 two 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 N and/or O atoms when attached to these. Condition (ii) also excludes the ketone 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 in greater accuracy by using their own group parameters. A CH=CH segment effectively acts as one group, in the context of this constraint. Therefore $n_{=\mathrm{CH}}$ is multiplied by 0.5. The presence of a $=\mathrm{CH_2}$ group makes one $=\mathrm{CH}$ group unavailable, therefore a $-0.5n_{=\mathrm{CH_2}}$ term is added.

$$\begin{aligned} c_7^m &= \left[n_{\mathrm{CH_2}} + 0.5n_{=\mathrm{CH}} - 0.5n_{=\mathrm{CH_2}} + n_{\mathrm{CF_2}} + n_{\mathrm{CHF}}\right] \\ &\quad - \left[n_{\mathrm{C{=}O}} + n_{\mathrm{COO}} + n_{\mathrm{NH_2}} + n_{\mathrm{NH}} + n_{\mathrm{N}} + n_{cO} + n_{\mathrm{eO}} + n_{\mathrm{OH}} - 1\right] \\ c_7^m &\geq 0 \end{aligned} \tag{4.7}$$

4.6 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 (OH–R–OH), two nitrogen groups (e.g. $-\mathrm{NH}-\mathrm{CH_2}-\mathrm{NH_2}$), or one nitrogen and one OH group (e.g. $-\mathrm{NH}-\mathrm{CH_2}-\mathrm{OH}$), respectively. Let the set of alcohol and nitrogen-atom containing groups be $\mathcal{G} = \{n_{\mathrm{OH}}, n_{\mathrm{NH_2}}, n_{\mathrm{NH}}, n_{\mathrm{N}}\}$, and the sum of all groups in $\mathcal{G}$ be $\sigma_{\mathcal{G}}$ (Equation 4.8). The binary variable y^g takes the value one only if $\sigma_{\mathcal{G}}$ takes the value 2 or more (Equation 4.9).

When $\sigma_{\mathcal{G}}$ is one or zero, geminal diols/aminals/hemiaminals are not possible by definition and no additional constraints are required. When $\sigma_{\mathcal{G}}$ takes the 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, 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 $\mathrm{CH_2}$ groups inside the chain 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

$$\begin{cases} n_{\mathrm{CH_2}} & \text{If the number of cO groups is zero} \\ n_{\mathrm{CH_2}} - n_{\mathrm{cO}} + 1 & \text{If the number of cO groups are non-zero} \end{cases}$$

To model both cases, we use the binary variable y^{cO} that is used to denote the presence of cO groups (Equation 4.10).

$$\begin{aligned} \mathcal{G} &= \{n_{\mathrm{OH}}, n_{\mathrm{NH_2}}, n_{\mathrm{NH}}, n_{\mathrm{N}}\} \\ \sigma_{\mathcal{G}} &= \sum_{g \in \mathcal{G}} n_g \end{aligned} \tag{4.8}$$

$$-M(1 - y^g) \leq \sigma_{\mathcal{G}} - 2 + \epsilon \leq M y^g \tag{4.9}$$

$$-M(1 - y^{cO}) \leq n_{\mathrm{cO}} - \epsilon \leq M y^{cO} \tag{4.10}$$

$$\begin{aligned} c_8^m &= [n_{\mathrm{CH_2}} + n_{\mathrm{CF_2}} + n_{\mathrm{CHF}}] + \left[n_{=\mathrm{CH}} - n_{=\mathrm{CH_2}}\right] \\ &\quad - \left[n_{\mathrm{cO}} - y^{\mathrm{cO}}\right] - 2(\sigma_{\mathcal{G}} - 1) \\ c_8^m &\geq -M(1 - y^g) \end{aligned} \tag{4.11}$$

4.7 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, keto-enol, and amine-imine, are considered here. Aliphatic enols are in equilibrium with the usually much more predominant ketone tautomer:

$$\mathrm{R{-}CH{=}CH{-}OH} \rightleftharpoons \mathrm{R{-}CH_2{-}CH{=}O}$$

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

$$\mathrm{R{-}CH{=}CH{-}NH_2} \rightleftharpoons \mathrm{R{-}CH_2{-}CH{=}NH}$$

By preventing OH, NH, and NH_2 groups from joining to =CH groups, the unstable minority tautomer is excluded, ensuring far more 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 cur-

rent form, it also excludes a few valid ether diols such as OH−CH_2−O−CH_2−O. Reformulating a tautomerism constraint that excludes all or most tautomers and does not exclude any valid molecules is the subject of future work.

$$\begin{aligned} c_9^m &= [n_{\mathrm{CH_3}} + n_{\mathrm{CF_3}} + n_{\mathrm{CHF_2}} + n_{\mathrm{CH_2F}} + n_{\mathrm{CHCl_2}} + n_{\mathrm{CH_2Cl}} \\ &\quad + n_{\mathrm{CH_2}} + n_{\mathrm{CF_2}} + n_{\mathrm{CHF}} - n_{\mathrm{cO}}] \\ &\quad - [n_{\mathrm{OH}} + n_{\mathrm{NH_2}} + n_{\mathrm{NH}}] \\ c_9^m &\geq 0 \end{aligned} \tag{4.12}$$

4.8 Constraints 10 & 11

These constraints prevent α-haloalcohols, molecules in which the alcohol group and a halogen atom are connected to the same carbon. For small molecules of size 2 groups, the OH group can only connect to CH_3. For larger molecules of size greater than 2, the OH group must connect to a CH_2 group.

$$-M(1-y^e) \leq \sum_{i=0}^{19} n_i - 2 - \epsilon \leq My^e \tag{4.13}$$

$$\begin{aligned} c_{10}^m &= n_{\mathrm{CH_2}} - n_{\mathrm{OH}} \\ c_{10}^m &\geq -M(1-y^e) \end{aligned} \tag{4.14}$$

$$\begin{aligned} c_{11}^m &= n_{\mathrm{CH_3}} - n_{\mathrm{OH}} \\ c_{11}^m &\leq My^e \end{aligned} \tag{4.15}$$

Chapter 5

VHC Benchmarks

VHC (MJ m^{-3})		T_{source} (K)				
		340	360	380	400	420
T_{sink} (K)	360	Ammonia (R-717) **23.9**	–	–	–	–
	380	Ammonia (R-717) **20.6**	Ammonia (R-717) **29.8**	–	–	–
	400	1,1,1,3,3-Pentafluoropropane (R-245fa) **2.6**	1,1,1,3,3-Pentafluoropropane (R-245fa) **4.40**	1,1,1,3,3-Pentafluoropropane (R-245fa) **7.3**	–	–
	420	Pentane (R-601) **1.2**	Pentane (R-601) **2.1**	Pentane (R-601) **3.6**	Pentane (R-601) **5.1**	–
	440	Pentane (R-601) **0.6**	Pentane (R-601) **1.2**	Water (R-718) **2.4**	Pentane (R-601) **4.3**	Pentane (R-601) **7.0**