



## DESIGNING ENVIRONMENTALLY SAFE REFRIGERANTS USING MATHEMATICAL PROGRAMMING

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**Abstract**—Computer-aided molecular design is a strategy in which a set of structural groups are systematically combined to form molecules with desired properties. In this paper, a mathematical programming-based approach to computer-aided molecular design is presented. Using a set of structural groups, the problem is formulated as a mixed integer nonlinear program in which discrete variables represent the number of each type of structural groups present in the candidate compound. The augmented-penalty/outer-approximation algorithm is used to solve the MINLP to obtain compound(s) with an optimum value of an appropriate performance index such that molecular structural constraints, physical property constraints and process design limitations are met. With the current renewed interest in the environment, the suggested approach is applied to refrigerant design with an environmental constraint. The results indicate the viability of this approach. Copyright © 1996 Elsevier Science Ltd.

### INTRODUCTION

The chemical industry is constantly exploring ways to synthesize compounds with improved properties. This search is in general very prolonged and expensive. A combination of heuristics and costly experimental studies have generally been employed to identify compounds which have physical property values appropriate to a given application. In these trial and error approaches, a compound is synthesized, its physical properties are estimated and compared with the desired properties for that application.

Computer-aided molecular design (CAMD) employs a reverse engineering approach of incorporating property and performance specifications directly into the design of the compound. The availability and the accuracy of the property estimation techniques employed to predict the target properties, restrict the scope of CAMD (Gani *et al.*, 1991). In the last decade, however, significant advances have been made in the use of group contribution methods for the prediction of pure-component and mixture properties (Reid *et al.*, 1987; Joback and Reid, 1987; Larsen *et al.*, 1987; Sander *et al.*, 1986; Dahl *et al.*, 1991; Lai *et al.*, 1987).

Gani and Brignole (1983) and Brignole *et al.* (1986) have presented methods of solvent design related to liquid–liquid extraction. Joback and Stephanopoulos (1989) have examined the design of replacement refrigerants for automotive air conditioners. They have considered refrigerant design based on pure-component properties and ideal mixing rules for properties of mixtures.

Gani *et al.* (1991) have outlined a flexible and structured CAMD approach which involves preselection

of structural groups, followed by generation of structurally feasible chemical compounds using a knowledge-based system. Subsequently, the properties are predicted using group contribution methods. Finally, the compounds are rated in terms of a performance index, which is a function of the explicit target properties. This approach was successfully used for selection of refrigerants in addition to the design of solvents for liquid–liquid extraction and solvents for gas absorption.

The approach employed by Macchietto *et al.* (1990) is to evaluate all feasible molecular structures implicitly within the framework of a constrained optimization problem which was solved assuming all the variables were continuous. This approach, though viable, dealt with the discrete variables associated with the structural groups by suitable rounding of continuous variables or by addition of integer forcing constraints. Solvents which were identified this way were not optimal. Odele and Macchietto (1993) later considered the selection of solvents for gas absorption and liquid extraction using a mixed integer nonlinear programming (MINLP) approach that dealt with discrete variables explicitly.

In this paper, a mixed integer nonlinear programming-based approach to computer-aided molecular design of refrigerants is presented. In the formulation, we have accounted for environmental considerations. Finally, a hybrid property estimation technique has been developed for the design.

The paper is organized as follows. We start with a description of the formulation of the refrigerant design problem (incorporating environmental restrictions) as an MINLP. Subsequently, the estimation techniques employed to predict the physical properties of refrigerants are presented. This is followed by the solution procedure and test examples to illustrate the viability of the approach.

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## MINLP MODEL

An MINLP-based methodology is used to design refrigerants with desired physical properties. Different combinations of pre-selected structural groups lead to the formation of different chemical compounds. Deciding which structural groups to include and which not to include in the basis is problem-dependent. For example, in refrigerant design, groups with double or higher number of bonds can make it highly possible for the resulting compounds to polymerize in a relatively short period of time (Rosendahl-Jensen, 1990). Thus, such groups are excluded from the basis. In addition, all those structural groups are to be excluded for which the parameters necessary to estimate the relevant physical properties are unavailable. The choice of the initial set of structural groups can be based on groups present in currently available refrigerants. Subsequently more groups can be added to this list so that the search for the "optimal" molecule is not too restrictive.

The refrigerant design problem can be mathematically formulated as the following nonlinear program:

$$\text{Max}_{\mathbf{n}, \mathbf{x}} p(\mathbf{n}, \mathbf{x})$$

subject to:

$$\begin{aligned} A\mathbf{n} &\leq b && \text{structural feasibility} \\ \mathbf{x} - g(\mathbf{n}) &= 0 && \text{physical property} \\ \mathbf{x}^l &\leq \mathbf{x} \leq \mathbf{x}^u \\ \mathbf{n} &: \text{integer (discrete) variable} \\ \mathbf{x} &: \text{continuous variable.} \end{aligned}$$

Here  $\mathbf{n}$  determines the kind of structural groups in the molecule. This is the only information required to estimate the physical properties ( $g(\mathbf{n})$ ) using the correlations in this paper. This initial formulation of the MINLP includes constraints that are nonlinear in the integer variables ( $\mathbf{n}$ ). A direct method of handling this nonlinearity efficiently does not exist however. Thus, the initial MINLP is modified by defining new continuous variables and new constraints in which these variables are set equal to the integer variables, thereby restricting the nonlinearity to the continuous variables only. The resulting formulation which is nonlinear only in the continuous variables  $\mathbf{x}$  can be expressed as

$$\text{Max}_{\mathbf{n}, \mathbf{x}} p(\mathbf{x})$$

subject to:

$$\begin{aligned} \mathbf{x}' &= \mathbf{n} && (1) \\ A\mathbf{n} &\leq b && (2) \\ \mathbf{x} - g(\mathbf{x}') &= 0 && (3) \\ \mathbf{x}^l &\leq \mathbf{x} \leq \mathbf{x}^u \\ \mathbf{n} &: \text{integer} \\ \mathbf{x} &: \text{continuous.} \end{aligned}$$

## Variables

In the above formulation,  $\mathbf{n}$  is a vector of integer variables characterizing the molecular configuration with scalar variables  $n_j$  indicating the number of structural groups of type  $j$  in the molecule.  $\mathbf{x}'$  is a vector of "pseudo-continuous" variables which are set equal to the integer variables through eq. (1). These variables are referred to as "pseudo-continuous" only to distinguish them from the other continuous variables.  $\mathbf{x}'$  is a subset of  $\mathbf{x}$ , which is a vector of all the continuous variables.

## Objective function

In the refrigerant design problem, the performance index  $p$  is expressed in terms of target property values. For example,  $p$  can be expressed in terms of the heat of vaporization ( $h_v$ ) and the liquid heat capacity ( $C_{pl}$ ) as

$$p = x_1/x_2 \quad (4)$$

where  $x_1$  and  $x_2$  are continuous variables set equal to  $h_v$  and  $C_{pl}$ , respectively, through eq. (3).

## Constraints

The three basic types of constraints for this MINLP can be listed as

(i) Assignment constraints ( $\mathbf{x}' = \mathbf{n}$ ):

These constraints are linear in the integer variables as well as the pseudo-continuous variables. The function of these equalities is to assign the values of the integer variables to the pseudo-continuous variables.

(ii) Structural feasibility constraints ( $A\mathbf{n} \leq b$ ):

Structural feasibility constraints are included in the MINLP formulation to ensure the structural feasibility of the synthesized molecules. These constraints are linear in the integer variables and do not involve the continuous variables.

The following constraints (Odele and Macchietto, 1993) have been employed:

$$\sum_j (2 - v_j) n_j = 2m \quad (5)$$

$$\sum_{i \neq j} n_i \geq n_j (v_j - 2) + 2 \quad \text{for all } j \quad (6)$$

$$\Rightarrow \sum_i n_i \geq n_j (v_j - 1) + 2 \quad \text{for all } j \quad (7)$$

$$n_j^l \leq n_j \leq n_j^u \quad (8)$$

$$2 \leq \sum_j n_j \leq n_{\max} \quad (9)$$

Equation (5) is a realization of the octet rule which provides a simple relation to ensure that a collection of groups has no free attachment.  $n_j$  and  $v_j$  are the number and valence, respectively, of groups of type  $j$ . For acyclic, monocyclic and bicyclic groups,  $m = 1$ , 0 and  $-1$ , respectively. In this paper, only acyclic compounds ( $m = 1$ ) have been considered since most of the conventional refrigerants are acyclic. This formulation of the octet rule is valid only for single bonded compounds.

Since only single bonded compounds are considered in refrigerant design, structural feasibility requires that two adjacent groups in the molecule may not be linked by more than one bond. In other words, for each structural group present, there must be at least as many other groups as available attachments. Inequalities (6) and (7) express this structural constraint. Through inequality (8), additional constraints are placed on the number  $n_j$  of groups of type  $j$  to keep it within lower and upper bounds  $n_j^l$  and  $n_j^u$ , respectively.

Group contribution methods, in general, become less accurate as the number of structural groups in a molecule increases. An upper bound ( $n_{\max}$ ) is therefore imposed on the sum of all the groups in the molecule through eq. (9). This can make the search for the "optimal" compounds restrictive, but it is a compromise that has to be made to avoid large inaccuracies in property prediction. As property estimation techniques become more accurate, large values of  $n_{\max}$  can be employed. In order to restrict the search to  $C_1$ – $C_4$  compounds (as higher compounds are not suitable for the refrigerant problem due to low vapor pressures),  $n_{\max}$  is chosen as 14 (four carbon atoms can bond with a maximum of ten hydrogen atoms or other functional groups thus making a total of 14). A lower limit is determined from the fact that at least two groups must be used to form a structurally feasible molecule. In addition, the following structural feasibility constraints have been included in this paper:

$$0 \leq \sum_j n_j \leq f_{\max} \quad \text{over all functional groups } j \quad (10)$$

$$n_R + f_{\max} (n_{\text{NH}_2} + n_{\text{NH}} + n_{\text{N}}) \leq f_{\max} \quad \text{for all halides R.} \quad (11)$$

General group contribution techniques cannot handle a large number of certain nonhydrocarbon groups (such as halides, alcohols and amines) efficiently. Therefore, eq. (10) is used to place an upper bound ( $f_{\max}$ ) on the total number of such functional groups. Here  $f_{\max}$  is chosen as 10 (a maximum of ten functional groups can be attached to a  $C_4$  chain). The lower limit is zero as it is possible to form molecules using just the hydrocarbon groups.

An implicit constraint considered by Gani *et al.* (1991) is that low boiling compounds containing halides and nitrogen have a strong tendency to explode and therefore, halogen and nitrogen groups should not exist together in the refrigerant molecule. It is also desired to have at most one of the three nitrogen groups ( $\text{NH}_2$ ,  $\text{NH}$ ,  $\text{N}$ ) in the molecule. Both of these constraints can be expressed together in terms of the integer variables through eq. (11)

(iii) *Physical property and process constraints* ( $x - g(x') = 0$ ):

These constraints assign the calculated physical property values to the continuous variables. They are nonlinear in the pseudo-continuous variables. The property values are estimated using a property es-

timination routine outside the MINLP framework. The function  $g(x')$  would include process variables such as the compressor displacement. The properties to be evaluated are (a) heat of vaporization, (b) liquid heat capacity, (c) vapor pressure, (d) ozone depletion potential and (e) compressor displacement. Compressor displacement is not a physical property of the refrigerant; however, it can be calculated directly from the other property values. The constraints on the physical properties and the process variable(s) are expressed as lower and/or upper bounds on the continuous variables.

#### TARGET MOLECULE PROPERTY ESTIMATION

Physical property estimation techniques are required to generate target property values for the different compounds obtained by combining the structural groups. The accuracy of these estimation methods is critical to the success of a molecular design strategy.

Target properties are of two types, pure component properties and mixture properties. Each type can be a primary property or a secondary property. Primary properties can be determined directly from a group contribution method, while secondary properties are determined by methods or correlations that use some of the primary properties.

In the refrigerant design problem, some important target properties are: (1) heat of vaporization ( $h_v$ ), (2) liquid heat capacity ( $C_{pl}$ ), (3) vapor pressure ( $P_{vp}$ ) and (4) ozone depletion potential (ODP). All of these are single-component properties. The ODP,  $C_{pl}$  and primary properties such as the normal boiling point ( $T_b$ ), critical temperature ( $T_c$ ) and critical pressure ( $P_c$ ) are evaluated by group contribution.  $T_b$ ,  $T_c$  and  $P_c$  are subsequently used by correlations to estimate  $h_{vp}$  and  $P_{vp}$ . Another important property (estimated using correlations) is the theoretical compressor displacement (CD) which determines the required size of the compressor for a given tonnage of the refrigerant.

Several group contribution techniques exist to estimate the normal boiling point and the critical properties. The choice of the estimation technique depends on the initial set of structural groups since many of these techniques are specific to certain kinds of groups. While designing a refrigerant, one needs an estimation technique which gives accurate prediction (to within 5% of experimental value) for halogenated compounds. There does not appear to be a group contribution technique good enough for the accurate prediction of  $T_b$  for a large class of highly halogenated compounds. Therefore, a hybrid of some of the group contribution approaches in the open literature was developed.

Details of the hybrid estimation technique are provided in the appendix and here we provide a summary of the technique. In the hybrid method, the following three group contribution techniques were used to predict the boiling points of halogenated derivatives of  $C_1$ – $C_4$  hydrocarbons: (a) a linear technique (Joback

and Reid, 1987), (b) the Miller method (Joback and Reid, 1987) and (c) a nonlinear technique (Lai *et al.*, 1987). The predictions of the three methods were then compared with the reported experimental values (Reid *et al.*, 1987). Subsequently, heuristics and statistical tools were employed to combine these methods in order to obtain a good fit for halogenated derivatives of  $C_1$ – $C_4$  hydrocarbons. The Miller method was found to be reasonably accurate for nonhalogenated compounds.

For example, for methane derivatives with one halogen atom, the normal boiling point as calculated by the hybrid method is given by

$$T_b = T_{\text{nl}} \quad (\text{nonlinear technique}). \quad (12)$$

For di-substituted methane derivatives,

$$T_b = 1.03T_{\text{linear}} \quad \text{if } -I \text{ is absent} \quad (13)$$

$$T_b = 1.07T_{\text{linear}} \quad \text{if } -I \text{ is present} \quad (14)$$

where  $-I$  represents an iodine group.

The critical temperature is estimated using Fedors' technique (Fedors, 1982), the Miller method and the linear method. The critical pressure is predicted using either the Miller method or the linear technique.

The boiling point, critical temperature and critical pressure are then used to evaluate the target properties as follows. The heat of vaporization at the normal boiling point is estimated using Vetere's modification of the Kistiakowsky equation (Vetere, 1973):

$$h_{vb} = S_{vb} T_b \quad (15)$$

For alcohols, acids and methylamine:

$$S_{vb} = 81.119 + 13.083 \log T_b - 25.769 T_b/M \\ + 0.146528 T_b^2/M - 2.1362 \times 10^{-4} T_b^3/M. \quad (16)$$

For other polar compounds:

$$S_{vb} = 44.367 + 15.33 \log T_b + 0.39137 T_b/M \\ + 0.00433 T_b^2/M - 5.627 \times 10^{-6} T_b^3/M. \quad (17)$$

For hydrocarbons:

$$S_{vb} = 58.2 + 13.7 \log M + 6.49 \\ \times \{ [T_b - (263M)^{0.581}]^{1.037} \} / M. \quad (18)$$

The advantage of Vetere's method is that it depends on just one estimated primary pure-component property (namely, the normal boiling point), thereby reducing the uncertainty in the prediction. From these equations, the predicted value of  $h_{vb}$  is almost always within 5% of the experimental value; for most cases the error is below 3% (Reid *et al.*, 1987). The Watson relation is used to estimate the heat of vaporization at any temperature,  $T$  (Thek and Stiel, 1967):

$$h_v = h_{vb} [(1 - T/T_c)/(1 - T_b/T_c)]^n \quad (19)$$

where

$$n = [0.00264 h_v / (R T_b) + 0.8794]^{10} \quad (20)$$

as recommended by Viswanath and Kuloor (1967).

The vapor pressure is estimated using the Riedel–Plank–Miller equation (Reid *et al.*, 1977):

$$\ln P_{\text{vpr}} = -G [1 - T_r^2 + k(3 + T_r)(1 - T_r)^3] / T_r, \quad (21)$$

$$G = 0.4835 + 0.4605h \quad (22)$$

$$h = T_{br} \ln P_c / [1 - T_{br}] \quad (23)$$

$$k = [h/G - (1 + T_{br})] / [(3 - T_{br})(1 - T_{br})^2] \quad (24)$$

where

$$P_{\text{vpr}} = P_{\text{vp}} / P_c, \quad T_{br} = T_b / T_c \quad \text{and} \quad T_r = T / T_c.$$

The liquid heat capacity is estimated using a group contribution technique (Chueh and Swanson, 1973).

Compounds with a minimum of one chlorine, bromine or iodine group are known to have a non-zero ozone depletion potential (ODP). However, ODP data are scarce and limited to a few halogenated compounds. For hydrochlorofluorocarbons with one or two carbon atoms, the ODP can be quantitatively expressed as (Nimitz and Skaggs, 1992):

$$\text{ODP} = 0.05013 n_{\text{Cl}}^{1.510} \exp(-3.858/\tau) \quad (25)$$

where the tropospheric lifetime  $\tau$  is given by

$$\tau = 0.787 (M/n_H) \exp(-2.060 n_{\alpha\text{-Cl}} \\ - 4.282 n_{2\text{C}} + 1.359 n_{\beta\text{-F}} + 0.926 n_{\beta\text{-Cl}}). \quad (26)$$

The  $\alpha$  designation implies that a substituent is attached to the same carbon atom as the hydrogen atom being considered;  $\beta$  means the substituent is attached to the carbon atom adjacent to the carbon atom bonded to the hydrogen. The subscript 2C indicates a term to be added only if two carbon atoms are present. Here  $n_{\alpha\text{-Cl}}$  represents the number of  $\alpha$  chlorine atoms present; the other symbols are similarly defined. Finally,  $n_H$  represents the number of abstractable hydrogen atoms.

The ODP values for a number of chlorofluorocarbons (CFCs) with one or two carbon atoms have been reported (Solomon *et al.*, 1992a, b; Lea, 1991; Stamm, 1989). Using these values, we formulate the following general expressions for the ODP of CFCs with one or two carbon atoms:

$$\text{ODP} = 0.585602 n_{\text{Cl}}^{-0.0035} \exp(M/238.563) \quad (27)$$

one carbon

$$\text{ODP} = 0.0949956 n_{\text{Cl}}^{-0.0404477} \exp(M/83.7953) \quad (28)$$

two carbon.

In addition to the above compounds, the ODP has been reported for other compounds (see the appendix). This leaves mainly  $C_1$ – $C_2$  bromides and iodides and higher carbon halides which are believed to have high ODPs. As such, the ODP is arbitrarily set to a large value for these remaining compounds.

The theoretical compressor displacement (CD) for a refrigerant is calculated as (Perry and Chilton, 1973)

$$CD \text{ (m}^3\text{/min)} = W_f V_g \quad (29)$$

where the weight flow ( $W_f$ ) is given by

$$W_f \text{ (kg/min)} = 200 \times 10^4 / (9.47831 \text{ RE}) \quad (30)$$

and the refrigerating effect (RE) is evaluated as

$$RE \text{ (J/kg)} = H_{vs} - H_{lc} \quad (31)$$

Here  $H_{vs}$  is the enthalpy of vapor leaving the evaporator and  $H_{lc}$  is the enthalpy of liquid leaving the condenser in the refrigeration cycle.  $H_{vs}$  and  $H_{lc}$  are evaluated from the primary properties using correlations (see the Appendix).  $V_g$  is the specific volume ( $\text{m}^3\text{/kg}$ ) of the suction vapor entering the compressor and it is also evaluated using correlations as shown in the Appendix.

#### SOLUTION OF MINLP

The augmented penalty outer approximation (AP/OA) algorithm (Viswanathan and Grossmann, 1990) is employed to solve the MINLP. This algorithm involves solving a finite sequence of nonlinear programming (NLP) *subproblems* and mixed integer linear programming (MILP) *master problems*.

NPSOL (Gill *et al.*, 1986) is used to solve the NLPs, while OSL (IBM Corp.) is used to solve the MILPs. Derivative information relating objective and constraint functions to all optimization variables, is employed in guiding the search for the optimum. If the derivatives cannot be calculated analytically, derivatives by perturbation techniques are employed.

The flowchart for the algorithm, which is described next, is given in Fig. 1. Initially, a relaxed form of the original MINLP problem in which the integer variables are considered to have continuous values, is solved using NPSOL. If all the variables in the  $\mathbf{n}$  vector (of the original MINLP) turn out to be integers, this solution to the relaxed problem is the optimal solution for the MINLP. If not, the noninteger solution serves as an initial guess for a mixed integer linear program (MILP) which yields an integer estimate of the solution. In the MILP, the nonlinear objective and constraint functions of the original MINLP are linearized at the current continuous solution. The optimization variables for this MILP are the original variables together with nonnegative slack variables which allow the linearizations of the objective and constraint functions to be violated at the expense of being penalized in a modified objective function. The penalty weights for the slack variables are set equal to a large value times the magnitude of the Lagrange multipliers of the nonlinear constraints obtained from the previous

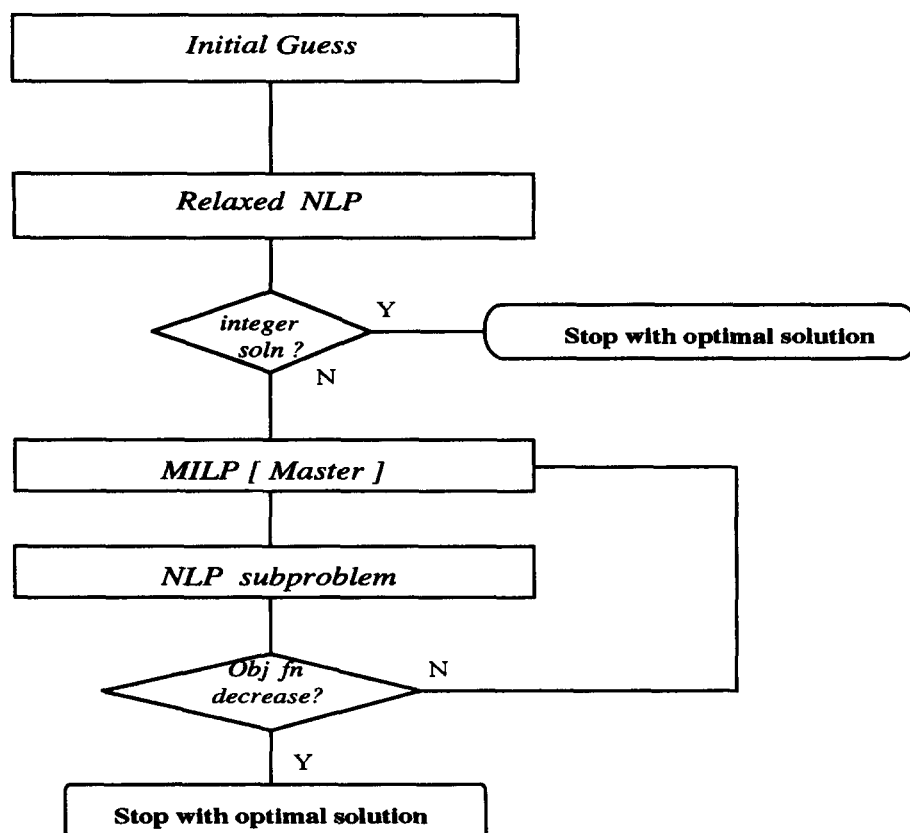


Fig. 1. Flowchart for the MINLP algorithm (for a maximization problem).

nonlinear program (NLP). OSL uses a branch and bound technique to solve the MILP.

The integer estimate obtained from the MILP is then used in an NLP subproblem to get new values of the continuous variables and thus a new point for linearizing the nonlinear functions in the next MILP. The MILPs and the NLPs are solved successively until there is a decrease (for a maximization problem) in the value of the objective function for successive feasible NLP subproblems. General integer cuts are added to the MILPs to exclude previously identified integer estimates from the search space.

It is possible that an MILP will yield an integer estimate for which there is no feasible solution from the corresponding NLP subproblem. In this case, there are two ways to handle the problem. One way is to disregard the infeasible continuous point for the linearization in the next MILP and just introduce an integer cut. This approach has been employed in this paper. The other option is to add the linearization at this infeasible continuous point to the master problem. However, in addition to this, information on the Lagrange multipliers is required to relax the equations.

The main function of the relaxed problem solution is to provide an initial guess for the MILP-NLP sequence. As such, even a nonoptimal solution to the relaxed problem can serve as an initial guess for the MILP-NLP iterations and yield an optimal solution to the MINLP. This was observed while solving case-study II, when the relaxed problem solution, though not optimal, was used to obtain an optimal solution for the MINLP. Due to the nonconvexity of the problem, this solution is only a local optimum.

#### CASE STUDY I

In this case study, the refrigerant design problem of finding alternative refrigerants to freon-12 (Joback and Stephanopoulos, 1989) is considered. Chlorofluorocarbon (CFC)-based refrigerants (such as freon-12) have found wide uses in home refrigerators and automotive air conditioners primarily due to their nontoxic, nonflammable nature (Masters, 1991) in addition to their overall efficiency. However, it is widely believed that CFC refrigerants damage the Earth's protective ozone layer (Stamm, 1989). A significant source of CFC-based refrigerant leakage into the environment is from automotive air conditioners. Thus, there is a need to find replacement refrigerants for automotive air conditioners.

The refrigeration process is defined by the following temperatures: (a) evaporating temperature ( $T_e$ ) = 30°F, (b) condensing temperature ( $T_{cd}$ ) = 110°F. Saturated conditions are assumed so that the superheat temperature ( $T_s$ ) is equal to the  $T_e$ .

The first step is to choose an initial set of structural groups. We have included an implicit constraint to ensure that the refrigerant would not polymerize over a long period of time. Thus, as mentioned earlier, double or triple bonds should not exist in the mole-

cule. In addition, most refrigerants used for automotive air conditioning are aliphatic compounds. It is practical therefore to concentrate on just aliphatic structural groups.

Based on the above criteria, a set of 15 structural groups is identified:

CH <sub>3</sub>	CH <sub>2</sub>	CH	C	F	Cl	Br	I
OH	O	NH <sub>2</sub>	NH	N	SH	S	

#### Objective function

The objective is to find a refrigerant as good as or better than freon-12; that is a refrigerant with a larger heat of vaporization ( $h_v$ ) and with a smaller liquid heat capacity ( $C_{pl}$ ) than that of freon. Subsequently, the objective function can be expressed as

$$p = x_1/x_2 \quad (32)$$

where,  $x_1$  and  $x_2$  are continuous variables which are set equal to  $h_v$  and  $C_{pl}$  in the MINLP formulation through eq. (A3).

#### Variables

The relevant physical properties for this problem are: (a)  $h_v(T_e)$ , (b)  $C_{pl}(T_{mean})$ , (c)  $P_{vp}(T_e)$  and (d)  $P_{vp}(T_{cd})$ . There exist 15 integer variables and hence 15 pseudo-continuous variables corresponding to the structural groups chosen. In addition, there exist four continuous variables corresponding to the above-mentioned properties.

#### Constraints

As explained earlier, there exist the assignment constraints, the structural feasibility constraints [described by eqs (25)–(31)] and the constraints which assign the calculated physical property values to the continuous variables. In addition, the following constraints on physical property values are expressed as bounds on the corresponding continuous variables:

$$h_v(T_e) \geq h_{v, \text{freon}}(T_e) \quad (33)$$

$$C_{pl}(T_{mean}) \leq C_{pl, \text{freon}}(T_{mean}) \quad (34)$$

$$P_{vp}(T_e) \geq 1.4 \text{ bar} \quad (35)$$

$$P_{vp}(T_{cd}) \leq 14 \text{ bar} \quad (36)$$

Equation (33) expresses the fact that a large  $h_v$  reduces the amount of refrigerant needed. The value for the enthalpy of vaporization of freon 12 (estimated by the hybrid method) is  $h_{v, \text{freon}}(30^\circ\text{F}) = 18.74 \text{ kJ/g mol}$ . Since the objective is to find a refrigerant better than freon-12, this value is used instead of the 18.4 kJ/g mol reported in the literature (ASHRAE, 1972).

It is desirable to have a low liquid heat capacity. A low value of  $C_{pl}$  reduces the amount of refrigerant which flashes upon passage through the expansion valve. The heat capacity constraint in eq. (34) is evaluated at an average temperature of 70°F. An estimated

value of  $C_{pl, \text{freon}}(70^\circ\text{F}) = 27.12 \text{ cal/g mol}$  is assumed for the liquid heat capacity of freon-12.

The lowest pressure in the cycle should be greater than the atmospheric pressure (Dossat, 1981) as expressed in eq. (35). This reduces the possibility of air and moisture leaking into the system. On the other hand, a high system pressure increases the size, weight and cost of equipment (Dossat, 1981). A pressure ratio of 10 is considered to be the maximum for a refrigeration cycle (Perry and Chilton, 1973); this value is used in eq. (36) to put a bound on the system pressure.

### Results

Table 1 lists the compounds obtained at each major iteration and their computed physical property values.  $F_{1.38} I_{0.62}$  was obtained after solving the relaxed problem and it serves as a starting point for the sequence of MILPs and NLPs.  $\text{CH}_3\text{Cl}$  was the optimal molecule identified. In the optimization algorithm employed here, structural feasibility constraints exist only in the MILP. Only if these constraints are nonlinear, do they have to be approximated by linearizations in the MILP. Thus, the linearity of all the structural feasibility constraints in our formulation further ensures that compounds at each major iteration are structurally feasible and as such are potential alternatives to the optimal compound.

For many initial guesses, the relaxed problem gave the same fractional solution  $F_{1.38} I_{0.62}$  and thus the

same starting point for the sequence of MILPs and NLPs. This may indicate that the fractional solution  $F_{1.38} I_{0.62}$  is the global optimum for the relaxed problem. However, the compound found after solving the sequence of MILPs and NLPs (in this case  $\text{CH}_3\text{Cl}$ ) represents only a local optimum for the chosen set of structural groups and constraints.

The MINLP approach can easily handle changes in the constraints or the objective function. For example, if the lower limit on the vapor pressure (at  $-1.1^\circ\text{C}$ ) is relaxed to 1.0 bar, the feasible region for the problem expands and a different iteration sequence is obtained (Table 2). Similarly, modifications made in the objective function will get reflected in a different iteration sequence and a different solution as well.

The MINLP formulation reduces to a feasibility problem if the objective function is set equal to a constant. This would yield compounds which satisfy the structural and physical property constraints of the problem. Table 3 lists a few compounds obtained using this approach and different initial guesses. At this point, however, there is no guarantee that the potential refrigerants obtained are environmentally "safe".

### CASE STUDY II

In the first case study, there is no guarantee that the alternative refrigerants obtained are environmentally friendly. In this case study, a quantitative measure (the

Table 1. Iteration sequence for objective function =  $h_v/C_{pl}$  ( $h_v [=]$  kJ/g mol;  $C_{pl} [=]$  cal/g mol;  $P_{vp} [=]$  bar)

Itn #	Compound type	Obj. function	$h_v$ ( $-1.1^\circ\text{C}$ )	$C_{pl}$ ( $21.1^\circ\text{C}$ )	$P_{vp}$ ( $-1.1^\circ\text{C}$ )	$P_{vp}$ ( $43.3^\circ\text{C}$ )
0	$F_{1.38} I_{0.62}$	1.9985	21.91	10.96	1.40	6.17
1	$\text{CH}_3 \text{ O F}$	1.0266	21.81	21.24	1.79	8.60
2	$\text{CH}_3 \text{ Cl}$	1.1737	<b>20.44</b>	<b>17.42</b>	<b>2.45</b>	<b>9.19</b>
3	$\text{CH}_3 \text{ NH}_2$	0.9686	22.11	22.82	2.29	8.51

Table 2. Iteration sequence for objective function =  $h_v/C_{pl}$  ( $P_{vp} \geq 1.0$  bar instead of 1.4;  $h_v [=]$  kJ/g mol;  $C_{pl} [=]$  cal/g mol;  $P_{vp} [=]$  bar)

Itn #	Compound type	Obj. function	$h_v$ ( $-1.1^\circ\text{C}$ )	$C_{pl}$ ( $21.1^\circ\text{C}$ )	$P_{vp}$ ( $-1.1^\circ\text{C}$ )	$P_{vp}$ ( $43.3^\circ\text{C}$ )
0	$F_{1.32} I_{0.68}$	2.0519	23.03	11.23	1.00	4.66
1	$\text{CH}_3 \text{ O F}$	1.0266	21.81	21.24	1.79	8.60
2	$\text{CH}_3 \text{ Cl}$	1.1737	<b>20.44</b>	<b>17.42</b>	<b>2.45</b>	<b>9.19</b>
3	$\text{CH}_2 \text{ F Cl}$	1.1372	22.69	19.95	1.24	5.40

Table 3. Feasible solutions (objective function = constant = 1.0) ( $h_v [=]$  kJ/g mol;  $C_{pl} [=]$  cal/g mol;  $P_{vp} [=]$  bar)

Compound type	$h_v$ ( $-1.1^\circ\text{C}$ )	$C_{pl}$ ( $21.1^\circ\text{C}$ )	$P_{vp}$ ( $-1.1^\circ\text{C}$ )	$P_{vp}$ ( $43.3^\circ\text{C}$ )
$\text{C Cl}_2 \text{ F}_2$	18.74	27.12	2.96	10.69
$\text{C F}_3 \text{ I}$	19.53	22.57	2.32	8.68
$\text{C F}_3 \text{ OH}$	24.52	24.68	2.70	13.51
$\text{CH}_3 \text{ Cl}$	20.44	17.42	2.45	9.19

ozone depletion potential or ODP) of the environmental damage caused by the depletion of the earth's ozone layer is incorporated in the refrigerant design objective in addition to the compressor displacement (CD).

The compressor displacement is directly proportional to the size of the compressor required in a refrigeration cycle and is thus a measure of the performance or the efficiency of the refrigerant used. For cost reasons, it is desirable to use refrigerants that have a low compressor displacement.

#### Objective function

The incorporation of the ODP and the CD ensure that the resulting refrigerant is environmentally safe and efficient. In the objective function, the ODP and the CD are traded off as follows:

$$p = -Wt_1 x_{CD} - x_{ODP} \quad (37)$$

where  $x_{ODP}$  and  $x_{CD}$  refer to the ODP and CD, respectively, in the MINLP formulation.  $Wt_1$  is a relative weight assigned to the CD term in the objective function.

#### Variables

In addition to the variables defined in the previous case study, there exist two continuous variables corresponding to the ODP and the CD.

#### Constraints

The performance or the efficiency of the refrigerant is reflected better in the compressor displacement than the heat of vaporization. There may exist refrigerants which have a low compressor displacement and are therefore efficient in spite of a low heat of vaporization. Imposing a strict lower bound on the heat of vaporization can exclude such efficient compounds from the search. Thus, the corresponding constraint is relaxed as follows:

$$h_v(T_e) \geq 10.0 \text{ kJ/g mol.} \quad (38)$$

The lower bound is arbitrarily chosen as 10.0. The remaining constraints, which include the assignment constraints, the structural feasibility constraints and the constraints which assign the calculated physical property values to the continuous variables are the same as those used in the first case study. The results are summarized in Table 4 with  $\text{CH}_3\text{CH}_2\text{F}$  as the locally optimal refrigerant.

Next  $Wt_1$  is set equal to 10.0 instead of 1.0. This means that a greater importance is placed on the compressor displacement than the ozone depletion potential in the objective function. Again, the relaxed problem yielded a fractional, nonoptimal solution which was used to initiate the search. Table 5 lists the

Table 4. Iteration sequence.  $Wt_1 = 1.0$ ,  $T_e = 30^\circ\text{F}$ ,  $T_s = 30^\circ\text{F}$ ,  $T_{cd} = 110^\circ\text{F}$  ( $h_v$  [ = ] kJ/g mol;  $C_{pl}$  [ = ] cal/g mol;  $P_{vp}$  [ = ] bar; CD [ = ]  $\text{m}^3/(\text{min})$  (ton))

#	Compound	Obj. fn.	$h_v(T_e)$	$C_{pl}(T_m)$	$P_{vp}(T_e)$	$P_{vp}(T_{cd})$	CD	ODP
0	$(\text{CH}_2)_{0.42}(\text{F})_{1.4}(\text{OH})_{0.5}(\text{O})_{0.09}$ $-(\text{NH})_{0.06}(\text{SH})_{0.08}(\text{S})_{0.16}$	-0.0807	22.76	17.67	3.17	14.00	0.0807	0.0
1	<b><math>\text{CH}_3\text{CH}_2\text{F}</math></b>	<b>-0.0806</b>	<b>17.78</b>	<b>20.14</b>	<b>4.21</b>	<b>13.11</b>	<b>0.0806</b>	<b>0.0</b>
2	$\text{CH}_3\text{CHF}_2$	-0.1404	20.61	21.96	2.07	7.85	0.1404	0.0

Table 5. Iteration sequence.  $Wt_1 = 10.0$ ,  $T_e = 30^\circ\text{F}$ ,  $T_s = 30^\circ\text{F}$ ,  $T_{cd} = 110^\circ\text{F}$  ( $h_v$  [ = ] kJ/g mol;  $C_{pl}$  [ = ] cal/g mol;  $P_{vp}$  [ = ] bar; CD [ = ]  $\text{m}^3/(\text{min})$  (ton))

#	Compound	Obj. fn.	$h_v(T_e)$	$C_{pl}(T_m)$	$P_{vp}(T_e)$	$P_{vp}(T_{cd})$	CD	ODP
0	$(\text{CH}_3)_{1.09}(\text{F})_{0.08}$ $(\text{Cl})_{0.75}(\text{NH}_2)_{0.08}$	-0.8919	19.42	17.56	3.19	11.49	0.0884	0.008
1	<b><math>\text{CH}_3\text{CH}_2\text{F}</math></b>	<b>-0.806</b>	<b>17.78</b>	<b>20.14</b>	<b>4.21</b>	<b>13.11</b>	<b>0.0806</b>	<b>0.0</b>
2	$\text{CH}_3\text{Cl}$	-1.123	20.44	17.42	2.45	9.19	0.1118	0.005

Table 6. Iteration sequence.  $Wt_1 = 1.0$ ,  $T_e = 40^\circ\text{F}$ ,  $T_s = 65^\circ\text{F}$ ,  $T_{cd} = 100^\circ\text{F}$  ( $h_v$  [ = ] kJ/g mol;  $C_{pl}$  [ = ] cal/g mol;  $P_{vp}$  [ = ] bar; CD [ = ]  $\text{m}^3/(\text{min})$  (ton))

#	Compound	Obj. fn.	$h_v(T_e)$	$C_{pl}(T_m)$	$P_{vp}(T_e)$	$P_{vp}(T_{cd})$	CD	ODP
0	$(\text{CH}_3)_{0.08}(\text{C})_{0.17}(\text{F})_{1.36}(\text{OH})_{0.5}$ $(\text{NH}_2)_{0.1}(\text{NH})_{0.07}(\text{SH})_{0.31}$	-0.0699	22.84	17.93	3.57	11.03	0.0689	0.00
1	<b><math>\text{SF}_2</math></b>	<b>-0.0589</b>	<b>17.48</b>	<b>16.03</b>	<b>5.33</b>	<b>13.87</b>	<b>0.0589</b>	<b>0.0</b>
2	$\text{CH}_3\text{CHF}_2$	-0.1109	20.27	21.96	2.51	6.80	0.1109	0.0



Table 7. Comparison of predicted properties to experimental values ( $Wt_1 = 1.0$ ,  $T_e = 30^\circ\text{F}$ ,  $T_s = 30^\circ\text{F}$ ,  $T_{cd} = 110^\circ\text{F}$ ,  $h_v [=]$  kJ/g mol;  $P_{ep} [=]$  bar;  $CD [=]$  ( $\text{m}^3/\text{min}$ )(ton)))

Mol.	$h_v(T_e)$		$P_{ep}(T_e)$		$P_{ep}(T_{cd})$		CD		ODP		Obj. func.	
	Pred.	Expt.	Pred.	Expt.	Pred.	Expt.	Pred.	Expt.	Pred.	Expt.	Pred.	Expt.
$\text{CH}_3\text{Cl}$	20.44	20.50	2.45	2.46	9.19	9.27	0.1118	0.1077	0.005	0.005	-0.1168	-0.1127
$\text{CH}_3\text{CHF}_2$	20.61	20.20	2.07	2.56	7.85	9.96	0.1404	0.1131	0.000	0.000	-0.1404	-0.1131

compounds obtained at each major iteration and their computed physical property values.

Reducing the importance of the ozone depletion potential in the objective function by increasing the value of  $Wt_1$  to 10.0, yielded a feasible solution ( $\text{CH}_3\text{Cl}$ ) with a low compressor displacement and a nonzero ODP. However,  $\text{CH}_3\text{CH}_2\text{F}$  has a lower compressor displacement and a zero ODP and, hence, it is still the optimal compound.

The generality of the MINLP approach to refrigerant design is demonstrated by applying it to another refrigeration process. This is achieved by changing the values of the evaporating temperature ( $T_e$ ), the condensing temperature ( $T_{cd}$ ) and the superheat temperature ( $T_s$ ). For the new process, the following values were used: (a)  $T_e = 40^\circ\text{F}$ , (b)  $T_s = 65^\circ\text{F}$  and (c)  $T_{cd} = 100^\circ\text{F}$ . The resulting iteration sequence is listed in Table 6 with  $\text{SF}_2$  as the optimal molecule. However,  $\text{SF}_2$  is not a known refrigerant and it is uncertain whether it is thermodynamically and kinetically stable.

Finally, the ODP was removed from the original MINLP problem and the resulting MINLP was solved. Four local optima were identified for the corresponding relaxed problem, using a series of initial guesses. Subsequently, the mathematical program was solved using each of these four optimal solutions as the initial guess. In three out of four cases,  $\text{CH}_3\text{Cl}$  was the optimal solution identified, whereas in the fourth case,  $\text{CH}_3\text{CH}_2\text{F}$  was the optimal compound obtained.

For the case studies considered, sensitivity and flexibility can be seen qualitatively by looking at the performance of two refrigerants ( $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{CHF}_2$ ) in terms of the predicted as well as experimental values (Meacock, 1979; Nimitz and Skaggs, 1992) of the target properties (see Table 7). Here the "experimental value" of the compressor displacement is the value that is calculated using experimental enthalpies and specific volumes (Meacock, 1979).

It can be seen that the property prediction is much better for  $\text{CH}_3\text{Cl}$  than  $\text{CH}_3\text{CHF}_2$ . However, the same ranking ( $\text{CH}_3\text{Cl}$  is a better refrigerant for this process) is seen to be retained even when the experimental values are compared.

#### CONCLUSIONS AND FUTURE WORK

For refrigerant design, the MINLP approach is novel and has been shown to be efficient and flexible. Taking into consideration recent renewed interest in the environment, constraints have also been incorporated in this formulation to exclude refrigerants which would deplete the earth's protective ozone layer. Toxicity and flammability are important properties of the refrigerant and need to be incorporated in the MINLP framework.

The accuracy of the physical property estimation techniques employed is of extreme importance since it is used to guide the search for the optimal compound(s). Therefore, in this paper, efforts have been made to develop a hybrid method for accurate estimation of physical properties. Performing analysis to

determine the sensitivity of the objective function and the constraints to uncertainties in property predictions need to be considered. An important step would be to incorporate flexibility [see e.g. Papalexandri and Pistikopoulos (1994) for explanation of this concept] into the MINLP framework and thus enable it to operate within a specified range of property predictions.

In addition to sensitivity and flexibility issues, the issue of stability (thermodynamic and kinetic) of the structures obtained need to be addressed. We are exploring the "Gibbs free energy" criterion to establish thermodynamic stability. The octet rule is not valid for all compounds. Violation of the octet rule exists in the form of odd-electron species, incomplete octets, expanded octets (Petrucci, 1982). These need to be considered also.

In the current formulation, the type and the quantity of the different structural groups forming a compound are known. However, the relative positions of the groups in the compound cannot be determined. We have developed a new formulation which incorporates a bond pattern. With this new formulation, one would be able to know not only the type and number of the groups that are present in the molecule, but also their connectivity and arrangement within the molecule. However, for refrigerant design, it was not deemed necessary to use the more powerful formulation, since the property estimation techniques that are employed cannot take advantage of connectivity information that the new formulation allows. Finally, as the problem size increases, there will be a need to consider decomposition techniques and parallel branch and bound algorithms [see e.g. Pekny and Miller (1992)].

#### NOTATION

CD	compressor displacement
$C_{pl}$	liquid heat capacity
$f_{\max}$	maximum number of functional groups
$H_{lc}$	enthalpy of liquid leaving the condenser
$h_v$	heat of vaporization
$h_{vb}$	heat of vaporization at the normal boiling point
$H_{vs}$	enthalpy of vapor leaving the evaporator
$M$	molecular weight
$\mathbf{n}$	vector of integer variables
$n_{\alpha\text{-Cl}}$	number of $\alpha$ chlorine atoms
$n_{\beta\text{-Cl}}$	number of $\beta$ chlorine atoms
$n_{\beta\text{-F}}$	number of $\beta$ fluorine atoms
$n_{\text{Cl}}$	number of chlorine atoms
$n_{\text{H}}$	number of abstractable hydrogen atoms
$n_j$	number of groups of type $j$
$n_j^l$	lower limit on $n_j$
$n_j^u$	upper limit on $n_j$
$n_{\max}$	maximum number of structural groups
$n_{\text{NH}_2}$	number of $\text{NH}_2$ groups
$n_{\text{NH}}$	number of $\text{NH}$ groups
$n_{\text{N}}$	number of $\text{N}$ groups
ODP	ozone depletion potential

$p$	performance index
$P_c$	critical pressure
$P_{vp}$	vapor pressure
$P_{vpr}$	reduced vapor pressure
RE	refrigerating effect
$S_{vb}$	entropy of vaporization at the normal boiling point
$\tau$	tropospheric lifetime
$T$	temperature
$T_b$	normal boiling point
$T_{br}$	reduced boiling point
$T_c$	critical temperature
$T_{cd}$	condensing temperature
$T_e$	evaporating temperature
$T_{\text{linear}}$	normal boiling point by the Linear technique
$T_{\text{mil}}$	normal boiling point by the Miller technique
$T_{\text{nl}}$	normal boiling point by the Nonlinear technique
$T_r$	reduced temperature
$T_s$	superheat temperature
$V_g$	specific volume of the suction vapor entering the compressor
$v_j$	valency of group of type $j$
$\text{Wt}_i$	relative weight in the objective function
$\mathbf{x}'$	vector of pseudo-continuous variables
$\mathbf{x}$	vector of continuous variables
$\mathbf{x}^l$	vector of lower bounds on continuous variables
$\mathbf{x}^u$	vector of upper bounds on continuous variables

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## APPENDIX

### (1) Group contribution based prediction of $T_b$ , $T_c$ and $P_c$ :

$n_{HAL}$  is the number of halogen atoms in the molecule,  $n_{CAR}$  is the number of carbon atoms in the molecule and  $T_{mil}$  is the boiling point using Miller's method,  $T_{lin}$  is with the linear method and  $T_{nln}$  is with the nonlinear method. Similarly,  $T_{cmil}$  and  $P_{cmil}$  are the critical properties found using Miller's method and  $T_{clin}$  and  $P_{clin}$  are those using the linear technique.  $T_{cfedors}$  is  $T_c$  using Fedor's method. Also,

$$T_{min} = \text{Min} (T_{mil}, T_{lin})$$

$$T_{cmin} = T_{cmil} \text{ (if } T_{mil} < T_{lin}); \quad T_{cmin} = T_{clin} \text{ (if } T_{lin} < T_{mil}).$$

The philosophy behind the hybrid property estimation was to obtain predictions that were within 5% of the experimental values. To achieve this goal, the experimental results were compared with the predicted values using the three methods (Miller, Linear and Nonlinear). Using these comparisons, the compounds were divided into different categories based on the number of carbon ( $n_{CAR}$ ) and halogen ( $n_{HAL}$ ) atoms present. These categories were further divided into subcategories.

The main categories were as follows (i) [ $n_{CAR} = 0$ ,  $n_{HAL} = 0$ ], (ii) [ $n_{CAR} \neq 0$ ,  $n_{HAL} = 0$ ], (iii) [ $n_{CAR} = 1$ ], (iv) [ $n_{CAR} = 2$ ] and (v) all others. Within each subcategory, the experimental boiling point  $T_{b,exp}$  was correlated (using least squares) with the estimated boiling point  $T_{b,method}$  from each of the three methods as follows: (a)  $T_{b,exp} = T_{b,method}$  (least squares not used) or (b)  $T_{b,exp} = \alpha T_{b,method}$  or (c)  $T_{b,exp} = \alpha T_{b,method}^{\beta} + \gamma$ . If model (a) was not deemed adequate then model (b) was used. Similarly, if model (b) was not deemed adequate, then model (c) was used. The final  $T_b$  for our studies was obtained using the relevant optimal parameters from the set  $[\alpha, \beta, \gamma]$ . For [ $n_{CAR} = 1$ ,  $n_{HAL} = 4$ ],  $T_{b,exp} = \alpha n_F + \beta n_{Cl} + \gamma n_{Br} + \delta n_I$  gave the best fit. In addition, for [ $n_{CAR} = 2$ ,  $n_{HAL} = 4$ ],  $T_{b,exp} = \alpha T_{b,method}^{\beta} + \gamma$  gave the best fit. For the critical temperature (or pressure), a model of the form  $T_{c,exp} = T_{c,method}$  ( $P_{c,exp} = P_{c,method}$ ) was found to be adequate. In certain instances, ([ $n_{CAR} = 1$ ,  $n_{HAL} = 3$ ], [ $n_{CAR} = 2$ ,  $n_{HAL} = 2$ ] and [ $n_{CAR} = 2$ ,  $n_{HAL} = 3$ ]) we deviated from these models.

#### (i) $n_{CAR} = 0$ , $n_{HAL} = 0$

$$T_b = T_{mil}$$

$$T_c = T_{cmil}$$

#### (ii) $n_{CAR} \neq 0$ , $n_{HAL} = 0$

$$T_b = T_{nln}$$

$$T_c = T_{cfedors}$$

#### (iii) For $n_{CAR} = 1$ (see Table A1)

#### (iv) For $n_{CAR} = 2$ (see Table A2)

#### (v) All other cases

$$T_b = T_{mil}$$

$$T_c = T_{cmil}$$

Table A1

$n_{\text{HAL}}$	Normal boiling point ( $T_b$ )	Crit. temp. ( $T_c$ )
1	$T_b = T_{\text{nlm}}$	$T_c = T_{\text{cfedors}}$
2	$T_b = 0.0303557 T_{\text{lin}}^{1.56543} + 80.7909$	$T_c = T_{\text{clin}}$
3	$T_b = 1.07 T_{\text{min}}$ (If $[n_{\text{Cl}} + n_{\text{I}}] = 3$ ) $T_b = T_{\text{min}}$ (If $[n_{\text{Cl}} + n_{\text{I}}] \neq 3$ and $n_{\text{F}} = 0$ ) $T_b = 0.95 T_{\text{min}}$ (If $[n_{\text{Cl}} + n_{\text{I}}] \neq 3$ and $n_{\text{F}} = 1$ ) $T_b = 0.92 T_{\text{min}}$ (If $[n_{\text{Cl}} + n_{\text{I}}] \neq 3$ and $n_{\text{F}} \geq 2$ )	$T_b = T_{\text{cmin}}$
4	$T_b = 34.8 n_{\text{F}} + 87.3 n_{\text{Cl}} + 115.45 n_{\text{Br}} + 152.25 n_{\text{I}}$ (If $n_{\text{F}} < 3$ ) $T_b = 36.3 n_{\text{F}} + 82.8 n_{\text{Cl}} + 106.45 n_{\text{Br}} + 141.75 n_{\text{I}}$ (If $n_{\text{F}} \geq 3$ )	$T_c = T_{\text{cmin}}$

Table A2

$n_{\text{HAL}}$	Normal boiling point ( $T_b$ )	Crit. temp. ( $T_c$ )
1	$T_b = T_{\text{nlm}}$	$T_c = T_{\text{cfedors}}$
2	$T_b = T_{\text{nlm}} - 30$ (If $n_{\text{I}} = 3$ ) $T_b = T_{\text{lin}} + 10$ (If $n_{\text{I}} \neq 3$ and $n_{\text{CH}_2} = 0$ ) $T_b = T_{\text{nlm}}$ (If $n_{\text{I}} \neq 3$ and $n_{\text{CH}_2} = 2$ )	$T_c = T_{\text{clin}}$
3	$T_b = T_{\text{mil}}$ (If $[n_{\text{CH}_2} + n_{\text{CH}}] = 2$ , $n_{\text{F}} = 3$ ) $T_b = T_{\text{mil}} + 10$ (If $[n_{\text{CH}_2} + n_{\text{CH}}] = 2$ , $n_{\text{F}} \neq 3$ ) $T_b = T_{\text{mil}} + 37$ (If $[n_{\text{CH}_3} + n_{\text{C}}] = 2$ , $n_{\text{F}} = 3$ ) $T_b = T_{\text{mil}} - 10$ (If $[n_{\text{CH}_3} + n_{\text{C}}] = 2$ , $n_{\text{F}} \neq 3$ )	$T_c = T_{\text{cmil}}$
4	$T_b = 13.0343 T_{\text{lin}}^{0.671403} - 98.6959 T_{\text{lin}}^{0.283678} + 248.779$	$T_c = T_{\text{clin}}$
5	$T_b = 5.55687e - 05 T_{\text{lin}}^{2.52569} + 184.692$	$T_c = T_{\text{clin}}$
6	$T_b = T_{\text{min}} - 40$ (If $n_{\text{Cl}} = 0$ ) $T_b = T_{\text{min}} + 18$ (If $n_{\text{Cl}} \geq 4$ ) $T_b = T_{\text{min}} - 20$ otherwise	$T_c = T_{\text{cmin}}$

Also,

$$P_c = P_{\text{clin}} \text{ (If } n_{\text{CAR}} = 3 \text{ or } 4 \text{)}$$

$$P_c = P_{\text{cmil}} \text{ otherwise}$$

(2) Reported ODP values of some halogenated compounds (see Table A3).

(3) Calculation of  $H_{\text{vs}}$  and  $H_{\text{lc}}$ :

The refrigeration process is specified by the evaporating temperature ( $T_e$ ), the condensing temperature ( $T_{\text{cd}}$ ) and the superheat temperature ( $T_s$ ). The enthalpy values  $H_{\text{vs}}$  and  $H_{\text{lc}}$  are calculated as follows (Smith and Van Ness, 1987):

$$H_{\text{vs}} = [h_v(T_0) - H^R(T_0) + \Delta H^{\text{ig}}(T_s)]$$

$$+ H^R(T_s)]/M + H_0 \quad (\text{A1})$$

and

$$H_{\text{lc}} = [h_v(T_0) - H^R(T_0) + \Delta H^{\text{ig}}(T_{\text{cd}}) + H^R(T_{\text{cd}}) - h_v(T_{\text{cd}})]/M + H_0 \quad (\text{A2})$$

where  $H_0$  is the enthalpy at the "zero" state ( $T_0 = 233.15 \text{ K}$ ) and is equal to 0. The residual enthalpy,  $H^R$ , (based on generalized second virial coefficients) is a function of the temperature and the pressure (Smith and Van Ness, 1987):

$$H^R(T) = R T_c P_r [B^0 - T_r dB^0/dT_r + \omega (B^1 - T_r dB^1/dT_r)] \quad (\text{A3})$$

Table A3

Compound	ODP
$\text{CH}_3\text{Br}$	0.56*
$\text{CHBrF}_2$	1.10†
$\text{CF}_2\text{ClBr}$	4.10*
$\text{CF}_3\text{Br}$	12.50*
$\text{C}_2\text{HF}_4\text{Br}$	0.30†
$\text{C}_3\text{HF}_5\text{Cl}_2$	0.04†
$\text{C}_2\text{F}_4\text{Br}_2$	6.10*

\* Solomon *et al.* (1992b).

† Senecal (1992).

where

$$B^0 = 0.083 - 0.422/T_r^{1.6} \quad (\text{A4})$$

$$dB^0/dT_r = 0.675/T_r^{2.6} \quad (\text{A5})$$

$$B^1 = 0.139 - 0.172/T_r^{4.2} \quad (\text{A6})$$

$$dB^1/dT_r = 0.722/T_r^{5.2} \quad (\text{A7})$$

and the accentric factor  $\omega$  is defined as

$$\omega = -\log P_{\text{vpr}} \text{ (at } T_r = 0.7) - 1.0. \quad (\text{A8})$$

The ideal gas enthalpy change accompanying a change of temperature from  $T_0$  to  $T$  is given by (Smith and Van Ness, 1987):

$$\Delta H^{\text{ig}}(T) = C_{\text{pm}}^{\text{ig}} (T - T_0) \quad (\text{A9})$$

where the mean ideal gas heat capacity,  $C_{pm}^{ig}$ , is given as (Smith and Van Ness, 1987)

$$C_{pm}^{ig}/R = C_{pa} + C_{pb} T_{am} + C_{pc} [4T_{am}^2 - TT_0]/3 + C_{pd} T_{am} (T^2 + T_0^2)/2 \quad (\text{A10})$$

where  $T_{am}$  is the mean temperature and  $C_{pa}$ ,  $C_{pb}$ ,  $C_{pc}$  and  $C_{pd}$  are found using the group contribution method of Rihani and Doraiswamy (see Smith and Van Ness, 1987).

(4) *Calculation of the specific volume ( $V_g$ ):*

The specific volume at a temperature  $T$  (based on generalized virial coefficient correlation) is given by (Smith and Van Ness, 1987):

$$V_g(T) = RT_c [T_r/P_r + B^0 + \omega B^1]/P_c. \quad (\text{A11})$$

For calculating the specific volume of the suction vapor entering the compressor,  $T$  is set equal to the superheat temperature ( $T_s$ ).