Process Synthesis Optimization and Flexibility Evaluation of Air Separation Cycles

Avinash R. Sirdeshpande and Marianthi G. Ierapetritou
Dept. of Chemical and Biochemical Engineering, Rutgers University, Piscataway, NJ 08854

Mark J. Andrecovich and Joseph P. Naumovitz
BOC Gases, Murray Hill, NJ 07974

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The solution is discussed of the process synthesis problem for cryogenic air separation using techniques from process synthesis optimization. The mass and energy balances for the process are represented by a simplified algebraic model in which material stream flows and pressures appear as continuous variables and the various equipment choices for components of the air separation cycle are represented by binary variables. The resulting model corresponds to a mixed-integer nonlinear programming (MINLP) formulation and enables numerical optimization of the cycle. The two problems addressed are the selection of the optimal equipment set for a given product slate and the flexibility determination of the chosen cycle. The flexibility analysis is complemented with unique visual techniques that depict the feasible region and use of the recently proposed convex-hull approach. The calculations are illustrated for low-purity (95%) oxygen plants using the Lachmann cycle.
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Introduction

The separation of air into oxygen, nitrogen, and argon is an important chemical process that finds applications in a variety of key market sectors such as refining, petrochemicals, metals, glass, electronics, medical gases, foods, beverages, pulp and paper, and environmental. The major processes for air separation may be classified as cryogenic and noncryogenic. In the cryogenic process, which has been practiced for nearly a century, separation of air is achieved through liquefaction followed by low-temperature distillation. Although the cryogenic process is more widely used, noncryogenic processes based on adsorption and membrane separation are finding their own niche. Cryogenic separation is the method of choice when large volumes [350–3500 metric tons per day (mtpd)], high purities, and liquefied products are needed.

Correspondence concerning this article should be addressed to A. R. Sirdeshpande at this current address: BOC Gases, 575 Mountain Ave., Murray Hill, NJ 07974; e-mail: Avinash.Sirdeshpande@.boc.com.

Cryogenic plants for the separation of air are known as air-separation units (ASUs) and the process is known as a *cycle*. The cycle configuration depends on the product slate and the economics. The product slate is defined by the total oxygen demand, oxygen purity, gaseous oxygen delivery pressure, total nitrogen demand, nitrogen purity, liquid oxygen production, liquid nitrogen production, and argon production. The economic factors include the values of the products, their anticipated demand, expected fluctuations, local cost of power ($/kW), and relative cost of power to capital investment.

The open literature on air separation cycles is limited and typically discusses only generic cycles. A review of the patent literature will reveal numerous cycles, each with subtle variations that achieve a specified objective related to the product slate or economics. Selection of an appropriate cycle is often the factor that determines the success of a new business proposal. The multitude of cycles available to the process engineer makes this a challenging problem that must often be solved in a short period.

The product slate, except for gaseous oxygen delivery pressure and oxygen purity, may be subject to variations. For

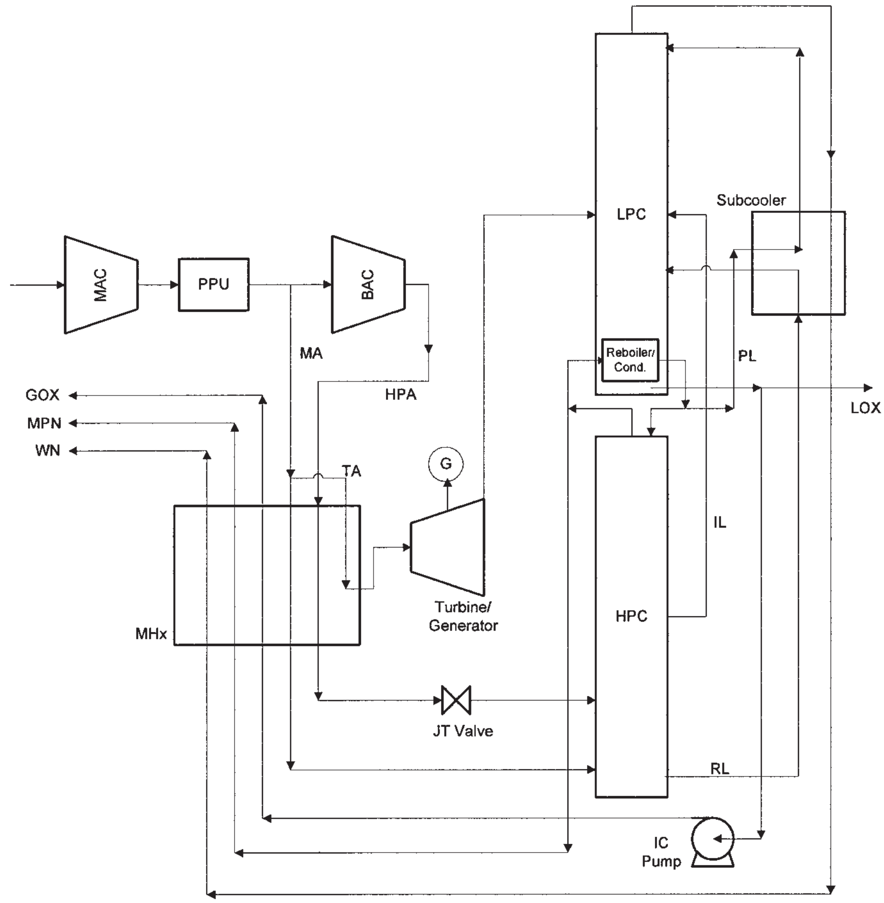

Figure 1. Block flow diagram of an air separation process based on the Lachmann cycle.

example, a customer may have an initial demand for 30 mtpd of liquid oxygen that is expected to grow linearly to 150 mtpd over the next 5 years. Having selected a cycle, knowledge of the flexibility of the chosen cycle in terms of variable product demand is thus of great importance.

The objective of this work is to demonstrate the application of techniques from process synthesis optimization to the selection of an optimal cycle and quantification of its flexibility. Having selected an optimal cycle, the chance of winning the new business is increased. It is expected that the man-hours required at the budgetary stage of new business proposals will be reduced through the use of this strategy. The investigation is limited to ASUs with a capacity to deliver 400 to 1200 mtpd gaseous oxygen, at pressures between 4 to 12 atm and a fixed oxygen purity of 95%, that do not produce nitrogen or argon products. However, the governing principles are general enough to be extended to cases that are more complex.

Process Description

Low-pressure, low-purity oxygen is often produced using the Lachmann cycle, especially when production of nitrogen and argon is not required. A schematic representation of an ASU using the Lachmann cycle is shown in Figure 1.

Air is first compressed in the main compressor (MAC) to a pressure of 6 to 7 atm and then purified to remove contaminants such as water vapor, carbon dioxide, nitrogen oxides, and hydrocarbons using an adsorption process. The cleaned air is split into three fractions: main air (MA), high-pressure air (HPA), and turbine air (TA). Of these, the HPA and TA portions may undergo further compression before all of the air is sent to the "cold box," a term used to denote an insulated system consisting of a main heat exchanger, a double-column distillation tower, a subcooler, cryogenic pumps, and associated pipework.

The air streams are cooled in a multistream brazed aluminum plate–fin heat exchanger (MHx), where they simultaneously exchange heat with returning product streams. The MA and HPA streams traverse the entire length of the exchanger and are cooled almost to the dew point of air. The TA stream is partially cooled before being drawn at an intermediate location and expanded in a turbine to produce a cold exhaust and mechanical work. The work extraction provides the necessary refrigeration to keep the plant cold. The three major refrigeration requirements are heat inleak from the ambient surroundings, the heat losses at the warm end of MHx, and production of any liquefied products.

The compressed and cooled air streams are distilled in a double-column system in which the higher-pressure column (HPC) operates at approximately 6.5 bar and the lower-pressure column (LPC) operates at about 1.5 bar. These pressures are chosen so that the two columns can be thermally coupled to share a common condenser/reboiler. The MA enters the bottom of the HPC as a saturated vapor. The HPA is compressed to a pressure that is sufficiently high to boil the liquid oxygen product stream. Upon leaving the MHx, the HPA is throttled across a valve to produce a colder, partially liquefied stream that enters the HPC at an intermediate location. A portion of the liquefied HPA stream is sent from the HPC to the LPC to improve the reflux conditions in that column, and is known as an intermediate liquid (IL) stream.

The Lachmann cycle represents the process where the TA stream is expanded to the pressure of the LPC and is fed to the LPC. In an alternative process known as the Claude cycle, the TA is expanded to the pressure of the HPC and fed to that column. Having the TA bypass the HPC reduces both the boil-up and the reflux in the LPC. Thus, increasing the TA flow rate to meet the refrigeration demand has an adverse effect on the recovery of oxygen from the process.

The MA and HPA entering the HPC undergo a preliminary separation into a nitrogen-rich liquid stream (PL) that provides reflux to the LPC and an oxygen-rich liquid stream (RL). The IL and RL enter the LPC at intermediate locations. The LPC produces a waste nitrogen stream (WN) from the top and a liquid oxygen stream from the bottom. After withdrawing a part of the LPC bottoms stream as product liquid oxygen (LOX), the remaining portion is pumped to an elevated pressure and vaporized in the MHx. Pressurized gaseous oxygen obtained this way is known as internally compressed oxygen (ICO). Included in the distillation process is a subcooler that cools the PL and RL streams against WN to recover refrigeration and enhance the recovery from the process.

Goal

The process for the separation of air may be modularized into the four basic operations of heat exchange, refrigeration, distillation, and compression. Rather than custom designing a plant for each product slate, modules may be predesigned for each unit operation to function over a range of conditions. This can save a significant amount of development and engineering costs. Presuming that this has been done, the building of a complete air-separation plant requires four basic modules to be chosen, one for each operation. The available modules differ in their capacity and applicability to the cycle.

In this work, the basic equipment set for any unit operation is denoted as a "main option. " Further, each main option may have additional alternatives known as "suboptions." For example, four main options are considered for distillation, each corresponding to a different range of total air flow to the plant. Each main option for distillation has two suboptions based on the MA flow that can be handled by the high-pressure column.

Table 1. Summary of Main Options and Suboptions for Unit Operations

Unit Operation	Main Options: Symbol	Main Options: No.	Suboptions per Main Option: Symbol	Suboptions per Main Option: No.
Heat exchange	Hx	2		
Refrigeration	Rf	4	RfSO	4
Distillation	Ds	4	DsSO	2
Compression	Cm	4	CmSO	2

In general, the number of options and suboptions could vary. Table 1 shows the numbers of main options and suboptions being considered for the various unit operations in this work.

An equipment set is a combination of main options and suboptions that define a complete plant for a given product slate. Each main option and suboption is denoted by a number (1, 2, 3, or 4). The choices representing the equipment sets are conveniently denoted by the string {*Hx*,*Rf*,*Ds*,*Cm*;*RfSO*,*DsSO*,*CmSO*}. Thus, {2144311} denotes the second main option for heat exchange, the first main option for refrigeration, the third suboption for distillation, and so forth. The main options (*Ds*, *Cm*) and suboptions (*RfSO*, *DsSO*, *CmSO*) are determined by the flow rates of MA, HPA, and TA in conjunction with the total air flow to the plant. On the other hand, the main options for *Hx* and *Rf* are all equally probable candidates for selection. In general, the size and cost of the equipment increases with option number. The main options for refrigeration represent four different ways of running the turbine. In options 1 and 2, the machine converts mechanical work through a generator that produces electricity. In options 3 and 4, the turbine is coupled with a compressor (TAC) that is driven by the work produced from the turbine. Further, the TA in options 2 and 4 is drawn from the discharge of the BAC as opposed to options 1 and 3, where it is drawn along with the MA after the MAC. The TAC further compresses the air drawn from the discharge of the MAC or BAC. Because the generated electricity in options 1 and 2 is available for export, it is counted as a power credit when determining the total work requirement. The turbine arrangement shown in Figure 1 conforms to $Rf = 1$.

Given a product slate, the overall goal is to choose an equipment set that maximizes the profitability of the project while delivering the specified products. Only some of the discrete equipment sets are capable of producing the product, and the most optimal among the feasible sets is to be determined. Feasible equipment sets are characterized by their subsidized gas cost

$$f = \frac{\text{Annualized capital cost} + \text{operating cost} - \text{sales of coproducts}}{\text{Gaseous oxygen production rate}} \quad (1)$$

The feasible set with the lowest value of *f* is the optimal set.

Process Model

A flowsheet model was set up in the HYSYS simulation environment to establish rigorous material and energy balances for a plant producing a given slate. Some of the data required to run the simulation are obtained by running stand-alone packages, developed in-house or available through other vendors, which cannot be linked to HYSYS. Because this is a complex model, it is not easily amenable to numerical analysis in terms of computational time or programmability. Thus, an algebraic model was developed that includes the essential variables governing the process and represents the superstructure of process/equipment alternatives. The coefficients of the model were obtained by regression using results obtained from detailed HYSYS simulations. Although there is an approximation error associated with this approach (Biegler et al., 1985), this was the only realistic solution technique. Final results from the algebraic model were always checked against the detailed simulation.

The final algebraic process model includes 11 continuous variables and 46 binary variables. Eight of the continuous variables are state variables (F_A, F_{MA}, F_{HPA}, F_{TA}, P_{MA}, P_{HPA}, P_{TA}, γ_r) representing the total air to the plant and the flows and pressures of streams entering the cold box (process). The recovery of oxygen from the plant (γ_r) is defined as the fraction of the oxygen in the feed to the plant that is contained in the product as pure oxygen (gaseous and liquid). The oxygen recovery is one example of a variable that was correlated using HYSYS simulations. The remaining three variables are design variables $\{F_{GOX}, F_{LOX}, P_{GOX}\}$ representing the product slate. In the text of this article, F_{GOX} and F_{LOX} are expressed in mtpd of pure oxygen and P_{GOX} is in atm. Thus, {800, 170, 9} denotes $F_{GOX} = 800$ mtpd, $F_{LOX} = 170$ mtpd, and $P_{GOX} = 9$ atm. However, in the model presented in the Appendix, F_{GOX} and F_{LOX} are expressed in kmol/h of the total stream to maintain dimensional consistency.

The various discrete equipment sets represented by the main options and suboptions were incorporated in the model by introducing 46 binary variables (**y**) that take the value of 0 or 1 to indicate whether a particular equipment set is excluded or included in the process (see Table 2).

Besides the material and energy balance equations, constraints are introduced for the selection of main options and suboptions, and to impose bounds on the flow rates (F_A, F_{MA}, F_{HPA}, and F_{TA}). The entire model and the values of the coefficients are given in the Appendix. Although the model was derived for general use, the coefficients used in this work do not represent the values for any real equipment or process in current use by BOC gases.

Solution Technique

The generic form of the equations corresponds to the following mixed-integer nonlinear programming (MINLP) model

Table 2. List of Binary Variables (*y*)

Equipment Set Operation	Main Options		Suboptions
Heat exchange	1	y_1	—
	2	y_2	—
Refrigeration	1	y_3	1–4 $\equiv y_{15}$–y_{18}
	2	y_4	1–4 $\equiv y_{19}$–y_{22}
	3	y_5	1–4 $\equiv y_{23}$–y_{26}
	4	y_6	1–4 $\equiv y_{27}$–y_{30}
Distillation	1	y_7	1, 2 $\equiv y_{31}, y_{32}$
	2	y_8	1, 2 $\equiv y_{33}, y_{34}$
	3	y_9	1, 2 $\equiv y_{35}, y_{36}$
	4	y_{10}	1, 2 $\equiv y_{37}, y_{38}$
Compression	1	y_{11}	1, 2 $\equiv y_{39}, y_{40}$
	2	y_{12}	1, 2 $\equiv y_{41}, y_{42}$
	3	y_{13}	1, 2 $\equiv y_{43}, y_{44}$
	4	y_{14}	1, 2 $\equiv y_{45}, y_{46}$

$$\phi = \min_{x,y} f(x, y) \tag{2}$$

subject to

$$h(x, y) = 0 \tag{3}$$

$$g(x, y) \le 0 \tag{4}$$

$$l \le x \le u \tag{5}$$

where $(x, l, u) \in R^{n_c}$, $y \in \{0, 1\}^{n_i}$, $h \in R^{n_c+n_i} \to R^{m_e}$, $g \in R^{n_c+n_i} \to R^{m_i}$, and $\phi \in R^{n_c+n_i} \to R^1$. An extended review of available techniques for solving MINLPs can be found in Floudas (1995). In this work, a Branch-and-Bound (B&B) method that belongs to the class of implicit enumeration techniques was used. A general code implementing the B&B was written in the F95 programming language. The code is modular in that it can be coupled to any continuous LP or NLP solver (Sirdeshpande et al., 2001). Depth-first, breadth-first, and combined depth–breadth search facilities are available. The relaxed subproblems were solved using the successive quadratic programming (SQP) technique. The SQP solver NPSOL (Gill et al., 1986) was successfully used on all the problems. The code was run on a Dell PC with a 1-GHz Intel Pentium III processor and the Windows 2000 Professional operating system. The programs were written in the Compaq Visual Fortran 6.5 environment. In the formulation of the current model for the B&B solver, $n_c = 11$, $n_i = 46$, $m_e = 23$, and $m_i = 10$.

Because the current optimization problem is nonconvex, the B&B method can fail to determine the true global optimum if local rather than global minima are encountered at the nodes of the tree. Unfortunately, convexification of the problem is not possible because the binary and continuous variables are often coupled and binary variables appear in highly nonlinear expressions also involving continuous variables. However, numerical experience with the model has shown that the results are reliable because of the absence of multiple minima, which was guaranteed by performing multiple runs with different starting points at every node.

Selection of Optimum Equipment Set

The general problem formulation presented in the previous section is used to solve two kinds of problems. In the Type I problem, the product slate is fixed and the optimization procedure is used to determine the equipment set with the lowest subsidized gas cost. For example, the product slate {930, 120, 9} was found to have an optimal equipment set {1244311} with a subsidized gas cost of 29.07 \$/mt. On the other hand, decreasing the production to {800, 60, 9} yields an optimal set of {1233111} with a subsidized gas cost of 31.81 \$/mt.

In the Type II problem, the product slate is allowed to vary over a range and the optimal equipment set is the one with the minimum cost that remains feasible. As an example, consider the case where the *LOX* demand varies in the range $0 \le F_{LOX} \le 80$ mtpd. The *GOX* demand is fixed at 400 mtpd and 5 atm. The optimal product slate was found to be {1412111} with a subsidized gas cost of 34.05 \$/Mt.

In some cases, there are multiple feasible equipment sets for the same product slate, where the term "feasible" represents the ability of the equipment set to satisfy the material and energy balances for the nominal conditions. Of these, only one is optimal in terms of subsidized gas cost. A by-product of the B&B calculations is a partial list of feasible equipment sets given by the number of nodes with all discrete variables having the value 0 or 1. Thus, the process engineer can confine his/her subsequent analysis to these equipment options. Further, the information required for the problem may be easily changed or updated as the need arises, making this technique a hands-on tool. The statistics of the B&B code execution, shown in Table 3, prove that the method is reliable, robust, and efficient for practical application.

Visualization Techniques

To represent the feasible region, a sampling approach was developed that determines the values of *GOX* and *LOX* flows that may be produced by a given equipment set. The values of *Hx* and *Rf* were fixed for a given P_{GOX}, and the values *GOX* and *LOX* were varied between zero and a specified maximum. For each data point $\{F_{GOX}, F_{LOX}\}$, the feasible point for the constraints was determined using the general problem formulation, and the equipment set and the subsidized cost were obtained. After generating a specified number of such points (usually 6000–10,000), the values of $\{F_{GOX}, F_{LOX}\}$ were grouped according to equipment set type. When mapped in a two-dimensional (2-D) plot with a different color to represent each equipment type, the map of equipment sets as a function of *GOX* and *LOX* flows proves to be a convenient visual tool to analyze the anatomy of the feasible region. Figure 2 shows the plot for $P_{GOX} = 9$ atm, $Hx = 1$, $Rf = 2$, $450 \leq F_{GOX} \leq 1200$ mtpd, and $0 \leq F_{LOX} \leq 300$ mtpd. Note that when multiple equipment sets are feasible for the same product slate, the procedure for determining the feasible point picks the equipment set with the smallest size or lowest capital cost.

Flexibility of Chosen Equipment Set

The problem addressed in this section is the determination of the feasible space for the optimal set of equipment options that has been obtained for a specified product slate. For example, the product slate {930, 120, 9} has the optimal equipment set {1244311}. Suppose the expected variations in *GOX* and *LOX* are each ±50 mtpd, or that the *LOX* demand is initially 10 mtpd but is expected to grow linearly to 100 mtpd over the next 5 years. It is then of interest to know whether the chosen equipment set will perform with a different product slate. The flexibility index formulation, which follows the work of Swaney and Grossman (1985), is used to determine whether the optimal configuration may be used in the face of changes in the nominal conditions.

Table 3. Statistics from B&B Runs*

	Problem 1	Problem 2	Problem 3
Problem type	I	I	II
F_{GOX} (mtpd)	930	800	400
F_{LOX} (mtpd)	120	60	$0 \leq F_{LOX} \leq 80$
P_{GOX} (atm)	9	9	5
Optimal equipment set	{1244311}	{1233111}	{1412211}
Subsidized gas cost ($/mt)	29.07	31.81	34.05
Oxygen recovery (%)	96.29	97.01	95.01
CPU time (s)	5.8	7.7	1.1
No. of integer solutions	3	1	1
No. of relaxed subproblems	42	60	6

*The starting guess for **y** was a vector of random numbers uniformly distributed between 0 and 1.

The input information consists of a nominal point that constitutes an optimal product slate and corresponding equipment options. Let the flow rates of *GOX* and *LOX* be denoted by θ_1 and θ_2, respectively. Then if $\Delta\theta_i^+$ and $\Delta\theta_i^-$ are the maximum expected deviations in the parameters from their nominal values θ_i^N, the expected range of each parameter is

$$\theta_i^N - \Delta\theta_i^- \leq \theta_i \leq \theta_i^N + \Delta\theta_i^+ \qquad i = 1, 2 \tag{6}$$

To determine whether the optimal equipment set is feasible over the expected parameter range, a new parameter δ is introduced, which allows the expected range to be represented by

$$\theta_i^N - \delta \cdot \Delta\theta_i^- \leq \theta_i \leq \theta_i^N + \delta \cdot \Delta\theta_i^+ \qquad i = 1, 2 \tag{7}$$

The flexibility index F for a given product slate and equipment set is the value of δ that defines the critical parameter range responsible for one or more inequality constraints to become active.

The value of F can be determined in two ways: the vertex enumeration strategy (VES) and the active set method (ASM). In the present context, the vertex enumeration strategy solves four problems, one at each vertex of the expected parameter range. The coordinates of the vertices V^k for a two-parameter problem are

$$V^1 = \{\theta_1^N + \delta \cdot \Delta\theta_1^+,\ \theta_2^N + \delta \cdot \Delta\theta_2^+\}$$

$$V^2 = \{\theta_1^N + \delta \cdot \Delta\theta_1^+,\ \theta_2^N - \delta \cdot \Delta\theta_2^-\}$$

$$V^3 = \{\theta_1^N - \delta \cdot \Delta\theta_1^-,\ \theta_2^N - \delta \cdot \Delta\theta_2^-\}$$

$$V^4 = \{\theta_1^N - \delta \cdot \Delta\theta_1^-,\ \theta_2^N + \delta \cdot \Delta\theta_2^+\} \tag{8}$$

where δ may be interpreted as the scaled step-length factor along each vertex direction.

At each vertex k, the following problem is solved

$$\Theta^k = \max(\delta) \tag{9}$$

subject to

$$h_i(x;\ \delta) = 0 \qquad i = 1, \ldots, m_e \tag{10}$$

$$g_i(x;\ \delta) \leq 0 \qquad i = 1, \ldots, m_i \tag{11}$$

Because the equipment set is fixed, the binary variables are not included in the above formulation. The value of δ may thus be determined using nonlinear programming techniques for continuous problems. The flexibility index is the smallest value

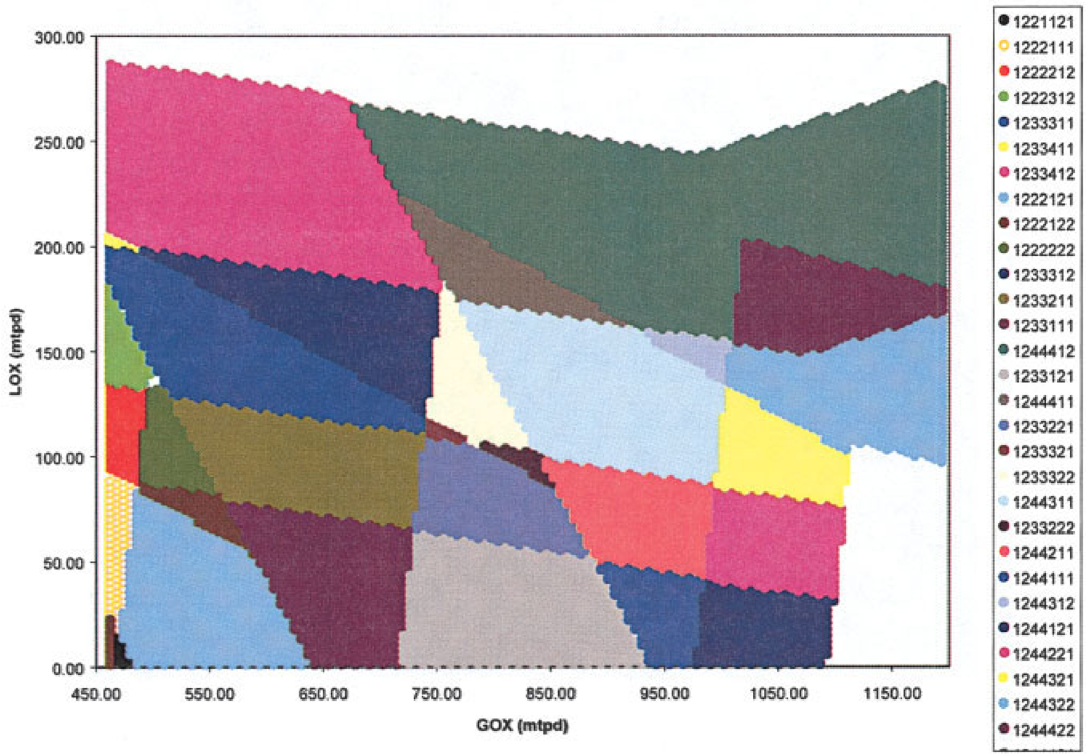

Figure 2. Map of feasible equipment sets (quilt plot) for *Hx* = 2 and *Rf* = 2.

among all the optima obtained from the solution of Eqs. 9–11 for each of the four vertices in Eq. 8

$$F = \min_{1 \le k \le 4} \{\Theta^k\} \tag{12}$$

The critical point is the vertex corresponding to the index of the problem responsible for the minimum value of Θ^k.

The VES assumes that the point of constraint violation, if it exists, occurs at one of the vertices of the expected parameter range. This need not be true, as shown by Biegler et al. (1997). Further, the number of optimization problems to be solved for a generic problem with n parameters is 2^n, which could be prohibitively large. In that case, the active set strategy must be used (Grossmann and Floudas, 1987).

The ASM exploits the fact that the value of F is determined by the active inequality constraints. In the present case, the flexibility index problem has only one active inequality constraint because the values of the parameters (*GOX* and *LOX* flow rates) can be independently set and there are no control variables such as reflux ratio or boil-up ratio that are adjusted. The active inequality constraint represents some equipment having reached its operability limit (such as a column approaching the flooding condition or an exchanger experiencing a pinch). Because the index of the active inequality constraint is not known in advance, the ASM reduces to the solution of m_i subproblems. In each subproblem k, the kth inequality constraint is treated as an equality constraint. The ASM formulation is represented by the following NLP

$$\psi^k(\delta) = \min \delta \tag{13}$$

subject to

$$h_i(x;\ \delta,\ \theta_1,\ \theta_2) = 0 \qquad i = 1, \ldots, m_e \tag{14}$$

$$g_i(x;\ \delta,\ \theta_1,\ \theta_2) \le 0 \qquad i = 1, \ldots, m_i;\ i \ne k \tag{15}$$

$$g_i(x;\ \delta,\ \theta_1,\ \theta_2) = 0 \qquad i = k \tag{16}$$

$$\theta_i^N - \delta \cdot \Delta\theta_i^- \le \theta_i \le \theta_i^N + \delta \cdot \Delta\theta_i^+ \qquad i = 1, 2 \tag{17}$$

Note that θ_1 and θ_2 appearing in the ASM formulation are related to δ through Eq. 7. The flexibility index is the smallest value among all the optima obtained from the m_i solutions of Eqs. 13–16 and 7 for each inequality constraint:

$$F = \min_{1 \le k \le m_i} \{\Psi^k\} \tag{18}$$

Thus, the ASM simultaneously determines the value of F and the critical values of the *GOX* and *LOX* flow rates.

Two examples of the determination of the flexibility index are considered. In the first case, the nominal product slate is {930, 140, 9} with an optimal equipment set {1244311} (see Problem 1, Table 3). If the expected variation is ±50 mtpd each in GOX and LOX, the plant may not continue to be feasible. To determine that, the flexibility index was calculated using both the VES and the ASM techniques. Both methods yield $F = 0.829$, with a critical production of {971.5, 161.5}. This indicates that the plant can accommodate an increase of

GOX and LOX demands only up to 42 mtpd, but any decrease in demand within the desired range.

The results from the flexibility analysis are shown graphically in Figure 3. The desired and predicted ranges of the feasible region, which are always rectangular according to the flexibility definition, are superimposed on the true feasible region obtained by sampling. The predicted feasible region is a subset of the desired feasible region because F is <1. The chosen equipment option does not remain feasible if both GOX and LOX production rates increase beyond 42 mtpd; all other variations in production within the stipulated extent of variation are permissible.

The second example considers a product slate of {800, 60, 9} with an optimal equipment set {1233111} (see Problem 2, Table 3). With an expected variation of ± 100 mtpd in GOX and ± 30 mtpd in LOX, the value of F is 0.193 with a critical production of {819.28, 54.22}. Again, both VES and ASM yield the same value of F. Thus, although this plant is optimal for the nominal case, it has a low flexibility and will not be an appropriate choice if there is an expansion in capacity. Figure 4 shows the feasible region determined by flexibility analysis.

The preceding examples show that the predicted shape of the feasible region does not adequately describe the true feasible region, which was obtained by sampling, because the geometric shape is restricted to be rectangular only. The actual shape is more complex and thus an alternative formulation is necessary. The convex-hull method (CHM) partially alleviates this problem by removing the rectangular restriction (Ierapetritou, 2001). To predict the feasible space for a problem with two uncertain variables, the CHM requires the solution of Eqs. 9–11 for eight vertices. In addition to the four vertices defined by Eq. 8, a search is made along the positive and negative x- and y-coordinate directions. The predicted feasible region is the convex hull of these eight points that may be determined using standard techniques, such as the convhull function in MATLAB® (The MathWorks, Natick, MA). Figure 5 compares the convex-hull and VES predictions of the feasible region with the exact boundary. The superiority of the convex-hull representation is clear, and thus this method will be investigated in detail in the future.

Summary

A plant for the cryogenic separation of air may be modularized based on the four basic unit operations of heat exchange, refrigeration, distillation, and compression. Having chosen a cycle, the final plant may be assembled by selecting predesigned equipment for each unit operation. In this work, the Lachmann cycle for low-purity (95%) oxygen was configured based on equipment sets whose selection depends on the state variables $\mathbf{x} = \{F_A, F_{MA}, F_{HPA}, F_{TA}\}$ and the design variables or product slate $\mathbf{d} = \{F_{GOX}, F_{LOX}, P_{GOX}\}$.

Because the number of combinations of possible equipment sets is prohibitively high ($2^{46} \approx 10^{14}$) for explicit enumeration techniques of selection to be practicable, a model that is amenable to MINLP techniques was developed. This algebraic model reproduces the essential information on material flows and stream pressures while maintaining mathematical simplicity. The parameters of the model are empirical correlations with coefficients regressed from the results of rigorous simulations using commercial and in-house process simulators. By introducing binary variables for equipment main options and suboptions into the model equations, an optimal equipment set for a given product slate may be chosen by minimizing the subsidized gas cost.

Two problems were solved. For a given product slate, the

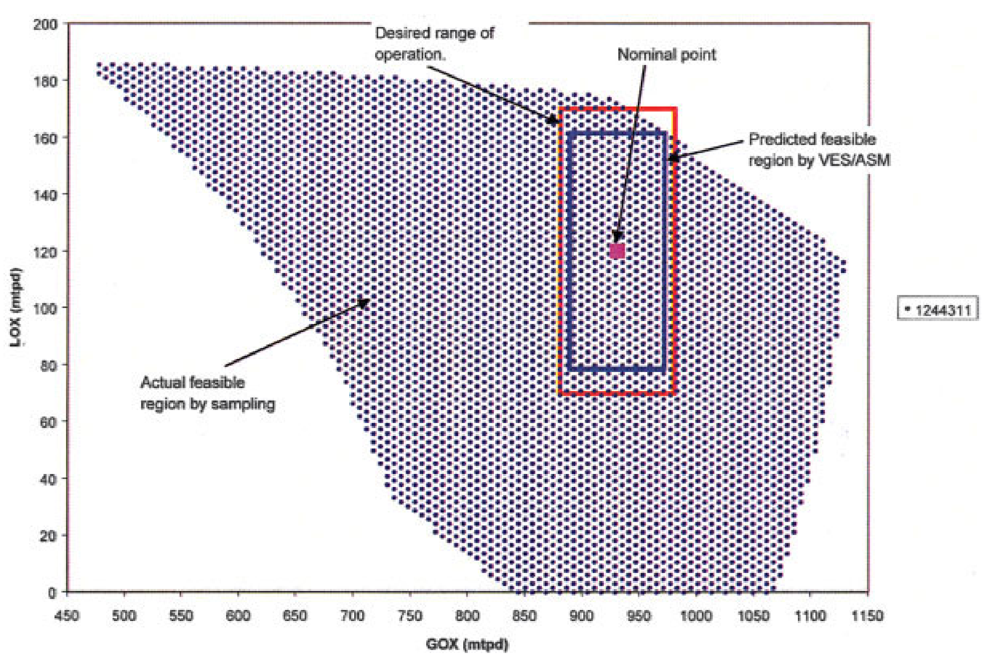

Figure 3. Predicted feasible region using VES and ASM for Problem 1.

Nominal slate = {930, 120, 9}. Optimal equipment set = {1244311}. Expected variation: GOX = ±50 mtpd, LOX = ±50 mtpd. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

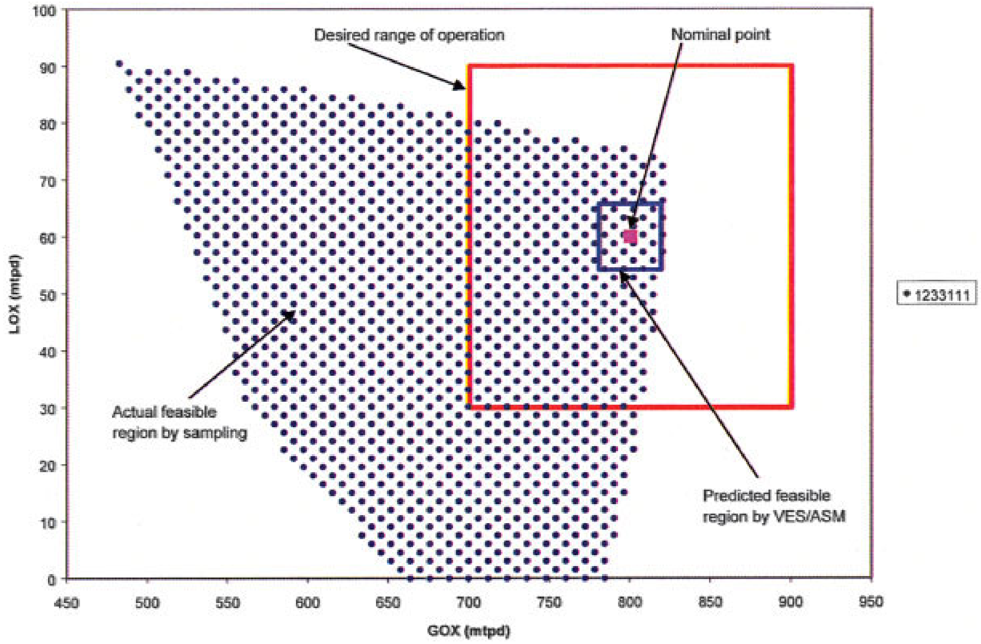

Figure 4. Predicted feasible region using VES and ASM for Problem 2.

Nominal slate = {800, 60, 9}. Optimal equipment set = {1233111}. Expected variation: GOX = ±100 mtpd, LOX = ±30 mtpd. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

optimal equipment set based on the gas cost was determined by solution of the MINLP with the Branch-and-Bound method. Then, the flexibility of the chosen configuration for variable *GOX* and *LOX* product rates was found using the vertex enumeration and active set strategies. The results from these problems were verified using maps depicting the feasible region. The VES and ASM techniques, which restrict the predicted feasible region in 2-D to be rectangular, were found to underestimate the true feasible region. An improved estimate of the feasible region was obtained using the convex-hull method.

Because the results are reliable and obtained efficiently, process synthesis techniques have been demonstrated to be viable tools for an application of industrial relevance. The modular nature of the model allows it to act as a repository for information from various areas. Future work will be directed to extend the model to more products (liquid and gaseous nitro-

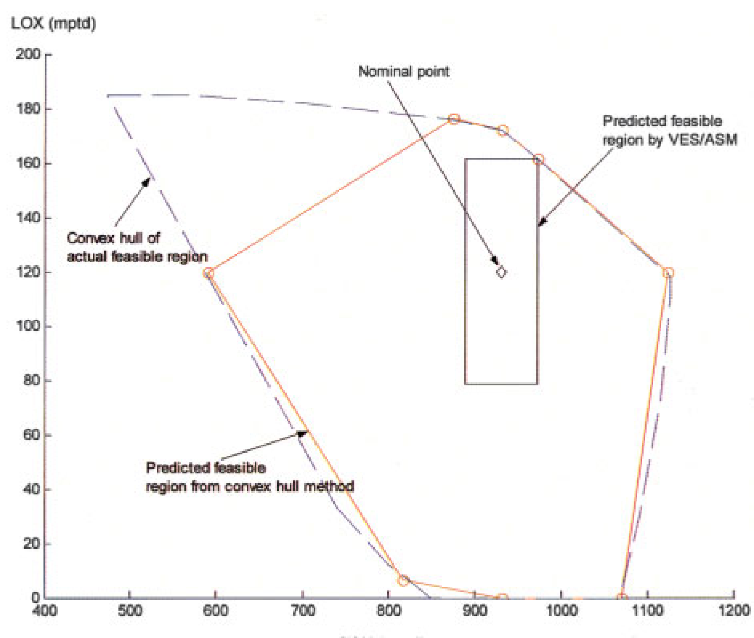

Figure 5. Convex-hull prediction of the feasible region for Problem 1.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

gen) over a wider range of delivery pressures and product purities. In addition to equipment choices, various types of cycles shall also be included.

Notation

C = capital cost, K$
$\mathbf{c}$ = vector of coefficients of optimization model, defined in Table A1
f = subsidized gas cost, $/mt
F = total stream molar flow rate, kmol/h
$\mathbf{h}$ = vector of generic equality constraints, defined in Eq. 3
H = enthalpy, kcal/kmol
HPC = high pressure distillation column
$\mathbf{g}$ = vector of generic inequality constraints, defined in Eq. 4
$\mathbf{l}$ = vector of lower bounds on continuous variables, defined in Eq. 5
LPC = low pressure distillation column
n_c = number of continuous variables
n_i = number of binary (discrete) variables
m_e = number of equality constraints
m_i = number of inequality constraints
mt = metric ton (=1000 kg)
mtpd = metric tons per day
P = pressure, atm
Q = energy, kcal
T = temperature, K
$\mathbf{u}$ = vector of upper bounds on continuous variables, defined in Eq. 5
W = mechanical work, kcal
$\mathbf{x}$ = vector of continuous variables
$\mathbf{y}$ = vector binary variables (0 or 1), defined in Table 2

Greek letters

ϕ = generic objective function of continuous and binary variables, defined in Eq. 2
γ_r = oxygen recovery, %
γ_p = oxygen product purity, %
η = efficiency, %

Subscripts

A = air to plant
BAC = booster air compressor
Cm = main compression option
$CmSO$ = suboption for compression
Ds = main distillation option
$DsSO$ = suboption for distillation
F = feed
GOX = gaseous oxygen
HI = heat inleak
HPA = high pressure air
Hx = main heat exchange option
ICO = internally compressed oxygen
in = inlet
iso = isothermal
LOX = liquid oxygen
MA = main air
MAC = main air compressor
MPN = medium pressure nitrogen product
P = product
PPU = prepurification unit
Rf = main refrigeration option
$RfSO$ = suboption for refrigeration
s = specific, per unit mass
TA = turbine air
T,s = turbine, specific
W,HPA = HPA to BAC
WN = waste nitrogen

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Appendix: Optimization Model

Objective function

$$f = \frac{361.69 c_{132} C_{Cap} + 3.63 c_{131} W_{tot} - c_{133} \gamma_p F_{LOX}}{\gamma_p F_{GOX}} \times \frac{\$}{\text{mt pure GOX}} \tag{A1}$$

Capital cost

$$C_{Hx} = \sum_{i=1}^{2} c_i y_i \tag{A2}$$

$$C_{Rf} = \sum_{i=1}^{16} c_{2+i} y_{14+i} \tag{A3}$$

$$C_{Ds} = \sum_{i=1}^{8} c_{18+i} y_{30+i} \tag{A4}$$

$$C_{Cm} = \sum_{i=1}^{8} c_{26+i} y_{38+i} \tag{A5}$$

$$C_{Cap} = C_{Hx} + C_{Rf} + C_{Ds} + C_{Cm} + \text{Storage cost} \tag{A6}$$

Constraints

Equipment Selection Constraints

- Main options

$$y_1 + y_2 = 1 \tag{A7}$$

$$\sum_{j=4i-1}^{2+4i} y_j = 1 \qquad i = 1, \ldots, 3 \tag{A8}$$

- Suboptions

$$\sum_{j=11+4i}^{14+4i} y_j = y_{2+i} \qquad i = 1, \ldots, 4 \tag{A9}$$

$$\sum_{j=29+2i}^{30+2i} y_j = y_{6+i} \qquad i = 1, \ldots, 8 \tag{A10}$$

Bounds on Flows for Specific Equipment Choices

- Distillation main option

$$\sum_{i=1}^{4} c_{34+i} y_{6+i} \le F_A \le \sum_{i=1}^{4} c_{38+i} y_{6+i} \tag{A11}$$

- Compression main option

$$\sum_{i=1}^{4} c_{42+i} y_{10+i} \le F_A \le \sum_{i=1}^{4} c_{46+i} y_{10+i} \tag{A12}$$

- Distillation suboption

$$\sum_{i=1}^{8} c_{50+i} y_{30+i} \le F_{MA} \le \sum_{i=1}^{8} c_{58+i} y_{30+i} \tag{A13}$$

- Compression suboption

$$\sum_{i=1}^{8} c_{66+i} y_{38+i} \le F_{W,HPA} \le \sum_{i=1}^{8} c_{74+i} y_{38+i} \tag{A14}$$

- Refrigeration suboption

$$\sum_{i=1}^{16} c_{82+i} y_{14+i} \le F_{TA} \le \sum_{i=1}^{16} c_{98+i} y_{14+i} \tag{A15}$$

- Ratio of turbine air to total plant air

$$0.06 \le F_{TA}/F_A \le 0.7 \tag{A16}$$

- Pressure restrictions

$$P_{MA} > 0.35 \tag{A17}$$

$$P_{TA} \le c_{201} \tag{A18}$$

Material and energy balances

$$F_A \frac{\gamma_r}{\gamma_p} = \frac{F_{LOX} + F_{GOX}}{c_{175}} \tag{A19}$$

$$F_A = F_{MA} + F_{HPA} + F_{TA} \tag{A20}$$

$$F_A = F_{GOX} + F_{LOX} + F_{WN} \tag{A21}$$

$$F_{HPA} = F_{GOX}(c_{153} + c_{154} P_{GOX}) \tag{A22}$$

$$P_{MA} = c_{155} + c_{156}\gamma_p \tag{A23}$$

$$P_{HPA} = P_{GOX}(c_{157} + c_{158} P_{GOX} + c_{159} P_{GOX}^2) \tag{A24}$$

$$P_{TA} = y_3 P_{MA} + y_4 P_{HPA} + P_{BTA} \tag{A25}$$

$$Q_F - Q_P + Q_{HI} = F_{TA} W_{T,s} \tag{A26}$$

$$W_{tot} = W_A + W_{HPA} - W_C \tag{A27}$$

Recovery correlation

$$\gamma_r = c_{150} + c_{151} \frac{F_{TA}}{F_A} + c_{152}\left(\frac{F_{TA}}{F_A}\right)^2 \tag{A28}$$

Auxiliary quantities

$$Q_{HI} = \sum_{i=1}^{4} c_{114+i} y_{6+i} \tag{A29}$$

$$Q_F = F_{MA} H_{MA} + F_{HPA} H_{HPA} + F_{TA} H_{TA} \tag{A30}$$

$$Q_P = F_{GOX} H_{GOX} + F_{LOX} H_{LOX} + F_{WN} H_{WN} \tag{A31}$$

$$H_i = c_{160} + c_{161} P_i \qquad i = MA, HPA, TA \tag{A32}$$

$$H_{GOX} = y_1(c_{165} + c_{166} P_{GOX}) + y_2(c_{167} + c_{168} P_{GOX}) \tag{A33}$$

$$H_{LOX} = c_{162} + c_{163} P_{GOX} + c_{164}\gamma_p \tag{A34}$$

$$H_{WN} = \sum_{i=1}^{2} c_{168+i} y_i \tag{A35}$$

$$\eta_{iso,MAC} = \sum_{i=1}^{4} c_{118+i} y_{10+i} \tag{A36}$$

$$\eta_{iso,BAC} = \sum_{i=1}^{8} c_{122+i} y_{38+i} \tag{A37}$$

$$P_{BTA} = y_5(c_{139} + c_{140} P_{MA} + c_{141} P_{MA}^2) + y_6(c_{139} + c_{140} P_{HPA} + c_{141} P_{HPA}^2) \tag{A38}$$

$$P_{T,s} = (y_3 + y_5) P_{MA} + (y_4 + y_6) P_{HPA} \quad (A39)$$

$$W_{T,s} = (y_3 + y_4) \sum_{i=1}^{4} (c_{141+i} P_{T,s}^{i-1}) + (y_5 + y_6) \sum_{i=1}^{4} (c_{145+i} P_{T,s}^{i-1}) \quad (A40)$$

$$W_{TA} = F_{TA} W_{T,s} \quad (A41)$$

$$F_{W,HPA} = (y_3 + y_5) F_{HPA} + (y_4 + y_6)(F_{HPA} + F_{TA}) \quad (A42)$$

$$W_A = \frac{F_A R_g T_{in}}{\eta_{iso,MAC} \eta_{motor} 10^{-4}} \ln \frac{P_{MA}}{P_{in}} \quad (A43)$$

$$W_{HPA} = \frac{F_{W,HPA} R_g T_{in}}{\eta_{iso,BAC} \eta_{motor} 10^{-4}} \ln \frac{P_{HPA}}{P_{MA} - 0.35} \quad (A44)$$

$$W_C = 0.95 \cdot W_{TA} (y_3 + y_4) \quad (A45)$$

Table A1. Values of Coefficients in the Optimization Model

i	c_i	i	c_i	i	c_i	i	c_i
1	1501.5	44	2583	87	0	130	75.85
2	2730	45	3780	88	0	131	0.065
3	955.5	46	4914	89	0	132	0.3
4	1023.75	47	3410	90	0	133	60
5	1126.65	48	4510	91	630	136	125
6	1263.15	49	6600	92	834.75	139	−2.8786
7	955.5	50	8580	93	1149.75	140	1.7459
8	1023.75	51	652.5	94	1102.5	141	0.0372
9	1126.65	52	832.5	95	630	142	3.0907
10	1263.15	53	832.5	96	834.75	143	47.999
11	887.25	54	1282.5	97	1149.75	144	−1.4522
12	887.25	55	1282.5	98	1102.5	145	0.0179
13	982.8	56	1755	99	1100	146	−64.958
14	1092	57	1755	100	1457.5	147	74.062
15	887.25	58	2002.5	101	2007.5	148	−2.2222
16	887.25	59	1595	102	2695	149	0.0278
17	982.8	60	2035	103	1100	150	88.276
18	1092	61	2035	104	1457.5	151	98.39
19	2218.65	62	3135	105	2007.5	152	−277
20	2265.9	63	3135	106	2695	153	1.3471
21	2798.25	64	4290	107	1100	154	0.0005
22	2893.8	65	4290	108	1457.5	155	−1.5705
23	3617.25	66	4895	109	2007.5	156	0.0807
24	3720.15	67	850.5	110	2695	157	3.2538
25	4299.75	68	1215	111	1100	158	−0.1432
26	4361.7	69	1134	112	1457.5	159	0.0045
27	5323.5	70	1620	113	2007.5	160	3841.1
28	5596.5	71	1669.5	114	2695	161	−1.5533
29	5460	72	2385	115	45650	162	818.5492
30	5801.25	73	2126.7	116	55700	163	0.938846
31	7507.5	74	3037.5	117	73800	164	3.130681
32	7917	75	1485	118	90250	165	4099.8
33	8190	76	2145	119	73.8	166	−1.9716
34	8667.75	77	1980	120	74.825	167	4129.6
35	1395	78	2860	121	75.85	168	−1.9163
36	1845	79	2915	122	76.875	169	3702.36
37	2700	80	4207.5	123	71.75	170	3732.34
38	3510	81	3712.5	124	72.775	171	0.98
39	3410	82	5500	125	72.775	172	300
40	4510	83	0	126	73.8	173	95
41	6600	84	0	127	73.8	174	1.9872
42	8580	85	0	128	74.825	175	0.20956
43	1953	86	0	129	74.825	176	33.5

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