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DESIGN OF DISTILLATE DESULFURIZATION REACTORS WITH GEOMETRIC PROGRAMMING

By

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ABSTRACT

The last few years have seen a simultaneous increase in the sulfur content of available crude oils and in the stringency of governmental limitations on the sulfur content of fuels. As a result, many refiners have been forced to construct new processing units to remove the sulfur from their products. Since the justification for desulfurization is regulatory rather than economic, it is prudent to try to minimize the cost of compliance with the standards. The method of geometric programming is used in this paper to address the problem of designing the desulfurization reactor at least cost. A geometric programming formulation for designing a high-pressure vessel with a specified volume is developed and evaluated. A method for generating a lower bound on the cost of such a vessel is also described. The second subject of this paper is a formulation of a geometric programming model for the design of a distillate desulfurization reactor which includes a complete kinetic evaluation.

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INTRODUCTION

In spite of massive research and development efforts aimed at finding alternatives to the use of petroleum as a fuel, the nation will continue to derive the largest portion of its energy from this source for several years. Unfortuneately, production from the mid-continent oil fields which have provided the inexpensive, clean (low sulfur) fuels for the rapid industrial growth of the last fifty years is declining at an ever-increasing rate. The imports and new domestic production which are replacing these low sulfur oils have, generally, a much higher sulfur content. Since fuels which contain sulfur produce toxic sulfur oxides on combustion, the environmental agencies at all levels of the government have determined that only fuels with less than some maximum sulfur level may be burned within their jurisdiction. As a result of this concurrent increase in the average sulfur level of available crude oil and heightened stringency of environmental constraints, many refiners have found that they can no longer meet statutory product specifications by blending stocks. These refiners have been forced to construct many new processing units to remove the sulfur in the last few years, even though the high equipment costs and uncertain effects of governmental regulation have greatly reduced most refinery construction.

The desulfurization of distillate stocks (kerosene, diesel, jet fuel, and furnace oil) has become especially important because the volume of use which this fraction receives is only slightly less than that of gasoline, and the sulfur compounds tend to concentrate in the heavier cuts. Distillate treating presents some special problems because the impurities (including nitrogen, oxygen, and olefins as well as sulfur) are often bound in large, highly complex molecules which may assume many different forms. In addition, the feed is normally only partially vaporized at reaction conditions, so the degree of catalyst contact and the velocity of the reactants vary with the temperature and pressure. Catalytic reactions, like this one, in which a two-phase feed flows through a bed of solid catalyst have been designated trickle-flow reactions.

Impurities are removed from petroleum streams by contacting the nitrogen, oxygen, and sulfur contained in the hydrocarbon with hydrogen on a cobalt-molybdenum or nickel-molybdenum catalyst to form ammonia, water, and hydrogen sulfide. These lighter gases can then be removed from the hydrocarbons by simple distillation. The hydrogen also reacts with olefins to form paraffins. This olefin saturation usually occurs in the first few inches of the catalyst bed, so it is seldom considered in sizing the bed. (If the olefins concentration is very high, however, the saturation reaction may cause an unacceptable increase in temperature in the top of the bed.) Nitrogen removal is usually harder to achieve than sulfur removal, so if the stock contains a significant amount of nitrogen, the unit design may be based on this consideration. For most stocks, however, the achievement of adequate sulfur removal is the principal design criterion. The analysis which follows considers only the removal of sulfur, but the reactor guidelines which are developed are applicable to most designs.

A distillate desulfurization unit is actually one of the least complex processing units in a modern refinery. (See the flow diagram in the Appendix.) The reactor is the heart of the unit because the conditions selected there provide nearly complete specification of the performance requirements of the other major pieces of equipment. The feed pump and hydrogen compressor must be capable of delivering their charges to the reactor at the desired pressure. In addition, the preheat exchangers and furnace must, in combination, add enough heat to the distillate and hydrogen streams to bring them to the reaction temperature. The design of the amine contactor and the distillate product stripper are not strongly dependent on the conditions at which the reaction occurs, being affected primarily by the total conversion. The geometric programming formulation which is developed in this paper concerns only the reactor itself since it is the most expensive single piece of equipment and it offers the greatest design flexibility.

This analysis accepts the statutory limits on sulfur in fuel as the desired level of sulfur removal. A complete economic evaluation might occasionally indicate that a higher level of sulfur removal is economic, but the price of sulfur varies so widely that such an economic evaluation would require an extensive study of the sulfur market. The long term price of sulfur will probably not provide justification for even the statutory sulfur removal because the sulfur which is being removed from fuels and other minerals currently exceeds the demand. In fact, sulfur prices now exceed the value which would be expected with the increased production of recent years simply because the sulfur being produced from the huge gas plants in western Canada does not yet have transportation routes to the market. The legal limits will, therefore, be the principal justification for sulfur removal for the foreseeable future.

The mathematical model of the reactor for a distillate desulfurization unit is a set of nonlinear equations in polynomial form in which all the coefficients are positive when the constraints are stated in less-than-or-equal-to-1 form. Since this is the form on which geometric programming is most effective, this method will be used for the analysis. The discussion is divided into three sections.

The first section prepares the equations for the physical configuration of a cylindrical vessel of a given volume with internal pressure. No reaction kinetics are included. A geometric programming formulation for the minimization of the cost of the vessel subject only to the configuration constraints is analyzed with an interactive computer program. Geometric programming provides some insight into why seemingly inconsequential changes in the model (i.e., corrosion allowance) may have a significant impact on the optimal solution. Examination of this model can provide a lower bound on the cost of any vessel at any pressure and a rule-of-thumb for selection of the length and diameter for a vessel with a specified volume.

The second section contains the development of the constraints which define the kinetics of the desulfurization reaction. Because so many species of sulfur compounds may be present and the reaction is affected by so many parameters, these constraints are quite complex.

The third section contains an analysis of the mathematical model which contains both the configuration constraints and the kinetic constraints. Solution of this model would provide the optimal reaction conditions as well as the reactor dimensions. In geometric programming form, the model is a posynomial with five degrees-of-difficulty, so that any solution which can be obtained will be a global minimum. The solution of this problem is beyond the scope of this paper because the kinetic expression and various other coefficients must be extracted from proprietary data. All of the exponents are available in the literature, however, so it is possible to formulate the dual constraints and find a feasible solution for the reduced dual. If an accurate set of coefficients could then be obtained, this feasible dual solution could be used to find a lower bound on the total cost.

CHAPTER 1

REACTION VESSEL MODEL

The first part of the model of a distilllate desulfurization unit is the set of equations which describe the reaction vessel itself. In a hydrotreater the catalyst is usually contained in a cylindrical vessel with ellipsoidal heads at pressures from 200 to 1000 pounds per square inch. For any set of operating conditions the pressure and required volume are specified, so the principal task is to select a length, diameter, and wall thickness in accordance with the specifications set by the American Society of Mechanical Engineers (ASME) in the code for unfired pressure vessels (1).

This problem has been discussed in the literature by several authors, with each presenting a different "optimal" solution. For example, Abakians (2) used calculus to determine the relationship between the length (L) and diameter (D) as follows:

$$L = D\left(1 + \frac{3DP}{4CSE}\right)$$

where:

P = design pressure, in psig

C = corrosion allowance, in in.

S = design stress limit, in psi

E = joint efficiency, percent

This approximation produces a L/D ratio which is much higher than any commonly used. (An error in the labeling of the nomograph which accompanies this article seems to make the method give results more consistent with traditional design practices.) Rudd (3), on the other hand, says that there is no root for the first derivative of the cost equation, so the cost is unbounded. His formulation differs from that of Abakians only in that he does not include an allowance for corrosion. Since the corrosion allowance is only a function of the stream composition, it does not seem logical that a least-cost reactor design can be formulated for a corrosive system, but not for a non-corrosive system. Analysis of this reactor model with geometric programming shows that a realistic optimum does not exist, but the inclusion of a corrosion allowance in the model will generate a design which provides a lower bound on cost. The cost function is quite flat, so the lower bound cost figure will have some relevance.

A detailed cost estimate for a vessel would include the length and type of welds, the complexity of the internal distributors, the cost of rolling the metal, transportation of the vessel to the plant, and erection of the vessel (4). Because the cost includes so many factors (several of them represented by discrete variables) the development of a general cost function is very difficult. For a large number of vessels, however, the cost function is flat enough that an expression of total cost based on only the total vessel weight will give a very reasonable preliminary estimate. The total weight consists of the sum of the weights of three parts: the cylindrical portion of the shell, the two ellipsoidal heads, and the internal distributors.

For vessels in which the shell thickness is small compared to the diameter, the weight of the cylindrical part of the shell may be approximated by the product of the inside surface area, the thickness, the metal density.

$$W_s = (\pi)(D)(L)(t)(\rho_m)/12$$

where: W_s = weight of the cylindrical portion of the shell, in lb

D = inside diameter of the vessel, in ft

L = length of the cylindrical portion of the shell, in ft

t = thickness of the vessel wall, in inches

ρ_m = metal density, in lb/cu ft

If the thickness of the wall is not small compared to the diameter, the more complicated formula for the volume of an annular object must be used instead.

High pressure vessels (above 100 psig) are most frequently closed with 2:1 ellipsoidal heads. That is, the depth of the head is equal to one fourth of the vessel inside diameter. Dimoplon (5) approximates the weight of one head with the following equation:

$$W_h = (1.084)(D)^2(t)(\rho_m)/12$$

where W_h is equal to the weight of one head in pounds.

An additional percent of the total weight must be added to account for the weight of the nozzles and other internals (6). This amount is estimated by the following equation (6):

$$W_i = K_5(W_s + 2W_h)^{A5} = K_5N^{A5}$$

where: W_i = weight of the internals, in lb

N = nominal weight of the empty shell, in lb

K_5 = 1.65

A_5 = 0.85

This factor is quite approximate because configurations and materials of construction vary quite widely.

The cost function for most process vessels may be approximately expressed as an exponential function of total weight (6).

$$\text{Cost} = K_1(W)^{-A1}$$

where: Cost = \$/pound of steel in the vessel

$$W = W_s + 2W_h + W_i = N + K_5N^{A5}$$

For a carbon steel vessel the values of the cost parameters are approximately as follows (6):

$$K_1 = 45$$

$$A_1 = 0.35$$

The principal constraint on the reactor cost is the requirement that the reactor volume be large enough to contain the amount of catalyst needed to complete the reaction. For processing purposes, the volume contained in the heads should not be considered because this volume does not contain catalyst. The top head contains trays and pipes of various configurations designed to distribute both the liquid and vapor portions of the feed evenly over the catalyst. The bottom head contains alumina balls or other inert materials as well as strainers to keep the catalyst from flowing out with the feed and to help the feed flow out smoothly. The total active volume is approximately

$$V = (\pi/4)(D)^2(L)$$

where V = the cylindrical volume of the vessel, in cubic feet.

An additional constraint is provided by the American Society of Mechanical Engineers' Pressure Vessel Code (1) in the specification of the minimum shell thickness.

$$t = \frac{6PD}{SE - 0.6P} + C$$

where: t = thickness of the vessel wall, in inches

P = internal pressure, in psig

S = stress limit of the shell material, in psi

E = joint efficiency

C = corrosion allowance, in inches

The corrosion allowance depends upon the nature of the substances contained in the vessel and the extent to which they will react with the vessel material.

The cost minimization problem is, therefore, as follows:

$$\text{Min:}\quad \text{Total Cost} = \text{Weight} \times \text{Cost}$$

$$= (W) \times K_1 W^{-A_1} = K_1 W^{1-A_1}$$

$$\text{s.t.:}\quad W = N + K_5 N^{A_5}$$

$$N = \pi\rho_m DL(t/12) + 2(1.084)\rho_m D^2(t/12)$$

$$t = 6PD/(SE - 0.6P) + C$$

$$V = (\pi/4)D^2 L$$

Since all of the constraints must be expressed in less-than-or-equal-to form for solution with geometric programming, (7), the sense of the constraints must be determined.

The first constraint expresses the total vessel weight as the sum of the weights of the constituents. Since W is to be minimized in the objective function, and it appears in no other constraint, it must be bounded from below in this constraint.

$$W \geq N + K_5 N^{A_5}$$

By similar reasoning, the second constraint must bound N from below in order to keep the weight of the shell from being forced to zero.

$$N \geq \pi\rho_m DL(t/12) + 2(1.084)\rho_m D\ (t/12)$$

The direction of the third constraint is made obvious by the fact that the reaction kinetics requires a minimum volume to achieve the desired conversion. The optimum dimensions must provide at least this minimum volume.

$$V \leq (\pi/4)D^2L$$

The acceptance of the ASME Pressure Vessel Code as a statutory lower bound on wall thickness fixes the direction of the fourth constraint.

$$t \geq 6PD/(SE - 0.6P) + C$$

For a specified pressure and volume, the geometric programming form of the problem statement becomes:

$$\text{Min:} \quad K_1W^{1-A_1}$$

$$\text{s.t.:} \quad N/W + K_5N^{A_5}/W \leq 1$$

$$(\pi\rho_m/12)DLt/N + (2.168\rho_m/12)D^2t/N \leq 1$$

$$(4V/\pi)D^{-2}L^{-1} \leq 1$$

$$(6P/(SE - 0.6P))D/t + C/t \leq 1$$

where W, N, D, L, and t are variables.

The geometric programming dual constraints may be formulated (7) as follows:

1. Orthogonality condition: $w_1 = 1$
2. Normality condition for W: $(1-A_1)w_1 - w_2 - w_3 = 0$
3. Normality condition for N: $w_2 + A_5w_3 - w_4 - w_5 = 0$
4. Normality condition for D: $w_4 + 2w_5 - 2w_6 + w_7 = 0$
5. Normality condition for L: $w_4 - w_6 = 0$
6. Normality condition for t: $w_4 + w_5 - w_7 - w_8 = 0$

where w_i = the weight associated with the ith term in the primal problem. The formulation has 8 terms, so there are 8 dual variables. The 6 equations in the constraint set mean that the problem has 2 degrees of difficulty. It is also posynomial and all of the constraints must be tight at optimality. As a result, the solution to the problem will be a global optimum (7).

The objective function for the dual problem is of the form:

$$\text{Max:} \quad = \Pi(C_i/w_i)^{w_i} \times \Pi(\Sigma w_j)^{\Sigma w_j}$$

where: C_i = coefficient of the ith term in the primal problem

Σw_j = sum of the weights associated with the terms in a constraint

Each of the w_i's may be expressed as a function of two basic variables in the reduced dual problem (7), r_1 and r_2. The only dual constraints are the requirements that the original dual variables be greater than zero. For this problem these constraints are

$$0.15r_1 - r_2 + 0.5525 > 0$$

$$0.65 - r_1 > 0$$

$$-0.30r_1 + 3r_2 - 1.105 > 0$$

A conversational program to solve this reduced dual problem has been written. (A listing and sample of the input and output are included in the Appendix.) Table 1 summarizes the results of eight runs, using different values for the pressure, the volume, and the corrosion allowance. The costs are for carbon steel vessels with no unusual internals. Examination of runs number 1, 2, and 3 will show that the length/diameter ratio (the usual expression of the dimension of the vessel) are impacted greatly by the change in the corrosion allowance. It may also be noticed, however, that the total cost is relatively insensitive to the exact dimensions of the reactor. For example, the length to diameter ratio for run 1 is 31.1 while that for run 2 is 18.9, but the cost for run 2 is only 3.5% higher. For a more reasonable L/D of approximately 5, the total cost is only 4.7% higher. As a result, this model can provide a quick lower-bound cost estimate.

TABLE 1

RESULTS OF COMPUTER RUNS

Run No.	1	2	3	4	5	6	7	8
Pressure, psia	700	700	700	700	700	400	400	400
Volume, cu ft	2000	2000	2000	4000	4000	2000	4000	4000
Corrosion Allow., in.	.0625	.1250	.2500	.0625	.1250	.0625	.0625	.1250
Cost, $	81570	84390	89140	125020	128730	58650	89460	93400
Diameter, ft	4.340	5.126	6.027	5.172	6.113	4.975	5.931	6.991
Length, ft	135.2	96.9	70.1	190.4	136.3	102.9	144.8	104.2
Length/diameter	31.1	18.9	11.6	36.8	22.3	20.7	24.4	14.9
Thickness, in.	1.028	1.265	1.591	1.213	1.485	0.689	0.809	1.005
Weight, lb	103000	108500	118100	198600	207800	62000	118700	126800

If the model is reformulated for a non-corrosive system, i.w. C=0, the problem has only eight terms and 1 degree of difficulty. The dual constraints are as follows:

1. Orthogonality condition: $w_1 = 1$
2. Normality condition for W: $(1-A_1)w_1 - w_2 - w_3 = 0$
3. Normality condition for N: $w_2 + A_5w_3 - w_4 - w_5 = 0$
4. Normality condition for D: $w_4 + 2w_5 - 2w_6 + w_7 = 0$
5. Normality condition for L: $w_4 - w_6 = 0$
6. Normality condition for t: $w_4 + w_5 - w_7 = 0$

It may be seen that $w_6 = w_4$, so substituting for w_6, equation 4 becomes:

$$-w_4 + 2w_5 + w_7 = 0$$

If this equation is added to equation 6, the following result is derived:

$$3w_5 = 0$$

There is no set of non-zero w's which satisfies all of the constraints. This discovery is consistent with Rudd's conclusion.

It seems very strange that the simple addition of an allowance for corrosion makes it possible for an optimum to be found. Further examination of the model will give an indication of why this is possible. The third primal constraint

$$(4V/\pi)D^{-2}L^{-1} \leq 1$$

will obviously be tight at optimality since the reactor will not be designed with a volume larger than the requirement. For any volume, therefore, L is proportional to $1/D^2$.

In addition, from the fourth primal constraint, thickness is a function of diameter

$$t = 6PD/(SE - 0.6P) + C$$

Substituting into the second constraint,

$$N = \frac{\rho m \pi}{12} D \left(\frac{4V}{\pi} D^{-2}\right)\left(\frac{6P}{SE-0.6P} D + C\right) + \frac{2.168 \rho m}{12} D^2 \left(\frac{6P}{SE-0.6P} D + C\right)$$

and, combining the constant terms

$$N = B_1 D^{-1}(D + C') + B_2 D^2 (D + C')$$

where $C' = C/(6P/(SE-0.6P))$. The second term, $B_2 D^2 (D + C')$ decreases as D decreases for all values of D. The first term exhibits a slightly more complex relationship with respect to D. When D is large compared to C', the first term is not a function of D, so N decreases as D decreases for all values of D, and the function is unbounded. On the other hand, if C' is not small compared to D, then a decrease in D will have a proportionally greater effect on the D in the denominator than on the (D+C') in the numerator, so the term may actually increase as D decreases.

Since all of the computer runs indicated that the "optimum" design for systems with a non-zero corrosion allowance was a very long, thin vessel, it is quite clear that the formulation needs an additional constraint. However, as a rule of thumb, the designer should try to make the L/D ratio as large as he can.

Several other constraints may act to keep the reactor diameter from getting as small as the results in Table 1. Five constraints which are most likely to be active are listed below:

1. Regional statutes may limit the height of the vessel.
2. The height of the cranes available at the site for dumping the catalyst into the vessel will place an effective upper limit on the vessel length.
3. The diameter must be large enough so that workmen can get inside to install the internals.
4. In a catalytic system, the cross-sectional area for flow must be large enough so that most of the stream is flowing through the catalyst rather than down the walls.
5. Pumping and compression costs may become excessive if the pressure drop through the bed becomes too high. Decreasing the diameter increases the velocity of the fluid through the bed, so the pressure drop per foot of bed length increases. In addition, the length of the bed increases to

provide adequate volume. This constraint may take the form of an upper bound on L/D^4. (Alternatively, an additional cost term, proportional to L/D^4, may be added to the objective function.)

In real design problems one of these constraints will be tight. Re-examination of the original primal problem, however, will reveal that the addition of one more constraint will result in a design model containing 5 constraints and 5 primal variables. Since all of the constraints will be tight and binding at optimality, there are no degrees of freedom and no optimization. Phillips and Beightler (8) included a constraint in the form of an upper bound on length in their formulation of this problem. They did not try to solve the problem and apparently failed to notice that all of the design variables were completely specified by the constraints.

In most catalytic refining units the fourth or fifth of the additional constraints listed above is most likely to be binding. For the discussion of the distillate desulfurization reactor which follows, the pressure drop constraint will be included because the hydrogen leaving the reactor is usually separated from the treated distillate and recycled to the reactor. Recompressing this hydrogen recycle stream is quite expensive, requiring both a large investment and high operating costs.

The calculation of pressure drop in a system with two-phase flow through a solid bed is quite complex (9), as is the calculation of compression cost (10). Over a narrow range of change, however, the pressure drop per foot of catalyst bed is approximately proportional to the square of the velocity of the liquid portion of the feed and the cost is proportional to the pressure drop.

$$\Delta P = Gs^2L$$

where ΔP = pressure drop, in psi

G = proportionality constant

L = bed length, in ft

s = velocity of the liquid flowing through the bed, in ft/hr

$= (F_1/\rho_1)(AR)^{-1}$

F_1 = liquid flow rate, in lb/hr

ρ_1 = liquid density, in lb/cu ft

AR = cross-sectional area, in sq ft

$= (\pi/4)D^2$

A summary of the three constraints which must be used to approximate the pressure drop through the catalyst bed in a distillate desulfurization reactor follows:

$$\Delta P \geq G s^2 L$$
$$s \geq (F_1/\rho_1)(AR)^{-1}$$
$$AR \leq (\pi/4)D^2$$

The directions of the constraints are determined by the requirement that the pressure drop not be understated for the physical design parameters. Since there is a cost associated with pressure drop, it must be lower bounded to keep it from going to zero. In geometric programming form, these constraints become:

$$G s^2 L(\Delta P)^{-1} \leq 1$$
$$(F_1/\rho_1)(AR)^{-1}s^{-1} \leq 1$$
$$(4/\pi)(AR)D^{-2} \leq 1$$

In conclusion, two results are derived from this analysis of the reactor vessel, even though a rigorously valid reactor model cannot be formulated. The results are:

1. As a general rule, the cost of a reactor of a given volume at a given pressure will be minimized if the vessel diameter is made as small as possible.
2. A geometric programming solution to the reactor formulation which includes a non-zero corrosion allowance may not give a reasonable design, but the resultant cost estimate should be a useful lower bound on the cost of the actual vessel.

This model, together with the pressure drop constraint, will be used with additional constraints describing the kinetics of desulfurization to create a geometric programming formulation from which the operating conditions and reactor physical design could be determined.

CHAPTER 2

KINETICS OF HYDRODESULFURIZATION

In spite of the commercial prominence of hydrodesulfurization of distillate stocks, the literature contains very little information on the reaction kinetics. Most of the published investigations consider only naphtha desulfurization, and the results are not transferrable because the naphtha is always completely vaporized at reaction conditions. The only complete analysis based on a commercial distillate feedstock available in the literature is the work of C. G. Frye and J. F. Mosby (11). Frye and Mosby studied the desulfurization of a light catalytic cycle oil (LCCO) containing 0.4 to 2.0 weight percent sulfur on commercial cobalt-molybdenum catalyst. The principal conclusions reached in the study were:

1. Reaction kinetics limit the extent of the conversion. The reverse reaction (combination of H_2S and hydrocarbons to form sulfur-containing organic compounds) occurs so slowly that the desulfurization is nearly irreversible, eliminating the possibility of thermodynamic limitation. The high activation energy indicates

that diffusion does not control.

2. The reaction is first order with respect to each individual sulfur compound. The studies of Satterfield and Roberts (12), Phillipson (13), and Wilson (14) confirm this conclusion. Some other investigators, Massagutov (15), and Beuther and Schmidt (16), have indicated that the reaction is approximately second order with respect to total sulfur concentration. Frye and Mosby illustrated that, though the reaction of each sulfur compound is first order, the rate of reaction for the various compounds varies so widely that the overall reaction may appear to be of higher order.
3. The reaction is first order with respect to hydrogen concentration. Only Frye and Mosby have determined this relationship experimentally though Phillipson (13) also assumed it.
4. Hydrogen sulfide and aromatic hydrocarbons inhibit the reaction because they are adsorbed by the catalyst and block active sites.

From their studies Frye and Mosby developed a kinetic model of the Langmuir-Hinshelwood type (17) which expressed the reaction kinetics for an individual sulfur compound.

The reaction rate constant for a typical compound, a trimethylbenzothiophene, was determined experimentally and the desulfurization of the whole fraction was correlated as a function of the removal of this particular compound and of the end point of the fraction. All of the coefficients derived are theoretically possible and consistent. The final equation is as follows:

$$\ln\frac{X_o}{X} = \frac{kAP_h}{(SV)(1-a+(a+H/M)P_v/P)(1 + K_{hs}P_{hs} + K_{ar}P_{ar})^2}$$

where:

X_o, X = concentration of the sulfur compound (trimethylbenzothiophene) in the feed and product, respectively

k = reaction rate constant = $B_r e^{E_r/RT}$ ($E_r \simeq -55260$)

A = catalyst activity

P_h = average hydrogen partial pressure, psi

SV = weight hourly space velocity

= lb/hr of oil flowing through the reactor per pound of catalyst

a = mole fraction vaporization of the feed

H/M = mole ratio of hydrogen to hydrocarbon

P_v = vapor pressure of the pure sulfur compound, psi

= $B_v\ e^{E_v/RT}$ ($E_v \simeq -23796$)

P = total reactor pressure, psi

K_{hs} = adsorption constant for hydrogen sulfide

$= B_{hs}e^{E_{hs}/RT}$ $(E_{hs} \simeq 1186)$

K_{ar} = adsorption constant for aromatic hydrocarbons

$= B_{ar}e^{E_{ar}/RT}$ $(E_{ar} \simeq 5040)$

P_{hs} = average hydrogen sulfide partial pressure, psi

P_{ar} = aromatics partial pressure, psi

T = reactor temperature, in degrees Rankine

R = gas constant = 1.987 Btu/lbmole-R

The rate and adsorption constants are all of the classical Arrhenius (17) form with an exponential dependence on temperature where the "E" in the exponent represents an activation energy. For adsorption, the activation energies are positive, indicating that adsorption decreases with an increase in temperature. The reaction rate constant, however, has a negative activation energy so the reaction rate will increase with an increase in temperature. (All of the "B" and "E" values must be determined experimentally.)

The space velocity, indicating the number of pounds of feed flowing through the reactor per hour for each pound of catalyst in the reactor, is the measure generally used to indicate residence time in a commercial reactor. It is also a measure of the required reactor volume and, as such, a principal design variable. The space velocity used in this formulation may also be called a weight hourly space velocity because it is determined by a ratio of two weights. (Another measure is the volume hourly space velocity, VHSV, which is defined as the cubic feet per hour of feed per cubic foot of catalyst.) The space velocity is equal to the feed rate in lb/hr divided by the product of the catalyst density and volume. ($SV = F/\rho_c V$, where F is the feed rate in lb/hr and ρ_c is the catalyst density in lb/cu ft.)

The term $(1-a+(a+H/M)P_v/P)$ represents the effect of the partial vaporization of the feed on the conversion. Liquids, because of the intermolecular attraction do not diffuse into the catalyst pores as readily as gases do, so the conversion is decreased. In addition, the liquid will not generally be as evenly distributed over the catalyst. The mole ratio of hydrogen to hydrocarbon in the feed (H/M) does not include any hydrocarbons contained in the hydrogen feed. The moles of hydrogen in the feed and recycle gas is available directly from the feed gas analysis. The moles of hydrocarbon feed is generally not available directly, but correlations (18) exist for estimating the number of moles from laboratory inspection data such as the API gravity (18) and the ASTM or TBP distillation (18).

The fraction vaporized, a, is the least readily determined value in the formulation. It is a direct function of the liquid-vapor equilibrium constant (19) which is, in turn, a function of the temperature, pressure, and composition of the hydrocarbon and hydrogen in the feed. Since the composition of the hydrocarbon portion is not known explicitily, the determination of the equilibrium constant becomes ambiguous. Techniques for arriving at a very rough approximation, however, do exist (18). For purposes of analysis, it will be most convenient to estimate the percent vaporization, then solve the geometric programming problem and re-calculate the fraction vaporized at the optimal conditions. If the change in a is not too great, the costs with the true percent vaporized may be determined with sensitivity analysis.

The functional relationships between the catalyst activity and the operating temperature and pressure have not been defined precisely in the literature. The qualitative relationships have been stated, however, and for the purposes of this analysis very approximate coefficients and exponents will be used. The activity is a function of the catalyst type and metals content, the operating temperature, and the hydrogen partial pressure. The variation with catalyst type is usually not especially significant. The activity decreases as hydrogen partial pressure is lowered because the hydrogen environment inhibits coke deposition on the catalyst. Any coke deposited on the active sites of the catalyst reduces the surface on which the desired reactions can occur. The temperature dependence is not easily defined. The activity decreases very slowly with increasing temperature up to a temperature where the crystalline structure of the alumina catalyst base begins to degrade. The activity loss becomes very rapid at this temperature, and it is irreversible. The temperature at which this conversion begins is dependent upon the stock being treated. A higher temperature can be tolerated in a naphtha unit than in one running middle distillates (11). The activity will be represented by an equation of the form:

$$A = B_{act}(e^{E_t/RT})(P_h)^{E_p}$$

To use this equation the coefficient and exponents (B_{act}, E_t, and E_p) would have to be determined experimentally for the particular stock to be treated. For this analysis, the following approximate values will be used: $E_t = 37620$ and $E_p = 0.3333$.

The expression $(1 + K_{hs}P_{hs} + K_{ar}P_{ar})^2$ represents the adsorption of hydrogen sulfide and aromatics on active catalyst sites. The adsorption constants (K_{hs} and K_{ar}) are decreasing functions of temperature of the exponential Arrhenius type and the rate of adsorption of each species is proportional to the partial pressure of the species. It was determined experimentally that the inhibiting effect was proportional to the square of the rate of absorption, indicating that the reaction occurs via a two-site mechanism; i.e., both the sulfur compound and the hydrogen are adsorbed on the catalyst surface when the reaction occurs (17).

The next step is determination of the direction of the constraints and reformulation in the form required for geometric programming.

In order to keep the algorithm from overstating the extent of the reaction consistent with a set of operating conditions, the expressions in the denominator must be bounded from below by the expressins which define them:

$$SV \geq F/\rho_c V$$

$$Q_2 \geq Q_3{}^2$$

$$Q_3 \geq 1 + K_{hs}P_{hs} + K_{ar}P_{ar}$$

$$Q_1 \geq 1 - a + (a-H/M)P_v/P$$

$$K_{hs} \geq B_{hs}(e^{1/RT})^{E_{hs}}$$

$$K_{ar} \geq B_{ar}(e^{1/RT})^{E_{ar}}$$

$$P_{hs} \geq (M_{hs}/M_t)\ P$$

$$P_{ar} \geq (f_{ar})a(M/M_t)\ P$$

$$P_v \geq B_v(e^{1/RT})^{E_v}$$

where: M_{hs} = moles H_2S in the reactor (average)

M_t = total moles in the reactor

f_{ar} = fraction aromatics in the distillate

Similarly, the quantities in the numerator must be upper-bounded:

$$k_r \le B_r(e^{1/RT})^{E_r}$$

$$A \le B_{act}(e^{1/RT})^{E_t}(P)^{E_p}$$

$$P_h \le (H/M_t)\ P$$

In geometric programming form, the constraints representing the reaction kinetics become:

$$R(SV)Q_1Q_2/(k_rAP_h) \le 1$$

$$F/\rho_cV(SV) \le 1$$

$$Q_3^{\,2}/Q_2 \le 1$$

$$1/Q_3 + K_{hs}P_{hs}/Q_3 + K_{ar}P_{ar}/Q_3 \le 1$$

$$(1-a)/Q_1 + (a-H/M)(P_v/P)(Q_1)^{-1} \le 1$$

$$B_{hs}(e^{1/RT})^{E_{hs}}(K_{hs})^{-1} \le 1$$

$$B_{ar}(e^{1/RT})^{E_{ar}}(K_{ar})^{-1} \le 1$$

$$(M_{hs}/M_t)(P/P_{hs}) \le 1$$

$$f_{ar}\ a(M/M_t)P(P_{ar})^{-1} \le 1$$

$$B_v(e^{1/RT})^{E_v}(P_v)^{-1} \le 1$$

$$(k_r/B_r)(e^{1/RT})^{-E_r} \le 1$$

$$(A/B_{act})(e^{1/RT})^{-E_t}(P)^{-E_p} \le 1$$

$$(P_h/P)(M_t/H) \le 1$$

These constraints can be used, in conjunction with the reactor vessel model and the pressure drop constraints to determine the reactor dimensions and the operating conditions (temperature and pressure) for a least-cost reactor design.

CHAPTER 3

THE COMPLETE MODEL

The optimal reaction conditions and vessel design parameters may be determined when the three sets of constraints are put together:

1. The reactor vessel design constraints
2. The kinetic model constraints
3. The pressure drop constraints

The cost function also has three parts: the cost of the reactor, the catalyst cost, and the compression cost. The entire model is as follows:

Min: $C_1(W)^{1-A_1} + C_2(\Delta P) + C_3(V)$

s.t.: Reactor Vessel Design Constraints

$$N/W + C_5N^{A_5}/W \leq 1 \tag{1}$$

$$(\pi\rho_m/12)DLt/N + (2.168\rho_m/12)D^2t/N \leq 1 \tag{2}$$

$$(4/\pi)VD^{-2}L^{-1} \leq 1 \tag{3}$$

$$(6/SE)PDt^{-1} + (0.6/SE)P \leq 1 \tag{4}$$

Kinetic Constraints

$$R(SV)Q_1Q_2/(k_rAP_h) \leq 1 \tag{5}$$

$$(F/\rho_c)V^{-1}(SV)^{-1} \le 1 \quad (6)$$

$$Q_3{}^2/Q_2 \le 1 \quad (7)$$

$$1/Q_3 + K_{hs}P_{hs}/Q_3 + K_{ar}P_{ar}/Q_3 \le 1 \quad (8)$$

$$(1-a)/Q_1 + (a- H/M)(P_v/P)/Q_1 \le 1 \quad (9)$$

$$B_{hs}(e^{1/RT})^{E_{hs}}(K_{hs})^{-1} \le 1 \quad (10)$$

$$B_{ar}(e^{1/RT})^{E_{ar}}(K_{ar})^{-1} \le 1 \quad (11)$$

$$(M_{hs}/M_t)(P/P_{hs}) \le 1 \quad (12)$$

$$(f_{ar})a(M/M_t)(P/P_{ar}) \le 1 \quad (13)$$

$$B_v(e^{1/RT})^{E_v}(P_v)^{-1} \le 1 \quad (14)$$

$$(1/B_r)(k_r)(e^{1/RT})^{-E_r} \le 1 \quad (15)$$

$$(1/B_{act})A(e^{1/RT})^{-E_t}(P)^{-E_p} \le 1 \quad (16)$$

$$(M_t/H)(P_h/P) \le 1 \quad (17)$$

Pressure Drop Constraints

$$Gs^2L(\Delta P)^{-1} \le 1 \quad (18)$$

$$(F_1/\rho_1)(AR)^{-1}(s)^{-1} \le 1 \quad (19)$$

$$(4/\pi)(AR)(D)^{-2} \le 1 \quad (20)$$

This formulation contains twenty-three variables. They are:

W, ΔP, N, D, L, t, V, P, SV, Q_1, Q_2, k_r,
A, P_h, Q_3, K_{hs}, P_{hs}, K_{ar}, P_{ar}, P_v, $e^{1/RT}$,
s, AR

There are also twenty-eight terms so the degree of difficulty (7) is five. It should also be noticed that all of the coefficients (with the possible exception of a-H/M) are positive and all of the constraints are in less-than-or-equal-to- 1 form. This means that, for any case in which H/M is less than a, and an optimal solution can be found, the solution is guaranteed to be a global minimum (7).

Before any attempt at analysis is made on the complete model, some combination of terms and elimination of variables is desirable. Reduction to seven constraints containing ten variables is possible without eliminating any of the fundamental variables: diameter, pressure drop, temperature, and pressure. The reduced formulation is as follows:

$$\text{Min:} \quad C_1(W)^{1-A_1} + C_2(\Delta P) + C_3(\Delta P)D^6$$

s.t.:

$$C_4N/W + C_5N^{A_5}/W \le 1 \qquad (1)$$

$$C_6D^5t(\Delta P)/N + C_7D^2t/N \le 1 \qquad (2)$$

$$C_8PD/t + C_9P \le 1 \qquad (3)$$

$$C_{10}Q_1Q_2(e^{1/RT})^{A_{10}}(P)^{A_{11}}(\Delta P)^{-1}(D)^{-6} \le 1 \qquad (4)$$

$$C_{11}(Q_3)^2/Q_2 \le 1 \qquad (5)$$

$$C_{12}/Q_3 + C_{13}(e^{1/RT})^{A_{13}}P/Q_3 + C_{14}(e^{1/RT})^{A_{14}}P/Q_3 \le 1 \qquad (6)$$

$$C_{15}/Q_1 + C_{16}(e^{1/RT})^{A_{16}}P^{-1}/Q_1 \le 1 \qquad (7)$$

The coefficients of the new model are defined in terms of the coefficients of the original model in the Appendix.

The dual to this problem is as follows:

Normality condition:

$$w_1 + w_2 + w_3 = 1$$

Orthogonality conditions:

$$W: \quad (1-A_1)w_1 - w_4 - w_5 = 0$$

$$\Delta P: \quad w_2 + w_3 + w_6 - w_{10} = 0$$

$$N: \quad w_4 + A_4 w_5 - w_6 - w_7 = 0$$

$$D: \quad 6w_3 + 5w_6 + 2w_7 + w_8 - 6w_{10} = 0$$

$$t: \quad w_6 + w_7 - w_8 = 0$$

$$P: \quad w_8 + w_9 + A_{10}w_{10} + w_{13} + w_{14} - w_{16} = 0$$

$$Q_1: \quad w_{10} - w_{15} - w_{16} = 0$$

$$Q_2: \quad w_{10} - w_{11} = 0$$

$$Q_3: \quad 2w_{11} - w_{12} - w_{13} - w_{14} = 0$$

$$e^{1/RT}: \quad A_{10}w_{10} + A_{13}w_{13} + A_{14}w_{14} + A_{16}w_{16} = 0$$

Since there are sixteen dual variables and eleven equations, the dual variables may be expressed in terms of 5 basic reduced dual variables, r_1, r_2, r_3, r_4, and r_5. Using the values of the A_i's given in the Appendix, the reduced dual constraints are as follows:

$$w_1 = 1 + r_1 - r_3$$

$$w_2 = 0.3250 + 0.2500r_1 - 0.5r_2 - 0.3250r_3$$

$$w_3 = -0.3250 - 0.2500r_1 - 0.5r_2 + 1.3250r_3$$
$$w_4 = 0.65 - 0.35r_1 - 0.65r_3$$
$$w_5 = r_1$$
$$w_6 = r_2$$
$$w_7 = -.65 + 0.5r_1 - r_2 - 0.65r_3$$
$$w_8 = 0.65 + 0.5r_1 - 0.65r_3$$
$$w_9 = -0.65 - 0.5r_1 + 5.4833r_3 - 0.7647r_4 - 3.7214r_5$$
$$w_{10} = r_3$$
$$w_{11} = r_3$$
$$w_{12} = 5.5r_3 - 0.7647r_4 - 4.7214r_5$$
$$w_{13} = r_4$$
$$w_{14} = -3.5r_3 - 0.2353r_4 + 4.7214r_5$$
$$w_{15} = r_3 - r_5$$
$$w_{16} = r_5$$

By examination, it was discovered that the following values of the basic reduced dual variables provide positive, non-zero values of all the dual variables:

$$r_1 = 0.1$$
$$r_2 = 0.1$$
$$r_3 = 0.6$$
$$r_4 = 0.1$$
$$r_5 = 0.5$$

Since all of the exponents in the primal problem are based on physical relationships (i.e.,activation energy and vessel physical parameters) these values of the basic reduced dual variables should be a feasible solution for the dual of a problem with any set of coefficients. Therefore, it should be possible to use the values to calculate a lower bound on total cost with the dual objective function.

The fact that a feasible dual solution does exist, though not guaranteeing a bounded solution, indicates that the variables are all independent.

Because a number of the coefficients (C_2, M_t, B_r, M_h, A, B_{act}, B_{hs}, B_{ar}, f_{ar}, a, M, B_v, and G) are available only from proprietary correlations, it is not possible to solve a sample problem.

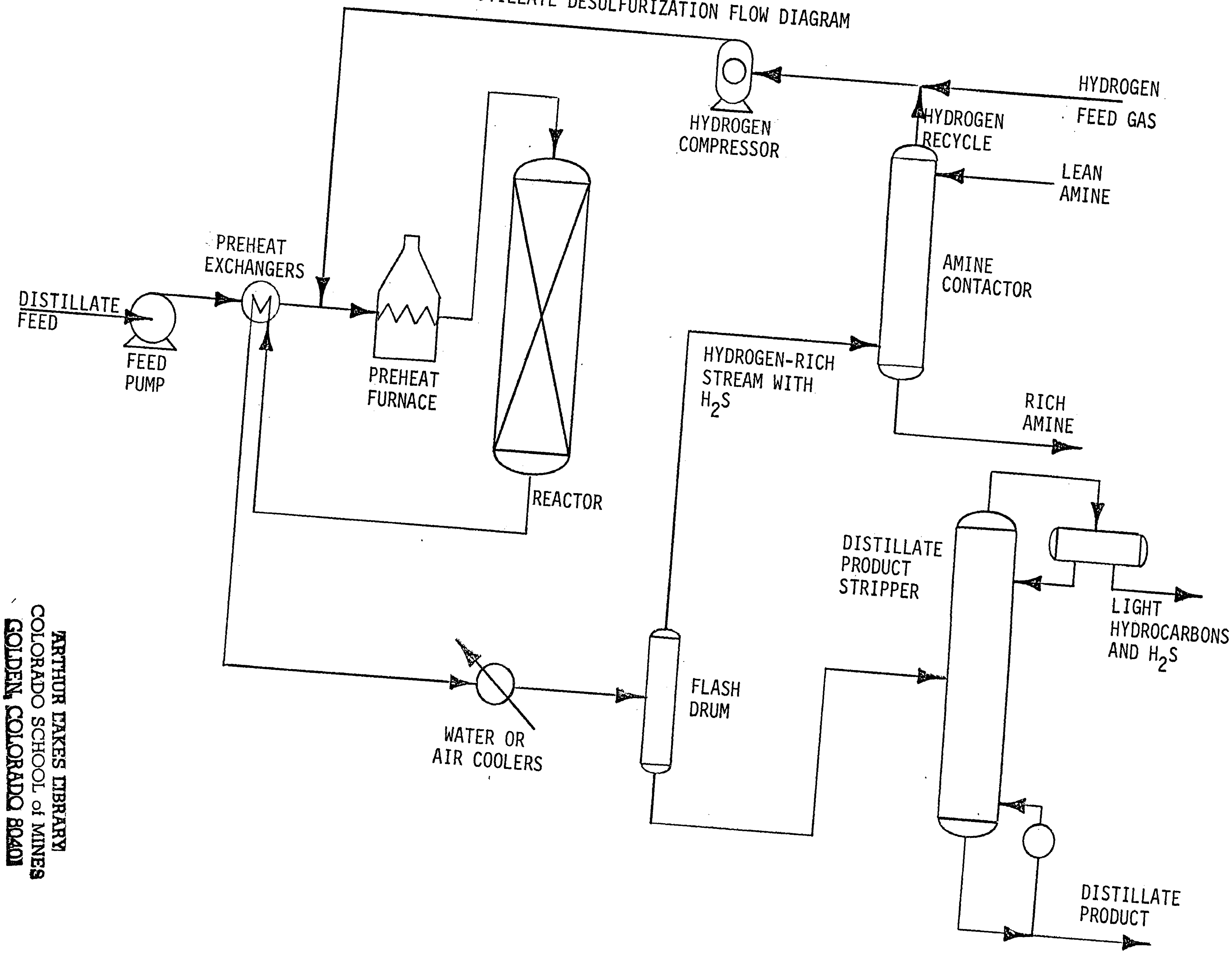
CONCLUSIONS

In the first chapter it was shown that a geometric programming model of a high pressure reactor with a specified pressure and volume can be used to find a lower bound on the total investment cost for such a reactor. It was also shown that the least cost design will have the smallest diameter which is practical.

The second and third chapters developed a formulation for determining the reaction conditions as well as vessel design parameters for a high pressure reactor to be employed for the desulfurization of middle distillate petroleum stocks. The cost to be minimized incorporates three components; in addition to the investment cost for the reactor, the catalyst cost and incremental pressure drop cost are considered. A level of sulfur removal must be set (this specification is usually based on a government standard for the product) then the reaction conditions and the vessel design which would achieve the specified removal at least cost could be determined with the method of geometric programming. A feasible solution for the dual problem was found. With data available from proprietary correlations this dual solution could be used to find a lower bound on cost and, perhaps, an optimal solution. For any formulation in which H/M is less than a, the problem is posynomial so any optimal solution determined is guaranteed to be a global minimum.

APPENDIX A

DISTILLATE DESULFURIZATION FLOW DIAGRAM



```
C                              APPENDIX B
C                    COMPUTER LISTING AND OUTPUT
C
C
C
C      THIS PROGRAM WILL CALCULATE A LEAST-COST DESIGN FOR A CARBON
C      STEEL VESSEL SUBJECTED TO INTERNAL PRESSURE.  USING THE METHOD
C      OF GEOMETRIC PROGRAMMING, THE PROGRAM CALCULATES THE TOTAL COST
C      DIAMETER, LENGTH, WALL THICKNESS, AND TOTAL WEIGHT FOR THE
C      OPTIMAL DESIGN.  THE PRESSURE, VOLUME AND  CORROSION ALLOWANCE
C      MUST BE SPECIFIED.  THE FOLLOWING ASSUMPTIONS ARE MADE:
C          THE CYLINDRICAL VESSEL IS CLOSED WITH 2:1 ELLIPSOIDAL HEADS.
C          THE METAL DENSITY IS 490 LB/CU FT.
C          THE STRESS LIMIT IS 21450 PSI.
C          THE JOINT EFFICIENCY IS 90 PERCENT.
C      COST CORRELATIONS ARE FROM AMOCO OIL.
C
       REAL LNK1,LNK2,LENGTH
       DIMENSION C(8),W(8),S(4)
1      FORMAT (G)
10     FORMAT (///' REACTOR DESIGN OPTIMIZATION'//' WHAT IS THE '
     1   ,'PRESSURE, IN PSIG?  '$)
11     FORMAT (' WHAT IS THE DESIGN VOLUME, IN CUBIC FEET?  '$)
12     FORMAT (//' ITERATION ',I3//'   DUAL VARIABLES')
13     FORMAT (' WHAT IS THE CORROSION ALLOWANCE, IN INCHES?  '$)
14     FORMAT (5X,'W(',I2,') = ',F10.8)
16     FORMAT (5X,'S(',I2,') = ',F10.9)
18     FORMAT (/5X,'DUAL OBJECTIVE = $',F10.3/)
20     FORMAT (5X,'GRADIENT 1 = ',E12.6/5X,'GRADIENT 2 = ',E12.6)
22     FORMAT (1X,'OPTIMAL SOLUTION'//3X,'DUAL VARIABLES')
23     FORMAT (///1X,'PRIMAL SOLUTION'//3X,'TOTAL COST = $',F6.0)
24     FORMAT (5X,'DIAMETER = ',4X,F6.3,' FEET'/5X,'LENGTH = ',
     1  6X,F6.2,' FEET'/5X,'THICKNESS = ',3X,F6.3,' INCHES'/5X,
     2  'COST = ',8X,F6.3,'$/POUND'/5X,'TOTAL WEIGHT = ',F7.0,
     3  ' POUNDS')
25     FORMAT (1X,'**THIS PROBLEM FAILED TO CONVERGE IN 30 ITERATIONS')
C
C      READ IN VARIABLES IN ORDER GIVEN ABOVE
C
       WRITE (4,10)
       READ (4,1) PRESS
       WRITE (4,11)
       READ (4,1) VOL
       WRITE (4,13)
       READ (4,1) CORALW
C
C      DETERMINE THE COEFFICIENTS
C
       C(1) = 45.
       C(2) = 1.0
       C(3) = 1.65
```

```
      C(4) = 128.2817
      C(5) = 82.52667
      C(6) = 4.*VOL/3.14159265
      C(7) = 6.*PRESS/(19300. - 0.6*PRESS)
      C(8) = CORALW
C
C     CALCULATE LNK1 AND LNK2
C
      LNK1 = ALOG(C(2)) - ALOG(C(3)) + 0.15*ALOG(C(5)) -
     1  0.30*ALOG(C(7)) + 0.45*ALOG(C(8))
      LNK2 = ALOG(C(4)) - ALOG(C(5)) +3.*ALOG(C(7)) - 3.*ALOG(C(8))
     1  + ALOG(C(6))
C
C     SET INITIAL VALUES OF REDUCED DUAL VARIABLES: R1=0.5,R2=0.6
C
      R1 = 0.5
      R2 = 0.6
C
C     CALCULATE VALUES OF DUAL VARIABLES
C
      K=1
100   W(1) = 1.0
      W(2) = R1
      W(3) = 0.65 - R1
      W(4) = R2
      W(5) = 0.15*R1 - R2 + 0.5525
      W(6) = R2
      W(7) = -0.30*R1 + 3.0*R2 - 1.105
      W(8) = 3.0*W(5)
      S(1) = 0.65
      S(2) = 0.15*R1 + 0.5525
      S(3) = R2
      S(4) = S(2)
C
C     CALCULATE THE VALUE OF THE DUAL OBJECTIVE FUNCTION
C
      OBJ = 1.0
      DO 120  I=1,8
120   OBJ = OBJ*(C(I)/W(I))**W(I)
      DO 130  I=1,4
130   OBJ = OBJ*(S(I))**S(I)
C
C     CALCULATE GRADIENTS
C
      GRAD1 = LNK1 - ALOG(W(2)) + ALOG (W(3)) - 0.15*ALOG(W(5))
      GRAD1 = GRAD1 + 0.30*ALOG(W(7)) - 0.45*ALOG(W(8))
      GRAD1 = GRAD1 + 0.15*ALOG(S(2)) + 0.15*ALOG(S(4))
      GRAD2 = LNK2 - ALOG(W(4)) + ALOG(W(5)) - 3.0*ALOG(W(7))
      GRAD2 = GRAD2 + 3.0*ALOG(W(8))
      IF (ABS(GRAD1).LE.0.001)  GO TO 150
      GO TO 180
```

```
150    IF (ABS(GRAD2).LE.0.001)  GO TO 250
C
C      CALCULATE THE ELEMENTS OF THE MATRIX
C
180    H11 = 1/W(2) + 1/W(3) + 0.0225/W(5)  + 0.09/W(7) + 0.2025/W(8)
       H11 = H11 - 0.0225/S(2) - 0.0225/S(4)
         H12 = -0.15/W(5) - 0.9/W(7) - 1.35/W(8)
       H22 = 1/W(4) + 1/W(5) + 9/W(7) + 9/W(8) + 1/W(6) - 1/S(3)
C
C      CALCULATE DELTA R'S
C
       DELR1 = (GRAD2*H11*H12 - GRAD1*H11*H22)
       DELR1 = DELR1/(H11*H12**2 - H11**2*H22)
       DELR2 = (GRAD1*H12 - GRAD2*H11)/(H12**2 - H11*H22)
C
C      WRITE OUT RESULTS FOR THIS ITERATION
C
       WRITE (4,12) K
       DO 200  I=1,8
200    WRITE (4,14) I,W(I)
       DO 210  I=1,4
210    WRITE (4,16)  I,S(I)
       WRITE (4,18)  OBJ
       WRITE (4,20)  GRAD1,GRAD2
C
C      CALCULATE ALPHA SUCH THAT ALL WEIGHTS ARE POSITIVVE
C
       ALPHA=0.7
240    RT1 = R1 + ALPHA*DELR1
       RT2 = R2 + ALPHA*DELR2
       WT1 = 0.65 - RT1
       IF(WT1.LE.0.001)  GO TO 245
       WT2 = 0.15*RT1 - RT2 + 0.5525
       IF(WT2.LE.0.001)  GO TO 245
       WT3 = -0.30*RT1 + 3.0*RT2 - 1.105
       IF(WT3.LE.0.001)  GO TO 245
       GO TO  248
245    ALPHA = ALPHA - 0.05
       GO TO 240
C
C      CALCULATE NEW VALUES OF R
C
248    R1 = RT1
       R2 = RT2
       K = K + 1
       IF(K.GT.30)  GO TO 300
       GO TO 100
C
C      CALCULATE THE VALUES OF THE PRIMAL VARIABLES AT OPTIMALITY
C
250    THICK = C(8)*S(4)/W(8)
```

```
      DIAM = THICK*W(7)/C(7)/S(4)
      LENGTH = C(6)/DIAM**2
      NOMWT = C(4)*DIAM*LENGTH*THICK*S(2)/W(4)
      TOTWT = NOMWT*S(1)/W(2)
      COST = C(1)/TOTWT**0.35
      COSTOT = COST*TOTWT
C
C     PRINT OUT OPTIMAL SOLUTION
C
      WRITE (4,22)
      DO 280  I=1,8
280   WRITE (4,14)  I,W(I)
      DO 290  I=1,4
290   WRITE (4,16) I,S(I)
      WRITE (4,20) GRAD1,GRAD2
      WRITE (4,23) COSTOT
      WRITE (4,24) DIAM,LENGTH,THICK, COST,TOTWT
      GO TO 350
300   WRITE (4,25)
350   STOP
      END
```

```
REACTOR DESIGN OPTIMIZATION

WHAT IS THE PRESSURE, IN PSIG?   700.0
WHAT IS THE DESIGN VOLUME, IN CUBIC FEET?  2000.0
WHAT IS THE CORROSION ALLOWANCE, IN INCHES?   .0625


ITERATION   1

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .50000000
    W( 3) =  .15000000
    W( 4) =  .60000000
    W( 5) =  .02750000
    W( 6) =  .60000000
    W( 7) =  .54500000
    W( 8) =  .08250000
    S( 1) = .649999999
    S( 2) = .627500005
    S( 3) = .600000002
    S( 4) = .627500005

    DUAL OBJECTIVE = $ 79341.136

    GRADIENT 1 = -.499668E+00
    GRADIENT 2 =  .334558E+01


ITERATION   2

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .49839886
    W( 3) =  .15160114
    W( 4) =  .61408211
    W( 5) =  .01317772
    W( 6) =  .61408211
    W( 7) =  .58772668
    W( 8) =  .03953315
    S( 1) = .649999999
    S( 2) = .627259828
    S( 3) = .614082113
    S( 4) = .627259828

    DUAL OBJECTIVE = $ 81560.903

    GRADIENT 1 = -.219191E-01
    GRADIENT 2 =  .153316E+00
```

ITERATION 3

DUAL VARIABLES

```
W( 1) = 1.00000000
W( 2) =  .49844728
W( 3) =  .15155272
W( 4) =  .61442409
W( 5) =  .01284300
W( 6) =  .61442409
W( 7) =  .58873810
W( 8) =  .03852900
S( 1) = .649999999
S( 2) = .627267093
S( 3) = .614424095
S( 4) = .627267093
```

DUAL OBJECTIVE = $ 81563.607

GRADIENT 1 = -.637936E-02
GRADIENT 2 = .446867E-01

ITERATION 4

DUAL VARIABLES

```
W( 1) = 1.00000000
W( 2) =  .49846245
W( 3) =  .15153755
W( 4) =  .61452159
W( 5) =  .01274778
W( 6) =  .61452159
W( 7) =  .58902602
W( 8) =  .03824335
S( 1) = .649999999
S( 2) = .627269372
S( 3) = .614521585
S( 4) = .627269372
```

DUAL OBJECTIVE = $ 81563.840

GRADIENT 1 = -.189720E-02
GRADIENT 2 = .132955E-01

```
ITERATION    5

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .49846705
    W( 3) =   .15153295
    W( 4) =   .61455040
    W( 5) =   .01271966
    W( 6) =   .61455040
    W( 7) =   .58911110
    W( 8) =   .03815897
    S( 1) = .649999999
    S( 2) = .627270058
    S( 3) = .614550404
    S( 4) = .627270058

    DUAL OBJECTIVE = $ 81563.858

    GRADIENT 1 = -.567766E-03
    GRADIENT 2 =   .397933E-02


ITERATION    6

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .49846844
    W( 3) =   .15153156
    W( 4) =   .61455902
    W( 5) =   .01271125
    W( 6) =   .61455902
    W( 7) =   .58913653
    W( 8) =   .03813375
    S( 1) = .649999999
    S( 2) = .627270266
    S( 3) = .614559017
    S( 4) = .627270266

    DUAL OBJECTIVE = $ 81563.864

    GRADIENT 1 = -.170060E-03
    GRADIENT 2 =   .119185E-02
```

OPTIMAL SOLUTION

```
  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .49846885
    W( 3) =  .15153115
    W( 4) =  .61456160
    W( 5) =  .01270873
    W( 6) =  .61456160
    W( 7) =  .58914413
    W( 8) =  .03812620
    S( 1) = .649999999
    S( 2) = .627270334
    S( 3) = .614561595
    S( 4) = .627270334
    GRADIENT 1 = -.509508E-04
    GRADIENT 2 =  .357270E-03
```

PRIMAL SOLUTION

```
  TOTAL COST = $81564.
    DIAMETER =        4.341 FEET
    LENGTH =        135.11 FEET
    THICKNESS =      1.028 INCHES
    COST =           0.792$/POUND
    TOTAL WEIGHT = 102979. POUNDS
```

```
REACTOR DESIGN OPTIMIZATION

WHAT IS THE PRESSURE, IN PSIG?   700.0
WHAT IS THE DESIGN VOLUME, IN CUBIC FEET?  2000.0
WHAT IS THE CORROSION ALLOWANCE, IN INCHES?   .1250


ITERATION   1

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .50000000
    W( 3) =  .15000000
    W( 4) =  .60000000
    W( 5) =  .02750000
    W( 6) =  .60000000
    W( 7) =  .54500000
    W( 8) =  .08250000
    S( 1) = .649999999
    S( 2) = .627500005
    S( 3) = .600000002
    S( 4) = .627500005

    DUAL OBJECTIVE = $ 84010.464

    GRADIENT 1 = -.187751E+00
    GRADIENT 2 =  .126614E+01


ITERATION   2

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .49950295
    W( 3) =  .15049705
    W( 4) =  .60534500
    W( 5) =  .02208044
    W( 6) =  .60534500
    W( 7) =  .56118412
    W( 8) =  .06624132
    S( 1) = .649999999
    S( 2) = .627425447
    S( 3) = .605345003
    S( 4) = .627425447

    DUAL OBJECTIVE = $ 84372.988

    GRADIENT 1 = -.430088E-01
    GRADIENT 2 =  .291502E+00
```

```
ITERATION    3

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .49943638
    W( 3) =   .15056362
    W( 4) =   .60636155
    W( 5) =   .02105391
    W( 6) =   .60636155
    W( 7) =   .56425373
    W( 8) =   .06316172
    S( 1) = .649999999
    S( 2) = .627415463
    S( 3) = .606361553
    S( 4) = .627415463

    DUAL OBJECTIVE = $ 84389.274

    GRADIENT 1 = -.122380E-01
    GRADIENT 2 =  .830353E-01

ITERATION    4

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .49942014
    W( 3) =   .15057986
    W( 4) =   .60663920
    W( 5) =   .02077382
    W( 6) =   .60663920
    W( 7) =   .56509157
    W( 8) =   .06232147
    S( 1) = .649999999
    S( 2) = .627413020
    S( 3) = .606639199
    S( 4) = .627413020

    DUAL OBJECTIVE = $ 84390.542

    GRADIENT 1 = -.361811E-02
    GRADIENT 2 =  .245565E-01
```

```
ITERATION    5

  DUAL VARIABLES
    W( 1)  = 1.00000000
    W( 2)  =   .49941555
    W( 3)  =   .15058444
    W( 4)  =   .60672034
    W( 5)  =   .02069199
    W( 6)  =   .60672034
    W( 7)  =   .56533636
    W( 8)  =   .06207598
    S( 1)  = .649999999
    S( 2)  = .627412334
    S( 3)  = .606720343
    S( 4)  = .627412334

    DUAL OBJECTIVE = $ 84390.655

    GRADIENT 1 = -.108076E-02
    GRADIENT 2 =   .733566E-02

ITERATION    6

  DUAL VARIABLES
    W( 1)  = 1.00000000
    W( 2)  =   .49941420
    W( 3)  =   .15058580
    W( 4)  =   .60674450
    W( 5)  =   .02066763
    W( 6)  =   .60674450
    W( 7)  =   .56540923
    W( 8)  =   .06200290
    S( 1)  = .649999999
    S( 2)  = .627412133
    S( 3)  = .606744498
    S( 4)  = .627412133

    DUAL OBJECTIVE = $ 84390.664

    GRADIENT 1 = -.323797E-03
    GRADIENT 2 =   .219786E-02
```

OPTIMAL SOLUTION

DUAL VARIABLES

```
W( 1) = 1.00000000
W( 2) =  .49941380
W( 3) =  .15058620
W( 4) =  .60675173
W( 5) =  .02066035
W( 6) =  .60675173
W( 7) =  .56543103
W( 8) =  .06198104
S( 1) = .649999999
S( 2) = .627412073
S( 3) = .606751725
S( 4) = .627412073
GRADIENT 1 = -.971947E-04
GRADIENT 2 =  .659704E-03
```

PRIMAL SOLUTION

```
TOTAL COST = $84392.
  DIAMETER =        5.126 FEET
  LENGTH =          96.91 FEET
  THICKNESS =       1.265 INCHES
  COST =            0.778$/POUND
  TOTAL WEIGHT = 108523. POUNDS
```

```
REACTOR DESIGN OPTIMIZATION

WHAT IS THE PRESSURE, IN PSIG?   700.0
WHAT IS THE DESIGN VOLUME, IN CUBIC FEET?  2000.0
WHAT IS THE CORROSION ALLOWANCE, IN INCHES?   .2500


ITERATION    1

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .50000000
    W( 3) =  .15000000
    W( 4) =  .60000000
    W( 5) =  .02750000
    W( 6) =  .60000000
    W( 7) =  .54500000
    W( 8) =  .08250000
    S( 1) = .649999999
    S( 2) = .627500005
    S( 3) = .600000002
    S( 4) = .627500005

    DUAL OBJECTIVE = $ 88954.590

    GRADIENT 1 =  .124165E+00
    GRADIENT 2 = -.813305E+00


ITERATION    2

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .50060703
    W( 3) =  .14939297
    W( 4) =  .59660789
    W( 5) =  .03098316
    W( 6) =  .59660789
    W( 7) =  .53464156
    W( 8) =  .09294949
    S( 1) = .649999999
    S( 2) = .627591059
    S( 3) = .596607894
    S( 4) = .627591059

    DUAL OBJECTIVE = $ 89121.685

    GRADIENT 1 =  .416286E-01
    GRADIENT 2 = -.273036E+00
```

```
ITERATION    3

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .50082409
    W( 3) =   .14917591
    W( 4) =   .59534407
    W( 5) =   .03227955
    W( 6) =   .59534407
    W( 7) =   .53078496
    W( 8) =   .09683864
    S( 1) = .649999999
    S( 2) = .627623618
    S( 3) = .595344067
    S( 4) = .627623618

    DUAL OBJECTIVE = $ 89142.331

    GRADIENT 1 =  .129908E-01
    GRADIENT 2 = -.852371E-01

ITERATION    4

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .50089351
    W( 3) =   .14910649
    W( 4) =   .59493539
    W( 5) =   .03269863
    W( 6) =   .59493539
    W( 7) =   .52953814
    W( 8) =   .09809590
    S( 1) = .649999999
    S( 2) = .627634026
    S( 3) = .594935395
    S( 4) = .627634026

    DUAL OBJECTIVE = $ 89144.407

    GRADIENT 1 =  .394651E-02
    GRADIENT 2 = -.258972E-01
```

ITERATION 5

DUAL VARIABLES

```
W( 1) = 1.00000000
W( 2) =  .50091477
W( 3) =  .14908523
W( 4) =  .59480985
W( 5) =  .03282737
W( 6) =  .59480985
W( 7) =  .52915514
W( 8) =  .09848210
S( 1) = .649999999
S( 2) = .627637215
S( 3) = .594809853
S( 4) = .627637215
```

DUAL OBJECTIVE = $ 89144.590

GRADIENT 1 = .118844E-02
GRADIENT 2 = -.779897E-02

ITERATION 6

DUAL VARIABLES

```
W( 1) = 1.00000000
W( 2) =  .50092118
W( 3) =  .14907882
W( 4) =  .59477192
W( 5) =  .03286626
W( 6) =  .59477192
W( 7) =  .52903940
W( 8) =  .09859877
S( 1) = .649999999
S( 2) = .627638184
S( 3) = .594771922
S( 4) = .627638184
```

DUAL OBJECTIVE = $ 89144.611

GRADIENT 1 = .357011E-03
GRADIENT 2 = -.234258E-02

```
OPTIMAL SOLUTION

   DUAL VARIABLES
     W( 1) = 1.00000000
     W( 2) =  .50092311
     W( 3) =  .14907689
     W( 4) =  .59476051
     W( 5) =  .03287795
     W( 6) =  .59476051
     W( 7) =  .52900462
     W( 8) =  .09863386
     S( 1) = .649999999
     S( 2) = .627638467
     S( 3) = .594760515
     S( 4) = .627638467
     GRADIENT 1 =  .107104E-03
     GRADIENT 2 = -.702858E-03


 PRIMAL SOLUTION

   TOTAL COST = $89142.
     DIAMETER =       6.027 FEET
     LENGTH =         70.10 FEET
     THICKNESS =      1.591 INCHES
     COST =           0.755$/POUND
     TOTAL WEIGHT = 118061. POUNDS
```

```
REACTOR DESIGN OPTIMIZATION

WHAT IS THE PRESSURE, IN PSIG?   700.0
WHAT IS THE DESIGN VOLUME, IN CUBIC FEET?  4000.0
WHAT IS THE CORROSION ALLOWANCE, IN INCHES?   .0625


ITERATION    1

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .50000000
    W( 3) =  .15000000
    W( 4) =  .60000000
    W( 5) =  .02750000
    W( 6) =  .60000000
    W( 7) =  .54500000
    W( 8) =  .08250000
    S( 1) = .649999999
    S( 2) = .627500005
    S( 3) = .600000002
    S( 4) = .627500005

    DUAL OBJECTIVE = $120258.676

    GRADIENT 1 = -.499668E+00
    GRADIENT 2 =  .403873E+01

ITERATION    2

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .50642858
    W( 3) =  .14357142
    W( 4) =  .61819895
    W( 5) =  .01026534
    W( 6) =  .61819895
    W( 7) =  .59766826
    W( 8) =  .03079603
    S( 1) = .649999999
    S( 2) = .628464289
    S( 3) = .618198946
    S( 4) = .628464289

    DUAL OBJECTIVE = $125028.024

    GRADIENT 1 =  .631379E-01
    GRADIENT 2 = -.209556E+00
```

```
ITERATION    3

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .50895129
    W( 3) =  .14104871
    W( 4) =  .61821017
    W( 5) =  .01063253
    W( 6) =  .61821017
    W( 7) =  .59694511
    W( 8) =  .03189759
    S( 1) = .649999999
    S( 2) = .628842697
    S( 3) = .618210167
    S( 4) = .628842697

    DUAL OBJECTIVE = $125040.797

    GRADIENT 1 =  .191722E-01
    GRADIENT 2 = -.653636E-01

ITERATION    4

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .50968831
    W( 3) =  .14031169
    W( 4) =  .61820240
    W( 5) =  .01075085
    W( 6) =  .61820240
    W( 7) =  .59670070
    W( 8) =  .03225256
    S( 1) = .649999999
    S( 2) = .628953248
    S( 3) = .618202396
    S( 4) = .628953248

    DUAL OBJECTIVE = $125041.981

    GRADIENT 1 =  .577571E-02
    GRADIENT 2 = -.198542E-01
```

```
ITERATION   5

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .50990769
    W( 3) =   .14009231
    W( 4) =   .61819899
    W( 5) =   .01078717
    W( 6) =   .61819899
    W( 7) =   .59662466
    W( 8) =   .03236150
    S( 1) = .649999999
    S( 2) = .628986158
    S( 3) = .618198991
    S( 4) = .628986158

    DUAL OBJECTIVE = $125042.101

    GRADIENT 1 =  .173494E-02
    GRADIENT 2 = -.597882E-02


ITERATION   6

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .50997335
    W( 3) =   .14002664
    W( 4) =   .61819787
    W( 5) =   .01079813
    W( 6) =   .61819787
    W( 7) =   .59660161
    W( 8) =   .03239440
    S( 1) = .649999999
    S( 2) = .628996007
    S( 3) = .618197873
    S( 4) = .628996007

    DUAL OBJECTIVE = $125042.112

    GRADIENT 1 =  .520799E-03
    GRADIENT 2 = -.179672E-02
```

```
OPTIMAL SOLUTION

   DUAL VARIABLES
      W( 1) = 1.00000000
      W( 2) =  .50999304
      W( 3) =  .14000696
      W( 4) =  .61819752
      W( 5) =  .01080144
      W( 6) =  .61819752
      W( 7) =  .59659466
      W( 8) =  .03240431
      S( 1) = .649999999
      S( 2) = .628998958
      S( 3) = .618197523
      S( 4) = .628998958
      GRADIENT 1 =  .156026E-03
      GRADIENT 2 = -.537634E-03


 PRIMAL SOLUTION

   TOTAL COST = $125042.
      DIAMETER =       5.173 FEET
      LENGTH =       190.35 FEET
      THICKNESS =      1.213 INCHES
      COST =           0.629$/POUND
      TOTAL WEIGHT = 198712. POUNDS
```

```
REACTOR DESIGN OPTIMIZATION

WHAT IS THE PRESSURE, IN PSIG?   700.0
WHAT IS THE DESIGN VOLUME, IN CUBIC FEET?  4000.0
WHAT IS THE CORROSION ALLOWANCE, IN INCHES?   .1250


ITERATION   1

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .50000000
    W( 3) =  .15000000
    W( 4) =  .60000000
    W( 5) =  .02750000
    W( 6) =  .60000000
    W( 7) =  .54500000
    W( 8) =  .08250000
    S( 1) = .649999999
    S( 2) = .627500005
    S( 3) = .600000002
    S( 4) = .627500005

    DUAL OBJECTIVE = $127336.056

    GRADIENT 1 = -.187751E+00
    GRADIENT 2 =  .195928E+01


ITERATION   2

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .50753266
    W( 3) =  .14246734
    W( 4) =  .60946184
    W( 5) =  .01916806
    W( 6) =  .60946184
    W( 7) =  .57112572
    W( 8) =  .05750419
    S( 1) = .649999999
    S( 2) = .628629901
    S( 3) = .609461837
    S( 4) = .628629901

    DUAL OBJECTIVE = $128684.385

    GRADIENT 1 = -.230756E-01
    GRADIENT 2 =  .359404E+00
```

```
ITERATION    3

  DUAL VARIABLES
    W( 1)  = 1.00000000
    W( 2)  =  .50980574
    W( 3)  =  .14019426
    W( 4)  =  .61090521
    W( 5)  =  .01806566
    W( 6)  =  .61090521
    W( 7)  =  .57477391
    W( 8)  =  .05419697
    S( 1)  = .649999999
    S( 2)  = .628970861
    S( 3)  = .610905208
    S( 4)  = .628970861

    DUAL OBJECTIVE = $128723.056

    GRADIENT 1 = -.601546E-02
    GRADIENT 2 =  .101005E+00

ITERATION    4

  DUAL VARIABLES
    W( 1)  = 1.00000000
    W( 2)  =  .51047538
    W( 3)  =  .13952462
    W( 4)  =  .61129896
    W( 5)  =  .01777235
    W( 6)  =  .61129896
    W( 7)  =  .57575426
    W( 8)  =  .05331706
    S( 1)  = .649999999
    S( 2)  = .629071310
    S( 3)  = .611298956
    S( 4)  = .629071310

    DUAL OBJECTIVE = $128726.059

    GRADIENT 1 = -.173577E-02
    GRADIENT 2 =  .297738E-01
```

```
ITERATION    5

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .51067512
    W( 3) =  .13932487
    W( 4) =  .61141407
    W( 5) =  .01768720
    W( 6) =  .61141407
    W( 7) =  .57603969
    W( 8) =  .05306159
    S( 1) = .649999999
    S( 2) = .629101269
    S( 3) = .611414075
    S( 4) = .629101269

    DUAL OBJECTIVE = $128726.317

    GRADIENT 1 = -.514789E-03
    GRADIENT 2 =  .888634E-02

ITERATION    6

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .51073495
    W( 3) =  .13926505
    W( 4) =  .61144835
    W( 5) =  .01766190
    W( 6) =  .61144835
    W( 7) =  .57612455
    W( 8) =  .05298569
    S( 1) = .649999999
    S( 2) = .629110247
    S( 3) = .611448348
    S( 4) = .629110247

    DUAL OBJECTIVE = $128726.327

    GRADIENT 1 = -.154056E-03
    GRADIENT 2 =  .266266E-02
```

```
OPTIMAL SOLUTION

   DUAL VARIABLES
     W( 1)  = 1.00000000
     W( 2)  =   .51075288
     W( 3)  =   .13924712
     W( 4)  =   .61145861
     W( 5)  =   .01765433
     W( 6)  =   .61145861
     W( 7)  =   .57614996
     W( 8)  =   .05296298
     S( 1)  = .649999999
     S( 2)  = .629112937
     S( 3)  = .611458607
     S( 4)  = .629112937
     GRADIENT 1 = -.462309E-04
     GRADIENT 2 =  .798941E-03


 PRIMAL SOLUTION

   TOTAL COST = $128726.
     DIAMETER =        6.113 FEET
     LENGTH =        136.31 FEET
     THICKNESS =       1.485 INCHES
     COST =            0.619$/POUND
     TOTAL WEIGHT = 207796. POUNDS
```

```
REACTOR DESIGN OPTIMIZATION

WHAT IS THE PRESSURE, IN PSIG?   400.0
WHAT IS THE DESIGN VOLUME, IN CUBIC FEET?  2000.0
WHAT IS THE CORROSION ALLOWANCE, IN INCHES?   .0625


ITERATION   1

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .50000000
    W( 3) =  .15000000
    W( 4) =  .60000000
    W( 5) =  .02750000
    W( 6) =  .60000000
    W( 7) =  .54500000
    W( 8) =  .08250000
    S( 1) = .649999999
    S( 2) = .627500005
    S( 3) = .600000002
    S( 4) = .627500005

    DUAL OBJECTIVE = $ 58183.089

    GRADIENT 1 = -.328936E+00
    GRADIENT 2 =  .163826E+01


ITERATION   2

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .49241044
    W( 3) =  .15758955
    W( 4) =  .60591965
    W( 5) =  .02044192
    W( 6) =  .60591965
    W( 7) =  .56503582
    W( 8) =  .06132575
    S( 1) = .649999999
    S( 2) = .626361571
    S( 3) = .605919652
    S( 4) = .626361571

    DUAL OBJECTIVE = $ 58625.592

    GRADIENT 1 = -.760367E-01
    GRADIENT 2 =  .333743E+00
```

```
ITERATION    3

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .49010321
    W( 3) =   .15989679
    W( 4) =   .60668036
    W( 5) =   .01933513
    W( 6) =   .60668036
    W( 7) =   .56801011
    W( 8) =   .05800539
    S( 1) = .649999999
    S( 2) = .626015484
    S( 3) = .606680356
    S( 4) = .626015484

    DUAL OBJECTIVE = $ 58641.829

    GRADIENT 1 = -.219979E-01
    GRADIENT 2 =  .940819E-01

ITERATION    4

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .48940093
    W( 3) =   .16059907
    W( 4) =   .60687179
    W( 5) =   .01903835
    W( 6) =   .60687179
    W( 7) =   .56879510
    W( 8) =   .05711505
    S( 1) = .649999999
    S( 2) = .625910141
    S( 3) = .606871791
    S( 4) = .625910141

    DUAL OBJECTIVE = $ 58643.102

    GRADIENT 1 = -.653674E-02
    GRADIENT 2 =  .277505E-01
```

```
ITERATION    5

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .48918926
    W( 3) =   .16081074
    W( 4) =   .60692637
    W( 5) =   .01895202
    W( 6) =   .60692637
    W( 7) =   .56902231
    W( 8) =   .05685607
    S( 1) = .649999999
    S( 2) = .625878394
    S( 3) = .606926367
    S( 4) = .625878394

    DUAL OBJECTIVE = $ 58643.215

    GRADIENT 1 = -.195558E-02
    GRADIENT 2 =  .828409E-02

ITERATION    6

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .48912567
    W( 3) =   .16087433
    W( 4) =   .60694249
    W( 5) =   .01892636
    W( 6) =   .60694249
    W( 7) =   .56908977
    W( 8) =   .05677909
    S( 1) = .649999999
    S( 2) = .625868850
    S( 3) = .606942490
    S( 4) = .625868850

    DUAL OBJECTIVE = $ 58643.223

    GRADIENT 1 = -.586318E-03
    GRADIENT 2 =  .248194E-02
```

```
OPTIMAL SOLUTION

   DUAL VARIABLES
     W( 1) = 1.00000000
     W( 2) =  .48910658
     W( 3) =  .16089342
     W( 4) =  .60694730
     W( 5) =  .01891869
     W( 6) =  .60694730
     W( 7) =  .56910993
     W( 8) =  .05675606
     S( 1) = .649999999
     S( 2) = .625865988
     S( 3) = .606947303
     S( 4) = .625865988
     GRADIENT 1 = -.175918E-03
     GRADIENT 2 =  .744939E-03


 PRIMAL SOLUTION

   TOTAL COST = $58643.
     DIAMETER =        4.977 FEET
     LENGTH =        102.80 FEET
     THICKNESS =       0.689 INCHES
     COST =            0.946$/POUND
     TOTAL WEIGHT =   61989. POUNDS
```

```
REACTOR DESIGN OPTIMIZATION

WHAT IS THE PRESSURE, IN PSIG?   400.0
WHAT IS THE DESIGN VOLUME, IN CUBIC FEET?  4000.0
WHAT IS THE CORROSION ALLOWANCE, IN INCHES?   .0625


ITERATION    1

  DUAL VARIABLES
    W( 1)  = 1.00000000
    W( 2)  =  .50000000
    W( 3)  =  .15000000
    W( 4)  =  .60000000
    W( 5)  =  .02750000
    W( 6)  =  .60000000
    W( 7)  =  .54500000
    W( 8)  =  .08250000
    S( 1)  = .649999999
    S( 2)  = .627500005
    S( 3)  = .600000002
    S( 4)  = .627500005

    DUAL OBJECTIVE = $ 88189.074

    GRADIENT 1 = -.328936E+00
    GRADIENT 2 =  .233141E+01


ITERATION    2

  DUAL VARIABLES
    W( 1)  = 1.00000000
    W( 2)  =  .50044016
    W( 3)  =  .14955984
    W( 4)  =  .61003648
    W( 5)  =  .01752955
    W( 6)  =  .61003648
    W( 7)  =  .57497738
    W( 8)  =  .05258864
    S( 1)  = .649999999
    S( 2)  = .627566025
    S( 3)  = .610036477
    S( 4)  = .627566025

    DUAL OBJECTIVE = $ 89437.100

    GRADIENT 1 = -.464809E-01
    GRADIENT 2 =  .352995E+00
```

```
ITERATION    3

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .50084232
    W( 3) =   .14915768
    W( 4) =   .61110171
    W( 5) =   .01652464
    W( 6) =   .61110171
    W( 7) =   .57805243
    W( 8) =   .04957392
    S( 1) = .649999999
    S( 2) = .627626352
    S( 3) = .611101709
    S( 4) = .627626352

    DUAL OBJECTIVE = $ 89457.679

    GRADIENT 1 = -.129266E-01
    GRADIENT 2 =   .991080E-01

ITERATION    4

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .50096688
    W( 3) =   .14903312
    W( 4) =   .61138748
    W( 5) =   .01625755
    W( 6) =   .61138748
    W( 7) =   .57887240
    W( 8) =   .04877265
    S( 1) = .649999999
    S( 2) = .627645031
    S( 3) = .611387484
    S( 4) = .627645031

    DUAL OBJECTIVE = $ 89459.232

    GRADIENT 1 = -.379938E-02
    GRADIENT 2 =   .292070E-01
```

```
ITERATION    5

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .50100452
    W( 3) =   .14899547
    W( 4) =   .61147065
    W( 5) =   .01618003
    W( 6) =   .61147065
    W( 7) =   .57911061
    W( 8) =   .04854008
    S( 1) = .649999999
    S( 2) = .627650678
    S( 3) = .611470655
    S( 4) = .627650678

    DUAL OBJECTIVE = $ 89459.362

    GRADIENT 1 = -.113308E-02
    GRADIENT 2 =  .871706E-02

ITERATION    6

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =   .50101584
    W( 3) =   .14898416
    W( 4) =   .61149539
    W( 5) =   .01615699
    W( 6) =   .61149539
    W( 7) =   .57918142
    W( 8) =   .04847096
    S( 1) = .649999999
    S( 2) = .627652377
    S( 3) = .611495391
    S( 4) = .627652377

    DUAL OBJECTIVE = $ 89459.371

    GRADIENT 1 = -.339272E-03
    GRADIENT 2 =  .261056E-02
```

OPTIMAL SOLUTION

```
   DUAL VARIABLES
     W( 1) = 1.00000000
     W( 2) =  .50101924
     W( 3) =  .14898076
     W( 4) =  .61150279
     W( 5) =  .01615010
     W( 6) =  .61150279
     W( 7) =  .57920259
     W( 8) =  .04845030
     S( 1) = .649999999
     S( 2) = .627652891
     S( 3) = .611502789
     S( 4) = .627652891
     GRADIENT 1 = -.101756E-03
     GRADIENT 2 =  .782728E-03
```

PRIMAL SOLUTION

```
   TOTAL COST = $89460.
     DIAMETER =        5.934 FEET
     LENGTH =        144.65 FEET
     THICKNESS =       0.810 INCHES
     COST =            0.754$/POUND
     TOTAL WEIGHT = 118711. POUNDS
```

```
REACTOR DESIGN OPTIMIZATION

WHAT IS THE PRESSURE, IN PSIG?   400.0
WHAT IS THE DESIGN VOLUME, IN CUBIC FEET?  4000.0
WHAT IS THE CORROSION ALLOWANCE, IN INCHES?   .1250


ITERATION    1

  DUAL VARIABLES
    W( 1)  = 1.00000000
    W( 2)  =  .50000000
    W( 3)  =  .15000000
    W( 4)  =  .60000000
    W( 5)  =  .02750000
    W( 6)  =  .60000000
    W( 7)  =  .54500000
    W( 8)  =  .08250000
    S( 1)  = .649999999
    S( 2)  = .627500005
    S( 3)  = .600000002
    S( 4)  = .627500005

    DUAL OBJECTIVE = $ 93379.116

    GRADIENT 1 = -.170199E-01
    GRADIENT 2 =  .251970E+00


ITERATION    2

  DUAL VARIABLES
    W( 1)  = 1.00000000
    W( 2)  =  .50154424
    W( 3)  =  .14845575
    W( 4)  =  .60129937
    W( 5)  =  .02643227
    W( 6)  =  .60129937
    W( 7)  =  .54843484
    W( 8)  =  .07929681
    S( 1)  = .649999999
    S( 2)  = .627731636
    S( 3)  = .601299368
    S( 4)  = .627731636

    DUAL OBJECTIVE = $ 93397.289

    GRADIENT 1 = -.469620E-02
    GRADIENT 2 =  .725572E-01
```

```
ITERATION   3

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .50200363
    W( 3) =  .14799637
    W( 4) =  .60166519
    W( 5) =  .02613536
    W( 6) =  .60166519
    W( 7) =  .54939449
    W( 8) =  .07840607
    S( 1) = .649999999
    S( 2) = .627800547
    S( 3) = .601665191
    S( 4) = .627800547

    DUAL OBJECTIVE = $ 93398.769

    GRADIENT 1 = -.137561E-02
    GRADIENT 2 =  .215178E-01


ITERATION   4

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .50214107
    W( 3) =  .14785893
    W( 4) =  .60177299
    W( 5) =  .02604818
    W( 6) =  .60177299
    W( 7) =  .54967664
    W( 8) =  .07814453
    S( 1) = .649999999
    S( 2) = .627821162
    S( 3) = .601772986
    S( 4) = .627821162

    DUAL OBJECTIVE = $ 93398.889

    GRADIENT 1 = -.409750E-03
    GRADIENT 2 =  .643307E-02
```

```
ITERATION   5

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .50218226
    W( 3) =  .14781774
    W( 4) =  .60180515
    W( 5) =  .02602219
    W( 6) =  .60180515
    W( 7) =  .54976077
    W( 8) =  .07806657
    S( 1) = .649999999
    S( 2) = .627827339
    S( 3) = .601805151
    S( 4) = .627827339

    DUAL OBJECTIVE = $ 93398.912

    GRADIENT 1 = -.122732E-03
    GRADIENT 2 =  .192833E-02


OPTIMAL SOLUTION

  DUAL VARIABLES
    W( 1) = 1.00000000
    W( 2) =  .50219461
    W( 3) =  .14780539
    W( 4) =  .60181478
    W( 5) =  .02601441
    W( 6) =  .60181478
    W( 7) =  .54978597
    W( 8) =  .07804323
    S( 1) = .649999999
    S( 2) = .627829194
    S( 3) = .601814784
    S( 4) = .627829194
    GRADIENT 1 = -.368021E-04
    GRADIENT 2 =  .578463E-03


PRIMAL SOLUTION

  TOTAL COST = $93401.
    DIAMETER =        6.993 FEET
    LENGTH =        104.14 FEET
    THICKNESS =      1.006 INCHES
    COST =           0.736$/POUND
    TOTAL WEIGHT = 126850. POUNDS
```

APPENDIX C

Definition of coefficients in the final form of the complete model of the reactor system:

C_1 = Reactor Cost Parameter = 45

C_2 = Compression Cost Parameter (Combination of Investment and Discounted Operating Costs)

C_3 = (Catalyst Density, lb/cu ft)(Catalyst Cost, \$/lb)

$C_4 = 1.0$

C_5 = Internals Weight Parameter ≈ 1.65

$C_6 = \pi^3(\rho_m)(\rho_1)^2/((12)(6)GF_1{}^2)$

$C_7 = (2)(1.084)\rho_m/12$

$C_8 = 6/SE$

$C_9 = 0.6/SE$

$C_{10} = (4/\pi)^3(M_t/M_h)^2(F_1/\rho_1)^2B_rR(F/\rho_c)GB_A$

$C_{11} = 1.0$

$C_{12} = 1.0$

$C_{13} = B_{hs}M_{hs}/M_t$

$C_{14} = B_{ar}f_{ar}aM/M_t$

$C_{15} = 1 - a$

$C_{16} = B_v(a - H/M)$

The exponents in this model are:

A_1 = cost exponent for the reactor = 0.35

A_2 = exponent on internals weight = -.85

$A_{10} = (-E_r)(-E_t) = 17640$

$A_{11} = -E_p - 1 = -1.3333$

$A_{13} = E_{hs} = 1186$

$A_{14} = E_{ar} = 5040$

$A_{16} = E_v = -23796$

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