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Ethylene Process Optimization. Constraint Relaxation And Bounds Adjustment

Kenneth R. Jinkerson

James L. Gaddy
Missouri University of Science and Technology

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(56) Haldeman, R. G., Colman, W. P., Langer, S. H., Barber, W. A., *Adv. Chem. Ser.*, **No. 47**, 116 (1965).
(57) Harwood, W. H., Hurd, R. M., Jordan, W. H., *Ind. Eng. Chem. Process Des. Dev.*, **2**, 72 (1963).
(58) Haver, F. P., Wong, M. M., "Recovering of Elemental Sulfur from Nonferrous Minerals", U.S. Dept. of the Interior, Bureau of Mines Rep. 7474 (1971).
(59) Haver, F. P., Wong, M. M., *J. Met.*, **23**(2), 15 (1971).
(60) (a) Horanyi, G., Novák, M., *Z. Phys. Chem.* (*Frankfurt am Main*), **75**, 323 (1971); (b) Hougen, O. A., Watson, K. M., Ragatz, R. A. "Chemical Process Principles", Part II, p 1004, Wiley, N.Y., 1959.
(61) Ibl, N., Selvig, A., *Chem. Ing. Tech.*, **42**, 180 (1970).
(62) Jackson, G. W., Dereska, J. S., *J. Electrochem. Soc.*, **112**, 1218 (1965).
(63) Jacques, W. W., *Z. Electrochem.*, **4**, 129 (1897).
(64) Juda, W., U.S. Patent 3 103 473 (Sept 10, 1963).
(65) Juda, W., U.S. Patent 3 103 474 (Sept 10, 1963).
(66) Juda, W., Moulton, D. M., *Chem. Eng. Prog.*, **63**(4), 59 (1967).
(67) Juda, W., Moulton, D. M., *Chem. Eng. Prog. Symp. Ser.*, **63**(71), 59 (1971).
(68) Kalinin, M. A., Stender, V. V., *J. Appl. Chem.* (*USSR*), **19**, 1045 (1946).
(69) Kemball, C., *J. Chem. Soc.*, **146**, 735 (1956).
(70) Kuhn, A. T., "Industrial Electrochemical Processes", pp 96, 106, 107, Elsevier, New York, N.Y., 1971.
(71) Kuhn, A. T., Wroblowa, H., Bockris, J. O'M., *Trans. Faraday Soc.*, **63**, 1458 (1967).
(72) Langer, S. H., Feiz, I., Quinn, C. P., *J. Am. Chem. Soc.*, **93**, 1092 (1971).
(73) Langer, S. H., Haldeman, R. G., *J. Phys. Chem.*, **68**, 962 (1964).
(74) Langer, S. H., Haldeman, R. G., *Science*, **142**, 225 (1963).
(75) Langer, S. H., Landi, H. P., *J. Am. Chem. Soc.*, **85**, 3043 (1963).
(76) Langer, S. H., Landi, H. P., *J. Am. Chem. Soc.*, **86**, 4694 (1964).
(77) Langer, S. H., Landi, H. P., U.S. Patent 3 248 267, (Apr 26, 1966).
(78) Langer, S. H., Miller, A. D., Pietsch, S. J., *J. Appl. Chem. Biotechnol.*, **27**, 176 (1977).
(79) Langer, S. H., Sakellaropoulos, G. P., *J. Electrochem. Soc.*, **122**, 1619 (1975).
(80) Langer, S. H., Yurchak, S., *J. Electrochem. Soc.*, **116**, 1228 (1969).
(81) Langer, S. H., Yurchak, S., *J. Electrochem. Soc.*, **117**, 510 (1970).
(82) LeDuc, J. A. M., French Patent 1 375 298 (1964); *Chem. Abstr.*, **62**, 86806 (1965).
(83) Liebhafsky, H. A., Cairns, E. J., "Fuel Cells and Fuel Batteries", Wiley, New York, N.Y., 1968.
(84) Lin, C. H., Winnick, J., *Ind. Eng. Chem. Process Des. Dev.*, **13**, 63 (1974).
(85) Löb, W., *Chem. Ber.*, **29**, 1390 (1896).
(86) Löb, W., *Chem. Ber.*, **29**, 1894 (1896).
(87) Martinyuk, G. A., Krylova, V. S., Khomchenko, G. P., *Izv. Timiryazev. Sel'skokhoz. Akad.*, **6**, 217 (1970); *Chem. Abstr.*, **74**, 82434*j* (1971).
(88) Mayell, J. S., *Ind. Eng. Chem. Prod. Res. Dev.*, **7**, 129 (1968).
(89) Misono, A., Osa, T., Yamagishi, T., Koduma, T., *J. Electrochem. Soc.*, **115**, 266 (1968).
(90) (a) McElroy, K. P., U.S. Patents 1 253 617 (Jan 15, 1918); 1 264 536 (Apr 30, 1918); (b) McMillan, G. W., U.S. Patent 2 485 982 (Oct 25, 1949).
(91) Miller, A. D., Langer, S. H., *J. Electrochem. Soc.*, **120**, 1695 (1973).
(92) Niedrach, L. W., *J. Electrochem. Soc.*, **109**, 1092 (1962).
(93) Niedrach, L. W., Alford, H. R., *J. Electrochem. Soc.*, **112**, 117 (1965).
(94) Ostwald, W., *Z. Elektrochem.*, **1**, 122 (1894).
(95) Pfeiffer, J. B., Ed., *Adv. Chem. Ser.*, **No. 139**, 1 (1975).
(96) Popp, F. D., Schultz, H. P., *Chem. Rev.*, **62**, 19 (1962).
(97) Price, F. C., *Chem. Eng.* (Apr 16, 1973).
(98) Reshetnikov, S. M., Sokol'skaya, *Kinet. Katal.*, **7**(2), 279 (1966).
(99) Sakellaropoulos, G. P., Ph.D. Thesis, Department of Chemical Engineering, University of Wisconsin, 1974.
(100) Sakellaropoulos, G. P., Langer, S. H., *J. Catal.*, **44**, 25 (1976).
(101) Sakellaropoulos, G. P., Langer, S. H., "The Role of Electrogenerative Processing in Environmental Protection and Energy Conservation", Meeting on Environmental Aspects of Non-Conventional Energy Resources, American Nuclear Society, Denver, Colo., (Mar 1–3, 1976).
(102) Sakellaropoulos, G. P., Langer, S. H., *J. Electrochem. Soc.*, **124**, 1548 (1977).
(103) Sakellaropoulos, G. P., Langer, S. H., *AIChE J.*, **24**, 1115 (1978).
(104) Schlatter, M. J., in "Fuel Cells", G. J. Young, Ed., pp 190–215, Reinhold, New York, N.Y., 1963.
(105) Schmid, A., *Helv. Chim. Acta.*, **7**, 169 (1933).
(106) Shmonina, V. P., Tsoi, A. A., Sokol'skii, D. V., *Khim. Khim. Tekhnol.*, **6**, 65 (1967); *Chem. Abstr.*, **71**, 35458*y* (1969).
(107) Sokol'skaya, A. M., Reshetnikov, S. M., Ryabinina, S. A., *Elektrokhimiya*, **3**(12), 1487 (1967).
(108) Sokol'skaya, A. M., Reshetnikov, S. M., *Izv. Vyssch. Ucheb. Zaved., Khim. Khim. Tekhnol.*, **10**(8), 867 (1967).
(109) Sokol'skii, D. V., "Hydrogenation in Solutions" (transl. by N. Kaner), Israel Program for Scientific Translations, Jerusalem, 1964.
(110) Sternberg, H. W., Markby, R. E., Wender, I., Mohilner, D. M., *J. Am. Chem. Soc.*, **89**, 186 (1967).
(111) Swann, S., Jr., in "Technique of Organic Chemistry", A. Weisberger, Ed., Vol. II, pp 385–523, Interscience, New York, N.Y., 1956.
(112) Szabó, S., Teles, I., Nagy, F., *Acta Chim.* (*Budapest*), **73**, 213 (1972).
(113) Tiedemann, W. H., Bennion, D. N., *J. Electrochem. Soc.*, **117**, 203 (1970).
(114) Thomas, J. M., Thomas, W. J., "Introduction to the Principles of Heterogeneous Catalysis", Academic Press, New York, N.Y., 1967.
(115) Vielstich, W., "Fuel Cells", (translation by D. J. G. Ives), Wiley-Interscience, London, 1970.
(116) Voss, E., *Chem. Ing. Tech.*, **42**(4), 199 (1970).
(117) Wiesener, K., *Electrochim. Acta*, **18**, 185 (1973).
(118) Williams, K. R., "An Introduction to Fuel Cells", Elsevier, Amsterdam, N.Y., 1966.
(119) Yoshizawa, S., Takehara, Z., Katsuya, H., *Denki-Kagaku*, **32**, 457, 519, 526 (1964).

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ARTICLES

Ethylene Process Optimization. Constraint Relaxation and Bounds Adjustment

Kenneth R. Jinkerson and James L. Gaddy*

Department of Chemical Engineering, University of Missouri, Rolla, Missouri 65401

Heavily constrained, mixed integer optimization problems present a difficult test for optimization algorithms. This paper examines optimization of the ethylene process (from ethane) using a flowsheet simulation model and the adaptive random search. Optimization resulted in an improvement in annual earnings of $1.15 MM over the usual ethylene process design. This process has both continuous and discrete variables and has sensitive implicit constraints in the pyrolysis furnace. The search efficiency was found to be improved by relaxing these constraints early in the search and then restoring the constraints as the optimum is approached. The search efficiency was also improved by testing each independent variable for its optimal explicit bound and using these bounds as the starting point for the optimization. Significant improvements in the economics ($0.7 MM per year) were found by examining and slightly adjusting the variable boundaries at the optimum. These results suggest that variable bounds should be established in conjunction with the optimization study.

In process design optimization, it is necessary to develop a model that accurately describes the interaction of the process variables in economic terms. An optimization algorithm is also needed to simultaneously consider the interactions of the variables in order to find the optimum combination. Because of the difficulties in finding a suitable algorithm most optimization studies have been simplified in one way or another.

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Parts of processes such as reactors (Barneson et al., 1970), absorber–strippers (Umeda and Ichikawa, 1971), and distillation column–condenser systems (Zellnik et al., 1962) have been studied using sophisticated optimization algorithms. Simplified processes have also been studied (Bracken and McCormick, 1968; Gottfried et al., 1970).

Recently, several complete processes have been optimized using modular flowsheet simulators which provide a convenient means to study complex processes. Friedman and Pinder (1972) optimized the production rate of a gasoline polymerization unit using the CHESS simulator. Gaines and Gaddy (1976) studied the same process, with the objective of maximizing the profitability of the process, using the PROPS simulator. The intermediate pressure methanol process was optimized by Ballman and Gaddy (1976) using PROPS. The study showed that the complex methanol process could be optimized without an unreasonable amount of computer time. Doering and Gaddy (1976), also using PROPS, studied the sulfuric acid process using metallurgical offgases as feed and showed that a flowsheet simulator could be used to examine the reliability and dependability of the process. Studies similar to those described above are needed to demonstrate the value of using a flowsheet simulator for process optimization.

The ethylene process was used commercially before 1920. Ethylene has become one of the largest volume chemicals in the world. Yet, few optimization studies of the ethylene process have been made. Loftus (1970) studied the reliability of the pyrolysis furnace and quench area using a simulation program with updating. Rothman (1970) and Gambro et al., (1972) used a linear program to optimize the process and determine optimum feedstocks and expected plant cost. In this study, the plant was considered as a series of process operation blocks. The design case was not considered. Simulation and optimization studies have been made on sections or simplified models of the ethylene process but there have been no published plant design and optimization studies.

The ethylene process presents an interesting optimization problem because it includes both continuous and discrete variables, which when combined pose difficult obstacles for most optimization algorithms (Campbell and Gaddy, 1975; Weisman and Holzman, 1969). The ethylene process also includes a series of reactors which have tight nonlinear constraints associated with the reactions. Such constraints are the cause of the failure of many optimization algorithms to successfully converge (Keefer, 1973; Friedman and Pinder, 1972). Since most search algorithms are designed to follow a definite pattern, repeated constraint violations occur when a constraint is encountered. The shape or location of the invalid region usually determines whether the search can proceed to the optimum. Penalty functions are sometimes used to help the constraint problem with some algorithms (Gottfried et al., 1970; Keefer, 1973), but collapse and failure are often the result.

When nonlinear constraints are combined with mixed integers, as in the ethylene process, the problem is particularly difficult. A possible method for handling these problems is to relax the sensitive constraints when encountered and then tighten the constraints as the search converges. This method would not be analogous to solving the unconstrained problem followed by gradual addition of the constraints from the unconstrained optimum, which would rarely lead to the optimum of the constrained problem without further search along the sensitive constraints. Relaxation of the constraints has the advantage of keeping the search in the region of the constrained optimum while allowing progress through particularly difficult regions.

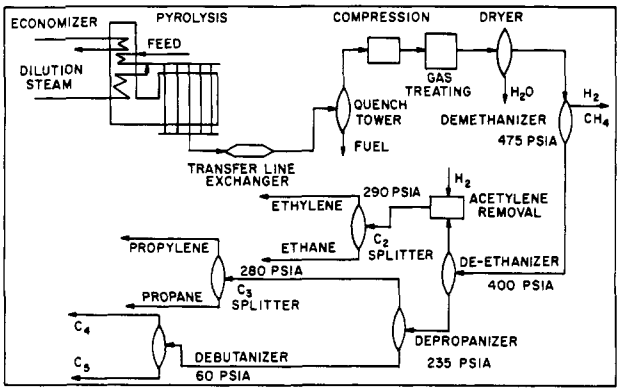

Figure 1. Flow diagram of the ethylene process.

Several process optimization studies (Ballman and Gaddy, 1976; Doering and Gaddy, 1976) have shown that the optimal values of several of the independent variables lie on or near the upper or lower boundaries of the independent variables. Therefore, it may be expeditious to initially test these boundary constraints and use the best boundary conditions as the starting values for the optimization. The explicit constraint boundaries are usually chosen somewhat arbitrarily to cover a wide range of operating conditions. If optimum variables lie on boundary constraints, expanding these constraints at the optimum may yield justifiable improvements in the process.

The purpose of this study was to develop a detailed model, with economics, of the ethylene process using ethane feed and to demonstrate the model's utility for optimization. The plant size studied is 500 000 TPY ethylene. Improvements in the economics of the ethylene process are compared with computer time needed for the study. The PROPS flowsheet simulator and the adaptive random search (ARS) technique (Heuckroth et al., 1976) are used to optimize the process. The ethylene process provides a severe test for an optimization algorithm and the ability of the ARS to handle this mixed integer, heavily constrained problem is examined.

A further objective of this study was to examine improvements in the search efficiency by initially relaxing rigid constraints on the most sensitive variables and then tightening the constraints gradually as the search proceeds. In order to improve the search efficiency even more, a third objective was to initially test the boundary constraints and allow the search to proceed from the best boundary point located. Finally, the improvements that can be realized by expanding the boundaries of any optimum variables that lie on a boundary were studied.

The Ethylene Process

The process chosen for this study is the ethylene process using ethane feed. A typical flow diagram is presented in Figure 1. Zdonik et al. (1970) have given a detailed description of the process and general design problems.

The feed enters the furnace convection section and is preheated to 1500–1750 °R by the flue gases before being further heated in a radiation section. Dilution steam, added to inhibit coke formation, is also preheated in the convection section before being mixed with the feed. The ethane–steam mixture is divided among parallel coils in the firebox. The mixture enters the radiation section at 60–80 psia where ethane is pyrolyzed to the primary products of hydrogen, methane, and ethylene, along with a mixture of smaller amounts of C_3 to C_5 hydrocarbons. The effluent leaves the furnace at 30–50 psia and 1950–1970 °R.

The furnace effluent is cooled in a transfer line exchanger (TLX) where 680.0 psia steam is recovered. The steam temperature (960 °R) is appreciably above the dew point of the furnace effluent, to avoid condensation. The final cooling of the effluent is performed in the quench tower where the vapor is cooled to about 560 °R, the cooling water temperature.

The gas effluent is next compressed to 500 psia in a steam-driven centrifugal compressor. To avoid fouling and polymer formation, the gas temperature must not exceed 710 °R. Usually, three to four stages of compression, with interstage cooling, are provided to meet the temperature requirement. Acid gas is removed with a caustic wash between the final two stages of compression. The gas is then dried with a fixed bed desiccant (24-h cycle) to a 410–460 °R dew point.

The dry gas is then sent to the product recovery section. Ethylene is recovered by low-temperature fractionation in the following sequence of steps: demethanizer, deethanizer; C_2 splitter; depropanizer; C_3 splitter; and debutanizer.

Demethanization is carried out at 465 psia and removes hydrogen and methane from the gas stream. Ethylene refrigerant at 310 °R is used to precool the gas and 97% of the hydrogen is removed by the use of a vapor–liquid separator. The demethanizer condenser uses 370 °R ethylene refrigerant to condense reflux and the reboiler temperature is usually below 525 °R. About 30 trays are sufficient to meet product specifications.

The demethanizer bottoms flow to the deethanizer, which operates at 390 psia. Forty trays and a reflux ratio of 0.8–1.3 are sufficient to split the ethylene–ethane distillate from the C_3 and heavier. The reboiler temperature is maintained at 615–625 °R and the condenser uses propylene refrigerant.

Acetylene is removed from the ethylene–ethane stream by catalytic hydrogenation to ethylene. A palladium-based catalyst is used at a process temperature of 710 °R.

The ethylene–ethane stream flows to the C_2 splitter. The column pressure is 290 psia and 100–120 trays with a reflux ratio of 4.5–5.5 are required to separate the streams because of very low relative volatility. Propylene refrigerant is used to condense reflux and the temperature of the reboiler is about 480 °R.

The depropanizer splits the C_3 from the C_4 and heavier streams. The column requires 35–45 trays and a pressure of 235 psia. Cooling water is sufficient to condense reflux and the reboiler is kept below 710 °R to minimize fouling and polymer formation.

The C_3 splitter separates propylene from propane at 275 psia. The low relative volatility necessitates 200 trays and a high reflux ratio.

The debutanizer separates the C_4 and C_5+ streams at 60 psia. Cooling water is used to condense reflux and steam is used to reboil the tower.

The refrigeration system is a very important part of any ethylene plant because of the complexity and interdependence of the process sections. A cascade refrigeration system, using both ethylene and propylene as refrigerants, is necessary to obtain temperatures well below the temperatures realized with cooling water.

Propylene refrigerant is compressed to 260 psia and condensed with cooling water. The refrigerant is used at two levels: 460 °R for the deethanizer condenser and 420 °R for the ethylene refrigerant and C_2 splitter condensers.

Ethylene refrigerant is compressed to 290 psia and condensed by using the vapor as a heat source for the demethanizer and C_2 splitter column reboilers. The remaining refrigerant vapor is condensed with propylene refrigerant. The demethanizer precooler and condenser uses the ethylene refrigerant at 310 and 370 °R, respectively.

Ethylene Process Simulation

The ethylene process using ethane feed was modeled using the Process Optimization System (PROPS), a modified version of CHESS. PROPS performs the material and energy balance, equipment design and cost, economic analysis, and the process optimization. A description of PROPS is available elsewhere (Gaines and Gaddy, 1974) and will not be reviewed here.

Standard equipment modules in PROPS were used for modeling heat exchangers, distillation columns, pumps, compressors, mixers, valves, dividers, reactors, and tanks in the ethylene process. Several additional equipment modules needed to be developed for this study: ethane pyrolysis reactor; TLX; quench tower; hydrogen addition controller; dryer–acid gas removal system; and a cascade refrigeration system.

The modules calculate the material and energy balance and determine the size and cost for each equipment item. A brief description of each module is presented in this section.

The pyrolysis furnace module uses the input feed temperature, flow rate, pressure, enthalpy, and composition to calculate: (1) the effluent composition, flow rate, temperature, pressure, and enthalpy; (2) the total furnace heat requirements and total heat recovered; and (3) the operating and capital cost of the furnace. The module carries out calculations for one coil in the pyrolysis furnace, then adjusts the output data for the total number of coils and furnaces in the plant.

Snow and Schutt (1957) give seven equations to describe the pyrolysis of ethane

$$C_2H_6 \rightleftarrows C_2H_4 + H_2 \quad (1)$$

$$C_2H_4 + 2H_2 \rightleftarrows 2CH_4 \quad (2)$$

$$C_2H_4 \rightleftarrows 0.25C_4H_6 + 0.125C_4H_8 + 0.125C_4H_{10} + 0.125H_2 \quad (3)$$

$$C_2H_4 \rightleftarrows C_2H_2 + H_2 \quad (4)$$

$$C_2H_4 \rightleftarrows 2C + 2H_2 \quad (5)$$

$$C_2H_4 + C_2H_6 \rightleftarrows 0.952C_3H_6 + 0.381C_3H_8 + 0.62H_2 \quad (6)$$

$$C_2H_4 \rightleftarrows 0.333C_6H_6 + H_2 \quad (7)$$

Schutt (1947) has also given data for effluent gas composition as a function of ethane conversion

$$N_{H_2} = 1.0044a - 4.036 \quad (8)$$

$$N_{C_2H_4} = 0.8022a + 3.950 \quad (9)$$

$$N_{C_3H_8} = 0.0083a - 0.205 \quad (10)$$

$$N_{CH_4} = 0.1786a - 2.500 \quad (11)$$

$$N_{C_4} = 0.0180a - 0.235 \quad (12)$$

$$N_{C_3H_6} = 0.0202a - 0.508 \quad (13)$$

$$N_{C_5} = 0.0203a - 0.662 \quad (14)$$

The conversion, a, for eq 8 to 14 is calculated using the following equation, presented by Fair and Rase (1954), for light hydrocarbon pyrolysis

$$\frac{k'\pi\Delta V}{F} = \frac{\Delta a_A}{1 - a_{A_2}}(1 + N_I + \delta a_{A_2}) \quad (15)$$

The equation requires a trial and error calculation for Δa_A and is valid when the increment of volume of the total coil

is small enough to allow k', π, and δ to be constant and the conversion in the increment to be between 3 and 7%.

The reaction velocity constant is calculated using the correlation of Zdonik et al. (1970)

$$k' = \frac{1.69824 \times 10^{14}}{RT} e^{(-65440/T)} \tag{16}$$

The pressure drop through the increment of the coil is determined by (Bennett and Myers, 1962)

$$-\Delta\pi = \frac{2fLG^2}{g_c D \rho_{av}} \times \frac{1}{144} \tag{17}$$

Equation 17 assumes that the Reynolds number does not change with pressure and thus the friction factor is constant. It is also assumed that there is not a large velocity change and as such the kinetic energy term is relatively small.

The calculation scheme, suggested by Fair and Rase (1954) and modified for the PROPS simulation, determines the outlet conditions of the furnace as follows. (1) Assume the temperature rise and pressure drop of an increment (31 ft). (2) Using the average temperature and pressure, calculate the conversion in the increment by trial and error using eq 15 and 16. (3) Compute the gas composition of the increment using eq 8 to 14. (4) Compute the heat of reaction of the increment using the HRX subroutine of PROPS and eq 1 to 7. (5) Use the PROPS physical properties subroutine, KHZT, to calculate the specific heat and density of the gas. (6) Calculate the temperature rise and use eq 17 to obtain the pressure drop of the increment and compare with the assumed values. (7) Repeat steps 1 to 6 with new values of the average temperature, pressure, and conversion until agreement is obtained.

The iteration continues until successive values of the temperature and pressure at the end of the increment differ by less than 1 °R and 0.5 psia. Once the increment converges, the calculations continue with the exit composition, temperature, conversion, and pressure as the initial points of the next increment. The procedure is complete when the desired total conversion is reached.

The conditions of the furnace must be checked to assure that coke deposition in the reactor coils will not be excessive. The criterion used (Snow and Schutt, 1957) is based upon an equilibrium approach (EA) rule. Through experience in reactor design, it has been concluded that coke formation is not excessive if the approach to equilibrium of the primary decomposition of ethane is kept below 0.65.

After the total furnace flow rate and heat duty are calculated, the fuel gas needed to satisfy the heat duty is obtained. The convection section calculations consist of subtracting the steam superheat and feed preheat duty from the flue gas enthalpy to determine the amount of 680.8 psia steam produced in the economizer section. An overall thermal efficiency of 75% is achieved by adjusting the quantity of steam produced.

The basis for the economic calculations has been obtained from Demarest (1977) and Schmitz (1977). The investment of the furnace is calculated from the total heat absorbed in the radiant, convection, and economizer sections. The operating cost is calculated from the fuel gas consumed and allowing credit for the steam produced in the economizer section.

The TLX unit recovers heat from the furnace product gases by producing 680.8 psia steam and enables the gas to be rapidly cooled below 1500 °R to suppress unwanted side reactions. The capital cost of the equipment items is based on the data of Rothman (1970). The operating cost consists of a credit for the steam produced.

The quench tower module further cools the reactor exhaust gases (between 560 and 660 °R) so the gas can be compressed without exceeding 710 °R where fouling and polymer formation occur. The cooling also reduces the dryer load by condensing moisture. The hot water produced is used as a source of heat for tower reboilers. A pump is included in the module to circulate this water.

The capital cost of the tower is based on the pounds of total hydrocarbons cooled (Rothman, 1970). The operating cost is established from the cost of the steam necessary to run the circulation pump, the credit for the amount of quench water used in downstream reboilers, and the cost of operating a cooling tower to cool the quench water.

Acetylene is removed from the ethylene product stream by catalytic hydrogenation using hydrogen obtained from the demethanizer overhead. Moisture is also unwanted in the product stream and is removed by passing the gas over a desiccant. Acid gas must also be removed, if present, using a caustic wash.

The hydrogen controller and dryer–acid gas removal module simulates both the controller for the hydrogen addition prior to entering the acetylene reactor and the dryer–acid gas calculations. The dryer–acid gas capital cost is based on data from Rothman (1970) while the operating cost is based on catalyst cost (Baba and Kennedy; 1976).

The refrigeration system is designed after all steam and refrigeration requirements have been determined. The system was modeled as a separate subroutine because of PROPS storage limitations. PROPS has space for 50 equipment items that are filled by the major pieces of equipment in the ethylene plant. There is not enough additional space to add the approximately 20 equipment items needed for the cascade refrigeration system. All the process equipment used by the system, such as heat exchangers, pumps, compressors and tanks are included in the module. The design and economic calculations for the additional units are drawn from the appropriate PROPS subroutine.

In addition to the modules described, modifications were made to the existing DIST and HXER subroutines. A partial condenser calculation was added to DIST to be used in conjunction with HXER when noncondensables exist in a stream, as is the case with demethanizer overheads. HXER was modified to accept the values of composition, flow rate, and temperature calculated in DIST and to place them in the appropriate variable locations. HXER can then calculate the area and water cooling or refrigeration necessary to handle the heat duty.

Optimization Technique

The ethylene process was optimized using the ARS technique. This technique guides the selection of new values of the independent variables by randomly searching in the region about the best known values of the objective function. The expression suggested by Gall (1966) and modified by Heuckroth et al. (1976) for determining values of the independent variables is given as

$$X_i = X_i^* + R_i/k\ (2\theta - 1)^k \tag{18}$$

The search region is centered about the best values of the variables and these values are replaced by improvements as the search progresses. The efficiency of the search is controlled by increasing the distribution coefficient, k, and reducing the range, R, as the optimum is approached. Although the procedure is random, it has been found to have equal or better efficiency than several other methods (Heuckroth et al., 1976). It is particularly advantageous to use the ARS technique with heavily

Table I. Starting Point for Base Case Optimization

variable	starting value
1. conversion, %, X_1	60
2. steam/hydrocarbon ratio, lb-mol/lb-mol, X_2	0.67
3. inlet temperature to radiation section, °R, X_3	1660
4. heat flux, Btu/h-ft²-°F, X_4	12000
5. inlet pressure to radiation section, psia, X_5	60
6. inside coil diameter, in., X_6	4.00
7. number of furnaces, X_7	8
8. number of coils/furnace, X_8	6
dependent variables	
1. investment, MM$	113.1
2. ROI, %	8.71
3. product flow rate, TPY × 10^5	5.0
4. product cost, ¢/lb	9.1
5. earnings, MM$	9.85
6. flow rate, lb/ft²-s	18.07

constrained problems, since the ARS has the ability to follow constraints. Equation 18 can be used to define values of continuous or discrete variables and, therefore, the ARS is appropriate for use with mixed integer problems (Kelahan and Gaddy, 1977).

To accomplish the objective of improving the search efficiency by initially testing the boundary constraints, the ARS technique was modified slightly. The only values of the independent variables possible for the search were either the upper or lower boundary values. After the best boundary point was determined, the search was allowed to proceed in the usual manner.

Optimization Results and Discussion

Four optimization searches were performed in this study. In addition, several single variable optimizations (case studies) were performed on column reflux ratios and system pressures and temperatures. Case studies were also performed about the optimum to ensure location of the global optimum.

A base case example was examined to measure the improvements in the objective function against the amount of computer time needed. This search revealed that the ethylene–hydrogen–ethane equilibrium approach (*EA*), which relates the operating conditions to coke formation, was extremely sensitive to changes in the independent variables. To try to improve the efficiency of the search, a second starting point was examined with the *EA* constraint relaxed. To further increase the efficiency, the optimal independent variable boundaries were found and used as starting values for the search. The boundary constraints were further examined by expanding the constraints and continuing the search. All cases use the objective of maximizing the return on investment (ROI) as determined by the PROPS simulator.

Base Case. The base case uses an ethane feed of 8658 lb-mol/h at a temperature of 560 °R with the following composition: 1% C_2H_4; 98% C_2H_6; 1% C_3H_6. The optimization problem is stated as follows.

$$\text{maximize: ROI} = f(X_1, X_2, X_3, ..., X_8) \qquad (19)$$

subject to: $0.55 \le X_1 \le 0.61$; $0.45 \le X_2 \le 0.67$; $1500 \le X_3 \le 1750$; $8500 \le X_4 \le 13500$; $60 \le X_5 \le 100$; $2.5 \le X_6 \le 5.0$; $7 \le X_7 \le 10$; $6 \le X_8 \le 10$; $6945 \le X_9 \le 11049$; $X_{10} \le 0.65$; $X_{11} \le 40$; and $25 \le X_{12}$.

The independent variables, X_1 through X_8, are defined in Table I, with the explicit constraints given in eq 19. The independent variables were selected in this study from Fair and Rase (1954) and Snow and Schutt (1957).

Table II. Comparison of Furnace Effluent

component	mol % PROPS	Zdonik et al.	Snow and Schutt
H_2	35.3	32.7	34.6
CH_4	5.2	6.3	7.2
C_2H_2	0.2	0.2	0.3
C_2H_4	33.2	33.8	31.7
C_2H_6	24.0	24.9	21.4
C_3H_6	1.1	1.0	2.3
C_3H_8	0.2	0.2	0.9
C_4	0.5	0.4	0.8
C_5	0.4	0.5	0.8

The variable X_9 is the quantity of ethane fed to the reactor. Ethylene production was chosen as 50 000 TPY for all cases. For a constant production rate, the ethane feed must be varied, depending upon the conversion chosen. The furnace is also implicitly constrained by a maximum flow rate in the furnace coils, X_{11}, a minimum outlet pressure, X_{12}, and a maximum *EA*, X_{10}. The function, f, defined by eq 19 represents all the computations performed by the PROPS flowsheet simulation.

The upper and lower bounds placed on the explicit and implicit constraints are set by the normal operating conditions or physical limitations of a pyrolysis furnace (Zdonik et al., 1970). The upper temperature constraint of 1750 °R to the radiation section was set below the point where incipient reaction occurs. The upper flux constraint of 13500 Btu/h-ft²-°F is set to avoid tube sag from overheating. The limits for the number of furnaces in a plant were obtained from Demarest (1977). The *EA* constraint (Snow and Schutt, 1957) is defined as

$$EA = \frac{N^*_{C_2H_4} N^*_{H_2} \pi}{N^*_{C_2H_6} N^* K_1} \qquad (20)$$

and

$$K_1 = 4.87 \times 10^{-6} e^{0.0078T} \qquad (21)$$

Since the coke formation mechanism is quite complex and not fully understood, a simple but effective relationship has been developed to represent conditions which give excessive coke formation. Experience in commercial furnace design has shown that an *EA* below 0.65 is effective in minimizing coke deposition.

Other variables were considered for optimization. The pressure to the recovery section was briefly examined using a case study optimization. The exit gas temperature from the TLX was also examined in the same manner. Neither affected the plant economics to an appreciable extent. Therefore, the optimal values of 480 psia and 1010 °R were used for these parameters in all cases. Since column reflux ratios can be optimized independently of other variables, these reflux ratios were studied after location of the optimal values of the other variables. The initial values of the reflux ratios were taken from the literature.

Verification of the base case was achieved by approximating the operating parameters of Snow and Schutt (1957). These parameters are listed in Table I. The furnace effluent composition, while operating under these conditions, compares closely to the data of Zdonik et al. (1970) and Snow and Schutt (1957) shown in Table II.

Baba and Kennedy (1976) have given an investment of $105.6 MM and a product cost of 8.6¢/lb for a 500 000 TPY plant. These data compare favorably with the economic results of the simulation. PROPS calculates an investment of $113.1 MM and a product cost of 9.1¢/lb as seen in Table I. Comparison of these data confirms the ability of the simulation model to accurately represent the

Table III. Results of Base Case Optimization

1. Independent Variables

improvement no.	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8
0	60	0.670	1660	12 000	60.0	4.00	8	6
3	61	0.670	1750	13 500	68.1	3.75	7	7
4	61	0.640	1750	13 500	68.0	4.25	7	6
10[a]	61	0.640	1750	13 447	67.3	4.25	7	6
11	61	0.640	1750	9 000	67.3	4.25	7	6
18	61	0.636	1750	9 047	67.6	4.25	7	6
19	61	0.609	1750	8 500	60.0	4.25	7	7

2. Dependent Variables

improvement no.	total no. of function explanations	X_{10}	X_{11}	total time, min	earnings, MM$	ROI
0	1	0.30	18.07	0	9.85	8.71
3	21	0.48	20.85	3.02	10.30	9.78
4	33	0.65	19.43	5.27	10.40	9.84
10[a]	52	0.63	19.40	9.34	10.50	9.92
11	53	0.52	18.61	11.67	10.97	10.30
18	70	0.53	18.65	16.28	10.99	10.45
19	76	0.55	16.39	17.48	11.00	10.50

[a] Case study search to aid optimization.

ethylene process and its associated economics.

Table III shows the history of the base case optimization. These results show that the search resulted in a substantial improvement in ROI of almost 2%. Earnings increased an additional $1.15 MM per year even though the starting values are the usual design conditions. The optimization required 18 min of computer time on the IBM 370/168. The cost of the simulation and optimization study is easily justified by the $1.15 MM improvement in earnings. In this case, optimization with a detailed simulation model would be a good investment, even for older and supposedly near optimal designs.

It is interesting to note that five of the eight variables lie on a constraint boundary. Conversion and inlet radiation section temperature lie on the upper bound while heat flux, the number of furnaces, and pressure to the radiation section, all lie on their lower bound.

Since an ethylene plant must be thermally efficient to be economical, the optimum combination of variables will tend to balance fuel costs with cost of equipment. The optimum conversion is found to be at its upper bound which would increase refrigeration but decrease compression and fuel gas costs. At constant ethylene production, the furnace cost is also less at high conversion. A high conversion adversely affects the *EA*. A higher steam to hydrocarbon ratio (S/HC) can be used to reduce the *EA*, but at the expense of lower hydrocarbon throughput and higher fuel gas and recovery costs. Therefore, the combination of maximum conversion and intermediate S/HC ratio is realistic.

Low heat flux requires more heat transfer surface and reduced gas velocity but improves the ethane decomposition equilibrium. High temprature enhances the reaction rate and reduces the heat transfer surface. Additional furnaces or coils and larger coil diameters increase the reaction volume and provide more surface for heat transfer. Increasing the coil diameter is cheaper than adding furnaces or coils and also reduces pressure drop, allowing a lower pressure which enhances the reaction. Thus, the combination of low flux, high temperature, and low pressure with intermediate coil diameter and minimum number of furnaces appears reasonable.

It should be noted that this study has an extremely difficult search region. The mixed integer variables along with the very sensitive *EA* combine to produce many local optima and invalid regions which decrease the search efficiency.

The base case simulation required 311 iterations with only 87 evaluations of the objective function and 19 improvements. A new simulation, with a new set of independent variables, was required each time a constraint violation was encountered. As the search approached the global optimum (improvement number 19), it slowed at a local optimum (improvement 10). The independent variables were changed individually in a separate case study, disregarding the *EA* constraint, in an effort to move the search further along. The heat flux was found to be far from the global optimum value, with a large invalid region separating the local and global optimum values. The search was started again using a value for the heat flux of 9000 Btu/h-ft^2-°F. The ARS technique then guided the search to the optimum (shown as improvement 19) with little difficulty.

Further individual changes of the independent variables about this optimum are shown in Table IV. The results show the S/HC ratio (X_2) is the most sensitive variable for controlling the *EA* parameter, which agrees with the findings of Petryschuk and Johnson (1968). It is also found that a slight improvement in ROI can be achieved by lowering the S/HC ratio. However, this nominal improvement is probably not worth the risk of additional carbon buildup with the *EA* value at 0.63. The other variables are tightly constrained, as shown by the many invalid regions. This narrow valid region leading to the optimum shows the difficult task the ARS technique had in reaching the optimum. Heat flux (X_4) is the only variable with a wide valid region about the optimum, but it also has the least effect on ROI. Pressure (X_5) is found to have the smallest valid region. As shown later, other cases converge to this same point, and it is concluded that the values in the last row of Table III are optimal.

Optimization with Relaxed Constraints. Because of the sensitivity of the *EA* constraint, relaxation of this constraint to improve the search efficiency was examined. A new starting point was chosen and the search begun as before, except the *EA* constraint was allowed to be as high as 1.2 and then restricted as the search moved closer to the optimum.

Table IV. Results of Case Study About the Optimum

independent variable						
X_2		0.58	0.59	0.60	0.61	0.62
	ROI	invalid	invalid	10.64	10.50	10.38
	X_{10}			0.63	0.55	0.53
X_4		8500	8550	8600	8700	8800
	ROI	10.524	10.520	10.517	10.520	10.500
	X_{10}	0.59	0.58	0.58	0.60	0.59
X_5		60	61	62	63	64
	ROI	10.52	invalid	invalid	invalid	invalid
	X_{10}	0.59				
X_6		3.75	4.00	4.25	4.50	4.75
	ROI	invalid	10.15	10.52	invalid	invalid
	X_{10}		0.34	0.59		
X_8		6	7	8	9	10
	ROI	9.67	10.52	invalid	invalid	invalid
	X_{10}	0.26	0.59			

Table V. Results of Optimization with Relaxed Constraints

1. Independent Variables

improvement no.	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8
0	55	0.550	1510	9 600	70.0	2.50	10	6
1	59	0.450	1682	10 395	60.0	5.00	10	7
5	61	0.605	1745	8 500	61.0	4.50	7	6
11	61	0.600	1747	8 500	68.0	4.25	7	6
18	61	0.604	1750	8 500	68.3	4.25	7	6
21	61	0.604	1750	8 500	60.0	4.25	7	7

2. Dependent Variables

improvement no.	total no. of function evaluations	X_{10}	X_{11}	total time, min	earnings, MM$	ROI
0	0	invalid point				
1	1	1.00	16.73	0.09	9.40	8.57
5	38	0.57	17.08	3.37	10.61	9.95
11	62	0.58	18.52	7.52	11.06	10.48
18	81	0.59	18.50	12.14	11.07	10.51
21	89	0.59	16.72	13.38	11.09	10.55

The results of this second search are shown in Table V. The optimum values of the variables agree with those found earlier within the accuracy of the simulation (0.1% ROI in this study). The search needed only 13.38 min computer time, with 276 iterations, 89 functional evaluations, and 21 improvements. This case resulted in a reduction of about 20% in computer time. This saving was achieved even though the starting point for the optimization with constraint relaxation was further from the optimum.

The search has no trouble in moving to the global optimum values. As the search approached the optimum, the *EA* moved below 0.65 but the problems with invalid regions were avoided. The loose *EA* constraint enabled the search to move through the invalid regions encountered in the base case search into the valid region about the global optimum. Tightening the constraints then directed the search to the optimum values. These results indicate that in problems with tight constraints that create irregular invalid regions that obscure the optimum, relaxation of these constraints can lead to improved search efficiencies.

Bounds Testing. A number of variables were observed to be optimal at a boundary, as noted before. Therefore, a further increase in the search efficiency was sought by first testing these boundaries to find an advantageous starting point. After locating the best bound point, the search was continued as before. Using this criterion, the search starts with all variables on an explicit constraint. The *EA* constraint was again relaxed to 1.2 and was then tightened to 0.65 as the search proceeded.

The results of the third search are shown in Table VI. The initial bounds testing required 2.91 min of computer time. A total of only 10.89 min was needed to complete the search. These results show a further improvement in the necessary computer time over the second case by about 19% and more than 35% over the base case.

It should be noted that the initial bounds testing does not assure optimality for those variables which are optimal at a boundary. This situation is observed in this study where X_4 and X_7 were optimal at upper bounds initially, whereas the true optima are at the lower bounds. Nevertheless, starting the search from an optimum boundary point and initially relaxing sensitive constraints can add to the efficiency of the optimization search.

Constraint Expansion. As several variables were optimal at their boundaries, it is appropriate to expand these explicit constraints and continue the search to see what improvements in the design might be possible. The minimum number of furnaces and the maximum temperature of the gas entering the radiation section were deemed to be physical limitations and therefore were unchanged. The conversion, inlet pressure to the radiation section, and heat flux constraints were expanded and the search continued.

The results of this study are shown in Table VII. The first expansion was made arbitrarily. The conversion

Table VI. Results of Bounds Testing Optimization

1. Independent Variables

improvement no.	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8
0	55	0.670	1750	13 500	60.0	2.50	10	10
1	61	0.450	1750	13 500	60.0	5.00	10	6
2[a]	61	0.450	1750	13 500	60.0	5.00	10	10
10	61	0.555	1750	13 209	63.0	4.25	7	10
12	61	0.548	1750	13 210	63.0	4.25	7	10
13	61	0.670	1750	8 500	68.0	4.25	7	6
15	61	0.610	1750	8 500	60.0	4.25	7	7

2. Dependent Variables

improvement no.	total no. of function evaluations	X_1	X_{11}	total time, min	earnings, MM$	ROI
0	0	invalid point				
1	1	0.97	9.10	0.08	10.07	9.29
2[a]	21	0.96	6.69	2.91	10.24	9.54
10	51	0.79	14.04	7.31	10.72	10.29
12	64	0.80	13.99	8.33	10.74	10.31
13	65	0.51	18.71	9.71	10.82	10.34
15	72	0.52	16.54	10.89	10.92	10.47

[a] End of bound testing, begin usual search.

Table VII. Results of Bound Expansion

1. Independent Variables

improvement no.	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8
0[a]	61.0	0.604	1750	8500	60.0	4.25	7	7
3[b]	61.0	0.607	1750	8000	68.0	4.25	7	6
7[c]	62.0	0.607	1750	7000	60.0	4.25	7	7
12	62.5	0.608	1750	7040	60.0	4.25	7	7
16	62.9	0.613	1750	7000	60.0	4.25	7	7
17	63.7	0.618	1750	7031	58.8	4.25	7	7

2. Dependent Variables

improvement no.	total no. of function evaluations	X_{10}	X_{11}	total time, min	earnings, MM$	ROI
0[a]	0	0.52	16.54	0	10.92	10.55
3[b]	17	0.59	18.35	4.12	11.16	10.60
7[c]	35	0.55	15.62	8.15	11.42	10.88
12	52	0.57	15.52	12.01	11.52	11.04
16	68	0.59	15.47	15.94	11.56	11.10
17	80	0.55	15.11	19.47	11.60	11.38

[a] Bounds: X_4 lowered to 8000; X_2 raised to 0.63. [b] Bounds: X_4 lowered to 7000. [c] Bounds: X_2 raised to 0.65; X_5 lowered to 55.0.

constraint was increased from 0.60 to 0.63, the heat flux constraint lowered from 12 000 to 8000 and the pressure constraint was left unchanged. As improvements were found, further expansions were made. Because of the ever decreasing flow through the coils, the *EA* constraint was also lowered, as recommended by Snow and Schutt (1957). A value of 0.55 was chosen as the *EA* constraint.

The new optimum found shows a marked improvement to 11.38% ROI. The search needed 19.49 min of computer time, but the new optimum showed an increase in earnings of $0.68 MM per year, well worth the expenditure of the additional computer time.

Table VII shows that the conversion increased from 61 to 63.7, while the flux and pressure decreased from 8500 to 7031 Btu/h-ft^2-°F and from 60 to 58.8 psia, respectively. The *EA* constraint of 0.55 stopped the variables from changing further.

These variable changes are not unexpected. A low pressure favors the reaction rate, as long as the minimum outlet pressure constraint is met. A low flux improved the equilibrium and furnace efficiency. A high conversion reduced compression and fuel costs. However, changing these variables in the above manner is constrained by the likelihood of coke deposition, requiring more frequent furnace cleaning and lost revenue. Further study might consider balancing the revenue lost due to furnace down-time to clean coke from the coils and the increased earnings from a looser *EA* constraint.

Column Optimization. As a final part of the study, the reflux ratios of several important columns were optimized. The demethanizer, deethanizer, and C_2 splitter columns are important because they use a large portion of the refrigeration and steam supplied to the recovery section.

The results of this study are shown in Table VIII. A very large increase in ROI (2.58%) is especially noted in the deethanizer optimization. Since the deethanizer splits the product gas into two major streams, minimizing the refrigeration and steam necessary to accomplish this split is much more economical than a larger column or more

Table VIII. Results of Column Optimization

column name						
DEET	R/R_{min}	1.1[a]	1.2	1.3	1.4	1.5
	ROI	13.10	12.92	12.53	12.89	12.83
C_2H_4	R/R_{min}	1.05[a]	1.1	1.15	1.2	1.5
	ROI	11.34	11.27	11.12	10.97	10.09
DEME	R/R_{min}	1.05	1.1	1.15	1.2	1.3
	ROI	10.54	10.58	10.55	10.52	10.47

[a] Minimum values considered feasible for these separations.

stages. The C_2 splitter and demethanizer also show an improvement (0.82 and 0.06%, respectively) in ROI. These results further demonstrate the benefits of a detailed model for optimization.

Conclusions

It is concluded that a flowsheet simulator can be used to optimize a complex process with a reasonable amount of computer time and is an excellent investment even for near optimal plants. The adaptive random search worked well for the cases studied. The optimization was not automatic, however, and some interaction with the simulation/optimization was necessary.

An improvement in the search efficiency was obtained in this tightly constrained optimization problem by relaxing the sensitive constraints. Restricting the constraint value as the search approached the optimum then guided the search to the final optimal values. A further improvement in the search efficiency was found by using the best boundary condition for the independent variables as a starting point. Additional study is needed to confirm these results for other optimization problems.

It has also been shown that expanding constraints can lead to substantial improvements in the economics of chemical processes. Such improvements are contingent upon the ability to realistically change the boundaries and the tolerances available for change. It is felt that in many cases, bounds are established somewhat arbitrarily, and if so, significant economic advantages may be lost. Simulation/optimization of the process offers a means of measuring these possible improvements.

Nomenclature

a = conversion, dimensionless
Δa = fractional conversion for one increment, dimensionless
D = diameter, ft
EA = equilibrium approach, dimensionless
f = friction factor, dimensionless
F = feed rate of key reactant, lb-mol/h
g_c = gravity constant, 32.17 lb_m-ft/lb_f-s^2
G = mass velocity, lb/ft^2-s
k' = reaction velocity constant, lb-mol/ft^3-h-psia
k = distribution coefficient (odd integer, 1, 3, 5...)
k_1 = equilibrium constant, psia
L = length of increment, ft
N_X = lb-mol of component X/100 mol of ethane charged
N_I = moles of inerts per mole of ethane entering
N_X^* = total moles of component X, lb-mol
N^* = total moles, lb-mol
R_i = allowable search region (range) for independent variables
R = gas constant, 10.73 psia-ft^3/lb-mol-°R
T = temperature, °R
ΔV = volume of one increment of coil, ft^3
X_i = new value of independent variable, i
X_i^* = value of variable X_i, which has produced the best value for the objective function

Greek Letters

δ = increase in number of lb-mol/lb-mol of ethane converted (expansion factor), dimensionless
θ = uniform random number between 0 and 1
π = total pressure, psia
$-\Delta\pi$ = pressure drop through one increment
ρ_{av} = average density over one increment of coil, lb/ft^3

Subscripts

A = key reactant
2 = denotes exit conditions

Literature Cited

Baba, T. B., Kennedy, J. R., *Chem. Eng.*, **83**(1), 116 (1976).
Ballman, S., Gaddy, J. L., *Ind. Eng. Chem. Process Des. Dev.*, **16**, 337 (1977).
Barneson, R. A., Brannock, J. G., Moore, J. G., Morris, C., *Chem. Eng.*, **77**(16), 132 (1970).
Bracken, J., McCormick, G. P., "Selected Applications of Nonlinear Programming", pp 94–100, Wiley, New York, N.Y., 1968.
Campbell, J. R., Gaddy, J. L., *AIChE J.*, **22**(6), 1050 (1976).
Demarest, K. D., personal communication, Foster Wheeler Energy Corp., Jan 25, 1977.
Doering, F. J., Gaddy, J. L., paper presented at the 69th Annual AIChE Meeting, Chicago, Ill., 1976; to appear in *Comp. Chem. Eng.*
Fair, J. R., Rase, H. K., *Chem. Eng. Prog.*, **50**(8), 415 (1954).
Friedman, P., Pinder, K. L., *Ind. Eng. Chem. Process Des. Dev.*, **11**, 512 (1972).
Gaines, L. D., Gaddy, J. L., "University of Missouri—Rolla PROPS User's Guide", University of Missouri, Rolla, Mo., 1974.
Gaines, L. D., Gaddy, J. L., *Ind. Eng. Chem. Process Des. Dev.*, **15**, 206 (1976).
Gall, D. A., "A Practical Multifactor Optimization Criterion", in "Recent Advances in Optimization Techniques", A. Lavi and T. P. Vagh, Ed., p 369, Wiley, New York, N.Y., 1966.
Gambro, A. J., Muenz, K., Abrahams, M., *Hydrocarbon Process*, **51**(3), 73 (1972).
Gottfried, B. S., Bruggink, P. R., Starwood, E. R., *Ind. Eng. Chem. Process Des. Dev.*, **9**, 518 (1970).
Heuckroth, M. W., Gaines, L. D., Gaddy, J. L., *AIChE J.*, **22**(4), 744 (1976).
Keefer, D. L., *Ind. Eng. Chem. Process Des. Dev.*, **12**, 92 (1973).
Kelahan, R. C., Gaddy, J. L., *Int. J. Numer. Methods Eng.*, **12**, 289 (1978).
Loftus, J., *Chem. Eng. Prog.*, **66**(12), 53 (1970).
Petryschuk, W. F., Johnson, A. I., *Can. J. Chem. Eng.*, **16**, 172 (1968).
Rothman, S. N., *Chem. Eng. Prog.*, **66**(6), 37 (1970).
Schmitz, P., personal communication, Shell Oil Co., Jan 14, 1977.
Schutt, H. C., *Chem. Eng. Prog.*, **43**(3), 103 (1947).
Snow, R. H., Schutt, H. C., *Chem. Eng. Prog.*, **53**(3), 133-M (1957).
Umeda, T., Ichikawa, A., *Ind. Eng. Chem. Process Des. Dev.*, **10**, 229 (1971).
Weisman, J., Holzman, A. G., *Trans. Am. Nucl. Soc.*, **12**, 141 (1969).
Zdonik, S. B., Green, E. J., Hallee, L. P., "Manufacturing Ethylene", Petroleum Publishing Co., Tulsa, Okla., 1970.
Zellnik, H. E., Sondak, N. E., Davis, R. S., *Chem. Eng. Prog.*, **58**(8), (1962).

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