flow conditions may be due to the dissimilar shape of particles which affects the in situ flow patterns. More experimental data are needed to explain this deviation.

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NOTATION

D = molecular diffusivity in liquid, cm^2/s
d_p = particle diameter, cm
G = superficial gas velocity, cm/s
J_D = mass transfer factor
k_{ls} = liquid phase mass transfer coefficient in particle-to-liquid transport cm/s
Re_L = liquid-phase Reynolds number, $(d_p u_L \rho_L)/\mu_L$
u_L = superficial velocity of liquid, cm/s
ρ_L = density of liquid, g/cm^3
μ_L = viscosity of liquid, g/(cm)(s)

LITERATURE CITED

Calderbank, P. H., and M. B. Moo-Young, "The Continuous Phase Heat and Mass Transfer Properties of Dispersions," *Chem. Eng. Sci.*, **16**, 39 (1961).

Farazimajd, A., "Effects of Flow Rates and Distributor Backmixing on Mass Transfer for Cocurrent Two-Phase Downflow in a Packed Bed," M.S. thesis, Univ. Tulsa, Oklahoma (1975).

Goto, S., and J. M. Smith, "Trickle-Bed Reactor Performance Part 1. Holdup and Mass Transfer Effects," *AIChE J.*, **21**, 706 (1975).

Goto, S., J. Levec, and J. M. Smith, "Mass Transfer in Packed Beds with Two-Phase Flow," *Ind. Eng. Chem. Process. Design Develop.*, **14**, 473 (1975).

Hirose, T., Y. Mori, and Y. Sato, "Liquid-To-Particle Mass Transfer in Fixed Bed Reactor with Cocurrent Gas-Liquid Downflow," *J. Chem. Eng. Japan*, **9**, 220 (1976).

Lemay, Y., G. Pineault, and J. A. Ruether, "Particle-Liquid Mass Transfer in a Three-Phase Fixed Bed Reactor with Cocurrent Flow in the Pulsing Regime," *Ind. Eng. Chem. Process Design Develop*, **14**, 280 (1975).

Reid, R. C., and T. K. Sherwood, "The Properties of Gases and Liquids," 2 ed., p. 559, McGraw-Hill, New York (1966).

Sato, Y., T. Hirose, F. Takahaski, and M. Toda, "Performance of Fixed-Bed Catalytic Reactor with Cocurrent Gas-Liquid Flow," PACHEC Section 8, 187 (1972).

———, and Y. Hashiguchi, "Flow Pattern and Pulsation Properties of Cocurrent Gas-Liquid Downflow in Packed Beds," *J. Chem. Eng. Japan*, **6**, 315 (1973).

Satterfield, C. N., A. A. Pelossof, and T. K. Sherwood, "Mass Transfer Limitations in a Trickle-Bed Reactor," *AIChE J.*, **15**, 226 (1969).

Satterfield, C. N., "Trickle-Bed Reactors (Journal Review)," *ibid.*, **21**, 209 (1975).

Sylvester, N. D., and P. Pitayagulsarn, "Effect of Transport Processes on Conversion in a Trickle-Bed Reactor," *ibid.*, **19**, 640 (1973).

———, "Mass Transfer for Two-Phase Cocurrent Downflow in a Packed Bed," *Ind. Eng. Chem. Process Design Develop*, **14**, 421 (1975).

Van Krevelen, D. W., and J. T. C. Krekels, "Rate of Dissolution of Solid Substances," *Rec. Trav. Chem.*, **67**, 512 (1948).

Weekman, V. W., and J. E. Myers, "Fluid-Flow Characteristics of Cocurrent Gas-Liquid Flow in Packed Beds," *AIChE J.*, **10**, 951 (1964).

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Process Synthesis Using Structural Parameters: A Problem with Inequality Constraints

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In this note, we shall expose a problem with the structural parameter method for process synthesis. The problem is almost obvious once stated, but until now, to the authors' knowledge, it has not been mentioned in the literature. It can seriously affect the expected results. The problem to be exposed does not mean that the method is valueless, as it clearly is not; it simply means that care must be taken to insure the method is really useful for a given problem.

A system of interconnected process subsystems can be modeled by the use of structural parameters which are defined by

$$x_i = \sum_{j=1}^{N} \alpha_{ij} y_j \quad i = 1, 2, 3, \ldots N$$

$$0 \leq \alpha_{ij} \leq 1, \quad \sum_{i=1}^{N} \alpha_{ij} = 1$$

where x_i and y_i are, respectively, the input and output variables of the i^{th} subsystem, N is the total number of subsystems in the entire system, and the parameters α_{ij} are the structural parameters; that is, each is the fraction of the output stream of the j^{th} subsystem which flows into the i^{th} subsystem.

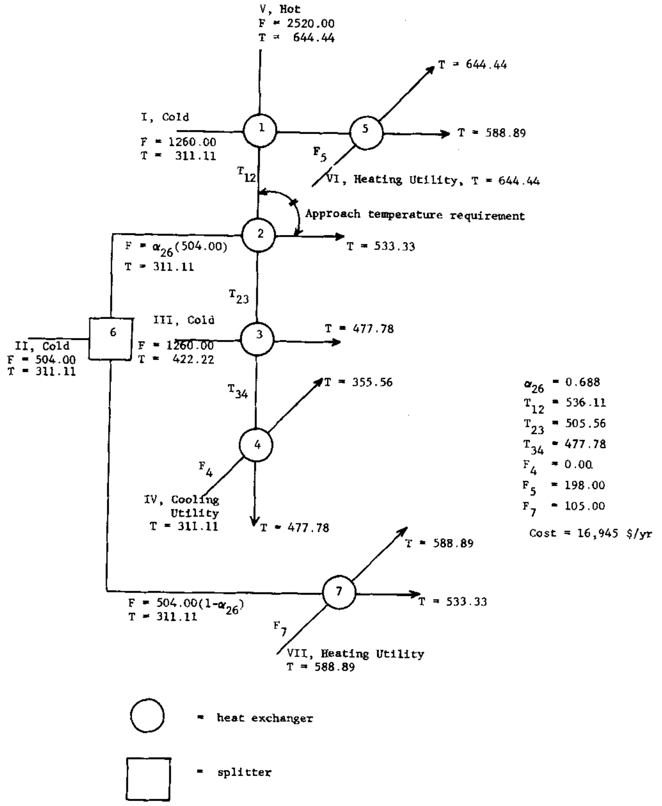

Fig. 1. The optimal values of the parameters.

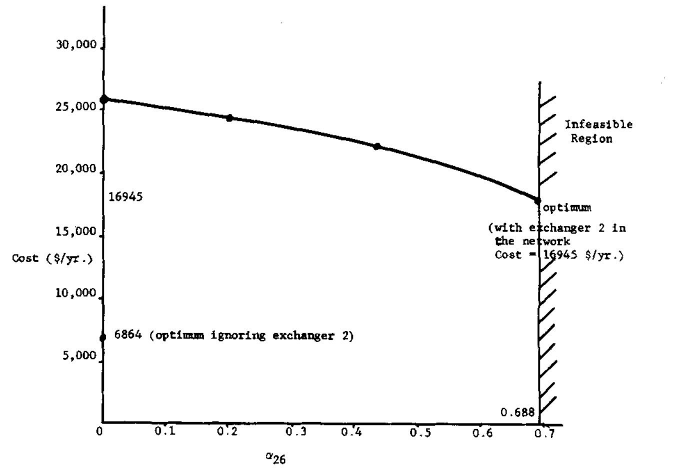

Fig. 2. The discontinuity in optimization.

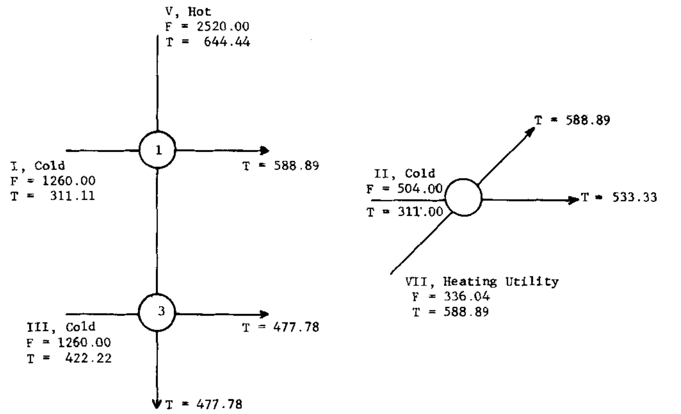

Fig. 3. The optimal network when the approach temperature requirement is ignored at the null exchanger 2.

By means of structural parameters, a system synthesis problem can be transformed into a nonlinear programming problem with continuous decision variables. This idea has been stated and demonstrated in the studies by Umeda, Hirai, and Ichikawa (1972), Ichikawa and Fan (1973), Osakada and Fan (1973), Mishra, Fan, and Erickson (1973), and Himmelblau (1975). In order to obtain an optimal structure, redundant subsystems are usually inserted into a super structure in which it is hoped that the optimal structure is imbedded. For example, Figure 1 illustrates one use of the method for synthesizing a heat recovery network. The problem data and the stream specifications are shown in Table 1, and the problem is described in the tradition of problems like 4SP1 in Masso and Rudd (1969) and Lee et al. (1970). A decision is to be made on whether or not to use cold stream II to aid in cooling hot stream V. The problem is formulated with potentially redundant exchangers 2, 4, and 5 and the structural parameter α_{26}. α_{26} is the fraction of cold stream II that goes through exchanger 2. The strategy is, in this formulation, to convert the discrete decision of whether or not to use cold stream II to aid in cooling hot stream V into a problem

Table 1. Stream Specifications and Problem Data

Description	Units	Stream I	II	III	IV	V	VI	VII
Flow	g/s	1 260.00	504.00	1 260.00	Unknown	2 520.00	Unknown	Unknown
Inlet temperature	K	311.11	311.11	422.22	311.11	644.44	644.44	588.89
Outlet temperature	K	588.89	533.33	477.78	355.56	477.78	644.44	588.89
Boiling point	K	755.56	755.56	755.56	373.33	755.56	644.44	588.89
Liquid heat capacity	$kJ/kg\,K$	4.19	4.19	4.19	4.19	4.19	4.19	4.19
Film heat transfer coefficient	$W/m^2\,K$	1 703.49	1 703.49	1 703.49	1 703.49	1 703.49	8 517.45	8 517.45
Cost	$/g	0.00	0.00	0.00	1.10×10^{-7}	0.00	22.05×10^{-7}	5.20×10^{-7}
Heat of vaporization	kJ/kg	697.80	697.80	697.80	1 786.368	697.80	1 628.20	1 395.60
Inlet vapor fraction		0.00	0.00	0.00	0.00	0.00	1.00	1.00
Outlet vapor fraction		0.00	0.00	0.00	0.00	0.00	0.00	0.00

Approach temperature = 2.78°K
Heat exchanger cost equation = $\delta(aA^b)$
where δ = annual rate of return = 0.1
$a = 350$
$b = 0.6$
equipment downtime = 280 hr/yr
The cost of the network is the cost of utility streams + the cost of the exchangers, $/yr.
All heat exchangers are assumed to be countercurrent.

of optimizing over the continuous decision variable α_{26}. To avoid a cost discontinuity caused by introducing an exchanger we must, of course, require the cost of an exchanger to approach zero as its area does.

The notion that we have converted a discrete decision problem to a continuous one is invalid here. It may be observed that hot stream V has sufficient heat content to drive cold stream I to its final temperature. However, the transfer of heat in exchanger 1 is limited because an inequality constraint in exchanger 2 has to be satisfied. This constraint is the approach temperature requirement between the inlet hot stream and the outlet cold stream ($T_{12} \geqq 533.33° + \Delta T$, where ΔT is a minimum allowed approach temperature of, say, 2.78°K). By numerical computation one finds that the overall cost can be lowered if α_{26} is increased (see Figure 2). This increase in α_{26} lowers the flows of cooling utilities IV and VII. Ultimately, when the flow of cooling utility IV is zero, an optimal structure is obtained with a cost of 16 945 \$/yr. At this point, $\alpha_{26} = 0.688$.

Note, however, that when the flow of the cold stream through exchanger 2 is zero, and the heat exchanger 2 is totally neglected, a network with a cost of 6 864 \$/yr is obtained, as shown in Figure 3. Thus, a significant discontinuity, which we had hoped we had eliminated, has reappeared. It should be emphasized that the data for the problem and its formulation are important only in that they are plausible and that they help make this point.

The main observation may be summarized as follows. When certain subsystems are rendered redundant during optimization (by the associated flow or a split fraction taking on a value of zero), and if inequality constraints are associated with these subsystems which force constrained behavior elsewhere, discontinuities very likely still exist in the problem. One must still make a discrete decision about whether or not to introduce that subsystem. This observation means that if the structural parameters are to be used for a synthesis problem, and if inequality constraints are involved, the problem has to be formulated very carefully, if indeed it can be, to make it a continuous one.

LITERATURE CITED

Himmelblau, D. M., "Optimal Design via Structural Parameters and Non-linear Programming," U.S.-Japan Joint Seminar on Application of Process Systems Engineering to Chemical Technology Assessment, Kyoto (June 23-27, 1975).

Ichikawa, A., and L. T. Fan, "Optimal Synthesis of Process Systems. Necessary Condition for Optimal System and Its Use in Synthesis of Systems," *Chem. Eng. Sci.*, **28**, 357 (1973).

Lee, K. F., A. H. Masso, and D. F. Rudd, "Branch and Bound Synthesis of Integrated Process Designs," *Ind. Eng. Chem. Fundamentals*, **9**, 48 (1970).

Masso, A. M., and D. F. Rudd, "The Synthesis of System Designs-II Heuristic Structuring," *AIChE J.*, **15**, 10 (1969).

Mishra, P. N., L. T. Fan, and L. E. Erickson, "Biological Wastewater Treatment System Design," *Can. J. Chem. Eng.*, **51**, 694 (1973).

Osakada, K., and L. T. Fan, "Synthesis of an Optimal Large-Scale Interconnected System by Structural Parameter Method Coupled with Multilevel Technique," *Can. J. Chem. Eng.*, **51**, 94 (1973).

Umeda, T., A. Hirai, and A. Ichikawa, "Synthesis of Optimal Processing System by an Integrated Approach," *Chem. Eng. Sci.*, **27**, 795 (1972).

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Effect of a Surface Active Agent on the Viscosity of Suspensions

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It has long been known that the apparent viscosity of suspensions is a function of the volume fraction of suspended solids for given solids shape, size distribution, and surface properties (Ting and Luebbers, 1957; Thomas, 1963). Ting and Luebbers (1957) derived the following equation relating the volume fraction of solids x_v to the viscosity of the suspensions μ_{sp}:

$$\frac{x_v}{\mu_{sp}} = x_{v,\infty} - x_v \tag{1}$$

where $x_{v,\infty}$ is a characteristic slurry property at a constant temperature. Ting and Luebbers measured the viscosities of suspension of glass spheres and other narrowly sized particles in dense liquid media prepared by blending different liquids to match the density of solids. The experimental slurry viscosities as measured by a Brookfield viscometer at 20°C were satisfactorily correlated with x_v by plotting x_v/μ_{sp} vs. x_v, yielding $x_{v,\infty}$ as the intercept on both axes.

Reduction of the viscosity of suspensions might be technically desirable in operations such as filtration, crystallization, and other solid-liquid separation processes. This can be done, in principle, through the interface modifying properties of surface active agents. For example, the reduction of the viscosity of colloidal suspensions by the addition of tetrasodium phosphate has been discussed by Sennett and Olivier (1964). Taki Fertilizer Company of Japan developed a phosphoric acid process via the crystallization of calcium sulfate hemihydrate that utilizes a sulfonic acid surfactant (Slack, 1968), which has the beneficial effect of significantly reducing the slurry viscosity.

The purpose of the present work is to demonstrate the effect of a surfactant in reducing slurry viscosity and to present, at the same time, an improved method of presenting slurry viscosity data.

EXPERIMENTAL

A Brookfield model LVT viscometer was used to measure the apparent viscosities of suspensions prepared from dried calcium sulfate dihydrate (or hemihydrate) and 30 to 40% P_2O_5 phosphoric acid, containing about 2% by weight of free sulfate ions. The slurry was mixed for 30 min in a 400 ml Pyrex beaker with