Incorporating Toxicology in the Synthesis of Industrial Chemical Complexes

by

I.E. Grossmann, R. Drabbant and R.K. Jain

DRC-06-21-81

November 1981

Incorporating Toxicology in the Synthesis of Industrial Chemical Complexes

I.E. Grossmann*, R. Drabbant and R.K. Jain
Department of Chemical Engineering
Carnegie-Mellon University
Pittsburgh, PA 15213

Paper to be presented in the Annual AIChE Meeting,
Hev Orleans, November, 1981.

* Author to whom correspondence should be addressed.

Abstract

A systematic procedure is presented for synthesizing chemical complexes in which toxicology aspects are incorporated in addition to the economic considerations* Based on previous work by Grossmann and Santibanez, it is proposed that the problem be formulated as a bicriterion mixed-integer programming problem, in which the two basic objectives that are considered are the maximization of the net present value and the minimization of toxicity in the overall system. The use of two different types of toxicity indices is explored, and solution strategies based on the theory of multicriterion optimization are developed. The application of the strategies is presented through a simple example.

Scope

The chemical industry is facing nowadays two formidable problems. One is the shortage of energy sources, and the other one is the increasing evidence of the adverse effect of toxic chemicals in the environment. Both problems pose challenging demands in the field of Chemical Process Design and require that effective solutions be obtained. Whereas considerable research effort is being done on the problem created by the energy shortage, not much attention has been paid as to how toxicology aspects can be incorporated systematically in the design of chemical processes. In fact, there is currently in practice little guidance for design engineers on how to deal simultaneously with toxicology, and economic considerations.

This paper presents an initial step directed at incorporating toxicology in an important class of process synthesis problems; namely, in the synthesis of industrial chemical complexes. In this problem a set of chemicals that can be produced from a set of interconnected processes are considered as candidates for integrating a chemical complex. Given limits on the supplies and demands on the different chemicals, the problem consists in selecting the chemicals and processes that will integrate the complex in order to attain one or several basic design objectives.

This work deals specifically with the case when the objectives are the maximization of the net present value and the minimization of toxicity. Two indices for measuring toxicity which reflect different environmental policies are considered, and the use of systematic solution strategies based on multicriterion optimization theory are proposed.

Conclusions and Significance

Toxicology considerations have been incorporated in the synthesis of industrial chemical complexes by formulating a bicriterion mixed-integer linear programming problem, where toxicity is minimized and the net present value is maximized. It has been shown that two types of toxicity indices can be used: one which is dependent on the amount of chemicals, and another one which is only species dependent. The c-constrained method and a meaningful method for ideal compromise solutions have been suggested for generating noninferior configurations for the complex. The numerical results of an example have shown that the proposed formulations provide a powerful tool for decision* makers in order to establish proper trade-offs between toxicity and economic objectives.

Introduction

In the synthesis of an industrial chemical complex it is assumed that NP chemical processes involving NC chemicals in the form of raw materials and intermediate and final products, are candidates for integrating an industrial processing scheme. Given limitations on the supplies and demands of the chemicals, and one or more objectives that should be achieved in the design, the problem consists in determining the products to be produced, the raw materials to be consumed and the actual processes that will integrate the chemical complex. In order to consider systematically the alternative schemes for the complex, a general network configuration is postulated in which NC nodes of chemicals and NP nodes of processes are interconnected through streams. As shown by Grossmann and Santibanez (1980), this synthesis problem can be formulated as a mixed-integer linear programming problem. By defining p_j^ℓ, s_j^ℓ, as the purchases and sales of chemical j in the market ℓ, w_k as the flowrate of stream k, and y_i as a 0-1 binary variable that denotes the existence of a chemical process i, the constraint set is given by:

a) Material balances for nodes of chemicals

$$\sum_{\ell \in M} p_j^\ell + \sum_{k \in I(j)} w_k = \sum_{\ell \in M} s_j^\ell + \sum_{k \in O(j)} w_k \qquad j = 1,NC \qquad (1)$$

b) Material balances for nodes of processes

$$w_k = \nu_k w_{m_i} \qquad k \in L_i \ , \ k \neq m_i \ , \ i = 1, NP \qquad (2)$$

$$w_k \geq 0$$

c) Constraints on sales and purchases

$$\left.\begin{array}{l} \underline{p}_j^\ell \leq p_j^\ell \leq \overline{p}_j^\ell \\ \underline{s}_j^\ell \leq s_j^\ell \leq \overline{s}_j^\ell \end{array}\right| \begin{array}{l} j = 1, NC \\ \ell \in M \end{array} \qquad (3)$$

d) Condition for existence of processes with bounded capacities

$$\left.\begin{array}{l} \underline{C}_i\, y_i \le w_{m_i} \le \overline{C}_i\, y_i \\ y_i = 0,1 \end{array}\right\} \quad i = 1,NP \qquad (4)$$

where the v_ℓ represents coefficients for the material balances in each process, m_i is the index for the main product produced by process i, I(j) is the index set of streams that produce chemical j, O(j) is the index set of streams that consume chemical j, M is the index set for the different markets and L_i is the Index set of streams associated with process i; $\underline{p}_j^\ell$, $\overline{p}_j^\ell$, $\underline{s}_j^\ell$, $\overline{s}_j^\ell$, $\underline{C}_i$, $\overline{C}_i$ are lower and upper bounds for purchases, sales and process capacities.

A suitable economic objective function for this problem is for instance the maximization of the net present value which can be expressed as

$$f_1 = NPV = -\sum_{i=1}^{NP} (\alpha_i w_{m_i} + \beta_i y_i + \varphi_i w_{m_i}) + \sum_{j=1}^{NC} \sum_{\ell \in M} (\gamma_j^\ell s_j^\ell - \mu_j^\ell p_j^\ell) \qquad (5)$$

where the first summation includes both the investment cost, $\alpha_i w_{m_i} + \beta_i y_i$, and operating cost, $\varphi_i w_{m_i}$ that corresponds to each process i in terms of the production of the chemical m_i. The second summation involves the sales and purchases of the chemicals in the different markets in terms of the prices γ_j^ℓ, μ_j^ℓ. Note that when the binary variable y_i is equal to zero, constraint (4) will force process i to be excluded from the general configuration. In the case when this variable is equal to one, process i is included in the configuration and a fixed cost charge β_i is incurred in (5) so as to reflect the economies of scale in the investment cost.

This synthesis problem has also been formulated previously in the literature in the context of the petrochemical industry as a linear programming problem with different objective functions. Stadtherr et al. (1976) considered the minimization of feedstocks as an objective, whereas Sophos et al. (1980) have considered a multlobjectIve formulation in which the change of thermodynamic availability is maximized, and the entropy creation and feedstock consumption are minimized. In this work it is proposed to incorporate toxicology considerations in this synthesis problem. Previous work has neglected the undesirable effects of toxic chemicals in industrial complexes, and since this is clearly a very relevant issue for which there is increasing concern in practice, there is a need to account systematically for this aspect in this synthesis problem.

Approaches for incorporating toxicology

The most common approach that is used to consider the effect of toxic chemicals in decision-making is the cost-benefit analysis. In the context of the synthesis problem of chemical complexes this would mean that the damage produced by toxic chemicals should be reflected ultimately as an "operating" cost. This would presumably have the advantage of establishing a unique and non-ambiguous trade-off between toxicity and the economic objective. However, as indicated by Fischhoff (1981), there are clearly many shortcomings in the cost-benefit approach. Firstly, it requires a large amount of information for which there is considerable uncertainty. For instance, it is very difficult to predict within a reasonable degree of accuracy the type and amount of damage that will be Inflicted upon various species in the environment. Secondly, this approach also requires assigning an economic value to the damage which in general is quite arbitrary, since other important issues that are of social nature and that cannot be quantified properly are also involved. Therefore, it is very questionable that a cost-benefit analysis can provide a solution that would be undisputed by industry, Government and the public. It should then be recognized that due to the Inherent conflict of minimizing toxicity and maximizing economic gains, the methodology that is to be used cannot be expected to provide simple and unique answers.

Since a systematic procedure for resolving the conflict between toxicity and an economic objective has to be more open-ended than the cost-benefit analysis, a more appropriate approach is to use a multicriterion optimisation formulation. This would imply that the toxic effects of chemicals should be reflected through an objective function or index that ought to be minimized. As shown below, indices for toxicity can be developed using the limited amount of information that can be obtained, in this way, the optimization of this index can be considered as an objective in its own right together with other specified objectives that are to be achieved. Although it is clear that the multicriterion optimization approach will not lead to unique answers, it can provide a powerful tool for rational decision-making as shown below.

The present paper will be restricted to the case when the two objectives that are involved in the synthesis of industrial chemical complexes are the maximization of the net present value and the minimization of toxicity. The crucial aspects in this work are the development of indices for measuring toxicity, and the derivation of meaningful solution strategies that provide guidelines to the decision-maker for resolving the conflict between the two objectives.

Indices for Toxicity

Toxicity is basically a relative term which reflects the potential of a chemical to do harm to biological tissue. In principle, no chemical is entirely safe nor entirely harmful since any chemical can come in contact with biological tissue without producing an effect on it, provided the concentration of the chemical is below a minimal effective level* Clearly, there are chemicals that are more toxic than others and, hence, some sort of quantitative measure of toxicity is required for the chemical products. In fact, several methods of reporting toxicity quantitatively have been suggested (Loomis, 1979). One of these, known as the lethal dose U>$_{50}$> is the dose of a compound which will produce death in 50% of the test animals, and is of course dependent on both the test specimens and the means by which they come into contact with the chemical. Another common method of reporting chemical toxicity is the threshold limiting value of the chemical which refers to maximum airborne concentrations of substances that can be allowed. Specifically, this value represents conditions under which it is believed that most humans may repeatedly be exposed to in their working environment on a daily basis without adverse effect.

Since both, LD_{50} and threshold limiting values are available for a large number of chemical (see for instance, Christensen and Luginbyhl, 1975), it would seem that an index which reflects toxicity of the chemicals involved in an industrial complex could be expressed in terms of these parameters. It must be noted, however, that this index would require the assumption of a particular biological species that would be affected and a given way of exposure (e.g. airborne, oral, skin) of the chemical. Given that such an assumption is made, two possible alternatives will be considered in this paper for the derivation of the toxicity index. In one of them the index reflects both the nature and amount of the chemicals, while the other is only dependent on the nature of the chemical. That is, in the latter the mere presence of a chemical is of importance regardless of the quantity.

For the first index, it will be assumed that for all chemicals there is the sane probability of exposure. The potential damage is then proportional to both the amount and toxicity of each chemical, and hence the index can be expressed as

$$f_2' = \sum_{j=1}^{NC} W_j/\tau_j \qquad (6)$$

where

$$W_j = \sum_{i \in M_j} p_i^f + \sum_{k \in n(j)} W_k \qquad (7)$$

represents the total amount of chemical j, and τ_j is either its corresponding LD_{50} or threshold limiting value.

When only the nature of the chemical species is considered the basic objective would be to minimize the presence of the most toxic chemicals. This can be achieved by defining the index

$$f_2'' = \max_j \{z_j/T_j\} \tag{8}$$

where y_j is a 0-1 binary variable that denotes the existence of chemical j in the complex. This binary variables must satisfy the constraint

$$y_j = 0,1 \qquad j = 1,NC \tag{9}$$

in order to reduce to zero the amount of chemical j when it is excluded from the configuration. Note that this constraint becomes redundant when the binary variable is one since U is an arbitrary upper bound.

In order to illustrate some inherent limitations with the index in (8) consider the simple example that is given in Table 1. When comparing alternatives A and B, this index is not able to discriminate between them since both alternatives involve the most toxic chemical, and hence $f_2'' = 2.8$. Furthermore, suppose that no feasible configuration can be obtained by eliminating this chemical in which case this index fails to provide any useful information. Clearly, when this case arises the procedure would be to remove the next chemical that is highest in toxicity. In fact, this can be achieved by defining the following index which is given as a weighted sum,

$$f_2'' = \sum_{j=1}^{NC} \nu_j z_j$$

$$\nu_1 = 1, \quad \nu_{j+1} = 2\nu_j \qquad j = 1, NC - 1 \tag{10}$$

where the chemicals are ranked in increasing order of toxicity, $1/T_j$. That is, the least toxic chemical has the weight ν_1 and the most toxic chemical has the weight ν_{NC}. In this way, the index in (10) will accomplish the objective of minimizing the largest toxicity that is feasible since $\nu_j > \sum_{k=1}^{j-1} \nu_k$. For instance, in the example of Table 1, the index would provide a value of 23 for alternative A and a value of 25 for alternative B, and hence the first alternative would be preferred since chemical 3 is less toxic than chemical 4. Note that actually the index f_2'' only requires information of relative degrees of toxicity, and therefore it is not very sensitive to the LD_{50} or threshold limiting values.

In summary, the two models to be considered for incorporating toxicology in the synthesis of industrial chemical complexes are given as follows:

a) For toxicity index that is amount dependent

$$\max_{x'} \; f_1 = NPV$$

$$\min_{x'} \; f_2' = \sum_{j=1}^{NC} w_j / T_j \qquad (11)$$

$$\text{s.t.} \quad x' \in Q'$$

b) For toxicity index that depends only on the nature of the chemical species

$$\max_{x''} \; f_1 = NPV$$

$$\min_{x''} \; f_2'' = \sum_{j=1}^{NC} \nu_j z_j \qquad (12)$$

$$\text{s.t.} \quad x'' \in Q''$$

where x and Q represent the variables and the constraint set as defined respectively for both cases in (1)-(4), (7),(9).

Solution strategies

Problems (11) and (12) correspond to mixed-integer bicriterion optimization problems. Hence, there will exist in general an infinite set of noninferior solutions which will define a trade-off curve as shown in Fig. 1. Note that at a noninferior solution it is not possible to obtain a simultaneous improvement in the two objectives for feasible perturbations in the variables. More specifically, a local noninferior point x^* is defined as the one for which there does not exist a small perturbation $\delta x \neq 0$, such that for $x^* + \delta x \in Q$

$$f_1(x^* + \Delta x) \geq f_1(x^*) \quad , \quad f_2(x^* + \Delta x) \leq f_2(x^*)$$

$$\text{and} \quad f_1(x^* + \Delta x) > f_1(x^*) \ \text{or} \ f_2(x^* + \Delta x) < f_2(x^*) \quad . \tag{13}$$

Assuming that a set of noninferior solutions exists for problem (10) and (11), basically two solution strategies can be considered. In the first one noninferior solutions are generated so that they can be analyzed by the decision-maker who may select one of them. In the second strategy an ideal compromise solution between the conflicting objectives is sought.

A simple procedure for generating noninferior solutions is the ε-constrained method (Haimes et al., 1975), in which one of the objectives is optimized subject to constraining the other objective to a limit ε. The logical choice for the constrained objective in this problem is the net present value f_1, which leads to the mixed-integer problem

$$\begin{aligned} \min_{x} \quad & f_2 \\ \text{s.t.} \quad & f_1 \geq \epsilon \\ & x \in \Omega \end{aligned} \tag{14}$$

where ε is an adjustable parameter that lies in the interval $[f_1^L, f_1^U]$ as shown in Fig. 1; f_1^L is obtained by minimizing f_1 over the domain Ω, and f_1^U is obtained by maximizing f_1 over the same domain. It should be noted that as long as the feasible region Ω is non-empty and a local minimum solution exists in (14), then this solution will correspond to a noninferior point (Haimes et al., 1975). This result holds even if the problem is nonconvex as in fact is the case of (14) since it corresponds to mixed-integer linear programming problem.

This strategy can then be used to determine configurations of chemical complexes in which the toxicity is minimized while satisfying a specified minimum ε for the net present value. By selecting different values of ε a set of noninferior configurations can be generated. Clearly, this procedure may bias the decision-maker towards schemes that are economically attractive, that is when ϵ is positive. But the important point is that toxicity will be minimized under the economic constraint that is imposed.

As indicated above, an alternative strategy for solving this bicriterion optimization problem is to search for an ideal compromise solution, in which both objectives sacrifice the least that is possible with respect to their maximum attainable benefit. This can be accomplished with the following solution procedure.

Suppose that f_1^U and f_2^L are the values of f_1 and f_2 when optimized respectively over the constraint set Ω. Then the point (f_1^U, f_2^L) can be defined in the output space as the utopia point which is illustrated in Fig. 1. In general this utopia point will be infeasible as it will lie outside from the feasible output space Λ given by

$$\Lambda = \left\{ (f_1, f_2) \mid x \in \Omega \right\} \qquad (15)$$

An ideal compromise solution can be obtained by determing the noninferior solution which is closest to the utopia point. This requires that the distance between the utopia point and the noninferior solution be at a minimum. This distance δ_p is dependent on the particular norm p that is selected since

$$\delta_p = \left[(f_1^U - f_1)^p + (f_2 - f_2^L)^p \right]^{1/p} \quad 1 \leq p \leq \infty \qquad (16)$$

The minimum distances with respect to the utopia point are illustrated in Fig. 1 for the norms $p = 1$ and $p = \infty$.

Clearly, the distance δ_p is not invariant to the relative magnitudes of f_1 and f_2, and hence the definition of an ideal compromise solution is rather arbitrary. However, a meaningful definition of the ideal compromise is obtained by scaling f_1 and f_2 between values of zero and one, such that the zero value corresponds to the minimum net present value and toxicity on the non-inferior surface, while the value of one would correspond to the maximum net present value and toxicity on the same surface. Thus, the following normalization can be employed

$$\hat{f}_1 = (f_1 - f_1^L) / (f_1^U - f_1^L)$$

$\hat{f}_2$ - « 2 - 0 / («2° - f2b (17)

where $1-\hat{f}_1$ and $\hat{f}_2$ represent fractional deviations with respect to the normalized Utopia point (1,0).

The resulting formulations for the ideal compromise solution in which the fractional deviations are minimized are then given as follows for the two extreme norms:

a) For p - 1 min (1 - ^) + ^ 2 (18)

x

S.t. X € Q

b) For p » oo min max {(1 - ^ H) , f^) (19a)

x

s.t. x e a

which can also be formulated as

min p

s.t. p ≥ 1 - ?x (19b)

x € a

By selecting the norms p = 1 and p » oo the formulations above give rise to mixed-integer linear programs since the objective functions in (18) and (19b) are linear. If the Eucledian norm p « 2 were to be selected the objective function would be quadratic, and hence the problem would be nonlinear. Yu (1973) has shown that the solution obtained with the norm p • 1 will always correspond to a noninferior point even if the output space is nonconvex. In the case of p • oo the solution may not necessarily be a noninferior point for the nonconvex case, although it should be pointed out that this failure will tend to occur only in pure integer programs.

It should be noted also, that the solutions obtained with the norms p » 1 and p * oo will in general not be the same. Since in the case of p = 1 the sum of fractional deviations is minimized, one can expect that the deviations of the objectives will be in general different* For the case p *oo, the largest deviation with respect to the Utopia point is minimized, and hence, one can expect that at the solution the deviation of the two objectives will be the same, and then the sum of fractional deviations will not necessarily be at a minimum. As shown by Freimer and Tu (1976) the solutions obtained with the two norms can be regarded as bounds for an ideal compromise. In the case of p = 1 the group utility is optimized, whereas in the case p «oo the regret of each individual objective is minimized. It is interesting to note that the latter case corresponds to criterion of minimizing equity regret that has been suggested by Ashford (1981) for regulatory decisions.

Example

Consider the general configuration of the chemical complex presented in Fig. 2 in which the following alternatives are included for seven different processes and nine different chemicals. Product G is to be produced from chemical E so as to satisfy a fixed demand in the local market. Chemical E can either be imported or produced from chemical B and D with the two different processes 2 and 3. D can be obtained from the raw material A and from chemical F which is a by-product in the manufacture of 6. The possibility of using F together with H so as to obtain products I and J is also included in the general scheme. It must be noted that except for 6, the purchases and sales of the other chemicals are optional and limited by upper bounds. Therefore, the simplest alternative is to have only process 4 to manufacture chemical 6. The economic data, coefficients for material balances and the toxicity data are given in Tables 2, 3 and 4. The numerical results that are presented below were obtained with the LINDO (1980) computer package for mixed-integer programming.

The configurations obtained by optimizing individually the net present value and the toxicity are shown in Fig. 3, and they represent the extreme choices as far as the two objectives are concerned. Therefore, the function values f_1 and f^ will provide lower and upper limits for each objective. As can be seen in Fig. 3 the maximization of the net present value leads to a complex where all the chemicals are included and only process 3 is excluded. The minimization of the two indices for toxicity lead to the same configuration which includes only process 4 for manufacturing chemical G. The index f_2' which is amount dependent and has been scaled by 10^{-6}, yields a negative net present value, whereas the other index f_2'' yields a positive net present value. This difference is due to the fact that in the former case the production of 6 is only the fixed local demand, whereas in the latter case the production is increased to **satisfy** also the International demand which results in increased revenues.

For the toxicity index f_2', the ε-constrained method was used to generate several points of the noninferior surface which is plotted in Fig. 4. The configurations of the complex corresponding to various values of c are shown in Fig. 5. It is interesting to note that significant changes occur in these configurations for different values of c* For instance, when e changes from $1150 x 10^6 to $1250 x 10^6, process 5 is removed and processes 1 and 3 are introduced. Increasing c to $2500 x 10^6, reintroduces process 5, and causes process 2 to be selected instead of process 3. The ideal compromise configurations for the norms p • 1 and p »oo are shown in Fig. 6. The main reason for the remarkable difference in these configurations is the nonconvexity in the noninferior surface as shown in Fig. 4. As is well known(Haimes et al.,1975), the noninferior solutions in the concave portion where the solution of p ^{3} GO is located, cannot be reached with the p » 1 norm. Note that for the latter norm the net present value has a deviation of 0.56 with respect to the Utopia point, whereas the toxicity has a deviation of only 0,24. For the case when p *oo both objectives have the same deviation of 0.4. Since with both norms the sum of deviations is 0.8, the p =oo solution would correspond to the fairest compromise.

The noninferior surface obtained with the toxicity index f_2^{if}, that is species dependent,is highly nonconvex as is shown in Fig. 7. Three configurations of the complex that were obtained with the e-constrained method are shown in Fig. 8. Note that since the index f_2^{it} does not penalize for the amount of the chemicals the net present values are substantially higher than the ones obtained with the index f^ as seen in Fig. 8. The ideal compromise configurations for p « 1 and p «oo are shown in Fig. 9. Deviation values of 0.09 and 0.27 were obtained respectively in the net present value and toxicity for the norm p * 1, and deviations of 0.26 were obtained for both objectives when p =orTi# in this case it would seem preferable to select the configuration for p • 1 since its deviation for the toxicity is only 0.01 higher than for p «oo, while its deviation for the net present value is reduced by 0.17.

Discussion

As shown in the example above, interesting insights can be obtained with simple bicriterion formulation that has been proposed for incorporating toxicology in the synthesis of chemical complexes. A simple example has been presented to emphasize the main ideas of the proposed approach. A large application example related to the petrochemical industry can be found in Drabbant (1981).

The formulation that has been presented in this paper clearly constitutes only an initial step for treating toxicology aspects in the synthesis of industrial chemical complexes. For instance, the fact that the toxicity indices that have been presented assume a particular biological species and a given way of exposure would suggest that perhaps it would be more appropriate to consider several toxicity indices, each one being related to different species and ways of exposure.

However, it should also be recognized that there are inherent limitations in the kind of information that is currently available in toxicology* For example, since experimental tests can not be performed on all biological species (particularly on humans), this implies that extrapolation of data to other species is inevitable. Therefore, one can expect that more general and meaningful toxicity indices will be developed only if further advances are made in the field of toxicology. Also, it should be pointed out that the formulation that has been presented could be extended in a number of ways by incorporating additional constraints and objective functions. An exsaple of the former would be limits on emissions of the chemicals, and an example of the latter would be the maximisation of energy conservation in the complex.

Despite the limitations cited above, the important point in the formulations that have been presented in the paper is that they provide a basic framework for establishing proper trade-offs between toxicity and the economic objective, without requiring excessive information on the damage that can be caused by the toxic chemicals. Note that no claim is made about obtaining unique solutions with the proposed approach as would be in the case of the cost-benefit analysis. Since choices such as toxicity indices, €-limits or norms for ideal compromise solutions are entirely dependent on the decision-maker, they can be used to provide a variety of useful guidelines and insights# However, it should be emphasized that the responsibility for the ultimate decision has to lie in the decision-maker and not in the proposed methodology.

References

Ashford, N.A., "Alternatives to Cost Benefit Analysis in Regulatory Decisions[11], Annals of the New York Academy of Sciences, 363, 129(1981).

Christensen, H.E. and T.T. Luginbyhl (Eds.), "Registry of Toxic Effects of Chemical Substances", Tracor Jitco, Inc., Rockville, Maryland (1975).

Drabbant, R., "Incorporating Toxicology into the Synthesis of Industrial Chemical Complexes[11], M.S. thesis, Carnegie-Mellon University (1981).

Fischhoff, B., "Cost-Benefit Analysis: An Uncertain Guide to Public Policy", Annals of the New York Academy of Sciences, 363, 173 (1981).

Freimer, M. and L. Tu, "Some New Results on Compromise Solutions for Group Decision Problems", Management Science, 22, 628 (1976).

Grossmann, I.E. and J. Santibanez, "Applications of Mixed-Integer Linear Programming in Process Synthesis", Computers & Chenu Eng., 4, 205 (1980).

Baimes, Y.Y., W.A. Hall and H.T. Freedman, "Multiobjective Optimization in Water Resource Systems", Elsevier Scientific, Amsterdam (1975).

Linear Interactive Discrete Optimizer (LINDO), Users Manual DEC-System (1980).

LoondLs, T.A., "Essentials of Toxicology", Lea and Ferbiger, Philadelphia (1978).

Sophos, A., E. Rotstein and G. Stephanopoulos, [lv]Multiobjective Analysis in Modeling the Petrochemical Industry[1]; Chem. Eng. Sci., 35, 2415 (1980).

Stadtherr, M,D. and D.F. Rudd, "Systems Study of the Petrochemical Industry", Chem. Eng. Sci., 31, 1019 (1976).

Yu, P.L., "A Class of Solutions for Group Decision Problems", Management Science, 19, 936 (1973).

Table 1, Alternative configurations Involving different chemicals

Chemical	$1/\tau_i$	ν_i	Alternatives A	Alternatives B
1	0.5	1	x	x
2	0.9	2	x	
3	1.6	4	x	
4	2.2	8		x
5	2.8	16	x	x

Table 2. Economic Data for the Chemical Complex

Life of project: **10 years**

Annual interest rate: 10%

a) Investment and operating cost of processes

Process	Operating cost ($/kg)	Investment cost Fixed(10^6 $)	Investment cost Variable($/kg)
1	0.1	45.3	0.9
2	0.12	45.2	1.15
3	0.25	32.2	3.09
4	0.15	48.1	1.64
5	0.12	23.3	1.27
6	0.28	46.2	1.31
7	0.35	32.8	2.23

Minimum capacity of processes: 10,000 tons/yr

b) Prices of chemicals

Chemical	Purchases Market	Price($/kg)	Upper limit(10^3 tons/yr)
A	Local	0.5	400
B	Local	0.7	50
	International	1.1	200
C	Local	1.2	320
E	International	3.7	200
H	Local	1.7	10
	International	1.9	50

Chemical	Sales Market	Price($/kg)	Upper limit(10^3 tons/yr)
F	Local	4.8	60
G	Local	6.5	10 (fixed)
	International	6.2	50
I	Local	4.6	100
	International	4.2	50
J	Local	7.2	40
	International	7.0	20

Table 3. Material Balance Parameters for Chemical Complex

Process	Main Product	Chemical (parameter)
1	D	A(1.2), F(0.2)
2	E	D(0.8), B(0.5)
3	E	D(0.7), B(0.4)
4	G	E(1.8), F(0.7)
5	H	A(0.3), C(1.1)
6	I	F(0.3), H(1.3)
7	J	I(1.1)

Table 4. Toxicity Data for Chemical Complex

	Chemical									
	A	B	C	D	E	F	G	H	I	J
LD_{50}(g/kg)	2	5	2.5	2	1	0.0714	0.4	0.6667	10	0.333

Figure 1. Plot of noninferior solutions and ideal compromise solutions for the bicriterion optimization problem.

Figure 2. General configuration of the chemical complex.

Figure 3. Optimal configurations for: (a) maximum net present value, (b) minimum toxicity with f_2', (c) minimum toxicity with f_2''.

Figure 4. Noninferior surface for normalized toxicity index f_2' and ideal compromise solutions for the norms $p=1$, $p=\infty$.

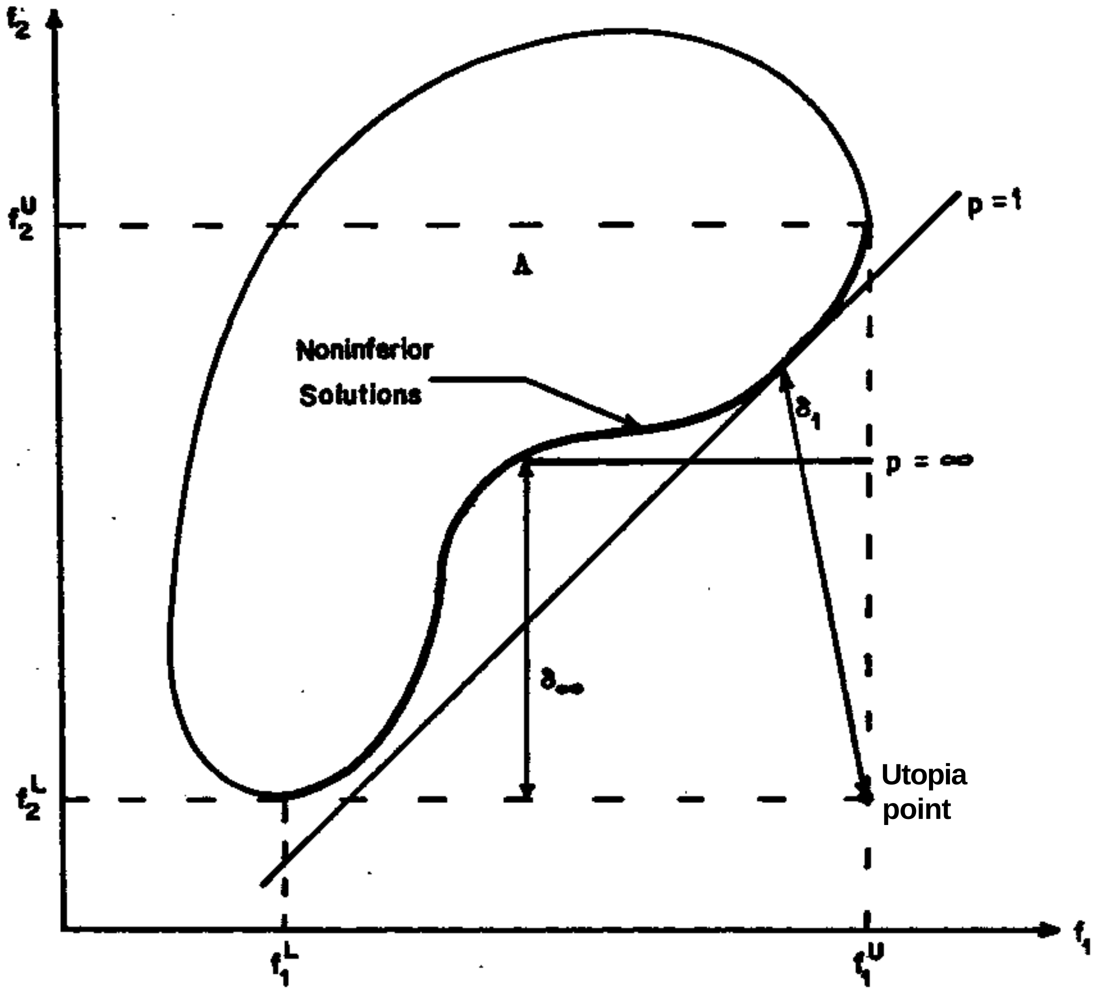
Figure 5. Configurations of the complex obtained by minimizing the index f_2^* with different values of ϵ.

Figure 6. Ideal compromise configurations obtained with the toxicity index f_2'.

Figure 7. Noninferior surface for normalized toxicity index f_2'' and ideal compromise solutions for the norms $p=1$, $p=\infty$.

Figure 8. Configurations of the complex obtained by minimizing f_2'' with different values of ϵ.

Figure 9. Ideal compromise configurations obtained with the toxicity index f_2''.



f2
f2U
f2L
A
Noninferior
Solutions
p = 1
p = ∞
δ1
δ∞
Utopia
point
f1L
f1U
f1

Fig. 1

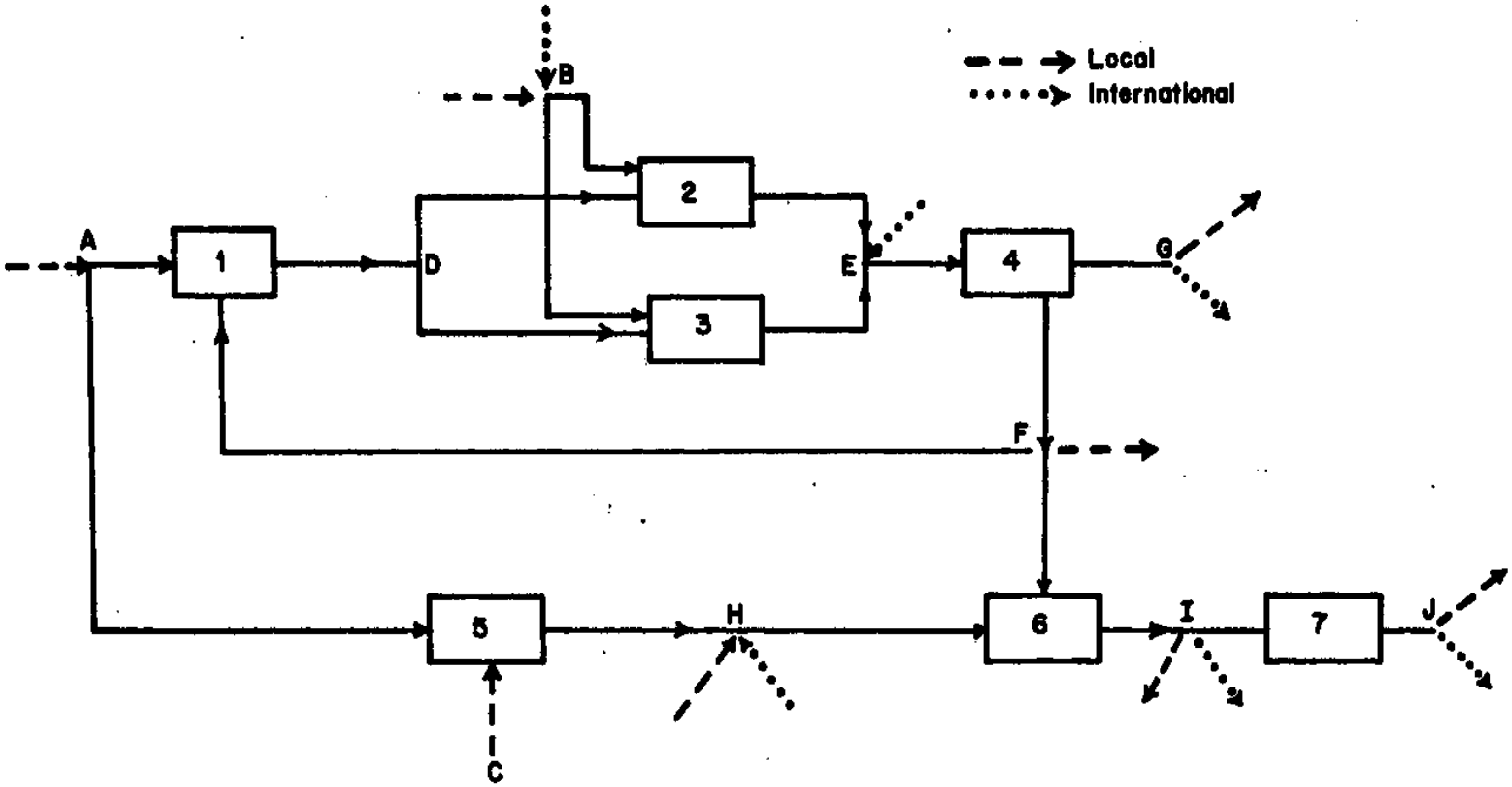
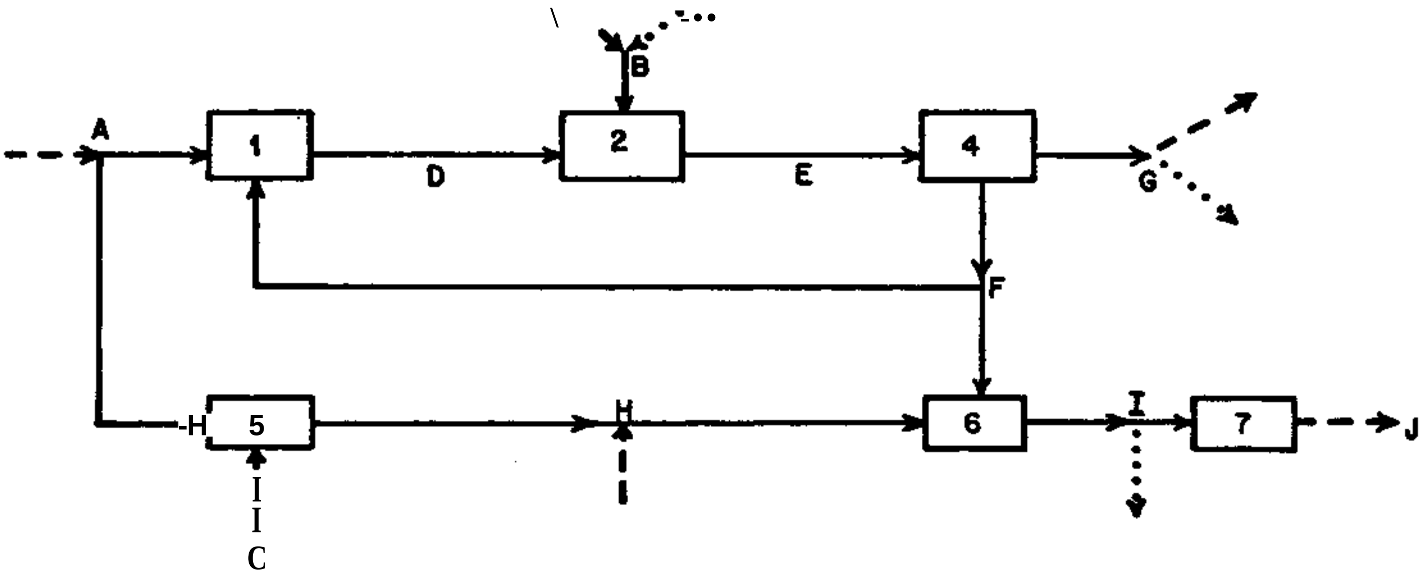
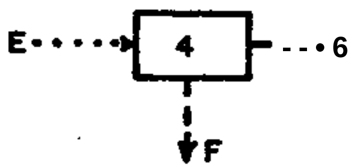


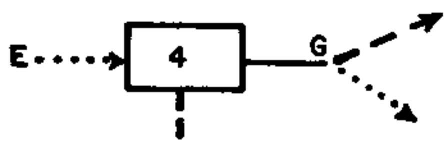
Fig. 2



(o) f, = \$ 3059 x10^6
f_2' =1266
f_2'' = 1023



(b) f, = -\$ 276 x10^6
f_2'=141



(c) t, = \$491x10^6
f_2'' = 672

Fig. 3

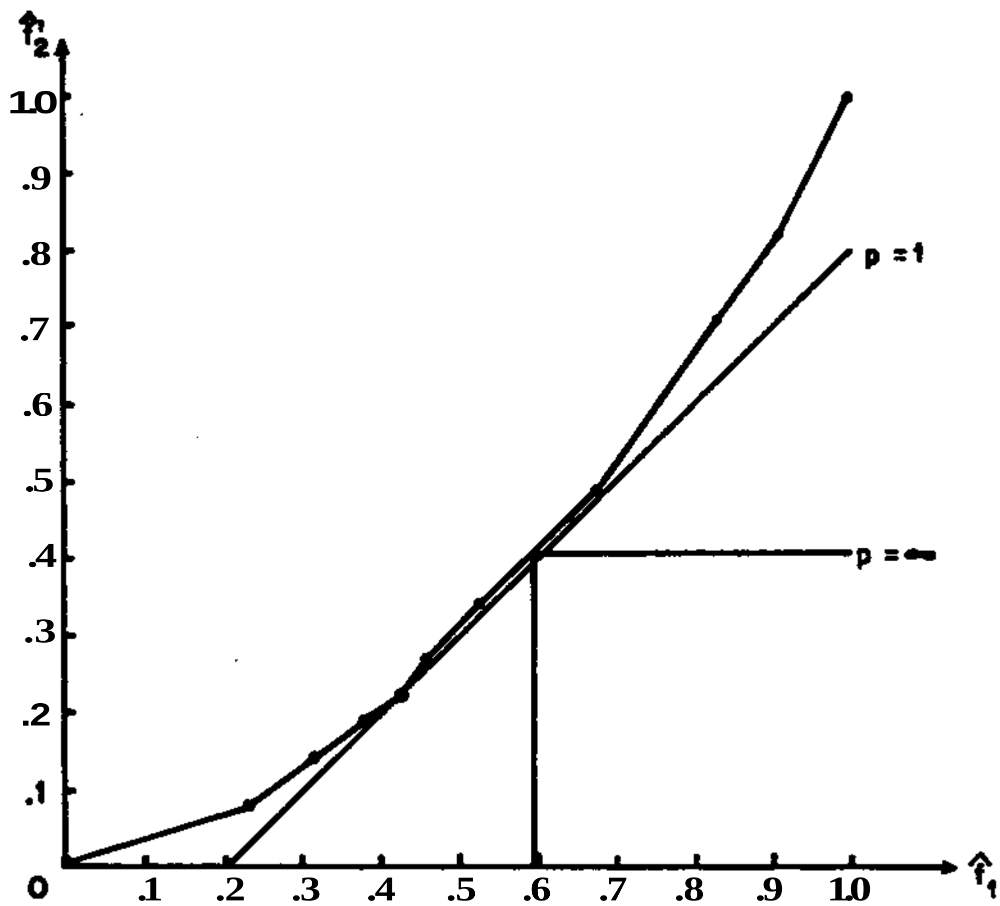
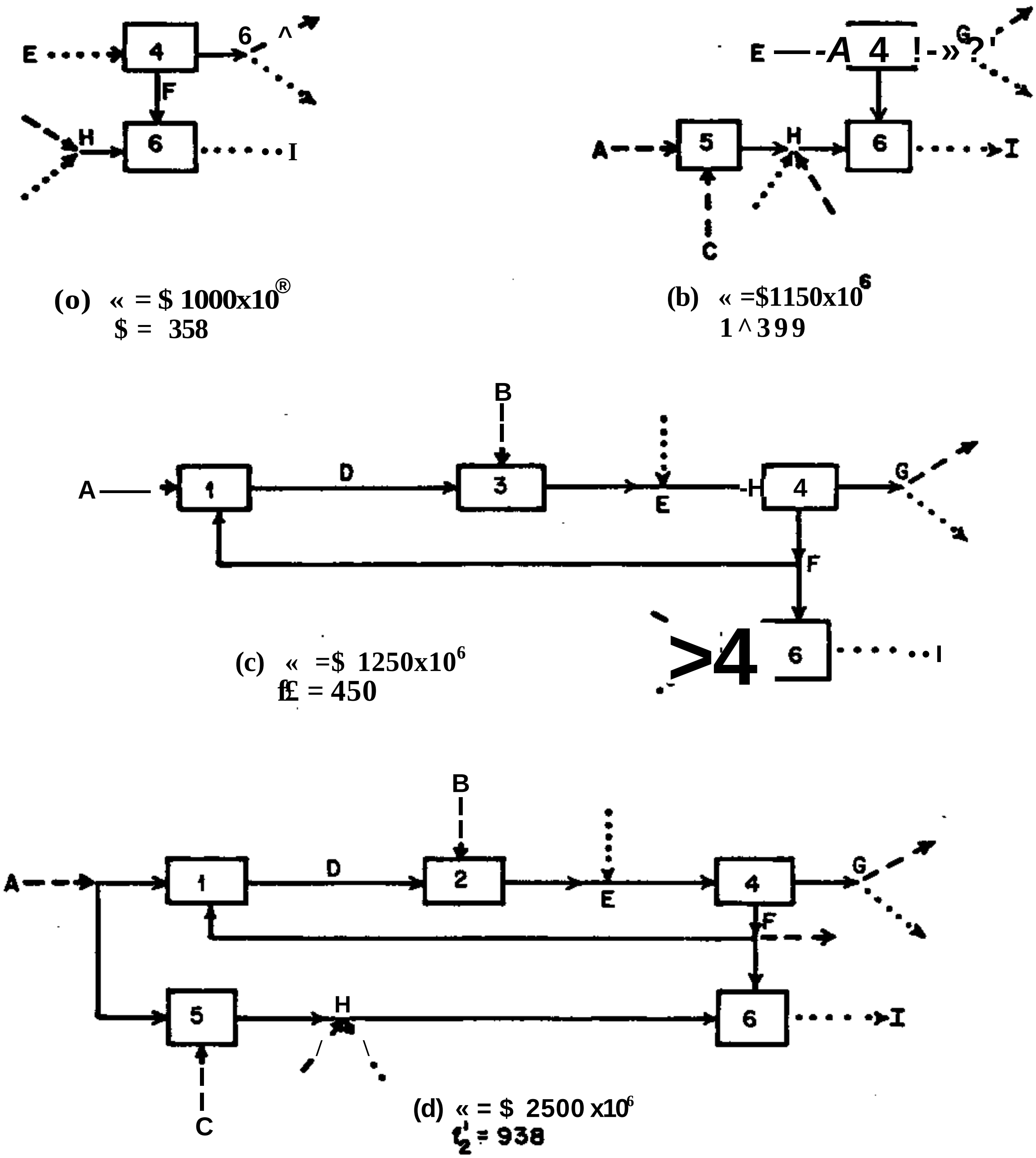


Fig. 4



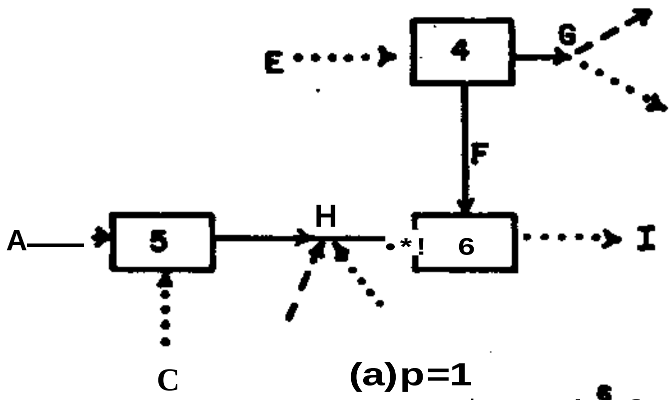
(o) « = $ 1000x10®
$ = 358

(b) « =$1150x10[6]
1^399

(c) « =$ 1250x10[6]
£ = 450

(d) « = $ 2500 x10[6]
t_2^1 = 938

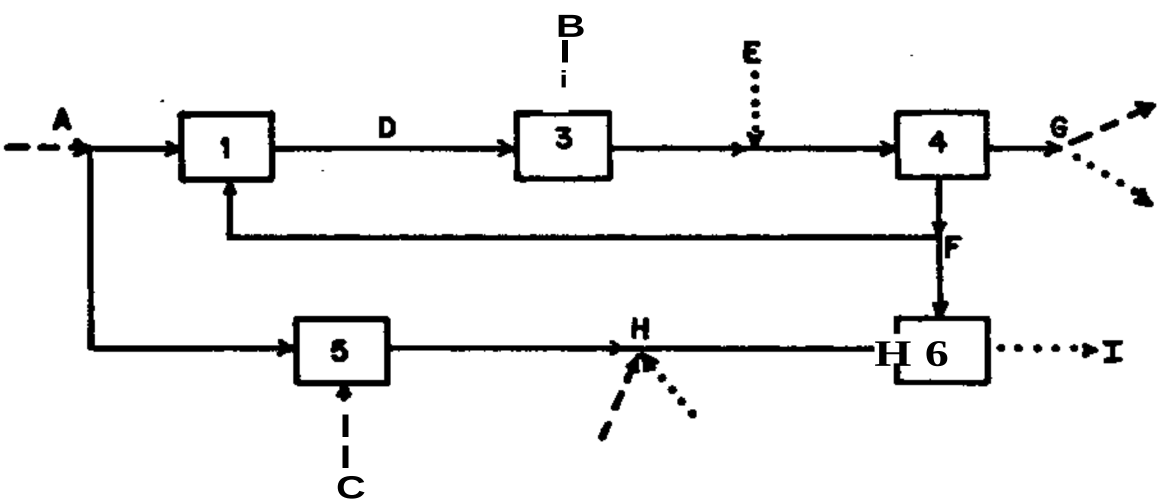
Fig. 5



(a) p=1

^ = $ 1199 x iO^{6}, f£ = 411

$\hat{\xi}_1$ = 0.44, f_{ξ_2} = 0.24



(b) P = -

^ =$1709x10*, 1^=596

$\hat{\xi}_1$ = 0.6 , \ = 0.4

Fig. 6

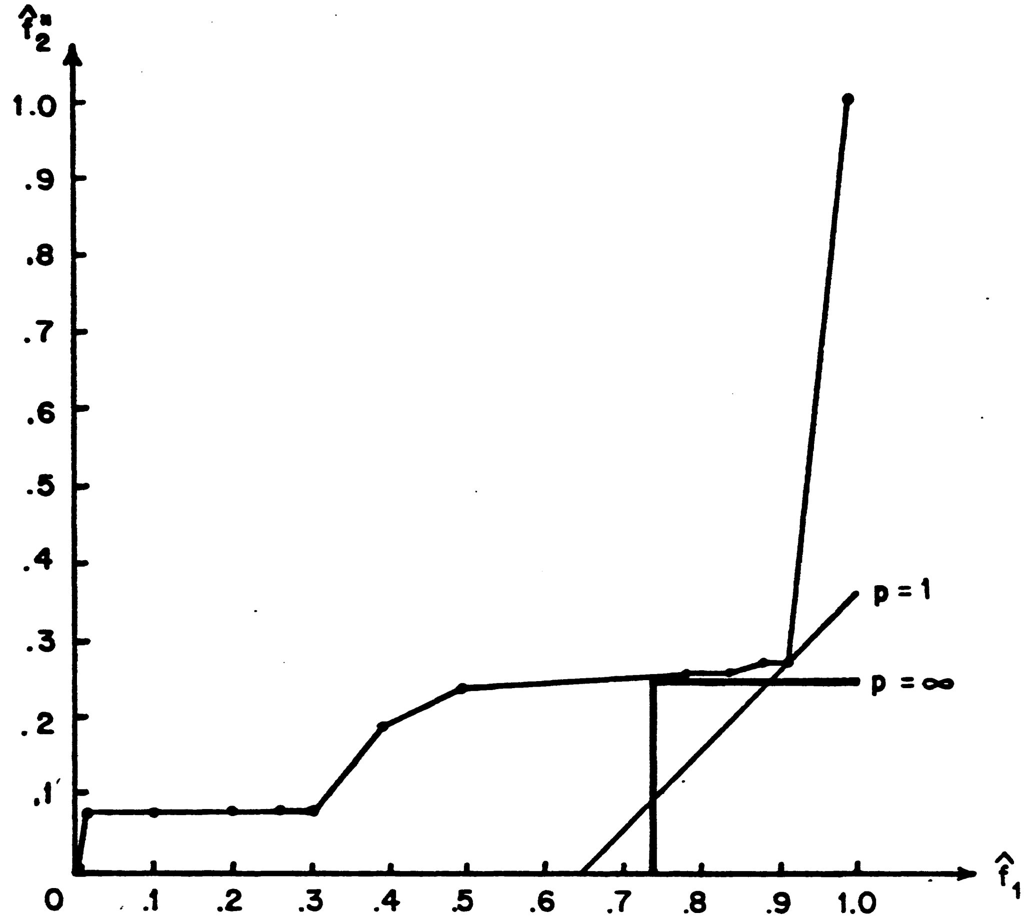
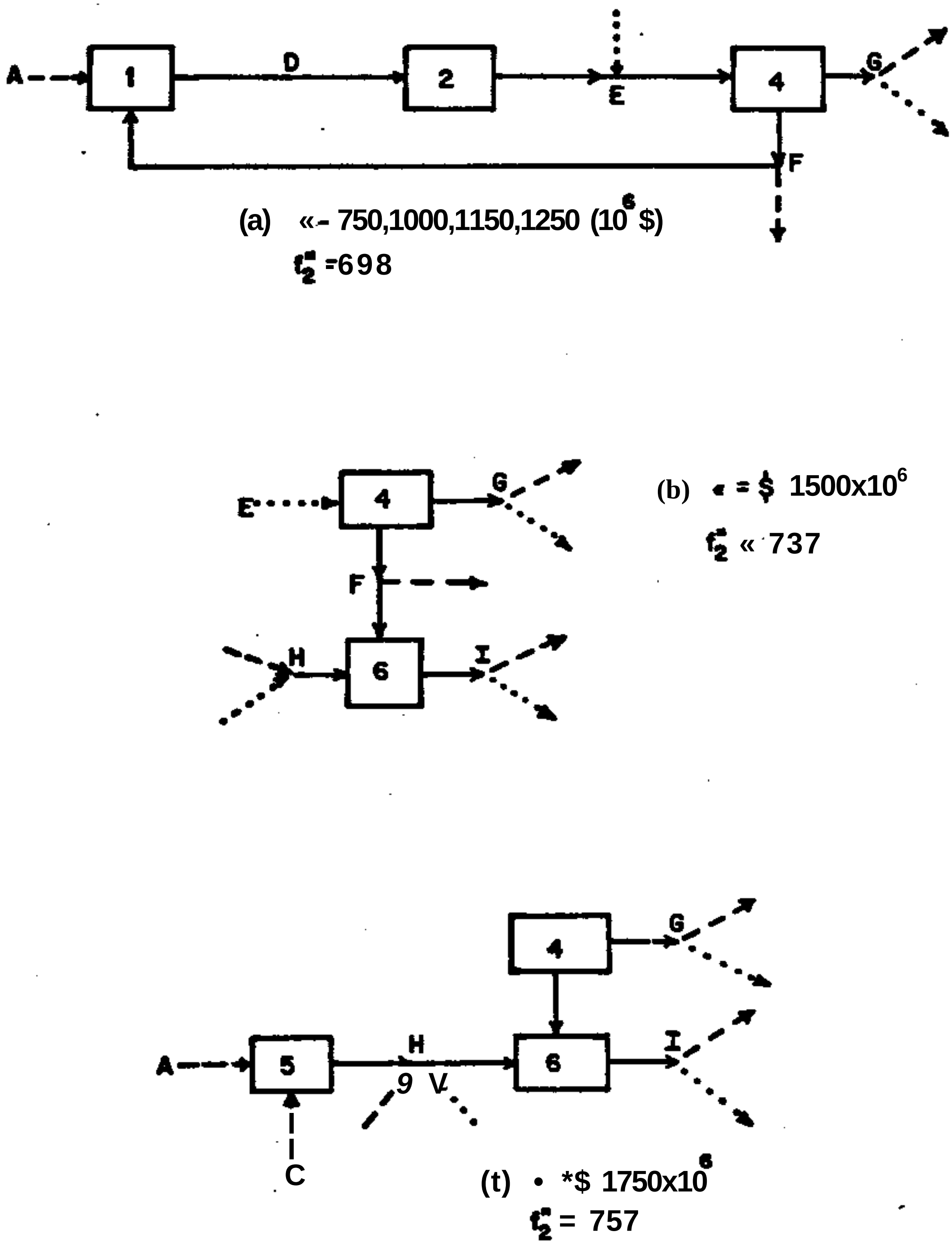
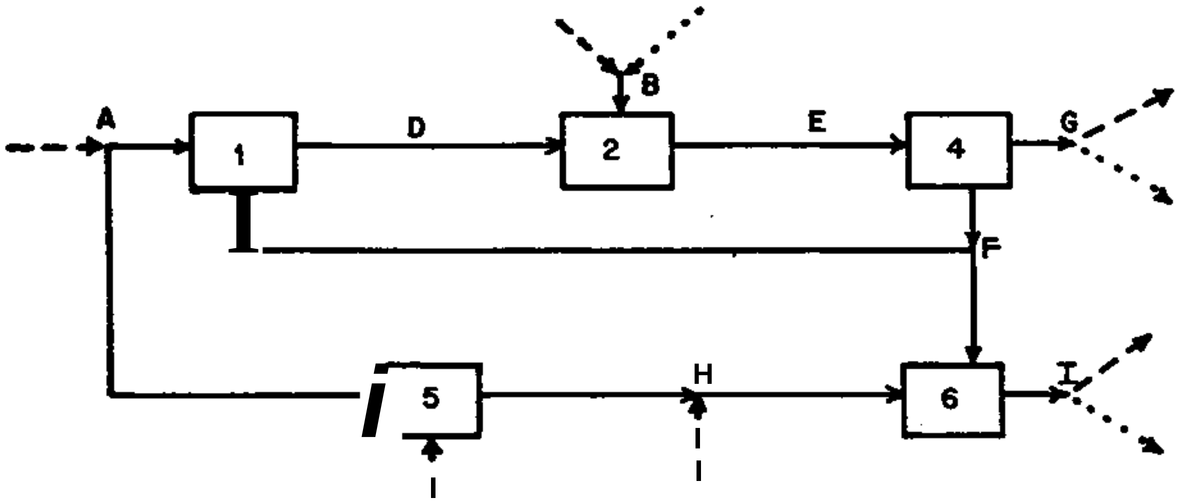


Fig. 7



A
1
D
2
E
4
G
F
(a) α = 750,1000,1150,1250 (10⁶ $)
t_2^* = 698
E
4
G
F
H
6
I
(b) α = $ 1500x10⁶
t_2^* = 737
4
G
A
5
H
6
I
C
(c) α = $ 1750x10⁶
t_2^* = 757

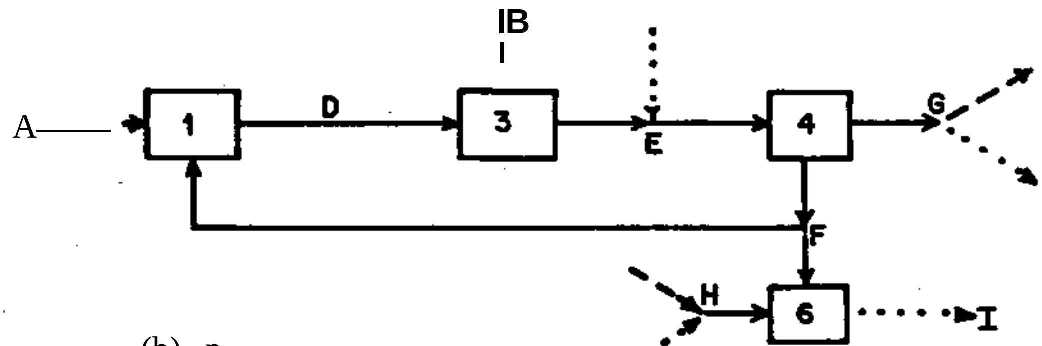
Fig. 8



(o) p –1

t, = $ 2863 x10^6, fg" =767

* 0.91, t2"= 0^7



(b) p s -

^ = $ 2393 x10^6, f^1' = 763

?t = 0.74 , ?i' = 0.26

Pig. 9