Reactor Network Targeting for Waste Minimization

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ABSTRACT

While process synthesis has matured in the areas of heat exchanger and separation synthesis, reactor network synthesis still remains a challenging problem. Advances in this area have been due to recent developments in methods for superstructure optimization as well as powerful concepts for reactor network targeting BEFORE a network is actually developed. In this paper we apply the latter approach to the synthesis of waste minimizing process flowsheets. This area has attracted much interest in the past five years, ^specially since waste minimization at the soorce is the most effective way to develop clean and efficient processes. Moreover, the characteristics of these flowsheets are primarily influenced by **the** reactor network.

This study deals with targeting concepts introduced by Horn (1964), developed by Glasses Hildebrandt and Crowe (1987) and adapted to an optimization framework by Balakrishna and Biegler (1992). Also, we apply concepts of waste minimization and multicriterion optimization, to incorporate the tradeoffs of minimum waste and maximum profit. This approach will be **demonstrated on the Williams Otto and Van de Vusse flowsheets, where the potential for developing profitable waste minimizing processes will be shown. Moreover, we demonstrate the ability of the targeting procedure to integrate the energy and separation** subsystems **as well. This further increases the potential** for **process improvement**

INTRODUCTION

Reactor network synthesis has been the topic of considerable research in the chemical engineering community in the past few decades, since the reaction is the most crucial unit operation in any chemical process. Reaction systems and reactor design often determine the character of the flowsheet. **The amount** of **waste produced,** the recycle structure and the downstream processing steps are directly influenced by selective conversion of raw materials to desired products in the reactor. Until recently the focus of research in process synthesis has been in the areas of heat exchanger network synthesis and separation schemes. There have been significant advances in these areas. However, research in reactor network synthesis has met with limited success, mainly due to the fact that the reactions are described by highly nonlinear differential algebraic models and uncertain rate laws. Also, the numerous possible reactor types and networks further complicate the problem of reactor network synthesis.

Mathematical programming strategies for synthesis of reactor networks may be classified into superstructure optimization and targeting. In superstructure optimization a fixed network of reactors is postulated and an optimal subnetwork which maximizes the performance index is derived (Chitra and Govind (1985a, b), Achenie and Biegler (1986), Kokosis and Floudas (1989)). This may be suboptimal since the solution obtained is only as rich as the initial superstructure chosen and it is difficult to ensure that all possible networks are included in the initial superstructure. In targeting, an attempt is made to find an achievable bound on the performance index of the system irrespective of the actual reactor configuration. A general functional representation is used to model the entire variety of reaction and mixing states. Bounds *an* then derived based on limits posed by reaction kinetics on the space of concentrations available by reaction and mixing.

Targeting for reactor network synthesis is based on the concept of the "attainable region" in concentration space, suggested by Horn (1964). The attainable region is the space of concentrations that can be achieved by reaction and mixing and which may not be extended any further by means of these processes. In essence, it is the convex hull of concentrations which can be achieved starting from the feed point by means of reaction and mixing intermediate or exit concentrations of the reactor with the feed or other intermediate points. Recently, Glasser et al (198?) and Hildebrandt et al (1990) attempted to map the entire region in the concentration space that is attainable from a given feed concentration using "geometric" concepts to represent reaction and mixing. Alternate plug flow reactor (PFR) and continuous stirred tank reactor (GSTR) trajectories were drawn to cover the attainable region and derive an optimal reactor network. Although this is an elegant method the geometric techniques are difficult to apply beyond three dimensions and pose a dimensionality problem.

Balakrishna and Biegler (1992a, b) developed a novel targeting strategy for reactor network synthesis. They adapted the geometric technique for targeting to an optimization based framework. A general targeting model based on optimizing flows between regions of segregation (PFR) and maximum mixedness (CSTR) was formulated as a mixed integer dynamic optimization problem. A simplified form of this model based on the segregated flow limit (PFR) was ppstuiated as a linear program for both yield and selectivity based objective functions. Necessary conditions for the optimaiity of this model were derived and if the conditions were not satisfied, successive Nonlinear Programs (NLP) were solved to improve the target. The solution of each ttLP results in a reactor extension (an additional reactor) from the segregated flow model. Since this is an optimization based procedure making use of operations research techniques, it overcomes the dimensionality problem of the previous geometric technique and could be easily extended to nonisothermal systems where temperature profile is an additional optimization parameter. Also, analytical expressions for the minimum utility consumption (Duran and Grossman, 1986) can be incorporated in the model to consider simultaneous energy integration of reactor networks. Simultaneous reaction and energy synthesis was found to be significantly more profitable than the sequential synthesis (Douglas, 1985). Balakrishna and Biegler (1993), also attempted to develop a unified targeting model for reaction, separation and energy management. A more comprehensive discussion of the targeting strategy is given in the next section.

Until recently optimal reactor network synthesis was based on maximizing yield, selectivity or profit based objective functions. Lately, waste minimization has also attained significance and attempts are being made to synthesize waste minimising process flowsheets. Moreover, waste minimization at the source is one of the best pollution control techniques, where, waste levels are reduced by modifying the manufacturing process. Apart from tighter regulations, the rising cost of waste treatment and disposal and the uncertainty of future waste levels and costs has further strengthened the need for research in this area. Other strategies for waste handling include recycling, treatment, incineration and disposal (Freeman, T990). Obviously, waste minimization at the source is the most attractive among these strategies. However, chemical plants need to adopt an optimal strategy involving all of the above.

Some bottlenecks faced by researchers in synthesizing waste minimizing process flowsheets, using either of the above mentioned techniques, arise from the fact that waste treatment costs are often hard to quantify. It includes "tangible" costs such as treatment and disposal costs and "intangible" costs like responsibility and public relations (for example, the concept of being a "good industrial citizen") the cost of which are difficult to determine. Also, changing regulations quickly alter these costs and require scenarios with additional capacity to be considered. Finally, since profit maximization is the "dominant" objective of the designer with waste minimization the "secondary"[9] objective, the problem needs to be modeled as a multiobjective optimization problem.

In this paper the possibility of developing targets when conflicting objectives need to be considered is explored. This is extremely significant since most real world problems require that more than one objective be considered. The problem of waste minimization at the source needs to be modeled as a multiobjective optimization problem since two conflicting objectives are involved: profit maximization being the " primary objective " and waste minimization the " secondary objective ". The model attempts to simultaneously maximize profits while minimizing waste production levels. The solution to the problem is a family of **points,** each with the characteristic that no objective can be improved without adversely meeting one of the competing objectives. The solution set is called the " noninferior " set, which in this case, is the set of solutions where profit cannot be increased without simultaneously increasing waste production. This is also known as the "efficient" solution or the "pareto" set.

TARGETING CONCEPTS

The targeting strategy used in this work involves:
(1) postulating an initial target, which could be a segregated flow target (PFR) or a continuous stirred tank reactor target (CSTR);
(2) optimize the objective with respect to the target chosen;
(3) consider reactar extensions (which could be CSTR or PFR extensions) from the initial target and examine if the reactor extensions improve the objective. If a reactor extension improves the objective then additional reactor extensions must be considered;
An important insight which is utilized in isothermal reactor network targeting is: the PFR trajectories are such that the rate vector at every point is tangent to the trajectory, thus the PFR trajectories cannot intersect each other. This property ensures that there cannot be a PFR extension to a PFR. However, in case of the CSTR trajectory, the rate vector at any point on the CSTR trajectory is collinear with the line joining that point and the feed point. Hence, there is almost always a PFR extension possible from a nonconvex CSTR target, if the entire attainable region is mapped (Hildebrandt et al 1990). The targeting strategy developed by Balakrishna and Biegler ensures an optimal reactor network in most cases except when the objective function is nonmonotonic with respect to the process variables. An improved targeting formulation which overcomes this problem is being tested and will be presented in a future paper. Typical segregated flow reactor and continuous stirred tank reactor targets are shown in Table 1.

The targets for isothermal reactor network synthesis may be easily extended to nonisothermal reactor network synthesis. One includes a temperature dependent rate expression and replaces the segregated flow reactor target with a cross flow reactor target to allow cold shot cooling (Balakrishna and Biegler, 1992b). Simultaneous synthesis of reaction, energy and separation subsystems was also attempted. Formulations developed by Duran and Grossmann (1986) for minimum utility consumption were incorporated in the energy targeting scheme to simultaneously synthesize the reaction and energy network.

Finally, simultaneous synthesis of reaction, separation and energy management was done by replacing the segregated flow target with a reactor-separator target that involved discretizing the reactor into elements of finite lengths and restricting the separation to the ends of each finite element (Balakrishna and Biegler, 1993). Binary Variables were associated with the separation network and the model formulated as an MINLP to ensure that separation of components occurs only if it is profitable to do so depending on separation costs.

Table 1: Segregated flow reactor and continuous stirred tank reactor targeting formulations for isothermal reactor network synthesis

PFR target	CSTR target
$X_{exit} = \int_0^{\infty} f(t) X_{seg}(t)\, dt$	$X_{exit} = X_0 + R(X)\Delta t$
$\bar{x} = \int_0^{\infty} t f(t)\, dt$	$\Delta t = t_{final} - t_{initial}$
$\int_0^{\infty} f(t)\, dt = 1$	
$dX_{seg}/dt = R(X_{seg}) \quad X_{seg}(0) = X_0$	

MULTIOBJECTIVE OPTIMIZATION APPROACHES

Two of the frequently used techniques to solve multiple objective optimization problems are the "ε constraint technique" and the "weighting method approach". In the weighting method approach (Rietveld et al 1090; Geoffrion 1967) the problem is formulated as a parametric optimization problem by weighting the objectives

$$\min_x \sum_i w_i f_i(x)$$

$$\text{Subject to } h(x) = 0$$

$$g(x) \leq 0$$

$$x \in X, \; w_i \geq 0, \; \sum_{i=1} w_i = 1$$

where ($f_1, \ldots, f_i \ldots f_n$) are the n different objectives and w_j are the weights associated with each objective. A drawback of the weighting method approach is that it can locate only those points which lie on the convex hull of the noninferior set. If the noninferior set includes points that do not lie on the convex hull then a weighted p &-norm, $(\sum (w_i f_i(x))^p)^{1/p}$, needs to be considered as a parametric objective (Lightened 1979)*

The e constraint technique (Haimes et al 1971) can be used to locate the convex and nonconvex regions of the noninferior set. The problem is formulated as

$$\min_{x} \{ f_1(x) \}$$

$$\text{subject to} \quad h(x) = 0$$

$$g(x) \leq 0$$

$$f_i \leq \varepsilon_i$$

$$x \in X$$

where

$$f_i(x) = (f_2(x),\ldots,f_i(x)\ldots f_n(x))^T$$

$$\varepsilon_i = (\varepsilon_2, \ldots, \varepsilon_i, \ldots, \varepsilon_n)^T$$

f i (x) are the n different objectives

Recently, Ciric and Jia (1992), considered the muitiobjective optimization problem and constructed noninferior surfaces using a sequential approximation algorithm which is a modification of the outer approximation algorithm (Duran and Grossman, 1986). Once die noninferior set of solutions of profit and waste levels has been determined, a sensitivity analysis may be performed to ascertain the variation of net profits (i.e. profit - estimated waste treatment cost) with respect to the uncertain waste treactment cost parameters (Huchette and Ciric, 1993).

PROBLEM FORMULATION

In this work the e constraint technique is adapted to consider waste minimization at the source. The muitiobjective optimization problem is formulated as

$$\min_{x,y} \{ -P(x,y),\ W(x,y) \} \qquad\qquad \min_{x,y}\ -P(x,y) \qquad (P3)$$

$$\text{subject to} \quad h(x,y) = 0 \qquad\qquad \text{subject to} \quad h(x,y) = 0$$

$$g(x,y) \leq 0 \qquad\qquad g(x,y) \leq 0$$

$$W(x,y) \leq W_{max} \qquad\qquad W(x,y) \leq \mu$$

$$x \in X \in R^m \qquad y \in Y \in R^q$$

$$\mu \in [W_{min}, W_{max}]$$

where x is the set of flowsheet parameters, y is the set of reaction and energy network variables and h(x,y) and g(x,y) are the constraints involved.

The algorithm used to generate the noninferior set of solutions is shown in figure 1. The algorithm first solves the primary problem, which yields the two extreme points of the non inferior curve, the maximum profit possible and the minimum waste level which may be achieved. The targeting strategy described in the previous section is used to generate the reactor network for both cases, with the production level of the desired product fixed at the required levels and the waste constrained to remain below the maximum allowed levels, which conform with regulatory constraints. The results of the primary problem are then used to initialize the secondary problem. The objective here is to maximize the profit. Targeting is used to postulate the reactor network and reactor extensions are considered. The ε constraint technique is adapted to map the "noninferior curve"[9] by making use of an additional constraint which varies the waste between the minimum and maximum possible levels depending on the value of μ in formulation P3. The solution, using this algorithm, yields the optimal reactor network, size of the reactors, maximum profit possible, waste production levels, fraction of recycle in the process and the noninferior curve between profit and waste levels.

The most significant outcome of finding the noninferior curve is that, since we cannot always be sure of what the allowable waste levels will be in the future, decision makers can get an estimate of what the profit would be at specific waste levels. After making educated guesses as to what the future specifications and costs would be, they can decide as to whether the project should be implemented or abandoned. Also, once the noninferior curve has been plotted, a sensitivity curve between net profit after waste treatment, and waste costs can be plotted. The approach has been tested on a few example problems.

AN EXTENSION

The above analysis has been done for a simple problem formulation with the waste being constrained below specified levels. Often, there are additional constraints which need to be considered. Since profit maximization is the primary objective, the resources allocated for a waste minimization plant may also be constrained. The constraint may be formulated as

$$\underbrace{C_O W}_{\text{operating costs}} + \underbrace{C_C W^B}_{\text{investment costs}} \leq \underbrace{C_{total}}_{\text{total waste treatment cost}}$$

where W is the waste flow rate, C_o the cost coefficient for the operating costs, C_c the annualized cost coefficient for the investment cost, B the exponential factor and Ctotal the resources available for waste treatment. These coefficients are difficult to estimate accurately although nominal values may be available. It has been assumed that investment costs are concave, monotonically increasing functions in the waste flow rate and the operating costs are linear functions of the waste flow rate. The problem may now be formulated as

$$\min_{x,y} \{ -P(x,y),\ W(x,y),\ C_o W + Q W\& \}$$

subject to $h(x,y) = O$
$g(x,y) \leq 0$

$W(x,y) \leq W$ aUowed
$C_c W^B + C_O W$ ^Qotal

$$\min_{x,y} \ -P(x,y) \qquad \text{(P4)}$$

subject to $h(x,y) = O$
$g(x,y) \leq 0$

$W(x,y)$ £ m
$W(x,y) \leq$ ^2

where $x \in X \in R^m$ $\quad y \in Y \in R^q$

$$Co^1 \leq C_o \leq Co^u \qquad C_c^l \leq C_c \leq C_c^u$$

HI e[Wniin. W ^ w e d] *Wl*et Wnrin,argmax(Q W^ + CoWSQotal)]
W

This problem formulation P4 is difficult to solve if C_o and C_c vary between a set of bounds. A rigorous analysis would involve a muitiperiod design which is considerably more complicated. Simpler solution techniques include an "expected value" design and a "worst case" design. In the former approach the expected values of Cc, Q> and 8, obtained from probability distribution dafia, are used to find the expected value of Wmax-

$$W_{max}e = \arg_W \{ \underset{CcCo,B}{E} (C_o W + C_c W^B = C_{total}) \}$$

In this study we merely consider a "worst case" design with variable coefficients Co, Cc and B. This allows a simple reformulation so that the constraints in W reduce to a single constraint. The constraint, which is valid, may be found by rewriting the constraint set as shown below and solving a simple optimization problem.

$$C_c W^B + C_o W \leq C\ total \iff W \leq \arg\max_W \{ (C_c W^{\wedge} + Q> W \leq C\ total) \}$$

$$W_{max} = \min \{ W_{allowed}, \min_{Cc,C_o,B} (\arg\max_W (CcW^6 + C_O W \leq Ctotal)) \}$$

subject to $Co^1 \leq C_o \leq C_o^u$
$C_c \leq C_c \leq C_c^u$

W_{max} is substituted into formulation P3 and instead of solving a number of different problems with estimated values of C_c and C_o and different values of \x\ the problem can be solved with just one constraint and the previous formulation P3 will be valid for the formulation P4. This simplification will accommodate all cost variations and will lead to a conservative design. While Ctotal may be easily quantified depending on the manufacturer's resources, C_c, B and C_o are difficult to estimate and it may only be possible to give nominal values to them. This formulation is illustrated in the first example.

Example 1: Reactor flowsheet integration with emphasis on waste minimization and separation of components from the reactor network.

The targeting procedure is coupled with the simultaneous solution strategy for reactor flowsheet integration with separation of components from the reactor network. The Williams Otto flowsheet, a typical flowsheet optimization problem (Ray and Szekely, 1973), is considered in this optimization. The schematic diagram of the flowsheet is shown in Figure 2. The raw materials A and B are fed to the reactor, where they react to form an intermediate C, desired product P, byproduct E and waste product G. Simultaneous reaction and separation of components may take place in the reactor.

$$A + B \xrightarrow{k}$$
$$C + B \xrightarrow{k_2} P + E$$
$$P + C \xrightarrow{k_3} G$$

The rate vector for the components A,B,C,P,E and G respectively is given by

$$R(x) = [-k_1 X_A X_B;\ -(k_1 X_A + k_2 X_C) X_B;\ 2k_1 X_A X_B - 2k_2 X_B X_C - k_3 X_P X_C;\ k_2 X_B X_C - k_3 X_P X_C;\ 2k_2 X_B X_C;\ 1.5\, k_3 X_P X_C]$$

where k_1 = 110.695 wt frac h^{-1}, k_2 = 561.088 wt frac h^{-1}, k_3 = 1248.748 wt frac h^{-1} and the X's denote the weight fractions of the components. The effluent from the reactor is cooled in a heat exchanger, followed by a decanter where the waste product G is separated from the other components. The waste G is then treated in a waste treatment plant while the remaining components are fed to a distillation column which separates the desired product P. Some of the bottoms product from the distillation column is recycled to the reactor inlet and the rest is used as fuel. Two cases are considered, first the simpler case of reaction without separation is examined and later simultaneous reaction and separation is considered. The objective function considered in the optimization is an annualized net profit which includes sales, cost of raw materials, sales and research expenditure, utility cost; depreciation costs and the last term annualizes the capital cost.

$$J = (8400 * (0.3 F_P + 0.0068 F_D - 0.02 F_A - 0.03 F_B) - 0.124 * (8400) * (0.3 F_P + 0.0068 F_D) - 2.22 F_R - 0.1 * (6 F_R * x) - 0.33 * (6 F_R * T)$$

where F_A, F_B and F_P are the flow rates of A, B and pure P. F_P is fixed at the desired level. F_D is the purge flow rate and F_R is the total flow of components within the reactor.

The variable t includes the residence time in the complete reactor network. The reactor cost is a function of residence time and is irrespective of the reactor type. This assumption is reasonable since the capital cost of the reactor is usually much smaller than the operating costs.

The problem is formulated as in formulation P4. The allowable waste level is assumed to be 12.0 lb waste/hr, the manufacturer is faced with an additional resource constraint which restricts the resources allocated for waste treatment to be a maximum of $340,000 a year. The values of the cost coefficients C_Q and C_C are uncertain, reasonable bounds for them are

$$1 < Go < 2.5 \quad \$/lb\ treated$$
$$50 < €_c < 100, \quad B«0.6$$

The problem needs to be solved using a multiperiod multiobjective optimization. For large flowsheets and complex reaction mechanisms the nonlinearities involved may make this a difficult problem to solve. However, making use of the analysis in the previous section, it is possible to simplify this problem to a direct multiobjective optimization problem, as in P3, with the set of constraints involving waste levels replaced by the constraint which is valid at the optimum. A simple optimization, taking into consideration 8400 hours of operation of the plant in a year, yields

$$Wmax = \min \{ Wallowed, \min_{Cc,C_o} (\arg\max_{W} (Cc\,W\& + Q>W \prec C_{to}tal))\}$$

$$= il.51b/hr$$

Case a) Without separation of components in the reactor network

Sequential reaction and separation followed by a global recycle are considered- The reactor in the flowsheet was replaced by an isothermal reactor targeting model as described in Table 1. The waste minimization algorithm was implemented to map the non inferior curve. The main purpose of this exercise was to stow that the levels of the annnalizeri profit are significantly loW without separation of components. The maximum annualized profit was found to be 133.21*1000 $/hr and the optimal network for the profit maximization case was found to be a PFR with a residence time of 0.020 hours. The noninferior curve is plotted in figure 3.

Case b) With separation of components in the reactor network

The objective function considered here is again an annualized profit which now includes the variable and fixed cost of separation.

$$J = (8400 * (0.3\ Fp + 0.0068\ FD - 0.02\ FA - 0.03\ FB - C_{sep}^{var}) - C_Sep^{flxed} - 0.124 * (8400) * (0.3\ Fp + 0.0068\ FQ) - 2.22\ FR - 0.1 * (6\ FR * Time + C_{se}p^{fixed}) - 0.33 * (6\ FR * Time + C_Sep^{flxed})$$

Csep is the cost of separation and is modeled as

$$C_{sep} = C_{sep}^{fixed} + C_{sep}^{var}$$

$$C_Sep^{flxed} = Cf_{1X}ed(mn)\ Ymn + \sum_{m:n=m+l} Pmn\,|\Delta\mu_{mn}|\,V$$

Cfixed(mn) = 5100 000 per separation between any two components m and n, the separation coefficient Pjnn = 0.0001, Y^hn is the binary variable associated with the separation of components and A|imn is the intensity of separation, iAjinin "'= * ie - sharp splits between components were assumed. Any intermediate degree of separation may be modeled by sharp splits followed by mixing. The order of volatility in the system is assumed to be [P, E, C B, A] and G is a heavy waste. Also, an azeotropic constraint needs to be considered since component P forms an azeotropic mixture with component E. This azeotropic constraint implies that wl>enever a separation between components P and E takes place, some P equivalent to 10 % weight fraction of E is lost along with stream E.

The reactor is replaced by a reactor-separation target to consider the possibility of simultaneous reaction and separation. The reactor is discretized using collocation on finite elements and the separation is restricted to the end of each element. The use of binary variables makes it possible to model the azeotropy constraint as

$$Fp[i+l,0] \wedge 0.1 * F_E[i,end] - M(l- Yi,PE)$$

where Fp[i+i,0] is the mass flow of P entering finite element i+l, FE[i,end] is the mass flow rate of E leaving finite element i, Yi, PE is the binary variable denoting separation between P and E in element i and M is a large positive number.

The model is a MINLP (mixed integer NLP) since discrete variables are associated with the separation of components. The optimization models were formulated within the GAMS modeling system ami DICOPT++ (Viswanathan and Grossmaon 1990) was used to solve the optimization problem. The results of the optimization (225 constraints and 232 variables) with separation of components from the reactor network is shown in Table 2. The optimal reactor network for the NPV maximization case is a PFR with a mean residence time of 0.007 hours, CSTR extensions did not improve the objective. The reactor network and the separation profile for a specific level of waste is shown in Figure 4. It indicates the separation of P,E and G from the reactor network, thus preventing the reaction of P with C to form G. Two sharp splits between PE and C and A and G occur at each separation node. The waste minimization algorithm was implemented and the non inferior curve with separation of components is shown in Figure 5 and the results of the optimization are given in Table 2.

Table 2: Reactor flowsheet integration with separation of components from the reactor and emphasis on waste minimization

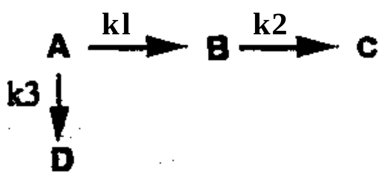
Ann. Profit x1000$/yr	WASTE lb/hr	Recycle Fraction	Mean Residence Time in hours PFR
471.727	11.3	0.861	0.007
465.523	8.5	0.866	0.008
458.707	7.6	0.867	0.008
447.143	6.6	0.868	0.009
427.401	5.7	0.869	0.009
393.015	4.7	0.870	0.010
328.143	3.8	0.871	0.011
228.185	2.8	0.905	0.010
117.932	1.9	0.919	0.010

The fraction of recycle in the system tends to increase with decrease in waste production, which conforms with intuitive reasoning. The residence time in the reactor is almost constant, this may be explained by examining the character of the flowsheet and the reaction kinetics. The production rate of pure product P is fixedin the optimization. Waste product G is separated put completely in die decanter* the only components recycled are E, C unrcacted A and B and a small amount of P. C is critical to the production of P and the presence of A, B and a small amount of E, P in the recycle does not affect the residence time in the reactor much for the desired rate of P to be produced. Also, the flowrate of reactants change at various levels of waste and hence the actual reactor sizes may be different.

The levels of annualized profit obtained with separation of components in the reaaor network is considerably higher than those obtained without separation of components. This indicates that simultaneous reaction and separation is preferable for this specific case with the separation costs being at the level considered in the optimization.

Example 2: Synthesis of optimal waste minimizing process flowsheets with simultaneous optimization of the reaction and energy network

The flowsheet considered in this optimization is shown in Figure 6. The feed A is mixed with the recycle gas stream consisting of unreacted A (99% purity), it is then preheated (stream Cl) before entering the reactor network. The reactions taking place in the reactor network follow nonisothermal Van de Vusse kinetics



where kio*8«6 * 10* h -1; k20»9.7 * 10$ h -1, kso*9.83 * Up JitmoH tr[1]
El « 15.00kcal/gmol E2^22.70kcal/gmol E3 = 6.920 kcjai/g mol
AH A—B=-0.4802kcal/gmol, A H ^ _ c =-0.918 kcaifgmol
A H A — D = -0.792 kcal/gmol

The mixture of A, B, C and D leaving the reactor is cooled before entering the distillation column. In the first column A is separated from the mixture and recycled, while in the second column, the desired product B is separated from the waste products C and D. The reactor is discretized into seven reacting finite element segments, this corresponds to 14 hot streams and 7 cold streams since the reaction is exothermic (HI - H13 and *Cl* - C7), streams H15, H16 and C8, C9 correspond to the condensers and reboilers in the distillation columns, the objective function is the total profit of the plant

J a 2* FB - 6.95* 10"^{5}* x *Fo - 0.4566 * FA (1+ 0.01 * (T^{in} H15 - 320))
-0/7 * (FB + FcD) -0.1• FAO-0.007 * Q_c -0.08 * Qh

where FA and FB are the flow rates of A and B respectively, the second term corresponds to the reactor capital cost, the third and fourth terms correspond to the capital costs of the distillation columns, the fifth term is the cost of raw material and the last two terms are the condenser and reboiler heat loads, with the operating costs of the column incorporated in them. The reaction and energy network are optimized simultaneously. The distillation columns arc assumed to operate with a constant temperature difference between the reboiler and the condenser (Andrecovich and Westcrberg 1985). Also, expressions developed by Duran and Grossmann (1986) for minimum utility consumption and hyperbolic approximations proposal by Balakrishna and Biegler to eliminate non differentiable expressions are incorporated in the formulation. The waste minimization algorithm is implemented and the noninferior curve is plotted in Figure 7. The results of the optimization for die profit maximization case, with a target production of 83,000 Ib / hr of B, art shown in Table 3. The simultaneous optimization model involved 560 equations and 525 variables and was solved in 2.99 CPU seconds on a HP-OX/9000-720 workstation for the profit maximization case. The optimal reactor network for this case was a PFR with a residence time of 0.25 seconds.

Table 3· Results for the profit maximization case in example 2

Overall Profit	75.432*105	$/yr
Overall Conversion	0.407	
Hot Utility Loald	6.47 *103	BTU/hr
Cold Utility Load	3.076*105	BTU/hr
Fresh Feed A	$12.6 * 10^4$	Lb/hr
WasteCD	$4.234*10^4$	Lb/hr
Unreacted(recycled A)	7.478*104	Lb/hr

CONCLUSIONS

Efficient use of muitiobjective optimization techniques has been made to formulate the problem of waste minimization at the source while simultaneously maximizing profits. A versatile waste minimization algorithm has been developed that presents a systematic technique to synthesize optimal reactor networks and flowsheets using targeting when conflicting objectives are involved in the optimization problem. The £ constraint technique is adapted to map the noninferior surface which is the set of efficient solutions. In this case the noninferior curve is simply a curve of profit versus waste where neither objective may be improved without affecting the other. The significance of this curve arises from the fact that EPA restrictions on allowable waste levels are becoming more and more stringent, especially on highly toxic wastes. The noninferior curve presents the data in a graphic and easily comprehensible manner. This analysis also gives the optimal reactor network sizes, flow rates of reactants, recycle ratios etc., these enable the decision maker to decide on whether the project should be implemented and a full scale design be done or whether it should be abandoned. For example in case a) of Example I) suppose it was expected that within a year waste levels shouiiJbe le$s than 3 lb/hr of pureTG. Then the decision maker can immediately see that the annualized profit would then be about 230,000 $/yr at the present level of costs of the raw materials and waste treatment/This is considerably less than the optimal annualized profit achieved at present and would definitely encourage the decision maker to consider other options, better raw materials, better treatment procedures for the wastes, consider alternative flowsheets and also try to improve selectivity. Hence a simple analysis helps to decide on the feasibility of the proposed model taking into consideration future changes.

Another advantage of identifying the noninferior curve is that a sensitivity analysis on variation of net profit after waste treatment with changes in waste costs is a direct consequence of this analysis. This is done by assuming nominal values of cost factors and evaluating the net profits with these values. Since the net profit is given by

$$NP(x,y,w) = P(x,y) - C_w W(x,y)$$

the relation between P(x,y) and W(x,y) is obtained from the noninferior curve and we may write the above expression as

$$NP(x,y,w) = P(W)-C_w W(x_t y)$$

and at the maximum of the net profit it may be seen that

$$C_w = 3P(W)/9W$$

Hence the noninferior curve may be transformed into a sensitivity plot. These relations were used by Huchette and Ciric (1992) to examine the sensitivity with respect to the waste costs.

The examples clearly demonstrate the feasibility of this approach to synthesize waste minimizing process flowsheets where the main emphasis is in the synthesis of the reactor network. The feasibility of handling caste when there are realistic constraints and uncertain costs involved has been demonstrated. However, a rigorous analysis would involve at least a multiperiod design with an assumption on the probability of occurrence of each period. On the other hand a conservative base case design may be done by doing a separate optimization on the uncertain cost factors and taking advantage of the nature of the problem constraints. Although, this analysis is valid and results in a good base case design at the synthesis stage, a more robust analysis may need be required at the design stage. It has been demonstrated that this technique is feasible even when there are discrete variables involved in the optimization. However, the reactor-separator target is a very simplistic model and needs to be improved to consider realistic processes such as reactive distillation.

The main advantage of using an optimization based targeting strategy is that simultaneous synthesis of the various subsystems involved in the synthesis of process flowsheets is feasible. It has been demonstrated in this paper that it is possible to synthesize waste minimizing process flowsheets while simultaneously optimizing the reaction network with the separation network and the energy network.

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Figure I: Waste Minimization Algorithm

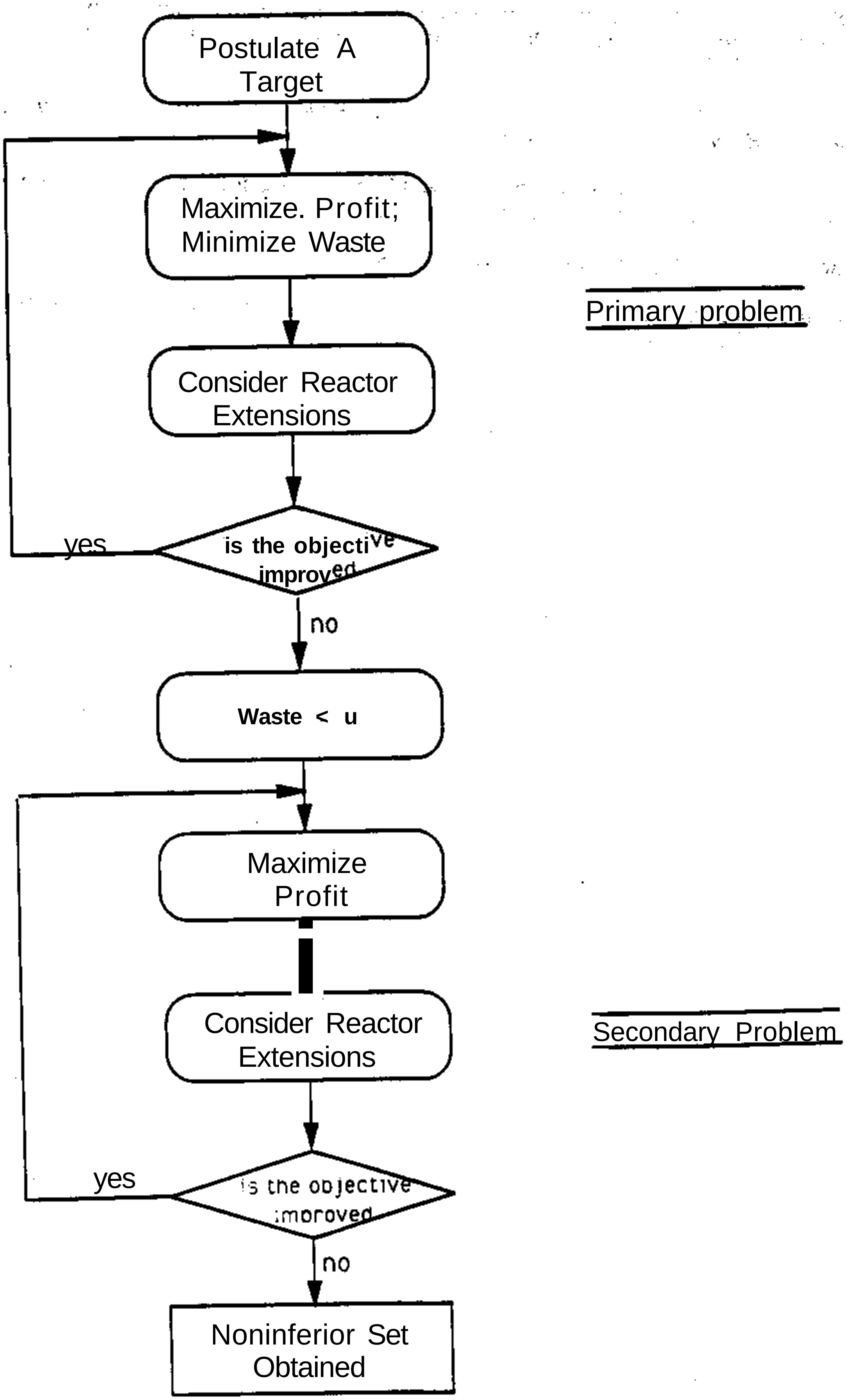

Figure 2: Flowsheet for the-Williams Otto process

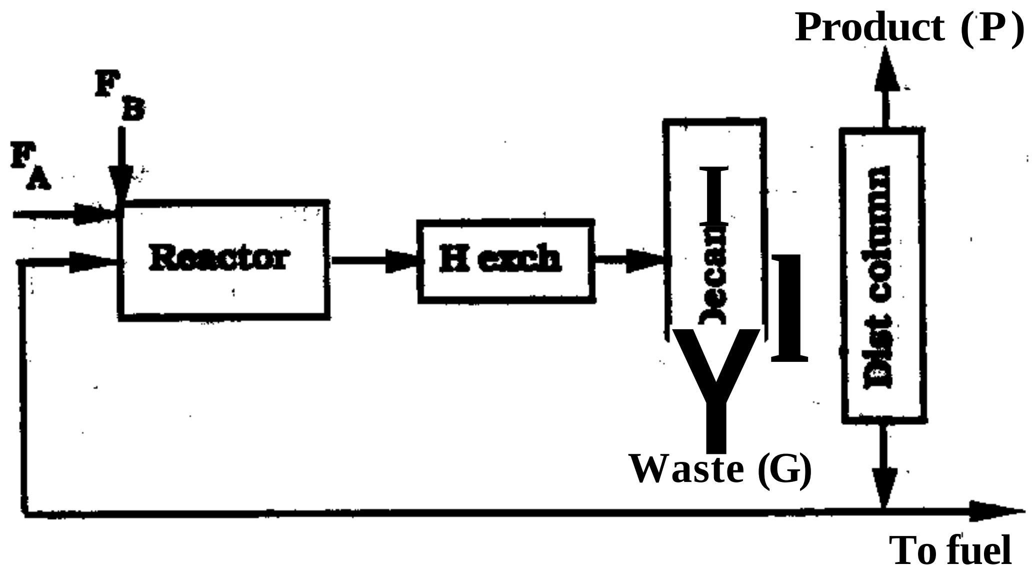

Figure 3: Non inferior curve for Example 1 without separation of components

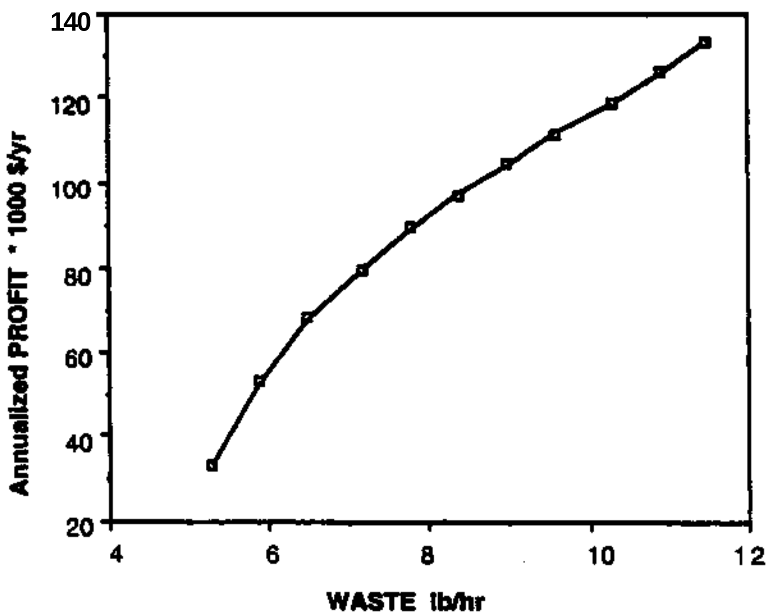

Figure 4: Reactor Network for a the Profit maximization case, mean RTD = 0.007 hr

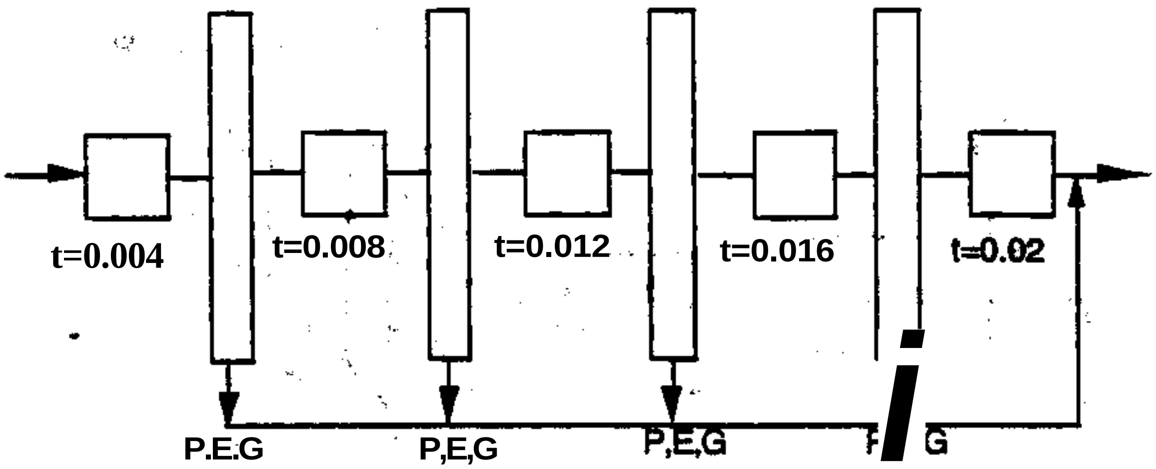

Figure S: Non inferior curve for Example 1 with separation of components

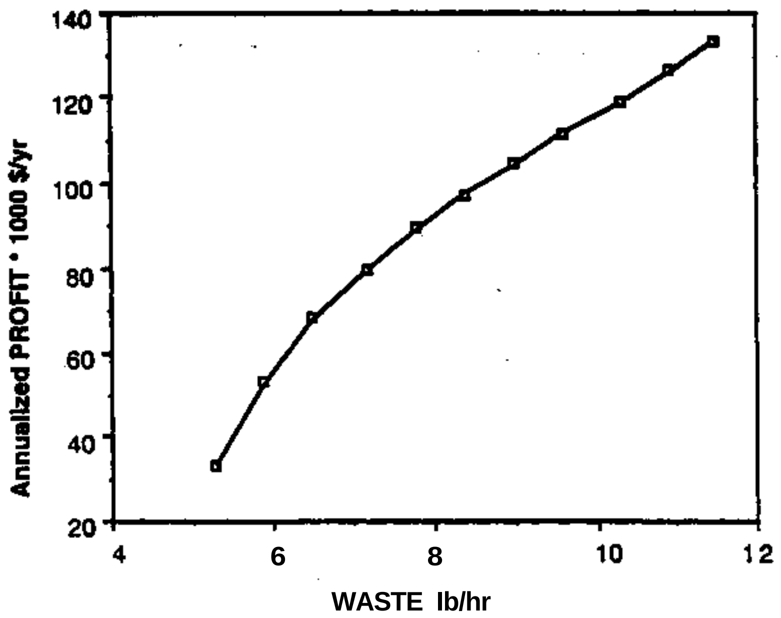

Figure 6: Process flowsheet for Van de Vusse waste minimization

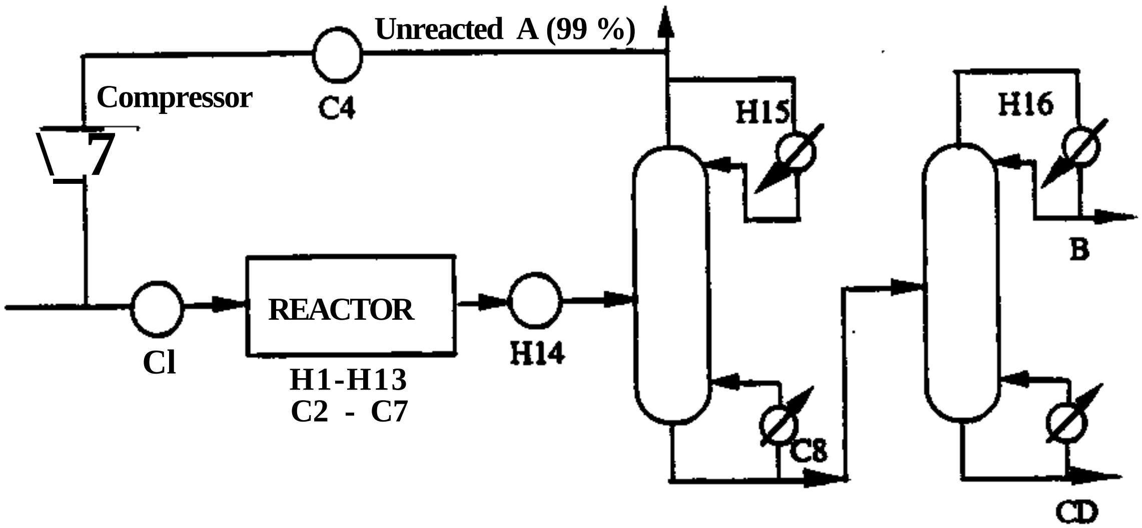

Figure 7: Noninferior surface for Van de Vusse waste minimization