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SYNTHESIS OF CHEMICAL REACTOR NETWORKS

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Abstract

An interesting problem in chemical reactor theory is finding bounds or targets on a given performance index in a reacting system. Moreover, performance of the reactor subsystem has a key impact on the design of other processing subsystems. It determines the recycle structure of the process, the separation sequence and has a strong influence on the energy and environmental considerations. However, this area of process synthesis has seen relatively little development when compared to heat integration and separation synthesis. As with the design of heat exchanger networks, this approach has evolved into the (discrete and continuous) *optimization of network superstructures* as well as the *performance targeting* of the optimal network prior to its construction. In this study we review both methods for reactor network synthesis but concentrate on advances with the latter approach.

The targeting approach is based on geometric interpretations of reaction and mixing. It uses a constructive approach to find the attainable region; that is, it effectively captures all possible reactor structures and finds the bounds on the performance of a reacting system. The approach also generates reactor structures which are candidates for the optimal system. It is however severely limited by the dimensionality of the problem and in practice only 2 and 3 dimensional problems have been solved. Nevertheless, insights gained from this geometric approach have led to an understanding of more general properties of optimal reactor structures. In particular the reactors that make up optimal structures are parallel - series systems of plug flow reactors, CSTR's and differential side stream reactors. Furthermore, the number of parallel structures is related to the dimensionality of the problem. In addition, these properties can be embedded within optimization formulations in order to deal with more complex problems. In particular, we describe several formulations that incorporate simpler properties derived from attainable region concepts. At this point, this approach is not as rigorous as the geometric approach but readily extendable to more complex reaction systems. In addition, it can be integrated with other process subsystems and allows for simultaneous approaches for heat integration, separation structures and reactor network design. In this way, trade-offs resulting from different parts of the process are properly taken into account in the optimization.

All of these concepts will be illustrated with numerous examples. Finally, future work will concentrate on the extension of geometric concepts to more general reactor systems as well as to separation systems. These will also lead to more compact optimization formulations and the consideration of larger and more complex process problems.

1. Introduction

Over the last thirty years the field of process synthesis has matured into an established research area. Significant progress has been made particularly in the synthesis of homogeneous systems related to energy and separation. On the other hand, the synthesis of reactor systems has not developed to the same degree, despite the fact that the reaction subsystem is the central focus of most chemical processes and its performance (yield, selectivity, energy requirements and byproducts) has a direct impact on the synthesis of all of the other subsystems.

There ^ a number of reasons that explain the lack of powerful tools for reactor networks. First, reactor design has a strong experimental component that is driven by the exploitation of new chemistries. As discussed in the previous paper (Mavrovouniotis and Bonvin, 1994) the exploration of new reaction paths is often the key to advancing the competitiveness of a process. However, given the competitive nature of the process industries, the primary goal of an experimental program is frequently not to obtain a detailed kinetic model, but rather to provide the

data necessary to design a scaled-up reactor. Consequently, the lack of a quantitative predictive model makes the derivation of systematic synthesis tools difficult.

The objective of reactor network synthesis is therefore to provide a scoping tool to aid in the design and scale-up of the reaction subsystem. This approach requires a predictive model, though not necessarily a mechanistic one. Moreover, this approach must incorporate the interactions of other process subsystems in order to exploit the synergy of a process effectively. However, even with a predictive kinetic model, the synthesis of reactor networks becomes difficult. First, there are numerous trade-offs to be made due to competing reaction and transport mechanisms. The choice of flow and mixing patterns as well as the addition and removal of heat at appropriate points is often impossible to evaluate entirely in an experimental program. Much more can be done with a predictive model, but even here these phenomena can lead to very difficult modeling and optimization problem formulations. Consequently, some idealization of the process is required.

Perhaps the most common idealizations of reactor networks occur in the choice of simple reactor types, plug flow reactors (PFRs), continuous stirred tank reactors (CSTRs), recycle reactors (RRs), etc. that are common to undergraduate textbooks (e.g., Levenspiel, 1962; Fogler, 1992). Here several well-known rules have been derived based on geometric and monotonicity concepts which apply to simple reaction systems (single reactions, series/parallel reactions, simple endothermic and exothermic reactions). However, while these concepts are expecially useful for single reactions they often cannot be generalized, or lead to conflicting advice when extended to more general systems.

A straightforward extension of this approach is to postulate a network of idealized reactors and perform a structural optimization on this enlarged network or "superstructure." This concept was investigated by Horn and Tsai (1967), Jackson (1968) and Ravimohan (1971) through the application of optimal control policies. Chitra and Govind (1985) exploited the extreme limits of recycle reactors and optimized serial structures of these reactors. The optimal control approach was again revisited by Achenie and Biegler (1986,1990) by treating a network of axial dispersion reactors. The same authors also explored a serial network of recycle reactors with bypass. A more general approach to the optimization of reactor superstructures was taken by Kokossis and Floudas (1990, 1991,1993). Here the problem was formulated as a mixed integer nonlinear programming problem (MINLP) and a very rich superstructure of CSTRs and PFRs (actually serially linked CSTRs) was postulated and the formulation was solved with generalized Benders decomposition. These authors also extended the formulation to include nonisothermal systems, interactions with separation systems and the consideration of stability in the synthesized reactor network.

While the superstructure approach can lead to an effective synthesis strategy, there are a number of drawbacks. First, because of the nonlinear nature of reaction processes, it is difficult to determine when a given superstructure is "rich enough" to deal with general reaction systems. Second, the resulting problem formulation contains many nonconvexities with the possibility of numerous local optima. As a result, global optimization tools, still under development, need to be applied here. Finally, the optimal network frequently has a nonunique structure; i.e., several networks can have the same yield or selectivity characteristics. As a result, an alternate approach of bounding or targeting in the concentration space is extremely useful. Reactor targeting has an intuitive analog with targets employed in heat exchanger networks (HENs). In both cases, strong bounds on network performance can be derived (in terms of concentrations for reactor networks and energy consumption for heat exchanger networks) without the explicit construction of a network. Generally the targeting information gives useful insights about the global solution (although not complete information) and is much easier to obtain.

A powerful concept for reactor network targeting is that of an attainable region (AR). The notion of an attainable region stems from Horn (1964) who noted that once an AR is identified in concentration space for a particular reaction system, the task of finding an optimal reactor network is greatly simplified. In particular, by exploiting geometric properties of attainble regions, a constructive approach is developed to find a region that is closed to the operations of mixing and reaction. As a result, the performance of a reactor network can be targeted and the network itself can be derived from boundaries of the attainable region.

This paper reports on the success of AR approaches for reactor network synthesis and develops a number of extensions to this approach. In the next section, geometric concepts for attainable regions are reviewed and a constructive approach for its approach is outlined. Moreover, while the constructive approach is most easily illustrated in two or three dimensions, general properties for any number of dimensions will be summarized. Section three extends these concepts to deal with more complex geometric aspects in AR approach. Of particular interest here are the incorporation of additional rate processes due to catalyst mixing and separation. In the fourth section optimization formulations will also be explored that build on the concepts of attainable regions. Here we will see that while these are not as rigorous as the geometric concepts, they allow us to "see" in higher dimensions in order to expand an attainable region. The fifth section further explores reactor network synthesis through the integration of the reaction subsystem to the rest of the process. Here optimization formulations are particularly useful to model the interactions between the reaction, energy and separation subsystems. Finally, section six summarizes and concludes the paper.

2. **Geometric** Concepts of Attainable Regions **for Reaction and** Mixing

Definition and Geometric Properties of the Attainable Region

For a given system of reactions with given kinetics and given feed(s), the attainable region A for reaction and mixing is defined as the set of all possible outcomes from all physically realizable steady state reactors in which the only processes occurring are reaction and mixing.

Consider a homogeneous, isothermal, constant density system with species i = 1, .., n participating in the reactions and where the objective function that we wish to optimize is only a function of output concentrations of the various species Q. The AR will lie in the space C = [C\, C2, ...» C_n} and we define the reaction vector $R(C) = (ri(C), r2(C),..., r_n(C))$, where the rate of formation of a species j, rj, is defined in terms of the concentrations of the various species Q, i.e. rj(C).

Now consider the geometric interpretation of the two processes, namely reaction and mixing that we are considering. If we have a mixture of composition C and we allow a differential amount of reaction, then the change in composition dC will be in the direction of R(Q i.e.[1]

$$dC = R(C) \, dx \text{ where } dx > 0 \qquad (1)$$

If we have a mixture of composition C and mix with material of composition C*\ then the composition of the resulting mixture C* lies on the line between C and C^ **i.e.**

$$C^* = a \, C + (1-a) \, C° \text{ where } 0 \le a < 1 \qquad (2)$$

Let us look first at the geometry of two ideal reactors: the PFR and CSTR, where Cfeed *s the feed concentration and x the residence time of the reactor. The PFR is described by:

$$dC/dx = R(C) \text{ where } C = \text{Cfeed at } x=0 \qquad (3)$$

which describes a trajectory in the space with the reaction vector R(C) tangent everywhere along the curve. The CSTR is described by:

$$\text{Cfeed-C} = - R(C) \, \tau \qquad (4)$$

which has the property that the reaction vector R(C) is linear with the mixing vector (Cfeed - Q and the two vectors point in opposite directions along the CSTR locus. Another reactor that will be of interest in the subsequent discussion is the differential sidestream reactor (DSR). In this reactor we have plug flow of material along the reactor

with addition of sidestream of composition $c9_9$ The DSR is described by:

$$dC/dx = R(C) + a(C) \, (C° - C) \text{ where } a(C) \ge 0 \qquad (5)$$

Thus the change in composition at any point along the DSR must lie between the reaction vector R(C) and the mixing vector (C° - C). Note that the limiting behavior of the DSR is either a PFR (a=0) or a CSTR (dC/dx=0). These are just a few examples of how we can describe a reactor in terms of the reaction and mixing occurring in the reactor and from this devise a geometric interpretation of the reactor. By considering the individual processes of reaction and mixing, we can show that A must satisfy the following necessary conditions:

1. All reaction vectors R on the boundary of A, dA, must be tangent, point inwards or zero. This follows from the PFR equation, because if, at some point on 3A, the reaction vector pointed outwards, then by reaction we could extend the region.

2. A must be convex. This follows if we had a concavity in A, we could fill in the concavity by mixing.

3. No reaction vector R in the complement of A can point backwards into A. This follows because if, at some point Ci in the complement of A, the vector R(Ci) could be extrapolated backwards into A, then a CSTR operating with a feed in A could achieve Ci.

A region that satisfies these necessary conditions is a candidate for the attainable region. Unfortunately we do not yet have a sufficiency condition for A; however a region that satisfies the necessary conditions is closed with respect to differential reaction and mixing, PFRs, CSTRs and DSRs.

One can construct A in a subset C' of the full concentration space when the objective function, bound or target depends only on the concentration of the species defining C' and when the rates of formation of the species defining C* also only depend on C*. The space can also be extended to incorporate variables other than concentration variables provided the new variables obey linear mixing laws, and can be incorporated in the definition of R. Examples of such variables are residence time in constant density systems and specific enthalpy. We can also extend this approach to non-constant density systems by using mass concentration variables as discussed by Hildebrandt et. al. (1990).

Once we have found A, an optimization problem can be solved relatively easily by searching over A to find where the objective function is optimized. The optimum can either lie on dA or in the interior of A. If the optimum lies in the interior of A, we can achieve this point in infinitely many different ways and in particular by mixing between appropriate points on 3A. We first look

at the geometric properties of 3A and how we can interpret these properties in terms of the combination reaction and mixing occurring in dA. By understanding the geometry, we will be able to translate this combination of reaction and mixing to determine the reactor structures that make up 3A.

The Geometry of the Boundary of Attainable Region

Results of the AR concepts are summarized below for $9t^n$. These are developed and proved in Feinberg and Hildebrandt (1994). Firstly, 3A is the union of straight lines and surfaces along which R is tangent. We interpret the surfaces as the union of PFR trajectories. This tells us that the structure of the boundary is rather simple and that the complexity of the reactors that make up the boundary is in fact fairly limited. If the objective function is optimized on a curved section of dA the optimal reactor structure that would produce this material will have a PFR as the last unit in the structure.

We next look at how the straight lines intersect the surfaces made up of PFR trajectories; we will refer to these intersections as connectors. When there is no unique tangent support hyperplane along the connector (i.e. PFR trajectories and straight lines do not intersect smoothly), the connector is itself a surface along which R is tangent and is thus a union of PFR trajectories.

If the PFR trajectories and the straight line sections do intersect smoothly, the tangent support hyperplane is uniquely defined along the connector and the mixing vectors and reaction vectors lie in the support hyperplane. We are really only interested in when the connector corresponds to *feed points* to the PFR trajectories, which will occur if the reaction vectors point away from the connector. This geometry implies that the connector is the union of CSTR operating points and DSR trajectories. We now look at the construction of A and at what these results imply in 2 and 3 dimensional space.

General results in $\mathfrak{R}^n$.

In $9t\,2_f\,J)A$ $J_S\,{}_t{}_h{}_e$ union of straight lines, PFR trajectories and equilibrium and feed points. Consider the sections of 3A made up of alternating PFR trajectories and straight lines. When one end of a straight line is a feed point to a PFR, this point, a connector, is achieved by a CSTR with its feed point being the other end of the straight line. Thus in SR^, the reactors that lie in 3A consist of alternating PFRs and CSTRs in series - parallel arrangements. We need at most 2 parallel structures to achieve any point in the boundary of the AR and at most 3 parallel structures to achieve any point in the interior of the region. No DSR is found to lie in the boundary of the AR in 2-dimensional examples. The construction of the AR is particularly easy in 2-dimensional space and a general construction algorithm can be given.

1. Start from the feed point and work toward equilibrium or endpoint by drawing a PFR from the feed point
2. If there is a concavity in the PFR trajectory, then straight lines would be drawn to fill in the concavities and find the convex hull of the PFR trajectory. If there is no concavity then we have found a candidate for dA and stop.
3. Else, we check along the straight line sections of the convex hull to see if reaction vectors point outwards. If no reaction vectors point outwards then we have a candidate for dA and stop.
4. Else, there exists a CSTR locus, starting from the PFR trajectory, that intersects the straight line at the point where the reaction vector becomes tangent. We then draw in the CSTR locus, with feed on the PFR trajectory, that extends the region the most. (Be sure to include all solutions (branches) if the CSTR can exhibit multiple steady states.) We next find the convex hull of the new extended region by filling in concavities in the CSTR locus. (The straight line that fills in the concavity from the feed point on the CSTR locus should not have reaction vectors pointing outwards if we have chosen die feed point to the CSTR correctly.)
5. Next, draw in a PFR trajectory from the end of the straight line filling in the CSTR concavity. If the trajectory is convex, then we have a candidate for 3A. Otherwise, repeat from step 3 until ail the concavities are filled in and have reached the equilibrium point

Note that this algorithm can also be applied to higher dimensional problems that can be projected into a two dimensional space. For example, Omtveit and Lien (1993) applied the principle of reaction invariants (Fjeld et al, 1974) to reduce the size of a steam reforming problem to two dimensions and then construct the AR.

We illustrate this approach by means of an example based on van de Vusse kinetics.

$$A \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} B \overset{k_2}{\rightarrow} C \text{ and } 2A \overset{k_3}{\rightarrow} D \qquad (6)$$

The reactions are elementary and the rate constraints are as follows: klf = 0.01, klr = 5, k2 = 10 and *3 = 100- We assume that the feed is pure A where $C^\wedge = 1$ and we define

$C = (C_A, C_R)$ where $R = (-0.01C_A + 5C_B - 100C_A^2, 0.01C_A - 5C_B - 10C_B)$. Applying the above procedure, both A as well as the reactors that make up dA are shown in Figure 1. We can see that although we have 4 different reactor structures lying in dA, the individual structures are simple combinations of CSTRs and PFRs. An advantage of the constructive approach is that we can give geometric

conditions for the critical operating points in the boundary, in this case points F and H. Point F is defined where the reaction vector, the tangent vector to the CSTR locus with feed A and the line AF are all collinear. Point H is defined as the point where the reaction vector on the PFR trajectory with feed F is collinear with the line from the origin.

Once we have determined A, we are in a position to solve any optimization problem where the objective function is a function of the concentration of A and B only. Thus for example if we wanted to maximize the concentration of B at some specified conversion of A, we could read the answer off from Figure 1 and we could also determine the optimal reactor structure as well as the operating conditions of the various reactors in the structure.

General results in 9j3

The reactors that lie in dA in *9&* are a series-parallel arrangement of PFRs, CSTRs and DSRs. At most 3 parallel structures are needed to produce a point that lies in dA while at most 4 parallel structures are required to achieve a point in the interior of A. The most common side stream addition arrangement in the DSR will be the addition of either an equilibrium or feed point. The DSR that lies in the boundary of the AR also lies in the surface described by:

$$R(C) \times (C^0\text{-}C) \cdot dR(C) (C^0\text{-}C) = \phi(C) = 0 \qquad (7)$$

This property stems from a lengthy derivation of the connector relations and states that, at the connector, the change in the reaction vector projected along the mixing vector must lie in the plane spanned by the reaction and mixing vectors. Furthermore, from (7) we determine the sidestream addition policy so as to keep the DSR in the above surface. Thus a can be determined by:

$$d(\triangleright)/dT = V(\triangleright(C)\text{-}dC/dT = V\triangleleft\triangleright(C)\text{-}(R(C) + oc(C^\circ\text{-}C)) = 0 \quad (8)$$

At present we have only a trial and error construction method for 3-dimensional examples, but we do know that if we propose a region, we can test whether the region satisfies the necessary conditions.

An illustration of a typical 3-dimensional attainable region that can be found from constructing the AR geometrically is the following. Consider an exothermic, reversible reaction: A » B, where rA = 5x10^ X exp(-4 OOO/T) + 5xlO⁸(l-X)exp(-8OOO/T),X = CA/C5,, *C%* is the feed concentration of A (pure A) and T is temperature. Let us look at the problem of finding the minimum volume of reactor for a given conversion of A. We have a feed of pure A at a temperature of 300 K and in addition to reaction and mixing, we are allowed to preheat the feed or a portion of the feed up to 400K. We can choose how much of the feed to preheat and its preheat temperature. We

assume constant density, constant heat capacity with ideal mixing. The energy balance for an adiabatic reaction is: T = Tθ + T_ad(1-X)_y where T is the temperature in K, T_ad is the adiabatic temperature rise (200 K) and Tδ is the basis temperature if the mixture were adiabatically reacted to form pure A. The AR can be constructed in SR^ where C ={CA» T, X) and x is the residence time. These variables (because of the assumptions used) follow linear mixing laws. We can also define a reaction vector R = {rA, -T_adrA» 1}, Note that the new variables T and x follow mixing laws and can be incorporated in R for the construction of A. The region for this example was constructed in Glasser et ai (1992) and is shown in Figure 2. The reactor structures that make up the boundary of the region are also shown on the figure. The DSR lies in the surface defined by <KQ which simplifies in this case to:

$$3rA/3X(X\text{-}l) + drpJ^T (T\text{-}300) = 0 \qquad (9)$$

Again notice from Figure 2 that there are a great number of different optimal reactor structures that form dA but all of these structures are very simple series-parallel combinations of the 3 basic reactor units.

We have constructed A for various 2 and 3 dimensional examples. We do not yet know, however, how to construct the region in higher dimensional spaces. The above results, on the other hand, have important implications as to the types of reactor structures that should be considered in optimization or targeting approaches in higher dimensions

The reactor structures that need to be considered are only series -parallel arrangements of PFRs, CSTRs and DSRs. This means that we need not consider recycle reactors and other complex types of reactors and we can thus discard a very large number of possible structures immediately. We also do not need to include recycle within the structure itself, which also adds considerably to the simplicity of the structure.

Generally, the maximum number of parallel branches needed in the structure is related to the dimensionality of the problem. A point in the interior of A can be achieved by infinitely many different reactor structures; we can however achieve the point by mixing between (n+1) points on dA (as is consistent with our two and three dimensional observations). This means we can achieve any point by mixing the output of at most (n+1) parallel optimal structures where each parallel structure consists only of PFRs, CSTRs and DSRs. Moreover, the equilibrium points, corresponding to dC/dx = 0, of DSR trajectories are CSTR operating points. Thus, by using only CSTRs and PFRs once can expect to achieve a reasonable approximation of A. This again reduces the complexity of the reactor superstructure that we need to consider for a particular problem.

3. Multirate Processes and Geometric Concepts

We can extend the concept of the AR for reaction and mixing to include more processes. The processes we can include must be described by the vector field, $P(C)$, in the space of the variables C. The field $P(C)$ must be such that if we have a mixture of composition C and we allow the process to occur differentially, then the change in composition dC is in the direction of $P(C)$ i.e., $dC = P(C) dx$, where $dx > 0$. Examples of such processes are separation by boiling and condensing, heating, cooling and allowing more than one reaction processes such as when there is a choice of catalyst. An outline of these ideas is presented in Godorr et al. (1994).

For simplicity in the following discussion we will regard mixing as a vector process described by $Pi = (C-C^\wedge)$, where both C and $C^*e A$. The set of processes that are allowed are thus mixing Pi, reaction $P2 = R$, and processes $P3, P4 ..., P_m$. We can incorporate all of these processes into $P = \{Pj\}$ where $i=l,..,m$. Geometrically we can say that at every point C in the space, there is a set of vectors defined such that the vectors point in the directions of change in C that can be achieved locally by allowing the individual processes Pi to occur differentially.

For a system of reactions with given kinetics and feeds, the AR is defined as the set of all possible outcomes from all physically realizable steady state systems in which only the processes defined in P are occurring. Thus, the necessary conditions and results given for reaction and mixing can be extended to incorporate the processes P. Firstly, along dA the components of P must not point outwards, that is they must be tangent, point inwards or zero. (This also implies that if $Pi 6 P$, then A must be convex if Pi is not to point outwards over dA). Other necessary conditions could be added including those that cover processes which could have multiple steady states.

Furthermore, we can make the following assertions about the properties of dA. For example, dA would be the union of trajectories tangent to single vector processes Pj. The equipment needed to achieve a point on a trajectory of dA will have a unit in which only a single process is occurring as the last unit in the structure. Thus the equipment could have a section which can be heating only, reaction only or boiling only before the material exits the equipment

Where do these trajectories originate from? Consider A in $9t^n$ where we have $k(n-l)$-dimensional hypersurfaces Sk that lie in dA, where $k \leq m$ and which intersect. Let the surfaces be such that each surface Si, $i=l,...,k$, is tangent to one of the elements of P and that all the other elements of P point into A. Furthermore, let each surface Sj be tangent to a different element of P. For simplicity let us assume that surface Si is tangent to Pj. Surface $S[$ can thus be regarded as the union of trajectories which are tangent Pi.

Consider now that $k=2$ and suppose that Si and $S2$ intersect smoothly and, furthermore, that Pi and $P2$ point away from the intersection. The intersection will be an $(n-2)$-dimensional hypersurface in dA and we can again call the intersection a connector. The support hyperplane to this connector will be tangent to both Pi and $P2$. It follows that this connector is the union of trajectories described by a differential equation which is a linear combination of Pi and $P2$- When $k=3$ and $Si, S2$ and $S3$ intersect smoothly, this connector/intersection will be an $(n-3)$-dimensional hypersurface in dA, and $Pi, P2$ and $P3$ will be tangent to the support hyperplane along the connector. If we consider only connectors that are feed points to the trajectories, i.e. connectors where $Pi, P2$ and $P3$ point away from the connector, then this connector is the union of trajectories which correspond to a process/operation defined by a differential vector equation which is a linear combination of $Pi, P2$ and $P3$.

We can further generalize these ideas. Firstly, n processes will operate simultaneously at isolated points in dA. Similarly, $(n-1)$ processes will operate simultaneously along a 1-dimensional curve in the boundary of dA. In general, $(n-m)$ processes will operate simultaneously along an (m)-dimensional hypersurface in dA, where $0<m<n$. We should then be able to translate this geometry into equipment or a unit process. Notice that the processes making up dA will again come out of the construction of A and do not have to be specified.

These results, together with the previous results regarding the number of parallel structures needed, can be used to propose a suitable candidate for the targeting approach. We could propose that the optimal structure would be series-parallel arrangements of units described by differential equations that are linear combinations of the individual elements of P. We should be able to relate these structures to unit operations or process equipment. If we allow mixing, condensing and boiling, the type of equipment that should be used will come out of the construction and it may turn out, for example, that distillation columns are not optimal and some other combination of flashes and mixing is better. (However, if the distillation column is described by a differential equation, as in van Dongen and Doherty (1985), then the resulting equation is a linear combination of a mixing vector and a vector describing boiling and thus can be a trajectory in dA.)

These results reduce the complexity of the required structure as well as the types of units that need to be considered in a proposed structure. A limitation of the approach is that it currently works only for single input single output problems, and many practical problems, for example, separation have multiple outputs. We are currently looking the implications of multiple outputs on the geometry. Moreover, the constructive approach to finding A in these types of problems is also limited by constructions in $9?^\wedge$ $_{an(j} \leq R3$ However, it is of interest to look at a few of these examples to illustrate the ideas and the implications of the geometry.

Reaction and Mixing with Catalyst Profile Optimization

The following problem has been looked at by various researchers. Suppose we are given two different catalysts that catalyze different sets of reactions. We wish to choose the reactor as well as the catalyst profile in the reactor in order to minimize the total catalyst volume used to produce some specified product. Given the following kinetics, catalyst 1 catalyzes the following two reactions:

Reaction 1: $A \Leftrightarrow B$ where $TAI =$
$(-k_1C_A+k_2C_B)/(1+k_P C_A^2)$

Reaction 2: $A+C \ll B+C$ where $TA2 =$
$-(k_3C_AC_C+k_4C_BC_C)/(1+k_P C_A^2)$

and catalyst 2 catalyzes two different reactions:

Reaction 3: $A \Leftrightarrow C$ where $rA4 =$
$(-k_5CA+k_6C_C)/(1+kpCi)$

Reaction 4: $A+B \gg C+B$ where $rA4 =$
$(-k_7C_AC_B+k_8C_BC_C)/(1+k_P C_A^2)$

We are given that the feed is pure A ($C_A^{0 = 1}$) ^{anc*we} are allowed to use 3 processes: reaction with catalyst 1 which we will describe by reaction vector $R|_9$ reaction with catalyst 2 which we will describe by reaction vector R2 and mixing. The reaction constants are $ki=k5=2$, $k2=k6=1$, $k3=k7=60$, $k4=ks=10$ and $k_p=20$. We can construct A in $91^{\wedge}$ $_{space}$ where $C = (C_B, C_C, X)$. The reaction vectors are thus given by $Ri = (rAl+i*A2Al)$ and $R2 = (0*i*A3^{+r}A4\gg l)$- We can thus see that Ri is parallel to the CB axis and R2 is parallel to the Cc axis. The solution to this problem is given in Godorr et. al. (1994) and the results for this example are shown in Figure 3. The projection of A onto CB-CC space together with the various optimal reactor structures are given in Figure 3. Note that LSRQC is the equilibrium for the system while O is the feed point.

Connectors PN and PM correspond to DSRs and lie in the 2-dimensional surfaces defined by equation (7), where the R refers to the relevant reaction vector. The mixing policy is described by $d \Leftrightarrow dT = 0$. Connector PR, on the other hand, is a new kind of connector. The PFR with mixed catalyst is described by:

$$dC/dx = (1-P) Ri(C) + p R2(C) \text{ where } 0 \leq P \leq l \quad (10)$$

and the connector lies in the 2-dimensional surface defined by:

$$\triangleleft D(C) = Ri(C) \times R2(Q - \{dRi(C) R_2(Q - dR2(C) Ri(C)\} = 0$$
$$(11)$$

Finally p, the fraction of catalyst 2 along the PFR, must be chosen to keep the mixed catalyst trajectory in the surface described by $O(C) = 0$. Thus from $dO/dx = 0$:

$$VO(C) \cdot dC/dx = V \triangleleft D(C) - \{(l-p)Ri(C) + p R_2(C)\} = 0 \quad (12)$$

Lastly, all 3 connectors intersect at point P, which corresponds to a point where all 3 processes occur simultaneously. Thus we interpret this as a CSTR with mixed catalyst. This example demonstrates all the types of connectors that were described earlier in the discussion.

Reaction, Mixing and Separation by Evaporation

We also consider the contribution of boiling to our multirate processes. If we have a liquid mixture with species $i=l,..,n$, where the mole fraction of species i of Xi we can describe the composition of the liquid by $X = (Xi, ..., X_n.i)$ and assume that the liquid molar density is constant. If we allow simple boiling (at constant pressure) to occur such that the vapor removed is in equilibrium with the liquid, we can describe the change in the composition of the liquid by:

$$dX/dx = N(X-Y(X)) = NS \quad (13)$$

where N is the molar rate of vapor removal per unit volume, Y is the mole fraction vector describing the vapor composition in equilibrium with the liquid of composition X and x is a scalar parameter. We will refer to $S = (X-Y(X))$ as the separation vector. We can also define a reaction vector R(X) at every point in X.

Consider now an example in $9?^{\wedge}$, where we have $A \gg B \gg C$ and $X = (XA, XB)$. Let us suppose that the reactions are first order and that $R = (-kifXA+ki_rXB. kifXA-ki_rXB-k2fXB + k2rO-XA-XB))$. We wish to find the maximum mole fraction of B that can be obtained for some specified mole fraction of A using reaction, mixing and separation by boiling only. Note that we are assuming that the vapor that is boiled off is "lost" and that it is not condensed and returned to the system. We have a feed of pure A and we adjust the temperature of the mixture to keep it as its bubble point assuming that the liquid and vapor behave ideally i.e. $YiP° = Xi p_i^{Va}P$, where P° is the total pressure (1 bar) and $p_I^{a}P$ is the vapor pressure of pure i. The temperature dependence of the vapor pressures is given by $a + b T$ (in °C), with a=0.4, 0.5 and 0.3 for components A, B and C, respectively, and b = 0.005 for all components. Thus $S = (XA - XA PX^{ap}(T)/p^0. {}^{X}B - XBP\mathcal{B}^{ap}(T)/p^0)$ and T is defined implicitly by: $S(Xi pV^{a}P (T)/P°) = 1$. We can find A for this problem and we would expect that at most 2 processes operate simultaneously at a point in dA and that nowhere in dA can all 3 processes occur simultaneously. Thus we would not expect to find, for example, a CSTR with

simultaneous reaction and boiling (3 processes occurring simultaneously) or even a PFR trajectory with simultaneous reaction and boiling in dA. If we have simultaneous mixing and boiling occurring at a point (i.e. a flash) we would find that the feed composition $Xf_{ee(j}$ would lie between X and Y on S. As the magnitude of S is generally not large, this means that the flash will not extend the region very much, if at all. We subsequently would not expect the flash to play an important role in extending dA.

The structures that make up dA arc in fact very simple and are shown in Figure 4. A PFR trajectory from the feed point operates between AB, the PFR trajectory is convex and S points inwards along the trajectory. B corresponds to reaction equilibrium. At B separation by boiling moves us along BCD which is concave. We can fill in that concavity by mixing B and D. Both R and S point inwards along line BD and so we claim that this region is fact A.

Note that one of the differences between this example and all the previous ones is that it is not clear from the construction how much material can be produced, as once we allow boiling, the quantity of material varies depending on how much vapor we have removed. Thus although all compositions along line BD can be achieved, the points along line BD correspond to different quantities of product.

Again, notice that in order to achieve a point on dA, we at most need 2 parallel structures with mixing at the outlet of the two structures. The dA is made up of curves along which only single processes are occurring, in this case reaction along AB and mixing along BD. In this example we do not have any points in dA where two processes operate simultaneously.

If we changed the vapor pressure relationships such that A had the lowest boiling point of the three components, then we would find that the whole mole fraction space was achievable in the limit by separation alone. Finally, it appears that we would have to look at $9*3$ or higher to find interesting examples where reaction, mixing and separation occurred simultaneously.

4. Optimization formulations for higher dimensions

The previous two sections demonstrated the effectiveness of geometric concepts and constructions to a wide variety of synthesis problems. While geometric concepts lead to powerful tools for visualizing and constructing an AR in concentration space, obtaining this region can be much more difficult in higher dimensions. In this section, on the other hand, we explore an optimization-based formulations for reactor network targeting. This approach applies many of the concepts of attainable regions from the previous section and poses them as optimization problems. This allows the designer to probe in higher dimensional spaces (in principle, without limitation) without the need of visualization. As developed so far, optimization-based formulations consist of small nonlinear programming problems (NLPs) that describe the performance of PFRs and CSTRs and lead to a analogous approach for determining the attainable region. This NLP approach has a number of advantages as well as shortcomings.

In particular, it should be noted that NLP formulations do not entirely replace insight gained from the construction of an attainable region. With geometric constructions, one obtains a family of reactors that is complete in concentration space. The NLP approach rather finds the family of reactors within an attainable region that improve a given objective. Here one assumes that steady improvement can be found for each NLP extension of the attainable region. This is not always possible and, as a result, the NLP-based procedure can terminate in suboptimal networks. Moreover, the optimization-based targeting approach has only been tackled with local optimization methods, and solutions arc obtained without a guarantee of a global optimum.

On the plus side, however, nonlinear programs can be formulated for arbitrarily large problems without restriction as to the features of the kinetics. As will be seen below, these formulations are quite easy to solve even for demanding kinetic problems. Moreover, while simple constraints can be incorporated into geometric constructions, the NLP approach offers greater flexibility in posing and synthesizing constrained reactor networks. This characteristic has its greatest advantage when integrating the reactor network within other process subsystems, as described in section S. This integration step is done quite naturally with optimization based formulations as links from other parts of the process are treated directly through equality and inequality constraints.

The NLP-based targeting strategy is summarized in Figure 5. Again, the basic properties of the attainable region are exploited and a constructive approach is developed in order to determine whether the best objective in the attainable region (but not the entire region itself) has been found. Here we modify the AR description slightly and first consider ARs in segregated flow, rather than simple PFRs. For isothermal problems, the segregated flow or PFR profiles arc generated off-line by solving the rate equations:

$$\frac{dX_{seg}}{dt} = R(X_{seg}) \qquad X_{seg}(0) = X_0$$

and form the data for the problem given below:

$$\text{Max} \qquad J(Xexit.x)$$
$$f(0 \tag{14}$$

$$Xexit = \int_0^\infty f(0\, X_{seg}(0\, dt$$

$$\int_0^\infty tf(t)dt = x \qquad \int_0^\infty f(t)dt = 1$$

Here, $f(t)$ and $X_{seg}(t)$ correspond to the residence time distribution and the dimensionless concentration vector

(e.g., C(t)/Cfeed)» respectively. It follows from section 2 **that** if the problem can be represented in two dimensions and if the PFR profiles are convex, then solution of (14) yields the optimal network and the attainable region is given by at most two plug flow reactors. Moreover, discretization of the integrals yields a simple linearly constrained nonlinear program (NLP). In fact, when the objective is yield or selectivity, (14) is easily solved as a linear programming problem. Balakrishna and Biegler (1992) also considered convex two dimensional projections for multi-dimensional problems and derived more general conditions under which PFR profiles remain sufficient for constructing the attainable region.

If PFR trajectories are insufficient, however, the attainable regions can be enhanced by NLP formulations **that** describe CSTR or RR extensions. Strictly speaking, any attainable region that is closed to CSTRs is also closed to recycle reactors, and vice versa. An advantage to the recycle reactor formulation is that it can model both plug flow and CSTR extensions. From any point within the segregated flow region, recycle reactors are sought to improve the objective at points outside of the attainable region, as shown in the formulation below:

$$\text{Max} \quad J(X_{exit}) \qquad (15)$$
$$R_e, f(i,j), \ ^f\text{model}(k)$$
$$\frac{dX_{rr}}{dt} = R(X_{rr})$$
$$X_{rr}(t=0) = \frac{R_e \ X_{exit} + X_{ypdate}}{R_e + 1}$$
$$X_{up}\text{date} = \int_0^\infty f(0 \ X_{seg} \ (0 \ dt$$

(or $X_U$pdate= previous point if further reactor extensions),

$$X_{exit} = \int_0^\infty frr(0 \ X_{rr} \ (t) \ dt$$

$$\int_0^\infty f(t)dt = 1, \qquad \int_0^\infty frr(0 \ dt = 1$$

Problems (14) and (15) are used in the algorithm of Figure 5. (15) is augmented by any additional extensions and an optimal network is claimed when no further improvement can be found by these formulations. As mentioned above, an important limitation is that an improvement in the objective is sought with every extension to the attainable region. However, there are cases where the attainable region can be extended without improving the objective - and from these extensions further improvements could still be found. This approach has been applied by Balakrishna and Biegler (1992a) to several isothermal examples, with as many as seven independent reactions. Their results are at least as good as or better than previous literature results.

Finally, the NLP formulation can be extended naturally to systems with variable feeds compositions and to nonisothermal systems with arbitrary temperature profiles. To deal with unknown or variable feed compositions, the formulation in (14) can be solved recursively in an inner loop with PFR profiles generated off-line for different feed conditions. This mimics the geometric approach where different attainable regions are constructed for a variety of feeds. However, a more direct approach involves a simultaneous NLP formulation that incorporates changes in segregated flow behavior, a differential equation model, with changing initial conditions. To reflect these in a nonlinear programming formulation, the differential and integral equations need to be discretized to algebraic equations. A natural way to do this is through collocation on finite elements. As a result, formulation (14) is transformed to:

$$\text{Max} \quad J(X_{exit}) \qquad (16)$$
$$\frac{dX_{seg}}{dt} = R(X_{seg})$$
$$h(X_{seg}(t=O), Xe_XH, y) = 0$$
$$X_{exit} = \int_0^\infty f(0 \ X_{seg} \ (t) \ dt$$

$$\int_0^\infty Jtf(t)dt = \tau, \qquad \int_0^\infty J \ f(t) \ dt = 1$$
$$^{-1} < \ ^x\text{max} \qquad l \le X_{exit} \le u$$

and solved as a discretized NLP. To generate extensions to the attainable region, the constraints related to recycle reactor behavior in (IS) can be added as before and the algorithm in Figure 5 can be executed in the same manner. As will be seen in section 5, the simultaneous formulation allows for a natural integration with other flowsheet subsystems. In particular, trade-offs are established among these subsystems in a direct manner.

To deal with nonisothermal systems, formulation (16) can be extended to add decision variables which describe optimal temperature profiles. In a similar manner as with (15), recycle reactor and CSTR extensions can also be added to expand the attainable region. Here each of the reactor extensions is allowed different temperatures as well. Finally, for purposes of heat transfer, and by extension, energy integration with other process subsystems, an effective means of controlling the temperature profile is through cold-shot cooling with the feed. This introduces only a slight modification of the nonisothermal formulation. Instead of an initial scheme based on reaction in segregated flow, the more general cross flow reactor model can be introduced as shown in Figure 6. Discretization of this model with the introduction of sidestreams at discrete points leads to the following NLP formulation:

$$\text{Max} \quad J(X_e xit, t) \qquad (17)$$

$$oc(t), f(t), T(t),$$

$$f -- \quad R(T(t),X) \quad + \quad {}^{\wedge} f_i (X_0 - X(t)),$$

$$X(0) = x_Q$$

$$x_{exit} = \int_0^{\infty} f(t) \, X(t) \, dt$$

$$\int_0^{\infty} f(t) \, dt = 1, \quad \int_0^{\infty} a(t) \, dt = 1$$

$$Q(t) / Q_0 = \int_0^t [\alpha(t') - f(t')] \, dt'$$

$$\int_0^{\infty} \int_0^t [a(f) - f(f)] \, df \, dt = x$$

Here, $a(t)$ is the feed addition profile for the cross flow model. Note that when $f(t)$ becomes a Dirac delta function, the cross flow model becomes the DSR model described in the previous section with the sidestream set to the feed composition. Consequently, the targeting model is compatible with the geometric properties presented above. Balakrishna and Biegler (1992b) discretized (17) using collocation on finite elements and thus solved this problem asanNLP.

Again, RR or CSTR extensions similar to (15), or even further cross flow extensions can be applied to the attainable region constructed from (17). However, in contrast to the simplest approaches in (14) and (IS) which often lead to LP formulations, (16) and (17) are more likely to lead to local optima. Clearly, the use of global optimization methods would be advantageous (see Floudas and Grossmann, 1994) but even with the use of faster local methods, good solutions to (17) can be obtained through incremental solutions of simpler problems. For example, solution of (17) with a fixed feed and temperature profile, and no sidestreams amounts to solving (14). With that solution, the feed compositions can be included as decisions (if desired) as in (16). Later with the solution from (16) or (14), temperature profiles can be varied and finally sidestreams can be allowed. While this approach does not guarantee global optimality, it builds on simple problem formulations and efficient solution procedures. In particular, more complex problem formulations are introduced only as they are needed. Numerous nonisothermal problems have been solved with this approach (Balakrishna and Biegler, 1992b). In the next section we will also see how this approach has advantages with flowsheet and heat integration.

5. Integration with other process subsystems

Reactor networks are rarely designed in isolation, but rather form an important part of an overall flowsheet. Moreover, since feed preparation, product recovery and recycle steps in a process are directly influenced by the reactor network, the synergy among these subsystems is a key factor in establishing an optimum process. Because of reactant recycling, overall conversion to product is influenced by selectivity to desired products rather than reactor yield, as noted by Conti and Patterson (1985). Douglas (1988) extends this notion of process synthesis by establishing trade-offs among conversion of raw materials, capital costs and operating costs. Here, although selectivity maximimization leads to optimum overall conversion to product, capital and operating costs affected by high recycles can improve if reactor yield is maximized instead. Hence, to balance these trade-offs, Douglas suggests a reactor network that operates between maximum yield and maximum selectivity.

A geometric approach to reactor/flowsheet integration was developed by Omtveit and Lien (1994) where separations and recycles were incorporated into the construction of the attainable region. Here, geometric constructions need to be performed ileratively as the reactor feed is unknown in the optimum flowsheet Omtveit and Lien (1994) therefore constructed a family of attainable regions and used constraints due to reaction limitations to represent this problem in only two dimensions. This approach was demonstrated on the HDA process (Douglas, 1988) as well as methanol synthesis. In both problems the optimal reactor turned out to be a plug flow reactor and quantitative trade-offs were established between the purge fraction, reactor yield and economic potential.

While the qualitative concepts mentioned above yield useful insights for process integration, many quantitative aspects along with discrete and continuous decisions still have to be made. A natural way to account quantitatively for process trade-offs and to represent the interactions of process subsystems is to develop targeting models based on NLP and MINLP formulations. Again, as with reactor network targeting the goal of these formulations is to predict process performance without explicitly developing the network itself. Consequently, concepts of attainable regions are extremely useful here and dimensionality limitations can be overcome through the NLP formulations presented above.

For example, with an isothermal network, Balakrishna and Biegler (1992a) demonstrated the effectiveness of NLP formulations for flowsheet integration on the Williams-Otto (1960) process. Originally, the reactor was represented as a stirred tank with an optimal return on investment of about 130%. Application of (16) and (IS) shows that much better performance can be obtained with a single plug flow reactor and the return on investment more than doubles to 278%.

For nonisothermal reaction systems and flowsheet integration, energy integration of the reactor network with separation units and process streams is a key consideration. Energy integration tools such as pinch technology have been extremely effective in reducing process operating costs, especially for existing processes, although often only the "sequential" energy integration problem is addressed. Here a heat exchanger network is targeted and synthesized only after the process is "optimized." On the other hand, numerous studies (Duran and Grossmann, 1986, Terrill and Douglas, 1987) have indicated the need

for simultaneous heat integration and process optimization. This is especially important in order to reflect the correct "costs" of energy resulting for integration and therefore to establish an accurate balance of the trade-offs between energy, capital and raw material costs.

To include the integration of energy into the synthesis of the reactor network a related simultaneous strategy can also be developed. Here the nonisothermal NLP formulation in (17) is adapted to deal with heat exchange from other process streams. Within the discretized cross flow reactor, temperature segments are identified as either hot or cold streams (for exothermic or endothermic reactions, respectively) and additional sources of heating or cooling are included with the possibility of intermediate feedstreams (as shown in Figure 7). With this framework and the identification of hot and cold reactor streams, we can now augment (17) with the Duran and Grossmann formulation for heat integration. In this approach additional constraints are constructed that reflect minimum utility consumption as a function of the flowrates and temperatures of the integrated system. Therefore, given a set of hot and cold streams, the minimum heating utility consumption is given by $QH = \max(zHP(y))$, where, ZHP is the difference between the heat sources and sinks above the pinch point for pinch candidate p. For hot and cold streams with inlet temperatures given by Th^{in} and tc^{in}; and outlet temperatures Th^{out} and tc^{out} respectively, $ZHP(y)$ is given by,

$$zH^P(y) = 2^\wedge w_c[\max\{0; tc^{out} - TP + AT_m\}$$
$$-\max\{O; tc^{in} - TP + AT_m\}])-$$
$$\pounds hW_h[\max\{0; Th^{in} - TP\} - \max\{0; Th^{out} - TP\}])$$

for $p = 1, Np$; where Np is the total number of heat exchange streams. Here, TP corresponds to all the candidate pinch points; these are given by the inlet temperatures for all hot streams and the inlet temperature added to AT_m for the cold streams. Wh and w_c are the heat capacity flows for the hot and cold streams and the vector y represents the set of all variables (temperatures, flowrates and compositions) in the reactor and energy network. The minimum cooling utility is given by a simple energy balance as $Qc = QH + ^\wedge(y)\gg$ where, $Q(y)$ is the difference in the heat content between the hot and the cold process streams, given by:

$$Q(y) = Zh\ Wh(T_h^{in} - T_h^{out}) - Ic\ w_c(T_c^{out} - T_c^{in}).$$

These relations can be incorporated with the flowsheet model and the targeting formulation of (17) in order to develop the following simultaneous formulation.

$$\text{Max} <\!t\!>((o,y,QH, Qc) -\!J\ (<\!a,y) - CHQH - cCQC$$
$$\text{s. t}\ ^\wedge = R\ (T(t), X) + \frac{\alpha(t)Q_0}{Q(t)}(X_0 - X(t)),$$

$$X(0) = X_0(co,y)$$

$$Xexit = \int_0^{\infty} f(0\ X(t)\ dt, \quad \int_0^{\infty} f(t)\ dt = 1$$

$$\int_0^{\infty} Ja(t)dt = 1, \quad \int_0^{\infty}\int_0^{t} [a(t\!>\!f(t')]dt^t dt = T$$

$$Q(t)/Qo = \int_0^{t} [a(f) - f(t')]\ dt'$$

$$W_h = C_{ph}(Th^{in})\ F_{h>} \qquad w_c = C_{pc}(t_c^{in})F_c$$

$$QC = QH - \pounds_h W_h[T_h^{in} *^T h^{0Ut}D -$$
$$\sum_c w_c[t_c^{out} - t_c^{in}])$$

$$QH \wedge z_H{}^P(y) \qquad p \in P$$

$$h(co,y) = 0 \qquad g(co,y) \le 0$$

Here Fh and F_c are the flowrates for all process and reactor streams, co is the set of flowsheet parameters and QH and QC represent hot and cold utility requirements. This optimization problem is expressed in a general abstract form, which is discretized in the same manner as (17). A discrete representation of this reactor targeting model is illustrated in Figure 7. In addition to discrete feed stream additions, any temperature profile can be determined through heating and cooling units at these points. Moreover, heats of reaction are directly incorporated through heat capacity flowrates of the reacting streams. Here in a discretized reacting segment, if QR is the exothermic (endothermic) heat of reaction to be removed (added) in order to maintain an isothermal segment, the equivalent Wh (w_c) is equated to QR and we assume a 1 K temperature difference for this reacting stream. Note that in addition to the performance of the reactor network, other process units and the energy network are captured in this compact formulation. Once this problem is solved, a formulation similar to (15) is employed to check for improvements in the network by extending the attainable region. Also, we note that no assumptions were made as to the structure of the reactor or heat exchanger networks.

This approach was applied to moderately sized process with van de Vusse kinetics, $A \rightarrow B \rightarrow C, A \rightarrow D$ as shown in Figure 8. In this case, the reaction is highly exothermic and numerous opportunities exist for the reactor to generate steam for the reboilers and thus reduce the overall energy load. In addition, the process produces a valuable main product (B) and potentially harmful byproducts, C and D. Consequently, reactor selectivity is a key component of this process in order to maximize the process profit. In order to demonstrate the synergy of the flowsheet subsystems we present two cases for comparison. In the first instance, the sequential case, a reactor network is synthesized within a flowsheet and energy integration is performed for this design. For the second, simultaneous case, the energy target is determined together with the reactor target.

Interestingly, in both cases, a single plug flow reactor is chosen with similar residence times and both reactors have falling temperature profiles, with the simultaneous profile about 10-20 K lower than for the sequential case. Because the side reactions are more exothermic than the main reaction (A --> B), the simultaneous result has a much better selectivity and a higher overall conversion of raw material A to product B (61.5% vs. 49.6%). As listed below, the simultaneous case has a lower conversion per pass (77% vs. 87%), a higher recycle rate and requires about 20% less raw material for the process. This occurs simply because cheaper energy costs due to heat integration allow more emphasis to be placed on raw material conversion in the optimization.

	Seq'l.	Simult.
Overall Profit(K)[5] $/yr)	38.98	74.02
Overall Conversion to B(%)	49.6	61.55
Hot Unidity Load (10^5 Btu/h)	3.101	2.801
Cold Utility Load (10^6 Btu/h)	252.2	168.5
Fresh Feed A (10^4 lb/h)	8.057	6.466
Byproducts C/D (10^4 lb/h)	4.045	2.44
Recycled A (10^4 lb/h)	1.22	1.963

A similar approach can also be adopted for the integration of reaction and separation systems. In previous studies, the separation sequence is considered to be a downstream process to recycle reactants, remove unwanted byproducts and purify the desired products. This approach allows for an easy decomposition of subsystems and this has been used to advantage in hierarchical decomposition (Douglas, 1988) and in MINLP synthesis (Kokossis and Floudas, 1991). In order to improve the synergy of these subsystems, strategies need to be developed lhat incorporate simultaneous reaction and separation. This topic is currently the focus of considerable research activity (Barbosa and Doherty, 1987, 1988; Omtveit and Lien, 1994; Balakrishan and Biegler, 1993). However, the synthesis of reaction-separation systems is still in its infancy. For instance, the targeting work described in Balakrishna and Biegler (1993) represents an idealized system that requires further development and generalization. Nevertheless, this topic has been spurred by significant industrial successes, where in lieu of clumsy conventional flowsheets, complex reactions and separations can be incorporated into a single reactor/separator (Agreda etal., 1990).

Finally, as new processes are invented and existing ones are revamped, the scope for minimizing waste and hazardous by-products becomes an important consideration. This aspect is directly focused on reactor performance. In addition to choosing new chemistries and reaction paths, insights gathered from attainable regions with knowledge of side reactions is a key element for waste-minimizing processes. As with any of the objectives used above for process synthesis, the application of geometric targeting approaches and the NLP extensions can be applied in a straightforward manner to waste minimization. Here constructive approaches can be applied to find an attainable region and subsequently to determine reactor networks with maximum selectivity, or minimum waste with a specified product yield. These results can then be embedded directly into an AR or NLP approach as well. Here, a useful decision-making tool, especially in dealing with uncertain waste treatment costs, is the use of multicriterion optimization and the generation of Pareto optimal or noninferior surfaces. Note here that on the noninferior curve, no objective can be improved without sacrifice to the values of the other objectives and trade-offs can be established clearly. In dealing with process profit vs. waste generation, Lakshmanan and Biegler (1994) adapted the NLP targeting approaches described in the previous section to develop these surfaces as well.

7. Summary and Conclusions

In this study, we have reviewed reactor network synthesis strategies based on attainable region concepts. These concepts have rigorous geometric foundations which can be used in complementary strategies; through direct constriction of the attainable region (AR) or by embedding AR concepts within optimization formulations. At present we can construct attainable regions for two and three dimensional problems. This allows us to solve bounds on reactor performance problems and then specify the reactor network and operating parameters. These AR approaches can be extended to include other processes such as heat exchange and separation. The theory behind the attainable region still needs to be developed but there are many postulates that can be made by extension from reaction and mixing. These are outlined along with example^s to demonstrate the constructive approach.

This constructive approach has not been extended to higher dimensional (> 3) problems as there are problems with the visualization of the region to higher dimensions. Furthermore as the approach effectively finds all possible output from all possible reactor networks, and then searches over this set of solutions for the optimal one, it is not a feasible approach in higher dimensional problems. However, by understanding the geometry of individual processes of reaction and mixing we are able to predict the way in which individual processes make up the boundary of the attainable region. This can then be interpreted in terms of the types of reactors and ways in which the reactors are interconnected. Hence we are able to make some suggestions on how to synthesize a reactor superstPicture rich enough to produce all possible output material, and then build these suggestions into the optimhation formulations for reactor network targeting.

Optimization-based approaches, on the other hand, have other characteristics that must be carefully considered. While geometric constructions yield a global picture of a given reactor system, optimization formulations frequently

rely on local tools. Clearly, the development of convex problem representations (as in segregated flow) or the application of global tools (Floudas and Grossmann, 1994) is an important topic for future work. At present, the application of small NLPs based on PFRs and CSTRs can be used as an approximation of the construction process. As a sequential approach, it ensures good, if not globally optimal solutions for higher dimensional problems.

In addition, NLP formulations have advantages as they can handle higher dimensional systems as well as problems in which the objective functions have parameters which cannot be incorporated in the constructive approach. Thus for example, constraints can be placed on the structure complexity and operating costs which cannot always be incorporated into the AR approach. Moreover, these formulations lead to straightforward integration of the reactor synthesis problem with other process subsystems in order to exploit their synergy. This was illustrated in a small process example.

In summary, this paper has explored ways in which the two approaches can be combined to exploit their strengths and advantages in reactor network synthesis, and ultimately for improved synthesis of process flowsheets. What we are aiming at is a method in which we can define the individual processes (i.e., reaction, mixing, separation, etc.), the process equipment and the flowsheet can be predicted, either by the construction approach currently used or through further understanding of the geometric properties, and subsequent optimization. Through this approach we ultimately aim for a synthesis approach based on the process phenomena and not on the traditional unit operations. This will serve as a significant motivator for novel future processes.

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