A Hierarchical Decision Procedure for Process Synthesis

A new procedure for synthesizing process flow sheets and base-case designs has been developed. The procedure is evolutionary in nature and proceeds through a hierarchy of decision levels, where more fine structure is added to the flow sheet at each decision level. Heuristics are used to obtain some of the structural elements of the flow sheet, and other heuristics are used to make some of the decisions required at the various decision levels. In many cases, no heuristics are available, so that process alternatives are generated. The analysis portion of the procedure has a strong focus on the economic tradeoffs that are associated with the significant design variables.

J. M. DOUGLAS
Chemical Engineering Department
University of Massachusetts
Amherst, MA 01003

SCOPE

Process design provides the backbone of the petroleum and chemical industries; it also is the capstone course in the undergraduate chemical engineering curriculum. However, there is no step-by-step procedure available in the literature that can be used to develop a process flow sheet or a base-case design. Furthermore, the logic and/or the order in which decisions for developing a first flow sheet are made have not been discussed previously in the literature.

CONCLUSIONS AND SIGNIFICANCE

A synthesis/analysis procedure for developing first flow sheets and base-case designs is presented. The procedure is described in terms of a hierarchy of decisions, where at each decision level more fine structure is added to a block flow sheet of the process. In many cases either previously published heuristics or some new heuristics can be used to guide the decisions, but in many other situations no heuristics are available. It is possible to identify the economic tradeoffs associated with decisions about design variables, but a case study approach is required to evaluate process alternatives. The synthesis/analysis does not necessarily lead to the "best" design, but it should be useful in developing "reasonable" designs.

INTRODUCTION

The problem of translating a chemist's discovery of a new reaction into a process flow sheet and a base-case design is always underdefined. Thus, it is necessary to introduce numerous assumptions in order to obtain a well-posed problem. These assumptions can be divided into three categories (Douglas, 1982):

1. Assumptions that fix parts of the process flow sheet.
2. Assumptions that fix some of the design variables.
3. Assumptions that fix the connections to the environment.

If we change the assumptions that fix parts of the process flow sheet, we generate process alternatives. For most processes we can generate over a million flow sheets in this way. If we change the assumptions that fix some of the design variables, we generate optimization problems. Westerberg (1981) has suggested that there are about 10 to 20 optimization variables per flow sheet. If we change the assumptions that fix the connections to the environment, we generate process operability and control problems. Normally, we do not consider these problems until after we have developed a base-case design (i.e., if a process has little chance of being profitable, we do not care about operability or control).

After an extensive series of discussions with industrial designers, there seems to be a consensus that the major errors in existing designs were caused by fixing the flow sheet too early in the development of a process. In other words, someone realized that there was a better process alternative when it was too late to make changes in the project definition. Thus, there is a need to have better tools available that can be used to generate and screen process alternatives.

Previous Work

There have been two major attempts to develop computer-aided design programs that would generate process flow sheets: AIDES (Siirola et al., 1971; Siirola and Rudd, 1971; Powers, 1972) and BALTAZAR (Mahelec and Motard, 1977). Both of these programs are designed to generate process flow sheets for multiproduct plants. They select the best raw materials to use and the best set of reactions for the process from a number of alternatives. Thus, the programs focus on the problem of species allocation. However, in their present forms neither program includes algorithms to calculate equipment sizes and costs, and therefore they do not produce a base-case design.

The scope of our procedure is much more modest. Only single-product plants with a specified set of raw materials and a specified reaction path are considered. Thus the species allocation problem can be solved using simple heuristics. The primary focus of our procedure is on the development of a reasonable base-case design, the significant economic tradeoffs that are associated with this design, and some process alternatives that should be evaluated.

Purpose of the Research

A major purpose of this research was to identify where design heuristics are missing, as well as to provide improved definitions of synthesis problems for pieces of the overall design. For example, at present there do not seem to be any heuristics available to help decide whether absorption, adsorption, or condensation should be chosen as a vapor recovery system. Similarly, current research on the selection of separation sequences is based on the problem statement: Given a single feed, what is the best selection of separating units to obtain the required set of pure products?

Our procedure indicates that in many processes there should be multiple feed streams that require separation, and that normally the specification of product compositions depends on interactions with the process. Thus, we expect that the procedure will provide a focal point for the definition of new research problems in design.

A valuable byproduct of the research should be an improved conceptual framework for the teaching of process design. Currently, most undergraduates are exposed to only a single case study, so that they develop no intuition or experience with the decisions required to develop other types of flow sheets. The synthesis procedure should make it possible to broaden this scope.

PROCESS SYNTHESIS: A NEW APPROACH

The process synthesis procedure decomposes the design problem into a hierarchy of decisions, as follows:

Level 1: Batch vs. Continuous
Level 2: Input-Output Structure of the Flow Sheet
Level 3: Recycle Structure of the Flow Sheet and Reactor Considerations
Level 4: Separation System Specification
  Level 4a: Vapor recovery system
  Level 4b: Liquid recovery system
Level 5: Heat Exchanger Network

The complete process is always considered at each decision level, but additional fine structure is added to the flow sheet as we proceed to the later decision levels. The newly developed synthesis techniques and heuristics are used by the designer, whenever they exist, as a guide in making the required decisions. By accumulating the decisions made by the designer for cases where there are no heuristics, or where the designer overrides the heuristics, we can develop a list of process alternatives that should be considered.

Each decision level terminates in an economic analysis. Experience indicates that less than one percent of the ideas for new designs are ever commercialized, and therefore it is highly desirable to discard poor projects quickly. Similarly, the later level decisions are guided by the economic analysis of the early level decisions.

The synthesis procedure is described in detail below. At present, the procedure is limited to continuous processes with vapor and liquid phases.

INPUT INFORMATION

The input information required to develop a process flow sheet and a base-case design is:

A. Reactions
  1. The stoichiometry, temperature, and pressure of each reaction.
  2. A correlation of product distribution vs. conversion (and temperature).
  3. The catalyst for each reaction (at present, the program will not handle catalyst deactivation).
  4. The desired phase condition of each reaction step.
B. Products
  1. Desired production rate and product purity.
  2. Product price, or price vs. purity.
  3. Value of all byproducts as chemicals or fuel.
C. Raw Materials
  1. Composition, temperature, and pressure of all raw material streams.
  2. Prices of all raw material streams, or price vs. purity.
D. Constraints
  1. Explosive limits and safety considerations.
  2. Coking limits, polymerization or decomposition limits, etc.
E. Plant and Site Data
  1. Utilities—fuel, steam levels, cooling water, refrigeration, etc.
  2. Waste disposal facilities and costs.

HDA EXAMPLE: HYDRODEALKYLATION OF TOLUENE TO BENZENE

In order to illustrate the procedure we consider a continuous process for producing benzene by the hydrodealkylation (HDA) of toluene. The reactions of interest are:

$$\text{Toluene} + H_2 \rightarrow \text{Benzene} + CH_4 \tag{1}$$

$$2\ \text{Benzene} \rightleftarrows \text{Diphenyl} + H_2 \tag{2}$$

The desired reactor pressure is 3,450 kN/m^2 (500 psia), and the reactor inlet temperature must exceed 895°K (1,150°F) in order to obtain a sufficiently large reaction rate. The selectivity (benzene produced at the reactor outlet divided by the toluene converted in the reactor) is given by

$$S = 1 \frac{0.0036}{(1-x)^{1.544}} \tag{3}$$

The reactor outlet must be kept below 978°K (1,300°F) to prevent hydrocracking reactions.

The desired production rate of benzene is 265 kgmol/hr at a purity $x_D = 0.9999$. A pure toluene stream is available at ambient conditions and a hydrogen stream containing 95% H_2 and 5% CH_4 is available at 311°K (100°F) and 3,790 kN/m^2 (550 psia). The hydrogen-to-aromatics ratio at the reactor inlet must exceed 5 and the reactor effluent must be rapidly quenched to 895°K (1,150°F) to prevent coking.

LEVEL 1: BATCH VS. CONTINUOUS

Since batch processes are time-dependent, they have a different structure and very different alternatives from continuous plants. The procedure in its current form is restricted to continuous processes.

LEVEL 2: INPUT-OUTPUT STRUCTURE OF THE FLOW SHEET

Since raw material costs are often in the range of 35 to 85% of the total processing costs (Grumer, 1967), we focus our initial attention on the design variables that might affect these stream costs. The decisions we make are:

1. Should we purify the raw material streams before processing, or process the feed impurities?
2. How many product streams will there be?
3. Do we need a gas recycle and a purge stream? What are the costs associated with a purge?
4. Should reversible byproducts be recovered or recycled to extinction?
5. What are the costs associated with selectivity losses for complex reactions?

Heuristics for Feed Impurities

If the impurities react, it is preferable to remove them before processing. If the impurities are inert, are present in fairly large amounts, but can be separated easily by distillation, it is preferable to remove them before processing. There does not seem to be any heuristic available to quantify the amount. Similarly, there does not seem to be any heuristic to decide whether it is better to use azeotropic distillation or other complex separation techniques to remove impurities. If an impurity in a feed stream is also a product component in one or more reactions, consider putting the feed stream into the process at the point were that impurity is recovered and removed. If a gas phase reactant stream contains light impurities (i.e., that boil at lower temperatures than propylene), process the impurities.

These heuristics are based on conventional industrial practice although they do not seem to have been published. It is apparent that it would be desirable to develop quantitative heuristics for each of the various cases.

Heuristics for the Number of Product Streams

We first assume that the reactor effluent will contain all of the components in the feed streams and all of the components in every reaction step (unless a component is known to be unstable, so that it completely reacts). If one or more of these components in the reactor effluent is highly corrosive, or might polymerize or decompose to undesirable byproducts, and if we can force this reaction to complete conversion in order to eliminate this type of undesirable component, we remove it from the list. Next, we classify all of the components in the reactor effluent as follows:

Reactant: recycle
Reaction intermediate: recycle
Reversible byproduct: either recycle or exit
Azeotrope with reactant: either recycle azeotrope or break azeotrope and recycle reactant
Primary product: exit
Valuable byproduct: exit
Fuel byproduct: exit
Waste byproduct: exit

Now we order the components by their normal boiling points, and we lump together neighboring components of the same type. The number of product streams is assumed to be the number of lumps.

This analysis is based on the heuristics that distillation is normally the least expensive separation and that it would be wasteful to separate two components and then give them identical treatment, e.g., send them both to a fuel supply or to waste treatment.

Heuristics for Recycle and Purge

If a reactant and either a feed impurity or a reaction byproduct both boil at a lower temperature than propylene (−48°C, −55°F), we assume that a gas recycle and a purge stream are required. This heuristic is based in part on the fact that propylene can be condensed with cooling water at high pressure, so that all materials less volatile than propylene can be recovered by distillation (or some other liquid separation scheme) using only cooling water. Of course, in ethylene plants we separate ethane from ethylene by distillation using refrigerated condensers and we even separate oxygen from nitrogen by distillation. However, for most processes the cost of recovering gaseous reactants (which normally are much less expensive than organics) from gaseous impurities is so large that it is cheaper to discard some of the reactant in a purge stream. Another alternative, however, is to use a membrane system to separate the gaseous components.

Material Balances and Stream Costs

The difficulty of solving the overall material balances for a fixed production rate of a desired component depends on the type of process, as shown below. In our initial analysis, we assume complete recovery of all valuable materials unless there is a gas recycle and purge stream. In other words, all unconverted reacting components are completely recovered and recycled. Thus, there are only two flow sheets of interest, Figure 1.

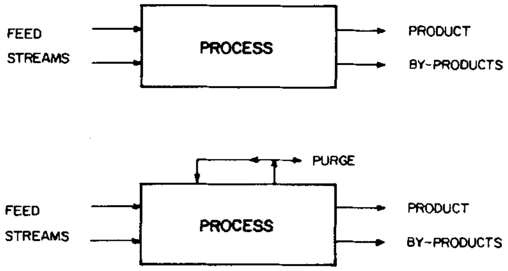

Figure 1. Input-output structure of flow sheet.

Single reaction. If there is a single reaction with no gas recycle and purge, it is always a simple matter to calculate the required raw materials and byproduct flows from the stoichiometry. (Note that all unconverted reacting components leaving the reactor are recycled to extinction.) Once the feed rates of the reactants have been determined, the impurity flows can be calculated from the known feed compositions. After the flows have been calculated, it is a simple matter to calculate the stream costs.

Gas recycle and purge. If there is a gas recycle and a purge stream for either single or complex reactions, some of the gaseous reactant is discarded. In order to calculate the overall material balances it is necessary to specify either the amount or the composition of the reactant in the purge stream. Large reactant compositions in the purge stream correspond to high raw material costs. On the other hand, if inerts are allowed to accumulate in the gas recycle stream so that the purge composition of reactant is small, there will be large gas recycle flows and large gas recycle costs. Thus there is always an optimum purge composition of reactants; unfortunately, there is no rule of thumb to help us guess this value. At the preliminary design stage, we plot the net stream value vs. the purge composition, where

$$\begin{matrix}\text{Net Stream}\\ \text{Value}\end{matrix} = \begin{matrix}\text{Economic}\\ \text{Potential}\end{matrix} = \begin{matrix}\text{Product}\\ \text{Value}\end{matrix} + \begin{matrix}\text{Byproduct}\\ \text{Value}\end{matrix} - \begin{matrix}\text{Raw}\\ \text{Material}\\ \text{Costs}\end{matrix} \tag{4}$$

Normally, there is a value of the reactant purge composition above which the net stream costs become negative, i.e., the value of the raw material discarded becomes so large that the process will never be profitable. Thus, we determine the range of purge compositions of reactant where potentially profitable operation is possible.

Recovery or recycle of reversible byproducts. If a reversible byproduct has a small concentration at the reactor exit, it is normally better to recycle this component. This approach saves on selectivity losses and usually requires one less separation unit. However, there does not seem to be any quantitative heuristic that helps to fix the composition. Some processes have been commercialized using both approaches, i.e., recovery and removal.

Complex reactions: In order to calculate the overall material balances for complex reactions it is necessary to specify the product distribution. For a large number of processes, the product distribution can be correlated against conversion (in some cases reactor temperature is important). Experience also indicates that the formation of byproducts and the raw materials required both increase rapidly as the conversion increases. Thus, the net stream value, Eq. 4, decreases and normally becomes equal to zero at some finite conversion. Of course, at very low conversions, where the selectivity losses usually approach zero, there will be a very large recycle of unconverted reactant.

Thus, there will be an optimum conversion that is fixed by the process economics, i.e., selectivity loss and reactor cost balanced against recycle cost. This optimum conversion is expected to be less than the conversion corresponding to the maximum yield. Normally there is a significant amount of by-product formation at the maximum yield, and therefore if we operate at smaller by-product

TABLE 1. CLASSIFICATION OF REACTOR EFFLUENT

Component	NBP, K	Component Type
H_2	20	reactant
CH_4	112	fuel byproduct
Benzene	353	product
Toluene	384	reactant
Diphenyl	528	fuel byproduct

formations and recycle the incremental amount of reactant we lower the total processing costs. Unfortunately, there are no heuristics which help us to estimate the optimum conversion. Thus, at the initial stages of design we plot the economic potential vs. conversion in order to find the region where potentially profitable operation might be possible.

Some Level 2 Decisions for the HDA Example

Since the methane impurity in the hydrogen feed stream is also produced by the primary reaction, there does not seem to be any incentive to purify the feed stream. Since the recycle of diphenyl to extinction has been patented by another company, we will evaluate the process alternative of recovering the diphenyl. Since both hydrogen (a reactant) and methane (both a feed impurity and a fuel byproduct) are lighter than propylene, we assume that we will need a gas recycle and a purge stream (a membrane separation of hydrogen from methane offers another process alternative).

Classification of reactor effluent. The classification of the reactor effluent is shown in Table 1. There are two liquid product streams (benzene and diphenyl) and a purge stream containing H_2 and CH_4. The flow sheet is shown in Figure 2.

Overall Material Balances. If we assume no losses of valuable materials (rather than the rule of thumb of greater than 99% recoveries), the toluene converted in the reactor will be equal to the toluene fresh feed rate. Then, for a production rate of benzene P_B, we find from the stoichiometry that the toluene fresh feed rate F_{FT}, is

$$F_{FT} = P_B/S \tag{5}$$

and the production of diphenyl, P_D, is

$$P_D = P_B \frac{1-S}{2S} \tag{6}$$

The hydrogen entering in the makeup gas stream, $0.95\,F_G$, will equal the net amount of hydrogen consumed by the reaction, $(P_B/S)[1-(1-S)/2]$, plus the amount lost in the purge, $y_{PH}P_G$; thus,

$$0.95\,F_G = \frac{P_B}{S}\left(1 - \frac{1-S}{2}\right) + y_{PH}P_G \tag{7}$$

A similar balance can be made for methane

$$0.05\,F_G + \frac{P_B}{S} = (1 - y_{PH})P_G \tag{8}$$

Thus, the makeup gas flow F_G and the purge flow are given by

$$F_G = \frac{P_B}{(0.95 - y_{PH})}[1 - \tfrac{1}{2}(1 - y_{PH})(1 - S)] \tag{9}$$

$$P_G = F_G + P_B\left(\frac{1-S}{2S}\right) \tag{10}$$

From these expressions, and Eq. 3, we see that the conversion, x, and the hydrogen composition of the purge stream, y_{PH}, must be specified in order to calculate the stream flows.

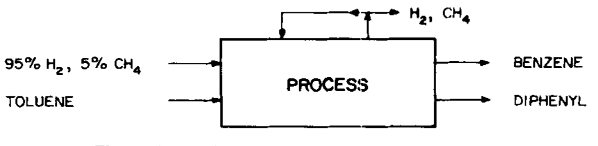

Figure 2. Block flow sheet for benzene process.

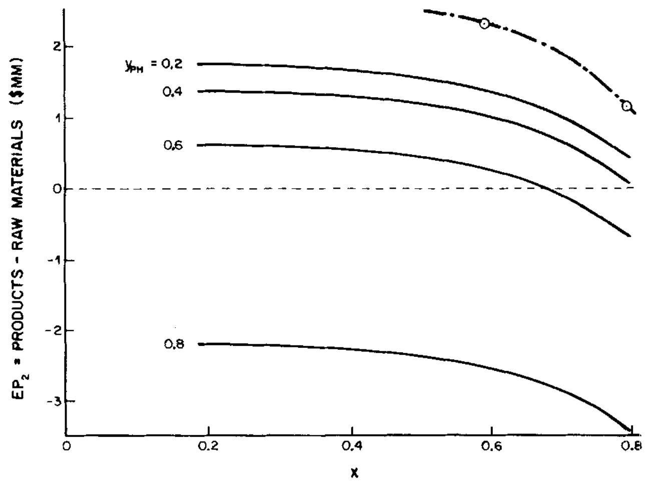

Figure 3. Economic potential at Level 2 vs. conversion and purge composition.

Stream Costs and Economic Potential. We define the economic potential at Level 2, EP_2, as

$$EP_2 = \begin{matrix}\text{Value of}\\ \text{benzene}\end{matrix} - \begin{matrix}\text{Cost of}\\ \text{toluene}\end{matrix} - \begin{matrix}\text{Cost of } H_2\\ \text{makeup}\end{matrix} + \begin{matrix}\text{Fuel value}\\ \text{of diphenyl}\end{matrix} + \begin{matrix}\text{Fuel value}\\ \text{of purge}\end{matrix} \tag{11}$$

Thus, we can plot the economic potential, as is shown in Figure 3.

Discussion of Level 2 Decisions

The idea of calculating product-plus-byproduct values minus raw material costs at the beginning of a design problem has been previously discussed by Rudd et al. (1973), Myers and Seider (1976), and others. We have extended this idea to processes where there is a gas recycle and a purge stream and to complex reactions. For these two cases, which are commonly encountered in practice, the overall material balances depend on the purge composition of reactant and/or the conversion, and therefore we plot the results to find the region where profitable operation is possible.

LEVEL 3: RECYCLE STRUCTURE OF THE FLOW SHEET

The most significant design variables for any flow sheet are the process flows. We have discussed the overall material balances in Level 2 decisions, and now we focus on the determination of the recycle flows. The simplified flow sheet that we use at this stage of the analysis is shown in Figure 4. Again, we assume that we can obtain complete recoveries of all valuable components that are less volatile than propylene. The decisions we make at Level 3 are:

1. How many reactors are required? If multiple reactors are used, which feed streams and recycle streams are associated with each reactor, and is some separation required between the reactors?
2. How many recycle streams are there?
3. Do we want to use an excess of one reactant at the reactor inlet?
4. Is a gas recycle compressor required? How does the compressor affect the economic potential?

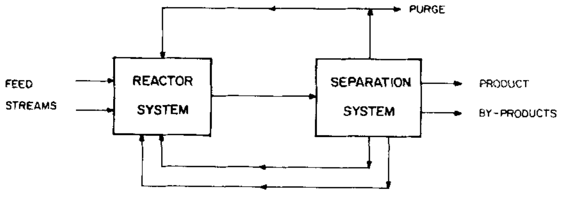

Figure 4. Recycle structure of flow sheet.

5. Should the reactor be operated adiabatically, with direct heating or cooling, or do we need a diluent or heat carrier?

6. If the reaction is equilibrium limited, do we want to shift the equilibrium using an excess composition, temperature, or pressure?

7. How do the reactor costs affect the economic potential?

Heuristics for Multiple Reactors

If some of the reaction steps take place at very different temperatures or pressures, or if different catalysts are used for different reaction steps, then we use different reactors for these steps. Since we know the temperature, pressure, and catalyst associated with each reaction step from the input information, we associate reaction steps with reactor numbers.

Heuristics for Reactor Feed Streams

Once we have associated each reaction step with a reactor number, we can identify the reacting components with a reactor number. Then we feed the raw material streams into the first reactor in the series where that reacting component is present.

Heuristics for Number and Destinations of Recycle Streams

In the Level 2 decisions we identified all of the components that would be recycled. Now we identify the reactor number where each of the recycle species first appears as a reacting component. We have previously ordered all of the components in the reactor effluent by their normal boiling points. We now lump neighboring recycle components that have the same reactor destination. The number of recyle streams will be the number of lumps; it would be wasteful to separate two components and return them to the same reactor.

Specification of Reactor Structure

After we have identified the feed and recycle streams associated with each reactor number, we can add more fine structure to the reactor system block on the flow sheet shown in Figure 4. An example of this type is shown in Figure 5. We need to identify this fine structure before we develop the recycle material balances.

Recycle Material Balances

The calculation of the recycle material balances depends on the type of system under consideration.

Single reactions: limiting reactant. For single reactions we must specify the reactor conversion of the limiting reactant in order to calculate the recycle flow of the limiting reactant. There is an optimum conversion which involves a tradeoff between large reactor costs at high conversions and large recycle costs at low conversions. A reasonable first guess seems to be to choose a conversion of 96% for irreversible reactions and 98% of equilibrium for reversible reactions.

Single reactions: no recycle. It should be noted that there is an optimum conversion for single reactions even if there is no recycle. For this case there is a tradeoff between reactor costs (which increase) and raw material costs (which decrease) as the conversion increases. In these situations, the optimum conversion often exceeds 99%.

Multiple reactants: single or complex reactions. Stoichiometric ratios of reactants give the highest reaction rates and smallest reactor volumes, but in many cases it is desirable to operate with an excess amount of one reactant at the reactor inlet. For example, an excess of one component can be used to shift the equilibrium conversion, to force another component to approach complete conversion, to decrease coke formation, etc. The greater the amount of excess used, the more benefit obtained, but the larger the cost will be to recover and recycle the excess component. There will always be an optimum amount of the excess, but this optimization normally is very difficult to quantify because coking data, for example, are not available. It is common pratice to base first designs on the excess ratio used in the laboratory or pilot plant.

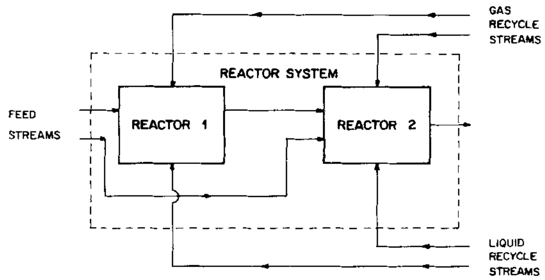

Figure 5. Reactor system.

Complex reactions. We found that it was necessary to specify the conversion of the limiting reactant for complex reactions in order to be able to calculate the overall material balances. We use this same value to estimate the recycle flows of the limiting reactant.

Gas Recycle Compressor

Compressors are one of the most expensive pieces of processing equipment; therefore we desire to estimate their effects on the total processing costs early in our design analysis. Since the gas recycle flow may depend on purge composition (if we have a purge stream) or conversion, we plot the effect of these variables on the costs. That is, we subtract the annual power cost and the annualized capital cost of the compressor from the economic potential given by Eq. 11.

Normally, we obtain an optimum (as a function of purge composition and conversion) from this procedure because the recycle flows become very large as the conversion or purge composition of reactant becomes very small. This is not the true optimum, however, because we have not included all of the recycle costs. Nevertheless, we can use these results to further restrict the region where the optimum design will be located (the values to the left of the maximum can be dropped from further consideration, since the true optimum will be at a lower level and shifted to the right).

Reactor Heat Effects

Once we have estimated the recycle flows, we can calculate the adiabatic temperature rise. The total heat generated in each reactor depends on the product distribution and the heat generated by the various reaction steps, and this heat generation (consumption) heats (cools) the products. Conventional computer-assisted design programs make this calculation simple, once the flows have been fixed.

Since we prefer to carry flow rate ranges through our preliminary analysis, we plot the adiabatic temperature rise, or the reactor exit temperature as a function of the design variables. If there is a temperature limitation because of side reactions at the reactor exit, this graph tends to further limit the range of the design variables where it is desirable to operate.

If the adiabatic temperature rise (fall) is unreasonable, then we evaluate the possibility of using direct heating (cooling) to obtain a reasonable temperature change. The possibility of direct heating (cooling) depends on the total heat generated (consumed) and the surface-to-volume ratio of the reactor. In many cases it is necessary to use a heat carrier (diluent) to modify the adiabatic temperature change. We prefer to use an increased recycle of either reactants or products as a heat carrier, because with this approach we do not need to add another separation unit to recover and recycle an extraneous component. If we introduce an extraneous component as a heat carrier (diluent), we want to choose one which is easy to recover, such as steam.

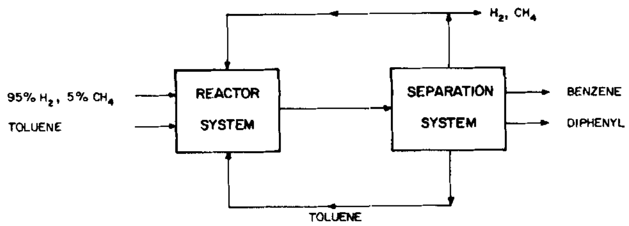

Figure 6. Recycle structure of benzene process.

Equilibrium Limitations

Providing that we write our overall balances in terms of component flow rates, we can always obtain simple solutions in terms of the conversion, purge composition or flow, or molar ratio of reactants. However, the conversions we choose arbitrarily might exceed the equilibrium values. The equilibrium conversions will put additional constraints on the cost curves, and will further limit the range of the design variables.

Of course, we can shift the equilibrium conversion by using an excess of one reactant, changing the reactor temperature, or changing the reactor pressure. For example, in the case of reversible, exothermic reactions, it is desirable to divide the reactor up into three or so adiabatic beds and to use interchangers (or cold shot cooling) to adjust the temperature changes in these beds.

Reactor Costs

At this point in the analysis we have all the information we require to be able to design a reactor. We are primarily concerned with obtaining a reasonable design, rather than the optimum design, because our analysis of the separation system might change the recycle flows. Once we calculate the reactor size and cost, we subtract the annualized cost from the economic potential. We expect that the maximum value on each curve will decrease in magnitude and shift to the right.

Some Level 3 Decisions for the HDA Example

Since both reactions take place at the same temperature and pressure, we use only one reactor. Since the H_2 and CH_4 are a gas recycle, which is separated from the liquid toluene recycle in Table 1 by the benzene product, we must use two recycle streams. Thus, the flow sheet is as shown in Figure 6. The input information requires that H_2/aromatics = 5 at the reactor inlet. Since we are recovering the diphenyl instead of allowing it to build up to its equilibrium level, we neglect equilibrium effects.

Recycle material balances. Again assuming complete recovery of all valuable materials, the toluene fed to the reactor, F_T, will be the sum of the unconverted toluene, $F_T(1-x)$, and the fresh feed toluene, i.e.,

$$F_T = F_T(1-x) + F_{FT}$$

or

$$F_T = F_{FT}/x = P_B/xS \tag{12}$$

This same result will be obtained for every process.

The recycle gas flow, R_G, is fixed by the H_2/aromatics ratio

$$0.95\,F_G + y_{PH}R_G = 5\,F_T = 5\frac{P_B}{Sx} \tag{13}$$

or

$$R_G = \frac{1}{y_{PH}}\left(5\frac{P_B}{Sx} - 0.95\,F_G\right)$$

This result clearly shows that the recycle gas flow becomes unbounded as we let inerts accumulate in the recycle gas stream (i.e., y_{PH} approaches zero), and that the recycle gas flow and compressor costs decrease as the makeup gas rate and raw material costs increase.

Using the results given above, we can easily calculate all of the other process flows.

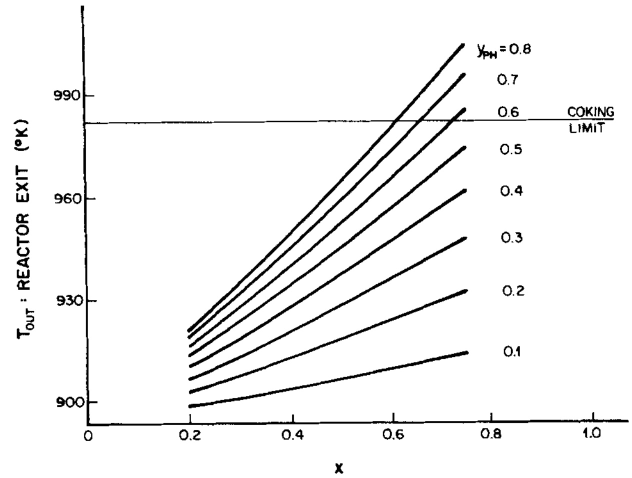

Figure 7. Reactor exit temperature.

Reactor heat effects. Now that we have estimated all of the process flows, we can fix the reactor inlet temperature at 895°K (1,150°F) and calculate the reactor exit temperature for the case of adiabatic operation as a function of conversion and purge composition of hydrogen, see Figure 7. The results indicate that an adiabatic reactor should be acceptable, providing that the conversion and purge composition of hydrogen satisfy the expressions $x < 0.8$, $y_{pH} < 0.6$. We could define these bounds more carefully, if necessary.

Revised economic potential. If we calculate the annualized compressor cost and the power cost for the compressor, as well as the annualized cost of an adiabatic reactor, as functions of conversion and purge composition of hydrogen, and we then subtract these costs from the economic potential at Level 2, we obtain a revised estimate of the economic potential for the Level 3 decisions, EP_3,

$$EP_3 = EP_2 - \begin{matrix}\text{annualized}\\ \text{compressor cost}\end{matrix} - \begin{matrix}\text{operating cost}\\ \text{of compressor}\end{matrix} - \begin{matrix}\text{annualized}\\ \text{reactor cost}\end{matrix} \tag{14}$$

The results, shown in Figure 8, indicate an optimum at various conditions. Since not all of the recycle costs have been included in the analysis, the true values of the optima must be lower and shifted to the right. Hence, we can ignore the operating conditions to the left of the optima.

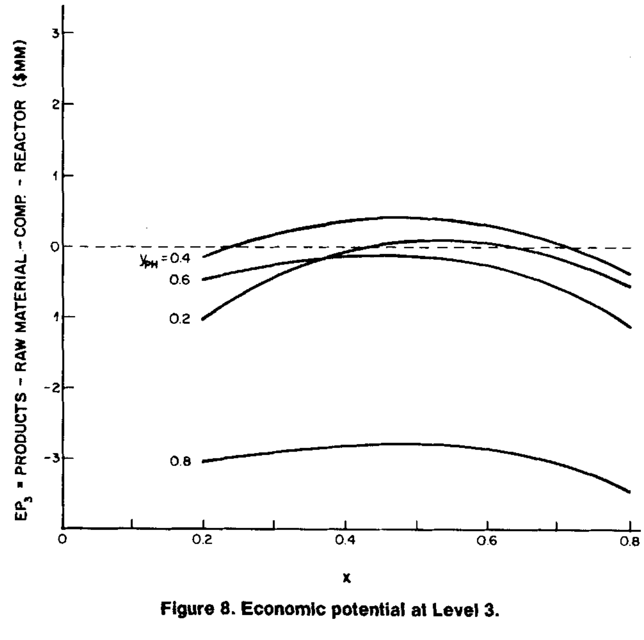

Figure 8. Economic potential at Level 3.

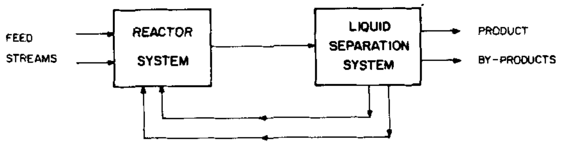

Figure 9. Reactor exit is liquid.

Discussion of Level 3 Decisions

It should not be surprising that we create many more process alternatives as we proceed through a design and that it becomes more difficult to provide heuristics to guide the decisions. In some cases we might undertake some small case studies of reactor alternatives in order to aid in making decisions. However, if the range of potentially profitable operation in Figure 8 is fairly small, we might defer these decisions and see if a preliminary analysis of the separation system will reveal that the process can never be profitable. We always want to minimize the effort we expend to terminate projects.

LEVEL 4: GENERAL STRUCTURE OF SEPARATION SYSTEM

The recycle flow sheet in Figure 4 considers a separation system that is lumped together in a single block. Our design heuristic is that a phase split is always the least expensive separation, and therefore we try to divide the separation system into a vapor recovery system and a liquid separation system. We consider this general problem first.

Once we have estimated all of the process flows, we can undertake a flash calculation of the reactor effluent stream in Figure 4. We use the heuristics below for the three alternatives.

1. If the reactor effluent stream is a liquid, we assume that we can separate the mixture in only a liquid separation system, Figure 9. The liquid separation system might contain distillation, extraction, azeotropic distillation, etc., but no vapor streams leave any of the units.
2. If the reactor effluent is a two-phase mixture at the reactor temperature and pressure, we phase-split the stream, Figure 10. The liquid stream leaving the phase splitter goes to the liquid recovery system. We cool the reactor vapor effluent to cooling water temperature, and phase-split it again. If the liquid leaving this low temperature flash is primarily reactant from that reactor, we recirculate it to the reactor (so that we have the equivalent of a reflux condenser). On the other hand, if the liquid leaving the low-temperature flash is not mostly a reactant from that reactor, we send it to the liquid recovery system. The flash vapor from the low-temperature flash drum is sent to a vapor recovery system.
3. If the reactor effluent is all vapor, we cool the stream to cooling water temperature and attempt a phase split, see Figure 11. If a phase split does not occur, we try to pressurize the reactor effluent and/or use refrigeration to accomplish a phase split (ethylene plants require both). In cases where a high pressure is needed, the possibility of pressurizing the reactor system should be considered. The flash liquid is sent to a liquid recovery system and the flash vapor is sent to a vapor recovery system. (In cases where the flash vapor and the lightest liquid component are recycled to the same reactor, we consider the possibility of operating the flash drum at a higher temperature.)

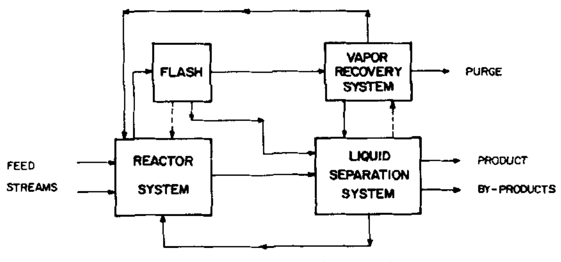

Figure 10. Reactor exit is two-phase.

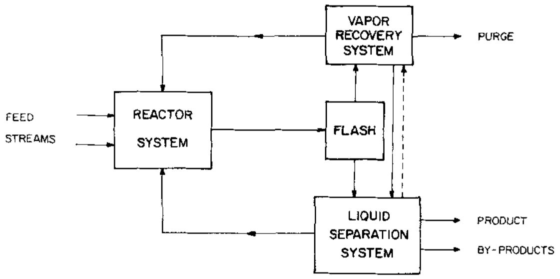

Figure 11. Reactor exit is vapor.

Level 4a Decisions: Vapor Recovery System

In both Figures 10 and 11 there is only one stream that enters the vapor recovery system. Also, from the flash calculations, we know the component flows in this stream. The decisions we make at this level are:

1. The stream location of the vapor recovery system.
2. The type of vapor recovery system.

Location of vapor recovery system. There are four possibilities:

a. If the flash vapor stream contains a significant amount (as compared to the economic potential) of valuable components that would be lost in the purge, put the vapor recovery system on the purge stream. (The purge stream normally has the lowest flow rate.)

b. If the flash vapor stream contains components that foul the catalyst or upset the reactor operability, put the vapor recovery system on the gas recycle stream. (The gas recycle stream normally has the second smallest flow rate.)

c. If both *a* and *b* above occur, put the vapor recovery system on the flash vapor stream (the largest flow rate).

d. If neither *a* nor *b* is significant, do not include a vapor recovery system.

It should be noted that unless *c* is chosen and the vapor recovery system is designed to achieve high recoveries, both the overall and the recycle material balances will change somewhat. Thus, an iteration step is often required in the analysis.

Type of vapor recovery system. There are four major possibilities:

a. Condensation—high pressure and/or low temperature.

b. Absorption—use an existing component as a solvent, if possible.

c. Adsorption—regeneration of the adsorption bed will affect the liquid recovery system.

d. Membrane separation processes.

Each of these (except membrane separation) has one or more streams which would be fed to the liquid recovery system; i.e., a vapor separation also requires a liquid separation. In addition, the absorption process (and usually an adsorption system) requires a solvent stream to be recirculated from the liquid separation system; i.e., an additional recycle loop is introduced into the process.

Fair (1969) has published a heuristic that adsorption is usually the cheapest alternative if the solute concentration is less than 5%. However, since absorption is much more widely practiced than adsorption in the petroleum industry, there is a tradeoff between design uncertainty and actual cost. In some cases it appears as if all of the processes have about the same cost. In summary, it appears that there are no heuristics that provide a clear decision between these alternatives.

Level 4b Decisions: Liquid Separation System

The decisions we make at this level are:

1. What separations can be made by distillation?
2. What sequence of distillation columns should be used?
3. How should the light ends be removed?
4. Should the light ends be vented to the atmosphere, sent to fuel, or recycled to the vapor recovery system?
5. How can we accomplish the other separations?

Heuristics for Using Distillation

We order the components by their normal boiling points (or the boiling point of azeotropes), and we determine the relative volatilities. Whenever $\alpha < 1.1$, we lump the components and then we look for a distillation sequence to separate the revised list of components. After we have established a distillation sequence, we consider ways of separating the lumped components. The alternatives available are:

a. Azeotropic distillation
b. Extractive distillation
c. Reactive distillation
d. Extraction, followed by distillation
e. Crystallization

It does not appear as if many heuristics are available for deciding among these alternatives or for selecting entrainers.

Light Ends Removal

In many cases there will be some light ends dissolved in the liquid leaving a flash drum, a condensed stream, or the solvent leaving a gas absorber. If these light ends will contaminate a product stream, or must be removed for some other reason, the alternatives available are to:

a. Drop the pressure and phase-split the stream.
b. Use a pasteurization section at the top of the first column.
c. Use a stabilizer column.

The appropriate alternative to choose depends on the amount of light ends present and the relative volatilities of the light ends compared to the next lightest component in our list. We usually send the light ends to a fuel supply, but if significant amounts of valuable materials leave with the light ends stream, we recycle this stream back through the vapor recovery system. A recycle flow of this type obviously introduces another recycle loop into the process.

Sequence of Distillation Columns

The selection of a sequence of distillation columns has received considerable attention in the literature in recent years; a complete review has been published by Nishida et al. (1981). However, most of this research has been based on a single feed entering the separation sequence, whereas Figures 10 and 11 indicate that we often expect to have multiple feeds.

Similarly, the heuristics were developed based on the assumption that we always desired pure products. If a component is a reactant that is recycled, then it is not always necessary for it to be pure. Moreover, since the optimum conversion depends on a balance between the sum of reactor and selectivity losses balanced against recycle costs, we might propose a new heuristic that it is always desirable to minimize the number of distillation columns in a liquid recycle loop.

Some of the most commonly accepted heuristics for sequencing columns are:

a. Recover the lightest component first.
b. Recover the most plentiful component first.
c. Make the most difficult splits last.
d. Favor equimolar splits.

It is not surprising that these heuristics can be contradictory. Heuristics *a* and *c* depend upon relative volatility, whereas heuristics *b* and *d* depend upon feed composition. If order of magnitude arguments are used to simplify the cost equations and an approximate solution of Underwood's equation is used to estimate the vapor flows, a quantitative criterion can be developed (Malone, et al.).

$$\text{Favor direct if } \frac{x_C}{x_A} > \frac{\alpha_A + 0.2}{1.2}\left[\frac{1}{1 + x_A(1 - x_A)\dfrac{\alpha_A - 1}{\alpha_B - 1}}\right] \tag{15}$$

A different quantitative heuristic based on an empirical function has been proposed by Lu and Motard (1982).

The results of Tedder and Rudd (1978a,b) indicate that perfect separations in either the direct or indirect sequence of columns are seldom the best. Instead, sidestream columns, sidestream strippers or reboilers, prefractionators, or other column configurations often appear to be more promising. There are a number of active research efforts focused on obtaining improved solutions to this problem.

The problem of energy integration of columns also is the subject of several research programs. The recent results of Andrecovich and Westerberg (1983) provide a useful approach, but they do not consider complex columns.

All of the heuristics discussed above for separation sequences are for ideal systems and are based on constant relative volatilities. Recent studies by Van Dongen and Doherty (1979), Levy et al. (1983), and Caldarola and Doherty (1982) provide relatively simple procedures for estimating the minimum reflux ratio, feed tray location, column design, and some sequencing heuristics for nonideal systems and homogeneous azeotropic mixtures.

Discussion of Liquid Separation Systems

Even though there have been a large number of studies that describe heuristics for the selection of separation sequences, there is still some uncertainty about how to select the best sequence. In particular, multiple feeds, the interaction of the separation system with the remainder of the process (in terms of specifying the fractional recoveries and the recycle of reactants), and nonideal separations need to be studied in much greater detail.

Some Level 4 Decisions for the HDA Example

Since the stream leaving the reactor is all vapor, we use Figure 11 as a flow sheet. Since we assume that any recycle of aromatics through the gas recycle loop is not detrimental to the reactor operation, we consider the installation of a vapor recovery system on the purge stream.

Vapor recovery system. For a nominal base-case design, $x = 0.75$, $y_{PH} = 0.4$ the purge losses are about \$350,000/yr. This amount is fairly significant as compared to the revised economic potential, so that a vapor recovery system on the purge stream should be considered.

However, the magnitude of the revised economic potential is becoming so small that we might want to consider abandoning the project. If we should decide to terminate the project, we want to minimize the amount of design effort that we expend. Hence, at this point we decide to postpone the decision about the design of a vapor recovery system on the purge stream until a later stage of the analysis.

A plot of a second revision of the economic potential, which includes the purge losses, i.e.,

$$EP_{4a} = EP_3 - \frac{\text{purge losses}}{\text{of aromatics}} \tag{16}$$

is shown in Figure 12. It should be noted that since we did not include a vapor recovery system on the flash vapor stream, we should revise our overall and recycle material balance calculations. However, the aromatics flow in the flash vapor is only about 2% of the total vapor flow, and therefore we temporarily neglect these corrections. Before we would decide to recommend the project for commercialization, we would undertake more rigorous balances, but if we should decide to terminate the project, we want to do so with a minimum amount of effort.

Liquid recovery system. We expect that we can accomplish all of the separations by distillation. The light ends, H_2 and CH_4, dissolved in the flash liquid will contaminate the benzene product, which has a very high-purity specification, i.e., $x_D = 0.9999$. Thus, we decide to use a stabilizer column to recover the light ends, and we assume that we send these light ends to a fuel supply since we did not install a vapor recovery system.

For a nominal base-case design condition, i.e., $x = 0.75$, $y_{PH} = 0.4$, the flash liquid flows of the aromatics are: Bz = 265, Tol = 91,

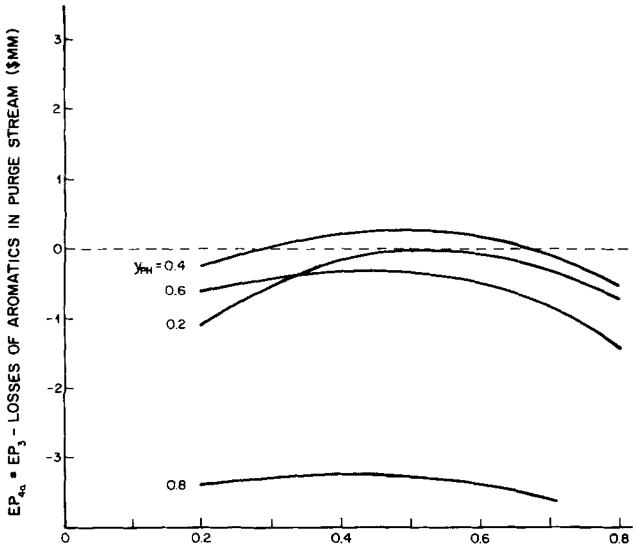

Figure 12. Economic potential at Level 4a.

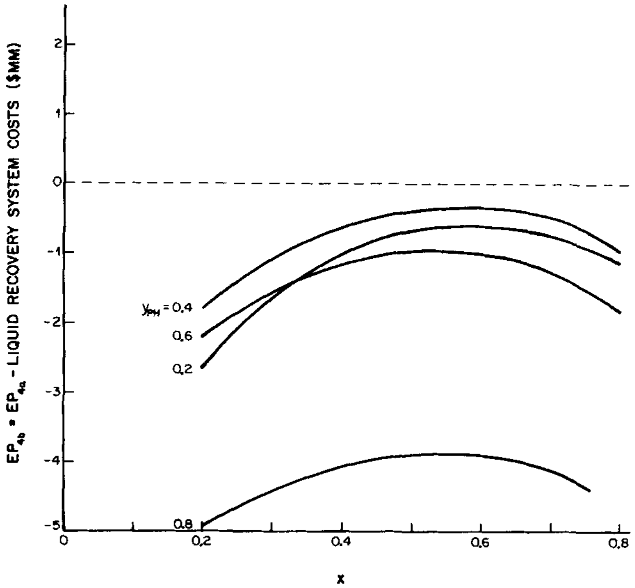

Figure 14. Economic potential at Level 4b.

Diph = 4. All of the sequencing heuristics (i.e., lightest first, most plentiful first, favor equimolar splits) indicate that the direct sequence is favored. Thus, for sharp splits and reasonably pure products, the flow sheet would be as is shown in Figure 13.

However, since toluene is a component that is recycled, we might consider recycling toluene as a sidestream. Similarly, it might be possible to use a pasteurization section on the top of the benzene column to recover the light ends. If both of these process alternatives were cheaper, the liquid separation system would be reduced to the single column.

Recycle of an impure toluene stream will require us to change our recycle material balances again if there are significant impurity levels. However, the incremental recycle costs must be balanced against the savings obtained by eliminating two distillation columns. Since there does not appear to be any simple way of guessing which is the best process alternative, we should at least use shortcut design procedures to evaluate all of the possibilities.

A plot of the third revision of the economic potential, i.e.,

$$EP_{4b} = EP_{4a} - \frac{\text{annualized distillation}}{\text{column costs}} \qquad (17)$$

is shown in Figure 14. We note that the economic potential is negative, but we also note that a relatively small increase in the price of benzene, i.e., 1%, will make the process profitable again. Therefore, instead of abandoning the project at this point, we proceed with a philosophy of cautious optimism. That is, one of the process alternatives might correspond to a profitable process or supply-and-demand factors might change the product price structure enough to make the process profitable.

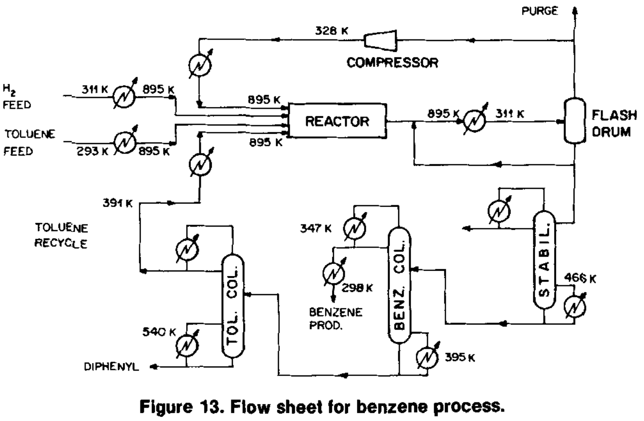

Figure 13. Flow sheet for benzene process.

LEVEL 5: HEAT EXCHANGER NETWORKS

The specification of targets for energy integration and the design of heat exchanger networks has received extensive study in recent years. Most of this material has been reviewed in detail in recent publications—Nishida et al. (1981), Linnhoff and Hindmarsh (1983), and Linnhoff et al. (1982). Extensions of the method to heat and power integration are available (Townsend and Linnhoff, 1983). Furthermore, some results on heat and distillation integration are also being developed (e.g., Andrecovich and Westerberg, 1983).

Since the methodology for the design of heat exchanger networks is well developed, and since a computer-assisted design program that implements the design procedure is available from Morari (1982), we will not discuss the details of the analysis. It should be noted, however, that the existing techniques are based on the assumption of a fixed flow sheet and fixed process flows. Since all of the process flows involve optimization problems and since there are no rules of thumb that can be used to fix the process flows, an iterative optimization analysis might be required to develop the best heat exchanger network.

SUMMARY

The procedure described above should lead to a "reasonable" process flow sheet and a base-case design. However, depending on the guesses of the design variables—i.e., conversion, recycle composition of inerts, etc.—and the guesses of the process alternatives, the result may be far from the best possible design. Nevertheless, we can use the procedure as a starting point for a more sophisticated evolutionary strategy or a structural parameter approach. Also, several new design heuristics were discussed in some detail.

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NOTATION

EP_i = economic potential for Level i decisions
F_{FT} = fresh feed rate of toluene
F_G = makeup gas flow rate
F_T = toluene flow enttering the reactor
P_B = production rate of benzene
P_D = production rate of diphenyl
R_G = recycle gas flow
S = selectivity: benzene produced at reactor exit/toluene converted
x = conversion
y_{PH} = mole fraction of hydrogen in the purge stream

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