

CONCEPTUAL DESIGN OF
CHEMICAL PROCESSES

McGraw-Hill Chemical Engineering Series

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DEDICATED TO:

The loves of my life,

My lovely wife, Mary E. (Betsy) Douglas,

My mother, Carolyn K., and the memory of my
father, Merrill H. Douglas,

My two wonderful kids, Lynn and Bob,

and to my colleagues, who have taught me so much about
design and control,

Mike Doherty, Mike Malone, Ka Ng, and Erik Ydstie,

and to my students, who have suffered so much.

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PREFACE

This book describes a systematic procedure for the conceptual design of a limited class of chemical processes. The goal of a conceptual design is to find the best process flowsheet (i.e., to select the process units and the interconnections among these units) and estimate the optimum design conditions. The problem is difficult because very many process alternatives could be considered. In addition, experience indicates that less than 1 % of ideas for new designs ever become commercialized. Thus, there are many possibilities to consider with only a small chance of success.

In many cases the processing costs associated with the various process alternatives differ by an order of magnitude or more, so that we can use shortcut calculations to screen the alternatives. However, we must be certain that we are in the neighborhood of the optimum design conditions for each alternative, to prevent discarding an alternative because of a poor choice of design variables. Hence, we use cost studies as an initial screening to eliminate ideas for designs that are unprofitable. If a process appears to be profitable, then we must consider other factors, including safety, environmental constraints, controllability, etc.

We approach the synthesis and analysis problem by establishing a hierarchy of design decisions. With this approach, we decompose a very large and complex problem into a number of smaller problems that are much simpler to handle. By focusing on the decisions that must be made at each level in the hierarchy (e.g., Do we want to add a solvent recovery system?), we can identify the existing technologies that could be used to solve the problem (e.g., absorption, adsorption, condensation) without precluding the possibility that some new technology (e.g., a membrane process) might provide a better solution. Moreover, by listing the alternative solutions we can propose for each decision, we can systematically generate a list of process alternatives.

In some cases it is possible to use design guidelines (rules of thumb or heuristics) to make some decisions about the structure of the flowsheet and/or to set the values of some of the design variables. We use order-of-magnitude

INPUT-OUTPUT STRUCTURE OF THE FLOWSHEET

TABLE 5.1-1
Hierarchy of decisions

1. Batch versus continuous
2. Input-output structure of the flowsheet
3. Recycle structure of the flowsheet
4. General structure of the separation system
a. Vapor recovery system
b. Liquid separation system
5. Heat-exchanger network

order-of-magnitude argument to say that this rule of thumb is equivalent to requiring that we completely recover and then recycle all valuable reactants. Thus, Fig. 5.1-1a indicates that no reactants leave the system.

Of course, if air and water are reactants in a process, they are sufficiently inexpensive, compared to organic materials, that it might be cheaper to lose them in an exit stream rather than to recover and recycle them. Hence, in a few rare cases, Fig. 5.1-1a might not be complete.

The other situation in which commonly reactants have been lost from a process occurs when we have a gaseous reactant and either a gaseous feed impurity or a gaseous by-product produced by one of the reactions. We want to recycle the gaseous reactant, but the inert-gas components must be purged from the process so that they do not continue to accumulate in the gas-recycle loop. In the past, it was so expensive to separate gaseous mixtures that some reactant was allowed to leave the process in a gas-recycle and purge stream (see Fig. 5.1-1b). However, the new membrane-separation technology, such as Monsanto's prism process, has cut the cost of gaseous separations so that gas recycle and purge might not be necessary.

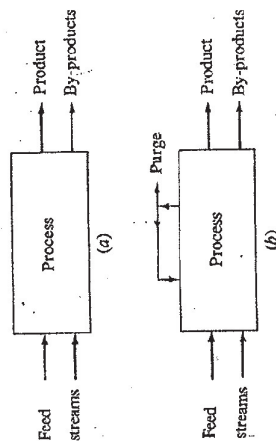


FIGURE 5.1-1
Input-output structure of flowsheet [From J. M. Douglas, *AIChE J.*, 31: 353 (1985).]

In Sec. 1.2 we described a hierarchical decision procedure for inventing process flowsheets and base-case designs. The decision levels are repeated in Table 5.1-1. The batch versus continuous decision of level 1 was discussed in Sec. 4.2, and in the subsequent chapters we discuss the other decision levels in detail.

5.1 DECISIONS FOR THE INPUT-OUTPUT STRUCTURE

To understand the decisions required to fix the input-output structure of a flowsheet, we merely draw a box around the total process. Thus, we focus our attention on what raw materials are fed to the process and what products and by-products are removed. Since the raw materials costs normally fall in the range from 33 to 85% of the total processing costs, we want to calculate these costs before we add any other detail to the design.

Flowsheet Alternatives

Almost every flowsheet has one of the two structures shown in Fig. 5.1-1a and b. There is a rule of thumb in process design (see Sec. 3.4) that it is desirable to recover more than 99% of all valuable materials. For initial design calculations we use the

TABLE 5.1-2
Level-2 decisions

1. Should we purify the feed streams before they enter the process?
2. Should we remove or recycle a reversible by-product?
3. Should we use a gas recycle and purge stream?
4. Should we not bother to recover and recycle some reactants?
5. How many product streams will there be?
6. What are the design variables for the input-output structure, and what economic trade-offs are associated with these variables?

We distinguish between Fig. 5.1-1a and b because the presence of a gas recycle and purge stream adds a degree of freedom to the design problem; i.e., either the reactant composition of the purge stream or the excess gaseous reactant fed to the process becomes a new design variable. We discuss the design variables later.

Level-2 Decisions

The decisions we must make to fix the input-output structure of the flowsheet are given in Table 5.1-2 and are discussed below.

Purification of Feeds

A decision to purify the feeds before they enter the process is equivalent to a decision to design a pre-process purification system. This is different from a decision to feed the process through a separation system that is required in any event. Since at this stage of our synthesis and analysis procedure we do not know what kind of separation system will be required for the process with no feed impurities, we cannot always make a definite decision.

Some design guidelines to be considered are as follows:

If a feed impurity is not inert and is present in significant quantities, remove it (otherwise, it will lead to raw-material losses, and usually a much more complicated separation system is required to recover the additional by-products). (5.1-1)

If a feed impurity is present in a gas feed, as a first guess process the impurity. (5.1-2)

If a feed impurity in a liquid feed stream is also a by-product or a product component, usually it is better to feed the process through the separation system. (5.1-3)

If a feed impurity is present in large amounts, remove it (there is no quantitative criterion available to indicate how "large" is large). (5.1-4)

If a feed impurity is present as an azeotrope with a reactant, often it is better to process the impurity. (5.1-5)

If a feed impurity is inert but is easier to separate from the product than the feed, it is better to process the impurity. (5.1-6)

If a feed impurity is a catalyst poison, remove it. (5.1-7)

PROCESS ALTERNATIVE. Unfortunately, not all these design guidelines are quantitative, so often we must base our initial decision on our best judgment (which might be merely a guess).

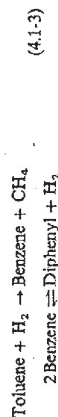
If we are not certain that our decision is correct, we list the opposite decision as a *process alternative*. (5.1-8)

With this approach, we have a systematic way of generating a list of process alternatives.

ECONOMIC TRADE-OFFS FOR FEED PURIFICATION. Our decision of purifying the feed streams before they are processed involves an economic trade-off between building a pre-process separation system and increasing the cost of the process because we are handling the increased flow rates of inert materials. Of course, the amount of inert materials present and where they will enter and leave the process may have a great impact on the processing costs. Therefore, it is not surprising that there is no simple design criterion that always indicates the correct decision.

Recover or Recycle Reversible By-products

The reactions to produce benzene from toluene are



Since the second reaction is reversible, we could recycle the diphenyl back to the reactor and let it build up in the recycle loop until it eventually reached an equilibrium level. That is, the recycled diphenyl would decompose to form benzene at the same rate as benzene would be producing diphenyl.

If we recycle the reversible by-product, we must oversize all the equipment in that recycle loop, to accommodate the equilibrium flow of the reversible by-product. However, if we remove it from the process, we pay an economic penalty because of the increased raw-material cost of reactant (toluene) that was converted to the reversible by-product (diphenyl), e.g., the raw-material cost of toluene minus the fuel value of diphenyl. Since our decision involves an economic trade-off between raw-material losses to less valuable by-products and increased recycle

costs, it should not be surprising that no simple design guideline is available to make this decision. The result will also be sensitive to the equilibrium constant of the by-product reaction. So we generate another process alternative.

Gas Recycle and Purge

If we have a "light" reactant and either a "light" feed impurity or a "light" by-product produced by a reaction, it used to be common practice to use a gas recycle and a purge stream; i.e., we want to recycle the reactant, but we must purge one or more components from the process. We define a *light component* as one which boils lower than propylene (-55°F , -48°C). We choose propylene as a breakpoint because lower-boiling components normally cannot be condensed at high pressure with cooling water; i.e., both high pressure and refrigeration would be required. Since gaseous reactants normally are less expensive than organic liquids, and since refrigeration is one of the most expensive processing operations, it usually was cheaper to lose some of the gaseous reactants from a gas recycle and purge stream than it was to recover and recycle pure reactant.

However, membrane technology, such as Monsanto's prism process, now makes gas separations less expensive. Unfortunately, there is not a sufficient amount of published information available concerning the costs of membrane processes to be able to develop new design guidelines. Thus, we treat the membrane separator as another process alternative. Because of the lack of published information, we would base our initial design on a process with gas recycle and purge, whenever our design guideline is satisfied:

Whenever a light reactant and either a light feed impurity or a light by-product boil lower than propylene (-55°F , -48°C), use a gas recycle and purge stream. (5.1-9)

A membrane separation process also should always be considered.

Do Not Recover and Recycle Some Reactants

One of our design guidelines states that we should recover more than 99% of all valuable materials. Since some materials, such as air and water, are much less valuable than organic ones, we normally do not bother to recover and recycle unconverted amounts of these components. Of course, we could try to feed them to the process so that they would be completely converted, but often we feed them as an excess to try to force some more valuable reactant to complete conversion.

For example, in combustion reactions, we usually use an excess amount of air to ensure complete conversion of the fuel. The greater amount of the excess we use, the closer to complete conversion of the other reactant we obtain. However, the capital and operating costs of the blower used to move the air, as well as preheating and cooling costs, increase as we increase the excess amount of air. Thus there is an

TABLE 5.1-3
Destination codes and component classifications

Destination code	Component classification
1. Vent	Gaseous by-products and feed impurities
2. Recycle and purge	Gaseous reactants plus inert gases and/or gaseous by-products
3. Recycle	Reactants
	Reaction intermediates
	Azeotropes with reactants (sometimes)
	Reversible by-products (sometimes)
4. None	Reactants—if complete conversion or unstable reaction intermediates
5. Excess—vent	Gaseous reactant not recovered and recycled
6. Excess—waste	Liquid reactant not recovered or recycled
7. Primary product	Primary product
8. Valuable by-product (I)	Separate destination for different by-products
9. Fuel	By-products to fuel
10. Waste	By-products to waste treatment

optimum amount of excess that should be used. Similarly, at some point, the cost of excess water used will become significant. Moreover, pollution treatment costs must be considered.

Number of Product Streams

To determine the number of product streams that will leave the process, first we list all the components that are expected to leave the reactor. This component list usually includes all the components in the feed streams and all reactants and products that appear in every reaction. Then we classify each component in the list and assign a destination code to each. The component classifications and destination codes are given in Table 5.1-3. Finally, we order the components by their normal boiling points, and we group neighboring components with the same destination. The number of groups of all but the recycle streams is then considered to be the number of product streams.

This procedure for determining the number of product streams is based on the common sense design guideline that

It is never advantageous to separate two streams and then mix them together. (5.1-10)

Also, it is based on the assumption that the components can be separated by distillation and that no azeotropes are formed. Thus, in some cases (i.e., solids) a different set of rules must be used to estimate the number of product streams.

Example 5.1-4. Suppose we have the 10 components listed in order of their boiling points and with the destination codes indicated. How many product streams will there be?

Component	Destination	Component	Destination
A	Waste	F	Primary product
B	Waste	G	Recycle
C	Recycle	H	Recycle
D	Fuel	I	Valuable by-product 1
E	Fuel	J	Fuel

Solution. The product streams are

1. A + B to waste (do not separate them and then mix them in the sewer)
2. D + E to fuel (do not separate them and then mix them to burn)
3. F—primary product (to storage for sale)
4. I—valuable by-product 1 (to storage for sale)
5. J to fuel (J must be separated from D and E to recover components F, G, H, and I, so we treat J as a separate product stream)

Example 5.1-2 Hydroalkylation of toluene to produce benzene. Find the number of product streams for the HDA process; i.e., see Example 4.1-1.

Solution. In Example 4.1-1 the components in the reactions are toluene, hydrogen, benzene, methane, and diphenyl. No additional components are present in either of the feed streams. If we arrange these components in order of their normal boiling points, we obtain the results shown in Table 5.1-4. Since both hydrogen (a reactant) and methane (both a feed impurity and a by-product) boil at a lower temperature than propylene, we decide to use a gas recycle and purge stream. Benzene is our primary product, and toluene (a reactant) is recycled. Diphenyl is a reversible by-product, and for this example we decided to remove it from the process and to use it as part of our fuel supply. These destination codes also are given in Table 5.1-4.

Thus, there are three product streams: a purge containing H₂ and CH₄, the primary product stream containing benzene, and a fuel by-product stream containing diphenyl. The initial flowsheet is given in Fig. 5.1-2.

TABLE 5.1-4
Toluene to benzene

Component	Boiling point	Destination code
H ₂	-253°C	Recycle and purge
CH ₄	-161°C	Recycle and purge
Benzene	80°C	Primary product
Toluene	111°C	Recycle
Diphenyl	253°C	Fuel

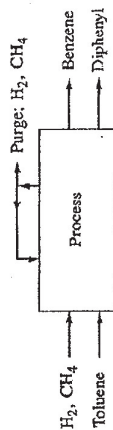


FIGURE 5.1-2
Input-output structure of HDA process. [From J. M. Douglas, *AIChE J.*, 31: 333 (1985).]

Evaluation of the Flowsheet

At each stage of the development of a flowsheet, this is essential:

- Be certain that all products, by-products, and impurities leave the process! (5.1-11)

For example, in our HDA process, there might be some other impurities in the hydrogen feed stream. We would expect them to leave with the purge. We also expect that there will be some impurities in the toluene feed stream. We attempt to identify these impurities by considering the source of our toluene, and then we look for where they will exit the process. Furthermore, we need to consider the possibility of other side reactions (such as the formation of terphenyl), and we must ensure that these new by-products leave the process or can be recycled.

If even a trace amount of a component is fed to a recycle loop and is not removed, the process will be inoperable. This is one of the most common mistakes made by inexperienced designers.

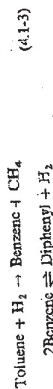
5.2 DESIGN VARIABLES, OVERALL MATERIAL BALANCES, AND STREAM COSTS

To calculate the overall process material balances and the stream costs, we must first assess whether the problem definition is complete or whether there are any degrees of freedom that must be specified to calculate the material balances. In general, the problem definition is not complete. Therefore, normally, it is impossible to develop a unique set of material balances for a process. Only a process with a single reaction and with no loss of reactants from the process has no degrees of freedom.

Of course, if the material balances are not unique, then the stream costs will also not be unique. Thus, we must develop the material balances and the stream costs in terms of the unknown design variables, and eventually we will look for the economic optimum values of these design variables.

Example 5.2-1 Toluene to benzene. Develop the overall material balances for the HDA process.

Solution. The reactions of interest are



and we are given that the desired production rate of benzene is $P_B = 265$ mol/hr (Example 4.1-1). If we use a gas recycle and purge stream for the H_2 and CH_4 , and if we recover and remove the diphenyl, then there are three product streams; see Example 5.1-2 and the flowsheet given in Fig. 5.1-2.

We note from Fig. 5.1-2 that all the toluene we feed to the process gets converted (i.e., no toluene leaves the system). However, this does not mean that the conversion of toluene in the reactor is unity. A low conversion per pass simply means that there will be a large internal recycle flow of toluene. However, we evaluate these recycle flows at a later stage of our design procedure. Of course, our assumption that all the feed toluene is converted neglects any toluene losses in any of the product streams, but this corresponds to our initial design assumption of complete recovery versus greater than 99% recoveries.

SELECTIVITY AND REACTION STOICHIOMETRY. We define the selectivity S as the fraction of toluene converted in the reactor that corresponds to the benzene flow at the reactor outlet. Also, we recover and remove all this benzene. Hence, for a production of P_B mol/hr, the toluene fed to the process F_{TF} must be

$$F_{TF} = \frac{P_B}{S} \quad (5.2-1)$$

Also, from the stoichiometry (Eq. 5.1-3), the amount of methane produced P_{R,CH_4} must be

$$P_{R,CH_4} = \frac{P_B}{S} \quad (5.2-2)$$

If a fraction S of toluene is converted to benzene, a fraction $1 - S$ must be lost to diphenyl. However, from the stoichiometry of Eq. 5.1-3, the amount of diphenyl produced P_D must be

$$P_D = F_{TF} \frac{1 - S}{2} = \frac{P_B}{S} \frac{1 - S}{2} \quad (5.2-3)$$

Since the toluene stream contains no impurities, we find the toluene fresh feed rate and the diphenyl by-product flow rate in terms of selectivity from the reaction stoichiometry and the given production rate. A relationship between selectivity and conversion is given in Example 4.1-1.

RECYCLE AND PURGE. The stoichiometry also indicates the amount of H_2 required for the reaction. If we feed an excess amount of hydrogen, F_E , into the

process, this hydrogen will leave with the purge stream. Thus, the total amount of hydrogen fed to the process will be

$$F_{H_2} = F_E + \frac{P_B}{2S}(1 + S) = y_{FH} F_G \quad (5.2-4)$$

which is equal to the amount of hydrogen in the makeup gas stream $y_{FH} F_G$. Similarly, the methane flow rate leaving the process will be the amount of methane entering the process, $(1 - y_{FH}) F_G$, plus the amount of methane produced by the reactions, $P_{R,CH_4} = P_B/S$, or

$$P_{CH_4} = (1 - y_{FH}) F_G + \frac{P_B}{S} \quad (5.2-5)$$

The total purge flow rate P_G will then be the excess H_2 , F_E , plus the total methane P_{CH_4} , or

$$P_G = F_E + (1 - y_{FH}) F_G + \frac{P_B}{S} \quad (5.2-6)$$

Rather than using the excess hydrogen feed F_E as a design variable, we normally use the purge composition of the reactant y_{FH} , where

$$y_{FH} = \frac{F_E}{P_G} \quad (5.2-7)$$

This purge composition is always bounded between zero and unity (actually there is a smaller upper bound which depends on the feed composition and sometimes on the conversion). The use of bounded variables makes the preparation of graphs simpler.

We can develop expressions for the makeup gas rate F_G and the purge rate P_G explicitly in terms of the purge composition of reactant y_{FH} either by using Eq. 5.2-7 to eliminate F_E from Eqs. 5.2-4 and 5.2-7 or by writing balances for the hydrogen and methane and then combining them. That is, the amount of hydrogen in the feed must supply the net reaction requirements as well as the purge loss

$$y_{FH} F_G = \frac{P_B}{S} - \frac{P_B}{S} \frac{1 - S}{2} + y_{FH} P_G \quad (5.2-8)$$

and the methane in the feed plus the methane produced must all leave with the purge

$$(1 - y_{FH}) F_G + \frac{P_B}{S} = (1 - y_{FH}) P_G \quad (5.2-9)$$

Adding these expressions gives

$$P_G = F_G + \frac{P_B}{S} \frac{1 - S}{2} \quad (5.2-10)$$

We can then solve for F_G :

$$F_G = \frac{P_D \left[1 - (1 - y_{PH}) \frac{1-S}{2} \right]}{S(y_{PH} - y_{PI})} \quad (5.2-11)$$

If we are given values of P_D , S , and either F_P or y_{PH} , we can use the above equations to calculate the fresh feed rate of toluene, F_{PT} (Eq. 5.2-1), the production rate of diphenyl, P_D (Eq. 5.2-3), the makeup gas rate F_G (Eq. 5.2-4 or 5.2-11), and the purge flowrate, P_G (Eq. 5.2-6 or 5.2-10). Thus, we have determined all the input and output flows in terms of the unknown design variables S and either F_P or y_{PH} .

MATERIAL BALANCES IN TERMS OF EXTENT OF REACTION. It is becoming common practice to describe material balance calculations in terms of the extent of reaction ξ_1 (or fractional extent of reaction). Thus, for the HDA process, we would say that ξ_1 mol (or moles/hr) of toluene react with ξ_1 mol of H_2 to produce ξ_1 mol of benzene plus ξ_1 mol of CH_4 . Also, $2\xi_1$ mol of benzene produces ξ_1 mol of diphenyl plus ξ_1 mol of hydrogen. Then, we combine these statements to say that

$$\text{Net benzene produced} = \xi_1 - 2\xi_1 \quad (5.2-12)$$

$$\text{Methane produced} = \xi_1 \quad (5.2-13)$$

$$\text{Diphenyl produced} = \xi_1 \quad (5.2-14)$$

$$\text{Toluene consumed} = \xi_1 \quad (5.2-15)$$

$$\text{Hydrogen consumed} = \xi_1 - \xi_1 \quad (5.2-16)$$

We can generalize these expressions and say that the number of moles (or moles per hour) of any component is given by

$$n_j = n_j^0 + \nu_{ij} \xi_i \quad (5.2-17)$$

where the ν_{ij} are the stoichiometric coefficients, which are positive for products and negative for reactants. Normally (for the purposes of initial design calculations) no products are fed to the process, $n_j^0 = 0$, and no reactants are allowed to leave, $n_j = 0$. Experience indicates that it normally is possible to correlate the extent of each reaction ξ_i against the per-pass conversion of the limiting reactant, although in some cases the molar ratio of reactants, reactor temperature, and/or reactor pressure must be included in the correlation.

EXTENT VERSUS SELECTIVITY. For the case of only two reactions, it often is simpler to describe the product distribution in terms of selectivity. Selectivity can be described in a number of different ways, such as the production of the desirable component divided by the amount of limiting reactant converted or the production

of the desired component divided by the production of the undesired component. For the HDA process, in the first case we would have

$$S_a = \frac{\xi_1 - 2\xi_2}{\xi_1} \quad (5.2-18)$$

whereas in the second case we would have

$$S_b = \frac{\xi_1 - 2\xi_2}{\xi_2} \quad (5.2-19)$$

It is essential to ensure that the definition of selectivity that is reported by a chemist (or in the literature) is clearly defined, but it is a simple matter to convert from one definition to another.

Example 5.2.2 Toluene to benzene. Develop the expressions relating the extents of reaction to production rate and selectivity for the HDA process.

Solution. From Eqs. 5.2-15 and 5.2-1 we find that

$$\xi_1 = \frac{P_D}{S} \quad (5.2-20)$$

Also from Eq. 5.2-12 we find that

$$\xi_1 - 2\xi_2 = P_D \quad (5.2-21)$$

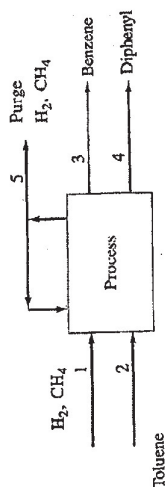
Thus we can write

$$\xi_2 = \frac{1}{2}(\xi_1 - P_D) = \frac{P_D}{2} \left(\frac{1-S}{S} \right) \quad (5.2-22)$$

Stream Tables

It is common practice to report material balance calculations in terms of stream tables. That is, the streams are numbered on a flowsheet, and then a table is prepared that gives the component flows in each of these streams which correspond to a particular set of values of the design variables. An example is given in Fig. 5.2-1. The temperatures, pressures, and enthalpy of each stream also are normally listed. Since we do not consider energy balances until the end of the synthesis procedure, we add these values to the stream tables later.

One major difficulty with this conventional practice is that the designer is forced to select values of design variables without knowing the optimum values. Moreover, once a set of values has been selected, it is often difficult to remember that they were selected arbitrarily. For this reason, we recommend that the stream tables list the values of the design variables and that the appropriate material balance equations, such as Eqs. 5.2-1, 5.2-3, 5.2-4, 5.2-6, etc., be programmed on a spreadsheet such as LOTUS. With this approach it is very easy to change the production rate and the design variables and then recalculate all the stream flows. We can use this same table as the basis for calculating the stream costs as a function of the design variables.



Production rate = 2665

Design variables: F_E and x

Component	1	2	3	4	5
H_2	F_{H_2}	0	0	0	F_E
CH_4	F_M	0	0	0	$F_M + P_B/S$
Benzene	0	0	P_B	0	0
Toluene	0	P_B/S	0	0	0
Diphenyl	0	0	0	$P_B(1 - S)/(2S)$	0
Temperature	100	100	100	100	100
Pressure	550	15	15	15	465

where $S = 1 - 0.0036/(1 - x)^{1.544}$ $F_{H_2} = F_E + P_B(1 + S)/2S$
 $F_M = (1 - y_{H_2})[F_E + P_B(1 + S)/S]y_{H_2}$ $F_C = F_{H_2} + F_M$

FIGURE 5.2-1
Stream table for the HDA process.

Stream Costs: Economic Potential

Since the "best" values of the design variables depend on the process economics, we want to calculate the stream costs, i.e., the cost of all raw materials and product streams in terms of the design variables. Normally, we combine these costs into a single term, which we call the economic potential (EP). We define the economic potential at level 2 as

$$EP_2 = \text{Product Value} + \text{By-product Values} - \text{Raw-Material Costs, } \$/\text{yr} \quad (5.2-23)$$

which for an HDA example would be

$$EP = \text{Benzene Value} + \text{Fuel Value of Diphenyl} + \text{Fuel Value of Purge} - \text{Toluene Cost} - \text{Makeup Gas Cost} \quad (5.2-24)$$

We would also subtract the annualized capital and operating cost of a feed compressor, if one is needed. (The calculations required are discussed in Sec. 6.5.)

TABLE 5.2-3
Cost data for HDA process

Value of benzene	\$0.85/gal = \$9.04/mol
Value of toluene*	\$0.50/gal = \$4.40/mol
Value of H_2 feed	\$3.00/1000 ft ³ = \$11.4/mol
Fuel = \$4.0/10 ⁶ Btu	
Fuel value: H_2	0.123×10^6 Btu/mol
CH_4	0.382×10^6 Btu/mol
Benzene	1.41×10^6 Btu/mol
Toluene	1.68×10^6 Btu/mol
Diphenyl†	2.688×10^6 Btu/mol

* Assume an internal transfer-price value versus the current prices of \$1.26/gal.

† We also assume that the fuel value of diphenyl is \$5.38/mol.

The economic potential is the annual profit we could make if we did not have to pay anything for capital costs or utilities costs. Of course, if the economic potential is negative, i.e., the raw materials are worth more than the products and by-products, then we want to terminate the design project, look for a less expensive source of raw materials, or look for another chemistry route that uses less expensive raw materials.

Example 5.2-3 HDA stream costs. If we use the cost data given in Table 5.2-3, where the values of H_2 , CH_4 , and diphenyl in the product streams are based on the heats of combustion of the components and a fuel value of \$4/10⁶ Btu, we can calculate the economic potential for the HDA process in terms of the design variables (we use reactor conversion per pass x , instead of S , and y_{H_2}). The results are shown in Fig. 5.2-2. The graph indicates that at high conversions the process is unprofitable

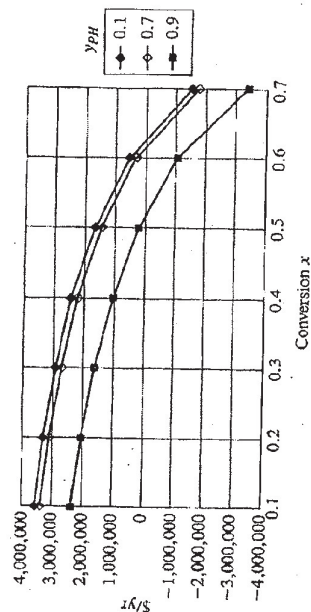


FIGURE 5.2-2
Economic potential—level 2.

TABLE 5.3-1
Alternatives for the HDA
process

- | |
|--|
| 1. Purify the hydrogen feed stream. |
| 2. Recycle the diphenyl to extinction. |
| 3. Purify the H_2 -recycle stream. |

(i.e., we convert so much toluene to diphenyl that this selectivity loss exceeds the increased value of the benzene that we produce). Also, at high purge compositions of hydrogen we lose money (we lose so much hydrogen to fuel that we cannot make up for this loss).

According to the graph, the most desirable values (i.e., the greatest profit) of the design variables correspond to $x = 0$ (i.e., no selectivity loss) and a reactant composition of the purge stream y_{RH} equal to zero (i.e., purge pure methane).

As we proceed through the design, however, we find that a zero conversion per pass ($x = 0$) corresponds to an infinitely large recycle flow of toluene and that purging no hydrogen ($y_{RH} = 0$) corresponds to an infinitely large gas-recycle flow. Hence, we develop the optimum values of x and y_{RH} as we proceed through the design.

5.3 PROCESS ALTERNATIVES

In our development of a design for the HDA process (see Fig. 5.1-2), we made the decisions (1) not to purify the hydrogen feed stream, (2) to remove the diphenyl from the process, and (3) to use a gas recycle and purge stream. If we change any of these decisions, we generate process alternatives. It is always good practice to make a list of these alternatives. Such a list is given in Table 5.3-1.

Evaluation of Alternatives

We could attempt to simultaneously develop designs that corresponded to each process alternative. However, if we remember that less than 1% of ideas for new designs ever become commercialized, our initial goal should be to eliminate, with as little effort as possible, projects that will be unprofitable. Thus, we prefer to complete the design for one alternative as rapidly as possible before we give any consideration to the other alternatives; for we might encounter some factor that will make all the alternatives unprofitable. Then, after we have completed a base-case design, we examine the alternatives. In the terminology of artificial intelligence (AI), we are using a *depth-first*, rather than a *breadth-first*, strategy.

5.4 SUMMARY, EXERCISES, AND NOMENCLATURE

Summary

The questions we must answer to fix the input-output structure of the flowsheet include the following:

1. Should we purify the feed stream?
2. Should we remove or recycle a reversible by-product?
3. Should we use a gas recycle and purge stream?
4. Should we use an excess of some reactant that we discard?
5. How many product streams will there be?
6. What are the design variables and the economic trade-offs at this level of analysis?

In some cases heuristics can be used to help make these decisions. When no heuristics are available, we make a guess and then list the opposite decision as a process alternative. We complete a first design based on our original guess before we consider any other alternatives (Since less than 1% of ideas for new designs are successful, we might learn something about the process that will make all the alternatives unprofitable.)

Some of the heuristics and design guidelines that were presented include the following:

- If a feed impurity is not inert, remove it.
- If an impurity is present in a gas feed stream, as a first guess process the impurity.
- If an impurity in a liquid feed stream is a product or by-product, usually feed the process through the separation system.
- If an impurity is present in large amounts, remove it.
- If an impurity is present as an azeotrope with a reactant, process the impurity.
- If a feed impurity is an inert, but is easier to separate from the product and by-product than from the feed, it is better to process the impurity.
- Whenever there is a light reactant and a light feed impurity or by-product (where light components boil lower than propylene, -48°C), use a gas recycle and purge stream for the first design. Also consider a membrane separator later.
- If O_2 from air or water is a reactant, consider using an excess amount of this reactant.
- For single-product, vapor-liquid processes, we determine the number of product streams by grouping components with neighboring boiling points that have the same exit destinations; i.e., we never separate streams and then remix them.
- Be certain that all by-products and impurities leave the process!
- The significant design variables are those that affect the product distribution and purge compositions of gas streams.
- Raw-material costs are often in the range from 33 to 85% of the total costs.

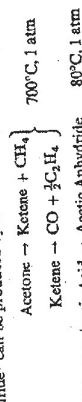
Exercises

- 5.4-1. Draw the input-output flowsheet and plot the economic potential for the HDA process for the case where the diphenyl is recycled.

134 SECTION 5.4 SUMMARY, EXERCISES, AND NOMENCLATURE

5.4-2. Draw the flowsheet and plot the economic potential for the HDA process for the case where the H_2 is separated from CH_4 before it is recycled and where diphenyl is removed from the process.

5.4-3. Acetic anhydride* can be produced by the reaction system

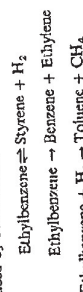


The selectivity (moles of ketene leaving the pyrolysis reactor per mole of acetone converted) is given by $S = 1 - 4x/3$ at low conversions. The desired production rate of anhydride is 1658 mol/hr at a purity of 99%. The cost data are: acetone = \$15.66/mol, acid = \$15.00/mol, anhydride = \$44.41/mol, and fuel at \$4.00/10⁶ Btu. Draw the flowsheet, and plot the economic potential.

5.4-4. A process for producing acetone from isopropanol is discussed in Exercise 1.3-4. The desired production rate is 51.3 mol/hr. The feed azeotrope contains 70 mol % IPA, and the costs are acetone = \$15.66/mol, IPA-H₂O azeotrope = \$9.53/mol, H₂ as fuel = \$0.49/mol, and H₂O as waste = -\$0.007/mol. Draw the input-output flowsheet, calculate the overall material balances, and plot the economic potential.

5.4-5. A simplified flowsheet for ethanol synthesis is discussed in Exercise 1.3-6. The desired production rate of the azeotropic product is 783 mol/hr (85.4 mol % EtOH), and the costs are: ethylene feed mixture = \$6.15/mol, process water = \$0.00394/mol, ethanol as azeotrope = \$10.89/mol, and the fuel at \$4.00/10⁶ Btu. Draw the input-output structure of the flowsheet, and plot the economic potential.

5.4-6. Styrene can be produced by the reactions



The reactions take place at 1115°F and 25 psia. We want to produce 250 mol/hr of styrene. The costs are: ethylbenzene = \$15.75/mol, styrene = \$21.88/mol, benzene = \$9.04/mol, toluene = \$8.96/mol, and fuel at \$4.00/10⁶ Btu. Werner and Dybdal[†] give correlations for the product distribution

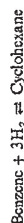
$$\begin{aligned} \text{Mol Benzene} &= 0.333x - 0.215x^2 + 2.547x^3 \\ \text{Mol Styrene} &= 0.084x - 0.264x^2 + 2.638x^3 \\ \text{Mol Toluene} &= 0.084x - 0.264x^2 + 2.638x^3 \\ \text{Mol Styrene} & \end{aligned}$$

where x = styrene conversion. The ethylbenzene feed stream contains 2 mol % benzene. Draw the input-output flowsheet and plot the economic potential.

* This problem is a modified version of the 1958 AIChE Student Contest Problem; see J. J. McKetta, *Encyclopedia of Chemical Processing and Design*, vol. 1, Dekker, New York, 1976, p. 271.

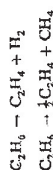
† R. N. Werner and E. C. Dybdal, *Chem. Eng. Prog.*, 44(4): 275 (1946).

5.4-7. Cyclohexane* can be produced by the reaction



The reaction takes place at 392°F and 370 psia. Pure benzene is used as a feed stream, but the hydrogen stream contains 2% methane. The desired production rate is 100 mol/hr, and the costs are: benzene = \$6.50/mol, H₂ = \$1.32/mol, cyclohexane = \$12.03/mol, and fuel at \$4.00/10⁶ Btu. Draw the input-output flowsheet, and plot the economic potential.

5.4-8. Ethylene can be produced by the thermal cracking of ethane[†]

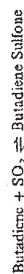


The reactions take place at 1500°F and 50 psia. We desire to produce 875 mol/hr of ethylene with 75% purity. Assume that the selectivity is given by

$$S = \frac{\text{mol } C_2H_4 \text{ Formed}}{\text{mol } C_2H_6 \text{ Converted}} = \frac{0.0381}{1 - (1 - x)^{0.241}}$$

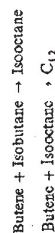
The ethane feed contains 5% CH₄ and costs \$1.65/mol. Ethylene at 95% composition is worth \$6.15/mol. Fuel is worth \$4.00/10⁶ Btu. Draw the input-output flowsheet and plot the economic potential.

5.4-9. Butadiene sulfone* can be produced by the reaction



The reaction takes place in the liquid phase at 90°F and 150 psia. The costs are SO₂ = \$0.064/mol, butadiene = \$6.76/mol, and butadiene sulfone = \$8.50/mol. We want to make 80 mol/hr of product. Draw the input-output flowsheet, and plot the economic potential.

5.4-10. Isooctane (gasoline)[†] can be produced by the reactions



The reactions take place in the liquid phase at 45°F and 90 psia; see Exercise 4.3-11. The desired production rate is 918 mol/hr, and the costs are: butene = \$14.56/mol, isobutane = \$18.59/mol, isooctane = \$36.54/mol, and fuel = \$4.00/10⁶ Btu. One feed stream contains 8% C₃, 80% butene, and 12% n-C₄, while the other contains 12% C₃, 73% i-C₄, and 15% n-C₄. Draw the input-output flowsheet, and plot the economic potential.

* J. R. Fair, *Cyclohexane Manufacture*, Washington University Design Case Study No. 4, edited by B. D. Smith, Washington University, St. Louis, Mo., Aug. 1, 1967.

† W. L. Rolles, *Ethylene Plant Design and Economics*, Washington University Design Case Study No. 6, edited by B. D. Smith, Washington University, St. Louis, Mo., 1970.

‡ This problem is a modified version of the 1970 AIChE Student Contest Problem; see J. J. McKetta, *Encyclopedia of Chemical Processing and Design*, vol. 5, Dekker, New York, 1971, p. 192.

§ This problem is a modified version of the 1977 AIChE Student Contest Problem; *AIChE Student Members Bulletin*, AIChE Headquarters, 1977.

Nomenclature

EP	Economic potential
F_E	Excess H_2 fed to the process, mol/hr
F_{FT}	Fresh feed rate of toluene, mol/hr
F_G	Makeup gas rate, mol/hr
F_{H_2}	H_2 consumed by the reactions, mol/hr
n_j	Final moles of component j
n_j^0	Initial moles of component j
P_R	Production rate of benzene, mol/hr
P_{CH_4}	Purge flow of methane, mol/hr
P_D	Diphenyl produced, mol/hr
P_G	Purge flow rate, mol/hr
P_{R,CH_4}	CH_4 produced by the reaction, mol/hr
S	Selectivity, mol benzene produced/mol toluene converted
y_{FH}	Feed composition of H_2
y_{PH}	Mole fraction of H_2 in the purge stream
Greek symbols	
ν_{ij}	Stoichiometric coefficients
ξ_i	Extent of reaction i