

Basic Chemicals Product Design Case Studies

13.0 OBJECTIVES

This chapter provides case studies to illustrate the steps in the design of *basic* chemical products using the Stage-Gate™ Product-Development Process. Emphasis is placed on the *concept* and *feasibility* stages in Figure PI.1. Only the key issues are summarized in the *development* stage.

After studying this chapter, the reader should:

1. Be able to use the elements of the Stage-Gate™ Product-Development Process for the design of *basic* chemical products.
2. Have an appreciation of how appropriate design methodology is invoked as needed using the Stage-Gate™ Product-Development Process.

13.1 INTRODUCTION

In this chapter, three case studies are presented involving *basic* chemical products. The first, which involves a plant to produce ammonia, focuses on process design to manufacture this well-understood basic chemical. A number of design innovations are considered in an attempt to reduce costs so as to compete with competitors. For the second, which involves the production of an environmentally friendly refrigerant to replace a refrigerant that is no longer acceptable environmentally, the focus is on the techniques for molecular structure design presented in Chapter 3. Finally, the third involves the design of a water-dispersible β -carotene product for the beverage industry, beginning with the basic chemical β -carotene.

These case studies follow the Stage-Gate™ Product-Development Process, as discussed in Chapter 2 and summarized in Figure PI.1, in solving the three product/process design problems.

13.2 AMMONIA CASE STUDY

Before proceeding with the ammonia case study, the reader should be conversant with the key steps in process design as introduced in Part One, specifically Chapters 4 to 9. Furthermore, since this case study is driven by economics, it is helpful to be familiar also with capital cost-estimation methods, introduced in Chapter 22, and with profitability analysis, introduced in Chapter 23.

Project Charter and New Technologies

As seen in Figure PI.1, it is recommended that the design team begin to develop a new product and process by creating a project charter. Before introducing the initial project charter prepared by the design team, a brief history of the manufacture and purchase of ammonia by Haifa Chemicals is reviewed. Haifa Chemicals is an international corporation, established in 1967, that produces and markets specialty fertilizers, food additives, and technical chemicals. Their production plants are located in Israel at Haifa Bay and in the northern part of the Negev region, and in Lunel, France.

In the 1970s, a 250-ton/day ammonia plant was located at Haifa Bay in close proximity to the Haifa Refinery, which provided naphtha that was converted to hydrogen in a reformer. Then, as demand increased in the late 1980s, the plant was shut down, with ammonia supplied by ship from external producers. To ensure continuous operation, a 12,000-ton storage vessel, containing a month's supply, was installed at Haifa Bay. The principal usage of ammonia in Israel is in the manufacture of $(\text{NH}_4)_3\text{PO}_3$, that is, fertilizer pellets for use in farming. Haifa Chemicals operates manufacturing facilities for ammonium phosphate in Ramat Hovav, which is in the Negev Desert in southern Israel, and in Haifa Bay, with ammonia being shipped by truck to Ramat Hovav, and phosphate rock being shipped by train to Haifa. As a result of the heightened security threat posed by the Lebanese Hezbollah in the summer of 2006, the State of Israel has been considering alternatives to relocate the storage tank to a remote location, such as the Negev Desert.

Table 13.1 Initial Project Charter

Project Name	Ammonia Production in Israel
Project Champions	Business Director of Haifa Chemicals, Inc.
Project Leaders	Speedy and Ploni Gonzales
Specific Goals	Produce and store NH ₃ from synthesis gas beginning with natural gas. Consider relocating the facility to a remote location to reduce the risk to population centers in the event of the release of NH ₃ that might result from terrorist rocket fire. Consider the initial design proposed by Emek Projects Ltd (EPL) as a possible starting point. Consider a joint facility with the State of Jordan and the purchase of natural gas from Egypt and/or the Palestinian Authority.
Project Scope	In-scope: <ul style="list-style-type: none"> • H₂ from natural gas • N₂ from air Out-of-scope: <ul style="list-style-type: none"> • Production and storage in port cities with large populations (e.g., Haifa, Ashdod)
Deliverables	<ul style="list-style-type: none"> • Business opportunity assessment • Technical feasibility assessment • Product life-cycle assessment
Time Line	Feasible processing package within 6 months

Consider the example project charter in Table 13.1 assembled by a typical design team in 2007. The goals of this project charter were centered around circumventing the safety hazard created by the storage of toxic ammonia in the Haifa area, which has a metropolitan population of over 1 million persons. At that time, the Israeli demand for ammonia was about 350 metric ton/day. This demand could have been augmented by the joint construction of a manufacturing plant with Jordan, which was storing approximately 30,000 metric tons of ammonia in Akaba that arrived by ship from external suppliers. In 2007, it was also significant that Egypt was constructing a 2,000-metric-ton/day ammonia plant in the Suez Industrial Zone, scheduled to begin operation in 2008, at an investment cost of \$540,000,000. While implicit in satisfying the need for ammonia product, an important objective was to provide guidance and recommendations to the Israeli government regarding policies for the storage of toxic chemicals. To protect the population, given the prices established by external suppliers of natural gas and ammonia, it may have been necessary for the government to consider the provision of tax breaks and low-cost loans. Initially, the preliminary design proposed by Emek Projects Ltd (EPL), an imaginary company, was available.

This initial project charter identified the production of synthesis gas using natural gas as the source of hydrogen and air as the source of nitrogen as *in-scope*. On the other hand, solutions involving the storage of ammonia in port cities, such as Haifa and Ashdod, were considered to be *out-of-scope*.

The first deliverable was a business opportunity assessment involving a profitability analysis. In addition, a techni-

cal feasibility assessment was to be provided, including the results of process simulations. And, finally, a product life-cycle assessment was to be conducted that addressed: (1) the danger of an ammonia release from a storage facility, (2) the release of carbon dioxide byproduct into the atmosphere, and (3) the possible conversion of ammonia to urea by reaction with carbon dioxide as a vehicle for curbing the release of the carbon dioxide byproduct. Note, however, that due to space limitations, this life-cycle assessment is the subject of Exercises 13.1–13.3.

Finally, the product time line required the delivery of a feasible process package within six months.

Innovation Map

Having created a project charter, the design team next turned to an examination of the customer needs (that is, the *customer-value proposition*) and the new technologies likely to play an important role in providing the ammonia product, as introduced in Section 1.3. These are shown linked together in the *innovation map* of Figure 13.1.

To construct this *innovation map*, the design team first identified the elements in its four levels, moving from the bottom to the top of the map:

1. *Process/Manufacturing Technology*: Improved heat integration, membrane separation to recover H₂ from the purge stream, and heat and mass exchange (HME) technology to enhance conversion in the NH₃

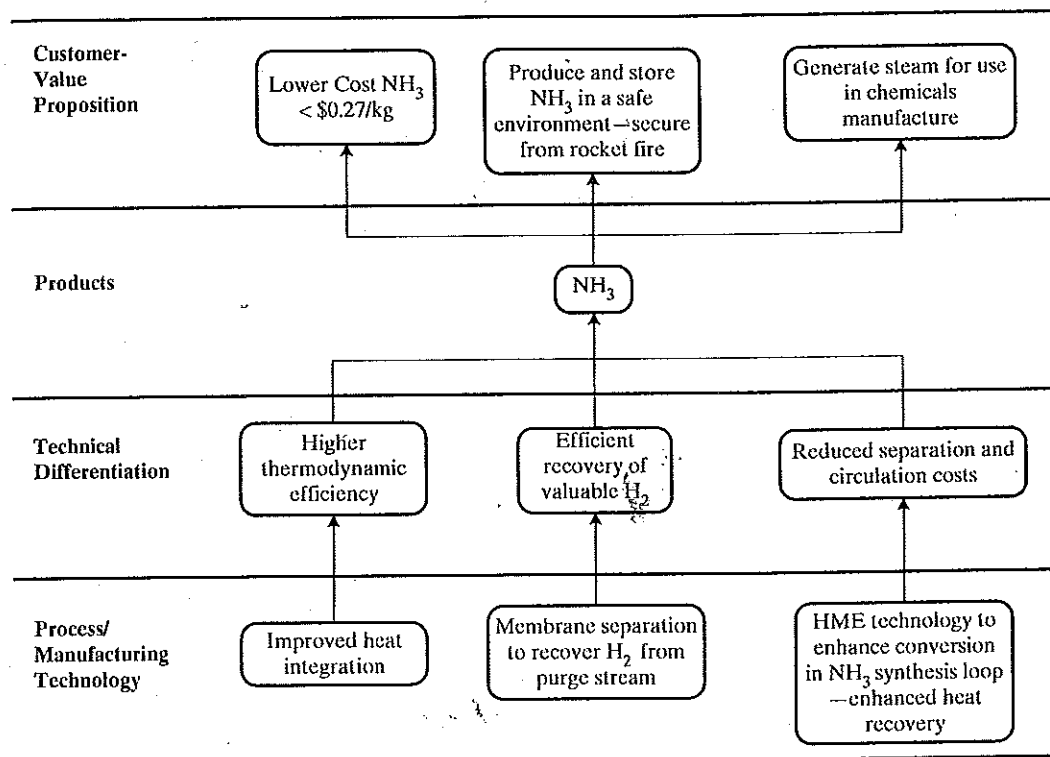


Figure 13.1 Innovation map for ammonia product.

synthesis loop and provide enhanced heat recovery. These were new technologies to be considered to enhance the profitability of the process under development.

2. *Technical Differentiation (Technical-Value Proposition)*: Higher thermodynamic efficiency, resulting from improved heat-integration methods; efficient recovery of valuable H_2 by utilizing membrane-separation technology; and reduced separation and recirculation costs in the synthesis loop by incorporating HME technology.

3. *Products*: NH_3 .

4. *Customer-Value Proposition*: Produce NH_3 to sell for $\$0.27/\text{kg}$ or less, while reducing the potential security impact of a rocket attack.

After identifying the elements at all four levels of the innovation map, their connectivity in the map was added to show the interplay between the technological elements, the *technical-value proposition*, and ultimately the *customer-value proposition*.

In this case, for a well-known commodity chemical product such as NH_3 , the new technologies that had the potential to satisfy the customer needs were process/manufacturing technologies. The first was the potential for improved heat integration using the algorithmic methods discussed in Chapter 9; that is, methods to increase the energy recovery. Yet another advance was possible through the use of membranes to recover valuable H_2 from the vapor purge stream that exits from the NH_3 synthesis loop. And, finally, the new heat and mass

exchange (HME) technology had the potential to significantly increase the conversion to NH_3 while providing enhanced heat recovery. Both of these separation technologies are discussed next.

Heat and Mass Exchange Technology

HME technology (Lavie, 1987) involves a heat-insulated pair of adsorbing vessels that perform their normal role of adsorption while also transferring heat from the hot regenerant stream to the cold process stream from which one or more species are removed by adsorption, as depicted schematically in Figure 13.2. In NH_3 production, the synthesis gas directed to the converter must be preheated, while the effluent stream from the converter must be cooled to condense the ammonia. This is normally accomplished by heat exchange between the two streams. Also, the maximum concentration of ammonia in the converter effluent is limited by equilibrium and is therefore essentially independent of the ammonia concentration in the feed to the converter. However, by installing an HME unit to completely or partially replace the heat exchanger, the

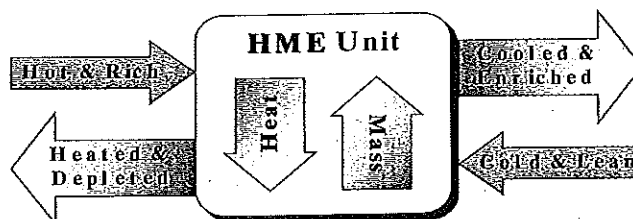


Figure 13.2 HME schematic.

converter effluent can also be enriched at the expense of its feed. This can increase the conversion-per-pass in the converter by a few percent, which translates into an increase of 10–20% in ammonia production from the same loop. The Hot & Rich stream fed to the HME unit should be at least 150°C.

Membrane Separation of Hydrogen from Synthesis Gas

The MEDAL™ membrane technology, commercialized by Air Liquide, <http://www.medal.airliquide.com/en/membranes/hydrogen/ammonia.asp>, enables hydrogen to be separated from a mixture as permeate, with the remaining gases removed as residue (retentate). A schematic of a typical separator, taken from the Air Liquide Web site, is shown in Figure 13.3, noting that the stream pressures and compositions shown do not apply directly to the separator's application in an ammonia process. The usage of highly selective polyvinylchloride membranes enables almost perfect separation of the hydrogen, with a recovery as high as 95 mol%. As discussed in the next section, this technology was not adopted by the EPL team, but was a strong candidate for the recovery of hydrogen from the purge gas stream.

In the innovation map, these new technologies were linked to their related technical differentiations, which permit the generation of the NH₃ product to satisfy the customer needs identified under the *customer-value proposition*. The first, which is imperative to achieve lower costs in energy-intensive processes that produce commodity chemicals, was to yield a high thermodynamic efficiency through the extensive use of heat integration. The second, which has been enabled by hollow-fiber membranes in recent years, was to recover valuable H₂ in purge streams rather than burn it in a flare device. And, finally, the application of HME technology led directly to reduced separation and circulation costs.

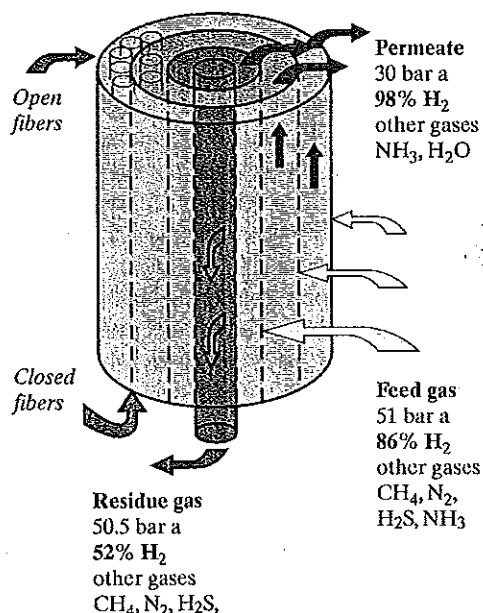


Figure 13.3 Typical membrane separator.

Combined, these technical differentiations had the potential to permit the production and storage of NH₃ in a remote environment, secure from rocket fire, and the generation of product steam to be used in related chemical processes, such as the manufacture of (NH₄)₃PO₃.

Concept Stage

Having assembled a promising *innovation map*, and after gaining approval to begin the SGPDP, as shown in Figure PI.1, the design team normally begins the *concept* stage with a market assessment to identify the *value creation* and *value capture*, and to create the *value proposition*, as discussed in Section 2.4.

- a. **Market Assessment.** For this NH₃ product, the added value to customers was unusual. In this case, the production and storage of NH₃ in a remote location would sharply reduce the danger of exposure to toxic NH₃ in the event of terrorist rocket attacks, a significant threat in Haifa, Israel.

The answers to the following questions also helped to define the *value creation*: Who are the customers? These were the fertilizer manufacturers, that is, the producers of (NH₄)₃PO₃, and the manufacturers of industrial refrigeration units, in both Israel and, possibly, Jordan. Of these customers, who are most likely to buy? Clearly, the Israelis were the most likely customers.

Turning to *value capture*, in this case, there was no clear competition. While the NH₃ could be purchased from external suppliers, especially the new NH₃ plant under construction in Egypt, unfortunately, it was not possible to import and store NH₃ in the Israeli ports Haifa and Ashdod, because they are large population centers.

Finally, the design team identified a concise statement that summarized the need for the new remote facility to produce the product NH₃. Their *value-proposition* statement, was: "To remove its dependence on imported NH₃, the Government of the State of Israel supports the construction of a new plant to produce NH₃ in the Negev Desert. This will permit the dismantling of the hazardous NH₃ storage facility in Haifa Bay."

- b. **Customer and Technical Requirements, and Superior Product Concepts.** For this commodity chemical, NH₃, the customer requirements were well established when the project charter was created. These were not further developed in the *concept* stage. Their translation into technical requirements (see Section 2.4) was rather straightforward: that is, to produce 99 mol% NH₃ containing 1 mol% water. The latter is needed to reduce stress-corrosion cracks (SCC) in the stainless steel containers exposed to pure ammonia. Normally, the next steps toward creating superior product concepts are to create a preliminary database and to carry out preliminary process synthesis, as shown in Figure PI.1 and discussed in Section 4.4. In this case, the most promising flowsheets of process operations are well

established for the conversion of natural gas to synthesis gas and for the NH₃ synthesis loop. For this reason, as discussed next, the design team opted to adopt, initially, the preliminary process flowsheet created by EPL as their base-case design. This flowsheet, in Figures 13.4 and 13.5, is described next. It was further developed in the *feasibility* stage of the SGPDP.

Feasibility Stage

As discussed above, for this case study a preliminary process flowsheet had been created by EPL. It provided the base-case design to be improved upon by the design team. Note that, in Figure PL.1, it is recommended that a base-case design be developed at the outset of the *feasibility* stage.

Proposed Design by EPL

Figures 13.4 and 13.5, to be described below, show the design proposed by EPL, which assumes a basis of 12,000 kg/hr of methane as feed, with raw material and product prices assumed as given in Table 13.2. Note that the EPL simulations were carried out using UNISIM, the Honeywell version of HYSYS. This design has a return on investment (ROI) of

Table 13.2 Prices of Raw Materials and Products

Commodity	Assumed Price (\$/kg)
Ammonia	0.27
Methane	0.20
Process steam	0.02

-15.4% and a venture profit (VP, computed as the profit minus a 20% return on investment; see Eq. (23.9)) of -\$25,500,000; that is, an annual *loss* of over \$25 million. EPL stated in their report that: "This poor economic evaluation is due to the relatively low market price for ammonia. It is impossible to design a more profitable process without a significant increase in the price of ammonia." During this *feasibility* stage, the design team disputed this assertion, believing that it was possible to generate an acceptable profit and that poor engineering practice led to EPL's negative assessment.

The popular route to ammonia, adopted by EPL, is from natural gas (largely methane). The process involves two main sections: one for synthesis gas generation (Figure 13.4) and the other for the ammonia synthesis loop (Figure 13.5). Full details of the original EPL design, as well as a complete project tender

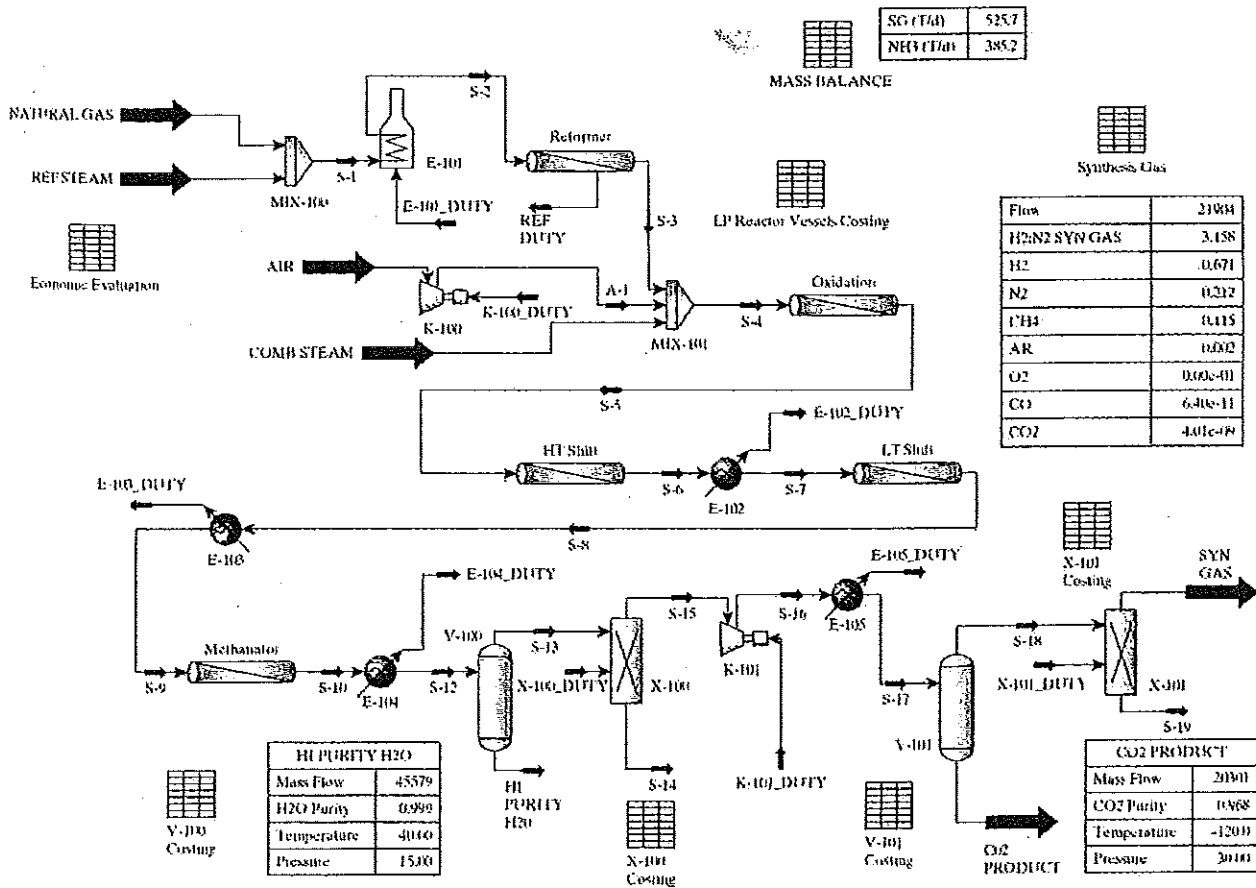


Figure 13.4 UNISIM PFD for the EPL design: Synthesis gas section. In the PFD, mass flows are in kg/hr, temperatures are in °C, pressures are in bar, and compositions are in mole fractions.

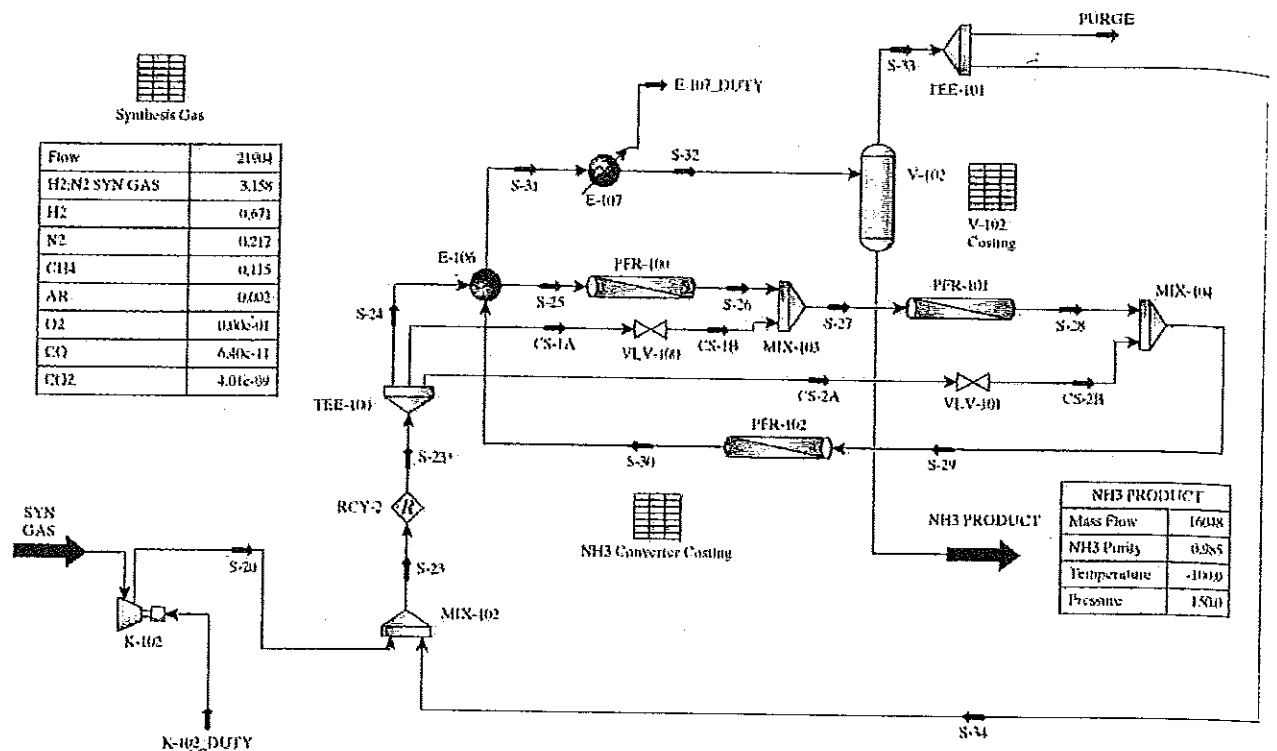


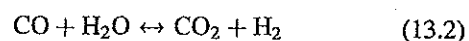
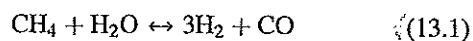
Figure 13.5 UNISIM PFD for the EPL design: Synthesis loop section. Units as in Figure 13.4.



that includes information about materials specifications and equipment costing information, can be found in the file Ammonia Project.pdf in the PDF Files folder, which can be downloaded from the Wiley Web site associated with this textbook.

Synthesis Gas Generation (see Figure 13.4). The objectives of this section are to maximize the production of synthesis gas and to ensure its purity. The specifications for synthesis gas are: (a) a molar ratio of hydrogen to nitrogen of 3 (ideally, this ratio needs to be 3:1 in the feed to the NH₃ converter); (b) water-free; (c) CO and CO₂ under 1 ppm each; (d) minimum inerts (argon and CH₄). To achieve these objectives, the following steps are employed:

- Methane is combined with reformer steam, preheated in furnace E-101, and fed to the reformer, in which most of the methane is converted to hydrogen. The reformer is a furnace in which the reaction mixture flows through tubes arranged along the furnace wall. It is modeled in UNISIM as an isothermal PFR (with the effluent temperature set at the feed temperature). In the EPL design, the operating temperature is selected as 700°C. The following reactions take place in the reformer:



According to Parisi and Laborde (2001), reaction rates for these two reactions are:

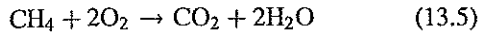
$$-r_{\text{CH}_4} = k_{1,\infty} \cdot \exp[-E_1/RT] \left(P_{\text{CH}_4} P_{\text{H}_2\text{O}} - \frac{P_{\text{CO}} P_{\text{H}_2}^3}{\exp\left[\frac{-27,464}{T} + 30.707\right]} \right) \quad [\text{kgmol}/\text{m}^3\text{-s}] \quad (13.3)$$

$$-r_{\text{CO}} = k_{2,\infty} \cdot \exp[-E_2/RT] \left(P_{\text{CO}} P_{\text{H}_2\text{O}} - \frac{P_{\text{CO}_2} P_{\text{H}_2}}{\exp\left[\frac{4,048}{T} - 3.765\right]} \right) \quad [\text{kgmol}/\text{m}^3\text{-s}] \quad (13.4)$$

Note that in the above equations, the species partial pressures are in atm, T is the temperature in K, and Eqs. (13.3) and (13.4) hold for $T > 860$ K. These authors provide the following kinetic parameters: $E_1 = E_2 = 16,000$ kJ/kgmol, $k_{1,\infty} = 200$ kgmol/m³-s, and $k_{2,\infty} = 100$ kgmol/m³-s.

- The reformer effluent is combined with air and steam to ensure a 3:1 mixture of hydrogen and nitrogen in the resulting synthesis gas. First, the effluent is reacted in the oxidation reactor, often referred to as a "secondary

reformer," modeled in UNISIM as an adiabatic PFR, where the oxygen in the air generates CO, which leads to additional hydrogen. In addition to reaction (13.1) above, the following reaction takes place in the oxidation reactor:



According to Wolf et al. (1997), its reaction rate takes the form:

$$-r_{\text{CH}_4} = \frac{k_{3,\infty} \cdot \exp[-E_3/RT] \cdot P_{\text{CH}_4} P_{\text{O}_2}}{(1 + K_{\text{CH}_4} P_{\text{CH}_4} + K_{\text{O}_2} P_{\text{O}_2} + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})^2}, \quad [\text{kgmol}/\text{m}^3\text{-s}] \quad (13.6)$$

Note that in the above equations, the partial pressures are in kPa and T is the temperature in K. Wolf et al. (1997) provide the following kinetic parameters:

$$K_{\text{CH}_4} = 1.1 \times 10^{-6} \cdot (-E_{\text{CH}_4}/RT), \quad E_{\text{CH}_4} = 32,200 \text{ kJ/kgmol}$$

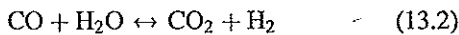
$$K_{\text{O}_2} = 1.1 \times 10^{-2} \cdot (-E_{\text{O}_2}/RT), \quad E_{\text{O}_2} = 28,400 \text{ kJ/kgmol}$$

$$K_{\text{CO}_2} = 1.5 \times 10^{-4} \cdot (-E_{\text{CO}_2}/RT), \quad E_{\text{CO}_2} = 32,900 \text{ kJ/kgmol}$$

$$K_{\text{H}_2\text{O}} = 5.3 \cdot (-E_{\text{H}_2\text{O}}/RT), \quad E_{\text{H}_2\text{O}} = 27,300 \text{ kJ/kgmol}$$

The two remaining parameters are selected to be: $E_3 = 32,000 \text{ kJ/kgmol}$ and $k_{3,\infty} = 1,000 \text{ kgmol}/\text{m}^3\text{-s}$.

- c. Since the first two reaction steps also generate CO, which poisons the ammonia synthesis catalyst, shift reaction steps are employed to convert CO to CO₂. These two reactors are modeled in UNISIM as adiabatic PFRs. In the EPL design, the oxidation reactor effluent is fed to the first shift reactor, HT shift. Then, heat exchanger E-102 reduces its effluent temperature to 500°C before it enters the second shift reactor, LT shift. Note that E-102 generates HT steam, providing a revenue source. The so-called water-gas shift reaction takes place in the shift reactors:



The same kinetic form is used as in Eq. (13.4), but two of the kinetic parameters are slightly different (Parisi and Laborde, 2001) because the reaction occurs at lower temperatures:

$$-r_{\text{CO}} = k_{2,\infty} \cdot \exp[-E_2/RT] \cdot \left(P_{\text{CO}} P_{\text{H}_2\text{O}} - \frac{P_{\text{CO}_2} P_{\text{H}_2}}{\exp\left[\frac{4,577}{T} - 4.33\right]} \right) [\text{kgmol}/\text{m}^3\text{-s}] \quad (13.7)$$

Note that the partial pressures are in atm, T is the temperature in K, and Eq. (13.7) holds for $T < 860 \text{ K}$. Parisi and Laborde (2001) provide the following kinetic parameters: $E_2 = 16,000 \text{ kJ/kgmol}$, and $k_{2,\infty} = 100 \text{ kgmol}/\text{m}^3\text{-s}$.

- d. According to reaction (13.1), any remaining CO reacts reversibly to methane in the methanator, which is modeled in UNISIM as an adiabatic PFR. Note that the reaction rate in Eq. (13.3) applies, with the operating temperature sufficiently low to ensure that the reverse reaction dominates. In the EPL design, the methanator feed temperature is selected as 250°C.
- e. The water produced in the previous reaction steps is removed next. In the design suggested by EPL, heat exchanger E-104 cools the methanator effluent to 40°C, condensing the water, which is removed largely in the flash vessel, V-100. Residual water is removed using adsorption beds, modeled using a separator, X-100, in UNISIM.
- f. The CO₂ produced in the previous steps is removed next. In the EPL design, the heat exchanger, E-105, cools the effluent from X-100 to -120°C, condensing CO₂, most of which is recovered in flash vessel V-101 as byproduct. The residual CO₂ is removed using adsorption beds X-101.

As shown in Figure 13.4, the EPL design produces very clean synthesis gas, easily satisfying the impurity constraints. However, only 526 T/day of synthesis gas is produced, given 12,000 kg/hr of methane feed, and the H₂/N₂ ratio is imprecisely maintained in excess of 3:1.

Ammonia Synthesis Loop (see Figure 13.5). The objectives of this section are to maximize the ammonia production and to ensure its purity ($\geq 98 \text{ mol}\%$). To achieve these objectives, the following steps are employed:

- a. The synthesis gas is compressed to the operating pressure of the synthesis loop in compressor K-102; that is, 150 bar in the EPL design.
- b. The synthesis gas is combined with the recycle stream from the vapor effluent of the flash vessel, V-102.
- c. The combined feed from the mixer, MIX-102, is split three ways, with the largest portion entering the ammonia converter through heat exchanger E-106, where it is preheated to the ignition temperature using the hot converter effluent from reactor PFR-102. In this design, the reacting synthesis gas progresses through three adiabatic PFRs, with intercooling provided by two cold shots in streams CS-1A/B and CS-2A/B. The reaction in the adiabatic beds is:



The rate of reaction is given by the following kinetic expression (Eq. 7.32):

$$-r_{\text{N}_2} = 10^4 \exp[-9.1 \times 10^4/RT] P_{\text{N}_2}^{0.5} P_{\text{H}_2}^{1.5} - 1.3 \times 10^{10} \exp[-1.4 \times 10^5/RT] P_{\text{NH}_3} \quad (13.9)$$

where $-r_{N_2}$ is the rate of nitrogen disappearance in $\text{kmol/m}^3\text{-s}$, T is the temperature in K, P_i are the partial pressures of the reacting species in atm, and the activation energies for the forward and reverse reactions are in kJ/kmol .

- d. The hot reactor effluent is cooled by exchange with the cold synthesis gas in heat exchanger E-106. It is further cooled in heat exchanger E-107, with the effluent temperature (of stream S-32) low enough to ensure sufficiently pure ammonia product. In the EPL design, cooler E-107 is cooled with expensive methane refrigerant. The cooled converter effluent is flashed in V-102 to liquid ammonia product, with the vapor stream recycled.
- e. A small purge stream is split away from the vapor recycle in TEE-101.

Sensitivity Analysis

For a complex process, it helps to identify the decision variables having the greatest effect on the profitability, with a comparable effect on the plant feasibility, like the critical-to-quality (CTQ) variables in product design. These decision variables are:

- **Production rate.** The design basis of 12,000 kg/hr methane adopted by EPL produces 385 T/day of ammonia, which meets Israel's needs. However, this scale of operation may not be profitable, as will be shown for the EPL base-case design. Clearly, a well-conceived design that generates a reasonable profit at minimum capacity is sought.
- **Steam/methane ratio.** This strongly affects the conversion of methane to hydrogen.
- **Air/methane ratio.** This affects the H_2/N_2 ratio in the synthesis gas fed to the synthesis loop. Note that the EPL design generates synthesis gas having a 3.16 H_2/N_2 ratio, which exceeds the stoichiometric ratio.
- **Feed temperatures of the shift reactors.** These control the conversion of CO, which poisons the ammonia synthesis catalyst, to CO_2 . Note that the EPL design doesn't control the feed temperature to the HT shift but sets the feed temperature to the LT shift to 500°C , leading to excessive CO in the effluent of the shift reactor train. This CO is subsequently converted to methane in the methanator, leading to highly inert (CH_4) concentrations in the synthesis loop, significantly reducing its efficiency and profitability.
- **Synthesis loop pressure.** The synthesis loop of the EPL design operates at 150 bar. While the conversion per pass increases with increasing pressure, as shown in the solution to Exercise 6.3, so do the equipment and operating costs. The impact of the synthesis loop pres-

sure on the profitability of the process is considered in Exercise 13.4.

- **Feed temperature to the ammonia converter.** This should be adjusted to the lowest possible value that guarantees a reasonable stability margin; that is, one that avoids operation in the vicinity of multiple steady states (see Section 7.2).
- **Control of "cold-shot" bypasses in the ammonia converter.** The fractions of feed in the bypasses permit the conversion per pass to be maximized, as discussed in Example 7.3.

In addition to the above, following Chapter 9, MER targeting should be carried out to compute hot and cold utility targets. Also, as will be shown, the grand composite curve helps to distribute the optimal utility sources. A heat exchanger network can then be designed that provides an adequate approach to the MER targets, thereby sharply reducing the usage of external utilities.

Refining the Solution

First, the design basis of 12,000 kg/hr methane feed in the EPL design is retained, with the aim being to estimate the best profitability achievable for this scale of operation. Then, economy-of-scale arguments are employed to estimate the effect of the production rate on the profitability of the process.

Refining the Solution for 12,000 kg/hr Methane Feed

There are several weaknesses in the EPL design: (a) too little hydrogen is produced in the synthesis gas section due to the poor performance of the reformers; (b) the $\text{H}_2:\text{N}_2$ ratio of the synthesis gas is 3.158, and 4.255 in the feed to the converter, due to the poor control of the quantity of air fed to the synthesis gas section; (c) the percentage of inerts in the synthesis gas, especially CH_4 , is excessive (the composition of methane is 11.5 mol%) due to: (i) the relatively poor conversion of CH_4 in the reformers, and (ii) the relatively large concentration of CO remaining in the synthesis gas effluent from the shift converters, which is subsequently converted to methane in the methanator; (d) the ammonia composition in the NH_3 converter effluent is about 8.5 mol% due to: (i) the excessive amount of inerts in the converter feed (over 44 mol%), (ii) the high $\text{H}_2:\text{N}_2$ ratio in the feed to the converter, which is far above stoichiometric, and (iii) poor performance of the converter, with the bypass fractions suboptimal and the feed temperature too high. All of these weaknesses are dealt with sequentially. Due to space limitations, only the key improvements are highlighted next:

Improving Hydrogen Yield. The main reason for the relatively low hydrogen yield is the low temperature in the reformer, with the yield increasing exponentially with temperature. Setting the operating temperature to 850°C , while

Table 13.3 Sensitivity of Primary and Secondary Reformer Performance to Steam Flow Rates. Outputs — H_2 (in Roman font) and O_2 Mass Flows (in *italics*) — in kg/hr

		Reformer Steam [kgmol/hr]			
		1,500	2,000	2,500	3,000
Combustion Steam [kgmol/hr]	600	4,334 <i>4.35×10^{-6}</i>	4,449 <i>1.15×10^{-5}</i>	4,514 <i>1.20×10^{-2}</i>	4,571 <i>4.27</i>
	900	4,302 <i>1.25×10^{-3}</i>	4,421 <i>2.02×10^{-6}</i>	4,494 <i>7.52×10^{-2}</i>	4,556 <i>2.47</i>
	1,200	4,268 <i>1.05×10^{-1}</i>	4,397 <i>3.01×10^{-6}</i>	4,476 <i>2.42×10^{-2}</i>	4,542 <i>1.17</i>
	1,500	4,234 <i>2.11×10^{-3}</i>	4,375 <i>2.56×10^{-6}</i>	4,460 <i>9.49×10^{-4}</i>	4,530 <i>4.48×10^{-1}</i>

adjusting the air flow rate to ensure a $H_2:N_2$ ratio of 3, reduces the methane composition in the effluent from the oxidation reactor from 3.6 to a very low 0.04 mol%. Furthermore, to maximize the hydrogen produced, a sensitivity analysis shows the effect of the steam molar flow rate in the reformer and oxidation reactor on the hydrogen mass flow rate in the oxidation reactor effluent. The results are presented in Table 13.3. As seen, the optimal operation is at a reformer steam flow rate of 2,500 kgmol/hr, rather than 2,000 kgmol/hr, and a combustion steam flow rate of 600 kgmol/hr, rather than 1,200 kgmol/hr. These settings ensure the highest possible hydrogen generation rate while keeping the oxygen level sufficiently low. With these settings, the methane composition in the oxidation reactor effluent drops further, from 0.04 to 0.009 mol%.

Minimizing CO Composition in the Shift Reactor Train Effluent. Next, the optimal operation of the two shift reactors is considered. To improve their performance, a cooler is inserted immediately before the HT shift reactor, allowing the feed temperatures to the two reactors to be selected independently. A sensitivity analysis shows their effect on the CO concentration in the effluent from the LT shift reactor as its feed temperature varies from 300 to 500°C. The results in Figure 13.6 show that the minimum CO concentration, at 1.33 mol%, is achieved when the feed temperatures to the HT and LT shift reactors are at 400 and 375°C, respectively. With these settings, the methane composition in the synthesis gas drops to 2.5 mol%. The new cooler also allows a large quantity of high-pressure steam (hps) to be produced, providing significant revenues.

As seen in Table 13.4, with these modifications to the synthesis gas section, the ROI and VP increase to -2.4 and -\$20,000,000, respectively. Although the profitability is improved, it remains unacceptable. Additional improvements are needed in the NH_3 synthesis loop.

Increasing Conversion in the Ammonia Converter. First, notice that the conversion in the ammonia reactors is very low. As shown in the

multimedia modules, which can be downloaded from the Wiley Web site associated with this textbook (*HYSYS* → *Tutorials* → *Process Design Principles* → *Ammonia Converter Design*), the conversion can be significantly enhanced by adjusting the cold-shot fractions. Consequently, both are increased from 0.1 to 0.2. Furthermore, the reactor feed temperature is reduced from 310°C to just above the extinction temperature, 250°C, further increasing the conversion, which is favored by low temperatures. Because multiple steady states are possible, to avoid operating problems, care is taken to select feed temperatures associated with unique steady states.

Reducing the Cost of Ammonia Separation. Because the ammonia purity is much higher than required, the operating temperature of V-102 can be increased, reducing the refrigeration costs. For example, using ammonia refrigerant at -30°C, the V-102 temperature can be as high as -20°C, assuming a minimum temperature approach of 10°C. With this change, the operating expenses of the process are reduced sharply, at the cost of increasing the NH_3 concentration in the recycle stream.

Hydrogen Recovery from the Purge Stream. The purge stream is at 4.3 T/hr and 61 mol% H_2 , which has been generated at considerable expense. As an alternative, hydrogen can be recovered using a membrane-separation unit, which is designed on the assumption of 95% hydrogen recovery. Because the hydrogen recovered is at 50% of the pressure of the synthesis loop, the single-stage compressor must be replaced by a two-stage compressor, including an intercooler, with the recovered hydrogen fed to the suction line of the second compressor. The additional equipment costs must be justified by the increased NH_3 production rates.

Figures 13.7 and 13.8 show the PFDs for the improved synthesis gas generation and synthesis loop sections. To achieve profitability, it is necessary to reduce the $H_2:N_2$ ratio of the synthesis gas, such that after the recovered hydrogen is recycled, the $H_2:N_2$ ratio entering the converter approaches three. As seen in Table 13.4, with these modifications to the



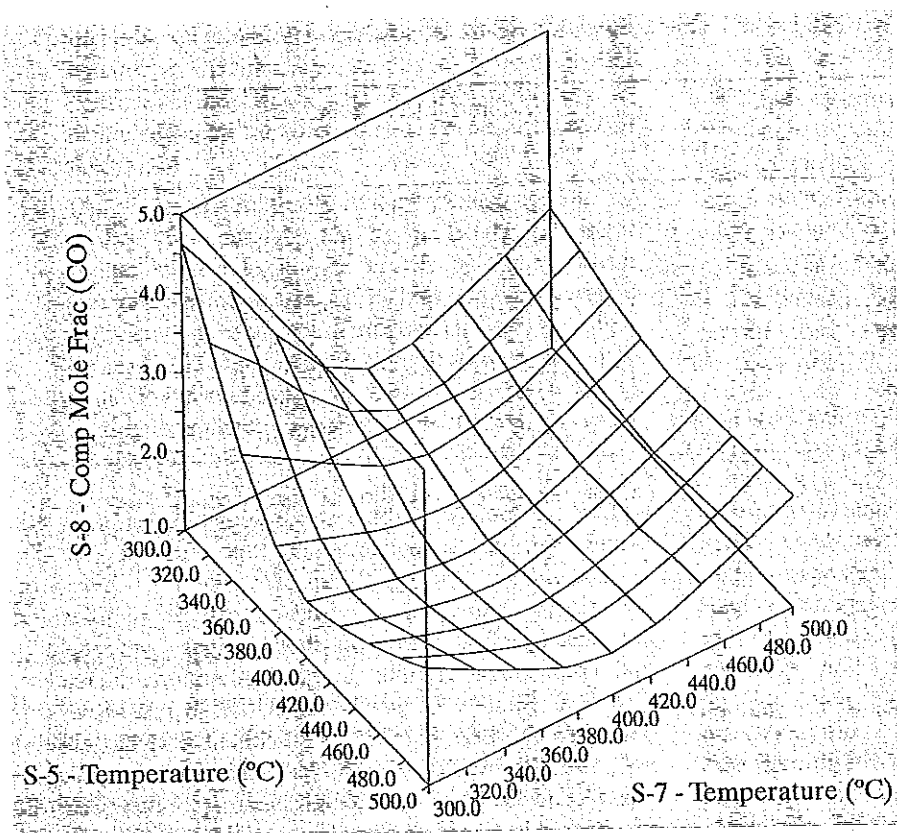


Figure 13.6 Effect of the feed temperatures to the two shift reactors on effluent CO.

Figur

Table 13.4 Profitability Analysis by Design Step (Basis: 12,000 kg/hr methane)

Step	NH ₃ (T/d)	GP (\$MM)	C _{TCI} (\$MM)	ROI (%)	PBP (yrs)	VP (\$MM)
EPL Design	385.2	-14.8	72.0	-15.4	n/a	-25.5
After modifications to synthesis gas section	530.5	-2.8	89.6	-2.4	n/a	-20.0
After modifications to synthesis loop section	608.9	16.1	96.0	12.5	7.8	-7.2
After implementing heat integration	608.8	17.5	89.3	14.7	6.8	-4.7
After implementing HME	610.2	19.0	88.5	16.1	6.2	-3.4

synthesis loop section, the ROI and VP are increased significantly to 12.5%, and -\$7,200,000. Next, heat integration is considered as a means of further improving the profitability:

MER Targeting, MER Design, and Optimal Energy Management

The objective of this step is to improve the profitability of the process by heat integration, using techniques discussed in Chapter 9. At the outset, note that the primary (NH₃) and secondary (purge) products are currently produced at -20°C, with valuable cooling resources not being exploited. To use these resources, two heaters are inserted into the flowsheet: E-109, which raises the CO₂ product temperature to its bubble point (the highest liquid temperature), and E-110, which raises the ammonia product temperature to its bubble

point. It is noted that ammonia storage is designed so that ammonia is stored either at ambient temperature (at about 10 bar) or at atmospheric pressure (thus requiring refrigeration to maintain the ammonia at its bubble-point temperature of -30°C). For this simplified design, it is assumed that the ammonia can be produced at the bubble-point temperature corresponding to the loop pressure.

Next, a preliminary analysis of the opportunities for heat integration is presented; that is, the demands of streams to be heated and cooled are listed below:

COLD_1: 24.02×10^6 kcal/hr is required between 185 and 850°C to preheat the reformer feed. The current design requires \$2,760,000/yr in fuel costs in a furnace (E-101) whose FOB purchase price is \$1,970,000.

Figur

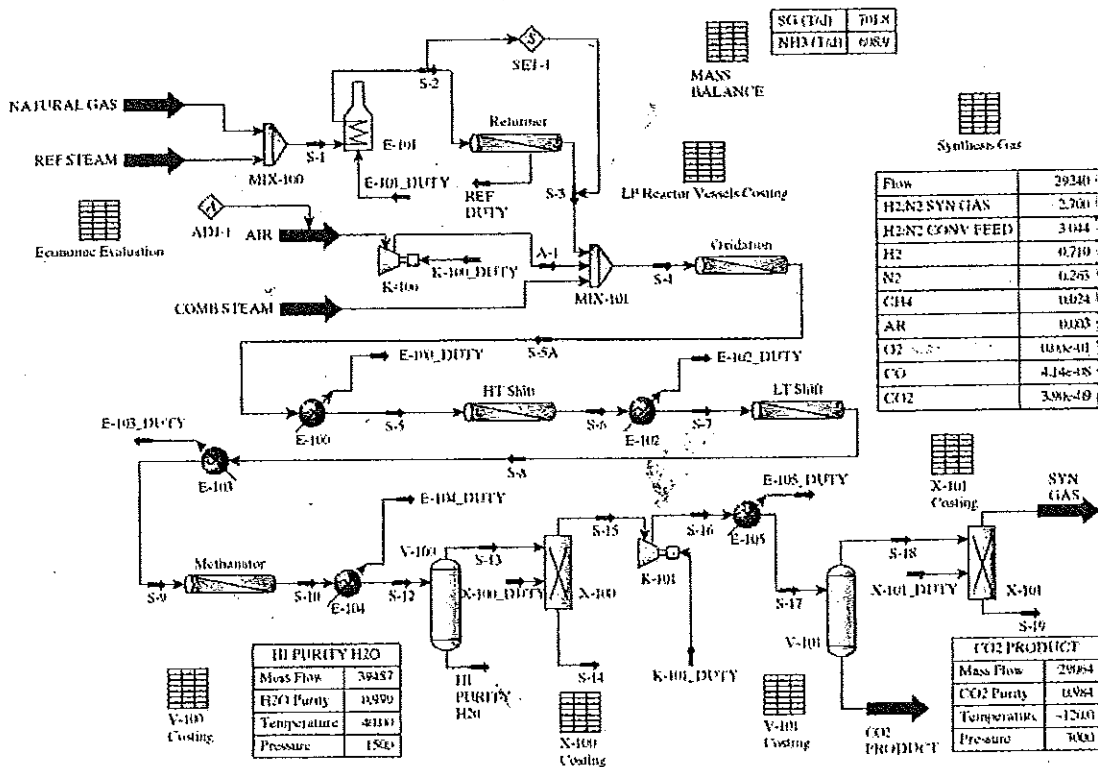


Figure 13.7 UNISIM PFD for the synthesis gas section after modifications. Units as in Figure 13.4.

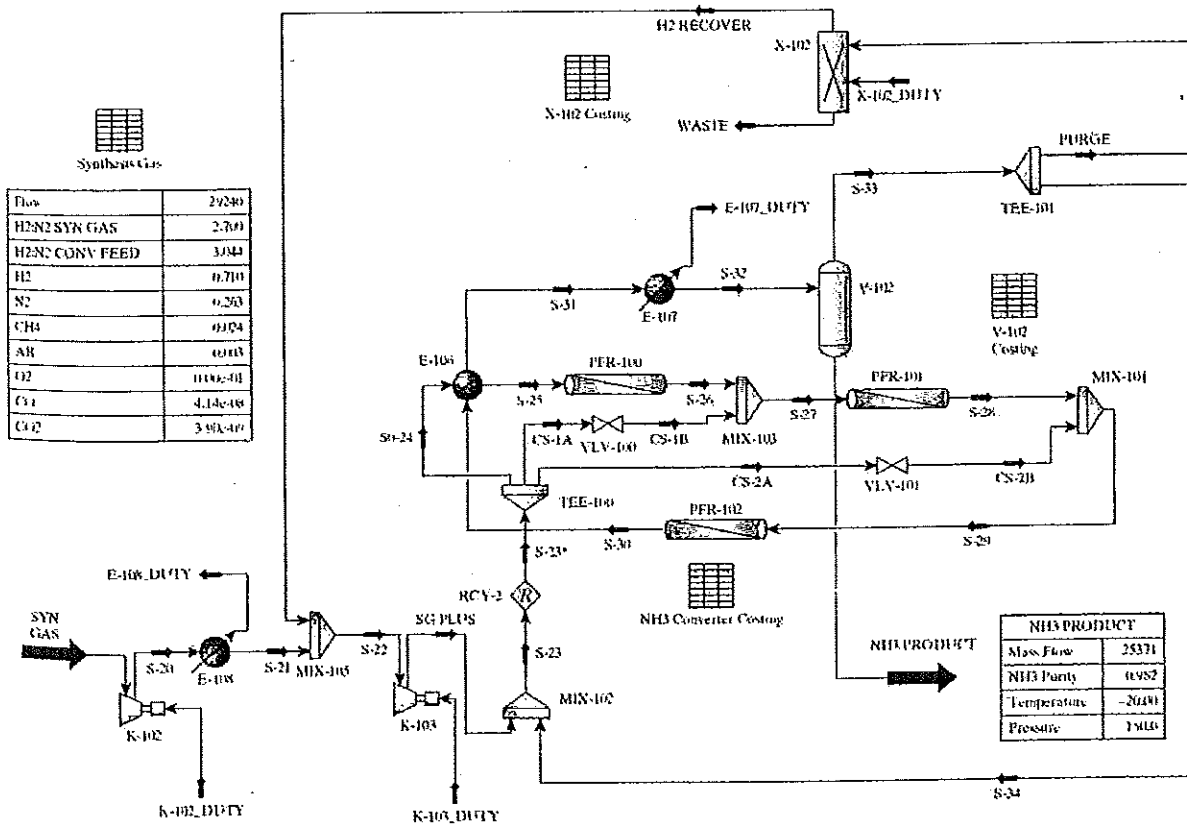


Figure 13.8 UNISIM PFD for the synthesis loop section after modifications. Units as in Figure 13.4.

COLD_2: 1.38×10^6 kcal/hr is required between -120 and -17°C to heat the CO_2 product. Alternatively, this cold stream can remain at -120°C if more economical.

COLD_3: 1.46×10^6 kcal/hr is required between -20 and 30°C to heat the NH_3 product. Alternatively, this cold stream can remain at -20°C if more economical.

HOT_1: 40.67×10^6 kcal/hr is available between 400 and $1,145^\circ\text{C}$ in the secondary reformer effluent. The current design generates HP steam with revenues at $\$10,170,000/\text{yr}$. Possibly, these revenues can be improved.

HOT_2: 3.80×10^6 kcal/hr is available between 375 and 449°C in the HT shift effluent. Again, the current design generates high pressure steam (hps) that provides $\$950,000/\text{yr}$. Perhaps this heat can be better utilized elsewhere.

HOT_3: 8.13×10^6 kcal/hr is available between 220 and 382°C in the LT shift effluent. Similarly, the current design generates HP steam with revenues at $\$1,220,000/\text{yr}$.

HOT_4: 35.21×10^6 kcal/hr is available between 40 and 302.8°C in the methanator effluent, noting that this stream exhibits a phase change. In the current design, this heat is removed using cooling water, which is clearly wasteful.

HOT_5: 9.83×10^6 kcal/hr is available between -120 and 125.7°C in the feed stream to V-101, noting that this stream exhibits a phase change. In the current design, this duty is removed using methane refrigerant (mr), at a cost of $\$4,920,000/\text{yr}$! Clearly, not all of this heat should be removed using such an expensive refrigerant.

HOT_6: 2.78×10^6 kcal/hr is available between 40 and 165°C in the effluent from K-102. Currently, this heat is removed using cooling water.

HOT_7: 27.58×10^6 kcal/hr is available between -20 and 232°C in the feed to V-102, noting that this stream exhibits a phase change. In the current design, this heat is removed using NH_3 refrigerant at a cost of $\$4,140,000/\text{yr}$! Clearly, not all of this heat should be removed using a refrigerant.

By selecting only the above streams as candidates for maximum energy recovery (MER) targeting, the heat-integrated NH_3 converter is left untouched. As noted above, its performance is sensitive to changes in its inlet temperature. Given its feed/product heat exchanger, E-106, it seems preferable to decouple the streams in the heat-integrated NH_3 converter from the remaining streams being considered for heat integration.

MER Targeting. To initiate the heat-integration calculations, heating and cooling curves are generated for the hot and cold streams. As shown in Figure 13.9, because most of the streams do not undergo phase changes, they exhibit near-linear behavior, enabling them to be approximated using constant heat capacities, C_p . Only streams HOT_4, HOT_5,

and HOT_7 undergo condensation (before flash drums V-100, V-101, and V-102, respectively), with highly nonlinear temperature variations. To a lesser extent, cold streams COLD_1 and COLD_2 exhibit nonlinear variations. Note that conservative approximations are made for the streams exhibiting nonlinear variations, with 7 and 17 cold and hot pseudo-streams, respectively, as detailed in Table 13.5, noting that the numbering convention used for the pseudo-streams, indicated on the plots in Figure 13.9, is adopted in the MER design.

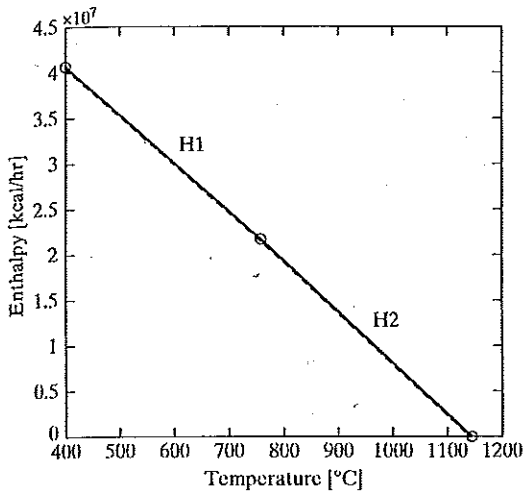
Table 13.6 shows the results of MER targeting for $\Delta T_{\min} = 10^\circ\text{C}$, indicating that a pinch does not exist. As discussed in Section 9.6, this threshold problem requires only cooling utilities. Note that a pinch appears with $\Delta T_{\min} > 300^\circ\text{C}$. The MER energy targets for $\Delta T_{\min} = 10^\circ\text{C}$ are $Q_{H\min} = 0$ kcal/hr and $Q_{C\min} = 101.2 \times 10^6$ kcal/hr. These compare unfavorably with $\sim 26.9 \times 10^6$ kcal/hr of heating utilities and $\sim 128 \times 10^6$ kcal/hr of cooling utilities in the current design. Clearly, the MER analysis shows that the furnace preheater and its fuel are not required and thus it should be possible to eliminate them. Note also that the difference between the total cold and hot utilities in the UNISIM simulation, 101.1×10^6 kcal/hr, is almost identical to the MER threshold target of 101.2×10^6 kcal/hr, an indication of the accuracy of the MER analysis. Note also that because zero heating utility is required, the residual heat flows between the temperature intervals are identical in columns 3 and 4 of Table 13.6.

The data in Table 13.5 are used to generate the grand composite curve (GCC) in Figure 13.10. Close inspection of the GCC suggests that a possible distribution of the total cold utility duty, 101.2×10^6 kcal/hr, is:

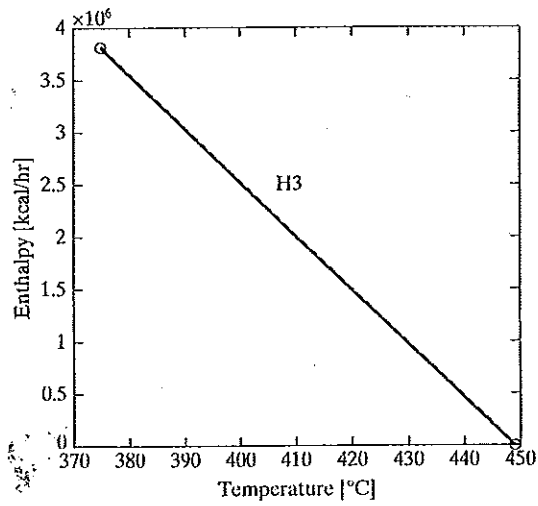
- Generate up to 27.6×10^6 kcal/hr of high-pressure steam (hps) using boiler feed water (bfw) at the appropriate pressure as a coolant.
- Generate up to 8.6×10^6 kcal/hr of intermediate-pressure steam (ips) using bfw at the appropriate pressure as a coolant.
- Use 50.2×10^6 kcal/hr of cooling water (cw).
- Use 10.2×10^6 kcal/hr of ammonia refrigerant (at -30°C).
- Use only 4.6×10^6 kcal/hr of methane refrigerant (at -160°C).

An alternative solution that does not involve cold streams COLD_2 and COLD_3 (i.e., with the CO_2 and NH_3 products delivered at the operating temperatures of V-101 and V-102, respectively) leads to the GCC shown in Figure 13.11, in which the MER cold utility target is 104×10^6 kcal/hr, distributed as follows:

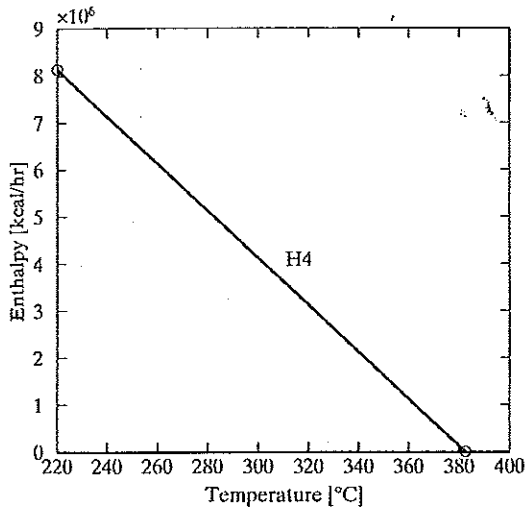
- Generate up to 27.6×10^6 kcal/hr hps using bfw at the appropriate pressure as a coolant.
- Generate up to 8.5×10^6 kcal/hr ips using bfw at the appropriate pressure as a coolant.



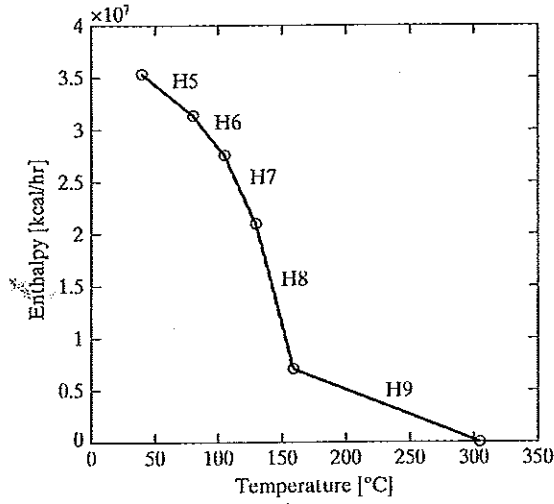
(a) HOT_1



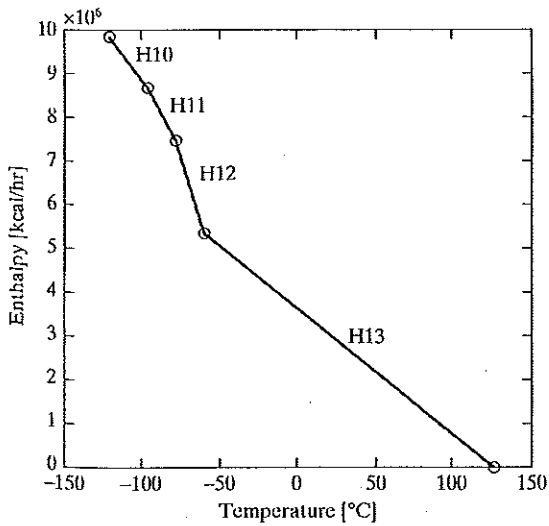
(b) HOT_2



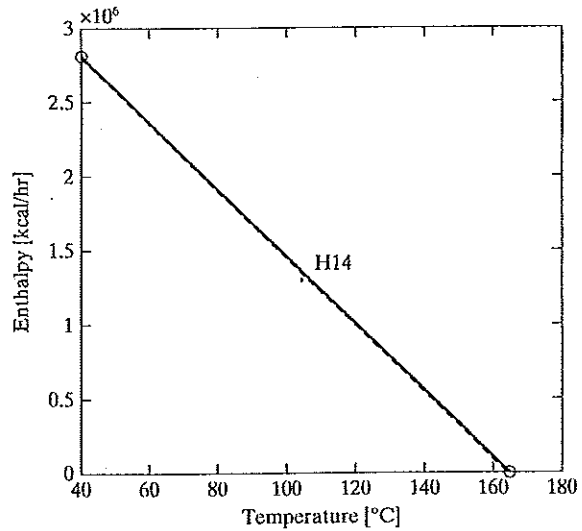
(c) HOT_3



(d) HOT_4

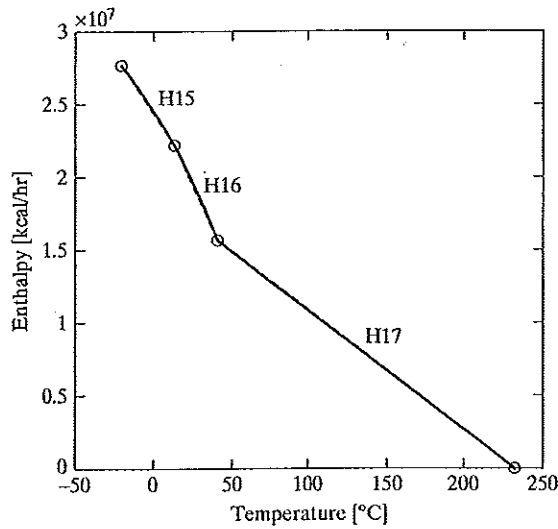


(e) HOT_5

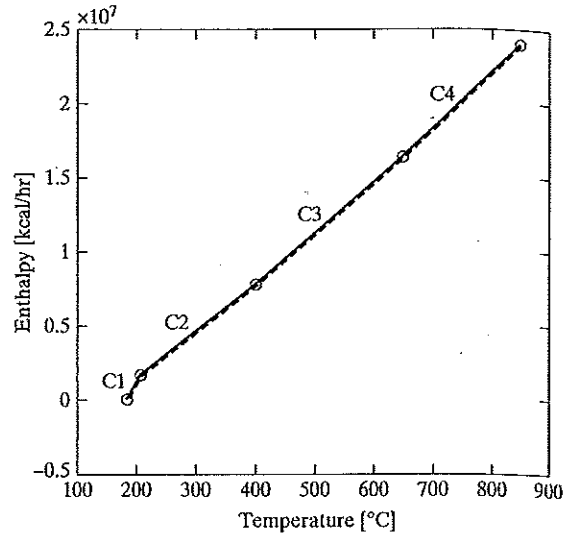


(f) HOT_6

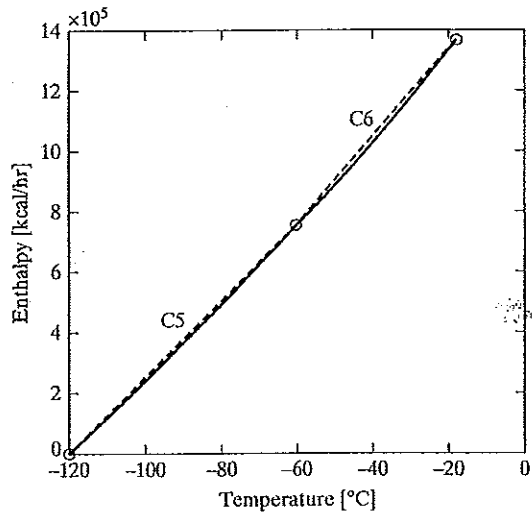
Figure 13.9 Heating and cooling curves for the streams in the HEN (Continued).



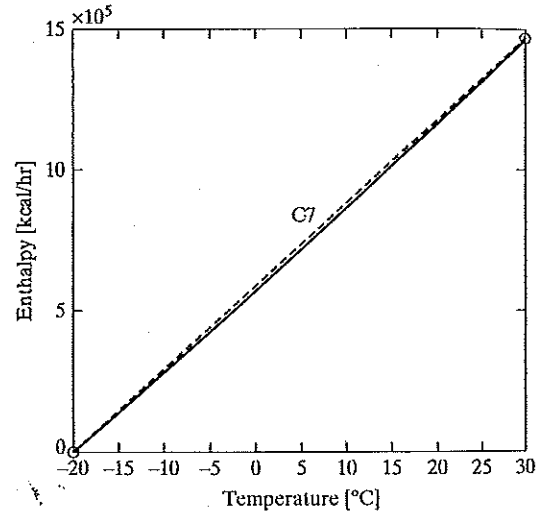
(g) HOT_7



(h) COLD_1



(i) COLD_2



(j) COLD_3

Figure 13.9 (Continued)

Table 13.5 List of Pseudo-Streams for HEN Synthesis (Output of MATLAB Script). THS, THT, TCS, and TCT are source and target temperatures of the hot and cold streams. CFH and CPC are heat-capacity flow rates of the hot and cold streams in $\text{kcal/hr}^\circ\text{C} \times 10^{-6}$. QH and QC are heat duties of the hot and cold streams in $\text{kcal/hr} \times 10^{-6}$

Hot Streams

	THS	THT	CPH	QH
H1:	4.0000e+002	7.6000e+002	5.2972e-002	-1.9070e+001
H2:	7.6000e+002	1.1450e+003	5.6104e-002	-2.1600e+001
H3:	3.7500e+002	4.4900e+002	5.1338e-002	-3.7990e+000
H4:	2.2000e+002	3.8200e+002	5.0210e-002	-8.1340e+000
H5:	4.0000e+001	8.0000e+001	1.0025e-001	-4.0100e+000
H6:	8.0000e+001	1.0500e+002	1.5200e-001	-3.8000e+000
H7:	1.0500e+002	1.3000e+002	2.6000e-001	-6.5000e+000
H8:	1.3000e+002	1.6000e+002	4.6567e-001	-1.3970e+001
H9:	1.6000e+002	3.0280e+002	4.8529e-002	-6.9300e+000
H10:	-1.2000e+002	-9.6000e+001	4.9708e-002	-1.1930e+000

(Continued)

Table 13.5 (Continued)

H11:	-9.6000e+001	-7.8000e+001	6.6667e-002	-1.2000e+000
H12:	-7.8000e+001	-5.9000e+001	1.1526e-001	-2.1900e+000
H13:	-5.9000e+001	1.2570e+002	2.8424e-002	-5.2500e+000
H14:	4.0000e+001	1.6560e+002	2.2237e-002	-2.7930e+000
H15:	-2.0000e+001	1.3900e+001	1.6165e-001	-5.4800e+000
H16:	1.3900e+001	4.1600e+001	2.3466e-001	-6.5000e+000
H17:	4.1600e+001	2.3260e+002	8.1675e-002	-1.5600e+001

Cold Streams

	TCS	TCT	CPC	QC
C1:	1.8500e+002	2.0800e+002	7.4348e-002	1.7100e+000
C2:	2.0800e+002	4.0000e+002	3.1510e-002	6.0500e+000
C3:	4.0000e+002	6.5000e+002	3.4560e-002	8.6400e+000
C4:	6.5000e+002	8.5000e+002	3.8100e-002	7.6200e+000
C5:	-1.2000e+002	-6.0000e+001	1.2583e-002	7.5500e-001
C6:	-6.0000e+001	-1.8000e+001	1.4643e-002	6.1500e-001
C7:	-2.0000e+001	3.0000e+001	2.9200e-002	1.4600e+000

Table 13.6 MER Targeting Results for $\Delta T_{\min} = 10^\circ\text{C}$ (Output of MATLAB Script)

Interval Temp ($^\circ\text{C}$) $1.0e+003 \times$	ΔH	Energy Flows $Q_H = 0$	Energy Flows $Q_H = 0$
1.1350	0	0	0
0.8500	0.0160	0.0160	0.0160
0.7500	0.0018	0.0178	0.0178
0.6500	0.0015	0.0193	0.0193
0.4390	0.0039	0.0232	0.0232
0.4000	0.0027	0.0259	0.0259
0.3900	0.0007	0.0266	0.0266
0.3720	0.0004	0.0270	0.0270
0.3650	0.0005	0.0275	0.0275
0.2928	0.0014	0.0288	0.0288
0.2226	0.0047	0.0335	0.0335
0.2100	0.0019	0.0354	0.0354
0.2080	0.0002	0.0356	0.0356
0.1850	0.0013	0.0369	0.0369
0.1556	0.0038	0.0407	0.0407
0.1500	0.0009	0.0416	0.0416
0.1200	0.0171	0.0587	0.0587
0.1157	0.0016	0.0602	0.0602
0.0950	0.0081	0.0683	0.0683
0.0700	0.0071	0.0754	0.0754
0.0316	0.0089	0.0844	0.0844
0.0300	0.0006	0.0850	0.0850
0.0039	0.0061	0.0911	0.0911
-0.0180	0.0035	0.0946	0.0946
-0.0200	0.0003	0.0949	0.0949
-0.0300	0.0018	0.0967	0.0967
-0.0600	0.0004	0.0971	0.0971
-0.0690	0.0001	0.0972	0.0972
-0.0880	0.0020	0.0992	0.0992
-0.1060	0.0010	0.1002	0.1002
-0.1200	0.0005	0.1007	0.1007
-0.1300	0.0005	0.1012	0.1012

- Use approximately 50.2×10^6 kcal/hr of cw.
- Use approximately 11.5×10^6 kcal/hr of ammonia refrigerant (at -30°C).
- Use approximately 5.8×10^6 kcal/hr of methane refrigerant (at -160°C).

Since this second alternative is much easier to implement and involves only 3% more cold utilities than the best possible option shown in Figure 13.10, it is selected as the basis for the HEN design.

Design of MER Network. Next, the HEN in Figure 13.12 is designed to meet the MER targets defined above for $\Delta T_{\min} = 10^\circ\text{C}$. A total of 12 heat exchangers are required, after grouping all contiguous pseudo-streams. Note that:

- A single process-process heat exchanger is required, in which heat is exchanged from the hot exothermic reactor effluent to the process feed (i.e., heat exchange from pseudo-streams H1-H2 to C1-C4), with a total duty of 24.02×10^6 kcal/hr. This eliminates the furnace heater, although a small heater for process startup may be necessary.
- The remaining system involves the usage of utility coolers. For process temperatures above 370°C , hps has been raised by using bfw as a coolant. Above 220°C , bfw is used to raise ips.
- As much as possible, cw has been used. For process temperatures above -20°C , ammonia refrigerant (ar) utility has been used, with methane refrigerant (mr) utility used for colder process temperatures.
- The above design uses the following distribution of external utilities:
 - $16.65 + 3.8 = 20.45 \times 10^6$ kcal/hr hps is raised using bfw.

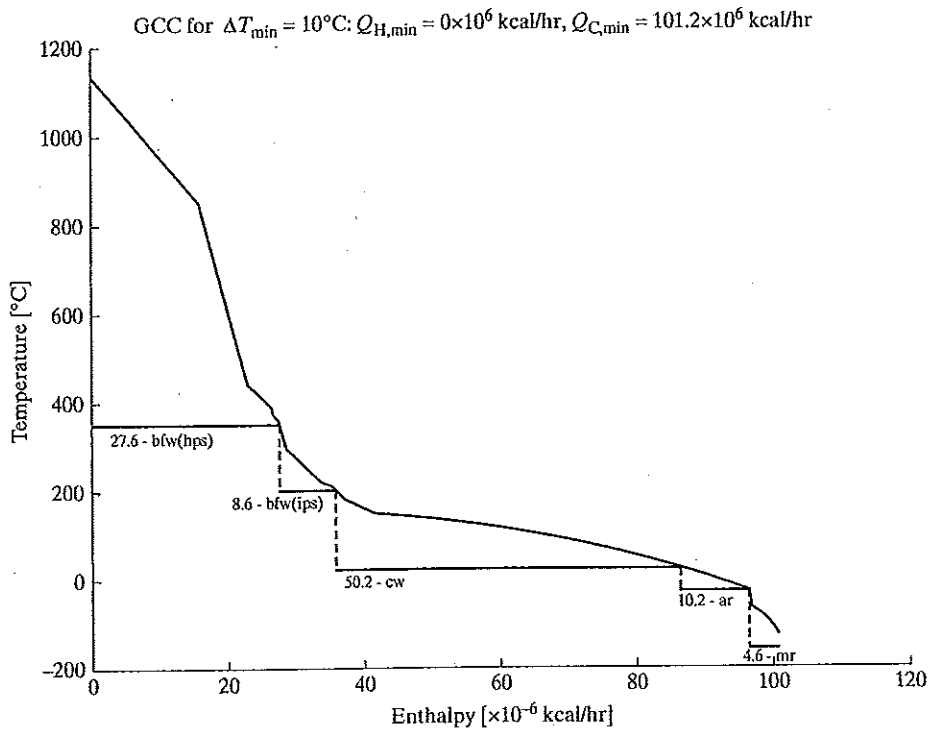


Figure 13.10 Grand composite curve for $\Delta T_{\min} = 10^\circ\text{C}$, showing a possible distribution of utilities; $Q_{H,\min} = 0$, $Q_{C,\min} = 101.2 \times 10^6 \text{ kcal/hr}$.

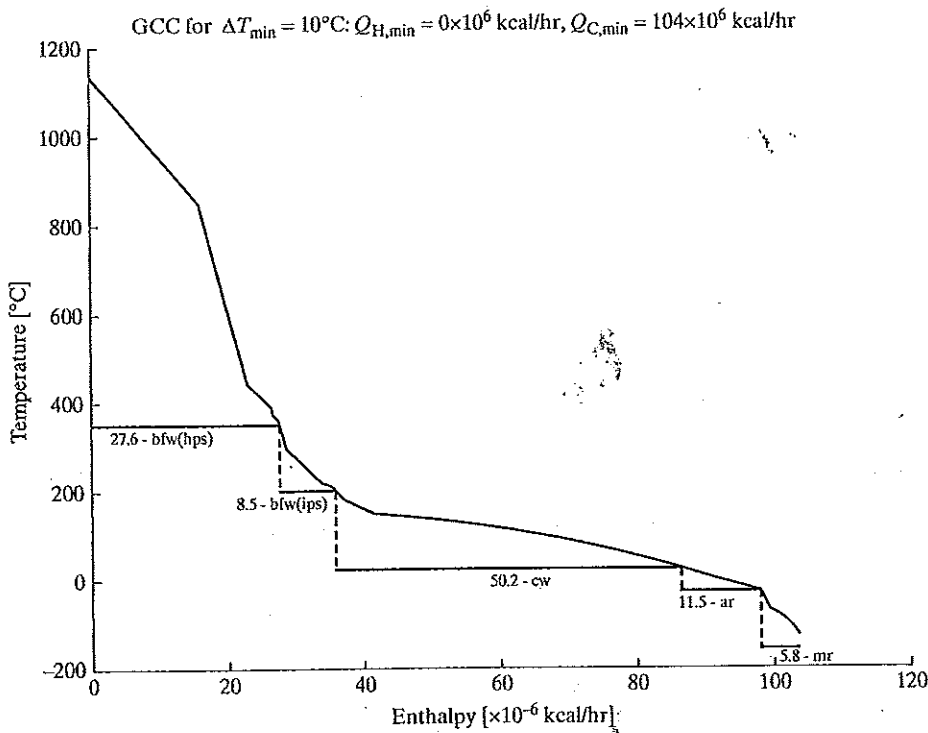


Figure 13.11 Grand composite curve for $\Delta T_{\min} = 10^\circ\text{C}$, with C1 as the only cold stream, showing a possible distribution of utilities; $Q_{H,\min} = 0$, $Q_{C,\min} = 104 \times 10^6 \text{ kcal/hr}$.

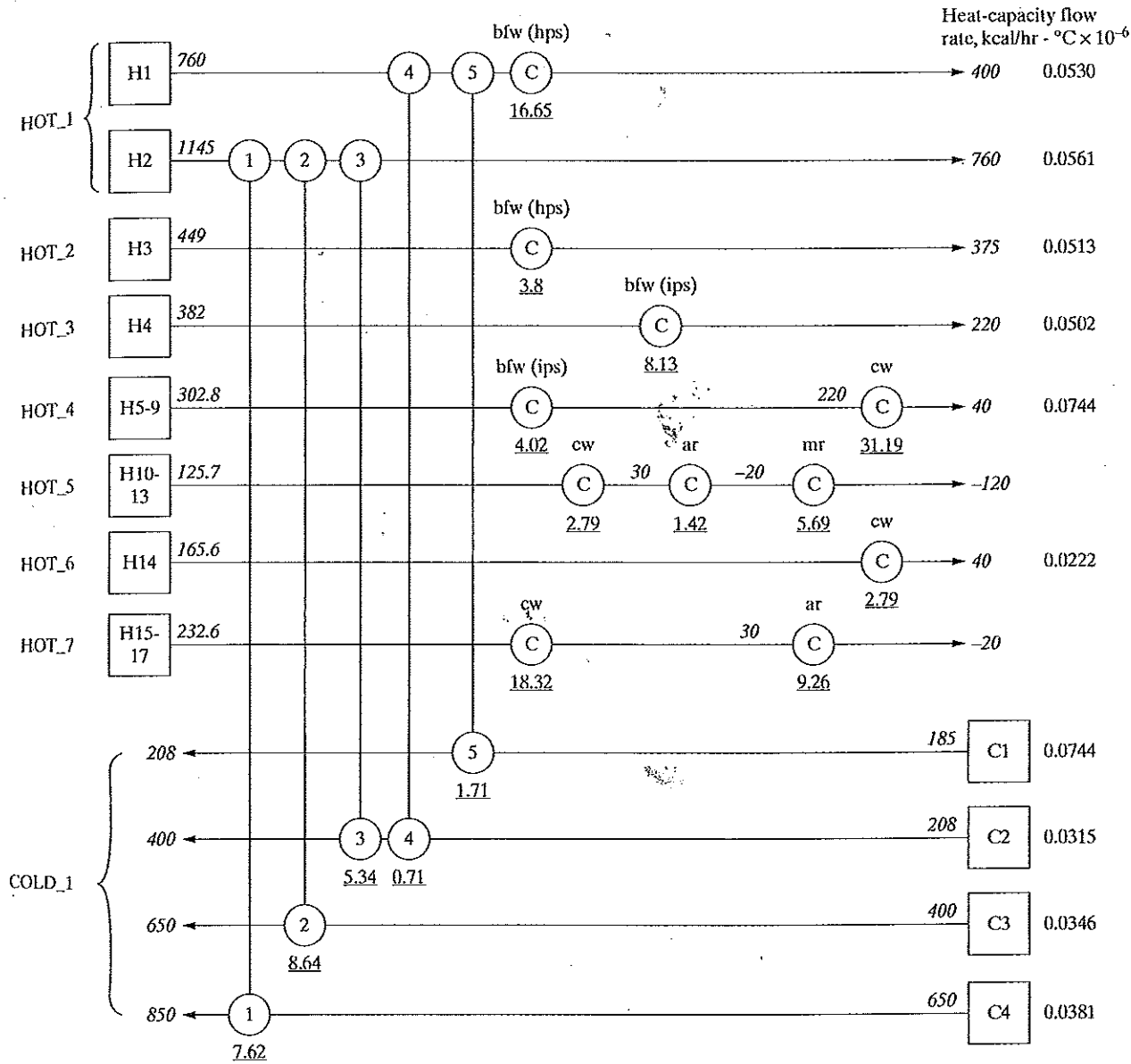


Figure 13.12 MER design for $\Delta T_{\min} = 10^\circ\text{C}$. The average heat-capacity flow rates for H10–H13 (HOT_5) and H15–H17 (HOT_7) are not shown. Temperatures in $^\circ\text{C}$ (italics). Heat duties in kcal/hr (Roman underlined).

- $8.13 + 4.02 = 12.15 \times 10^6$ kcal/hr ips is raised using bfw.
- A total of 55.02×10^6 kcal/hr of cw.
- 10.68×10^6 kcal/hr of ammonia refrigerant is used (at -30°C).
- 5.69×10^6 kcal/hr of methane refrigerant is used (at -160°C).

Figures 13.13 and 13.14 show the UNISIM PFD for the heat-integrated process, which implements the HEN in Figure 13.12. As shown in Table 13.4, this heat integration further increases the ROI and VP to 14.7% and $-\$4,700,000$.

Installing a HME into the Synthesis Loop

As shown in Figure 13.15, the heat and mass exchanger (HME) is installed such that the HOT RICH stream is the effluent of a new heat exchanger, E-112, installed to generate ips (S-34B), and the COLD LEAN stream is the combination of the vapor recycled from the flash vessel, V-102, and the makeup synthesis gas stream (Total_SG). The COOLED ENRICHED stream is fed to cooler E-111 (cooled with cw), and the HEATED DEPLETED stream is fed directly to the ammonia reactors. The degrees of freedom for the HME are defined as: (a) 50% of the ammonia in the HOT RICH stream is transferred to the

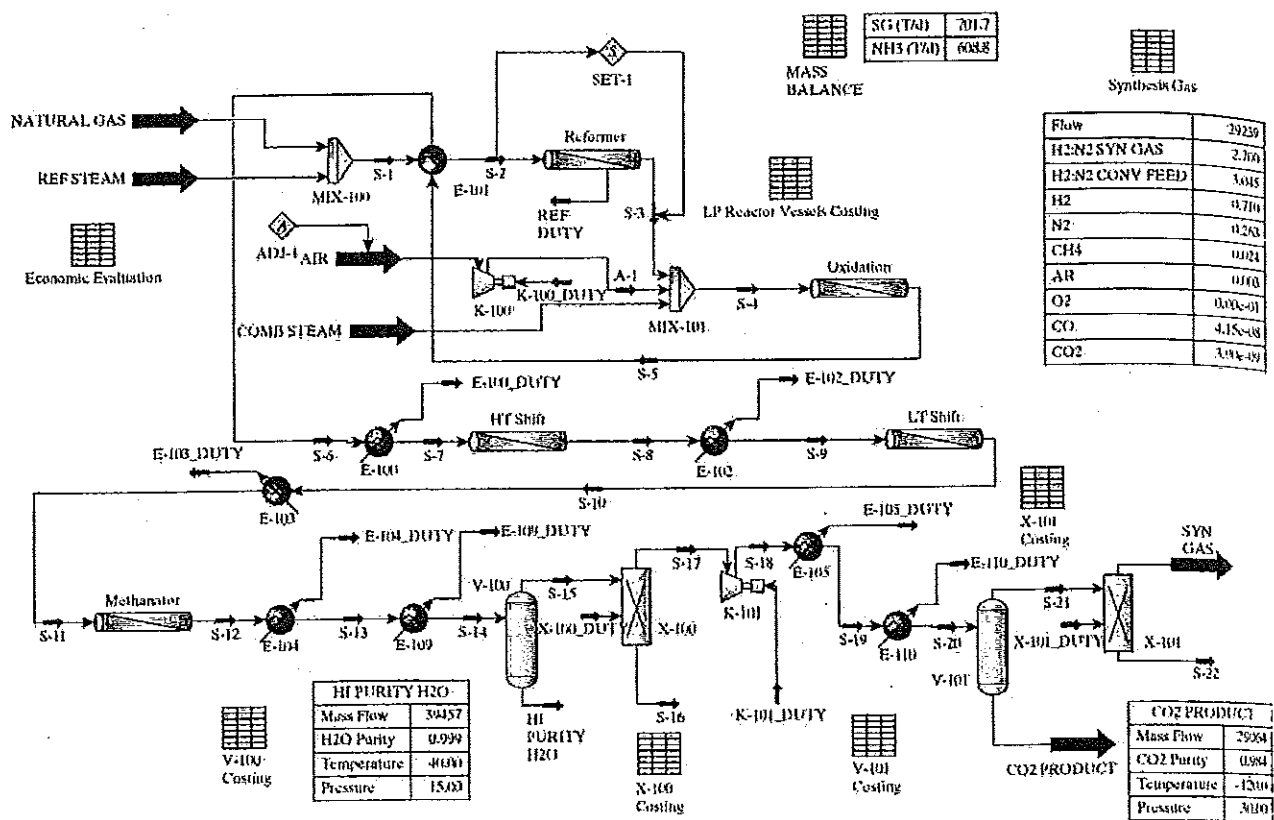


Figure 13.13 UNISIM PFD for the synthesis gas section after heat integration. Units as in Figure 13.4.

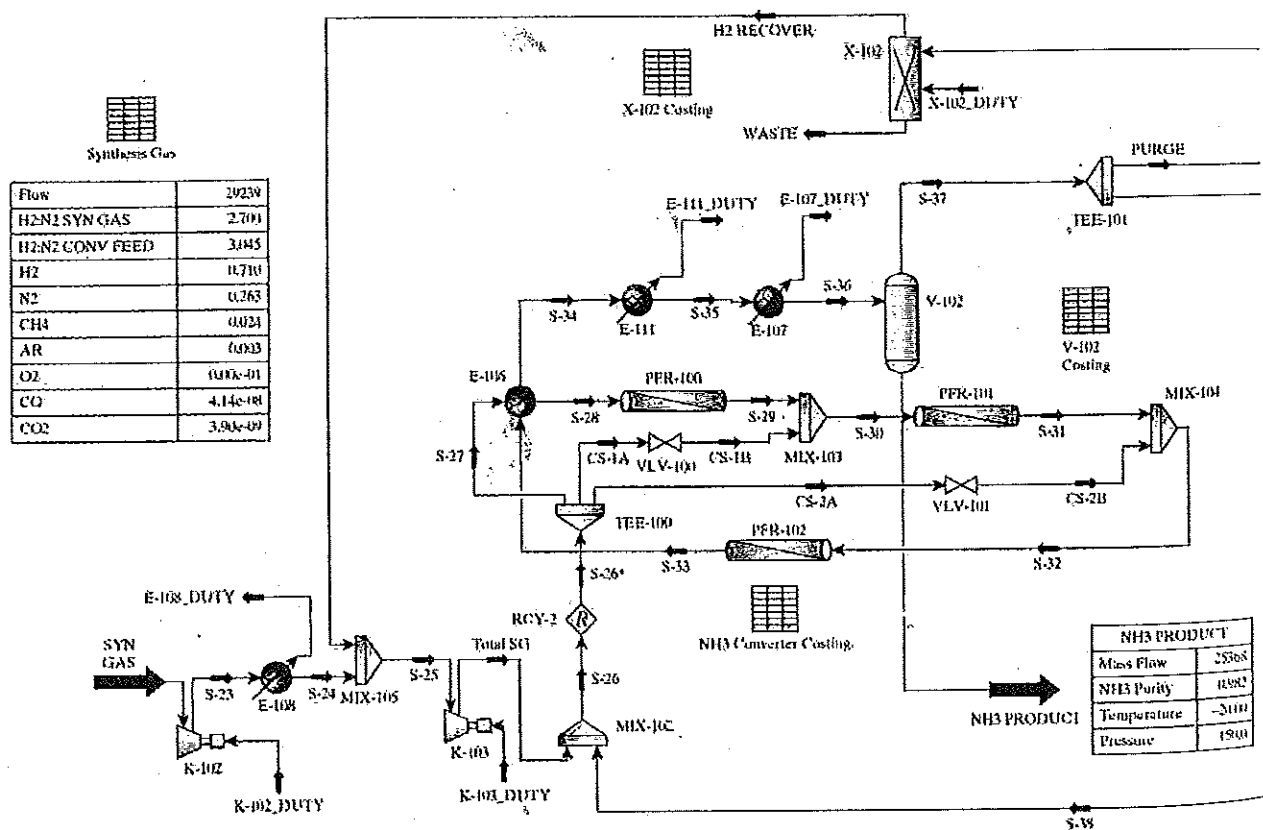


Figure 13.14 UNISIM PFD for the synthesis loop section after heat integration. Units as in Figure 13.4.

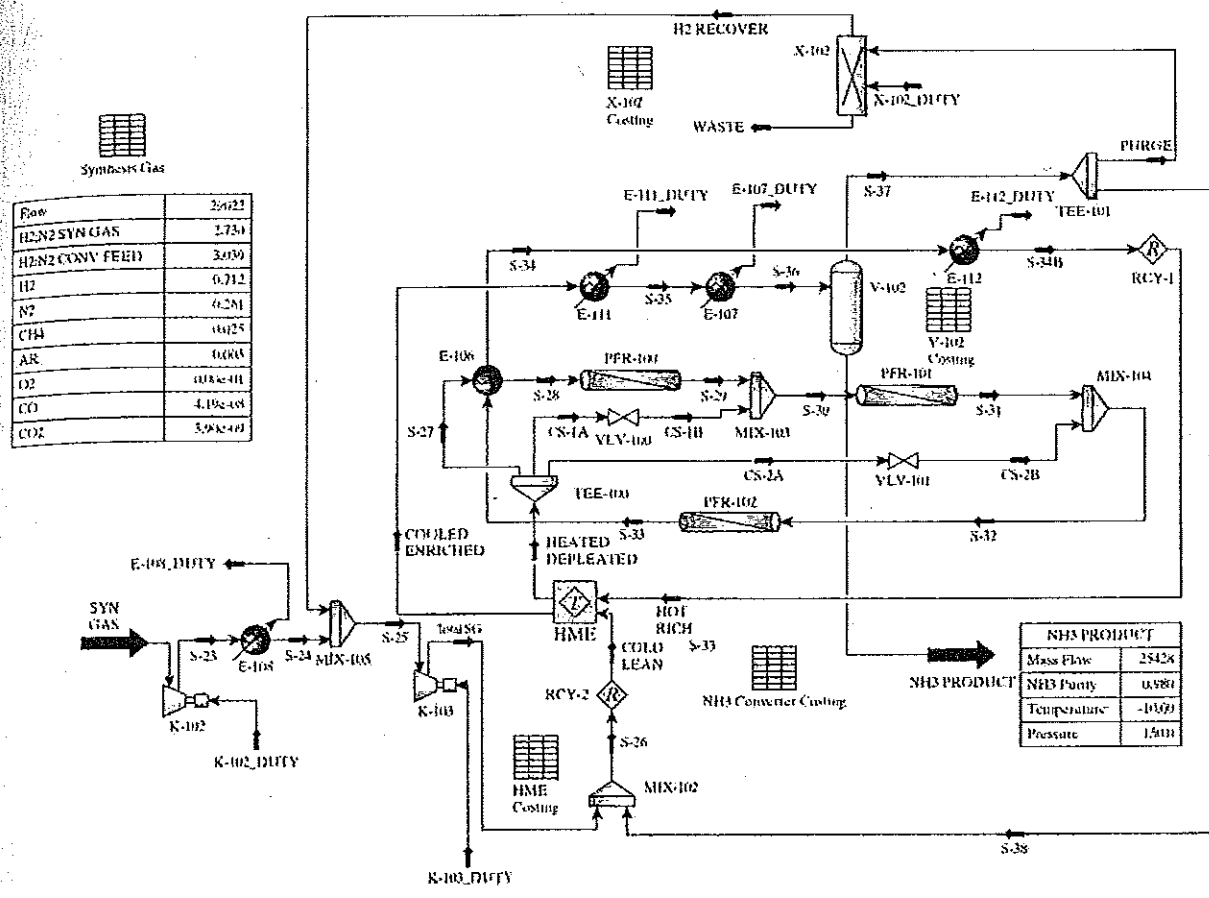


Figure 13.15 UNISIM PFD for the synthesis loop section after installing an HME. Units as in Figure 13.4.

COOLED ENRICHED stream; (b) the temperature of the HEATED DEPLETED stream is 50°C less than that of the HOT RICH stream. Note that the internals of the HME block in the PFD are as given in the project tender in Figure 6 (see the file Ammonia Project.pdf in the PDF Files folder, which can be downloaded from the Wiley Web site associated with this textbook).

The installation of the HME alters the material balance in the synthesis loop, requiring a small adjustment in the H₂:N₂ ratio in the makeup stream to maintain the H₂:N₂ ratio in the reactor feed close to the optimal value of 3. Furthermore, because the reactor feed temperature is increased, the optimal cold-shot fractions move from 0.6, 0.2, and 0.2 to 0.34, 0.33, and 0.33. The reactor feed temperature is also reduced to 240°C. These modifications increase the NH₃ composition in the stream fed to the flash vessel, V-102, to 18.7 mol% (from 16.5 mol%). Also, the feed temperature to the flash vessel is increased to -10°C (thus saving significant refrigeration costs). This, of course, increases the NH₃ composition in the recycle stream, but this is corrected for by the action of the HME. Finally, note that about \$1,000,000/yr of revenue is obtained from ips generation in E-112.

As shown in Table 13.4, the introduction of the HME, while not optimally designed, further increases the ROI and

VP to above 16% and -\$3,400,000, with a payback period that just exceeds 6 years. Clearly, the process at the EPL production rate is only marginally acceptable. To secure an adequate profit, a larger production rate is required, as considered next.

Economy-of-Scale

In this section, the venture profit is estimated at various levels of operation using *economy-of-scale* methods. As defined in Eq. (23.9), the venture profit, VP, is:

$$VP = (1 - t)GP - i_{\min}C_{TCI} \quad (13.10)$$

where *t* is the income tax rate, GP is the annual pretax earnings (*S* - *C* = gross profit), *S* is the annual sales, *C* is the annual cost of production, *C_{TCI}* is total capital investment, and *i_{min}* is the minimum acceptable return on investment.

For the ammonia process, the annual cost of production is:

$$C = NG + OP + WD + LAB, \quad (13.11)$$

where *NG* is the annual cost of natural gas, *OP* is the annual cost of operations, *WD* is the annual cost of waste disposal, and *LAB* is the annual cost of labor. Returning to Table 13.4, the most profitable configuration (after implementing the HME) for a feed of 12,000 kg/hr methane has *C_{TCI}* =



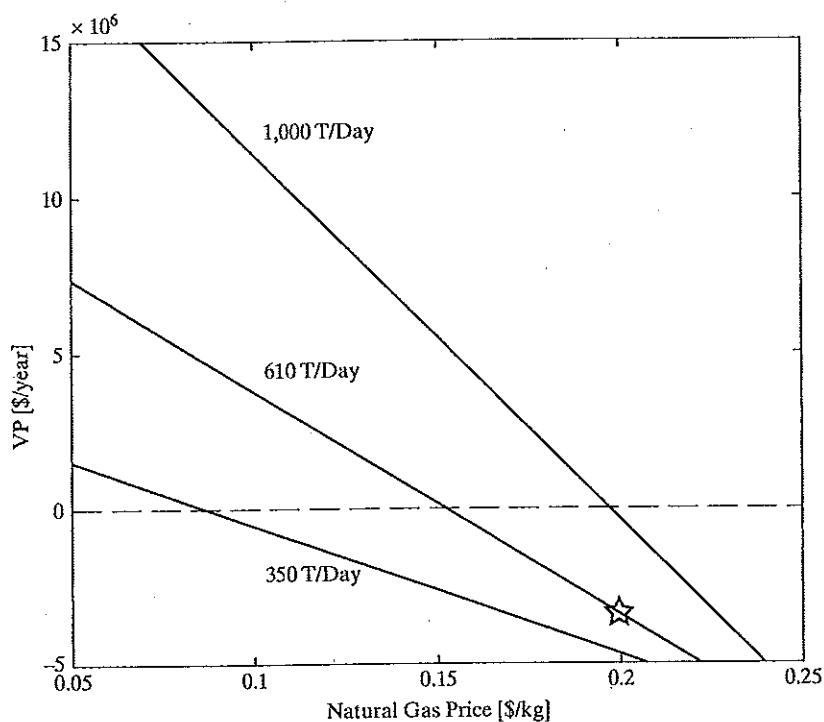


Figure 13.16 The effect of production scale on VP.

\$88,500,000, $OP = \$3,300,000$, $WD = \$1,430,000$, and $LAB = \$2,770,000$. NG and REV are computed using the unit costs of methane and ammonia and assuming 330 days of production per year. A power law is commonly used to scale the C_{TCI} with the production level; that is, for the ammonia process, $C_{TCI} = 0.993P^{0.7}$ million dollars. Taking $i_{min} = 0.2$ and $t = 0.25$, the VP is estimated as a function of the production level, with the results shown in Figure 13.16 as a function of the price of methane. Several obvious conclusions are:

- Ammonia cannot be produced at a level that satisfies the Israeli national demand unless the cost of natural gas is about half its current level. Given that methane prices are expected to rise, this eliminates the feasibility of production to satisfy the Israeli market demand only. The possible impact of governmental incentives on the feasibility of production at this level is considered in Exercise 13.5.
- A plant that produces approximately twice the Israeli national demand would be feasible if the cost of methane is subsidized by 25%. However, the surplus ammonia produced would have to be exported, probably by sea, requiring bulk storage facilities in population centers—an infeasible option.
- A plant to produce three times the Israeli national demand, that is, 1,000 T/day, is feasible economically. If this solution were adopted in Haifa, the storage facilities would be doubled, with two-thirds of the production exported using the city's port facilities, which is also an infeasible option. Alternatively, a joint venture with Jordan, whose ammonia demand is approximately twice that of Israel's, could be encouraged.

The combined Israeli–Jordanian demand matches the minimum level of production that is economically viable. This suggests a production facility in the Negev Desert, close to the Israel–Jordan border.

Development Stage

As indicated in Figure PI.1, the main task in the *development* stage of the SGPDP, as applied to the design of *basic chemical* products, is to carry out a detailed plant design and draw conclusions about the feasibility of the project. This stage remains to be implemented for the ammonia product; see Exercise 13.6.

Postscript

This case study documents the final-year design project undertaken by undergraduate students of the Department of Chemical Engineering at the Technion, Class of 2007. The project tender, provided in the file Ammonia Project.pdf in the PDF Files folder, which can be downloaded from the Wiley Web site associated with this textbook, was addressed to the students. The project attracted considerable media attention in the wake of the 2006 Lebanese War and the missile bombardment of Haifa. The following is an article published in the *Jerusalem Post*:

<http://www.jpost.com/servlet/Satellite?cid=1185379003413&pagename=JPost%2FJPostArticle%2FShowFull>

A joint Israeli–Jordanian factory for the production of ammonia—for making fertilizer and other products—to solve the problems of Haifa Bay's ammonia storage



facility has been proposed by researchers at the Technion-Israel Institute of Technology in Haifa.

Prof. Danny Lewin and students from the chemical engineering faculty were invited by the Haifa City Association to find ways to transfer the ammonia facility from Haifa to the South because of environmental and security risks in its present location. The students' three-semester project was to suggest a way to turn the money-losing facility into a profitable one while ensuring safety and protecting the environment. An ammonia leak could endanger the lungs of neighbors and even pose the danger of death.

Ammonia is not manufactured in Haifa, but imported and stored in the Haifa tanks. During the Second Lebanon War, residents were very fearful that a Hezbollah rocket would hit the facility and set off an environmental disaster.

Lewin said he wanted students to finish their studies less as technocrats and more as involved with people's problems and taking a global approach. They worked for three semesters on a problem that experienced engineers had failed to solve and came up with a way to manufacture ammonia naturally, safely and efficiently.

They reached the conclusion that it was not economically viable to manufacture ammonia for Israel alone, as any facility would produce three times what Israel needs. Instead, they said a partnership should be formed with Jordan to manufacture the chemical at Rotem in the South, close to the Jordanian border. The area already has a facility to manufacture fertilizers from Haifa Chemicals' ammonia.

13.3 ENVIRONMENTALLY FRIENDLY REFRIGERANT CASE STUDY

In Section 3.2, the issues involved in designing environmentally friendly refrigerants are discussed. These employ molecular-structure design to locate molecules involving C, N, O, S, and H atoms, and the halogens F, Br, and I (and not Cl), that have: (1) a large latent heat of vaporization, to reduce their throughput when removing a specified heat duty; (2) a low viscosity, to reduce the recirculation power; and (3) a low freezing point, to reduce the possibility of freezing. Note that Cl was banned in the Montreal protocol of 1987 because the composition of Cl-containing refrigerants had increased to parts-per-billion in the stratosphere, with the chlorine atoms reacting with ozone, decreasing the earth's ozone layer. Hence, in 1987, the product design problem was to design environmentally friendly molecules, that is, refrigerants that exclude Cl.

For this case study, it is presumed that a design team was assembled in the late 1980s to create a new environmentally friendly refrigerant product. In hindsight, of course, many refrigerants were designed. The purpose of this case study is to trace the steps in product design, following Figure PI.1, as they may have been carried out by design teams at that time. Note that these scenarios are postulated by the authors, who were not involved in the design teams.

Project Charter

As discussed in Section 2.2, and shown in Figure PI.1, most design teams begin to develop a new product by creating a project charter. For an environmentally friendly refrigerant product, a typical project charter—containing specific goals, a project scope, deliverables, and a time line—is given in Table 13.7. Clearly, the project charter summarizes the objectives above and sets the time line with deliverables.

Molecular-Structure Design

The next step in Figure PI.1 requires that the design team answer the question: "Is materials technology invention required?" In this case, of course, it is necessary to "find chemicals or chemical mixtures that have the desired properties." This involves molecular-structure design, as discussed under "Refrigerant Design" in Section 3.5.

In the strategy described, the design team begins by selecting the extreme temperatures in refrigeration cycles for which the refrigerant is needed; that is, the temperatures at which heat is to be absorbed in the evaporator and rejected in the condenser of a refrigerator. For a typical refrigeration cycle, see Figure 9S.20. Then, k atoms and molecular groups are selected to be included in the candidate molecules, each of which may appear n times.

First, Example 3.3 considers 13 atoms and molecular groups—CH₃, CH₂, CH, C, OH, O, NH₂, NH, N, SH, S, F, and Cl—with Cl included in the search to show that molecules containing chlorine are the most desirable when the ozone layer is disregarded. Then, in Example 3.4, when an ozone depletion potential (ODP) is included, refrigerants without Cl are obtained.

For these examples, the refrigerant is designed to absorb heat at temperatures as low as 30°F (−1.1°C) and reject heat at temperatures as high as 110°F (43.3°C). In an optimization formulation, the refrigerants are selected to have:

1. A vapor pressure, $P^s\{-1.1^\circ\text{C}\} > 1.4$ bar, to ensure that leaks are from the refrigerant system (rather than from vacuum operation, into which air and water vapor can leak),
2. $P^s\{43.3^\circ\text{C}\} < 14$ bar, to keep the compression ratio from exceeding 10,
3. An enthalpy of vaporization, $\Delta H^u\{-1.1^\circ\text{C}\} > 18.4$ kJ/mol, to reduce the amount of refrigerant needed (where 18.4 kJ/mol is the latent heat of vaporization of Freon 12, the chlorine-containing refrigerant banned in 1987), and
4. A liquid heat capacity, $c_{pl}\{21.1^\circ\text{C}\} < 32.2$ cal/(mol K), to reduce the amount of refrigerant that flashes across the valve (where 32.2 cal/(mol K) is the heat capacity of liquid Freon 12). Note that 21.1°C is the average of the extreme temperatures.