CHEMICAL REACTOR DESIGN
FOR PROCESS PLANTS

Volume Two:
Case Studies and Design Data

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CASE STUDY 111

Steam Reforming

THIS IMPORTANT PROCESS, the function of which is to generate hydrogen for such uses as ammonia synthesis (Fig. CS-5.1), affords an opportunity to demonstrate equilibrium and equilibrium-approach techniques in design (see p. 549[I]). Operating conditions are purposely selected to correspond to a reported industrial installation so that the calculated results may be compared with the known operating data (1).

Because of the high endothermic heat of reaction and the rapidity of the reactions, high heat fluxes, attainable conveniently with a direct-fired furnace, are required.

Problem Statement

Determine the number of 5-in. ID × 40 ft tubes required for a methane steam reforming unit to produce 50 million SCFD of H_2 with 95% purity when dry (60°F and 1 atm).

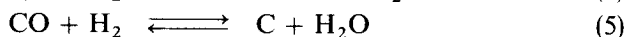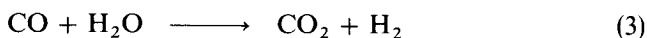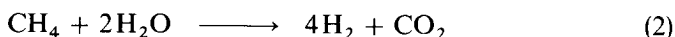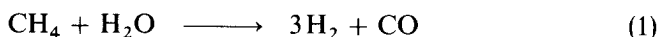| Feed Composition	Mole %
H_2O	84.07
H_2	1.56
CH_4	12.83
C_2H_6	0.61
C_3H_8	0.27
C_4H_{10}	0.07
N_2	0.58

Steam-to-carbon ratio: 5.5528

Catalyst

The catalyst is in the form of $\frac{5}{8}$ in. $\times$ $\frac{5}{8}$ in. $\times$ $\frac{3}{16}$ in. Raschig rings with $\rho_b =$ 53 $\pm$ 4 lb/ft^3, crush strength 90 lb, fusion temperature of 2500°F, and negligible shrinkage up to 2300°F. It contains 15% Ni and a maximum of 0.03% S and 0.2% SiO_2. Poisons are as listed in Table 2.13. Catalyst life varies from 1 to 5 yr depending on treatment. Excessive temperatures above 1000°C for periods longer than 1 hr cause irreversible growth of nickel crystallites and corresponding loss in active surface area (5). At low steam rates carbon deposits rapidly and causes the catalyst to disintegrate.

Chemistry and Thermodynamics

It is generally conceded that the following reactions can occur (1,2,4–6).

$$CH_4 + H_2O \longrightarrow 3H_2 + CO \tag{1}$$

$$CH_4 + 2H_2O \longrightarrow 4H_2 + CO_2 \tag{2}$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \tag{3}$$

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \tag{4}$$

$$CO + H_2 \rightleftharpoons C + H_2O \tag{5}$$

$$CH_4 \rightleftharpoons C + 2H_2 \tag{6}$$

$$2CO \rightleftharpoons C + CO_2 \tag{7}$$
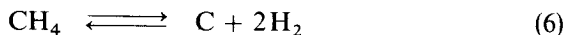
This group of reactions does not represent a mechanism, but is consistent with the known chemistry. Any pair among the first four reactions is adequate for representing equilibrium compositions, and it has been customary to select reactions 1 and 3. This conclusion applies when the ratio of steam to methane is high enough to prevent the presence of carbon at equilibrium (8). For carbon not to be present it is necessary that the steam to methane ratio be such that the following apply as calculated from simultaneous equilibrium of reactions 1 and 3.

$$\frac{a_{H_2O}}{a_{H_2}a_{CO}} \geq K_5, \quad \frac{a_{H_2}^2}{a_{CH_4}} \geq K_6, \quad \text{and} \quad \frac{a_{CO_2}}{a_{CO}^2} \geq K_7 \quad \text{(CS-11.1)}$$

Under these conditions any carbon formed will consume product and form reactants in the respective reactions until the value of K is reached. It has been shown that as the ratio applying to reaction 7 is satisfied, the other two are also satisfied (5,8). Thus the minimum steam ratio (moles steam-to-methane in feed) corresponds to $a_{CO_2}/a_{CO}^2 = K_7$. This theoretical value is invariably well below the ratios normally employed in modern reactors.

The combined or overall reaction comprising reactions 1 and 3 ($CH_4 + 2H_3O \rightarrow CO_2 + 4H_2$) has an endothermic heat of reaction of 79,900 BTU/lb mole at 1000°F and increases approximately 650 BTU for every 100°F increase in reaction temperature. The very negative adiabatic factor (-682) and $q_p = -24.5$ (Table 6.4) confirm the need for a direct-fired furnace, as shown in Fig. 11.17 (p. 551[1]).

Since the gas as received for reforming is under pressure, energy is saved by operating the reformer at elevated pressures even though an increase in moles is involved. The negative effects of this higher pressure on the forward progress of reaction 1 can be overcome by increased temperature and high steam-to-methane ratios. The operating range to accomplish this favorable conversion requires high radiant flue-gas temperatures, and the combustion gases leaving the furnace contain a great deal of useable energy (9). A major portion of the furnace design is thus concerned with heat recovery usually by generating high-pressure steam.

Although kinetics and mechanism have been studied and it is known that the reaction path involves alternate oxidation and reduction of the active nickel centers, it has been established that in the usual operating range of heat flux [17,000 to 21,000 BTU/(hr)(sq ft)] the rapid reactions are controlled by the rate of heat transfer (1,3,5).

The chemical steps are very rapid causing low effectiveness factors, such that the reaction rates are proportional to the outside surface of the pellet (10). The Raschig-ring form of catalyst increases the utilizeable area and acts to reduce pressure drop.

In the aforementioned heat-flux range, the composition at the outlet of the converter corresponds to the equilibrium composition for reaction 3 at the outlet temperature and pressure and to the equilibrium composition of reaction 1 calculated at the outlet pressure and a temperature variously reported as 15–25°C below the actual (3,5,7). This equilibrium approach criterion is dependent on contact time and steam ratio. A conservative design value (3) is a ΔT of 50°F (~ 28°C).

Design Calculations

It is possible in this case to ignore kinetics provided one confines economic studies within the narrow range of heat flux stated. Higher heat fluxes are now possible because of improved materials which permit high tube-wall temperatures. If these higher fluxes are used, the reaction could become more strongly rate limiting such that a simple equilibrium approach criterion would no longer be accurate or valid. In such a case a kinetic model would be required. For the heat flux range quoted above, however, a kinetic model would be a waste of time. The following algorithm based on equilibrium and heat transfer is adequate (3).

Algorithm

1. Set inlet composition, flow rates (including steam-to-methane ratio), and temperature. Set catalyst size, tube length, and tube diameter. Also select an average design heat flux. Set also the outlet temperature, pressure and approach to equilibrium.
2. Calculate the equilibrium constant K_1 for the stream reforming reaction at the outlet temperature minus ΔT approach.

$$K_1 = \exp(30.53 - 4.8486 \times 10^4/T + 2.421748 \times 10^6/T^2 + 2.49 \times 10^9 T^3) \tag{CS-11.2}$$

3. Calculate the equilibrium constant K_3 at the reactor outlet temperature.

$$K_3 = \exp(-2.930632 + 3606.211/T + 5.0424 \times 10^6/T^2 - 1.815388 \times 10^9/T^3) \tag{CS-11.3}$$

4. Solve for corresponding compositions.

$$K_1 = \frac{(n_{H_2})_a{}^3 (n_{CO})_a}{(n_{CH_4})_a (n_{H_2O})_a} \frac{P^2}{n_{T_a}{}^2} \tag{CS-11.4}$$

where $(n_{H_2})_a$ etc. are moles of indicated component per moles of equivalent methane fed and n_{T_a} is the total moles on same basis. [Since hydrocarbons other than methane are rapidly converted to methane near the inlet by hydrocracking, the initial or equivalent moles of methane should be (1), $\sum n\mathscr{F}_n$ for all values of n, where n is the number of carbon atoms in hydrocarbon, and $\mathscr{F}_n$ is the flow of hydrocarbon in moles t^{-1}.]

$$K_3 = \frac{(n_{H_2})_a (n_{CO_2})_a}{(n_{CO})_a (n_{H_2O})_a} \tag{CS-11.5}$$

Solve simultaneous Eqs. 11.4 and 11.5 by trial and error with $(n_{CH_4})_a = n$, $(n_{CO_2})_a = m$, $(n_{H_2})_a = \frac{1}{2}H - 3n - \overline{O} + 1 + 2m$, $(n_{H_2O})_a = \overline{O} - (1 - n) - m$, $(n_{CO})_a = 1 - n - m$, n_{T_a} = total moles including inerts, where $\overline{O}$ and H are equivalent atoms of oxygen and hydrogen in total feed per mole of equivalent methane fed.

5. Based on the selected tube size and length, and heat flux calculate number of tubes required.

$$\text{No. of tubes} = \frac{(\text{Heat Load})}{(\text{Heat Flux})\pi D Z_H}$$

where Z_H is the heated length (in this case 37 ft).

$$\text{Heat Load} = \sum_{j=1}^{n} \mathscr{F}_{j_e}(H_{f_j}{}^\circ + H_j - H_j{}^\circ)_e - \sum \mathscr{F}_{j_0}(H_{f_j}{}^\circ - H_j - H_j{}^\circ)_0$$

where $H_{f_j}{}^\circ$ is the heat of formation at 25°C for component j, H_j and $H_j{}^\circ$ are the enthalpies of component j at temperatures T and 25°C, respectively. The outlet molar flow rates $(\mathscr{F}_{j_e})$ are determined from material balance based on equilibrium calculations.

6. Calculate G:

$$G = \frac{\text{mass flow/hr}}{(\pi D^2/4)(\text{number of tubes})}$$

7. Calculate pressure drop.

Equations for pressure drop on p. 491[1] may be used with a multiplying factor of 0.6 to account for the lower ΔP of Raschig-ring shapes (3). For this system the following special manufacturer's equation was used based on an average viscosity (11).

$$\Delta P = 5.922 \times 10^{-9} G^{1.9}\left(\frac{1-\varepsilon}{\varepsilon^3}\right)\frac{1}{\rho_f D_p{}^{1.1}} Z, \quad \text{psi}$$

where D_p is the effective pellet diameter in inches, G is the mass velocity lb/hr ft^2, Z is the tube length in feet, and ρ_f is the fluid density in lb/ft^3.

Results

A major catalyst supplier provides a computer program based essentially on the previously described algorithm (11). It was used at typical operating conditions so it could be compared to published results as shown in Table CS-11.1. An equilibrium approach ΔT of 50°F was used and an average heat

Table CS-11.1   Comparison of Plant Operating and Calculated Data

	Plant Data (7)	Calculated
Tube length [heated length], ft	40[37]	[a]40[37]
Inside diameter, in	5	[a]5
Inlet pressure, atm	14.3	14.33
Outlet pressure, atm	12.2	[a]12.2
Gas inlet temp. °F	687	[a]687
Gas outlet temp. °F	1460	[a]1460
Feed carbon converted, %	91.7	90.7
No. of tubes	260	226
Approximate average heat flux, BTU/(hr)(sq ft)	17,000	17,000
Mass flow rate, lb/(h)(sq ft)	5476	6188

[a] Designates input data.

flux of 17,000 BTU/hr ft^2 was studied. The results are certainly within the errors associated with gathering plant data and in the model itself. The hydrocracking reactions for example, are exothermic but this heat is not considered in the model.

In applying the program, hydrocarbons other than methane are assumed to hydrocrack to methane at the initial portion of the tube. It has been observed that no hydrocarbon heavier than methane can be detected after contact with catalyst for a significant time (1). The fired length for heat transfer of a 40-ft tube was taken as 37 ft.

It appears that the method is quite adequate for design purposes. The 50°F approach is obviously conservative since a lower equilibrium approach would be required to reproduce the slightly higher observed conversion. The technique could be used to study the effect of pressure, inlet temperature, and steam-to-carbon ratio in order to determine the most economical allocation and recovery of energy, which is surely the major component in operating costs.

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