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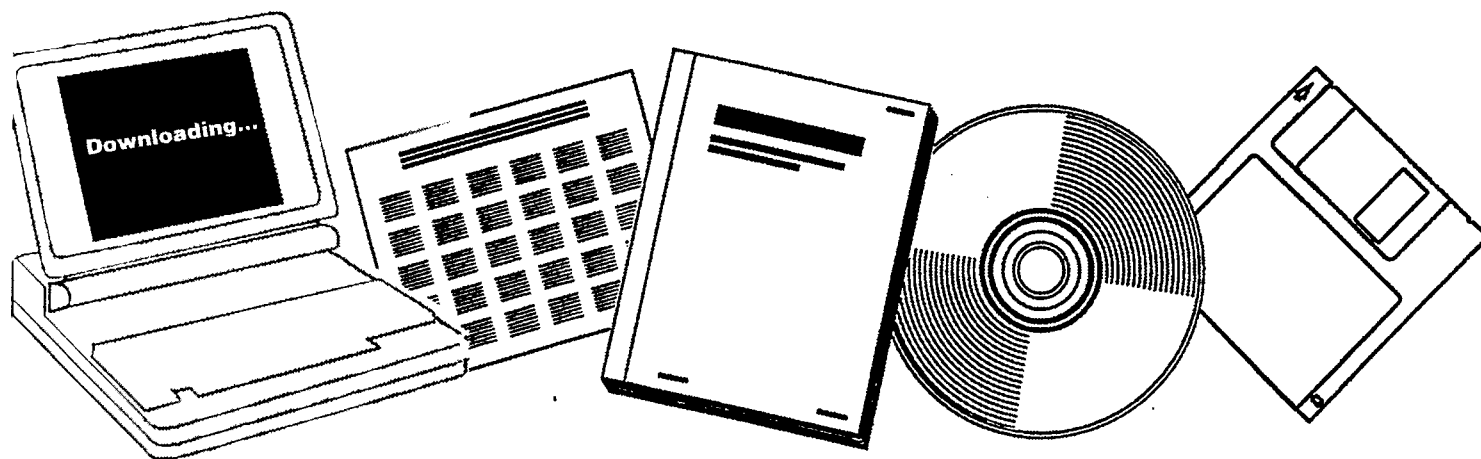
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# OPTIMIZATION OF FIXED BED METHANATION PROCESSES

WEST VIRGINIA UNIV., MORGANTOWN.  
ENGINEERING EXPERIMENT STATION

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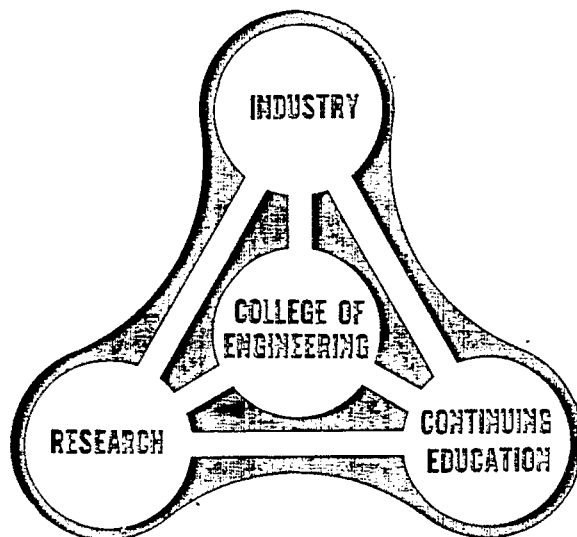
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OPTIMIZATION OF FIXED  
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## OPTIMIZATION OF FIXED BED METHANATION PROCESSES

### ABSTRACT

As a part of the study on optimization of coal gasification processes for the production of pipeline gas, optimization of methanation processes is performed.

Since the heat of reaction for the methanation reaction is so large, heat removal from the reactor is the major problem in process design.

Various systems of catalytic fixed bed reactors are considered. They are the adiabatic system, the heat extraction system, the cold quench system and the recycle system. The size of the plant considered is for the production of  $250 \times 10^9$  Btu/day of pipeline gas. Three different feed gas compositions likely to result from the primary gasification phases are treated. Only the total equipment cost of the methanation processes is considered.

Prior to the optimization of the methanation processes, the heat exchanger optimization is performed. A computer simulation of the methanation process is then programmed based on the kinetic information, the cost information and heat and material balance. Suitable techniques of optimization for the methanation processes are selected and the optimum conditions and designs of the various systems are found.

The result indicates that for the low CO case, an adiabatic reactor without internal or intermediate cooling is the most economical system. For the intermediate CO and high CO cases, the cold quench system offers the minimum total equipment cost. Cost of equipment associated with heat removal is found to occupy the major portion of the total equipment cost.

From the operational and maintenance point of view, the recycle system seems to be the easiest while the heat extraction system seems to be most difficult to control.

The effects of temperature and pressure on the optimum design of the process are discussed. The system parameters which affect the optimum design of the processes are identified.

Information on the methanation catalyst is not complete particularly the reaction rate at high CO concentration and the temperature effect on activity and durability should be further investigated.

## 1. INTRODUCTION

The gasification of coal to produce methane as a substitute or a supplement to pipeline natural gas is currently being extensively studied under the sponsorship of the Office of Coal Research, Department of the Interior.

Although a variety of routes and several raw materials are being investigated, it appears that any system for gasification of coal will require additional units for conversion of excess carbon monoxide and hydrogen to methane to achieve heating value equivalent to natural gas.

The magnitude of methanation will vary considerably, depending on the undecided choice of the process in the primary gasification phases. The degree of methanation may vary from a major operation involving conversion of the feed gas containing a minor amount of methane to simple gas composition clean-up.

Since it is presently impossible to predict the exact composition of the gaseous effluent from the various primary coal gasification processes, the compositions of the three different feeds as listed in Table 1-1 will be considered as approximate gas mixtures.

Although CO concentration as high as 25% can be considered, lacking actual experimental reaction rate data at such a high CO concentration level, it is not possible to make a reasonable assessment of the process for this case. Besides, for such a high CO concentration feed, recycle system is more than likely to be used for excess heat removal, some methane will be present at the reactor entrance. The gas compositions listed in Table 1-1 may result from the primary gasification phases now under investigation after the adjustment of the composition by the water-gas shift reaction and purification is made.

Since the methanation reaction is a highly exothermic reaction, the heat removal from the reacting gas becomes the major problem in economic optimization. Several types of methanation reactors, such as fixed beds and fluidized beds, have been tested on pilot plant scale.

Fluidized bed operation is found to be difficult because of technical problems involved. Particle elutriation caused by the breaking of catalyst pellets may become severe. Lack of ruggedness of the catalyst and the unavailability of small particle sizes prevents good fluidization of catalysts. Therefore, three types of fixed bed downflow catalytic reactors are considered. They are:

1. The heat extraction system
2. The cold quench system
3. The recycle system

TABLE 1-1 FLOW RATE AND CONCENTRATION  
OF FEED AND PRODUCT GASES

A. 950 Btu/SCF Gas

Low CO Case

	Feed Gas		Product Gas	
	[lb.mole/hr.]	[mole%]	[lb.mole/hr.]	[mole%] (dry base)
CH <sub>4</sub>	23,962.8	75.500	25,355.1	92.100
CO	1,419.9	4.474	27.5	0.100
H <sub>2</sub>	5,594.4	17.626	1,417.4	5.148
CO <sub>2</sub>	63.5	0.200	63.5	0.231
H <sub>2</sub> O	31.7	0.100	1,424.1	0.000
N <sub>2</sub>	666.5	2.100	666.5	2.421
Total	31,738.8	100.0	28,954.1	100.0

Intermediate CO Case

	Feed Gas		Product Gas	
	[lb.mole/hr.]	[mole%]	[lb.mole/hr.]	[mole%] (dry base)
CH <sub>4</sub>	21,378.8	62.100	24,115.0	92.100
CO	2,762.4	8.024	26.1	0.100
H <sub>2</sub>	9,562.3	27.776	1,353.8	5.170
CO <sub>2</sub>	68.9	0.200	68.9	0.263
H <sub>2</sub> O	34.4	0.100	2,770.6	0.000
N <sub>2</sub>	619.7	1.800	619.7	2.367
Total	34,426.5	100.0	28,954.1	100.0

High CO Case

	Feed Gas		Product Gas	
	[lb.mole/hr.]	[mole%]	[lb.mole/hr.]	[mole%] (dry base)
CH <sub>4</sub>	16,397.5	41.400	21,724.3	92.100
CO	5,350.3	13.508	23.6	0.100
H <sub>2</sub>	17,107.2	43.192	1,126.9	4.777
CO <sub>2</sub>	118.8	0.300	118.8	0.504
H <sub>2</sub> O	39.6	0.100	5,366.4	0.000
N <sub>2</sub>	594.1	1.500	594.1	2.519
Total	39,607.5	100.0	28,954.1	100.0

TABLE 1-1 (CONT.)

B. 900 Btu/SCF Gas

Low CO Case

	Feed Gas		Product Gas	
	[lb.mole/hr.]	[mole%]	[lb.mole/hr.]	[mole%](dry base)
CH <sub>4</sub>	24,632.3	75.500	25,663.8	87.000
CO	1,061.0	3.252	29.5	0.100
H <sub>2</sub>	6,149.3	18.848	3,054.9	10.356
CO <sub>2</sub>	65.3	0.200	65.3	0.221
H <sub>2</sub> O	32.6	0.100	1,064.1	0.000
N <sub>2</sub>	685.1	2.100	685.1	2.323
Total	32,625.6	100.0	30,562.7	100.0

Intermediate CO Case

	Feed Gas		Product Gas	
	[lb.mole/hr.]	[mole%]	[lb.mole/hr.]	[mole%](dry base)
CH <sub>4</sub>	22,004.3	62.100	24,439.8	87.000
CO	2,463.6	6.953	28.1	0.100
H <sub>2</sub>	10,221.7	28.847	2,915.2	10.377
CO <sub>2</sub>	70.9	0.200	70.9	0.252
H <sub>2</sub> O	35.4	0.100	2,470.9	0.000
N <sub>2</sub>	637.8	1.800	637.8	2.271
Total	35,433.7	100.0	30,562.7	100.0

High CO Case

	Feed Gas		Product Gas	
	[lb.mole/hr.]	[mole%]	[lb.mole/hr.]	[mole%](dry base)
CH <sub>4</sub>	16,919.1	41.400	22,071.4	87.000
CO	5,177.7	12.670	25.4	0.100
H <sub>2</sub>	17,994.1	44.030	2,537.1	10.000
CO <sub>2</sub>	122.6	0.300	122.6	0.483
H <sub>2</sub> O	40.9	0.100	5,193.2	0.000
N <sub>2</sub>	613.0	1.500	613.0	2.417
Total	40,867.4	100.0	30,562.7	100.0



The distinguishing features among the three systems are the manners by which heat is removed and the temperature is controlled in the reactors.

The goal of this study is to economically evaluate their relative technical merits for prospective application in coal gasification processes. To achieve this, it will require all three reactor systems being analyzed from both the technical and economic points of view. Each component information must be integrated by programming it into the computer for simulation. Finally, optimum conditions must be searched by an appropriate technique to arrive at the best economic process and design.

The following specifications and bases are chosen in this study.

1. Production rate is  $250 \times 10^9$  Btu/day of pipeline gas.
2. The product gas should have a heating value of approximately 950 Btu/S.C.F. or the product gas should contain approximately 92.1% methane on a dry base. In addition, the concentration of CO must be less than 0.1%. Product gas with heating value of 900 Btu/S.C.F. is also considered.
3. Three different feeds; low CO case, intermediate CO case and high CO case, are considered. The temperature of the feed gas is fixed at 100°F for comparison. However, the effect of feed gas temperature will be discussed. The pressure of the feed gas is varied up to 1065 psia.
4. The compositions of feed gases and corresponding product gases are listed in Table 1-1. In addition, the feed gas containing 20% CO is also discussed.

Since it is presently impossible to estimate the costs of the various feed gases which depend largely on the primary gasification phases, only the equipment costs are considered. However, in the optimization study of heat exchangers, in addition to equipment cost, coolant water cost and steam benefit are also considered.

After optimization of the sub-system which involves the primary gasification phases, purification phases and other necessary phases including methanation phases has been completed, the overall plant optimization will be performed. Costs not included in the methanation study will then be taken into consideration in the overall plant optimization study. However, the optimization based on the equipment costs alone at this stage should be sufficient to provide necessary information for the selection of the best system among those considered for methanation.

## 2. REACTION KINETICS

### (1) Reaction Rate Expressions for Methanation Reaction

The reactions taking place in the methanation process are:

#### 1. Methanation Reactions:



#### 2. Water-Gas Shift Reaction:



#### 3. Carbon Deposition Reactions:



Although reactions (2-1), (2-2), (2-3) and (2-4) must take place to a larger or smaller extent regardless of the feed compositions employed, for a high hydrogen concentration feed, only a small amount of  $\text{CO}_2$  has been detected experimentally [1]. Therefore, reactions (2-2), (2-3) and (2-4) may be regarded as secondary reactions.

Because carbon deposition reduces the catalyst activity drastically, it is imperative that a range of temperature, pressure and feed compositions within which no carbon deposition takes place must be found. These conditions will become the constraints in the optimization of the processes.

A number of catalysts have been investigated for methanation reactions. The best catalyst for which kinetic data are available seems to be Harshaw Ni-0104 T and Harshaw Ni-0116 T having an average particle diameter of 1/4 inch and 1/8 inch, respectively. This catalyst contains 59% Ni, it has been shown that the catalyst behaves satisfactorily in the temperature range from 550°F to 850°F and the pressure range from 14.7 to 1000 psia without any carbon deposition [15].

A quantitative kinetic rate expression of the methanation reaction on the Harshaw catalyst is very difficult to obtain because extensive accurate kinetic data are not available. Therefore, it is necessary to simplify the reaction mechanism to consider only reaction (2-1). The experimental data obtained from I.G.T. [15] using Harshaw catalysts

can be correlated by two empirical equations, one for the temperature range at 550 to 600°F where reaction rate is controlling and another equation for temperature range of 600 to 850°F where diffusion is the rate controlling factor.

The empirical rate equations obtained are:

1. For temperature between 550°F and 600°F:

$$r_{\text{CH}_4} = 120 \exp \left[ -\frac{15,660}{R(T+460)} \right] P_{\text{CO}}^{0.7} P_{\text{H}_2}^{0.3} \quad (2-8)$$

2. For temperatures between 600°F and 850°F:

$$r_{\text{CH}_4} = 0.0696 P_{\text{CO}}^{0.7} P_{\text{H}_2}^{0.3} \quad (2-9)$$

These equations are adequate for the present optimization purpose in getting a reasonably accurate assessment of the various processes and subsequent study shows that the overall optimum cost of the reactor system is not very strongly affected by the kinetic expressions.

## (2) Approach to Equilibrium

Although the above kinetic expressions were obtained from the experimental rate data of the methane forming reactions on the Harshaw catalyst including the runs under equilibrium hindrance, the equations do not provide the reverse reaction term. It would then be necessary to assure that the rate equations are not applied to conditions too close to the equilibrium.

The equilibrium constant based on mole fraction for the methanation reaction expressed as

$$K_{x_1^*} = \frac{(x_{\text{CH}_4}^*)(x_{\text{H}_2\text{O}}^*)}{(x_{\text{CO}}^*)(x_{\text{H}_2}^*)^3} \quad (2-10)$$

and computed from the values given by the Bureau of Standards [14], is plotted in Figure 2-1 with the operating pressure as the parameter. Here,  $x_2$  refers to the equilibrium mole fraction of each component. As shown in the figure the equilibrium constant,  $K_{x_1^*}$ , is affected by the

pressure and very strongly by the temperature. The equilibrium constant for the water gas shift reaction expressed as

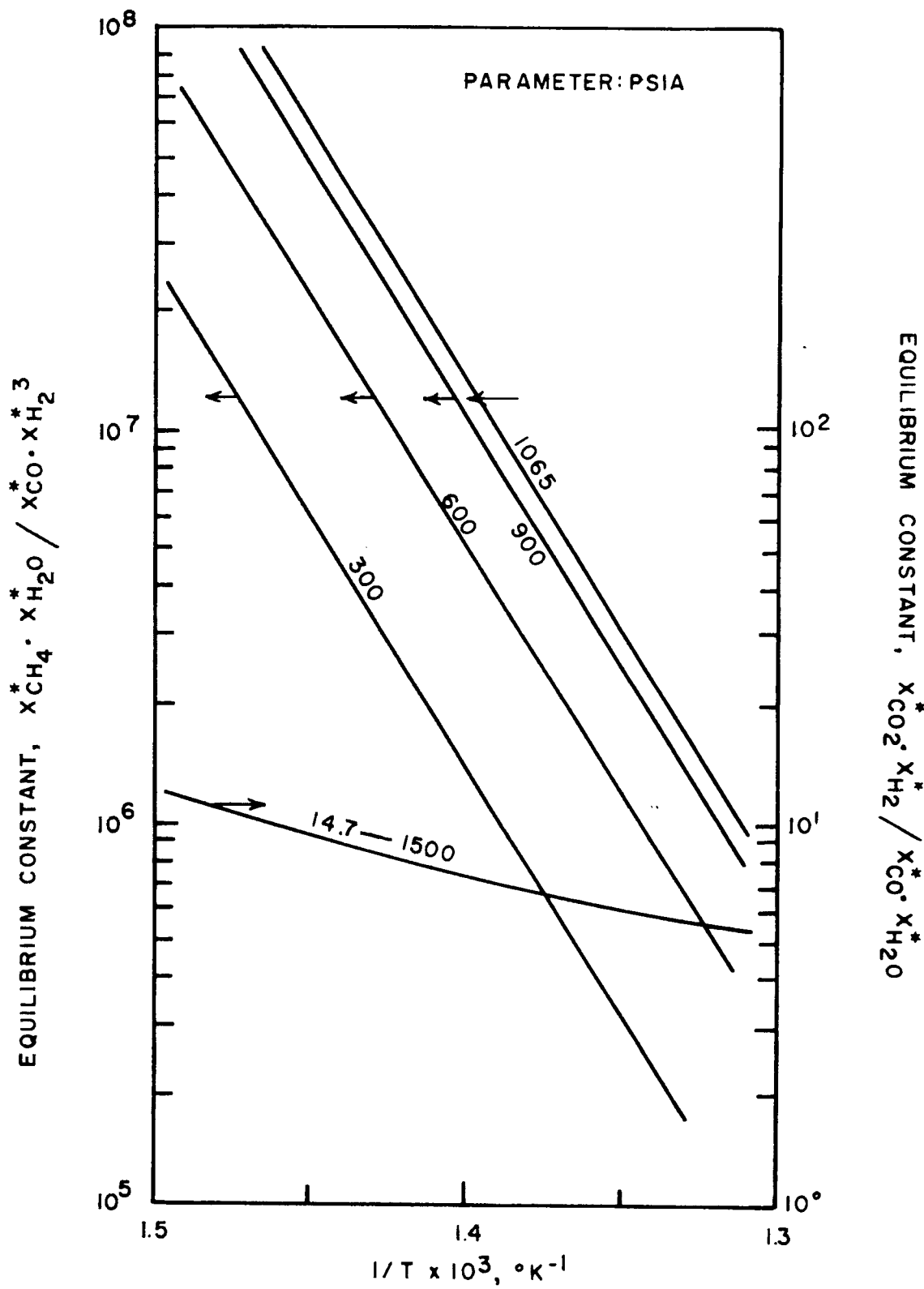


FIGURE 2-1 EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANTS FOR REACTIONS  $CO + 3H_2 \rightarrow CH_4 + H_2O$  AND  $CO + H_2O \rightarrow CO_2 + H_2$

$$K_{x_2^*} = \frac{(x_{CO_2}^*)(x_{H_2}^*)}{(x_{CO}^*)(x_{H_2O}^*)} \quad (2-11)$$

is also calculated from the Bureau of Standards [14] and is plotted in Figure 2-1. The extent of approach to the equilibrium for the methane reaction can be evaluated by computing the mass action law ratio of the product gases,  $K_{x_1}$ , defined as

$$K_{x_1} = \frac{(x_{CH_4})(x_{H_2O})}{(x_{CO})(x_{H_2})^3} \quad (2-12)$$

$x$ 's are the mole fraction of each component present in the reactor. It is decided arbitrarily to maintain  $K_{x_1} < K_{x_1^*}/10$  at all times to

assure the negligible reverse reaction. Whenever the above criterion is exceeded in the reactor, the temperature of the reactor is lowered to the point where the above condition is again satisfied. Such provision is necessary for the high CO case particularly near the exit of the reactor.

### (3) Mass and Heat Transfer Within Catalyst Bed

Since the methanation reaction is highly exothermic and quite rapid, it will be necessary to examine the possible temperature and concentration difference between the bulk phase of reacting gas and the surface of the catalyst. Temperature difference between the bulk phase and the catalyst surface can be approximated by

$$T_s - T_b = \frac{r_s \Delta H}{h_p \pi d_p^2} \quad (2-13)$$

When particle-fluid radiation may be neglected,  $h_p$  can be calculated by [17]

$$J_H = \frac{h_p}{G G_p} N_{Pr}^{2/3} = 1.95 \left( \frac{d_p G_p}{\mu} \right)^{-0.51} \quad (2-14)$$

A maximum temperature difference ( $T_s - T_b$ )<sub>max</sub> can be calculated when

the maximum reaction rate is used. When the temperature difference is too great, many undesirable phenomena may take place. A minimum mass flow rate corresponding to an allowable temperature difference exists for a given reaction rate. This becomes one of the constraints in the reactor optimization. Experimental measurement of temperature difference on the Harshaw catalyst carried out by I.G.T. [15] indicates a maximum temperature difference of approximately 11°F for the intermediate CO case under complete mixing of gas stream.

As the reaction is quite exothermic, it is also necessary to check the temperature gradient in the catalyst particles. If the reaction takes place uniformly in the catalyst particle, the heat balance equation in the catalyst can be written as

$$\frac{d^2 T}{dr^2} + \frac{2}{r} \frac{dT}{dr} = \frac{r_s}{k_e} \Delta H \quad , \quad (2-15)$$

where  $k_e$ , the effective thermal conductivity of the catalyst particles, is expressed as

$$\frac{1}{k_e} = \frac{1}{(1-\theta)k_s + \theta k_g} \quad (2-16)$$

Using the proper boundary conditions, Equation (2-15) can be solved for the temperature within the catalyst pellet as,

$$T = T_s + \frac{1}{6} \left( -\frac{r_s}{k_e} \Delta H \right) \left[ \left( \frac{d_p}{2} \right)^2 - r^2 \right] \quad (2-17)$$

Numerical calculation shows the largest temperature difference in the catalyst particle to be about 30°F.

The concentration difference between the bulk phase and at the surface of catalyst pellets can be estimated by

$$C_s - C_b = \frac{r_s}{k_f \pi d_p^2} \quad (2-18)$$

where  $k_f$  is the fluid-particle mass transfer coefficient in a packed bed and is computed by [8]

$$\frac{J_M}{(1-\epsilon)^{0.2}} = 1.40 \left[ \frac{d_p G}{\mu(1-\epsilon)} \right]^{-0.41} \quad (2-19)$$

Numerical calculations show no appreciable difference between the catalyst surface concentrations and the bulk gas concentration of each component.

### 3. REACTOR PERFORMANCE EQUATIONS

Flow behavior in a fixed bed usually can be represented either by the dispersion model or by the cells-in-series model.

The following material balance equations are obtained around the n-th cell based on the cells-in-series model:

$$F_1^n = F_1^{n-1} + \rho_c V_c^n r_{CH_4} \quad (3-1)$$

$$F_2^n = F_2^{n-1} - \rho_c V_c^n r_{CH_4} \quad (3-2)$$

$$F_3^n = F_3^{n-1} - 3\rho_c V_c^n r_{CH_4} \quad (3-3)$$

$$F_4^n = F_4^{n-1} \quad (3-4)$$

$$F_5^n = F_5^{n-1} + \rho_c V_c^n r_{CH_4} \quad (3-5)$$

$$F_6^n = F_6^{n-1} \quad (3-6)$$

The heat balance equations around the n-th cell can be obtained similarly as

$$T^n \sum_{i=1}^6 C_{P_i}^n F_i^n - T^{n-1} \sum_{i=1}^6 C_{P_i}^{n-1} F_i^{n-1} = (\Delta H) \rho_c V_c^n r_{CH_4} - Q^n \quad (3-7)$$

The heat of reaction,  $\Delta H$ , is in Btu per pound mole of  $CH_4$  formed and is given as

$$\Delta H = 87787.8 + 11.87 T^n - 0.00668 (T^n)^2 \quad (3-8)$$

The pressure drop across the n-th cell can be computed based on Ergun's equation [6]:

$$\Delta P = \frac{150(1-\epsilon) \left(\frac{\mu}{d_p G}\right) + 1.75}{[\epsilon^3 / (1-\epsilon)] (d_p / C_L) (g\rho / G^2)} \quad (3-9)$$

#### 4. COST INFORMATION

The costs of equipment required in the methanation processes are estimated based on the following equations:

(1) In methanation processes, heat exchangers are required to preheat the feed gas, to cool the product gas and to cool the intermediate product in the case of the cold quench system.

The following equation is used to estimate the heat exchanger cost based on the required heat transfer area,  $A_o$  (sq.ft.) [12]:

$$E_H = C_y I_f \left[ 850 \left( \frac{A_o}{50} \right)^{0.56} \right], \quad A_o > 1,000 \text{ ft}^2 \quad (4-1)$$

(2) In the heat extraction system, heat generated in the reactor must be removed internally. The fin tubes may be used effectively for this purpose by embedding them into the catalyst. The cost of fin-tubes based on the bare tube heat transfer area,  $A_b$  (sq.ft.), used in the computation is given as [12],

$$E_F = C_y I_f \left[ 350 \left( \frac{A_b}{60} \right)^{0.88} \right], \quad A_b > 1,000 \text{ ft}^2 \quad (4-2)$$

(3) The cost of the Harshaw catalysts used may be expressed as [5]

$$E_C = 2.5 W_C \quad (4-3)$$

(4) The estimated cost of high pressure reactor shell is based on the weight of an empty reactor. The thickness of the reactor wall,  $T_h$  (inches), is calculated based on the ASME boiler and pressure vessel code section 8 [2] given as,

$$T_h = PR / (SE - 0.6 P) \quad (4-4)$$

The top and the bottom of the reactor are calculated based on an equivalent flat blank diameter necessary to form the required dome.

The weight of the reactor,  $W_R$ , is then computed by

$$W_R = \rho_m \left\{ \left[ \frac{\pi}{4} \left( D + \frac{T_h}{6} \right)^2 - \frac{\pi}{4} D^2 \right] L + 2 \left( \frac{\pi F_d^2}{4} \right) \left( \frac{T_h}{12} \right) \right\} \quad (4-5)$$

The cost of the reactor becomes

$$E_R = C_R I_f W_R \quad (4-6)$$

(5) Cost of mild steel catalyst support trays:

$$E_S = 0.195 I_f (D + 5)^{3.13} \quad (4-7)$$



For a chrome-type tray:

$$E_S = 0.216 I_f (D + 5)^{3.13} \quad (4-8)$$

The total tray cost is

$$E_{ST} = N \cdot E_S \quad (4-9)$$

(6) The cost of a control valve can vary widely depending on the sizes and is rather difficult to estimate. An average of \$4,000 per valve is used in this estimation.

(7) Since the heat insulation cost of the reactor is rather small, an approximate cost of 1.5% of the total fixed cost is added as the insulation cost [3].

(8) Compressors are needed for compressing the feed gas or product gas if necessary, and for recycling the product gas. The following equations are used to estimate the brake horse power [11]

$$B = \frac{T_a}{520} \frac{0.0643 q_p}{E\eta} \left[ \left( \frac{P_b}{P_a} \right)^\eta - 1 \right] \quad (4-10)$$

The feed compressor cost can be computed by [4]

$$E_{cp} = 696 (B)^{0.81} \quad (4-11)$$

The cost of recycle compressor may be determined using the following equations:

$$Br = \frac{(T^N)(0.0643) q_r}{520 E\eta} \left[ \left( \frac{P^0}{P^N} \right)^\eta - 1 \right] \quad (4-12)$$

and

$$E_{CR} = 698 (Br)^{0.81} \quad (4-13)$$

(9) Pumps are required to deliver the water coolant. The following equations are used to estimate pump costs [4,11]

For steel-made water pump,

$$B_P = \frac{q' \rho_w \Delta h}{246,800E} \quad (4-14)$$

and

$$E_P = 684 (B_P)^{0.467} \quad (4-15)$$

In the process optimization of the heat exchangers, water is used for cooling. The costs of treated and spent water are \$0.12 per thousand

gallon and \$0.05 per thousand gallon, respectively. The prices for 400 psia steam and 35 psia steam produced in the heat exchangers are \$0.35 per thousand pound and \$0.15 per thousand pounds, respectively. The annual capitalization charge for the equipments are calculated at 13% of the initial cost per year, as recommended by the Office of Coal Research, Department of the Interior.

## 5. PROCESS OPTIMIZATION OF HEAT EXCHANGERS

Since a large amount of heat is released in the methanation reaction, heat removal from reactors and product gases become the major problem in the optimization study. Three different types of heat exchangers are required in the methanation process, namely the preheater, the product gas cooler and the intermediate cooler. In this section, a process optimization of these heat exchangers is discussed.

### (1) Preheater

The feed gas must be preheated to a temperature above the reaction initiation temperature. The feed gas preheating is accomplished by exchanging heat between the product gas and the feed gas.

The total annual cost for the preheater can be represented by the following equation [13]

$$C_T = A_o K_F C_{Ao} + A_o E_i H C_i + A_o E_o H C_o \quad (5-1)$$

The area for heat transfer,  $A_o$ , is a function of  $h_i$ ,  $h_o$  and  $t_m$  as given by the following equation

$$\frac{F_T \Delta t_m}{q} = \frac{1}{U_P A_o} = \frac{1}{A_o} \left( \frac{D_o}{D_i h_i} + \frac{1}{h_o} + R_{dw} \right) \quad (5-2)$$

Thus Equation (5-2) may be written in terms of  $h_i$ ,  $h_o$  and  $A_o$  as,

$$G = A_o K_F C_{Ao} + A_o \alpha_i h_i^{3.5} H C_i + A_o \alpha_o h_o^{4.75} H C_o \quad (5-3)$$

where  $\alpha_i$  and  $\alpha_o$  are the proportionality constants which depend on designing condition and fluid properties.

Applying the "Lagrange multiplier method," Equation (5-3) becomes

$$G = A_o K_F C_{Ao} + A_o \alpha_i h_i^{3.5} H C_i + A_o \alpha_o h_o^{4.75} H C_o + \lambda' \left[ \frac{F_T \Delta t_m}{q} - \frac{1}{A_o} \left( \frac{D_o}{D_i h_i} + \frac{1}{h_o} + R_{dw} \right) \right] \quad (5-4)$$

where  $\lambda'$  is the Lagrange multiplier. A computer program of Equation (5-4) is already available [9]. From this computation, the optimum overall heat transfer coefficient is found to be about 70 Btu/ft.<sup>2</sup>hr.°F. This value is used in the subsequent design calculation of the preheaters associated with the various methanation processes.

(2) Product Gas Cooler

After flowing through the preheater, the product gas is cooled to 100°F by three heat exchangers. The exit product gas from the preheater has the temperature ranging between 400°F and 750°F. 400 psia steam is produced in the first heat exchanger while steam of about 35 psia is produced in the second heat exchanger. The product gas cooler is finally cooled down to 100°F by the counter-current product gas cooler. The coolant water enters at a temperature of 85°F and leaves at 150°F. If the inlet gas temperature to the first heat exchanger is below 500°F, only two heat exchangers are required.

In the first heat exchanger, treated water enters the tube side. Approximately 50% of the water entered is vaporized producing high pressure steam. The product gas flows in the shell side providing the main heat transfer resistance of this exchanger. The shell side film coefficient can be calculated by

$$\left(\frac{h_o}{k}\right) = 0.36 \left(\frac{D_e G_s}{\mu}\right)^{0.55} \left(\frac{C_p \mu}{k}\right)^{1/3} \quad (5-5)$$

Pressure drop for shell side fluid is calculated by the following equation [10]

$$\Delta P_s = \frac{f G_s^2 D_s L_H}{5.22 \times 10^{10} D_e s B'} \quad (5-6)$$

and

$$f = 1.2 \times 10^{-2} \left(\frac{D_e G_s}{\mu}\right)^{-0.189} \quad (5-7)$$

If the combined pressure drop of the three product gas coolers is limited to 10 psia, the corresponding maximum mass velocity is about 100,000 lb./ft.<sup>2</sup>hr. The shell side film heat transfer coefficient corresponding to this mass velocity is about 110 Btu/ft.<sup>2</sup>hr.°F.

Since two phases exist in the tube side, the inside tube film heat transfer coefficient may vary from 200 to 1000 Btu/ft.<sup>2</sup>hr.°F. The overall heat transfer coefficient of the first heat exchanger then becomes approximately 85 Btu/ft.<sup>2</sup>hr.°F.

Similar to the previous case treated, water is introduced into the second heat exchanger with 50% of the water being vaporized in the tube side. The product gas is passed through the shell side which again provides the main heat transfer resistance of this exchanger. However, when the temperature of the product gas is reduced below 370°F., partial condensation of the water takes place in the shell side. The quantity of condensation depends upon the partial pressure of water in the product gas.

Heat flux accompanied by steam condensation is expressed as

$$q_c = K_G M_v \lambda_c (P_v - P_c) \quad (5-8)$$

Since steam condensing on the tube may be regarded as simultaneous heat and mass transfer phenomena,  $K_G$  may be expressed as

$$K_G = \frac{h_o (C_p \mu / k)^{2/3}}{C_p P_g f_m (\mu / \rho k_d)^{2/3}} \quad (5-9)$$

The total heat flux is a sum of the heat flux due to non-condensing vapor and the heat flux accompanied by the condensation. Hence,

$$q_T = h_o (T_g - T_c) + K_G M_v \lambda_c (P_v - P_c) = h_c (T_g - T_c) \quad (5-10)$$

Calculation using Equations (5-5) and (5-10) give the range of the shell side film heat transfer coefficient to be between 110 and 210 Btu/hr.ft.<sup>2</sup>°F under an allowable combined pressure drop of 10 psi.

The tube side film heat transfer coefficient is practically the same as that for the first heat exchanger. The overall heat transfer coefficient of the second heat then becomes approximately 90 Btu/ft.<sup>2</sup>hr.°F.

In the third heat exchanger, process water is used in the tube side and product gas is passed through the shell side. Using Equations (5-5) and (5-10), the film coefficient of shell side fluid, which is also affected by the partial condensation of water, is calculated to be between 110 to 150 Btu/hr.ft.<sup>2</sup>°F under the allowable pressure drop. The tube side heat transfer coefficient is about 250 ~ 300 Btu/hr.ft.<sup>2</sup>°F for this operating condition. Thus, the overall heat transfer coefficient of the third heat exchanger is calculated to be approximately 80 Btu/hr.ft.<sup>2</sup>°F.

In the process optimization of product gas coolers, the optimum temperatures of gas entering the second and the third heat exchanger are to be found so as to minimize the total equipment and operation costs of the three heat exchangers under the specified temperature constraints. The total cost consisting of the equipment cost of the three heat exchangers, the water cost and the steam benefit, is expressed as

$$C_T = \phi' E_H + (C_1 W_1 + C_2 W_2) - (C_3 W_{S1} + C_4 W_{S2}) \quad (5-11)$$

The heat duties of the first, the second and the third heat exchanger are expressed as:

$$q^I = \bar{M} W^N \left( \frac{P}{C_P} T^P - \frac{I}{C_P} T^I \right) \quad (5-12)$$

$$q^{II} = \bar{M} W^N \left( \frac{I}{C_P} T^I - \frac{II}{C} T^{II} \right) + 18 \left( \frac{P}{P_t} - \frac{P^{II}}{P_t} \right) \lambda_c W^N \quad (5-13)$$

$$q^{III} = \bar{M} W^N (C_p^{II} T^{II} - C_p^F T^F) + 18 \left( \frac{P^I v}{P t} \right) c W^N \quad (5-14)$$

The heat transfer area of the first exchanger is calculated as follows:

First, the water flow rate through the first exchanger is calculated from

$$WC^I = \frac{q^I}{C_{pw}(t_{c1} - t'_c) + 0.5\lambda_c} \quad (5-15)$$

After entering the first heat exchanger, the water is preheated to the vaporization temperature. This assures a near constant water temperature in the tube as long as the constant steam pressure is maintained. The product gas temperature corresponding to the point at which steam starts to vaporize can be found from,

$$T_m^I = T^I + \frac{WC^I \cdot C_{pw}}{\bar{M} W^N C_p^I} (t_{c1} - t'_c) \quad (5-16)$$

The heat transfer area of the first heat exchanger is

$$A^I = \frac{WC^I}{U^I} \left( \frac{C_{pw}(t_{c1} - t'_c)}{\Delta t_1} + \frac{0.5\lambda_c}{\Delta t'_1} \right) \quad (5-17)$$

where  $\Delta t_1$  and  $\Delta t'$  are the log-mean temperature difference corresponding to the liquid phase and the subsequent vaporization phase, respectively. Next the heat transfer area of the second heat exchanger is calculated by the same procedure as the first exchanger.

The heat transfer area of the third heat exchanger is calculated as follows:

$$A^{III} = \frac{q^{III}}{U^{III} \Delta t_3} \quad (5-18)$$

where  $\Delta t_3$  is the log-mean temperature difference in the third heat exchanger. The water flow rate in the third heat exchanger is calculated from

$$W_2 = \frac{q^{III}}{C_{pw}(t_{c3} - t_c)} \quad (5-19)$$

Therefore, all terms in Equation (5-11) are expressed as the function of the inlet gas temperatures of the second and third heat exchangers. According to the numerical calculation, the optimum inlet gas temperatures of the second and third heat exchangers are 460°F and 270°F, respectively.

It is not possible however, at this stage to estimate how much process steam will be required for each of the various routes to be considered. Therefore, low costs of steam, \$0.35/1,000 lb. for 400 psi steam and \$0.15/1,000 lb. for 35 psi steam are used.

### (3) Intermediate Cooler

In the cold quench system with a high CO content feed gas, the heat generated in the reactor is so large that it is necessary to cool the product to a suitable temperature to recycle them. In this intermediate cooler, high pressure steam (400 psia) is recovered. The gas enters the heat exchanger at 850°F and must leave at a temperature higher than the reaction initiation temperature of 550°F. Since steam benefit is the over riding factor, it is clear that the optimum outlet temperature of the intermediate cooler must approach the temperature of 550°F. Since the fluid properties in the intermediate cooler are almost the same as that in the first heat exchanger of the product gas cooler, the overall heat transfer coefficient of this heat exchanger may be taken to be 85 Btu/hr.ft.<sup>2</sup>°F. Water flow rate,  $W_{im}$ , and steam rate obtained in the intermediate cooler are,

$$W_{im} = \frac{w^o(C_p^N T^N - C_p^A T^A)}{C_{pw}(t_{c1} - t_c'') + 0.5\lambda_c} \quad (5-20)$$

The heat transfer area of the intermediate cooler is obtained from

$$A_{im} = \frac{W_{im}}{UI} \left( \frac{C_{pw}(t_{c1} - t_c'')}{\Delta t_A} + \frac{0.5\lambda_c}{\Delta t_B} \right) \quad (5-21)$$

where  $\Delta t_A$  and  $\Delta t_B$  are log-mean temperature differences in the intermediate cooler corresponding to the liquid phase and the subsequent vaporization phase, respectively.

## 6. THE HEAT EXTRACTION SYSTEM

### (1) Process Analysis

The gaseous effluent from the primary gasification system, is fed into the methanation system at 100°F and 1065 psia. The gas has been preheated to 550°F, a temperature high enough to initiate the reaction before it is introduced to the top of the reactor.

In the upper portion of the reactor, reaction is carried out adiabatically until the maximum allowable temperature of 850°F (1) is reached. The reaction thereafter is carried out isothermally by removal of the excess heat of reaction from the reactor through the embedded fin tubes. In the high CO case, the temperature near the exit of the reactor is reduced to 810°F in order to avoid equilibrium hindrance. Heat is removed from the reactor by generating 400 psia steam in the fin tubes.

The exit gas pressure of the methanation process is fixed at 1015 psia. Therefore the total pressure drop, both in the reactor and in the heat exchangers must be kept less than 50 psia. These are the constraints in the design of the optimum reactor diameter.

### (2) Calculation Procedure

As previously stated, in the heat extraction system the reactor is operated adiabatically until the temperature of 850°F is reached, after which the reactor is operated isothermally. Thus, the heat balance around the n-th cell can be written as,

For  $T_1 < T < 850^\circ\text{F}$

$$\sum_{i=1}^6 C_{P_i}^n F_i^n T^n - \sum_{i=1}^6 C_{P_i}^{n-1} F_i^{n-1} T^{n-1} = (\Delta H) \rho_c V_c^n r_{\text{CH}_4} \quad (6-1)$$

and  $T = 850^\circ\text{F}$ ,

$$Q^n = (\Delta H) \rho_c V_c^n r_{\text{CH}_4} = U_o A_t^n (T^n - T_w) \quad (6-2)$$

Since the main resistance to heat flow is across the gas film outside of the fin tubes, the resistance across the tube wall and that due to inside film of the coolant can be neglected. The overall heat transfer coefficient based on the outside surface of the fin tube is approximated to be 11 Btu/hr.ft.<sup>2</sup>°F.

From the equations developed, the concentration of each component, the temperature and the pressure at each cell can be calculated under the adiabatic condition from the previous cell. The calculation is



continued until the reactor temperature reaches 850°F. The calculation thereafter is repeated but under the isothermal condition until the concentration of methane reaches 92.1% of a dry base. Since heat transfer area in a single cell does not have a practical meaning, an average heat transfer area of 40 cells-in-series which make up one tray length is calculated.

Since the heat generated in the low CO case is not very great, no heat removal from the reactor is necessary for this case. For the high CO case, the heat generation rate near the entrance of the reactor is so large, that tubes are packed partially with catalyst in order to keep the gas temperature at 850°F. Also the temperature near the exit of the reactor is reduced to 810°F to avoid equilibrium hindrance of the methanation reaction.

The heat transfer areas of the preheater and the product gas cooler are calculated by the method mentioned in Section 5.

The total cost of the system can be computed from the summation of the individual costs; preheater, product gas cooler, catalyst, insulation, reactor, supporting tray, control valves and fin tubes. Here, the number of the control valves and their cost is estimated from the number of trays.

From the optimization point of view, the decision variables are the reactor diameter,  $D$ , the inlet pressure,  $P^0$ , and the inlet gas temperature to the reactor,  $T^{(1)}$ . A search technique as described in the next section is developed to determine these three variables by minimizing the total equipment cost. Since the gas temperature at the reactor inlet should be kept as low as possible to minimize the heat removal cost, the problem is reduced to that involving two decision variables; the reactor diameter and the inlet pressure.

### (3) Optimum Search Techniques

In this study, the method of the steepest descent is used for the optimization study. This method starts with locating the direction of the steepest descent from an initial point, then search along this line until no further improvement can be made along this line. A new direction of the steepest descent is located at this point and searching is continued along the new line until no further improvement is possible. At this point, another new direction is found and the search continues.

For the search involving two independent variables, once the starting point is selected the search direction can be located by varying one variable at a time. When there are more than two variables involved, Powell's method which does not require the computation of derivatives is more conveniently employed. However, this procedure has no way of recognizing constraints on the variables and consequently this method is not effective for the problems with inequality constraints [7]. Computer programs were written to carry out the optimization calculations.

#### (4) Results and Discussion

The optimum process conditions and the optimum equipment costs for the three feeds are listed in Tables 6-1 and 6-2.

Since the heat generated in the low CO case is not very large, no heat removal from the reactor is necessary. The reactor is essentially operated adiabatically without internal heat removal or quenching.

Although the decision variables selected for optimization are the reactor diameter, the inlet pressure and the feed gas temperature, the feed gas temperature has been fixed at 550°F in actual calculation. This is because the reaction is not affected by temperature significantly after 600°F is reached probably due to the slow catalyst pore diffusion. Hence, there is no reason to increase the inlet temperature above 600°F.

As is evident from Tables 6-1 and 6-2, the heat exchanger costs, particularly the preheater cost and the product gas cooler cost, are the major items of the total equipment cost. Any effective scheme to reduce the size of heat exchanger will reduce the total cost most significantly. Had the reactor been permitted to operate at a feed gas temperature of 500°F, the total cost would have been reduced further.

Each section of the reactor between the two adjacent trays is made up by forty cells equivalent to 40 inches of fixed bed packed with catalyst and fin tubes. The fin tubes have equal heat transfer area in each section. Therefore, the temperature in the isothermal portion of the reactor is not necessarily maintained at the specified 850°F. The temperature deviation is not serious, however, with the largest deviation of only 16°F occurring at the final tray in the high CO case.

TABLE 6-1 OPTIMUM PROCESS CONDITIONS  
IN TWO DIFFERENT FEEDS  
FOR HEAT EXTRACTION SYSTEM

	Intermediate CO	High CO
Inlet temperature, °F	100	100
Outlet temperature, °F	100	100
Inlet pressure, psig	1,050	1,050
Outlet pressure, psig	1,000	1,000
Reactor diameter, ft.	7.0	8.0
Reactor height, ft.	15.2	23.5
Space velocity,* hr. <sup>-1</sup>	1,420	1,270
Catalyst weight, lbs.	17,390	22,340
Total heat transfer surface area of fin tube, ft. <sup>2</sup>	31,400	94,500
Heat transfer surface area of preheater, ft. <sup>2</sup>	10,320	13,520
Heat transfer surface area of product gas cooler II, ft. <sup>2</sup>	10,900	18,360
Heat transfer surface area of product gas cooler III, ft. <sup>2</sup>	20,000	21,140
Flow rate of 35 psia steam in heat exchangers, lb/hr.	55,530	76,670
Flow rate of treated water in heat exchangers, lb./hr.	111,000	153,400
Flow rate of process water in heat exchangers, lb./hr.	149,200	157,600
Flow rate of 400 psia steam in fin tubes, lb./hr.	105,790	356,600
Flow rate of treated water in fin tubes, lb./hr.	105,790	356,600

\* Based on inlet condition. (550°F, 1065 psia)

TABLE 6-2 OPTIMUM EQUIPMENT COSTS  
IN TWO DIFFERENT FEEDS  
FOR HEAT EXTRACTION SYSTEM

	Intermediate CO	High CO
Catalyst, \$	43,500	55,900
Reactor and tray, \$	124,800	223,000
Control valve, \$	20,000	28,000
Fin tube, \$	49,600	131,140
Preheater, \$	81,600	81,400
Product gas cooler I, \$	0	0
Product gas cooler II, \$	84,130	112,800
Product gas cooler III, \$	118,300	122,000
Separator drum and recycling pump (in fin tube system), \$	20,250	36,850
Total equipment, \$	542,180	754,240

## 7. THE COLD QUENCH SYSTEM

### (1) Process Analysis and Calculation Procedure

In the cold quench system, only a small portion of the fresh feed is preheated and enters the top of the reactor. The remainder of the fresh feed at relatively low temperature enters at prescribed intervals into the reactor in such a way that the effluent from the preceding bed is cooled substantially to maintain the reactor temperature below the maximum allowable temperature. In effect, the excess heat generated by the reaction is absorbed into the sensible heat of the feed gas. If the excess heat generated by the reaction is more than that can be absorbed by the sensible heat of the feed gas, it is necessary to use more than one reactor with provisions for intermediate cooling. The maximum allowable temperature is again taken to be 850°F for all cases except for the high CO case in which the exit temperature from the last reactor is reduced to 810°F for reasons previously discussed. The pressure drop in both the reactor and the product gas cooler is limited to less than 50 psia.

Since the amount of heat generated by the reaction,  $Q_c$ , is strongly affected by the feed gas composition as can be seen from

$$Q_c = (\Delta H) F^0 \cdot y^N \quad (7-1)$$

As mentioned previously, the heat generated for the low CO case is less than the sensible heat of the reactant gas so it is not necessary to perform cold quenching. From the heat generation as well as from the economics point of view, only one reactor without the intermediate cooling will be necessary for the intermediate CO case. However, for the high CO case, three reactors with two intermediate coolers will be needed.

#### 1. Intermediate CO Case

A portion of the feed gas is preheated to  $T^{(1)}$  by the preheater prior to entering the top of the reactor. The first cold shot of feed is introduced to cool the reacting gas at a point where the gas temperature has reached the maximum allowable value of 850°F. Since the reaction rate is not significantly affected by the temperature above 600°F, an exact amount of cold quench that will bring down the gas temperature to 600°F should be introduced.

The heat balance across the reactor can be written as

$$T^N \sum_{i=1}^6 C_{P_i}^N F_i^N = (1 - \lambda'_1) T^F \sum_{i=1}^6 C_{P_i}^F F_i^0 + \lambda'_1 T^{(1)} \sum_{i=1}^6 C_{P_i}^{(1)} F_i^0 + Q_c \quad (7-2)$$

If  $T^{(1)}$  is known,  $\lambda'_1$  is calculated from Equation (7-2). The concentration of each gaseous component and temperature profiles can then

be calculated by the same method described in the heat extraction system. The calculation is continued until the temperature in the reactor reaches 850°F.

In the cold quench system, the reactor is subdivided into a number of sections which are separated by the cold quench point. At each quenching point, both the flow rate of the cold quenching gas required and the gas composition after the quenching, can be calculated from the flow rate and the temperature of the gas before quenching. Therefore knowing the inlet temperature,  $T^{(1)}$ , the concentrations of each component and the temperature distribution in the reactor can be calculated.

The total equipment cost for the intermediate CO case is obtained by the summation of the individual equipment cost; preheater, product gas cooler, catalyst, reactor and tray, control valves and thermal insulation. These costs are calculated from the design condition of the reactor and the heat exchangers together with the cost equations described in Section 4.

In obtaining the reactor and tray cost, the distance between the two adjacent sections of catalyst allowed for the quenching gas to mix with the hot gas, is taken to be 0.5 feet.

The decision variables studied in the optimization of this system for the intermediate CO case are the gas temperature at the reactor inlet,  $T^{(1)}$ , and the reactor diameter,  $D$ . Optimization technique used is the same as that for the high CO case in the cold quench system.

## 2. High CO Case

Since a large amount of heat is released in this case, a single reactor cannot accommodate the necessary conversion. Two process arrangements are considered. In System I, a portion of the fresh feed gas is preheated and enters the top of the first reactor. The remainders of the feed are introduced at intervals along the reactor in order to cool the reactant gas.

When the gas temperature in the first reactor reaches 850°F after the final quenching, the reactant gas leaves the first reactor and is cooled by the preheater and the intermediate cooler I.

A portion of the reactant gas then enters the top of the second reactor. The remainder of the reactant gas is cooled by the intermediate cooler II and is fed at intervals along the second reactor to cool the reactant gas. After leaving the second reactor, the product gas is cooled in the product gas coolers I, II and III to 100°F. 400 psia steam is recovered from the intermediate cooler I and the product gas cooler I and 35 psia steam is recovered by the intermediate cooler II and the product gas cooler.

In System II, the arrangement for the first reactor is the same as in System I. When the gas temperature in the first reactor reaches 850°F after the last quenching, the reactant gas is introduced to the intermediate cooler I and is cooled to  $T^{(2)}$  and fed to the second reactor. When the temperature in the second reactor reaches 850°F, the reactant gas leaves the second reactor and is cooled by the intermediate cooler II to  $T^{(3)}$  and therefore enters the third reactor.

As the product gas leaves the third reactor, it is cooled by the feed gas preheater and subsequently by the product gas coolers I, II and III to 100°F. Again 400 psia steam is recovered from the intermediate coolers I and II and the product gas cooler I, while 35 psia steam is recovered from the product gas cooler II.

A rough calculation shows that the total heat exchanger cost for System II is smaller than that for System I and the steam benefit for System II is larger than that for System I. It also shows that the catalyst weight for System II is smaller than that for System I because no quenching for the second and the third reactor is required. Therefore, System II is selected for the optimization study. The calculation procedure for the optimization of System II is as follows:

The heat balance across the third reactor can be written as

$$T^E \sum_{i=1}^6 C_{P_i}^E F_i^E - T^{(3)} \sum_{i=1}^6 C_{P_i}^{(3)} F_i^{(3)} = \Delta H F^0 (y^N - y^{(3)}) \quad (7-3)$$

If the temperature,  $T^{(3)}$ , is known, the conversion,  $y^{(3)}$ , is calculated from Equation (7-3).

The heat balance across the second reactor is

$$T^N \sum_{i=1}^6 C_{P_i}^N F_i^{(3)} - T^{(2)} \sum_{i=1}^6 C_{P_i}^{(2)} F_i^{(2)} = \Delta H F^0 (y^{(3)} - y^{(2)}) \quad (7-4)$$

If the inlet temperature  $T^{(2)}$  is known, the conversion  $y^{(2)}$  is calculated from Equation (7-4).

The heat balance across the first reactor can be written as,

$$T^N \sum_{i=1}^6 C_{P_i}^N F_i^{(2)} = (1 - \lambda'_1) T^F \sum_{i=1}^6 C_{P_i}^F F_i^0 + \lambda'_1 T^{(1)} \sum_{i=1}^6 C_{P_i}^{(1)} F_i^0 + \Delta H \cdot F^0 \cdot y^{(2)} \quad (7-5)$$

If the inlet temperature of the first reactor  $T^{(1)}$  is given, the fraction of feed gas required for the first quenching,  $\lambda'_1$ , is calculated by Equation (7-5). The catalyst weight and reactor sizes of three reactors are calculated from  $\lambda'_1$ ,  $y^{(2)}$  and  $y^{(3)}$ .

The total equipment cost for the high CO case is obtained by the summation of the individual equipment costs; preheater, product gas coolers I, II and III, intermediate coolers I and II, catalyst, reactors and trays, control valves, and heat insulation.

In optimization of System II, the decision variables are the diameters and inlet temperatures for the three reactors. The inlet temperatures for the first reactor should be as low as possible, because under this condition the preheater cost is the lowest and steam benefit for the product gas cooler I is the highest. The inlet temperature of the second and the third reactors also should be as low as possible because the steam benefits for the intermediate coolers I and II are the highest under this condition. Thus, the optimum inlet temperature for the three reactors must be selected at 550°F. Hence the optimization problem for this case is reduced to that of searching the optimum reactor diameters.

## (2) Results and Discussion

Table 7-1 and 7-2 show the operating conditions and the optimum equipment costs for the cold quench system under the two different feeds.

The quantity of the quenching gas and the locations of the quenching points are determined by assuming the reactant temperature before and after quenching to be at 850°F and 600°F, respectively. The reactor and catalyst costs calculated based on such temperature constraints are not necessarily the true optimum values, however. According to Tables 6-3 and 7-2, the catalyst cost for the cold quench system is no more than 1.3 times that for the heat extraction system. Therefore the cost of reactor and the catalyst estimated can be considered to be very close to the true optimum value.

TABLE 7-1 OPTIMUM PROCESS CONDITIONS  
IN THREE DIFFERENT FEEDS  
FOR COLD QUENCH SYSTEM

	Low CO	Intermediate CO	High CO
Inlet temperature, °F	100	100	100
Outlet temperature, °F	100	100	100
Inlet pressure, psig	1,050	1,050	1,050
Outlet pressure, psig	1,000	1,000	1,000
First reactor diameter, ft.	5.9	6.2	6.2
First reactor height, ft.	10.1	18.75	3.4
Second reactor diameter, ft.	--	--	6.6
Second reactor height, ft.	--	--	3
Third reactor diameter, ft.	--	--	7.2
Third reactor height, ft.	--	--	8.5
Space velocity,* hr. <sup>-1</sup>	1,890	1,080	1,200
Catalyst weight, lbs.	12,030	22,930	23,740
Heat transfer surface area of preheater, ft. <sup>2</sup>	9,015	2,175	6,090
Heat transfer surface area of intermediate cooler I, ft. <sup>2</sup>	--	--	7,680
Heat transfer surface area of intermediate cooler II, ft. <sup>2</sup>	--	--	7,530
Heat transfer surface area of product gas cooler I, ft. <sup>2</sup>	--	8,480	6,075
Heat transfer surface area of product gas cooler II, ft. <sup>2</sup>	5,920	11,930	15,670
Heat transfer surface area of product gas cooler III, ft. <sup>2</sup>	18,600	26,630	21,240
Flow rate of 400 psia steam in intermediate cooler I and II, lb./hr.	--	--	336,670
Flow rate of treated water in intermediate cooler I and II, lb./hr.	--	--	336,670
Flow rate of 400 psia steam in heat exchangers, lb./hr.	--	108,100	22,000
Flow rate of 35 psia steam in heat exchangers, lb./hr.	38,450	101,000	138,130
Flow rate of treated water in heat exchangers, lb./hr.	76,900	202,000	276,280
Flow rate of process water in heat exchangers, lb./hr.	138,000	1,249,500	1,319,470

\*Based on inlet condition. (55°F, 1065 psia)



TABLE 7-2 OPTIMUM EQUIPMENT COSTS  
 IN THREE DIFFERENT FEEDS  
 FOR COAL QUENCH SYSTEM

	Low CO	Intermediate CO	High CO
Catalyst, \$	30,000	57,300	59,350
Reactor and tray, \$	66,100	88,270	167,400
Control valve, \$	12,000	18,000	14,000
Preheater, \$	75,510	34,000	53,490
Intermediate cooler I, \$	--	--	62,270
Intermediate cooler II, \$	--	--	61,560
Product gas cooler I, \$	--	73,030	56,360
Product gas cooler II, \$	55,730	88,470	92,720
Product gas cooler III, \$	109,260	118,600	110,160
Total Equipment, \$	348,600	477,670	677,320

## 8. THE RECYCLE SYSTEM

### (1) Process Analysis and Calculation Procedure

In the recycle system, total heat generated in the reactor is absorbed by the portion of the product gas being recycled to absorb the heat.

From the heat balance across the reactor, the following equations are obtained.

$$T^N \sum_{i=1}^6 C_{P_i}^N F_i^N - T^{(1)} \sum_{i=1}^6 C_{P_i}^{(1)} F_i^{(1)} = Q_c \quad (8-1)$$

and

$$F_i^{(1)} = F_i^0 + F_i^r \quad (8-2)$$

If the total amount of heat generated in the reactor,  $Q_c$ , is known, the recycle flow rate  $\sum_{i=1}^6 F_i^r$  is calculated from Equations (8-1) and (8-2).

The inlet flow rate and the compositions are then calculated. The reactor size and the catalyst weight for this system are determined from the performance equations.

When the enthalpy of the inlet gas  $T^{(1)} \sum_{i=1}^6 C_{P_i}^{(1)} F_i^{(1)}$  is larger than both  $T^N \sum_{i=1}^6 C_{P_i}^N F_i^r$ , it is necessary to preheat the feed gas to  $T^{(PF)}$ . The temperature  $T^{(PF)}$  to which the gas must be preheated is calculated from the heat balance around the point where the feed mixes with the recycle gas, according to the following equation:

$$T^{(PF)} \sum_{i=1}^6 C_{P_i}^{(PF)} F_i^0 + T^N \sum_{i=1}^6 C_{P_i}^N F_i^r = T^{(1)} \sum_{i=1}^6 C_{P_i}^{(1)} F_i^{(1)} \quad (8-3)$$

The size of the preheater required is calculated from  $T^{(PF)}$  by the same procedure described in Section 5.

When the enthalpy of the inlet gas is smaller than that of the feed gas and the recycle gas, it is necessary to cool the recycle gas to  $T^{(Nr)}$ . The temperature  $T^{(Nr)}$  of the gas leaving the recycle gas cooler is calculated from the heat balance around the mixing point as

$$T^F \sum_{i=1}^6 C_{P_i}^F F_i^0 + T^{(Nr)} \sum_{i=1}^6 C_{P_i}^{(Nr)} F_i^r = T^{(1)} \sum_{i=1}^6 C_{P_i}^{(1)} F_i^{(1)} \quad (8-4)$$

The size of the recycle gas cooler producing 400 psia steam is calculated from  $T^{(Nr)}$  by the same procedure used in the intermediate cooler. The size of the recycle pump is calculated based on the pressure drop in the reactor and the flow rate of the recycle gas.

TABLE 8-1 OPTIMUM PROCESS CONDITION  
IN TWO DIFFERENT FEEDS FOR  
RECYCLE SYSTEM

	Intermediate CO	High CO
Inlet temperature, °F	100	100
Outlet temperature, °F	100	100
Inlet pressure, psig	1,050	1,050
Outlet pressure, psig	1,000	1,000
Number of reactors	4	8
Reactor diameter	5.8	6.0
Reactor height, ft.	6.02	5.95
Catalyst weight, lbs.	28,030	58,730
Space velocity, hr. <sup>-1</sup>	882	484
Heat transfer surface area of preheater, ft. <sup>2</sup>	1,593	--
Heat transfer surface area of recycle gas cooler I, ft. <sup>2</sup>	--	6,140
Heat transfer surface area of product gas cooler I, ft. <sup>2</sup>	8,500	10,150
Heat transfer surface area of product gas cooler II, ft. <sup>2</sup>	11,775	15,630
Heat transfer surface area of product gas cooler III, ft. <sup>2</sup>	19,900	21,195
Flow rate of treated water in heat exchangers, lb./hr.	320,000	317,930
Flow rate of spent water in heat exchangers, lb./hr.	1,236,170	1,316,140
Flow rate of 400 psia steam in heat exchangers, lb./hr.	108,330	178,330
Flow rate of 35 psia steam in heat exchangers, lb./hr.	95,330	139,670
Recycle ratio	0.7796	2.911
Flow rate of treated water in recycle gas cooler, lb./hr.	--	147,860
Flow rate of 400 psia steam from recycle gas cooler, lb./hr.	--	147,860

\* Based on inlet condition. (550°F, 1065 psia)

## (2) Effect of Temperature of the Feed Gas on Total Equipment Cost

In the optimization of this process, the decision variables considered are the reactor diameter, the inlet and outlet temperature of the gas  $T^{(1)}$  and  $T^N$ , and the number of reactors in parallel. In the recycle system, volumetric flow rate in the reactor and consequently the reactor diameter is so large, especially for the high CO case, it is necessary to find the optimum number of reactors for this case. In the cost estimation of this process, as the number of reactors is increased, \$8,000 per each reactor is added as the costs of control valves and other instrumentation.

However, as the temperature difference between  $T^{(1)}$  and  $T^N$  increases, the recycle gas rate is decreased, reducing the reactor cost, catalyst cost and recycle pump cost. Therefore, the optimum gas temperature at the reactor inlet is 550°F for each CO case and the optimum gas temperatures at the outlet of the reactor are 850°F for the intermediate CO case and 810°F for the high CO case, respectively.

Consequently, the remaining decision variable, the numbers of reactors in parallel, and the reactor diameters are searched in the optimization study of this system.

## (3) Results

Figure 8-1 and 8-2 show the effect of the reactor diameter on the total equipment cost with the number of reactors as parameter for the intermediate CO case and the high CO case, respectively. From Figure 8-1, the optimum number of reactors in parallel is seen to be 4, and the optimum reactor diameter to be 5.8 ft. for the intermediate CO case. From Figure 8-2, the optimum number of reactor and the reactor diameter for the high CO case are 8 and 6.0 ft., respectively. Comparing Figure 8-1 with 8-2, a considerable effect of the number of reactors in parallel on the total equipment cost is noted for the cases where large diameter reactors are used. The differences between the optimum equipment cost for one reactor and that with optimum number of reactors in parallel are \$190,000 for the high CO case, but only \$13,000 for the intermediate CO case. Table 8-1 and 8-2 list the optimum operating conditions and the optimum equipment costs for the recycle systems.

From Table 8-2, the reactor and catalyst costs for this system are seen to be most expensive among the three systems. In addition, recycle pumps are also considerably expensive resulting in the highest total equipment cost among the three systems investigated.

TABLE 8-2 OPTIMUM EQUIPMENT COSTS IN TWO  
DIFFERENT FEEDS FOR RECYCLE SYSTEM

	Intermediate CO	High CO
Catalyst, \$	70,080	146,830
Reactor and tray, \$	169,970	363,560
Valve and flow meter, \$	48,000	80,000
Preheater, \$	28,540	0
Recycle gas cooler, \$	0	60,930
Product gas cooler I, \$	73,170	80,880
Product gas cooler II, \$	87,840	103,030
Product gas cooler III, \$	117,990	122,230
Recycling compressor, \$	81,000	244,000
Total equipment, \$	676,590	1,201,460

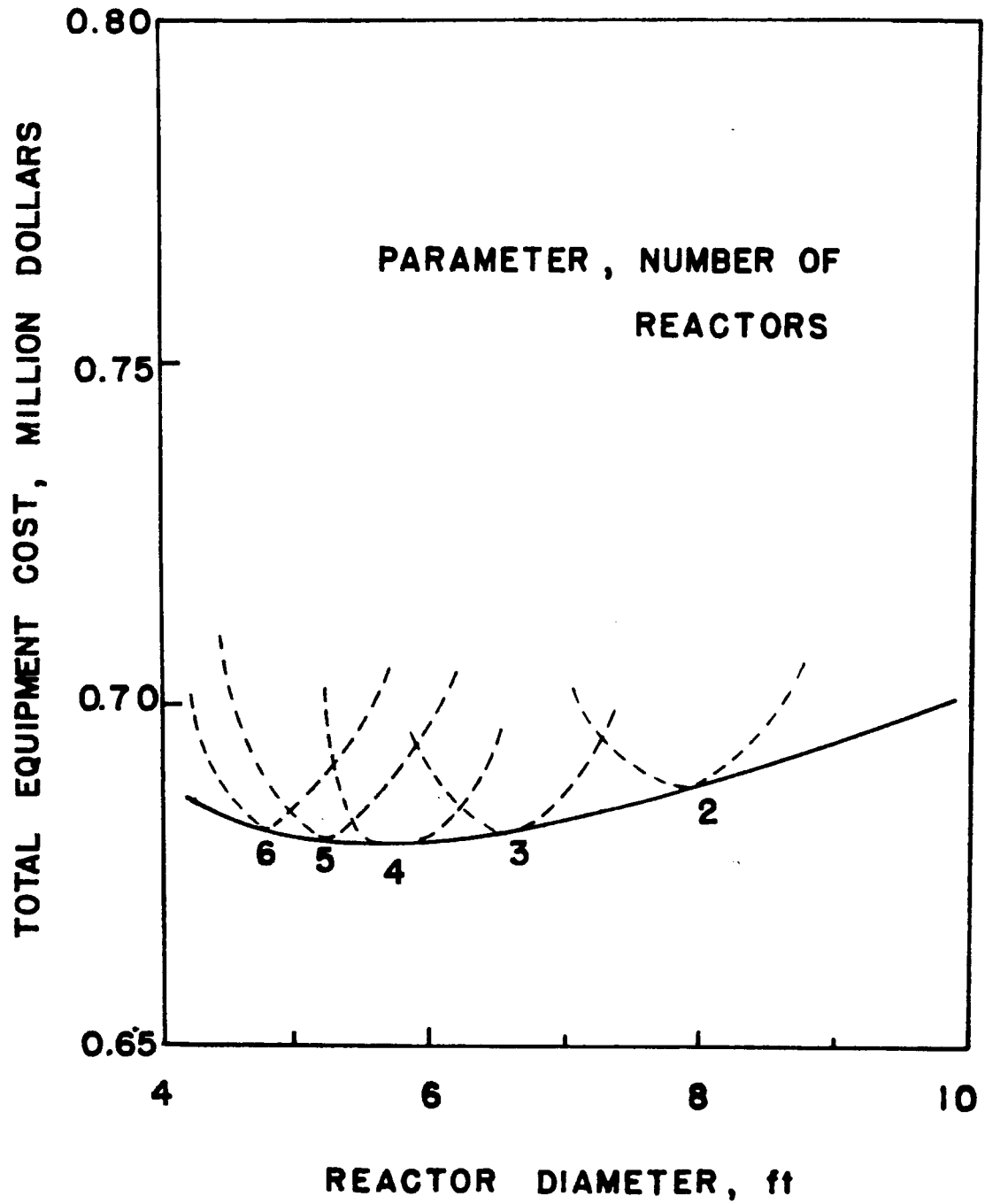


FIGURE 8-1 TOTAL EQUIPMENT COST VERSUS REACTOR DIAMETER  
IN INTERMEDIATE CO CASE FOR RECYCLE SYSTEM

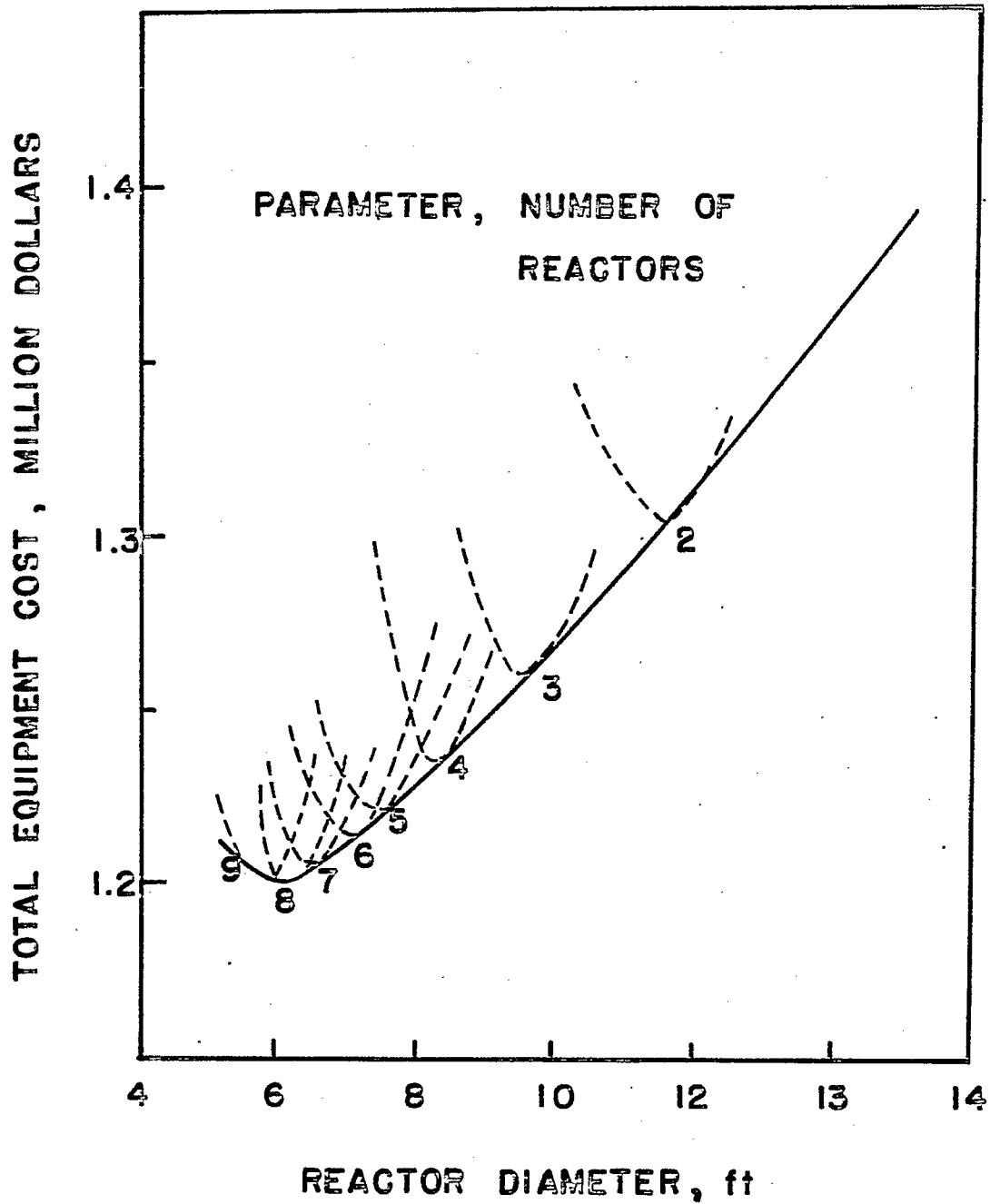


FIGURE 8-2 TOTAL EQUIPMENT COST VERSUS REACTOR DIAMETER  
IN HIGH CO CASE FOR RECYCLE SYSTEM

## 9. DISCUSSION OF RESULTS

### (1) Comparison of the Equipment Costs for the Three Different Feeds

#### 1. Heat Exchanger Costs

For heating and cooling of the process fluids, preheaters, product gas coolers, intermediate coolers, recycle coolers and embedded fin tubes are used. The preheater cost for the heat extraction system is more expensive among the three systems considered. This is because the entire feed gas must be heated to the required inlet reactor temperature. In the cold quench system, only a fraction of the feed gas is preheated while in the recycle system, the preheater is not needed except for the intermediate CO case.

It appears evident that the cost of the product gas cooler is highest for the recycle system and is lowest for the heat extraction system. For the cold quench system, the cost of the product gas cooler depends largely on the fraction of the feed gas introduced to the top of the reactor,  $\lambda_1'$ , and is in general between that of the recycle system and the heat extraction system. As to the costs of the fin tubes, intermediate coolers and recycle gas coolers, they are related to the amount of heat removed during the reaction and therefore are higher as the CO content of the feed gas is increased.

#### 2. Catalyst and Reactor Costs

It is readily seen that the catalyst cost for the heat extraction system is the cheapest and that for the recycle system is the most expensive among the three systems. The catalyst cost for the cold quench system ranks in the middle of the two, leaning closely to that of the heat extraction system. In contrast to the lowest catalyst cost for the heat extraction system, the reactor cost is larger than the cold quench system because a large reactor volume is occupied by the embedded fin tubes. However, for the high CO case when three reactors are needed to accomplish the cold quenching, the reactor costs of the two systems becomes approximately the same.

The reactor cost for the recycle system is the highest since the catalyst volume required is the largest among the three systems.

In view of the high reactor and the catalyst costs as well as the high recycle gas compressor cost in the recycle system, this system is the least economical system.

Figure 9-1 shows the relation between the total equipment cost and the concentration of CO in the feed gas. From this figure, it may be concluded that the cold quench system is the most economical system among the three systems for the intermediate CO case and the high CO case.



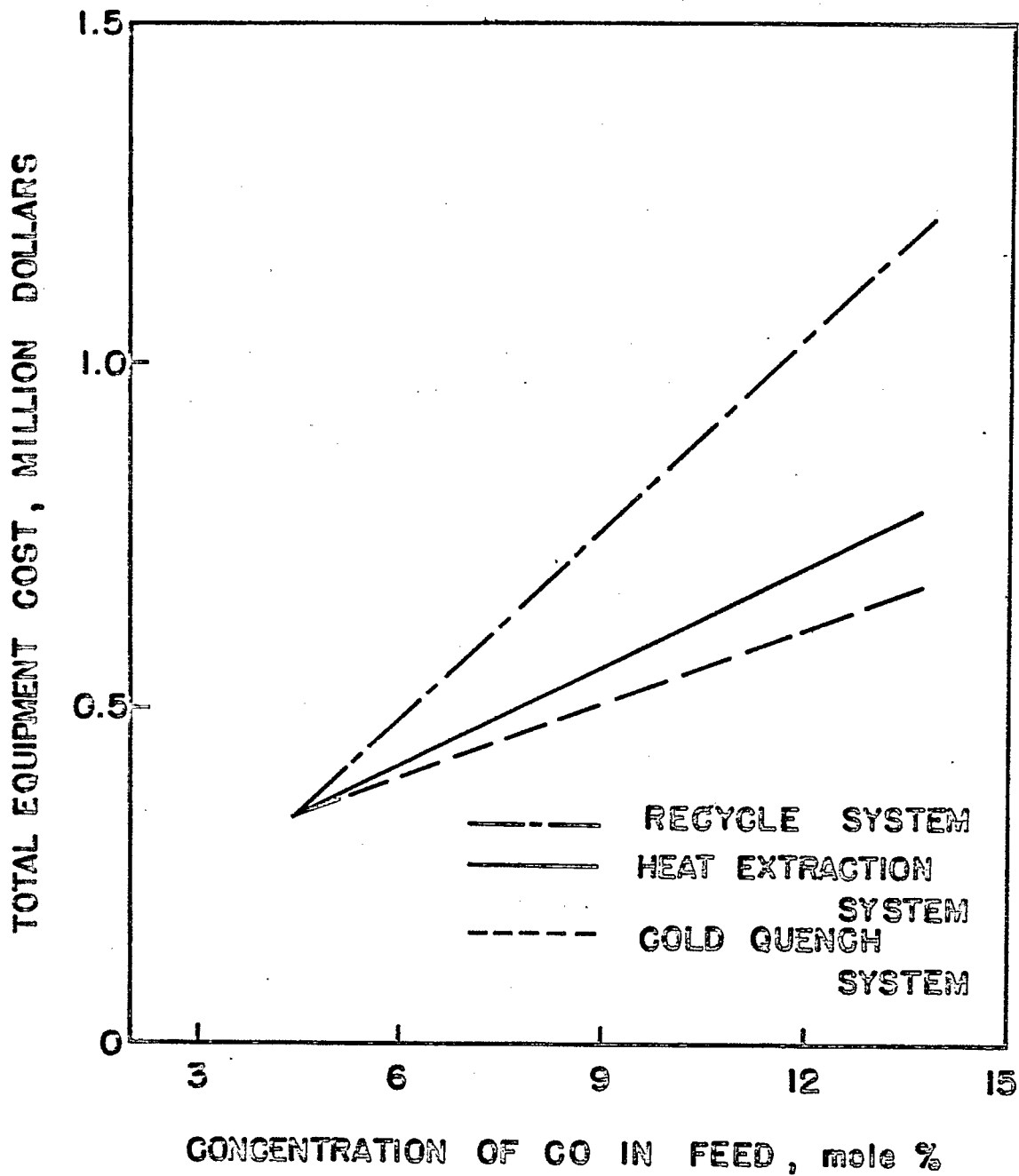


FIGURE 9-1 RELATION BETWEEN TOTAL EQUIPMENT COST AND CONCENTRATION OF CO IN THE FEED GAS FOR THREE DIFFERENT SYSTEMS.

Although in this study the feed gas is assumed to be available at a temperature of 100°F and a pressure of 1065 psia, the optimum temperature and pressure are largely affected by the undecided choice of the primary gasification phases and to a lesser extent by the gas purification phase and the water-gas shift reaction phase which precedes the methanation phase. It is therefore necessary to study how the feed gas temperature and pressure will affect the equipment cost and what the optimum temperature and pressure should be as far as the methanation process is concerned.

Figure 9-2 shows the relation between the total equipment costs and the feed gas temperature for the low CO case in the adiabatic reactor and for the intermediate CO case and the high CO case in the cold quench systems.

### (2) Effect of Pressure of the Feed Gas on Total Equipment Cost for Two Different Product Gas Heating Values

Figure 9-3 shows the relation between total equipment cost and the pressure of the feed gas with the feed CO composition as parameter. Since it is necessary to maintain the outlet product gas pressure above 1000 psig in order to meet pipeline transportation, the product gas must be compressed to this pressure when the gas effluent from the methanation reactor does not have enough pressure to meet this requirement. The operating pressure of the primary gasification system has the predominating effect on the compressor requirements, compressor placement and the methanation reactor pressure so that the methanation processes cannot be optimized without the selection and co-optimization of primary gasification. However, the compressor cost is by far the largest portion of the total equipment cost. If we neglect the cost of compression, Figure 9-3 shows that the equipment cost decreases with pressure of the feed gas.

The product gas having the heating value of 900 Btu/S.C.F. is believed to be enough to meet pipeline gas qualities. Its total equipment cost versus feed CO composition with pressure of the feed gas as parameter is also shown in Figure 9-3.

### (3) Parameter Sensitivity Analysis

In this study, the optimum conditions (decisions) are obtained based on the specific values of system parameters which characterize the performance (kinetic constants, heat transfer coefficient, etc.) to minimize the total equipment cost (the objective function). The values of these parameters are usually obtained from the experimental studies or from careful evaluations based on established correlations. Often these values are somewhat inaccurate due to lack of time and funds required for an accurate evaluation. If the performance of the system under the optimal conditions is significantly dependent on these parameters, and if these values are uncertain, the actual system performance may deviate considerably from the specification. Therefore,

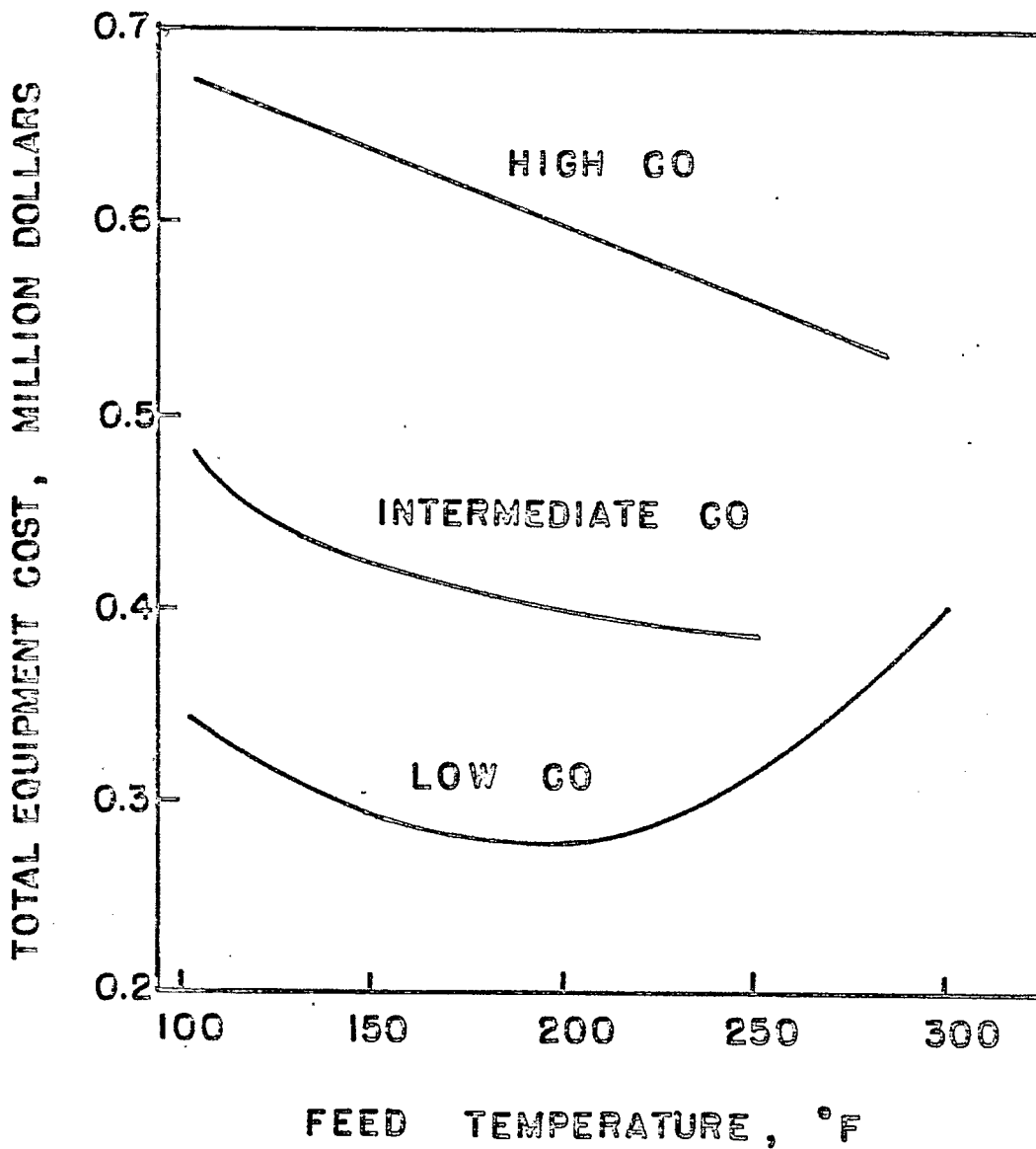


FIGURE 9-2 TOTAL EQUIPMENT COST VERSUS FEED TEMPERATURE IN LOW CO CASE AND IN TWO CASES FOR GOLD QUENCH SYSTEM

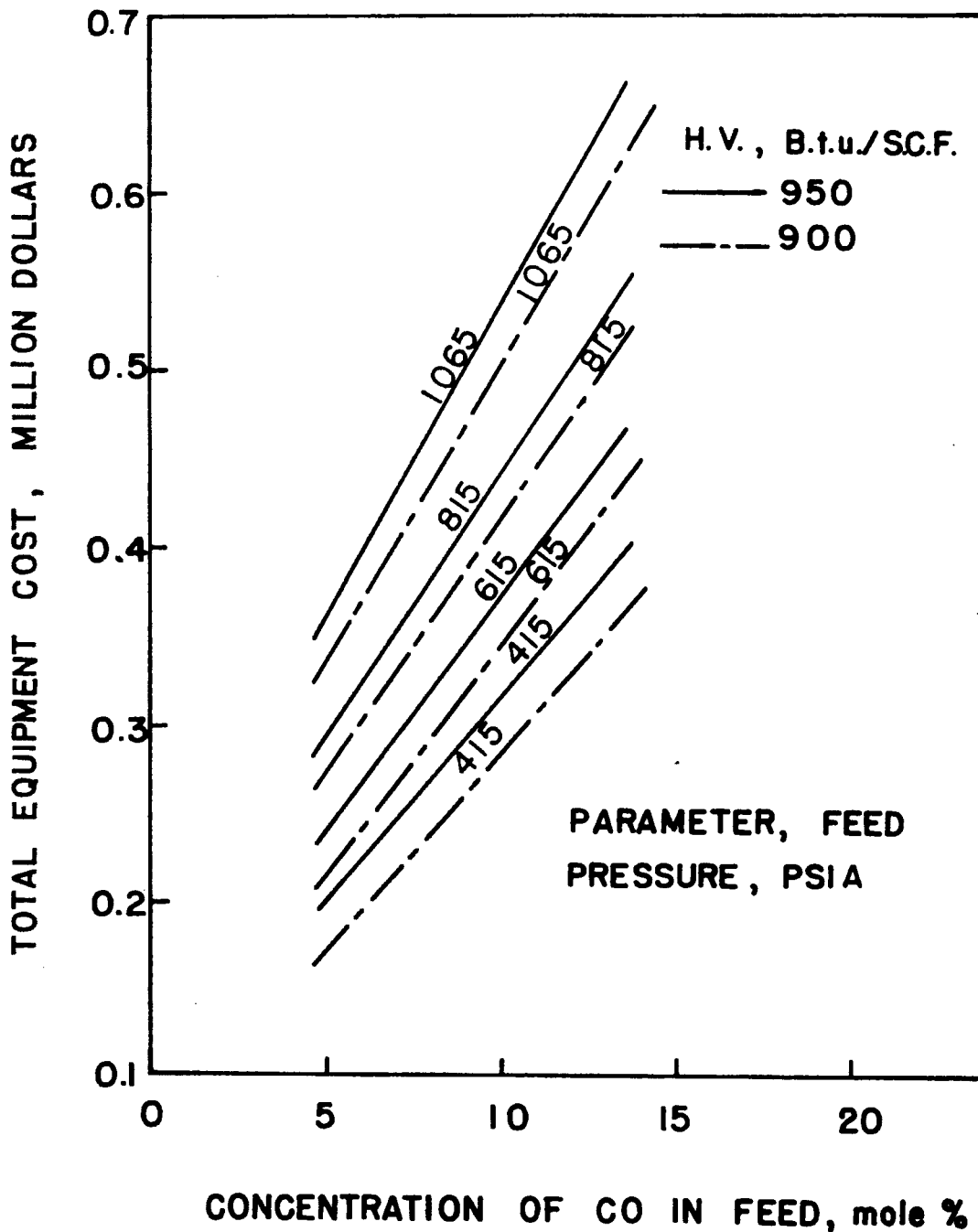


FIGURE 9-3 TOTAL EQUIPMENT COST EMPLOYING COLD QUENCH SYSTEM VERSUS FEED CO COMPOSITION FOR TWO DIFFERENT HEATING VALUES WITH FEED PRESSURE AS PARAMETER

to ensure a better system performance, it is necessary to analyze how sensitive the system parameters are to the objective function (total equipment cost).

The sensitivity of a given parameter,  $\sigma$ , is defined [16] as

$$\sigma = [(\alpha - \bar{\alpha}) / [(\beta - \bar{\beta}) / \bar{\beta}]] \quad (9-1)$$

The result of parameter sensitivity study on the total equipment cost based on the low and the high CO cases for optimum methanation processes is shown in Table 9-1. Among the parameters studied, the maximum allowable temperature,  $T^N$ , is a moderately sensitive factor, particularly for the high CO case. This means if the maximum allowable temperature could be higher than 850°F, the total equipment cost may be decreased, provided of course that the equilibrium hindrance is avoided by cooling the gas near the exit of the reactor. From the heat removal point of view the maximum temperature at which the catalyst can be operated without deactivation due to local sintering or carbon deposition, should be as high as possible. However, high temperatures also limit the material for construction of the reactor and equilibrium concentration for methane. Therefore, further study of catalyst reactivity, durability and regenerability are required.

Since the heat transfer coefficient is directly related to the cost of heat exchangers, an increase in the heat transfer coefficient will directly decrease the total equipment cost, particularly for the low CO case. Among the heat transfer coefficients studied as shown in Table 9-1, the coefficient of the product gas cooler III seems the most sensitive one, this is due to its large heat transfer area required. Comparatively speaking, the heat transfer coefficients are least sensitive among the parameters studied.

The kinetic expression seems to be the most sensitive factor among the parameters considered for both the low and the high CO cases.

Other factors studied gave negligible sensitivities on the total equipment cost.

#### (4) Uncertainty Analysis of Kinetic Expression

Lacking the reliable experimental data, it is difficult to obtain an accurate kinetic rate expression. However, in the previous section, the frequency factor,  $k$ , and the orders of the reaction,  $m$  and  $n$  are found to be very sensitive, therefore it becomes necessary to study how the optimum policy changes over a range of uncertainty in  $k$ ,  $m$  and  $n$ .

In this analysis, a range of uncertainty in the kinetic rate expression is obtained based on the positive and the negative maximum deviations in the Arrhenius plot. The orders of reaction  $m$  and  $n$  are varied from 0.2 to 0.4 and from 0.6 to 0.9, respectively. The optimum

TABLE 9-1 PARAMETER SENSITIVITY ON  
TOTAL EQUIPMENT COST  
OF OPTIMUM METHANATION PROCESSES

Parameters	Sensitivity	
	Low CO	High CO
$U^I$	--	-0.051
$U^{II}$	-0.103	-0.087
$U^{III}$	-0.196	-0.104
$U_P$	-0.131	-0.051
$\mu$	$-0.263 \times 10^{-4}$	$-0.13 \times 10^{-6}$
$\rho$	$0.398 \times 10^{-2}$	$0.486 \times 10^{-3}$
$T^N$	-0.175	-0.331
$T^E$	--	0.161
$T^O$	--	0.077
$k^*$	-0.155	-0.126
$m^*$	-0.435	-0.357
$n^*$	-0.764	-0.627

\*Based on the rate equation:

$$r_{CH_4} = k e^{-E/RT} P_{H_2}^m P_{CO}^n$$

reactor design as well as the total equipment cost for various sets of  $m$ ,  $n$  and the corresponding maxima and minima values of  $k$  for the low CO case are shown in Table 9-2.

The result indicates that the range of uncertainty in the rate expression can cause the total optimum equipment cost to vary from \$490,200 when the minimum rate expression is used to \$287,900 when the maximum rate expression is used. For other rate expressions inside the range of uncertainty, the cost falls between them. Since the optimum design is considerably affected by the kinetic rate expression, a more extensive investigation of the reaction kinetics and further development of improved catalyst are necessary for methanation reaction. The dependency of the rate equation on concentration and temperature should be more firmly established.

(5) Use of Harshaw Ni-0116T - 1/8" Catalyst

Instead of Harshaw Ni-0104T - 1/4", Harshaw Ni-0116T - 1/8" catalyst pellet may be used. The pressure drop across the reactor bed and the kinetic rate expression are affected and therefore must be adjusted. Again it is rather difficult at present to obtain an accurate rate equation, a rough correlation is obtained. The orders of the reaction are considered to be the same and a value of 240 for the frequency factor,  $k$ , is used. The optimum reactor design as well as the total equipment costs for the low CO case for the adiabatic reactor system and for the high CO case for the cold quench system are shown in Table 9-3. Apparently, the reactor diameters are about the same and the reactor heights are about halves as those when 1/4" pellets are used. This is due to the pressure drop across the reactor bed being twice as big as previous case. The total equipment cost is also slightly decreased in both cases.

(6) Feed with CO Composition Higher Than 15%

Since the experimental kinetic data are available only up to 15% of feed CO concentration, the present optimization study is restricted within this range. However, when the feed CO composition is higher than 15%, reactors with better heat removal systems must be considered. One of the ways to reach better heat removal is to utilize the sprayed catalyst on heat transfer surface to facilitate quick removal of heat. Also, there is the hot-gas-recycle system in which two methanators are used. The bulk of the methanation, 80 to 90 percent conversion of the feed gas, occurs in the main reactor over steel catalysts; the remainder of the methanation occurs in the second reactor over a Raney nickel catalyst.

In order to obtain a rough estimate of the total equipment cost for the feed CO concentration higher than 15%, a feed containing approximately 20% of CO is studied. Since a large amount of heat is generated in the reactor, the heat extraction system is poor for the heat removal under this condition and the cold quench system is difficult due to the

TABLE 9-2 UNCERTAINTY STUDY OF KINETIC RATE EXPRESSION FOR  
OPTIMUM METHANATION PROCESSES IN LOW CO CASE

k	m	n	Reactor Diameter ft	Reactor Height ft	Total Equipment cost, dollar
100	0.3	0.7	6.1	11.3	366,000
110	0.3	0.7	6.0	10.7	355,800
120	0.3	0.7	5.9	10.1	348,600
130	0.3	0.7	5.8	9.7	343,160
140	0.3	0.7	*5.7*	9.3	338,230
200	0.2	0.6	6.8	18.15	441,200
148	0.2	0.6	7.1	22.4	490,200
142	0.2	0.9	5.4	7.17	317,940
104	0.2	0.9	5.7	8.75	334,570
157	0.4	0.6	5.4	7.58	320,360
115	0.4	0.6	5.7	9.25	337,720
85	0.4	0.9	4.8	3.5	287,900
62	0.4	0.9	5.0	4.2	295,100

TABLE 9-3 OPTIMUM REACTOR DESIGN AND TOTAL EQUIPMENT  
COST IN TWO DIFFERENT FEEDS FOR TWO DIFFERENT CATALYST

	LOW CO		HIGH CO	
	Ni-0104T 1/4"	Ni-0116T 1/8"	Ni-0104T 1/4"	Ni-0116T 1/8"
First Reactor Diameter, ft.	5.9	5.9	6.2	6.2
First Reactor Height, ft.	10.1	5.2	3.4	2.1
Second Reactor Diameter, ft.	--	--	6.6	6.8
Second Reactor Height, ft.	--	--	3.0	1.5
Third Reactor Diameter, ft.	--	--	7.2	7.2
Third Reactor Height, ft.	--	--	8.5	4.42
Total Equipment Cost, \$	348,600	315,650	677,320	627,840



fact that the reactor temperature quickly reaches the maximum allowable reactor temperature causing the cold shot difficulty. Besides, the temperature difference between the catalyst surface and the bulk gas phase could become excessive due to the large reaction heat generated. The "temperature run-away" may cause the catalyst sintering and the carbon deposition. A recycle system is therefore considered. The flow rate and composition in both feed and product gases are listed in Table 9-4. Assuming that all the properties including kinetic rate expression used in the previous optimization study can be applicable and the exit reactor temperature is changed to 790°F due to the equilibrium hindrance, the system is optimized by the similar way as used in the high CO case for the recycle system. Figure 9-4 shows the effect of the reactor diameter on the total equipment cost with the number of reactors in parallel as parameter. In the cost estimation, as the number of reactors is increased, \$8,000 per each reactor is added as the costs for control valves and other instrumentation. The optimum number of reactors in parallel is seen to be 16, the optimum reactor diameter to be 5.8 feet, and the optimum reactor height is 4.75 feet. The optimum total equipment cost is \$1,799,780 and is much larger than the previous cases studied.

#### (7) Miscellaneous

In this study, only the equipment costs are considered in the objective function due to the difficulty in estimating the costs of various feed gases which depend greatly upon the primary gasification phases. After the optimization of the other sub-system, such as the primary gasification phases, purification phases and other necessary phases has been completed, the overall plant optimization must then be performed.

TABLE 9-4 FLOW RATES AND CONCENTRATION OF FEED AND  
 PRODUCT GASES FOR THE FEED CONTAINING  
 APPROXIMATELY 20% OF CO

	Feed Gas		Product Gas	
	[lb.mole/hr.]	[mole %]	[lb.mole/hr.]	[mole %](dry base)
CH <sub>4</sub>	8,267.1	17.200	17,822.2	92.100
CO	9,574.5	19.920	19.3	0.100
H <sub>2</sub>	29,357.6	61.080	692.3	3.577
CO <sub>2</sub>	96.1	0.200	96.1	0.497
H <sub>2</sub> O	48.1	0.100	9,603.2	0.000
N <sub>2</sub>	721.0	1.500	721.0	3.726
Total	48,064.4	100.0	28,954.1	100.0

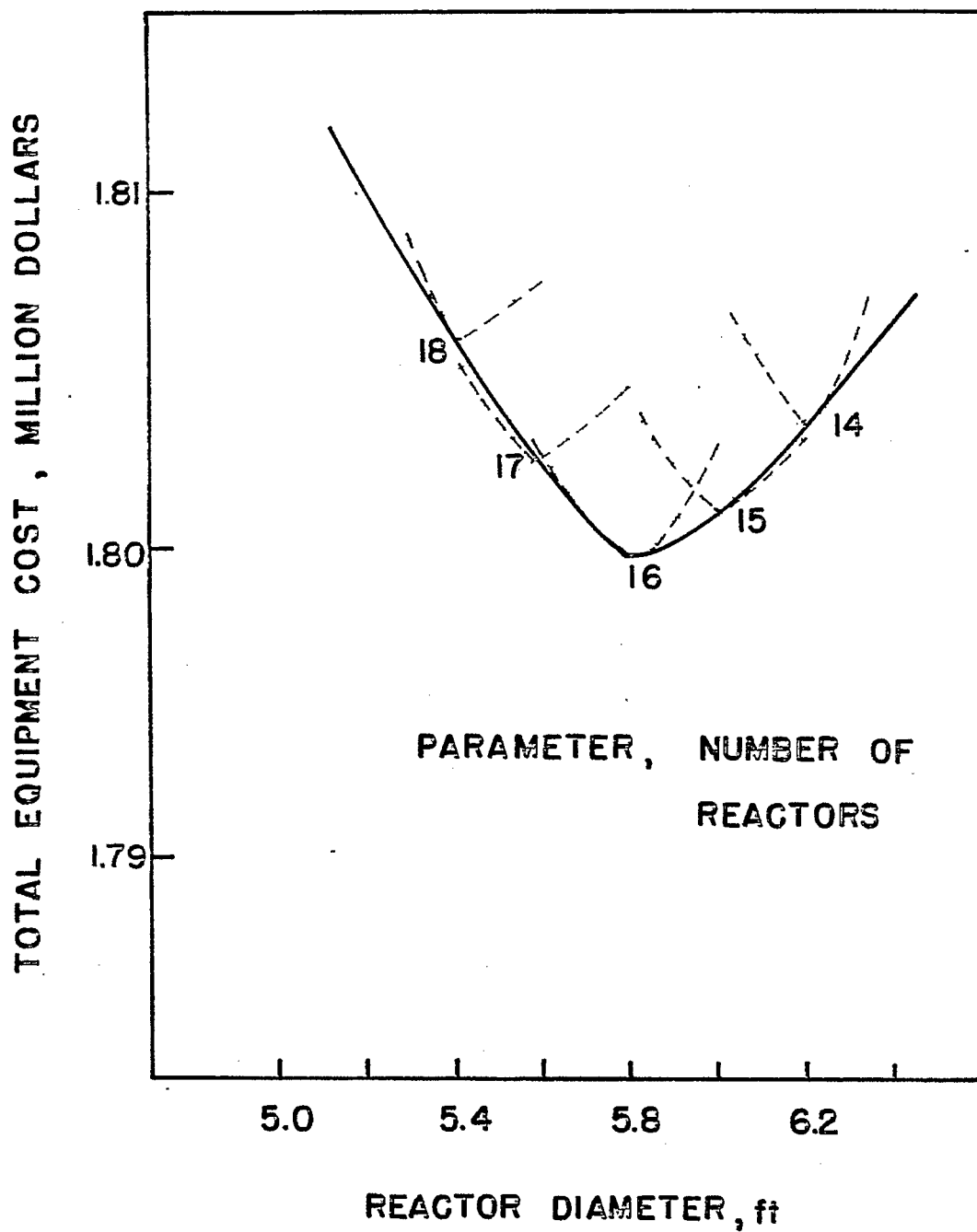


FIGURE 9-4 TOTAL EQUIPMENT COST VERSUS REACTOR DIAMETER FOR FEED CONTAINING 20 PERCENT CO EMPLOYING RECYCLE SYSTEM

## 10. CONCLUSION

An optimization study of methanation processes in the coal gasification plant has been performed. Three different feed compositions, namely the low CO case, the intermediate CO case and the high CO case have been considered. Four different systems employing fixed bed downflow, catalytic reactors have been examined. They are the adiabatic reactor system, the heat extraction system, the cold quench system and the recycle system. The heat exchanger optimization has also been simulated due to the fact that it occupies a major portion of the total equipment cost. The following conclusions are drawn from the results of the study.

1. Owing to the extremely large heat of reaction, removal of heat from the reacting gas is the major problem associated with methanation process. The cost of equipment involved in heat removal such as heat exchangers, etc., occupies a major portion of the total equipment cost. The problem of heat removal becomes more complicated when the feed gas contains a large amount of CO.

2. In the low CO case, since CO concentration in the feed gas is less than 4.6%, an adiabatic reactor system is sufficient to achieve a product gas equivalent to the pipeline gas quality. The consideration of other systems is unnecessary. The adiabatic reactor system then becomes the optimum system for the low CO case.

In the intermediate and high CO cases, since CO concentration in the feed gas is over 4.6%, some devices for removal of the heat are needed. Among three systems considered, the cold quench system offers the least total equipment cost followed by the heat extraction system. The recycle system is by far the most expensive system.

The above analysis is based on the feed gas temperature of 100°F, the inlet reactor temperature of 550°F and the maximum reactor temperature of 850°F.

3. Among three systems considered in the intermediate and high CO cases, from the total equipment cost point of view, the heat extraction system is not too far away from the cold quench system, but from the maintenance and operational points of view, the heat extraction system is not easy to control during the operation and may become unstable when small disturbances in the operating conditions are present.

The recycle system on the other hand may be most costly, but is easiest to control, particularly when the CO concentration in the feed gas is high and when the gas distribution through the catalyst bed is not uniform.

4. The total equipment cost is also affected by the feed gas temperature and pressure. There is an optimum feed temperature for a given concentration. The optimum feed gas temperature for the low CO

case is 200°F, for the intermediate CO case is 250°F and for the high CO case is 300°F. Since the smaller volumetric flow rate would significantly reduce the cost of the compressor, the gas should be compressed to meet the pipeline gas specifications after the methanation process and the feed pressure to the methanation process should be as low as possible.

5. The minimum total equipment costs for the methanation processes are  $\$348.6 \times 10^3$  for the low CO case employing the adiabatic reactor system,  $\$477.67 \times 10^3$  for the intermediate CO case and  $\$677.32 \times 10^3$  for the high CO case both employing the cold quench system.

6. Sensitivity analysis of the system parameters shows that the accuracy of the kinetic rate constants and the orders of reaction would have some effects on the total equipment cost. Also the maximum allowable temperature does have moderate effect on total equipment cost. The heat transfer coefficients are comparatively less sensitive.

7. Uncertainty study of uncertainty of kinetic rate expression demonstrates how the optimum reactor design and the total equipment cost change over the ranges of uncertainty in the frequency factor,  $k$  and the order of the reaction,  $m$  and  $n$ . The result indicates that the kinetic rate expression greatly affects the optimum design of the processes and a more extensive study of the methanation reaction kinetics is needed.

8. Instead of Harshaw Ni-0104T - 1/4" catalyst, Harshaw Ni-0116T - 1/8" catalyst pellets are used to optimize the processes by adjusting the kinetic rate expression and using the same operation conditions. The result shows that the pressure drop across the reactor bed causes the reactor height to reduce to one half of the previous cases. The optimum reactor diameter is about the same.

9. Since the experimental kinetic data are available only up to 15% of feed CO concentration, the present optimization study is restricted within this range. If the feed CO composition is higher than 15%, reactors with better heat removal systems, such as utilizing the sprayed catalyst on the heat transfer surface to facilitate the quick removal of heat and the hot-gas-recycle system should be considered.

Assuming that the kinetic rate expression used in this study is applicable, the recycle system is optimized employing a feed containing approximately 20% of CO. The optimum number of reactors in parallel is found to be 16, the optimum reactor diameter of 5.8 feet, and the optimum reactor height of 4.75 feet and the optimum total equipment cost of \$1,799,780 are obtained from the results.

SYMBOLS

$A_o$	heat transfer area	(ft. <sup>2</sup> )
$A_t^n$	total heat transfer area of fin tube in n-th cell	(ft. <sup>2</sup> )
$A^I, A^{II}, A^{III}$	heat transfer area of first, second and third product gas cooler, respectively	(ft. <sup>2</sup> )
$A_b$	bare tube heat transfer area of fin tube	(ft. <sup>2</sup> )
$B_p$	brake horse power	(HP)
$B_r$	brake horse power of recycle compressor	(HP)
$B'$	baffle spacing	(ft.)
$C_{AO}$	installed cost of heat exchanger per unit heat transfer area based on outside	(\$/ft. <sup>2</sup> )
$C_b$	concentration of product gas in bulk of gas phase	(lb.mole/ft. <sup>3</sup> )
$C_i$	cost for supplying one ft.-lb. force to pump fluid flowing through inside of tubes	(\$/ft.-lb.force)
$C_L$	height of an unit cell	(ft.)
$C_o$	cost for supplying 1 ft.-lb. force to pump fluid flowing through shell side	(\$/ft.lb.force)
$C_p$	heat capacity of gases	(Btu/lb. <sup>o</sup> F)
$C_p^{(I)}_i$	molar heat capacity of i-th component at temperature $T^{(I)}$	(Btu/lb.mole <sup>o</sup> F)
$\bar{C}_p^{(I)}$	heat capacity of product gas at temperature $T^{(I)}$	(Btu/lb. <sup>o</sup> F)
$C_{pw}$	heat capacity of water	(Btu/lb. <sup>o</sup> F)
$C_R$	cost per pound of material used for construction of reactor shell	(\$/lb.)
$C_S$	concentration of product gas at surface of catalyst	(lb.mole/ft. <sup>3</sup> )
$C_T$	total annual variable cost	(\$/years)
$C_Y$	cost year index	(--)
$D$	inside diameter of reactor	(ft.)
$D_e$	equivalent diameter for heat transfer tube	(ft.)

$D_i$	inside diameter of tube	(ft.)
$D_S$	inside shell diameter of heat exchanger	(ft.)
$d_p$	diameter of catalyst particle	(ft.)
$E$	efficiency of longitudinal joints or mechanical efficiency	(—)
$E_C$	catalyst cost	(\$)
$E_{CP}$	compressor cost	(\$)
$E_{CR}$	recycle compressor cost	(\$)
$E_F$	embedded fin tube cost	(\$)
$E_E$	heat exchanger cost	(\$)
$E_i$	power loss inside tube per unit of outside tube area	(ft.lb.force/hr.ft. <sup>2</sup> )
$E_o$	power loss outside tube per unit of outside tube area	(ft.lb.force/hr.ft. <sup>2</sup> )
$E_R$	reactor cost	(\$)
$E_S$	cost of unit tray	(\$/unit tray)
$E_T$	total equipment cost	(\$)
$F_1^n$	molar flow rate of CH <sub>4</sub> at n-th cell	(lb.mole/hr.)
$F_2^n$	molar flow rate of CO at n-th cell	(lb.mole/hr.)
$F_3^n$	molar flow rate of H <sub>2</sub> at n-th cell	(lb.mole/hr.)
$F_4^n$	molar flow rate of CO <sub>2</sub> at n-th cell	(lb.mole/hr.)
$F_5^n$	molar flow rate of H <sub>2</sub> O at n-th cell	(lb.mole/hr.)
$F_6^n$	molar flow rate of N <sub>2</sub> at n-th cell	(lb.mole/hr.)
$F^0$	total molar flow rate of feed gas	(lb.mole/hr.)
$F_i^0, F_i^n, F_i^r$	molar flow rate of i-th component in feed, product and recycle gas, respectively	(lb.mole/hr.)
$F_i^{(2)}, F_i^{(3)}$	molar flow rate of i-th component at inlet of second and third reactor, respectively	(lb.mole/hr.)
$F_d$	flat blank diameter of top and bottom of domes of reactor	(ft.)

$F_T$	correction factor on $\Delta t_m$	(--)
$G$	superficial mass velocity	(lb./ft. <sup>2</sup> hr.)
$G_S$	shellside mass velocity	(lb./ft. <sup>2</sup> hr.)
$\Delta H$	heat of reaction	(Btu/lb.mole CH <sub>4</sub> )
$H_y$	hours of operation per year	(hr./year)
$\Delta h$	hydraulic head	(ft.H <sub>2</sub> O)
$h_i$	inside film heat transfer coefficient of tube	(Btu/ft. <sup>2</sup> hr.°F)
$h_o$	outside film heat transfer coefficient of tube	(Btu/ft. <sup>2</sup> hr.°F)
$h_p$	fluid-particles heat transfer coefficient	(Btu/ft. <sup>2</sup> hr.°F)
$I_f$	cost factor	(--)
$J_H$	heat transfer factor	(--)
$J_M$	mass transfer factor	(--)
$K$	ratio of specific heats	(--)
$k$	thermal conductivity of fluid	(Btu/ft.hr.°F)
$k_d$	diffusion coefficient	(ft. <sup>2</sup> /hr.)
$K_F$	annual fixed charges	(--)
$K_G$	mass transfer coefficient	(lb.mole/hr.ft. <sup>2</sup> atm.)
$K_{X_1}^*$	equilibrium constant of methanation reaction	(--)
$K_{X_2}^*$	equilibrium constant of shift reaction	(--)
$K_{X_1}$	mass action law ratio of product gas in methanation reaction	(--)
$k_e$	effective thermal conductivity of catalyst particles	(Btu/ft.hr.°F)
$k_f$	fluid-particle mass transfer coefficient	(ft./hr.)
$k_g$	thermal conductivity of gas	(Btu/ft.hr.°F)
$k_s$	thermal conductivity of catalyst	(Btu/ft.hr.°F)
$L$	length of reactor	(ft.)
$L_H$	length of heat exchanger	(ft.)



$\bar{M}$	average molecular weight of product gas	(lb./lb.mole)
$M_m$	mean molecular weight of fluid	(lb./lb.mole)
$M_v$	molecular weight of steam	(lb./lb.mole)
$N$	number of trays	(--)
$N_{Pr}$	Prandtl number	(--)
$\Delta P$	design pressure	(psig)
$P$	pressure drop per unit cell	(lb/ft. <sup>2</sup> )
$P_a$	pressure at suction to compressor	(atm.)
$P_b$	pressure at discharge from compressor	(atm.)
$P_c$	partial pressure of steam at surface of tube	(atm.)
$P_{gf}$	logarithmic-mean pressure difference of non-condensing gas	(atm.)
$P^N$	outlet pressure of reactor	(atm.)
$P^O$	inlet pressure of reactor	(atm.)
$\Delta P_S$	shell side pressure drop in heat exchanger	(psi)
$P_v$	partial pressure of steam at bulk fluid	(atm.)
$P_v^{II}$	vapor pressure of water at temperature $T^{II}$	(atm.)
$P_w$	partial pressure of steam in product gas	(atm.)
$P_{CO}$	partial pressure of CO	(atm.)
$P_{H_2}$	partial pressure of H <sub>2</sub>	(atm.)
$Q_c$	total amount of heat generated in reactor	(Btu/hr.)
$Q^n$	amount of heat removed from n-th cell	(Btu/hr.)
$q$	total heat transfer rate in heat exchangers	(Btu/hr.)
$q^I, q^{II}, q^{III}$	heat duties of first, second and third product gas coolers, respectively	(Btu/hr.)
$q^v$	volumetric flow rate	(gal./min.)
$q_c$	heat flux accompanied with condensation	(Btu/hr.ft. <sup>2</sup> )

$q_p$	volume of gas compressed	(S.C.F./min.)
$q_r$	recycle gas flow rate	(S.C.F./min.)
$R_{dw}$	resistance to heat flow due to scaling	(ft. <sup>2</sup> hr.°F/Btu)
$r$	distance from center of catalyst particle	(ft.)
$r_s$	reaction rate per unit catalyst particle	$\left(\frac{\text{lb.mole CH}_4}{\text{hr.unit catalyst}}\right)$
$r_{CH_4}$	reaction rate	$\left(\frac{\text{lb.mole CH}_4}{\text{hr. lb. catalyst}}\right)$
$S$	maximum allowable stress	(psig)
$s$	specific gravity	(--)
$T$	temperature	(°F)
$T^{(1)}, T^{(2)}, T^{(3)}$	inlet temperatures of first, second and third reactors, respectively	(°F)
$T^I, T^{II}$	outlet gas temperature from first and second product gas coolers, respectively	(°F)
$T^A$	outlet gas temperature from intermediate cooler	(°F)
$T^E$	exit temperature of final reactor for high CO case	(°F)
$T^F$	feed gas temperature	(°F)
$T^N$	exit gas temperature of reactor	(°F)
$T^{Nr}$	gas temperature leaving recycle gas cooler	(°F)
$T^n$	temperature at n-th cell	(°F)
$T^P$	outlet product gas temperature from preheater	(°F)
$T^{(PF)}$	outlet feed gas temperature from preheater for recycle system	(°F)
$T_a$	temperature at suction to compressor	(°F)
$T_b$	bulk gas temperature in reactor	(°F)
$T_h$	thickness of reactor	(in.)
$T_s$	surface temperature of catalyst particles	(°F)
$t_{C1}, t_{C3}$	outlet coolant temperature of first, and third product gas coolers, respectively	(°F)

$t'_c$	inlet water temperature of first product gas cooler	(°F)
$t_c$	temperature of treated or spent water	(°F)
$\Delta t_m$	logarithmic-mean temperature difference	(°F)
$U^I, U^{II}, U^{III}$	overall heat transfer coefficients of first, second and third product gas coolers, respectively	(°F)
$U_o$	overall heat transfer coefficient of fin tubes	(Btu/ft. <sup>2</sup> hr.°F)
$U_p$	overall heat transfer coefficient of preheater	(Btu/ft. <sup>2</sup> hr.°F)
$V_c^N$	catalyst volume per unit cell	(ft. <sup>3</sup> )
$W^N$	molar flow rate of product gas	(lb.mole/hr.)
$W_1, W_2$	flow rate of treated and process water in product gas coolers, respectively	(lb./hr.)
$WC^I$	water flow rate through the first exchanger	(lb./hr.)
$W_C$	catalyst weight	(lb.)
$W^O$	mass flow rate of feed gas	(lb./hr.)
$W_R$	weight of reactor tube	(lb.)
$W_{S1}, W_{S2}$	flow rate of 400 psia steam and 35 psia steam in product gas cooler, respectively	(lb./hr.)
$X_{CH_4}^*$	equilibrium mole fraction of CH <sub>4</sub>	(--)
$X_{H_2O}^*$	equilibrium mole fraction of H <sub>2</sub> O	(--)
$X_{CO}^*$	equilibrium mole fraction of CO	(--)
$X_{H_2}^*$	equilibrium mole fraction of H <sub>2</sub>	(--)
$X_{CO_2}^*$	equilibrium mole fraction of CO <sub>2</sub>	(--)
$X_{CH_4}$	mole fraction of CH <sub>4</sub> in product gas	(--)
$X_{H_2O}$	mole fraction of H <sub>2</sub> O in product gas	(--)
$X_{CO}$	mole fraction of CO in product gas	(--)
$X_{H_2}$	mole fraction of H <sub>2</sub> in product gas	(--)
$Y^{(2)}, Y^{(3)}$	conversion of CO to CH <sub>4</sub> at inlet of second and third reactors	(--)
$Y^N$	total conversion of CO to CH <sub>4</sub>	(--)

### Greek Letters

$\alpha, \bar{\alpha}$	objective function and that at optimum, respectively	
$\beta, \bar{\beta}$	system parameter subject to variation and a specific value of system parameters, respectively	
$\epsilon$	void fraction of reactor	(--)
$\theta$	internal porosity of catalyst	(--)
$\lambda'$	Lagrange multiplier	(--)
$\lambda'_1$	fraction of feed gas passing through preheater	(--)
$\lambda_c$	heat of condensation for steam	(Btu/lb.)
$\mu$	gas viscosity	(lb./ft.hr.)
$\rho$	gas density	(lb./ft. <sup>3</sup> )
$\rho_c$	catalyst density	(lb./ft. <sup>3</sup> )
$\rho_m$	density of reactor shell	(lb./ft. <sup>3</sup> )
$\rho_w$	density of cooling water	(lb./ft. <sup>3</sup> )
$\sigma$	sensitivity defined as $[\alpha - \bar{\alpha}/\bar{\alpha}] / [\beta - \bar{\beta}/\bar{\beta}]$	(--)
$\emptyset$	cost factor	(--)
$\eta$	$(K-1)/K$	(--)

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