Pilot Plant Operation of a Nonadiabatic Methanation Reactor

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INTRODUCTION

The development of efficient catalytic methanation reactors is essential to the commercialization of plants for converting coal to substitute natural gas. One of the most important problems facing researchers in this area is that of effective removal of the heat of reaction from the catalyst bed. The Energy Research and Development Administration, Pittsburgh Energy Research Center, is conducting bench-scale and pilot-plant scale studies of a variety of types of catalytic methanation reactors. Some of the earlier investigations (1, 2) included fixed-bed and fluidized-bed experiments using an assortment of supported catalysts and promoters. Later studies (3, 4, 5, 6) concentrated on Raney nickel catalyst thermally deposited onto stainless steel substrates and operated in reactors of varying geometrical configurations and differing modes of operation.

Two distinctly different types of methanation reactors utilizing thermally sprayed Raney nickel catalyst had heretofore been investigated; one, an isothermal reactor in which the Raney nickel was thermally sprayed onto either the internal or external surface of a tube with the heat of reaction being removed by circulating Dowtherm, the other, an adiabatic reactor with the catalyst bed consisting of parallel plate grid assemblies. The plates were constructed of stainless steel and coated on both sides with Raney nickel. The catalyst temperature in the adiabatic reactor is controlled by diluting the reactants in the feed stream to the reactor with recycled product gas. There are advantages and disadvantages to both reactor schemes and the present work is an effort to encorporate desirable features of each methanation scheme into a more efficient reactor system.

The hybrid reactor, as we have christened it, employs a Dowtherm jacket to remove an appreciable amount of the heat of reaction, while at the same time, some product gas is recycled through the reactor to control the reaction rate. The catalyst bed is in the form of an x-shaped stainless steel insert, thermally sprayed with Raney nickel. This insert may be easily replaced when the catalyst becomes deactivated.

REACTOR DESCRIPTION

The hybrid reactor experiments, HYB-17, 18, 19 and 20, were performed in a pilot plant scale reactor constructed of type 304 stainless steel 2 inch schedule 40 pipe. Surrounding the two inch reactor tube was a four inch diameter pipe jacket containing boiling Dowtherm in the annular space to remove a portion of the heat of reaction. The Dowtherm cooling system is depicted in figure 1. The temperature of the coolant is regulated by controlling the pressure in the cooling system. Nucleate boiling is assumed to take place on the outer surface of the reactor tube thereby providing a natural convective circulation of the Dowtherm. Dowtherm vapor is condensed via cooling water and returned to the reservoir.

The catalyst bed consisted of an x-shaped insert coated with Raney nickel catalyst. The cross member insert was two stainless steel 1 x 1 x 1/8 inch angles welded together, 14 ft long. The catalytic surface of the insert was prepared by sand-blasting the stainless steel surface with an iron-free grit and then depositing a

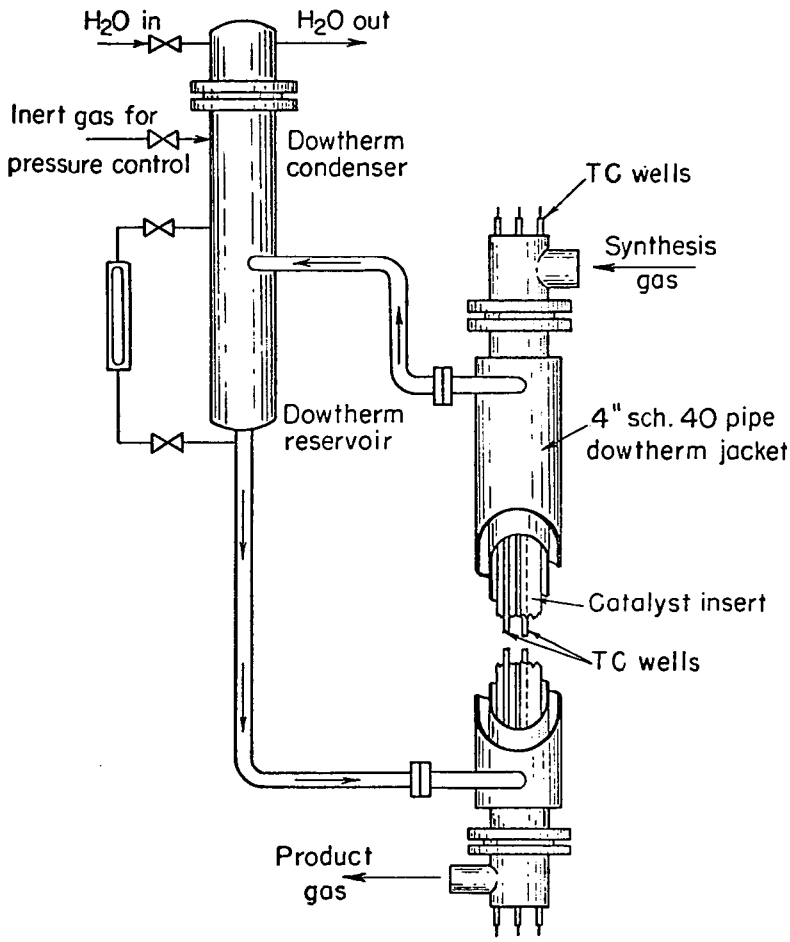

Figure 1. - Hybrid methanation reactor with Dowtherm cooling system.

light coat of bonding material consisting of 80% Ni and 20% Al to a thickness of about .007 inches. Subsequent to the bond coat, Raney nickel alloy powder (80-200 mesh) was thermally deposited onto the bond surface until the desired thickness was achieved (.023 inches). Two different methods were employed for the thermal deposition of Raney nickel onto the substrate. In runs 17 and 18 the catalyst was flame sprayed onto the surface with an oxy-hydrogen flame. A plasma arc with nitrogen as the carrier gas was used to deposit the catalyst for runs 19 and 20. Prior bench-scale studies indicated that plasma sprayed catalyst exhibited longer stability, hence, the method of catalyst deposition was one of the more important parameters studied in this sequence of runs.

The catalyst insert was placed in the reactor and then activated by passing a 2 wt. percent solution of NaOH through the reactor until approximately 70 percent of the aluminum in the Raney alloy was reacted. The extent of reaction was determined by measuring the quantity of hydrogen which evolves according to 3 moles of H_2 for every 2 moles of Al reacted. After activation, the catalyst was washed with distilled water until the pH of the effluent water was within one or two tenths that of the distilled water. The reactor was maintained under hydrogen until the temperature and pressure of the system was brought to synthesis conditions. Synthesis feed gas was then introduced gradually to the system to initiate the run.

Figure 2 illustrates a simplified flowsheet of the hybrid methanation pilot plant. Synthesis gas consisting of approximately 3 parts hydrogen and one part carbon monoxide is blended with recycled product gas. Product water vapor is condensed from the recycle stream before the recycle is mixed with the fresh feed gas. The ratio of recycled gas to fresh gas was from 5 to 8, depending upon the exposure velocity, for a fresh catalyst bed. The recycle ratio required to maintain some preselected maximum catalyst temperature then tended to increase as the catalyst activity declined with age. The mixed gas stream was preheated to the desired temperature before being introduced to the reactor. This temperature was generally the same temperature as that of the Dowtherm coolant.

A second stage clean-up methanator, not shown in figure 2, was used only during the latter periods of the runs when conversion in the primary reactor was declining. The clean-up reactor, an adiabatic reactor charged with a supported commercial nickel catalyst, was utilized to upgrade the quality of the product gas from the primary reactor.

OPERATING PROCEDURES AND RESULTS

The system pressure for all four hybrid reactor runs was 300 psig. The Dowtherm temperature in the cooling jacket as well as the inlet gas temperature was maintained at 300° C throughout all of the runs except for the last few hundred hours of Run 20, when these temperatures were raised to 325° C. Similarly, the maximum catalyst temperature was held at 400° C by adjusting the rate of recycled product gas. The maximum catalyst temperature was allowed to increase to 425° C during the latter portion of Run 20.

Catalyst temperature and gas temperature were measured at 3 inch intervals throughout the reactor on a daily basis. This was accomplished through the use of movable thermocouples in thermowells positioned as shown in figure 3. The thermocouple measuring the gas stream temperature was positioned in the geometrical center of one of the quandrants defined by the x-shaped insert and held in place by ceramic spacers. The thermowell designed to measure the catalyst temperature was first fastened into the "vee" formed by two fins. The bond and catalyst coatings were then sprayed over the thermowell at the same time that the fins were coated. A configuration of this type, with the catalyst essentially surrounding the thermowell,

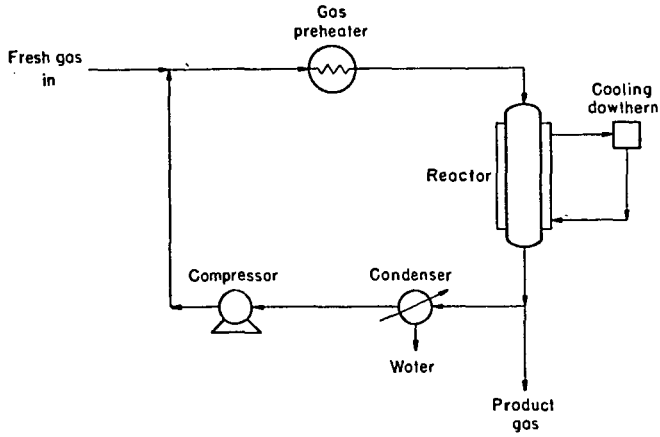

Figure 2. - Flow scheme of HYBRID reactor system.

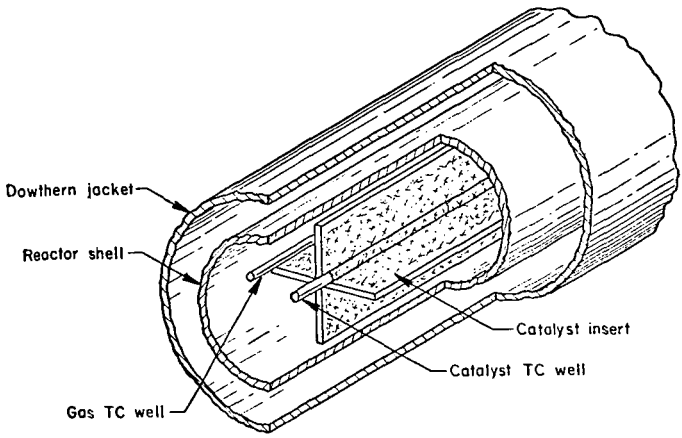

Figure 3. - View of catalyst insert and thermocouple wells.

should yield an excellent measurement of maximum temperature that the catalyst experiences. The gas stream composition was also measured as a function of distance through the catalyst bed. Gas samples were taken every one-eighth of the reactor length with a movable probe which was guided by a slit tube. The gas composition profile was measured only when operating conditions were changed rather than on a daily basis.

Run HYB-17: Seven two ft. inserts coated with flame sprayed Raney nickel were used in Run HYB-17. The reactor was operated at exposure velocities of 20, 30, and 40 scfh/ft^2. Exposure velocity is calculated as the ratio of scfh of synthesis gas (3 parts H_2 to 1 part CO) to the superficial catalyst surface area. An exposure velocity of 30 scfh/ft^2 corresponds to a space velocity of 806 hr^{-1}. Once again, the space velocity is based on a 25 percent CO fresh feed gas flow rate. This first hybrid reactor experiment lasted only 671 hours. The run was terminated when CO conversion decreased to 96.6 and the concentration of CO in the product gas reached 3 percent. Overall performance of this catalyst bed was not outstanding with a production of only 15.0 mscf of CH_4 per pound of catalyst (before leaching). Operating parameters and product gas characteristics are presented in figure 4. Catalyst bed data for Run HYB-17 as well as the three successive runs are listed in Table 1.

Table 1. - Catalyst Bed Data

	HYB-17	HYB-18	HYB-19	HYB-20	HYB-21
Catalyst Type	Flame-Sprayed Raney		Plasma Sprayed Raney		Cast Raney
Wt Pct Nickel	42[a]	42[a]	42[a]	42[a]	42[a]
Pct Activated	71.4[b]	70.6[b]	70.1[b]	70.0[b]	100.0[c]
Reactor Diameter X Length, in.	2 x 168	2 x 168	2 x 168	2 x 168	2 x 170
Reactor Volume, ft^3	0.326	0.326	0.326	0.326	0.330
Weight of Unactivated Catalyst, lb	2.78	2.24	2.43	1.70	10.64
Superficial Area of Catalyst, ft^2	8.75	8.75	7.58	8.46	11.20
Fin Thickness, in.	0.124	0.122	0.125	0.129	0.150
Avg. Bond Coat Thickness, in.	0.008	0.007	0.007	0.006	—
Avg. Catalyst Thickness, in.	0.03	0.023	0.023	0.013	0.050

[a] before leaching

[b] theoretical (based on H_2 evolution)

[c] 100% theoretical leaching of 0.05 inches

Run HYB-18: Flame sprayed Raney nickel was again used in Run HYB-18. Operating conditions were comparable to those of HYB-17 with the exception that the catalyst was exposed to a higher space velocity (1344 hr^{-1}, 50 scfh/ft^2) during a large portion of the run. This experiment lasted almost 3 times longer than the previous run. The run was voluntarily terminated after 2073 hours on stream when the CO conversion reached 95.6 percent and the CO concentration in the product gas was nearly 4 percent. It should be noted in figure 5 that decreasing the Dowtherm temperature from 300° C to 275° C at about 1950 hours on stream was responsible for a large decrease in conversion. CO conversion just prior to this time was

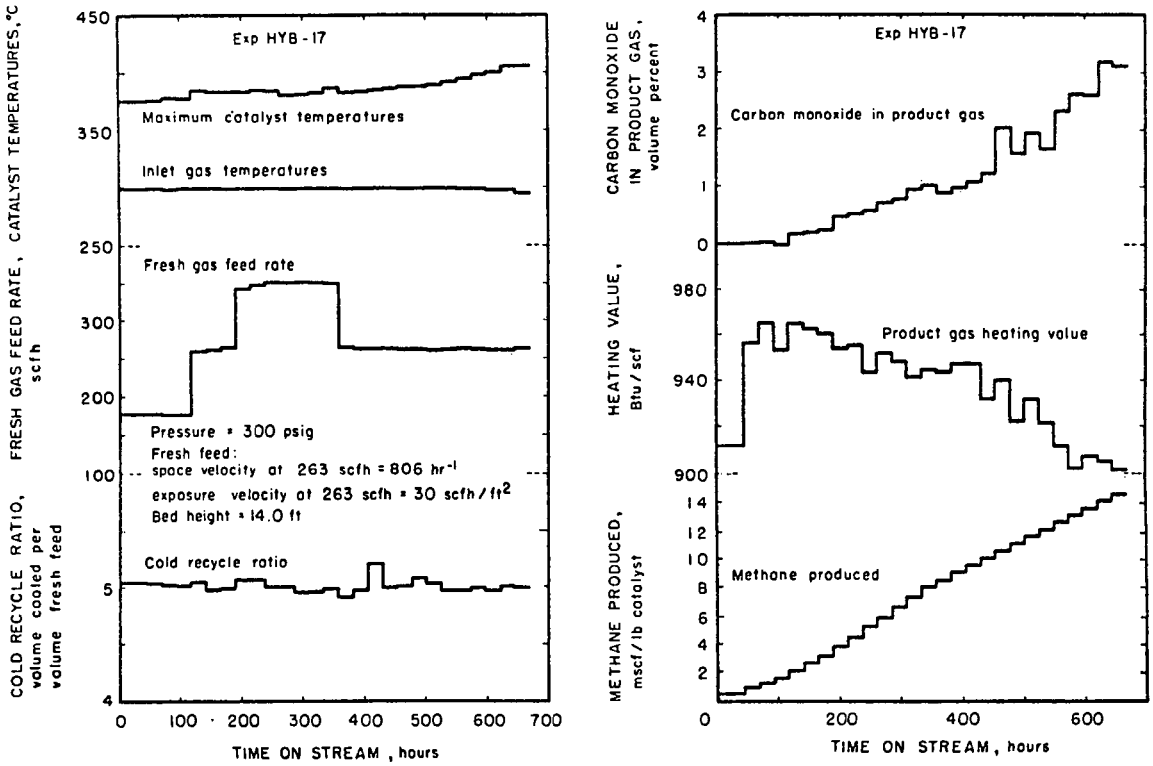

Figure 4. - Reactor conditions and product gas characteristics for Run HYB-17.

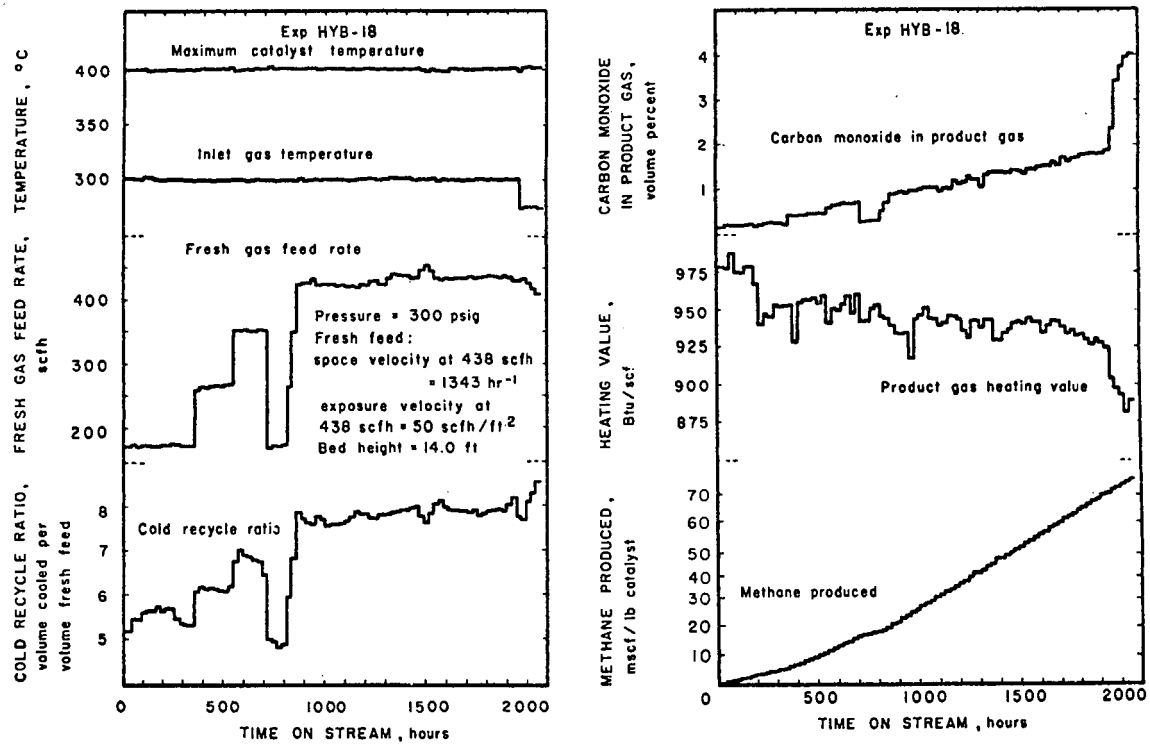

Figure 5. - Reactor conditions and product gas characteristics for Run HYB-18.

still rather acceptable at 98 percent. Due to greater catalyst stability, methane production was much higher for Run HYB-18 with a total of 75.2 mscf per pound of catalyst. Data pertinent to Run HYB-18 are illustrated in figure 5.

Typical stream flowrates and compositions are listed in table 2 for experiment HYB-18. These are data averaged over a 24 hour period and representative of the operating conditions during each of the exposure velocities investigated (20, 30, 40 and 50 scfh/ft^2). The last period represents the reactor operation with a Dowtherm temperature of 275° C. It should be noted that, at this temperature, CO conversion decreased significantly, and as a direct result, the heating value of the product gas decreased to 898.1 Btu/scf.

Run HYB-19: Recent experiments performed on bench-scale methanation reactors using plasma sprayed Raney nickel catalyst indicated that catalyst coatings prepared in this manner demonstrated a longer life. In an effort to test these findings in a larger scale reactor, an x-shaped substrate, identical to that used in runs HYB-17 and HYB-18 was plasma sprayed with catalyst and operated under conditions similar to those used in the previous two runs. Deactivation of the catalyst was rather rapid, with the experiment lasting only 1100 hours. Final CO conversion declined to 97.3 percent with 2.35 percent CO in the product gas. Methane production for this run was 36.6 mscf per pound of catalyst. Operating conditions for this run are shown in figure 6. One plausible explanation for the relatively poor performance of the catalyst in this experiment might lie in the leaching procedure. The activation time required for 70% aluminum leaching was much shorter, 4.6 hours compared to 18 hours in Run HYB-18. It was discovered that the NaOH solution was inadequately mixed resulting in an initial caustic concentration higher than the usual 2 percent.

Run HYB-20: This experiment was, essentially, a duplication of Run HYB-19. Operating parameters and product gas characteristics are given in figure 7. Methane production for this plasma sprayed catalyst was significantly better than HYB-19 with a total of 75 mscf per pound of catalyst. Final CO conversion stood at 97 percent with 2.55 percent CO in the product gas. The reactor was on stream for a total of 2081 hours. As indicated in figure 7, the Dowtherm temperature was increased to 325° C during the last portion of this run. Correspondingly, the maximum catalyst temperature was allowed to increase to 425° C. The increase in catalyst temperature was accompanied by a decrease in the quantity of recycled product gas required. Contrary to what might be expected, however, an increase in catalyst temperature did not significantly improve CO conversion. The conversion remained about the same, at 97.7 percent.

HYB-21: A fifth hybrid test has just been initiated. Preliminary results of this run are given in figure 8. The catalyst bed in this run differs from the previous four in that cast Raney nickel inserts were used rather than a thermally spray coated stainless steel insert. The castings were made of 42-58 percent Ni-Al alloy; each being six inches long and having 8 fins. The castings were formed with a hole along the axis to accomodate a thermocouple well to measure catalyst temperature. The catalyst surface was activated to a depth of .05 inches and operated under conditions similar to those for Run HYB-20. The data shown in figure 8 for the first 384 hours on stream indicate greater initial CO conversion and no detectable catalyst deactivation.

At the termination of each run, samples of spent Raney nickel catalyst were removed from the catalyst insert and subjected to wet chemical analysis, x-ray diffraction, BET surface and pore size distribution analysis. Two catalysts, one flame sprayed Raney nickel and one plasma sprayed Raney nickel, were measured for nickel surface area. Table 3 summarizes the results from chemical analysis and x-ray diffraction of the samples taken from the four runs. An appreciable carbon

Table 2. - Experiment HYB-18, Selected Test Data

Time on Stream.....hr	335	527	695	1640	2000
Temperatures					
Dowtherm.....°C	300	300.	300.	300.	275.
Gas Inlet.....°C	300.	300.	300.	300.	276.
Maximum Catalyst.....°C	400.	400.	400.	400.	401.
Pressure.....psig	300.	300.	300.	300.	300.
Feed Gas					
Rate.....scfh	175.	269.5	354.1	433.6	433.7
H_2.....vol pct.	75.5	76.1	74.6	75.9	75.9
CO..... "	23.8	3.0	23.6	23.7	23.4
CO_2..... "	.3	.3	.1	.2	.2
N_2..... "	.2	.4	1.5	.1	.4
CH_4..... "	.2	.2	.2	.1	.1
H_2O..... "	.0	.0	.0	.0	.0
Exposure Velocity.....scfh/ft^2	20.	30.8	40.5	49.6	49.6
Space Velocity.....hr^{-1}	673.	1036.5	1361.9	1667.7	1668.1
Mixed Feed Gas					
Rate.....scfh	1112.2	1912.4	2748.4	3870.1	3779.1
H_2.....vol pct	17.9	16.0	16.1	14.5	19.4
CO..... "	3.9	3.7	3.7	4.0	5.1
CO_2..... "	0.2	.2	.2	.7	.5
N_2..... "	0.7	.8	.7	1.2	.3
CH_4..... "	77.2	79.2	79.2	79.5	74.0
H_2O..... "	.1	.1	.1	.1	.1
Inlet Velocity.....ft/sec	1.4	2.5	3.6	5.0	4.7
Inlet Reynold's No..... "	3357.	5885.	8465.	12042.	11548.
Exposure Velocity.....scfh/ft^2	127.1	218.6	314.1	442.3	431.9
Space Velocity.....hr^{-1}	4278.	7355.	10571.	14885.	14535.
Volume Recycle/Volume Fresh Gas	5.4	6.1	6.8	7.9	7.7
Product Gas					
Rate..... scfh	40.9	64.4	88.4	105.9	112.1
H_2.....vol pct	6.8	6.0	7.2	6.6	11.6
CO..... "	.2	.5	.7	1.5	3.3
CO_2..... "	.1	.2	.2	.7	.6
N_2..... "	.8	.9	.6	1.2	.3
CH_4..... "	87.9	89.2	87.9	87.1	81.3
H_2O..... "	4.2	3.2	3.4	2.9	2.9
Conversion					
CO..... pct	99.7	99.5	99.2	98.4	96.2
H_2..... pct	97.7	98.0	97.4	97.8	95.9
Heating Value.....Btu/scf	953.7	955.6	948.4	935.1	898.1
Carbon Recovery..... pct	91.6	98.3	98.8	93.5	95.6
Hydrogen Recovery..... pct	92.2	89.1	97.2	90.0	90.7
Oxygen Recovery..... pct	98.9	89.1	103.3	99.1	100.4

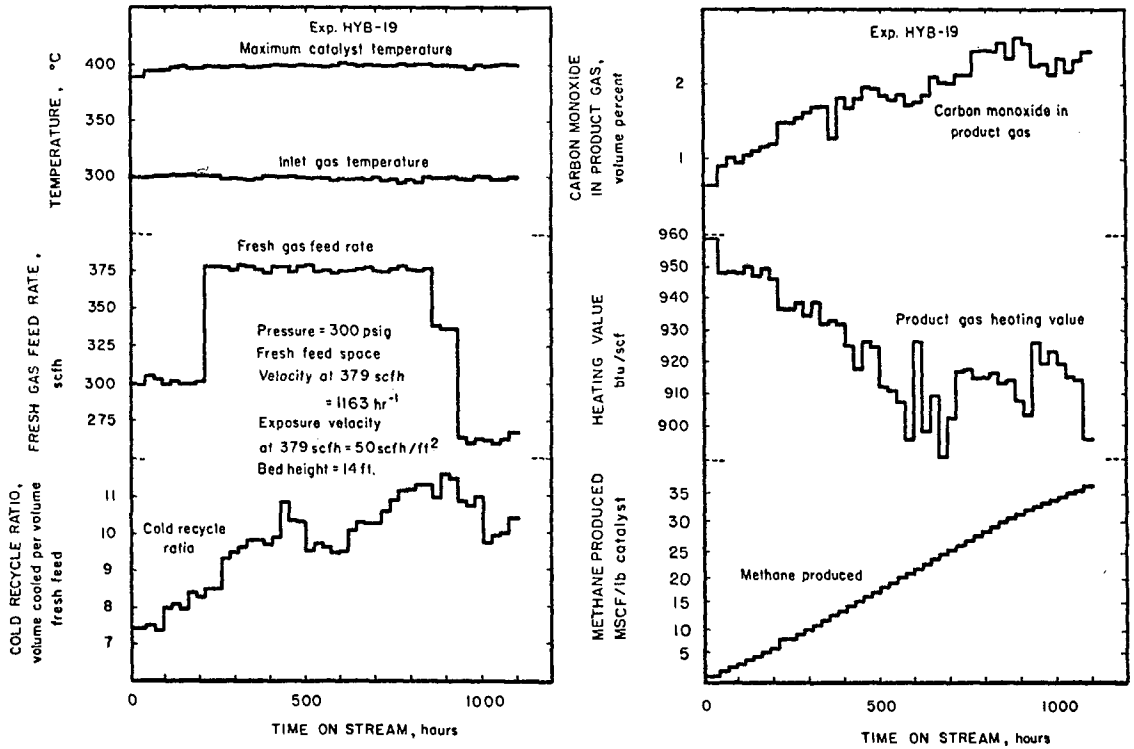

Figure 6. - Reactor conditions and product gas characteristics for Run HYB-19.

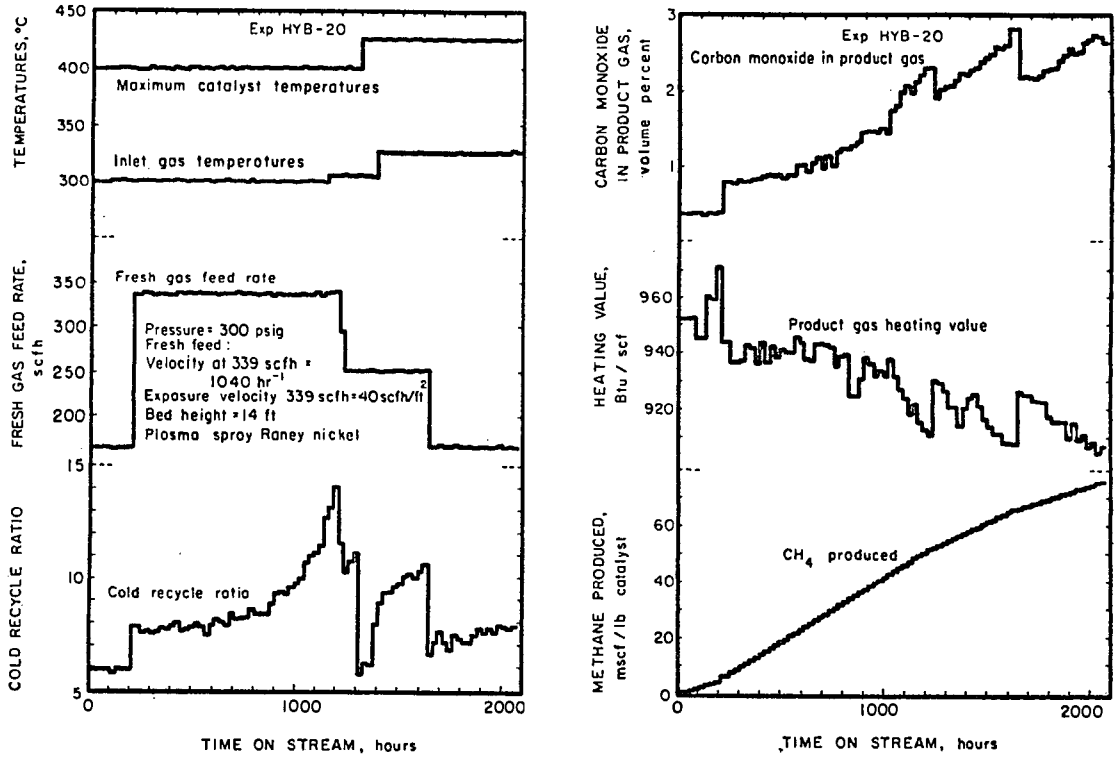

Figure 7. - Reactor conditions and product gas characteristics for Run HYB-20.

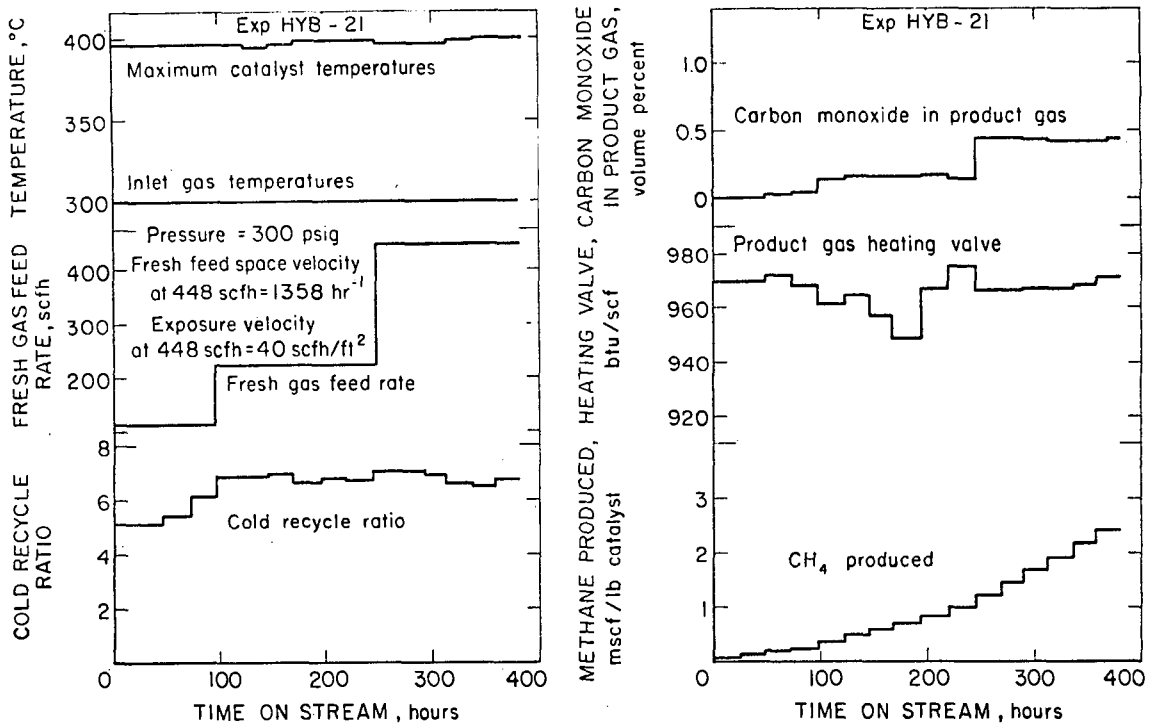

Figure 8. - Reactor condition and product gas characteristics for Run HYB-21.

Table 3. - Analysis of Spent Catalysts

	Ni	Al	C	S	Fe	Na	Species
HYB-17							
Inlet	68.1	8.6	4.68	-	0.27	0.08	Ni_3C
Center	74.6	8.8	1.71	-	0.24	0.08	Ni_3C, Ni
Outlet	72.3	9.0	0.20	-	0.25	0.08	Ni
HYB-18							
Inlet	64.1	10.4	2.0	0.3	0.5	4.5	Ni_3C
Center	68.0	11.7	0.7	0.2	0.4	4.9	-
Outlet	69.0	11.6	0.5	0.3	0.7	6.5	Ni
HYB-19							
Inlet	75.7	8.6	3.0	0.2	0.5	0.08	Ni, Ni_3C
Center	77.1	7.3	1.6	0.3	0.5	0.03	Ni
Outlet	75.7	6.6	1.1	0.2	0.4	0.03	Ni
HYB-20							
Inlet	76.5	8.8	3.4	0.1	0.3	<0.01	Ni_3C
Center	80.3	8.3	1.0	0.4	0.4	<0.01	Ni
Outlet	79.4	8.4	0.3	2.2	0.4	<0.01	Ni

profile along with nickel carbide is found in every case. Other contaminants such as S, Fe, and Na are not present in amounts significantly greater than those found in unactivated catalyst except for high sodium concentrations on Run HYB-18 catalyst. This probably is indicative of insufficient rinsing of the catalyst subsequent to the activation step. The high sulfur concentration measured at the exit of HYB-20 is unexplained. Possibly sampling and/or analysis errors are involved. Analysis of this sample is being repeated. Iron contamination had been a problem in experiments prior to the hybrid reactor tests. Iron carbonyl can form by reaction of CO at high pressure and low temperature (100° - 200° C) with carbon steel piping. The carbonyl is carried into the hot reactor where it thermally decomposes according to the reaction:

$$2Fe\ (CO)_5 \rightarrow 5C + 2Fe + 5CO_2$$

and deposits on the nickel catalyst creating an iron catalyst. At methanation temperatures, carbon deposition occurs on the iron and further fouls the catalyst. Iron concentrations as high as 22 percent in the catalyst at the reactor inlet had been detected in previous runs. This was accompanied by high carbon content. Before initiating the hybrid reactor experiments, all carbon steel piping in the pilot plant was replaced with stainless steel. Examination of the iron concentrations found on the spent catalyst samples from the hybrid runs in table 3 indicates that this was successful in alleviating the iron contamination problem. The BET surface areas, pore volumes and pore radii are shown in table 4. Measured BET surface area for HYB-17 and HYB-20 appear to be somewhat smaller than those for the other runs. No other trends in the data were clearly evident. Also shown on table 4 are the nickel metal surface area measurements as determined by hydrogen chemisorption. Metal surface area measurements were performed on a flame-sprayed catalyst, Run HYB-18, and a plasma sprayed catalyst, Run HYB-20. In both instances, metal surface area is lower at the reactor exit than at the inlet while in general, being lower for HYB-20 than for HYB-18. There is no immediate explanation for these trends in the data. Nickel metal surface area for freshly activated catalyst is in the neighborhood of 12 m^2/gm. The tentative conclusion regarding the cause for catalyst deactivation for this series of experiments, in view of the limited amount of data available, is the formation of nickel carbide and possibly additional carbon formation on the catalyst surface. It was not possible to distinguish free carbon from carbidic carbon.

Table 4. - Surface Areas Of Spent Catalysts

	Surface Area m^2/gm	Pore Volume cm^3/gm	Avg. Pore Radius Å	Nickel Surface Area m^2/gm
HYB-17				
Inlet	30.5	.076	50.07	
Outlet	23.7	.055	46.07	
HYB-18				
Inlet	53.4	.053	45.05	6.0
Outlet	50.2	.060	53.51	4.5
HYB-19				
Inlet	44.3	.095	42.8	
Outlet	32.8	.11	66.7	
HYB-20				
Inlet	32.77	.067	40.6	2.5
Outlet	23.73	.078	65.7	<1.0

MATHEMATICAL MODELING

Several recent publications (7, 8, 9, 10, 11) have discussed a one-dimensional mathematical model along with several applications of the model to tube-wall and parallel-plate, adiabatic (hot-gas-recycle) methanation reactors. Incorporated in the model was a postulated poisoning mechanism which obeyed an irreversible Langmuir-Hinschelwood type of rate equation. This one-dimensional model has been appropriately modified to describe the chemical and physical processes occurring in the hybrid methanation reactor.

The kinetic rate expression for the conversion of carbon monoxide to methane according to the reaction

$$CO + 3H_2 \rightarrow CH_4 + H_2O,$$

is taken to be that proposed by A. L. Lee (12, 13) which provides a reasonable fit to data reported by IGT. Lee's rate expression, developed from data for supported commercial nickel catalysts is of the form,

$$-r_{CO} = \frac{A\, e^{(-E/RT_C)}\, \tilde{C}_{CO}\, \tilde{C}_{H_2}^{\,1/2}}{1 + k_1 \tilde{C}_{H_2} + k_2 C_{CH_4}} \qquad 1)$$

Since the catalyst is deposited in a very thin layer, the catalyst thickness is neglected in the model and is considered to be only an active superficial surface. The kinetic rate is expressed as the number of moles of CO converted per unit time per unit superficial surface area of catalyst. The symbols, $\tilde{C}$, signify that these are concentrations at the surface of the catalyst as opposed to concentrations in the bulk stream. It should be noted that the concentration of methane at the catalyst surface is assumed to be the same as the bulk methane concentration. Due to the relatively large quantity of product gas that is recycled through the catalyst bed, methane is the major constituent in the gas at every point in the reactor. The assumption is made that negligible error is introduced by ignoring the methane concentration gradient between the bulk gas and the catalyst surface.

The construct envisioned for the description of the processes occurring in the hybrid reactor is the following. The reacting gas, flowing through a conduit in turbulent flow, is considered to be thoroughly mixed in the radial direction, i.e., there are no thermal or concentration gradients across the turbulent core (see figure 9). The reactants (CO and H_2) are transported across the laminar sublayer, adsorbed, react to form methane and water, and the products diffuse back into the turbulent core. There will be thermal and concentration gradients across the laminar film, the magnitudes of which depend upon the extent of diffusion control. Energy released in the methanation reaction is removed from the catalyst by convective heat transfer to the cooler bulk gas and thence to the cooling jacket and by radiation from the catalyst to the cooling jacket. A portion of the heat of reaction is also removed as sensible heat to the gas.

At steady state conditions there is no net change in reactant concentrations at the catalyst surface, thus, the rate of reaction must equal the rate at which CO and H_2 diffuse to the surface. The mass transfer rates are given by,

$$-r_{CO} = k_C\,(C_{CO} - \tilde{C}_{CO}) = j_{CO} \qquad \text{2-a)}$$

$$-r_{H_2} = -3r_{CO} = k'_C\,(C_{H_2} - \tilde{C}_{H_2}) = j_{H_2} \qquad \text{2-b)}$$

where k_C and k'_C are the film mass transfer coefficients for CO and H_2 respectively. The mass transfer coefficients are calculated, for a given Reynold's number, from the standard j-factor correlation (14, 15).

The following equations are taken to describe the heat transfer in the system.

$q = r_{CO}\mathcal{H}$ rate of heat generated by reaction 3-a)

$q_1 = h(T_C - T_G)$ heat flux between catalyst and turbulent core 3-b)

$q_2 = k\varepsilon\,(T_C^{\,4} - T_W^{\,4})$ radiation heat flux between catalyst and cooling jacket 3-c)

$q_3 = h'\,(T_C - T_W)$ heat flux by conduction through direct contact of insert with cooling wall 3-d)

$q_4 = h\,(T_G - T_W)$ heat flux between turbulent core and cooling wall 3-e)

$C_P M \dfrac{\partial T_G}{\partial a}\,\delta a = q_1\delta a - q_4\delta a'$ rate change of sensible heat of the gas 3-f)

In addition, we have the equation for the conservation of energy,

$$q = q_1 + q_2 + q_3. \qquad \text{3-g)}$$

In order to calculate the global rate of reaction at any point in the reactor, equations 1), 2), and 3) must be solved simultaneously. The method of finite differences is utilized to calculate local bulk concentrations and temperatures throughout the length of the reactor. The model used to describe catalyst deactivation in previous experiments has been reported elsewhere (7, 8) and will not be reiterated. This deactivation mechanism was found to inadequately predict deactivation rates for the hybrid methanation reactor. It is possible that, due to system plumbing

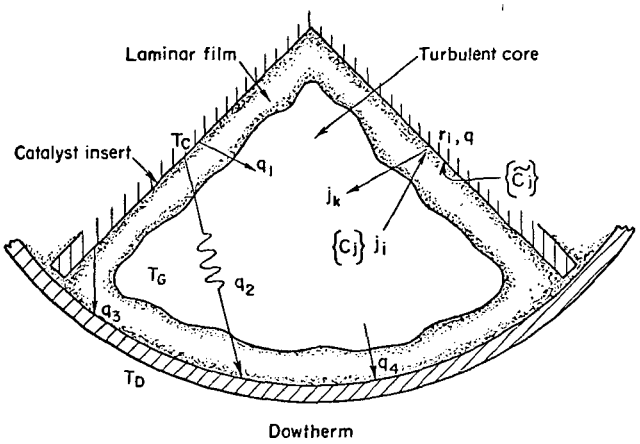

Figure 9. - Cross-section view of a quadrant of the reactor.

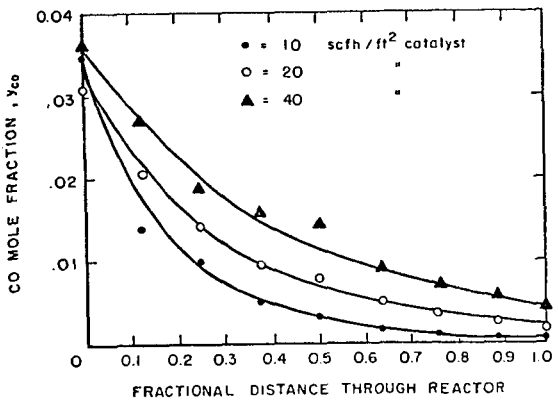

Figure 10. - Carbon monoxide mole fraction profiles for Run HYB-21. Solid lines indicate model predictions.

modifications, i.e. the substitution of carbon steel with stainless steel pipes, catalyst activation procedures, or the intrinsic difference in mode of reactor operation, the principal agent responsible for catalyst deactivation differs between the hybrid reactor and reactors previously operated. Nevertheless, the model is capable of satisfactorily predicting initial reactor performance. As an example, figures 10 and 11 illustrate the fit of the model to experimental composition and temperature profile data from Run HYB-21. Figure 10 is a plot of CO mole fraction as a function of distance through the reactor. Gas stream compositions were measured at 21 inch intervals through the reactor. The data represente operation at exposure velocities of 10, 20 and 40 scfh/ft^2 catalyst and wer taken early in the run before any deactivation of the catalyst was evident. The points indicate experimentally measured values whereas the solid lines represent the profiles calculated from the model. Agreement between model and experiment is seen to be quite good.

Temperature profiles for both catalyst and gas phase are illustrated in Figure 11. The three plots, once again, represent operation at 10, 20 and 40 scfh/ft^2 catalyst. The open circles are measured catalyst temperature while the ▲'s are gas phase temperatures. The temperatures predicted by the model (solid lines) are in good agreement with measured values. At the higher exposure velocities, the differences between model and measured values are, at most, 10-15° C. The percentages of the total heat liberated by the reaction which is transferred to the Dowtherm coolant are 86, 73 and 61% for the exposure velocities 10, 20, and 40 scfh/ft^2 catalyst, respectively.

SUMMARY

Four experiments were completed using the hybrid methanation reactor. A fifth experiment utilizing cast Raney nickel inserts has been initiated and preliminary results are encouraging. Each of the first four runs was terminated voluntarily with final CO conversions no less than 95-97 percent. The reactor was satisfactorily operated at an exposure velocity of 50 scfh/ft^2, comparable to those attainable in the tube-wall reactor, yet, as a result of the bed design, the catalyst can be easily replaced. The recycle ratio in a hot-gas-recycle methanator required to maintain a 100° C gas temperature difference across the catalyst bed is about 10/1. At comparable exposure velocities, the recycle ratio required to hold the catalyst temperature below 400° C in the hybrid reactor is as little as 5/1 - 6/1.

Although the hybrid reactor had a higher average productivity of methane per pound of catalyst than previous TWR and HGR experiments, it is possible that this is the result of decreasing the amount of iron carbonyl in the system rather than the nature of the reactor. Data, resulting from the four completed runs, do not indicate that plasma sprayed Raney nickel catalyst demonstrates a greater life at the pilot plant scale than flame sprayed Raney nickel. Data from the test using cast Raney nickel inserts are, of course, incomplete at the present time. Catalyst stability continues to be of prime concern in the research efforts at Pittsburgh Energy Research Center.

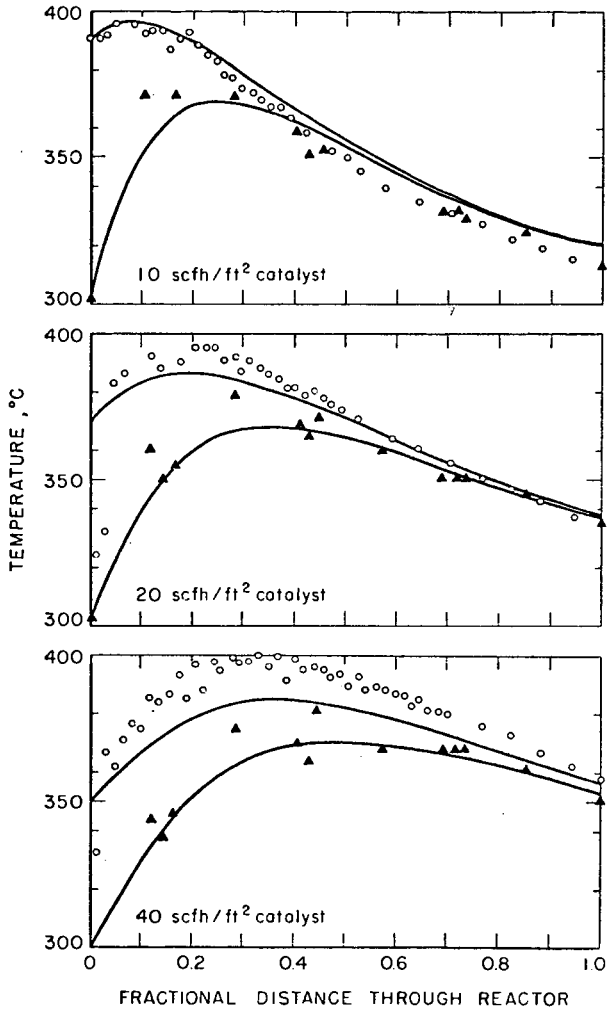

Figure 11. - Catalyst (O) and Gas (▲) temperature profiles for Run HYB-21. Solid lines indicate model predictions.

NOMENCLATURE

A= preexponential factor

C= concentration in bulk gas (lb mol/ft^3)

$\tilde{C}$= concentration at catalyst surface (lb mol./ft^3)

C_p= specific heat of gas (Btu/lb.mol. - °F)

E= activation energy (Btu/lb mol)

$\mathcal{H}$= heat of reaction (Btu/lb mol)

h= heat of transfer coefficient (Btu/hr-ft^2 - °F)

j= mass flux (lb. mol./hr-ft^2)

k= constant (Btu/hr-ft^2 - $°R^4$)

k_C= mass transfer coefficient (lb.mol./hr-ft^2-concentration difference)

k_1,k_2= equilibrium constant's

M= gas molar flowrate (lb.mol./hr)

q= rate of heat generated (Btu/hr-ft^2)

q_1= heat flux from catalyst to gas (Btu/hr-ft^2)

q_2= radiation heat flux between catalyst and cooling jacket (Btu/hr-ft^2)

q_3= heat flux by conduction through direct contact of insert with cooling wall (Btu/hr-ft^2)

q_4= heat flux from gas to cooling wall (Btu/hr-ft^2)

R= gas constant (Btu/lb.mol. - °R)

r= rate of reactant conversion (lb.mol./hr-ft^2 catalyst)

T= temperature (°R)

ε= emissivity (dimensionless)

δa= incremental catalyst surface area (ft^2)

δa'= incremental cooling wall surface area (ft^2)

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