Development of Catalysts and Reactor Systems for Methanation

J. H. Field, J. J. Demeter, A. J. Forney, and D. Bienstock
U. S. Bureau of Mines, 4800 Forbes Avenue,
Pittsburgh, Pennsylvania 15213

INTRODUCTION

The continued increase in the consumption of natural gas, the slowly declining reserves-to-consumption ratio, and the slow but steady increase in the price of natural gas have extended the interest in production of high-Btu gas from coal. Estimates of the time when supplemental gas will be required range from about 10 to 25 years, depending on the estimated rise in consumption and ultimate reserves (4).[1] Despite record production, reserves of natural gas are still increasing slowly. For example, while U.S. production increased to 13.75 trillion cubic feet in 1962, the reserves at the end of 1962 were 285.3 trillion cubic feet, an increase of 8 trillion cubic feet for the year, with gas well completions at an all time high at 5,848 (5). Importation of gas from Canada and Mexico and possibly of liquefied methane by tanker are other factors that will affect the need for supplemental gas. Nevertheless, synthetic pipeline gas from coal can insure a long-time domestic source of gas from an abundant raw material.

Research is continuing on the principal methods of producing high-Btu gas by coal hydrogenation, $C + 2H_2 \rightarrow CH_4$, and catalytic methanation of synthesis gas, $3H_2 + CO \rightarrow CH_4 + H_2O$. The synthesis gas is obtained by gasifying coal with steam. Direct hydrogenation has a higher possible thermal efficiency and requires only about half as much gas as methanation--1,500 to 2,000 cubic feet of hydrogen as compared with 3,000 to 4,000 cubic feet of synthesis gas per 1,000 cubic feet of methane. The 1,500-cubic-foot value is achieved by utilizing some of the hydrogen in the coal and converting only part of the carbon. The lower requirement of 3,000 cubic feet of synthesis gas for catalytic methanation can be realized when a gasification process is employed that yields a gas containing about 10 percent methane.

Despite the inherent advantage of hydrogenation over catalytic methanation, there are two reasons justifying continued development of the catalytic method. First, catalytic methanation, being a gas phase reaction conducted at mild conditions of about 300° to 350° C and 20 to 30 atmospheres, is much simpler to operate and technical feasibility is apparent. However,

1/ Underlined numbers in parentheses indicate items in the bibliography at the end of this paper.

process improvements are needed to improve the economics of catalytic methanation and its continued development is warranted. Additionally, catalytic methanation may be necessary in conjunction with direct hydrogenation to increase the heating value of the gas by converting the carbon oxides and residual hydrogen to methane.

In the past 20 years catalytic methanation has been investigated in fixed-bed and fluidized reactors. The principal objectives have been to develop reactor systems that permit effective removal of the exothermic heat of reaction in order to provide adequate temperature control and maintain a long catalyst life. Important contributions in catalytic methanation have been made in the past 20 years by Dent (2), Dirksen and Linden (3), Schlesinger, Demeter, and Greyson (6, 7) and Wainwright (8), and their coworkers. Our group at the Bureau of Mines has reported previously the development of a hot-gas-recycle system (1). This paper covers further methanation studies using hot-gas recycle and bench-scale tests of a newer reactor system, the tube-wall reactor, in which the wall of the tube is coated with catalyst.

EQUIPMENT AND EXPERIMENTAL RESULTS

In the hot-gas-recycle system, the temperature is controlled by recycling several volumes of tail gas to the reactor inlet per volume of feed gas. Low resistance to gas flow across the bed is necessary to keep the pressure drop low and to avoid the high compression cost of gas recycle. Earlier work using two reactors in series has been reported (1). A simplified flowsheet of the system is shown in figure 1. The bulk of the synthesis gas was converted over steel lathe turnings as catalyst in the first reactor; the remainder was converted over nickel catalyst in a second reactor. This system was tested in 3- and 12-inch-diameter reactors.

Recently, catalyst prepared by flame spraying a thin coat of Raney nickel on metal plates has been tested, figure 2, using $3H_2+1CO$ synthesis gas or the product gas from a reactor using steel turnings. This gas contains hydrogen, carbon monoxide, carbon dioxide, methane, and C_2 to C_5 hydrocarbons, and is similar to the product gas from hydrogenation except that it is somewhat higher in carbon oxides. It is, however, essentially sulfur-free. As shown in table 1 (column 2), the sprayed nickel after extraction and activation is highly effective for reacting product gas to increase the heating value. Most of the carbon oxides are hydrogenated, and the C_2 to C_5 hydrocarbons are hydrocracked to methane. The inlet and outlet reactor temperatures in the test shown were 300° and 338° C and the gas recycle ratio was 8 to 1.

In the tests using $3H_2+1CO$ gas with sprayed catalyst in a single reactor, gas with a heating value of 900 Btu per cubic foot has been produced. Typical results are shown in table 1 (column 1). Rather limited conditions have been tried to date. By modifying the gas throughput, temperatures, and gas recycle ratio, increased gas conversion and heating value can be obtained.

Recently most of the emphasis in methanation has been given to studies of a tube-wall reactor. The reactor, shown in figure 3, consists of two concentric pipes; the inner is made of 3/4-inch pipe or 1-1/8-inch tubing, and the outer is made of 1-1/2-inch stainless steel pipe. The outer surface of a 6-inch length of the inner tube is coated with a layer of catalyst about 0.02 inch thick, and the synthesis gas passes over the catalyst in the annulus of about 0.15 to 0.18 inch between the tubes. A concentric tube arrangement is used because the catalyst is applied by flame spraying and the inner wall of a small diameter pipe cannot be coated by this technique. The heat of reaction generated on the tube surface during methanation is transferred effectively to Dowtherm located within the center tube. The outer tube of stainless steel is not a methanation catalyst at the operating temperatures employed. Temperature measurements along the catalyst surface are made with a sliding thermocouple positioned in a well located in the annulus.

Tubes sprayed with Raney nickel are activated by immersing them in a 2-percent solution of sodium hydroxide at 30° to 95° C until 60 to 85 percent of the aluminum in the coating is converted to $NaAlO_2$ or Al_2O_3. The tube is washed thoroughly to remove excess alkali.

After a pretreatment with hydrogen, synthesis follows with $3H_2+1CO$ gas, usually at an hourly space velocity of 7,000 based on the annular volume. Gas recycle is seldom used because it is not required for heat removal or temperature control. Synthesis is continued until the heating value of the product gas is less than 900 Btu per cubic foot (CO_2- and N_2-free). The catalyst coating must be activated and pretreated in a prescribed manner to obtain a long catalyst life. Several tests were made in which the conversion declined rapidly within 100 hours or less of synthesis because the catalyst spalled and dropped off the tube surface. X-ray analysis showed that the spalled material was largely nickel carbide. In other tests at similar operating conditions, the catalyst remained intact and active, and nickel carbide was not present. It is believed that alkali remaining from the activation promoted the reaction

$$3Ni + CO + H_2 \rightarrow Ni_3C + H_2O.$$

This problem was overcome by prolonged rinsing of the catalyst following the activation.

TABLE 1.- Experiments using sprayed Raney nickel catalyst

	Experiment 30	Experiment 29
Metal base	Carbon steel	Stainless steel
Feed gas	$3H_2+1CO$	1/
Space velocity	1,500	5,800
Recycle ratio, recycle-to-fresh	26:1	8:1
Reactor temperature, °C		
Top, inlet	242	300
Bottom, outlet	284	338
Conversion, pct		
H_2	92.3	---
CO	95.6	---2/
H_2+CO	93.1	98.0
Heating value of product gas, Btu/cu ft3/	907	943
Product gas composition, vol-pct		
H_2	22.6	7.5
CO	4.3	0.8
CO_2	0.2	2.1
CH_4	65.3	87.2
C_2H_6	4.6	1.0
C_3-C_5	2.6	0.6
N_2	0.4	0.8

1/

H_2	56.7 pct
CO	4.0
CO_2	8.7
CH_4	23.6
C_2H_6	3.5
C_3-C_5	2.4
N_2	1.1
	100.0 pct

2/ Overall conversion of H_2+CO in synthesis gas.
3/ Volumes of dry gas at 60° F and 30 inches Hg.

Following the water rinse and drying, a hydrogen pretreatment has been found desirable for maximum catalyst activity. As shown in table 2, while the catalyst had considerable activity without hydrogen treatment (experiment 46), for most of the time on stream the heating value was lower than for comparable experiments. The gas conversion decreased from 97.4 to 95.4 percent relatively quickly in experiment 46, whereas in the other experiments in which the catalyst had been pretreated with hydrogen, the conversion remained near the initial level for several weeks. The heating value of the product gas changes appreciably with small changes of the conversion at these high conversion levels. Thus for experiment 46 it had declined to 905 Btu per cubic foot at 300 hours, while in experiments 43 and 44 it was about 950 Btu per cubic foot. The maximum prolonged high activity was obtained in experiment 44 where the catalyst was pretreated at 300° C and 100 psig for 20 hours and at 300 psig for 0.1 hour.

In experiments 19, 39, and 41 the effect of varying the thickness of the catalyst layer was studied. Data for these tests are given in table 3. Synthesis could not be sustained on the 0.009-inch layer used in experiment 19, and the desired heating value of the product gas could be obtained for only 8 hours. In tests 39 and 41, where the catalyst thicknesses were 0.019 and 0.057 inch, respectively, no difference in conversion and catalyst life was observed. It was possible to renew the activity of the thicker coating used in experiment 41 by scraping the fouled surface and repeating the caustic treatment of the new surface. However, it is not likely that the ultimate life of the 0.057-inch layer would be three times that of the 0.019-inch layer to compensate for the additional amount of catalyst applied.

Plots of the heating value of the product gas with time on stream for typical tests are shown in figure 4. The product contains 80 to 85 percent CH_4 and the balance H_2, CO_2, and CO as shown in table 4. The maximum operating time to date with the prescribed minimum heating value of 900 is slightly more than 1,200 hours. The production of high-Btu gas within this period amounted to 180,000 cubic feet per pound of catalyst, giving a low catalyst cost of under 1 cent per 1,000 cubic feet based on a cost of $1.50 per pound for the applied and treated catalyst.

Temperature control has been excellent in the tube-wall reactor. Figure 5 shows temperature profiles along the catalyst surface as indicated from the readings of the movable thermocouple during an early and later period of operation. The temperature peak indicating the area where the bulk of the reaction occurs is located initially about 1 inch below the gas inlet, and then moves down the tube with time on stream. A possible explanation for this occurrence is that the surface gradually becomes deactivated because traces of sulfur in the synthesis gas react with the nickel. Analyses of the coating indicate some localized accumulation of sulfur.

TABLE 2.- Variation of hydrogen pretreatment[1]

Expt. No.	Hydrogen pretreatment		Time on synthesis, hr. 20	300	500	Synthesis[2] life, hr.
43	20 hr. at 25 psig, 350° C; 0.3 hr. at 300 psig, 350° C	H_2+CO conversion, pct.	98.1	97.5	95.2[3]	479
		Heating value, Btu/cu ft[4]	964	952	898	
44	20 hr. at 100 psig, 300° C; 0.1 hr. at 300 psig, 300° C	H_2+CO conversion, pct.	97.7	97.7	97.4	1,200
		Heating value, Btu/cu ft	953	956	949	
46	No pretreatment	H_2+CO conversion, pct.	97.4	95.4	95.2	730
		Heating value, Btu/cu ft	949	905	901	

1/ Catalyst coating about 0.02 inch; 12.4 gram catalyst activated; activated with 2 percent NaOH solution and water washed 24 hours to remove excess alkali.
2/ Hours at 7,000 hourly space velocity with the heating value of the product at least 900 Btu/cubic foot.
3/ At 479 hours.
4/ Volumes of dry gas at 60° F and 30 inches Hg.

TABLE 3.- Variation of thickness of catalyst coating

Expt. No.	Thickness catalyst layer, in.	Catalyst activated, gram		Time on synthesis, hr. 20	300	500	Synthesis[1] life, hr.
19	0.009	6.7	H_2+CO conversion, pct.	--	--	--	8
			Heating value, Btu/cu ft[2]	--	--	--	
39	.019	12.0	H_2+CO conversion, pct.	98.2	97.4	95.7	650
			Heating value, Btu/cu ft	967	949	912	
41	.057	12.1	H_2+CO conversion, pct.	98.0	97.3	96.4	678
				957	944	926	

1/ Hours at 7,000 hourly space velocity with the heating value of the product at least 900 Btu per cubic foot.
2/ Volumes of dry gas at 60° F and 30 inches Hg.

TABLE 4.- Operating and yield data, tube-wall reactor, experiment 44

Catalyst age, hr.	263	1,107
Hourly space velocity of feed gas	7,000	7,000
Average catalyst temperature, °C	363	366
Maximum catalyst temperature, °C	390	390
Location of maximum temperature, inches from top	1	2.3
H_2 conversion, pct.	97.0	95.2
CO conversion, pct.	100	98.8
H_2+CO conversion, pct.	97.8	96.1
Product gas analysis, vol pct.		
H_2	7.7	12.0
CO	0	1.0
CO_2	5.2	5.6
CH_4	85.2	80.1
C_2H_6	0.1	0.4
N_2	1.8	0.9
Heating value of product gas (CO_2- and N_2-free), Btu/cu. ft.1/	957	920

1/ Volumes of dry gas at 60° F and 30 inches Hg.

The effectiveness of heat removal in the tube-wall reactor can be shown from the heat transfer coefficient. Based on the estimated heat release and the differential between the average temperature of the tube surface and that of the boiling Dowtherm of 30° F, an overall heat transfer coefficient of 250 Btu per hour-square foot-° F has been calculated for the reactor. This high value indicates that convective heat transfer is of little significance and that the heat is evolved at the catalyst surface and is removed through the tube wall to the boiling Dowtherm.

CONCLUSIONS

Progress has been made in developing reactor systems for methanation that provide effective heat transfer and excellent temperature control. Raney nickel sprayed on plates or tube surfaces and extracted with alkali has proved to be an active and durable catalyst. The nickel is thoroughly utilized by being applied in a thin layer. The life of the catalyst has been sufficient to attain a low catalyst cost per unit of product gas. This is an important objective because the catalyst is the most expensive item in the methanation step regardless of the type of reactor. Because either $3H_2$+1CO synthesis gas or partially converted gas can be reacted, product gas from hydrogenation of coal can be upgraded in heating value.

A tubular reactor with a catalyst coating on the wall shows promise for methanation. Potentially the tube-wall reactor has advantages of need for little or no gas recycle, efficient catalyst utilization, low pressure drop and power consumption, and the combined function of reactor and heat recovery in one vessel. Low capital and operating costs for the methanation step can result from these features. Thus far, only a small tube has been used, and further investigation will be made in a larger reactor. For full-scale operatinn the reactor is visualized as a common multipass tube and shell heat exchanger with the tubes coated on their outer surface and the gas passing across the baffled tubes. Six reactors, each comprised of a 10-foot-diameter shell containing 2-inch tubes on 3-3/8-inch centers and 30 feet long, would be ample for a 90-million-cubic-foot-per-day methanation plant.

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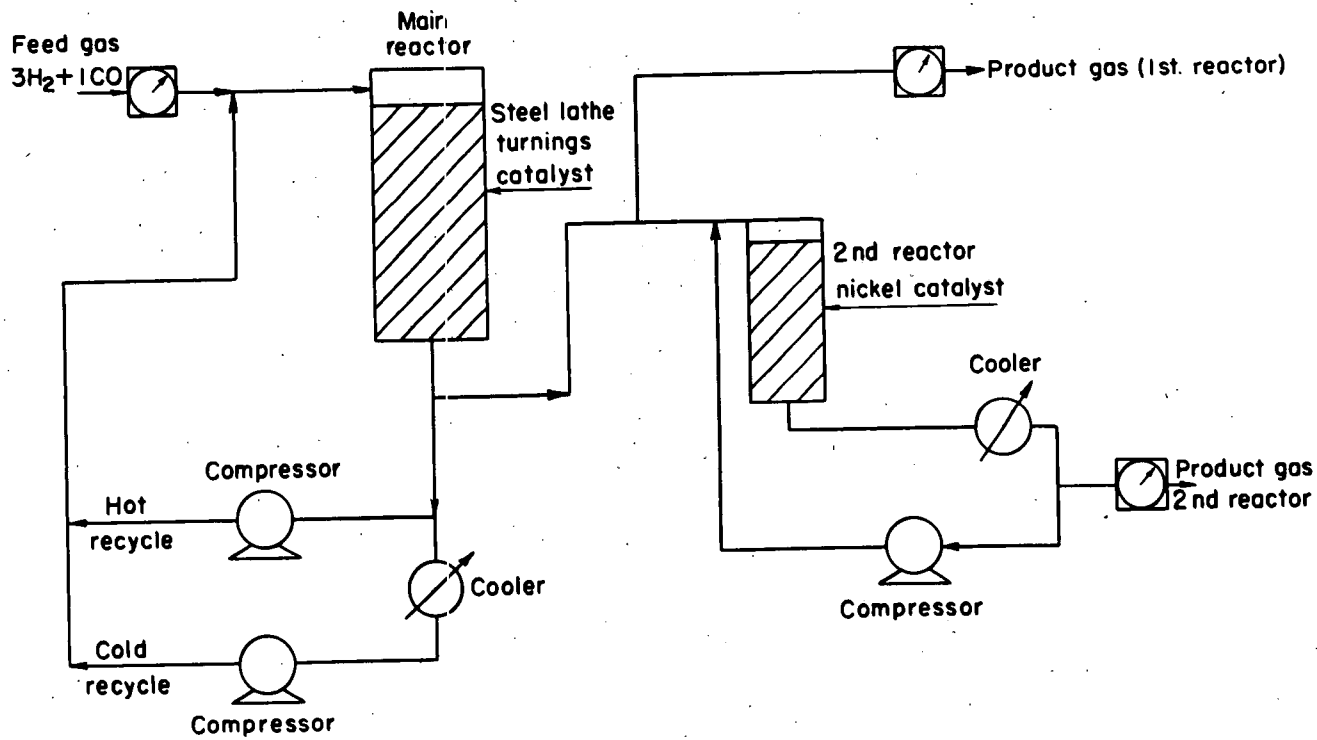

Figure 1. - Flowsheet of hot-gas-recycle process.

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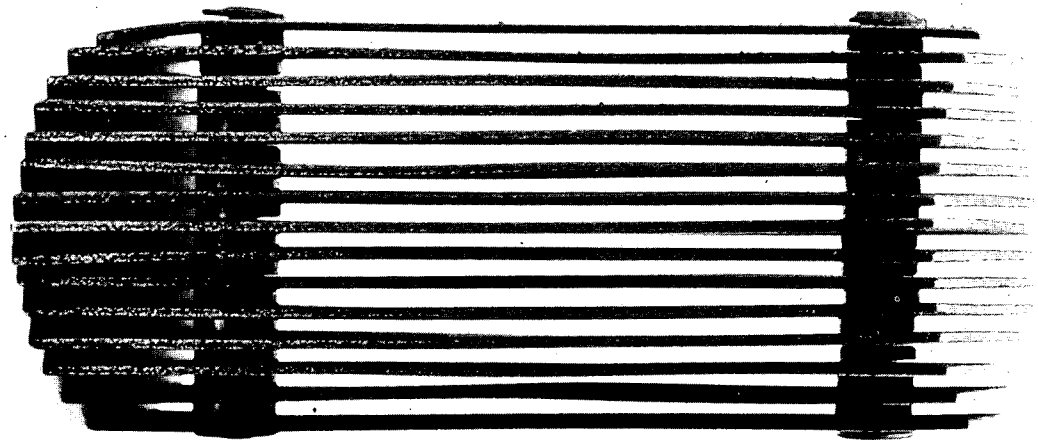

Scale, inches

Figure 2.- Catalyst prepared by flame spraying a thin coat of Raney nickel on metal plates.

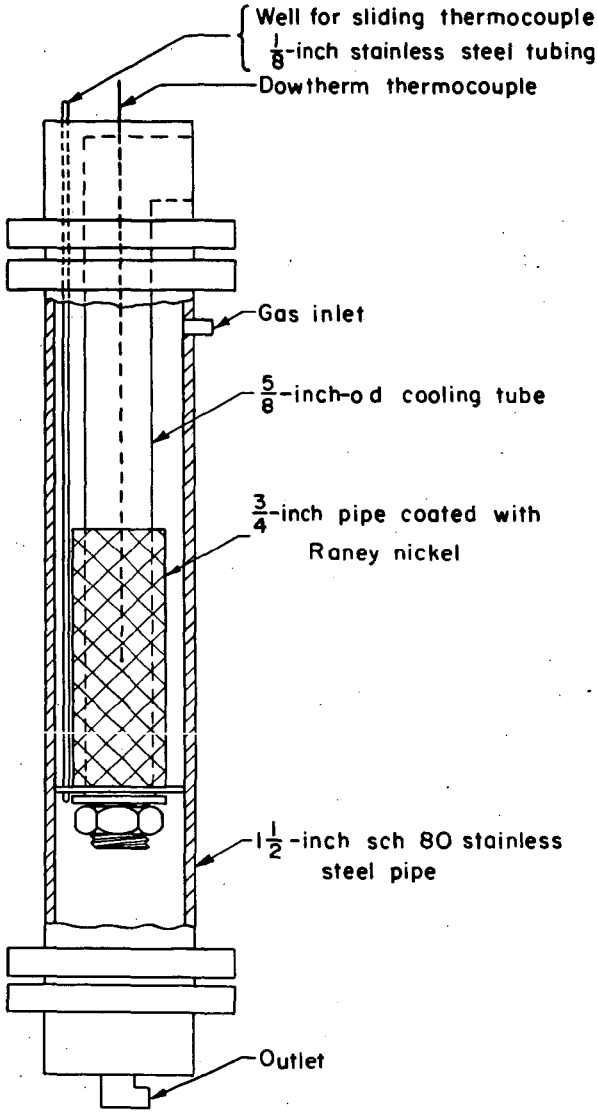

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Figure 3.- Reactor for testing Raney nickel in catalyst coated tubes.

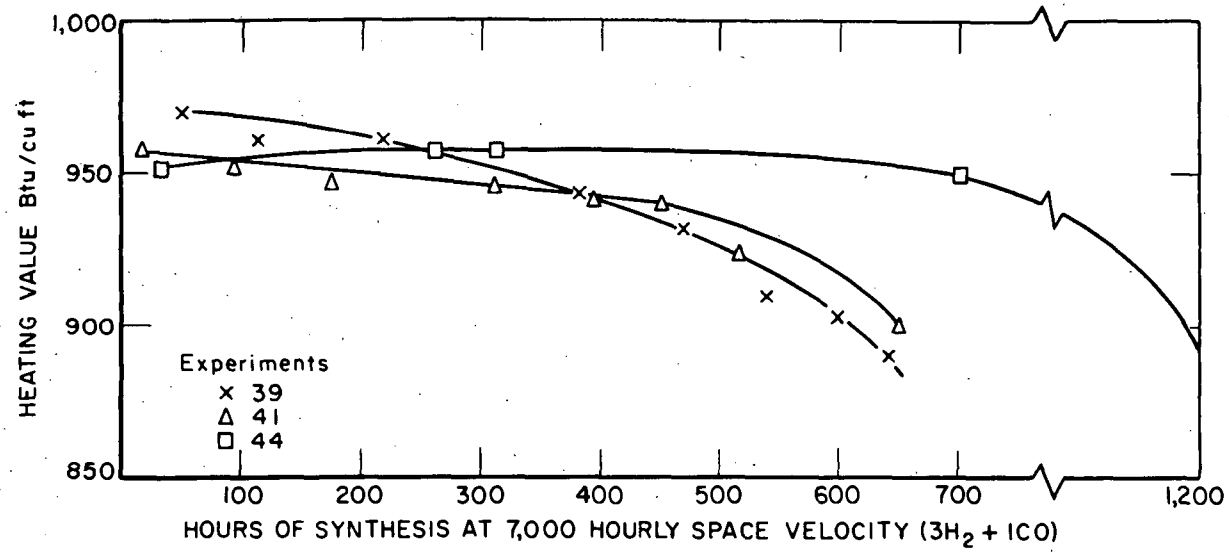

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Figure 4.- Tube-wall reactor: Heating value changes with time of operation.

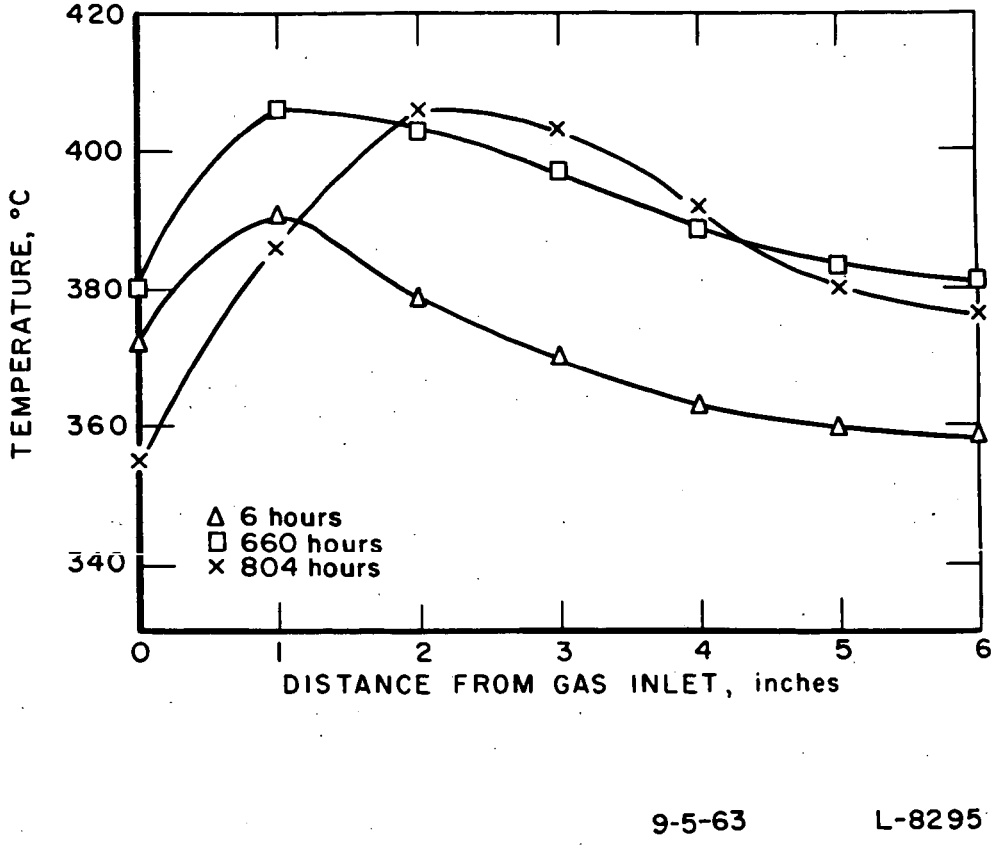

Figure 5.- Temperature profile, tube-wall reactor.