OPERATION OF A SPRAYED RANEY NICKEL TUBE WALL REACTOR FOR PRODUCTION OF A HIGH-BTU GAS

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INTRODUCTION

Almost all processes for the production of high-Btu gas from coal require a clean-up methanation step to upgrade the product gas to a heating value of at least 900 Btu/SCF. Such upgrading is needed both after steam-oxygen gasification of coal and after most processes for hydrogasification of coal. Methanation over a nickel catalyst is one of the most promising methods of achieving the required heating value. A major difficulty in the development of a suitable catalytic methanation reactor is in controlling the temperature of the highly exothermic reaction $3H_2 + CO \xrightarrow[400^\circ C]{Ni} CH_4 + H_2O$, where the heat of reaction is about 65 Btu/SCF of feed gas converted. Efficient heat removal is required to prevent excessive reaction temperatures and catalyst deterioration.

Catalytic synthesis of methane has been studied in various reactor configurations, such as :

(a) Fixed-bed reactor, with cooling achieved through heat exchange surface; (1) (2)[1/]

1/ Numbers in parentheses refer to references at end of paper.

(b) Fixed-bed reactor, cooled directly by gas recycle (3) (4) (5);

(c) Fluidized-bed reactor, cooled indirectly by heat exchange surface (6) (7); and

(d) Tube-wall reactor, where the catalyst is cooled because of being integral with or bonded to heat-exchanger tubes (8) (9).

The bench-scale developmental work performed at the Bureau of Mines on 1.2" and 1.3" outside-diameter single-tube tube-wall reactors has indicated that such reactors, with tubes coated with Raney nickel catalyst, provide excellent temperature control and result in high yields per weight of catalyst of up to 300,000 SCF of high-Btu gas per pound of catalyst (10). Development of the tube-wall reactor, therefore, is proceeding at the pilot-plant level in a multitube reactor unit. The initial experimental work performed in the pilot plant unit is reported in this paper.

Equipment

The tube-wall reactor used in this series of experiments was a multitube unit, as shown in figures 1 and 2. The shell of the reactor is 8-inch, schedule-40 stainless-steel pipe, with an overall length of 11 ft. The unit contains 7 catalyst tubes, each 2 inches in diameter by 7 ft long. The outer surface of each tube is thermally sprayed with Raney nickel over a length of 6 feet and to a depth of

0.020-0.030 inch. Each catalyst tube has a 1-inch diameter dip-tube down the center. Liquid Dowtherm* passes down the dip-tube and then boils as it passes upward through the annulus to remove the heat of reaction. The Dowtherm vapor enters the condenser above, is indirectly cooled and condensed with water, and then by gravity feeds back into the center tube. To achieve good contact between gas and catalyst, the coated lengths of the sprayed tubes are baffled so that the synthesis gas, as it passes upward through the reactor, is forced by the horizontal baffles to take a tortuous path across the tube surfaces.

Thermocouple wells were mounted along the length of the catalyst surface of four tubes. Three thermocouples were placed in each well and were spaced 2 feet apart. A calibrated and motorized drive moved these thermocouples a total of 2 feet to permit measurement of catalyst temperatures in 1-inch increments along the entire 6-foot length of each of the four tubes.

A schematic flowsheet of the reactor system is shown in figure 3, where it is shown that the feed gas to the reactor is preheated by a series of three heat exchangers. The first exchanger is steam-heated, the second exchanger recovers sensible heat from the hot product gas, and the third is heated by Dowtherm vapor. Product water is condensed from the product gas stream; then part of the dry product gas is returned to the feed gas stream. Recycle of dry product gas reduces

* Reference to trade names is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

the water vapor concentration of the reaction gas and thereby helps to maintain the activity of the catalysts as well as increase the yield of methane (10).

Fresh synthesis gas is made from natural gas in a Girdler plant and stored in 60,000 ft^3 holders until needed. The gas then is compressed to 500 psi, passed through a silica gel trap for dehumidification, then through two charcoal traps in series to remove sulfur compounds. A continuous analyzer records the sulfur concentration in the feed gas which is maintained below 0.1 grain H_2S/1000 SCF. Analyses of fresh gas and product gas were performed by mass spectrometry and gas chromatography. Impurities O_2, N_2, and CO_2 were present in the fresh synthesis gas in the range of 0.1, 0.4, and 0 to 1 percent, respectively.

Operation

After the reactor system was assembled and leak-tested, the Raney nickel catalyst (42% Ni + 58% Al) was activated in place by treatment at 90° C temperature with 2 wt pct sodium hydroxide solution. After the aluminum was leached to the extent desired, as indicated by measurement of hydrogen evolution, the caustic solution was displaced with water, and the catalyst was washed with 20 gal per hr of cold tap water for about 24 hours. Distilled water was then used until a reasonably constant pH was attained in the wash water. In experiment TWR-1, a pH of 5.7 was reached after 48 hours washing; in experiment TWR-2, a pH of 9.0 was reached after 45 hours. These values were about 0.2 above pH of the fresh distilled water. After the water was drained, the activated catalyst was kept under a hydrogen

atmosphere until synthesis gas was fed to the reactor. The amount of aluminum digested was 85 percent in the first experiment and 50 percent in the second experiment. Catalyst in experiment TWR-2 was activated an additional 20 pct after 964 hours operation.

After activation of the catalyst, the unit was brought to operating pressure and temperature under an atmosphere of hot recycling hydrogen. Before the synthesis gas was admitted to the system, catalyst tube surface temperatures ranged from 325° to 339° C in experiment TWR-1 and from 369° to 387° C in experiment TWR-2.

Synthesis gas was fed into the system which was then brought to desired steady-state conditions by adjustment of gas flows, reactor pressure, and catalyst temperature. A minimum synthesis temperature of 390° C was reached within 5 hours in experiment TWR-1 and within 1 hour in experiment TWR-2.

Results

Most of the operating conditions over the length of experiments TWR-1 and TWR-2 are shown in figures 4 and 5. Heating values of the N_2-, O_2-free dry product gas are shown. Values of the H_2:CO ratio of the feed gas are not shown, but they ranged from 2.27 to 3.35.

Additional data, including H_2/CO ratios, conversions, product gas analysis, and yields, at selected times in experiments TWR-1 and -2 are presented in tables 1 and 2. The average temperatures shown

in tables 1 and 2 represent the average of temperatures of 4 tubes at some common distance from the gas inlet determined to be the hottest point in the reactor. The maximum temperatures are plotted in figures 4 and 5.

Discussion of Results

General Performance

The length of experiment TWR-1 was 338 hours. During the initial 100 hours of operation at a feed rate of 600 SCFH and maximum catalyst temperature of 398° to 401° C, the heating value of the product gas gradually decreased from 950 to 910 Btu/SCF[2/]. This decrease indicated that the catalyst immediately began to lose activity. Overall loss of catalyst activity by the end of the experiment was so great that the heating value of the product gas fell to 720 Btu/SCF when the feed rate was 600 SCFH and maximum catalyst temperature was 403° C.

The length of experiment TWR-2 was 1055 hours, including the hours of synthesis after the second activation; this indicates that loss of catalyst activity was much slower than in the case of test TWR-1. After 675 hours of operation, product gas of 900 Btu per SCF heating value was being produced at 402° C maximum catalyst temperature, 300 psi, and 600 SCFH fresh feed rate. The increase in catalyst life in experiment TWR-2 is attributed to the repression of nickel carbide formation which is discussed later.

2/ Heating values are based on N_2- O_2-free gas with SCF taken at 60° F, 30 in. Hg. and dry.

The second activation of the catalyst in experiment TWR-2 improved the catalyst activity significantly, as is indicated by resultant increases in the heating value of the product gas. For example, as shown in figure 5, before the second activation at 964 hours, the product gas heating value was 690 Btu/SCF for a feed gas rate of 2400 SCFH; after the second activation and at 1055 hours, the heating value increased to 765 Btu/SCF for the same feed gas rate. The catalyst life in experiment TWR-2 might have been longer had the catalyst been activated to 70 pct initially rather than 50 pct. Dirksen and Linden (6) indicated that at activation of at least 65 pct of the catalyst is required for long catalyst life.

Although the system had charcoal traps to remove organic sulfur from the fresh synthesis gas, sulfur concentrations of up to 0.8 wt pct were determined on samples of the used catalyst in experiment TWR-2. This suggests that sulfur poisoning contributed to the decrease in catalyst activity.

Heat removal and control of catalyst temperature by means of the Dowtherm coolant was excellent. In both experiments, there were no runaway temperatures at any time.

Conversion and Gas-Feed Rate

As shown in tables 1 and 2, in the first part of experiment TWR-1, conversion of $CO + H_2$ was as high as 99 pct at a gas feed rate of approximately 600 SCFH; and 97.9 pct at approximately 1200 SCFH. In comparison, conversion of $CO + H_2$ during the early part

of experiment TWR-2 was lower; for example, at 71 hours conversion was 95.5 pct at about 1200 SCFH feed gas rate. This relatively lower conversion in experiment TWR-2 was caused by the excess of hydrogen in the feed gas, as shown by the H_2:CO ratios greater than 3:1. Such hydrogen excess lowers the heating value of the product gas by acting as a diluent, but at the same time, favors CO usage.

The comparatively lower values of CO in the product gas of experiment TWR-2 are notable. Such high usage of CO is desired because it represses carbide formation, indicates good catalyst activity, and provides a pipeline gas of low toxicity.

As gas feed rates were increased to about 2400 SCFH or 106 SCFH per sq ft catalyst surface, CO + H_2 conversion decreased significantly. For example, in experiment TWR-2 at 71 hours and 267 hours, respectively, conversion dropped from 95.5 pct at 1216 SCFH feed rate to 89.4 pct at 2432 SCFH feed rate. This performance is considerably lower than that achieved in earlier bench-scale experiments (10) on a signle-tube tube-wall reactor where conversions of greater than 98 pct were sustained for more than 1200 hours at gas feed rates of 105 SCFH per sq ft catalyst surface. Two other possible reasons (in addition to the presence of excess hydrogen) for the lower performance in the multitube reactor are that diffusional distances from the bulk gas to the catalyst surface for the multitube unit were several-fold greater than for the single tube unit and that turbulent mixing in the large multitube unit was poorer than in the

highly baffled bench-scale unit. Future modifications to the multi-tube reactor will improve these two factors.

Carbide Formation

In experiment TWR-1, formation of nickel carbide and flaking of the catalyst from the surface are suspected of contributing to the rapid decline in catalyst performance. Nickel carbide formation was verified by X-ray analyses of samples scraped from the surface of the spent catalyst tubes. The analyses showed in order of declining abundance: Ni_3C; Ni; aluminum nickel catalyst (cubic F.C.); and Ni_xC ($x>4$). Nickel carbide predominated at both the gas outlet and inlet ends of the catalyst tubes and in catalyst particles accumulated in the reactor bottom. Formation of nickel carbide was the result of too much exposure of the catalyst to CO at temperatures favoring carbide formation, less than 370° C.

Experiment TWR-2 was conducted with the aim of repressing carbide formation and achieving higher catalyst performance than was achieved in TWR-1. One step taken to minimize carbide formation was to get the catalyst temperature above the carbide formation region as soon as possible (within 1 hour) during start of synthesis and to maintain the catalyst temperature above 390° C throughout synthesis. The quick start-up was achieved by preheating the reactor and feed gas to higher temperatures than those used in experiment TWR-1. Another step

taken to inhibit carbide formation was to use a feed gas that contained excess hydrogen. These approaches proved effective, as shown by X-ray analyses of the catalyst surface at the conclusion of the experiment. Free nickel was the major constituent found on the catalyst surface, while nickel carbide (Ni_3C) was found to a lesser extent. No carbide was found at the gas outlet end of the catalyst tubes.

Catalyst Bonding

Inspection of the tube bundle at the conclusion of test TWR-1 showed that large segments of the catalyst had flaked from the tubes. Figure 6 is a photograph of a section where flaking occurred. Such flaking was not evident at the end of test TWR-2. A suggested explanation of the more stable bond in test TWR-2 is that the lower percent activation of the catalyst with caustic solution resulted in less initial disturbance of the bond between catalyst and tube than had occurred in test TWR-1.

Temperature Profile and Heat Removal

Temperature profiles measured along the catalyst tubes indicated that the amount of reaction occurring along the length of the catalyst tubes was dependent upon the following: velocity and direction of gas flow, distance from point of gas entry, and location of baffle plates.

Figure 7 shows a typical temperature profile of one of the catalyst tubes (tube F) in experiment TWR-1 after 50 hours of operation; feed gas rate is about 600 SCFH and recycle ratio is 1:1. The direction of gas flow was parallel, rather than normal, to the tube surface at the points of temperature measurement. On tube F, temperature peaks generally coincide with the location of a baffle plate. Temperature profiles of some of the other tubes showed peak temperatures at every other baffle plate. No satisfactory explanation of these patterns has been established. It has been noted that average tube temperatures may vary by up to 5° C from tube to tube.

Dowtherm temperatures remained relatively constant along the length of the catalyst tube. Typically, at 532 hours operation in experiment TWR-2, Dowtherm temperatures as measured in tube G were 386° C at the bottom, 386° C at the middle, and 387° C at the top. This indicates that Dowtherm circulation was good. Based on a heat release of 65 Btu per SCF synthesis gas converted during the 532-hour period and a difference of 18.2° F between the average tube surface temperature and the average Dowtherm temperature, the calculated overall heat transfer coefficient of the reactor is 182 Btu per hour per sq ft per ° F. This is of the same magnitude as the value of 275 Btu per hr per sq ft per ° F reported for a 3-ft single tube bench-scale unit (10).

Conclusion

A pilot-plant size tube-wall methanation reactor has been operated satisfactorily in two tests, providing excellent temperature control and needing a modicum of gas recycle. Catalyst life and yields of product gas were not as great as those achieved in previous bench-scale tests. However, use of higher temperatures and excess hydrogen in the second test inhibited carbide formation and increased catalyst life significantly over that of the first test. In future tests, a further increase in catalyst life should be achieved by a more rigorous removal of sulfur from the feed gas and a more complete activation of the catalyst. A satisfactory 900 Btu per SCF product gas was yielded at a specific feed rate of about 54 SCFH per sq ft catalyst. A reduction in excess hydrogen fed to the reactor and, possibly, an improvement in contacting of the gas and catalyst are needed to yield a satisfactory product gas at the higher gas feed rate of 105 SCFH per sq ft of catalyst surface, formerly achieved in the Bureau of Mines bench-scale units.

TABLE 1. - Selected operating results at various times in Experiment TWR-1

Synthesis, hours	22	48	145	192	312	336
System pressure, psig	300	300	300	300	400	400
Fresh gas rate, SCFH	677	607	1214	2383	1213	614
Fresh gas/catalyst area, $SCFH/ft^2$	30.1	27.0	54.6	106.2	54.0	27.3
Vol. recycle/vol. fresh gas	0.86	0.87	1.11	1.04	1.94	1.97
Vol. product gas/vol. fresh gas	0.27	0.267	0.276	0.406	0.406	0.343
H_2/CO in fresh gas	2.40	2.43	2.93	2 59	2.59	2.73
Catalyst temperature, ° C:						
Average	380	393	399	398	398	400
Conversion, pct:						
H_2	99.0	98.8	97.0	76.5	77.8	86.2
CO	98.7	100.0	99.8	78.0	72.2	85.5
$CO + H_2$	99.0	99.0	97.9	76.9	75.9	86.0
Product gas composition, vol. pct (N_2-free):						
H_2	2.9	3.5	7.9	42.2	38.1	28.5
CO	1.3	0.0	0.2	14.2	21.2	12.4
CO_2	3.6	4.8	3.8	3.0	2.4	1.3
CH_4	92.2	91.7	88.1	40.2	38.2	57.7
C_2H_6	--	--	--	0.4	0.1	0.1
Product gas heating value, Btu/SCF 1/	948	941	919	598	581	720
Product water, lb/hr	4.17	3.91	14.5	13.3	11.4	5.45

1/ SCF based on 60° F and 30 in. Hg., dry

TABLE 2. - Selected operating results from Experiment TWR-2

Synthesis, hours	71	167	267	387	508	532	731	916	922
System pressure psig	300	300	300	300	300	300	300	400	400
Fresh gas rate, SCFH	1217	2388	2432	2419	604	1217	1222	1213	1218
Fresh gas/catalyst area, $SCFH/ft^2$	54.2	106.5	108.3	107.8	27.0	54.3	54.4	54.1	54.3
Vol. recycle/vol. fresh gas	2.0	1.0	0.99	1.01	2.96	1.47	0	2.00	0
Vol. product gas/vol. fresh gas	0.251	.309	.341	0.345	.280	0.296	0.319	0.307	0.324
H_2/CO in fresh gas	3.18	3.02	3.34	3.35	3.09	3.09	2.93	3.16	2.93
Catalyst temperature, ° C:									
Average	406	407	408	411	405	408	405	406	408
Conversion, pct:									
H_2	94.0	92.7	86.0	85.0	94.4	92.9	89.3	91.4	89.6
CO	100	99.3	100	99.4	100	100	100	96.4	100
$CO + H_2$	95.5	95.4	89.4	88.6	95.7	94.6	88.1	92.7	92.3
Product gas composition, vol. pct. (N_2-free):									
H_2	18.0	17.9	30.9	32.8	15.3	18.2	24.2	20.5	23.5
CO	----	0.5	----	0.4	----	----	----	3.1	----
CO_2	0.2	1.2	0.8	0.9	.3	1.3	3.5	3.0	2.8
CH_4	81.8	79.1	68.3	65.9	84.4	80.5	72.3	69.1	73.5
C_2H_6	----	----	-----	----	----	----	----	----	0.2
Product gas heating value, Btu/SCF 1/	887	861	792	775	905	875	811.1	777	825
Product water, lb/hr	12.1	25.7	26.5	25.4	6.59	13.3	10.4	15.8	10.8

1/ SCF based on 60° F and 30 in. Hg. dry

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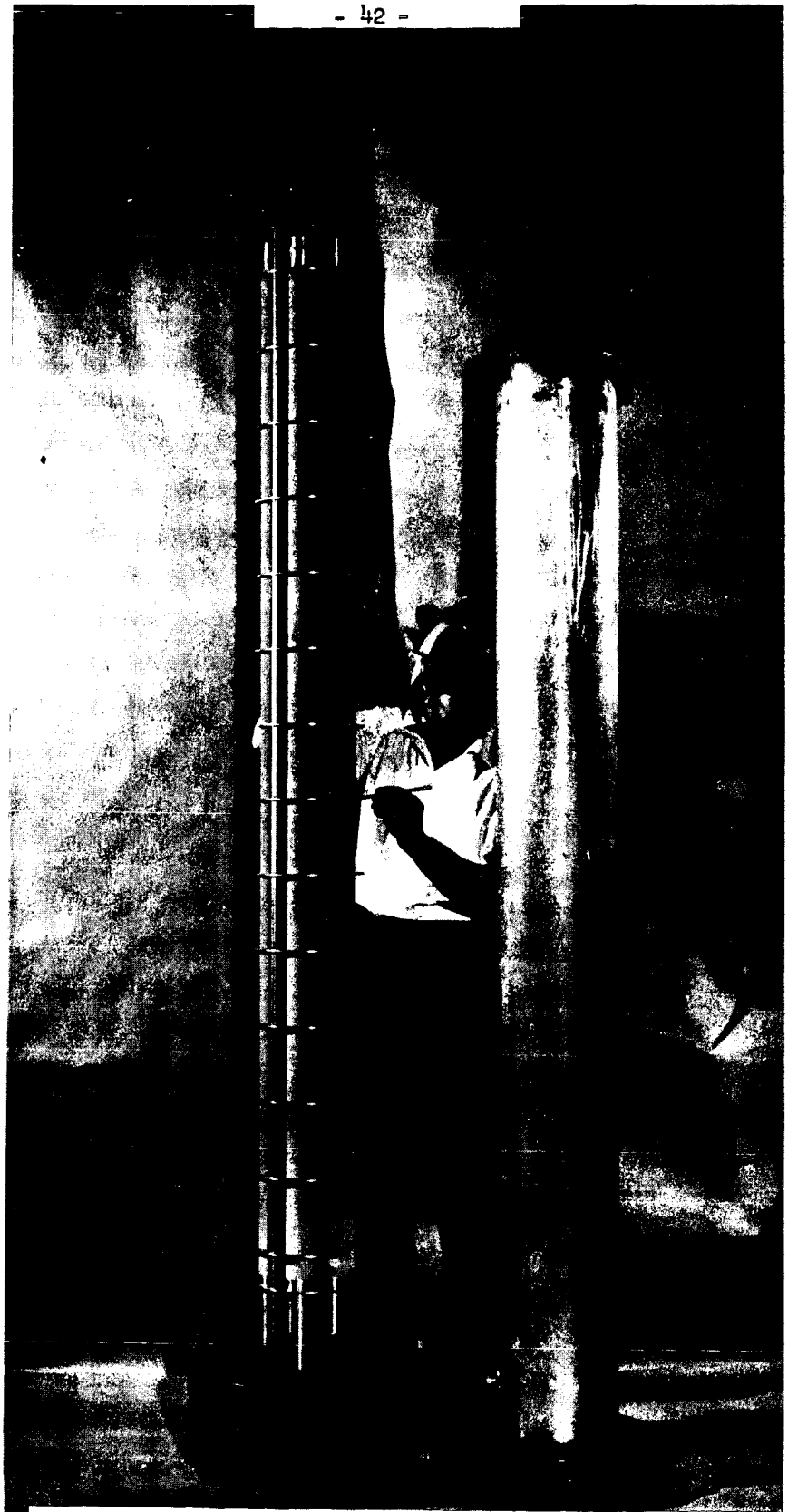

Figure 1. Catalyst Tubes and 8-inch Shell of Multitube Methanation Reactor

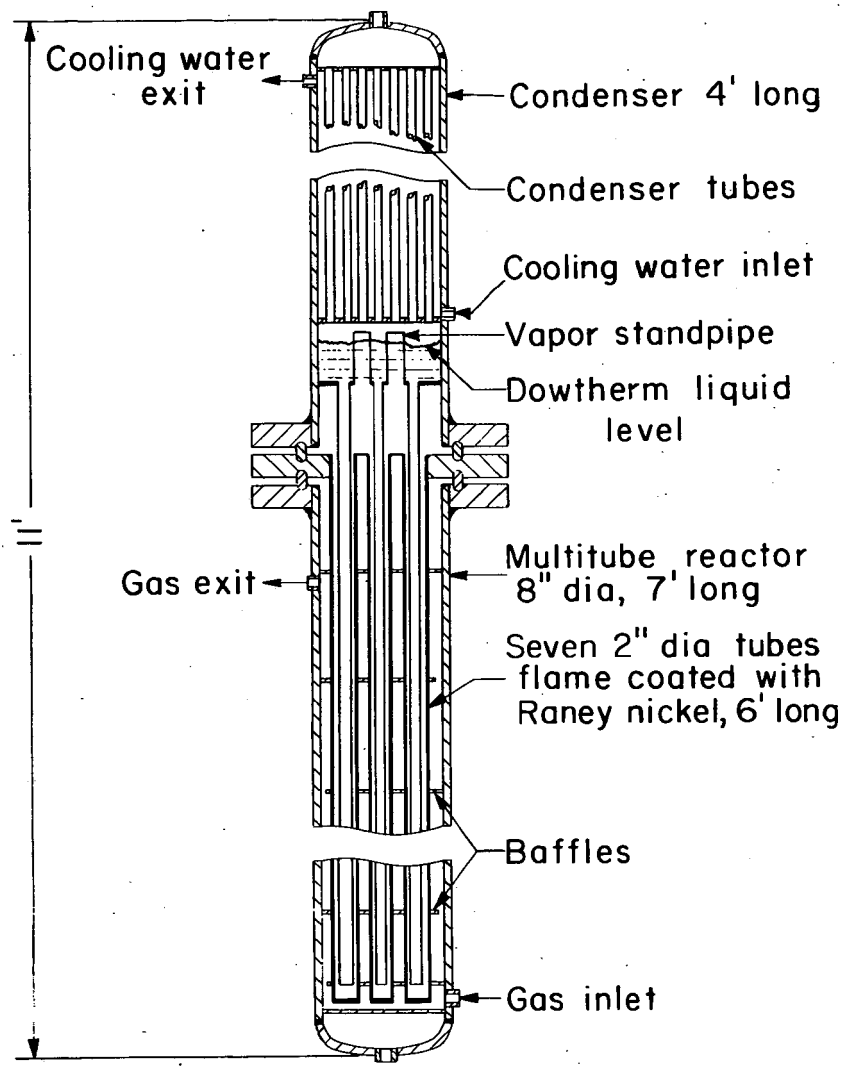

Figure 2. Multitube Reactor for Synthesis of High-Btu Gas

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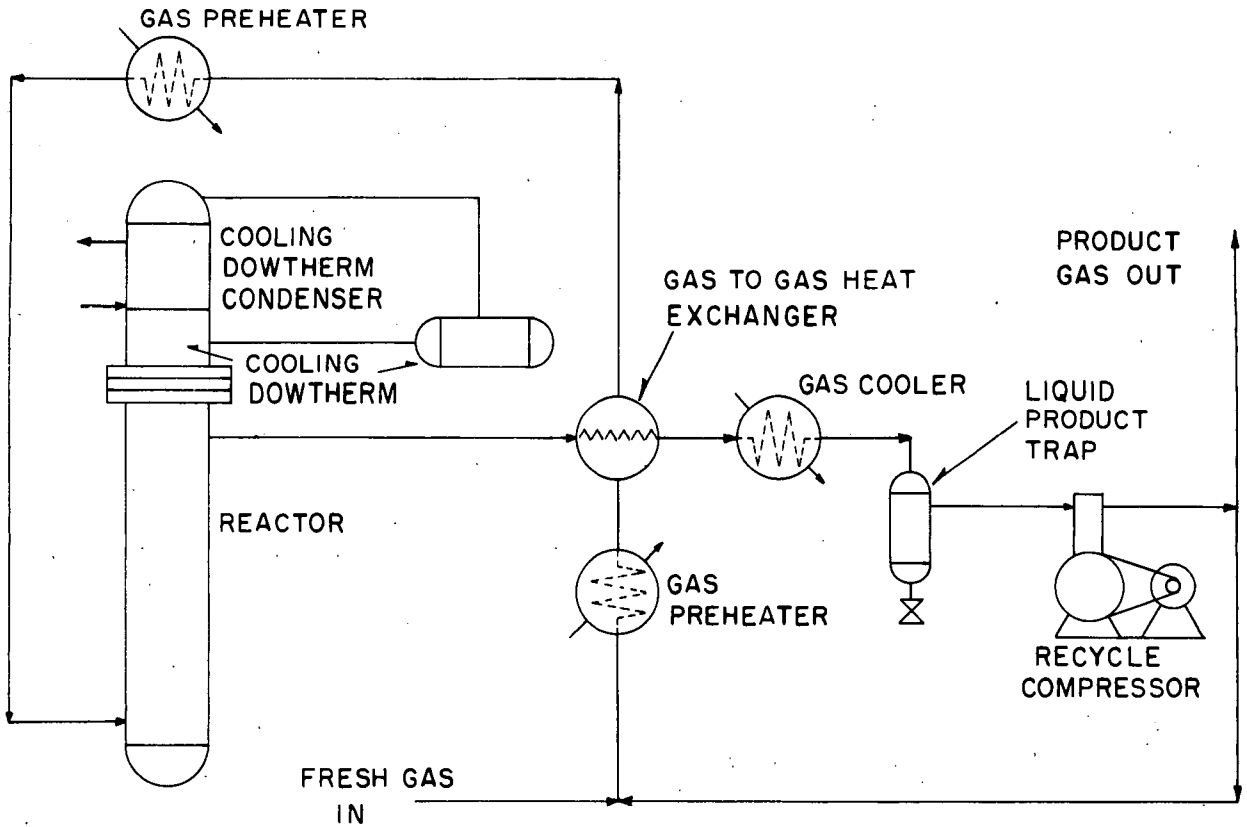

Figure 3. Schematic of Multitube Reactor Pilot Plant for Making High-Btu Gas

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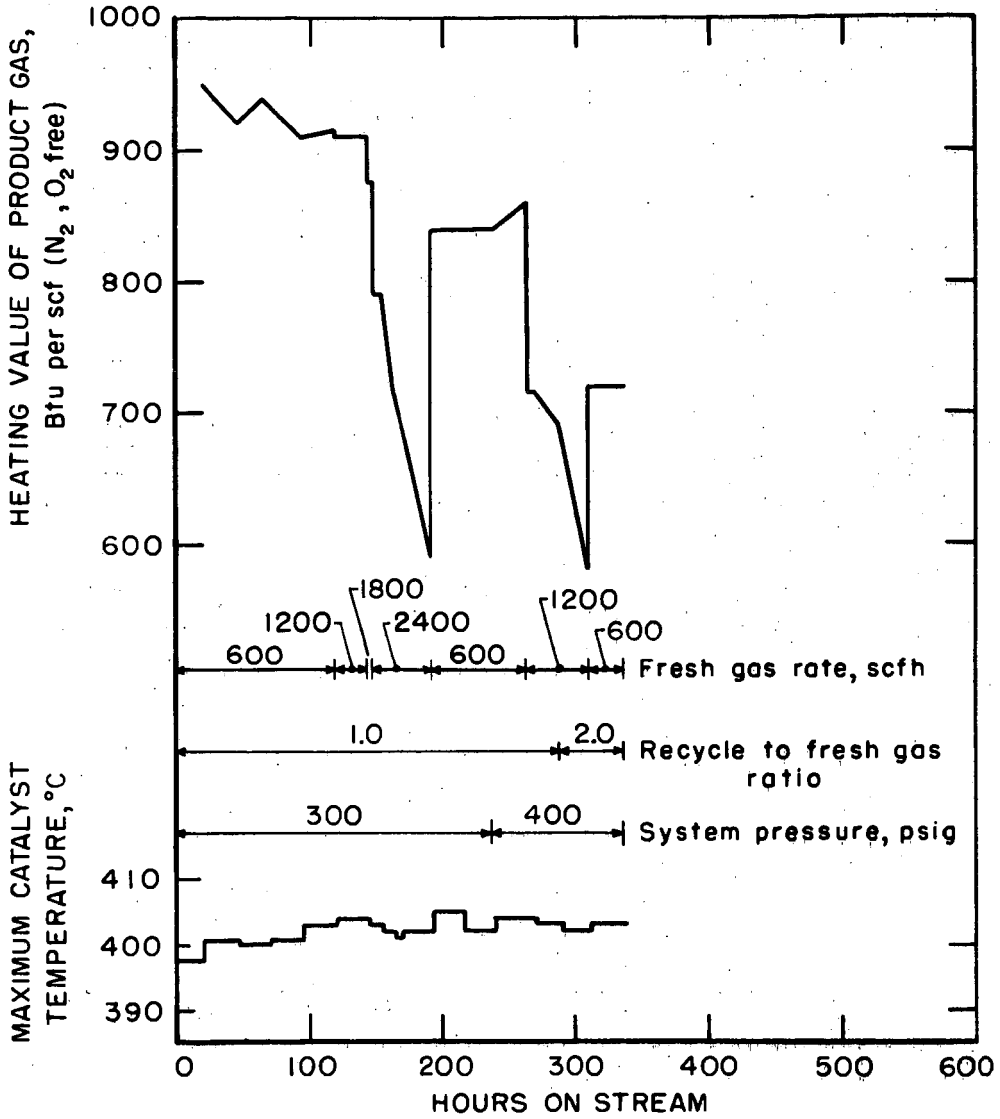

Figure 4. Operating Conditions - Experiment TWR-1

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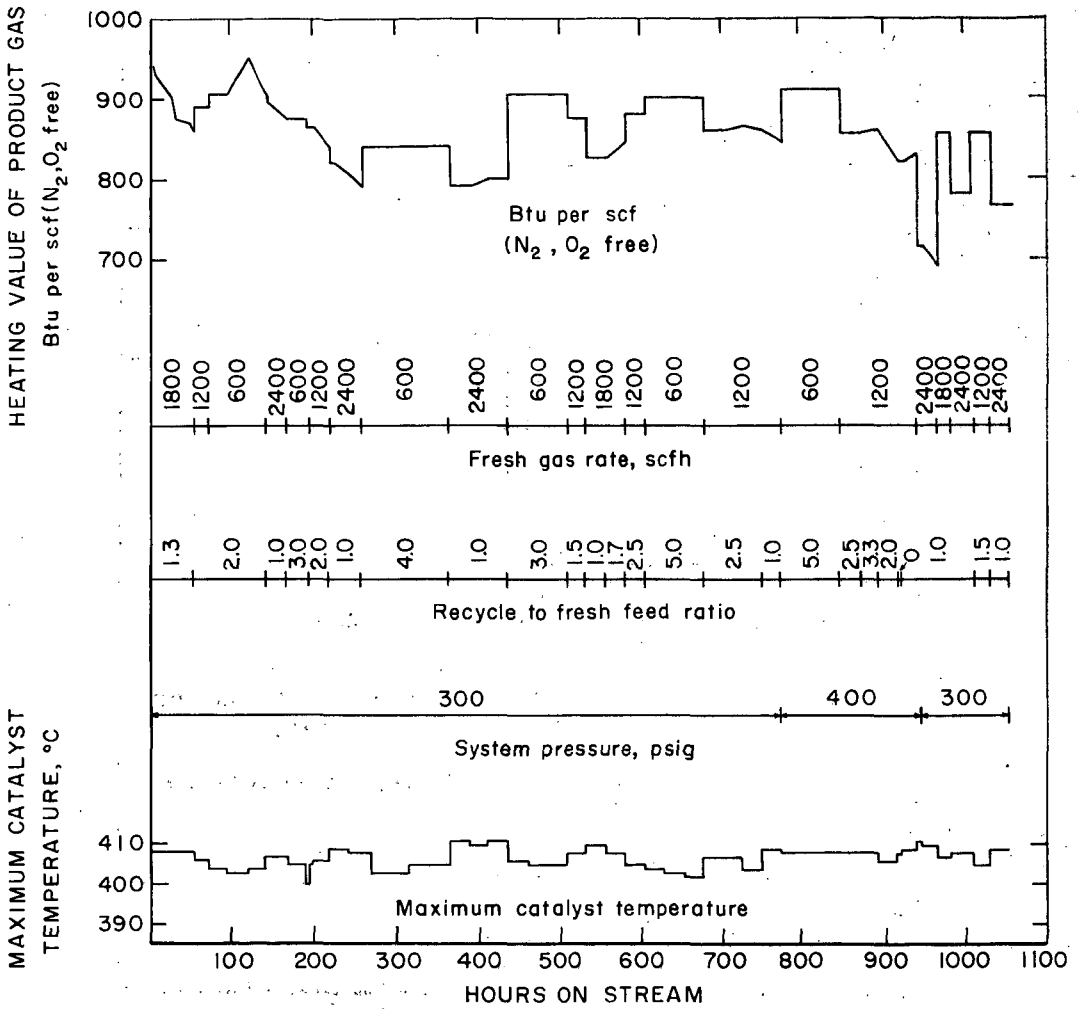

Figure 5. Operating Conditions - Experiment TWR-2

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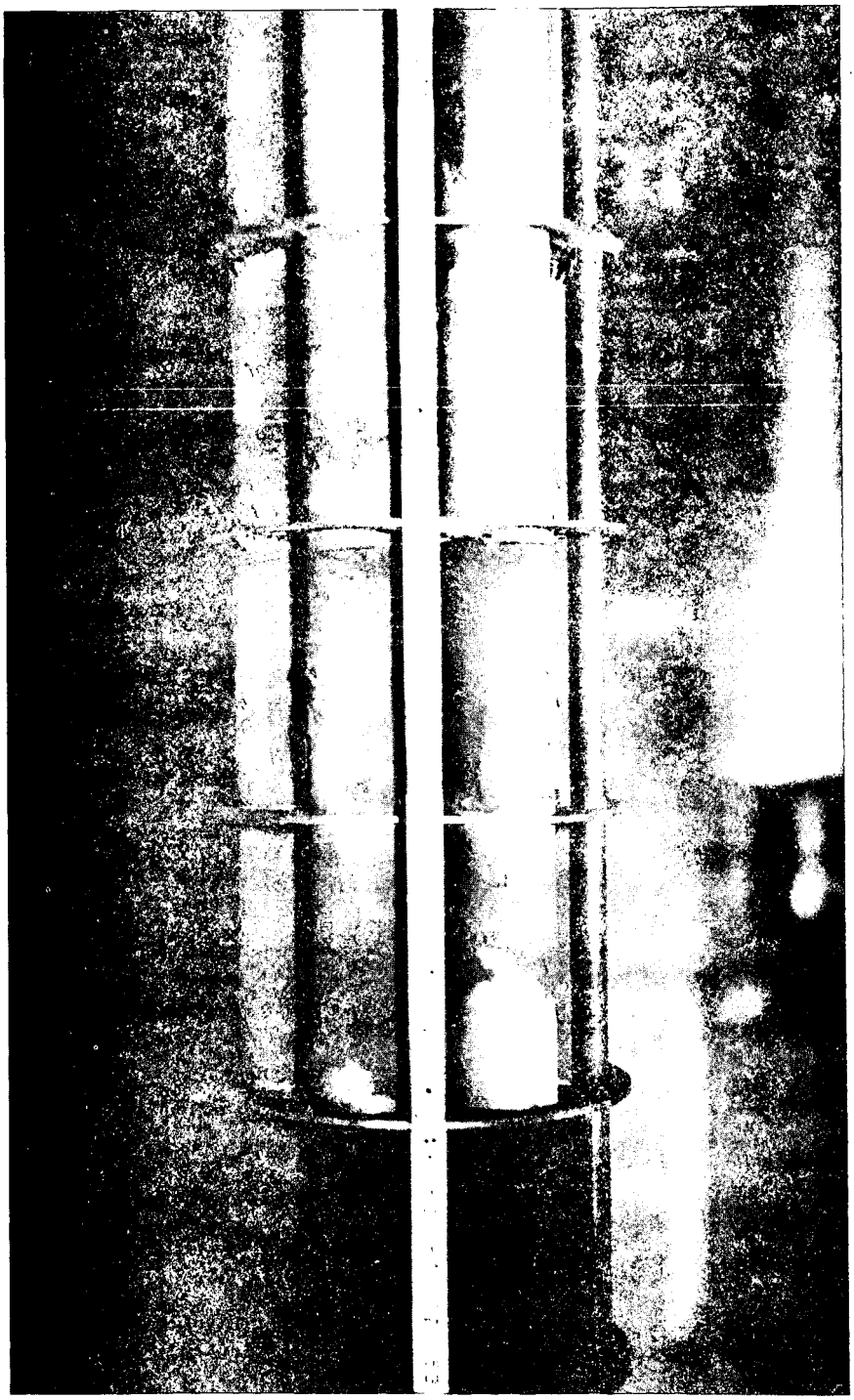

Figure 6. Section of Reactor Where Flaking Occurred

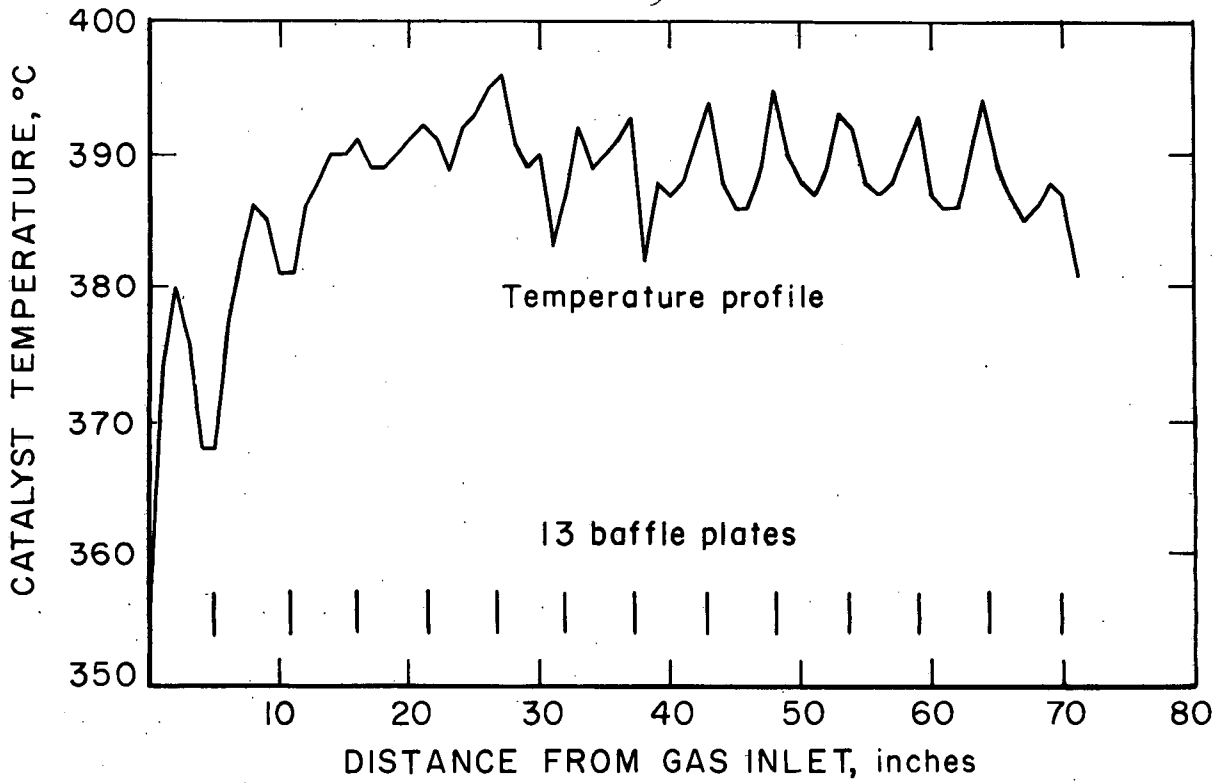

Figure 7. Temperature Profile of Tube F at 50 Hours Synthesis, Experiment TWR-1; and Location of Baffle Plates

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