

## EXPERIENCE WITH METHANATION CATALYSTS

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## Introduction

Nearly all process schemes for making synthetic natural gas from coal include a catalytic methanation step for upgrading the raw synthesis gas to a high Btu pipeline gas. The Bureau of Mines, Pittsburgh Energy Research Center, has conducted bench-scale and pilot-plant studies of the methanation reaction with a variety of catalysts and reactors. This report discusses some of the work, comments on the preparation of the various types of catalysts and their performance, and outlines results of a recent tube-wall reactor pilot-plant test.

## Laboratory-Scale Fixed-Bed Studies

Greyson and coworkers (3)<sup>1/</sup> examined the performance of many catalysts both in fixed-bed and fluidized-bed reactors. The fixed-bed reactors were single, steel-tube reactors, 0.622 inch ID by 12 inches long, cooled by boiling Dowtherm. Figure 1 shows a schematic diagram of the fixed-bed catalyst reactor. Various catalysts were tested in this unit.

Preparation of impregnated catalysts involved impregnating a catalyst support material with metal and promoters. To do this, a solution of the nitrate salts of the desired metals was added to a quantity of support to form a slurry. (Catalyst supports were cracking catalyst base and activated charcoal.) The slurry was then evaporated to dryness over a steam bath and then dried further in an oven at 600° C to convert the nitrate salts to oxides. The oxidized material was crushed to 6 to 8 mesh (U.S.). Activation of the catalyst for synthesis was achieved by reduction with hydrogen for 8 hours at 350 to 400° C and atmospheric pressure.

If a precipitated material was desired, the slurry of nitrate salts and support was treated with a solution of potassium carbonate. The treated slurry was then heated to the boiling point with constant stirring and filtered. The filter cake was washed with hot water and dried in an oven for about 16 hours. Supports for the precipitated catalysts included kaolin, kieselguhr, alumina, silica gel, and zirconia cement. The precipitated catalysts were crushed to 6 to 8 mesh sizes and then reduced with hydrogen prior to synthesis in the same manner as were the impregnated catalysts.

Preparation of iron nitride catalyst involved first a hydrogen reduction of 90 percent of the iron oxide and then treatment of the reduced iron with anhydrous ammonia at 350° C and atmospheric pressure until X-ray analysis showed that Fe<sub>2</sub>N was obtained.

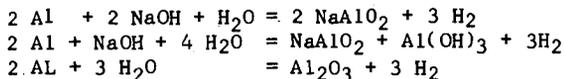
A magnetite and ball clay catalyst was prepared by firing a dried mixture of magnetite and ball clay at about 600° C. The sinter was then crushed, sized, and nitrided.

Raney nickel and Raney cobalt catalysts were partially oxidized with steam and then reduced with hydrogen. Plain nickel pellets were also subjected to the same activation treatment before the methanation reaction.

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<sup>1/</sup> Numbers in parentheses refer to list of references at the end of this paper.

Raney catalysts were also activated by extraction of the aluminum. A solution of sodium or potassium hydroxide was used to remove part of the aluminum from the alloy. The reactions proceeding during leaching are:



The remaining catalyst material consisting of unreacted alloy,  $\text{Al}_2\text{O}_3$ , and elemental nickel or cobalt was washed with water and charged wet into the reactor.

The simplest catalyst prepared was iron ore reduced with hydrogen. Table 1 lists some typical catalysts treated, the space velocities, and ratio of  $\text{H}_2$  to CO of the feed gas. Selected methanation conditions as well as causes for termination of tests are also shown. These tests showed that the precipitated nickel catalysts and the extracted Raney nickel catalyst were the most active, yielding methane concentrations of more than 90 percent. The nickel impregnated catalysts ranked second in activity, generally yielding 40 to 60 percent methane in the product gas. The iron catalysts were third, yielding product gas with less than 40 percent methane. The iron catalysts also produced a considerable amount of liquid hydrocarbon, which is an undesirable byproduct with respect to a high-Btu gas plant. Carbon deposition was excessive on all catalysts whenever  $\text{H}_2/\text{CO}$  ratio in feed gas was 1. When the  $\text{H}_2/\text{CO}$  ratio was 2.5, carbon deposition was still excessive on iron catalysts but nearly eliminated on the nickel catalysts.

#### Laboratory-Scale Fluidized-Bed Studies

Various iron and nickel catalysts were prepared and studied in laboratory-scale fluidized-bed reactors. Figure 2 is a sketch of a 0.96-inch diameter by 72-inch long fluidized-bed reactor used in the tests. This reactor introduced the feed gas at three locations to minimize the temperature gradient in the catalyst bed. Provisions were also made for recycling the cold product gas. The recycle gas was preheated before entering the catalyst bed.

Iron catalysts were reduced or nitrided for fluidized-bed operation in the same manner as for fixed-bed operation, except that the catalyst particle size <80 mesh was smaller for fluidized-bed operation. Initial forms of iron catalyst tested included synthetic ammonia, Alan Wood magnetite, steel shot, and magnetite in ball clay. Performance of both the reduced and the nitrided iron catalysts was the same as it was during fixed-bed operation. At typical operating conditions of  $340^\circ \text{C}$ , 300 psig, and space velocities<sup>2/</sup> of 880 to  $3000 \text{ hr}^{-1}$ , carbon deposition was excessive, even with  $\text{H}_2\text{O}$  ratios in the feed gas as high as 3; methane content of the product gas was generally less than 30 percent; heating value of the product gas was 400 to 600 Btu/scf, well below the desired minimum of 900 Btu/scf; and yields of higher molecular weight hydrocarbon,  $\text{C}_3^+$ , were still high, amounting to up to 3 wt pct of the fresh feed.

Addition of over 2.6 percent steam to the feed gas prevented carbon deposition, but it also decreased the catalyst activity. Addition of up to 5 percent carbon did not reduce carbon deposition.

The procedures for preparing the nickel catalysts was essentially the same as that followed in the series of fixed-bed tests, except that ingredients and proportions were varied, and particle size was kept below 80 mesh. Because the nickel

<sup>2/</sup> Space velocity is volume per hour of fresh feed gas at standard conditions ( $0^\circ \text{C}$ , 1 atm.) per settled volume of catalyst.

Table I. Fixed Bed Experiments

Selected methanation conditions									
Catalyst composition and pretreatment	H <sub>2</sub> /CO ratio	Space <sup>1/</sup> velocity hr <sup>-1</sup>	Temp., °C	Pres- sure, psig	CH <sub>4</sub> <sup>2/</sup> per- cent	Heating value <sup>3/</sup> Btu/scf	Termination of run due to	Space <sup>1/</sup> velocity hr <sup>-1</sup>	
								100-300	300
Cuban iron ore - reduced	1	100-300	321	300	37.5	896	Excessive carbon		
Fused Fe <sub>3</sub> O <sub>4</sub> , reduced and nitrided N/Fe = 0.44	2	100-300	395	300	30.5	738	Excessive carbon		
Fe <sub>3</sub> O <sub>4</sub> (50%) and ball clay, reduced and nitrided N/Fe = 0.48	2	100-300	312	300	27.5	691	Excessive carbon		
Fe-Ni-MgO-SiO <sub>2</sub> (58.8:12.4:2.21:0.2) N/Fe = 0.314, reduced and nitrided	1	300	273	300	39.7	706	Sufficient data, some carbon		
Ni, ThO <sub>2</sub> -Cr <sub>2</sub> O <sub>3</sub> ppt. on kieselguhr (30.9:7.6:1.6:59.9) - reduced	1	100-300	320	0	60.8	785	Excessive carbon		49
10% Ni impregnated on steam-treated cracking catalyst base reduced	1	300		No appreciable activity					
5% Ni impregnated on cracking catalyst base - reduced	1, 2	300	398	300	44.6	874	Excessive carbon		
5% Ni impregnated on cracking catalyst base plus K <sub>2</sub> O-reduced	2.5	300	400	300	39.1	635	Excessive carbon		
1% Ni impregnated on activated charcoal - reduced	1	100-300		No appreciable activity					
10% Ni ppt. on silica - reduced	1	100-300	355	300	48.3	(720)	Excessive carbon		
NiO-Al <sub>2</sub> O <sub>3</sub> ppt. on kaolin (100:200:125) - reduced	2	300	300	300	98.9	1071	Decreased activity		
NiO-MgO ppt. on kaolin (100:200:125) - reduced	2.5	300	264	300	97.3	(1060)	Sufficient data		
28% Ni, 5.5% Mn, 2.4% Al ppt. on kaolin - sintered and reduced	2.5	300		No appreciable activity					
NiO, MnO, Al <sub>2</sub> O <sub>3</sub> ppt. on cracking catalyst - reduced	2.5	300	404	300	17.3	(470)	Insuff. activity		
Ni pellets steam-treated - reduced	2.5	100-300		No appreciable activity					
Raney cobalt (50% Co, 50% Al), Al partly extracted with NaOH	2.5	300-2,800	286	300	92.1	(1050)	Excessive carbon		
Raney nickel (42% Ni, 58% Al), steam-treated - reduced	2.5	300		No appreciable activity					
Raney nickel (42% Ni, 58% Al), Al partly extracted with NaOH	2.5	300-1,500	300	300	96.9	(1060)	Sufficient data		

<sup>1/</sup> Space velocity = Std volumes feed gas per hour per vol catalyst    <sup>2/</sup> CO<sub>2</sub>, H<sub>2</sub>O free    <sup>3/</sup> ( ) estimated.

catalysts were extremely active in comparison with the iron catalysts, the feed gas was more evenly distributed in the fluidized-bed reactor by a multiple feed system as shown in figure 2 rather than by a single feed system. Provision was also made to recycle product gas. Variation of the distribution of fresh feed gas in the reactor and variation of the ratio of recycled product gas to fresh feed permitted minimizing the temperature gradients in the catalyst bed to within 10° to 15° C, as opposed to the temperature gradients in excess of 100° C obtained when the fresh gas was introduced through a single port.

Table 2 describes the nickel catalysts tested and summarizes their performance.

The thorium-promoted nickel-alumina catalyst (L-6053) proved to be very active and, chemically, one of the most stable catalysts of the precipitated and impregnated type nickel catalysts. Special tests with the thorium-promoted nickel alumina catalyst suggests that drying the catalyst at 180° C, as compared with drying at 120° C or 220° C, resulted in an optimum in catalyst life. Operating at 370° C, 300 psig, fresh gas space velocity of 7000 hr<sup>-1</sup>, H<sub>2</sub>/CO ratio of 3.0, and recycle ratio of 1:1, maximum life of the thorium-promoted nickel alumina catalyst (dried at 180° C) was 550 hours, giving a methane productivity of 6500 lb/lb Ni (145,000 scf CH<sub>4</sub>/lb Ni). Methane content of the product gas was generally more than 80 percent.

In fluidized-bed operation, partially activated Raney nickel catalyst (80-230 mesh size) performed as well as the thorium-promoted nickel catalyst (5). The Raney nickel catalyst was activated by extracting about 3 to 5 percent of the aluminum with caustic solution, and then washing the extracted material with water until the wash water gave a neutral reaction with litmus or pH paper. The wet catalyst was then charged into the reactor and dried with a flow of hot hydrogen until the catalyst bed became fluidized. The reactor was put into operation by pressurizing it to 300 psig under hydrogen, starting the flow of synthesis gas, and finally heating the catalyst from room temperature up to operating temperature. Operating at 370-394° C, 300 psig, H<sub>2</sub>/CO = 2.94, a settled-bed space velocity of 7700 to 10,000 hr<sup>-1</sup>, and recycle-fresh feed ratio ranging from 0.4 to 1.0, production of high-Btu product gas proceeded for a total of over 1000 hours. To achieve this length of service, the catalyst required two additional partial activations with caustic solution, one after 492 hours and another after 964 hours of operation.

Particle attrition is a suspected cause of substantial losses of nickel catalysts operating in fluidized-bed reactors. Weight loss in catalysts ranged from 8 percent for 6 hours of operation for an impregnated catalyst (L-6092) to 37 percent for 220 hours of operation for a precipitated catalyst (L-6036). An attrition-resistant nickel catalyst needs to be developed for fluidized-bed reactor operation.

#### Hot-Gas Recycle Reactor Catalyst

Catalysts for use in hot-gas recycle reactors were developed especially to give a low-pressure drop across the reactor (4, 2). The hot-gas recycle reactor removes the exothermic reaction heat by utilizing the sensible heat capacity of large volumes of recycle gas passing through the catalyst bed. A fraction of the recycle stream is cooled to remove the reaction heat and to condense out product water. Figure 3 shows a simplified sketch of the hot-gas recycle (HGR) methanator system.

One type of iron catalyst used in the HGR system consisted of lathe turnings cut from either 1018 carbon steel or wrought iron. Void volumes were about 87 percent to give acceptably low-pressure drops. The turnings were activated by oxidizing 20 percent of the iron to Fe<sub>3</sub>O<sub>4</sub> with 600° C steam flowing at a space velocity of 400 hr<sup>-1</sup> and then reducing the turnings with hydrogen for 60 hours at 400° C at a space velocity of over 4000 hr<sup>-1</sup>.

Table II. Fluidized-bed Catalyst Evaluation

Theoretical catalyst composition <sup>1/</sup>	Catalyst No.	H <sub>2</sub> /CO	Average temp. ° C.	Fresh feed, SVH	Recycle ratio	Life, hrs	Process life, lbs CH <sub>4</sub> /lb Ni
NiO-100 (21.1%), Al <sub>2</sub> O <sub>3</sub> 159, kaolin 97	L-6025	2.5	350	7,100	1:1	45	-
NiO-100 (35.6%), Al <sub>2</sub> O <sub>3</sub> 7.3, MnO 25.6, kaolin 97	L-6036	2.5	330	2,800-10,000	0.8:1-1.3:1	220	-
NiO-100 (36.8%), Al <sub>2</sub> O <sub>3</sub> 7.3, MnO 25.6, kaolin 97	L-6036.2	3.0	345	7,500	1.5:1	132	1,200
NiO-100 (36.1%), Al <sub>2</sub> O <sub>3</sub> 7.3, MnO 25.6, activated alumina 75	L-6039	2.5	360	7,500	1:1	171	900
NiO-100 (7.1%), Mn 48, activated alumina 143	L-6042	2.5	345	7,500	0.8:1	6	-
NiO-100 (27.1%), Al <sub>2</sub> O <sub>3</sub> 7.3, MnO 25.6, Filtrol S-185	L-6051	3.0	350	7,500	0.7:1	237	2,500
NiO-100 (17.3%), Al <sub>2</sub> O <sub>3</sub> 7.3, ThO <sub>2</sub> 11.0, activated alumina 240	L-6053	3.0	368	7,000	1:1	550	6,500
NiO-100 (42.4%), ThO <sub>2</sub> 13.6, kieselguhr 78.4	L-6057	3.0	370	7,000	1:1	380	4,000
Co-100, Al 99	L-6049	3.0	381	14,000	2:1	1	-

<sup>1/</sup> Based upon wt of ingredients ( ) Percentages of NiO determined analytically. <sup>2/</sup> Above 69% CO<sub>2</sub>-free dry gas contraction.

NOTE: All catalysts except L-6049 were reduced at 350-400° C. 100 psig (All runs at 300 psig).

All catalysts were prepared by precipitating nitrate salts on various supports with K<sub>2</sub>CO<sub>3</sub> except following:  
 L-6042 - Supports impregnated with nitrate salts which were later precipitated with K<sub>2</sub>CO<sub>3</sub>.  
 L-6049 - Raney cobalt 1% Al extracted with KOH solution

Nickel catalysts tested in the HGR system were in the form of parallel plate assemblies. The assemblies were made of plates sawed from an ingot of Raney nickel or of carbon steel plates, stainless steel plates, or aluminum plates that had been thermal-sprayed with either Raney nickel or nickel oxide powder. Thickness of the solid Raney nickel plates was 1/8-inch; thickness of the sprayed coatings ranged from 0.020 to .040 inch. Distance between plates was 1/8-inch. The Raney nickel catalysts were activated by caustic leaching of 10 to 20 percent of the aluminum followed by water washing to remove all caustic as previously described. The wet activated catalyst was charged to the reactor for synthesis. The sprayed nickel oxide coatings were activated in the reactor by reduction with hydrogen in the same manner as that used to reduce the iron catalysts.

Test results on performance of the iron and nickel catalysts confirmed the general superiority of the nickel catalysts over the iron in several respects. Activities of the nickel catalysts were several-fold that of the iron catalysts. Depending upon reactor conditions, estimated rates of conversion of  $\text{CO} + \text{H}_2$  per unit geometric surface area were about 20 to 50 scfh/ft<sup>2</sup> for the nickel catalysts and about 2 scfh/ft<sup>2</sup> for the steel lathe turnings catalysts.

Carbon deposition was negligible for the nickel catalysts, whereas carbon deposition continued to build up on the iron catalyst and, in some cases, plugged the reactor.

Nickel catalysts yielded the higher heating value product gas with no oil byproducts, while the iron catalysts tend to yield about 3 to 4 percent of the hydrocarbon product as oil. Table 3 shows typical product gas yields over steel turnings, catalyst, the solid Raney nickel plate, and the sprayed nickel oxide plates. Much of the heating value of the product gas from the steel catalyst is due to the presence of  $\text{C}_2\text{-C}_5$  hydrocarbons rather than a high yield of methane.

#### Tube-Wall Reactor Catalysts

The tube-wall reactor (TWR) system was developed to provide highly effective cooling of the catalyst by means of heat transfer through catalyst-coated tubes to boiling Dowtherm and thereby extend catalyst life. This type of cooling is efficient and permits operation with a much lower gas recycle ratio than that required in the HGR system; the recycle ratio ranges from 0 to 5 for the TWR system as compared with a range of 12 to 20 for the HGR system.

Figure 4 shows a sketch of a multi-tube tube-wall reactor pilot plant. The methanation reaction occurs on the outer surface of the catalyst coated tubes, while boiling Dowtherm removes the heat of reaction from the inner surface of the tubes.

Preparation of the flame-sprayed catalyst tubes for the TWR involves first a sand-blasting of the tube-wall surface, followed by flame-spray application of a commercial nickel aluminide about 0.003-inch thick for bonding purposes. A final flame-spraying of the surface is done with Raney nickel to obtain a catalyst thickness of about .020 to .025 inch. The catalyst is activated by the previously described procedure of alkali leaching at up to 95° C followed by water washing. Water washing must be sufficient to remove all excess alkali, as it is postulated that the presence of excess alkali promotes formation of  $\text{Ni}_3\text{C}$  during synthesis.

Bench-scale experiments with TWR indicated that a rapid decline in catalyst activity occurred with the activated Raney nickel catalyst if the reaction temperature was below 390° C. (1). Nickel carbide formation was the suspected cause of such rapid decline in activity. X-ray analyses of the spent catalyst and of loose material spalled from the spent catalyst tubes showed large amounts of  $\text{Ni}_3\text{C}$ . Nickel carbide formation is also a suspected cause of the short life of nickel catalysts

Table III. Hot Gas Recycle Methanation Results

Experiment No.	18 K	18 P	31 D	31 B	32 A
Catalyst bed size	3" dia x 10'	3" dia x 10'	3" dia x 3'	3" dia x 3'	3" dia x 2'
Catalyst	1018 steel turnings, oxidized 20%, reduced with 400° C H <sub>2</sub>	1018 steel turnings, oxidized 20%, reduced with 400° C H <sub>2</sub>	Solid Raney nickel plates, 20% activated, with caustic	Solid Raney nickel plates, 20% activated, with caustic	Sprayed nickel oxide plates, reduced with 400° C H <sub>2</sub>
Pressure, ..... psig	400	400	400	400	400
Temperature, °C.....(top)	300	300	300	301	300
.....(bottom)	340	340	397	353	361
(Av.)	320	320	380	330	324
Feed gas space velocity std vol/vol cat/hr	800	800	1284	1767	1830
Fresh feed, H <sub>2</sub> :CO	3:1	2.5:1	2.92:1	2.94:1	2.95:1
Hot recycle: fresh feed	19:1	17:1	10:1	6:1	0
Cold recycle: fresh feed	4:1	4:1	2:1	8:1	11:1
Results:					
Conversion, ..... % feed	88.4	91.0	99.0	98.1	93.5
Heating value, ...Btu/scf dry	810	868	933	923	808
Product Gas Composition, %					
CH <sub>4</sub>	43.6	38.8	90.4	88.5	71.2
C <sub>2</sub> -C <sub>5</sub>	10.6	15.7	.1	.2	.1
H <sub>2</sub>	38.8	31.2	4.0	5.2	24.4
CO	1.3	2.2	.6	2.0	1.9
CO <sub>2</sub>	4.4	11.0	3.2	2.3	.8
N <sub>2</sub>	1.3	1.1	1.7	1.8	1.6
Oil production, % of total HC	3.2	3.7	0	0	0
Water vapor in recycle gas, %	4.8	4.7	8.1	2.8	2.1

Table V. Catalyst Analysis - TWR-6

<u>Sample Description</u>	<u>Chemical analysis, wt. percent</u>						<u>X-ray analysis</u>	<u>Surface area determination, M<sup>2</sup>/gm</u>
	<u>Ni</u>	<u>Al</u>	<u>Fe</u>	<u>C</u>	<u>S</u>	<u>Na</u>		
Upper 9" of tubes (Gas Out)	70.1	12.5	0.2	4.3	0.1	0.1	Ni <sub>3</sub> C	31.4
Middle 9" of tubes	67.9	14.4	.2	4.7	.1	.1	Ni <sub>3</sub> C	33.4
Lower 9" of tubes (Gas In)	70.3	14.1	.3	5.4	.2	.1	Ni <sub>3</sub> C	33.9
Loose material from baffles	68.7	11.3	.5	7.2	.1	.1	Ni <sub>3</sub> C	30.3
Raney nickel unactivated	41.4	55.6	.1	--	.19	-	-	-

## Conclusions

Suitable methanation catalysts of various forms can be prepared from iron or nickel, but nickel is far more effective in yield, activity, and desired selectivity. The activity of nickel catalysts is highly sensitive to sulfur poisoning and carbide formation; other important factors yet undetermined may exist. Major catalyst improvements needed include greater attrition resistance for fluidized-bed operation, less sensitivity to catalyst poisons and to temperature gradients for the HGR operation, and less sensitivity to catalyst poisons for TWR operation.

In the Bureau of Mines program, flame-sprayed Raney nickel catalyst in the TWR system has given the best methanation system thus far.

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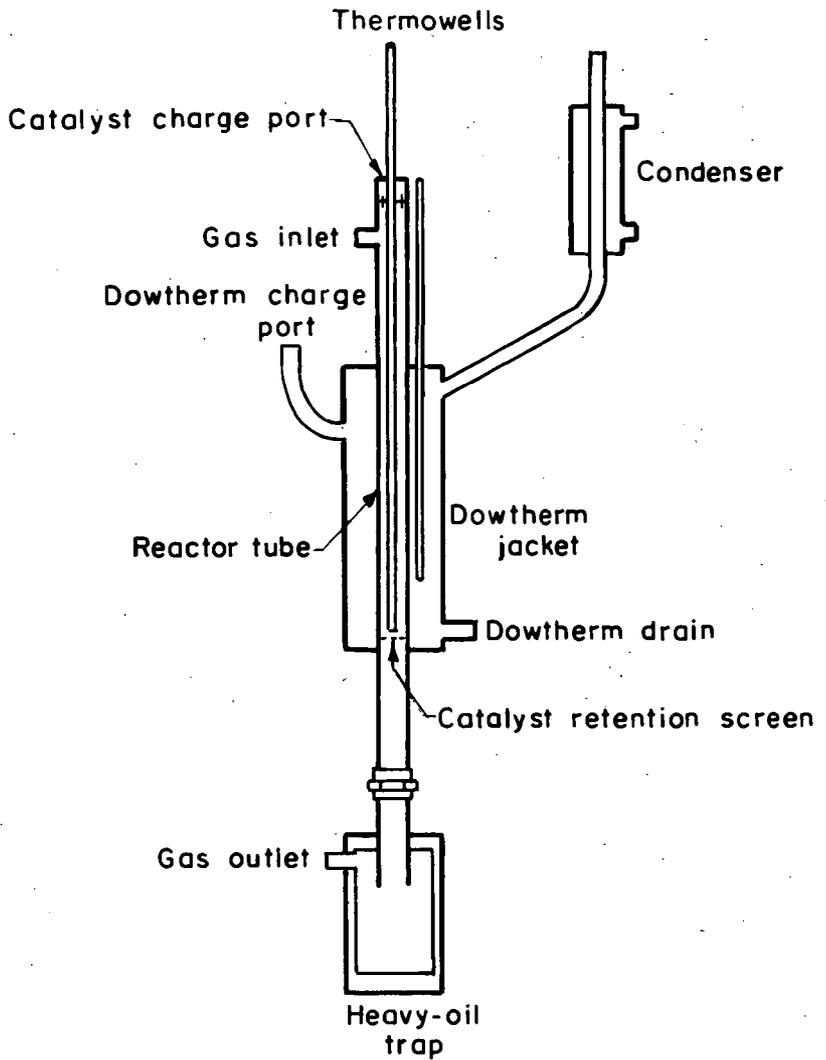


Figure 1— Fixed-bed catalyst reactor.

L-12580

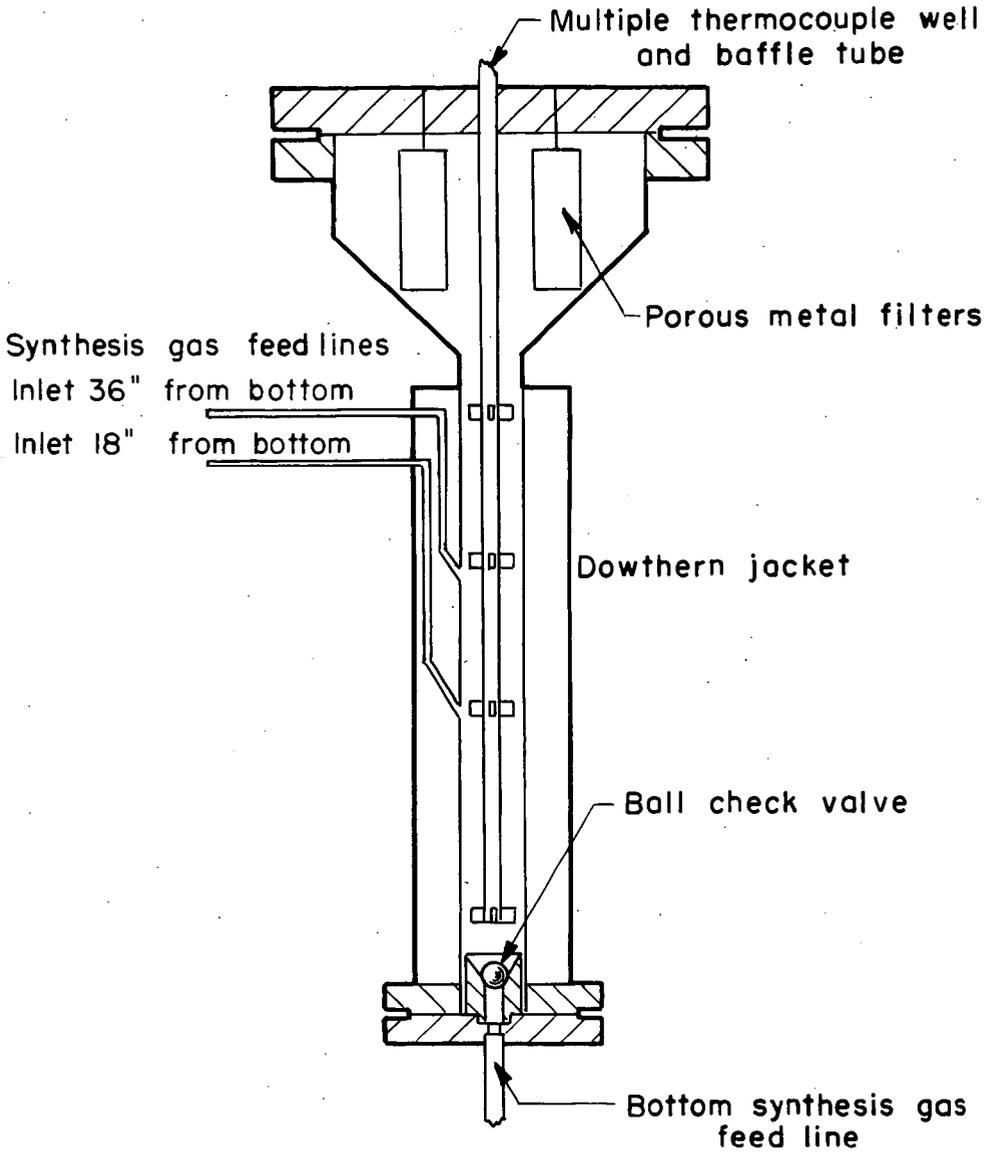


Figure 2 - Multiple-feed, fluidized-catalyst reactor.

L-12 581

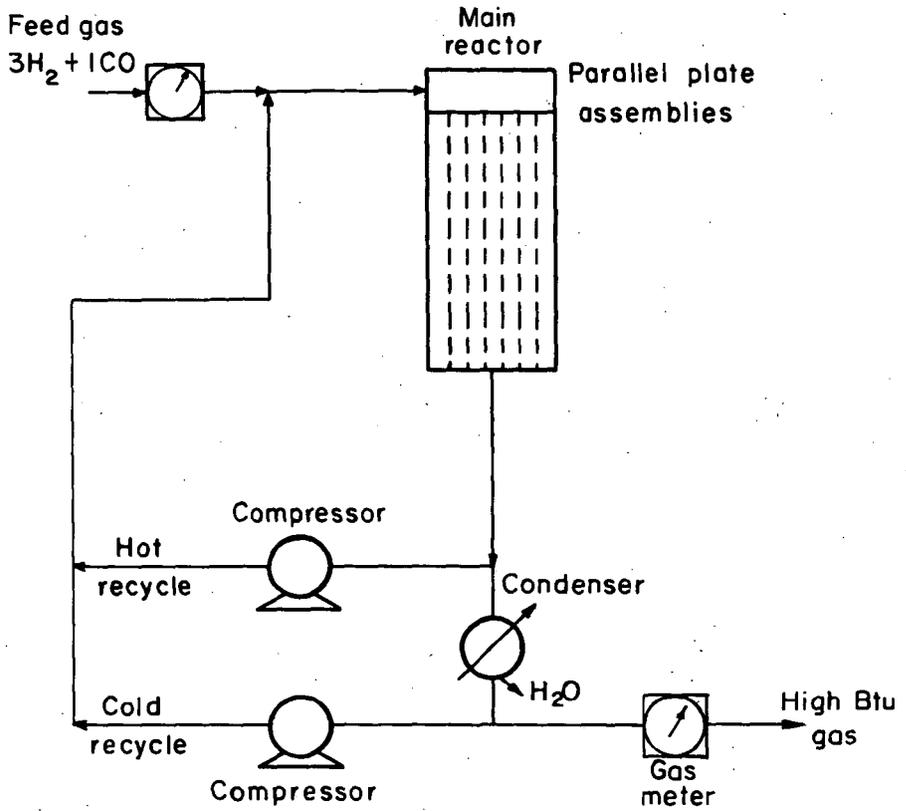


Figure 3-Flowsheet of hot-gas recycle process.

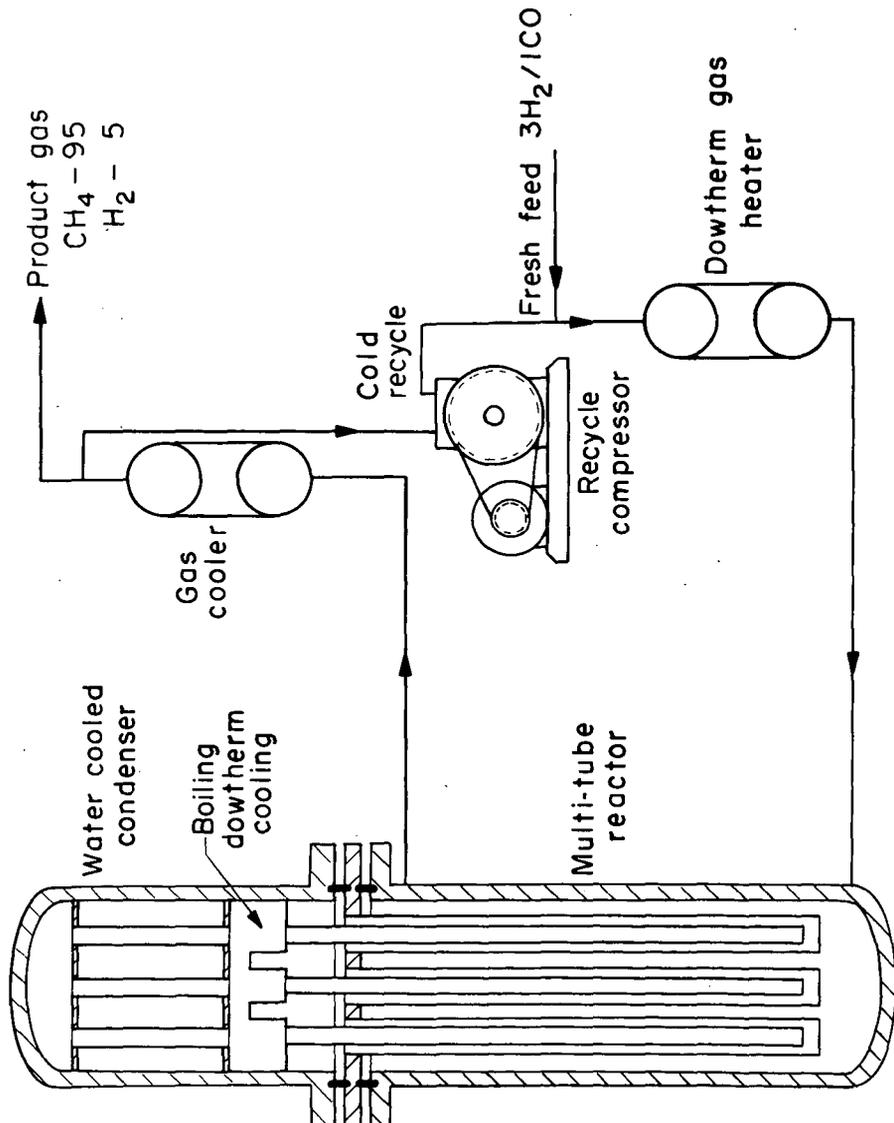


Figure 4-Simplified flowsheet of pilot plant for producing high-Btu gas

10-20-72 L-11657 K6

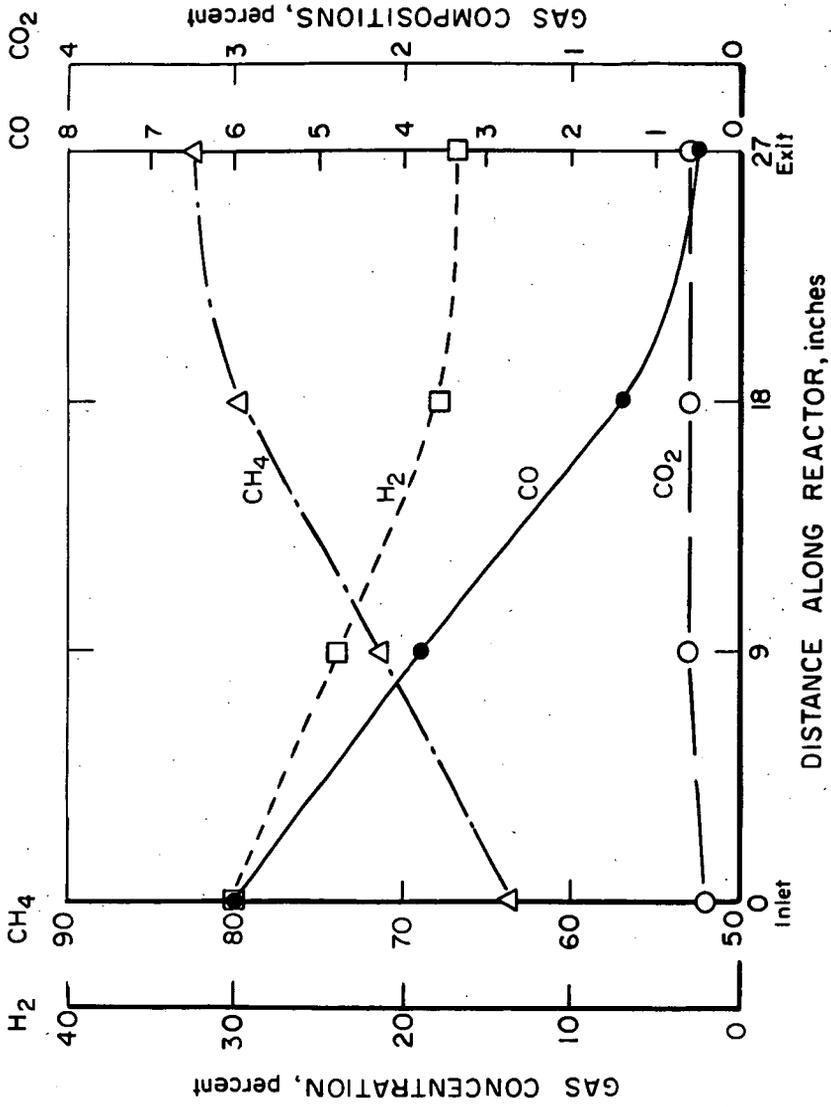


Figure 5 — Profile of gas composition (N<sub>2</sub>, H<sub>2</sub>O -free) along TWR reactor.  
Condition: 800 hours on stream, 390 °C average temperature,  
300 psig, 500 scfh and 3:1 recycle.

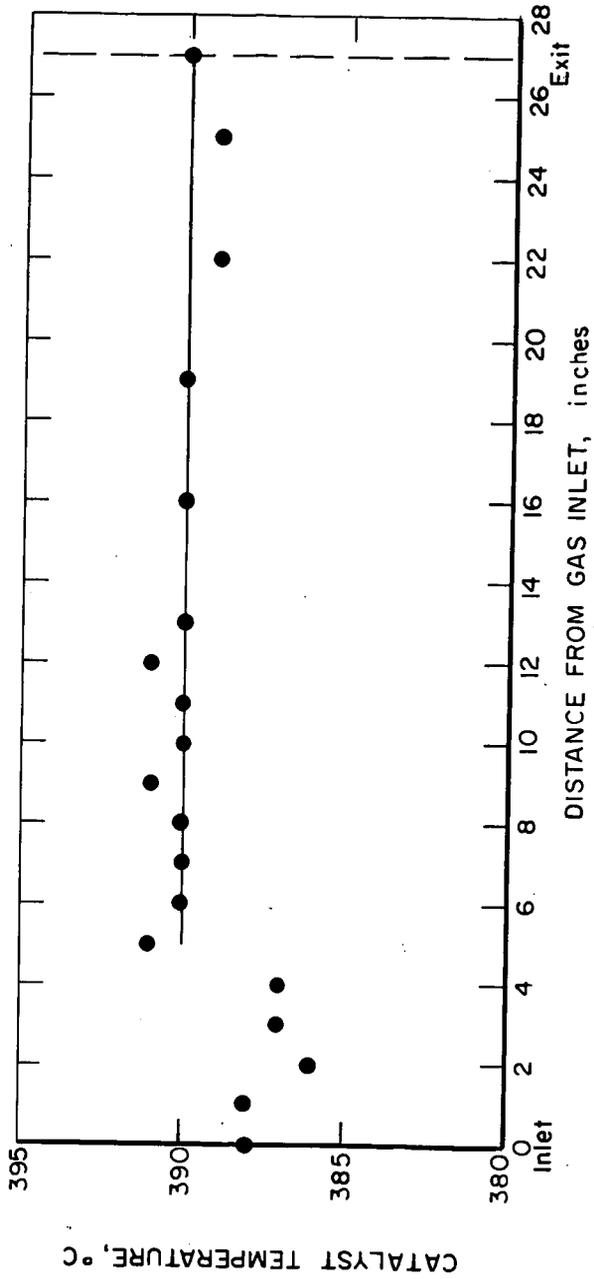


Figure 6 — Temperature profile — TWR-6, 526 hours on stream.