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METHANATION IN COAL GASIFICATION PROCESSES

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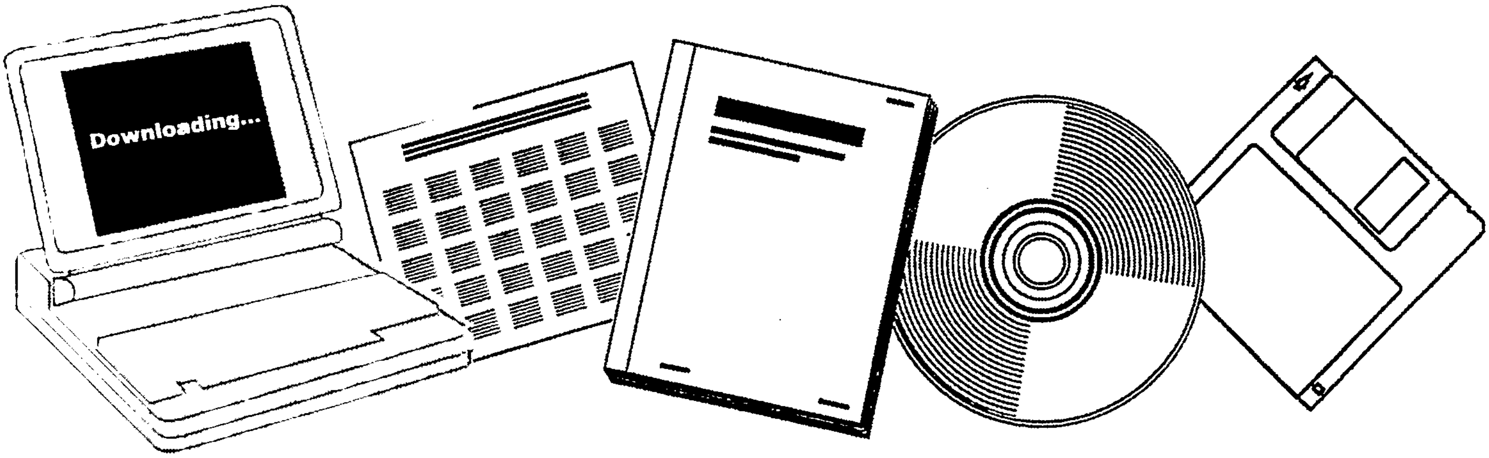

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Introduction

Studies of catalytic methanation, the conversion of carbon oxides to methane, date back to 1902. This reaction has become commercially important in recent years in the production of synthetic ammonia. The synthesis gas after several stages of shift and removal of carbon dioxide normally contains up to one percent of carbon oxides which will cause deactivation of the ammonia synthesis catalyst. They are therefore catalytically converted to methane which is inert towards the catalyst.

Although the methanation reaction is very exothermic, the low concentration of carbon oxides limits the temperature rise to less than 75° C and a simple adiabatic packed bed reactor is used. These converters are normally designed to operate with an exit temperature below 450° C. Concentration of carbon oxides is generally reduced to below 5 ppm. Also, the hydrogen is present in large excess (≈74 percent).

Methanation in coal gasification processes presents a considerably different problem in that the carbon monoxide concentration is much higher than that of an ammonia synthesis gas.

Typical dry compositions of a raw gasifier product, the shifted and purified feed to the methanators, and the final methanator product, are shown below for the SYNTHANE process.

	Gasifier Product	Methanator Feed	Methanator Product
H_2	23.6	45.1	1.8
CO	15.2	14.7	0.1
CO_2	34.9	1.0	1.7
CH_4	23.1	35.5	91.9
C_2H_6	0.7	1.1	--
N_2	1.7	2.6	4.5
H_2S	0.8	--	--

The compositions in most other coal gasification processes are generally similar.

The difficulty with the high carbon monoxide concentration is that in an adiabatic reactor, the heat of reaction causes the temperature to rise by 60° C for each one percent of CO converted to methane; so, with a feed concentration of 14 percent CO, the temperature rise would be high enough to cause catalyst sintering and decomposition of the product methane to carbon. Novel reactor configurations are used to circumvent this problem.

In the SYNTHANE process, over 60 percent of the product methane is made in the gasifier itself. This reduces the load on the methanation system and reduces the size requirements of the equipment downstream of the gasifier due to the volumetric contraction.

To be interchangeable with natural gas, a substitute natural gas (SNG) must satisfy several characteristics and it should be evaluated by combustion tests. In 1965, the Office of Coal Research issued guideline objectives for gas from coal. The gas should be pumpable at 1000 psig and interchangeable with natural gas and should have the following desirable characteristics:

Heating value > 900 Btu/SCF (higher heating value)
$CO < 0.1\%$
$H_2S < 0.25$ gr/100 SCF
Total S < 10 gr/100 SCF
Inerts <5%
$CO_2 < 3\%$
Water < 7 lb/million SCF
Specific gravity 0.59 to 0.62 recommended
Hydrocarbon dewpoint <-40° at 1000 psig
No poisonous compounds or gum formers

Mixtures containing 16 percent H_2 and 84 percent CH_4 will have a heating value of 900 Btu/SCF. Others [1] calculate that a hydrogen concentration of 25 percent gives acceptable burning characteristics. The sulfur requirement is no problem since it must be removed to very low levels prior to methanation.

Reactions-Thermodynamics

The pertinent reactions are shown below along with the heat of reaction and equilibrium constant at 700° K.

1. $CO + 3H_2 \rightleftarrows CH_4 + H_2O$ $\Delta H(700K) = -52.69$ kcal/gm mol
   $K(700K) = 3{,}726.5$

2. $CO + H_2O \rightleftarrows CO_2 + H_2$ $\Delta H(700K) = -9.064$ kcal/gm mol
   $K(700K) = 9.01$

3. $CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O$ $\Delta H(700K) = -43.63$ kcal/gm mol
   $K(700K) = 413.7$

4. $2CO + 2H_2 \rightleftarrows CH_4 + CO_2$ $\Delta H(700K) = -61.75$ kcal/gm mol
   $K(700K) = 33{,}566.$

5. $(2n+1)\ H_2 + n\ CO \rightleftarrows C_nH_{2n+2} + n\ H_2O$
   $2n\ H_2 + n\ CO \rightleftarrows C_nH_{2n} + n\ H_2O$

6. $C_2H_6 + H_2 \rightarrow 2CH_4$
   $C_3H_8 + 2H_2 \rightarrow 3CH_4$

Reaction (1) is the primary methanation reaction. A 3/1 ratio of hydrogen to carbon monoxide is needed and the gasifier product is usually adjusted to a slightly higher value in the shift reactor. This reaction is highly exothermic by nearly 53 kcal/gm mole of CO converted leading to approximately a 60° C temperature increase for each one percent CO converted. Equilibrium is not a limiting consideration in most methanation processes.

Reaction (2) is the shift reaction which also occurs in the methanator. It is mildly exothermic causing approximately an 11° C temperature increase for each one percent CO converted. Frequently, as a catalyst becomes spent, the CO_2 concentration in the product increases due to this reaction. Measured mass action coefficients for the shift reaction in the Hot Gas Recycle reactor of the SYNTHANE process are generally below 1.0 while the equilibrium value at the reactor exit temperature is 11.7.

The third reaction is the methanation of CO_2. This reaction is also the result of subtracting (2) from (1) so it is not an independent reaction. It has been found experimentally that CO_2 is not methanated as long as the concentration of CO is greater than a few hundred ppm.

Reaction (4) is the methanation of CO with a 1/1 ratio of H_2 to CO. Under these conditions carbon deposition will normally occur so this reaction is not used.

The formation of higher hydrocarbons (the Fischer-Tropsch synthesis) as shown in reaction (5) takes place at lower temperatures than used in methanation and at lower H_2/CO ratios. Iron catalysts, which are used for Fischer-Tropsch synthesis, lead to carbon deposition when used for methanation.

Reaction (6) is the hydrogenolysis of higher hydrocarbons. This takes place over the usual nickel catalyst and all the ethane made in the gasifier is converted to methane. This is unfortunate since a reduction in heating value occurs.

Reaction Mechanism

One of the mechanisms for methanation on nickel catalysts that seems most reasonable was proposed by Vlasenko and Yuzefovich [2] in 1969. It is based on the evidence presented by reaction kinetics, infrared spectra, contact potential differences, and adsorption measurements.

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O$$

1. $[\ ] + e + H_2 \rightarrow [H_2]^-$
2. $[\ ] + CO \rightarrow [CO]^+ + e$
3. $[CO]^+ + [H_2]^- \rightarrow [HCOH]^+ + e$ slow step
4. $[HCOH]^+ + [H_2]^- \rightarrow [CH_2] + H_2O + [\ ]$
5. $[CH_2] + [H_2]^- \rightarrow CH_4 + e + [\ ]$

$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O$
1. $2\,[\ ] + 2e + H_2 \rightarrow 2\,[H]^-$
2. $2\,[H]^- + CO_2 \rightarrow [HCOOH] \rightarrow 2\,[\ ] + C{<}^{OH}_{OH} + 2e$ slow step
3. $C{<}^{OH}_{OH} + H_2 \rightarrow HCOH + H_2O$
4. $HCOH + H_2 \rightarrow CH_2 + H_2O$
5. $CH_2 + H_2 \rightarrow CH_4$

The important difference between these reactions is that the methanation of CO takes place with molecularly adsorbed hydrogen while the methanation of CO_2 requires hydrogen adsorbed in the atomic form. Carbon monoxide adsorbs on the surface and poisons the surface for the adsorption of atomic hydrogen. Thus, when CO is present, CO_2 is not methanated.

For many hydrogenation reactions, CO acts as a strong poison by preventing atomic adsorption of hydrogen. Also, note that the adsorbed methylene radical has a chance to polymerize in step 5 of the first reaction but no adsorbed methylene radicals are present in the CO_2 methanation. This agrees with the fact that no higher hydrocarbons are formed in the methanation of CO_2.

Catalysts

Catalysts are covered in detail in an excellent review article by Mills and Steffgen [3]. The order of activity has been found to be:

Ru > Ir > Rh > Ni > Co > Os > Pt > Fe > Mo > Pd > Ag

of which only Ru, Ni, Co, Fe, and Mo can be considered commercially important. Ru is used in some ammonia plants as a cleanup methanation catalyst but its availability is limited and the tonnages required for coal-to-gas plants would not be available. Nickel is cheap, very active, and very selective to CH_4. Thus almost all commercial catalysts are nickel based. Cobalt is less active and less selective. Iron is less active and forms carbon readily. Molybdenum is of very low activity and fairly selective but it has the advantage of being sulfur resistant.

Commercial nickel methanation catalysts contain 25 to 70 percent Ni on an alumina or kieselguhr base, and are pelleted. Precipitated catalysts are more active than impregnated ones. Prices vary from about \$100 to \$130/ft^3 for the low nickel catalysts to \$207 to \$235/ft^3 for the high nickel catalysts. Most catalysts require reduction of the NiO with H_2 before service. A reduced and stabilized version is available which can be put into methanation service without further reduction. It costs about \$55/ft^3 more.

In the SYNTHANE process, a Raney nickel catalyst is used. This is an alloy containing 42 percent Ni and 58 percent Al. It is activated by leaching with sodium hydroxide according to the following reactions:

$$2\ Al + 2\ NaOH + 2H_2O \rightarrow 2\ NaAlO_2 + 3H_2$$
$$2\ Al + NaOH + 4H_2O \rightarrow NaAlO_2 + Al(OH)_3 + 3H_2$$
$$2\ Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$$

The reaction is continued until 70 percent of the aluminum is removed, as determined by hydrogen evolution, then the catalyst is rinsed with demineralized water until the pH of the effluent is close to that of the rinse water. This leaves a spongy skeletal Ni catalyst that is very active in methanation. The activated catalyst is then placed in service.

Catalyst Deactivation

Several mechanisms for catalyst deactivation are possible and are shown below:

1. $Ni + H_2S \rightarrow NiS + H_2$
2. $Ni\ (75\ \text{Å}) \rightarrow Ni\ (1000\ \text{Å})$
3. $2\ CO \rightleftarrows C + CO_2$
   $CH_4 \rightleftarrows C + 2H_2$
4. $3\ Ni + 2\ CO \rightleftarrows Ni_3C + CO_2$
   $3\ Ni + CH_4 \rightleftarrows Ni_3C + 2H_2$
5. $Ni + 4\ CO \rightleftarrows Ni(CO)_4$
6. $Fe(CO)_5 \rightleftarrows Fe + 5\ CO$

Sulfur rapidly poisons methanation catalysts via reaction (1). The effect of increasing sulfur concentrations on catalyst life has been shown [4]. We try to keep sulfur concentration below 0.1 ppm to prevent sulfur poisoning, a poisoning which appears to be irreversible.

Reaction (2) depicts the sintering effect. Nickel crystallites grow in size and a loss of surface area results. B.E.T. surface areas of spent Raney nickel catalyst decreases to about one-half that of the freshly activated catalyst (as high as 64 m^2/gm).

Carbon deposition is another reason for catalyst deactivation. Decomposition of carbon monoxide is favored by lower temperatures while decomposition of methane increases with temperature. Carbon deposition boundaries have been calculated by Greyson et al [5] and are shown in figure 1. Ternary equilibrium diagrams are given in reference [6].

Nickel carbide can form according to reaction (4). We find that nickel carbide is catalytically inactive but the carbiding can be reversed by treatment with hydrogen above about 250° C to give an active catalyst.

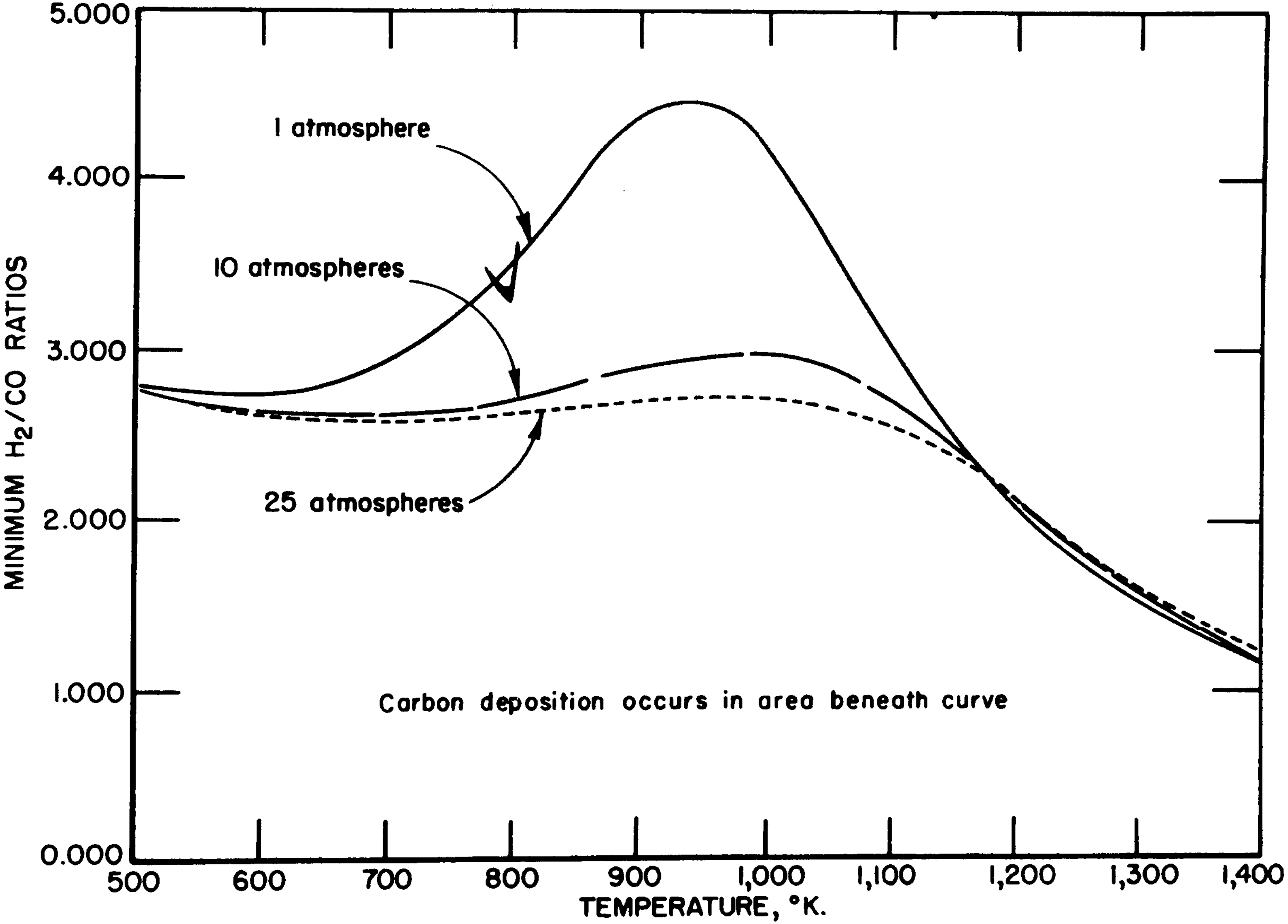

Figure 1 - Carbon deposition boundaries. (5)

We have, however, detected nickel carbide in several samples of spent catalyst. Formation of Ni_3C can also cause spalling of flame sprayed Raney nickel catalysts.

Nickel carbonyl can form via reaction (5) at low temperatures and cause loss of the nickel catalyst. It is easily avoided by only contacting the catalyst with synthesis gas at high temperature (T>275° C). The maximum allowable exposure to $Ni(CO)_4$ has been set by OSHA at 1 ppb and care should be taken to avoid opening reactors that have been exposed to low temperature syngas.

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 decomposes according to reaction (6) and deposits on the nickel catalyst creating an iron catalyst. At methanation temperatures, carbon deposition occurs on the iron and fouls the catalyst. We have detected iron concentrations as high as 22 percent in the catalyst at the reactor inlet. This was accompanied by high carbon content. We have taken steps to replace all carbon steel piping with stainless steel in the pilot plant.

Methanation Systems

Existing methanation systems generally use either heat extraction or dilution to control the temperature rise created by the high exothermic heat of reaction. We have developed methanation systems using both principles. Both of these systems will be tested in the SYNTHANE pilot plant.

SYNTHANE Hot Gas Recycle (HGR)

The simplest system is the Hot Gas Recycle reactor. Product gas is recycled back to the inlet of the reactor to dilute the feed and reduce the CO concentration so that a conversion of about 2 percent CO is obtained in the reactor. Thus, with an inlet temperature of 300° C, the exit temperature does not exceed 400° C. These limits apply to the Raney nickel catalyst. Other catalysts are claimed to operate at higher temperatures. In our small pilot plant we use a feed gas containing about 23 percent CO with a H_2/CO ratio slightly in excess of 3/1 for which the required recycle volume is 10 times the feed volume (10/1). If all this recycle were returned hot so that no moisture was removed, the steam concentration would approach 50 percent which is undesirable from an equilibrium standpoint and may cause catalyst oxidation. Therefore, 30 percent of the recycle stream is cooled to room temperature and water is condensed. Thus we use a 7/1 hot recycle ratio and a 3/1 cold recycle ratio.

Pressure drop is an important consideration in these systems. If the hot gas recycle reactor is used with pelleted catalysts, pressure drop can be quite high as the following calculated pressure drops show:

	Pressure Drops - Psi	
	20 ft bed	10 ft bed
HGR	0.23	0.035
Pellets	85.5	10.8

This is for a 2000 space velocity based on fresh feed, 10/1 recycle, 1000 psi operating pressure. At this point in the process a full scale plant will be circulating up to 5×10^9 SCFD.

The low pressure drop is a result of applying the catalyst to flat plates which are arranged in parallel and stacked in bundles in the HGR. Flame spraying or metallizing is the process used to deposit the catalyst. For the HGR plates Raney nickel alloy powder (80–200 mesh) is fed through a hydrogen-oxygen flame where it partially melts and solidifies on the surface of the flat plate. This process is normally used to apply corrosion resistant coatings, for hard-facing soft metals with hard coatings, and for building up worn journals. A bond coat, .006" thick, containing 95 percent Ni and 5 percent Al is first applied to the stainless steel substrate to improve adhesion, then a coating of Raney nickel, 0.019" thick, is sprayed onto the plate. It is then activated by leaching and kept under hydrogen until contacting the SYNGAS at elevated temperature.

Details of the HGR runs have been presented [7]. Relatively high space velocities of 2000 to 3000 based on fresh feed have been used which correspond to a total feed space velocity of 22,000 to 33,000. Raney nickel catalyst on parallel plates has been compared to a commercial pelleted methanation catalyst in a 3-inch diameter by 2-foot deep bed and results are shown in figures 2 and 3.

Space velocity followed the same program with a 2000 fresh feed space velocity and one period at 3000. The bed of parallel plates coated with Raney nickel was much more reactive as shown by the lower carbon monoxide in the outlet gas. Catalyst life for the parallel plates was 2307 hours while the precipitated catalyst had a life of 1368 hours. Productivity, measured by ft^3 of methane produced/lb of catalyst, was higher for the parallel plates (32.0 vs 11.5 mscf/lb). A higher deactivation rate is experienced during the period at the higher space velocity as shown by the slope of the plots. Other precipitated catalysts which are reputedly superior to this one have been developed recently as well as other forms of Raney nickel. These catalysts will be evaluated in the near future.

The HGR will also be tested in the 75 ton/day SYNTHANE pilot plant. It is designed to handle about 1/8 of the gas produced in the gasifier. The

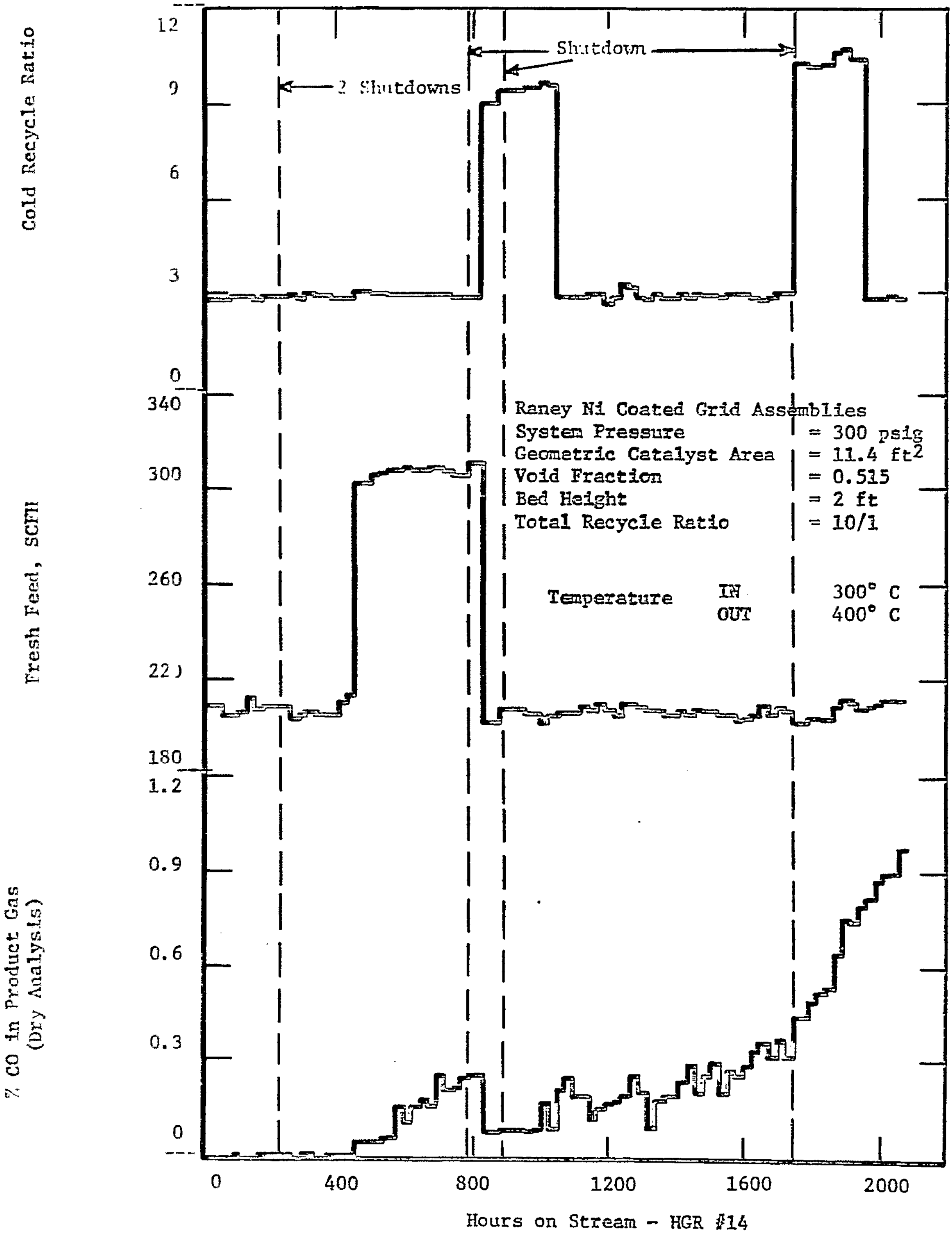

FIGURE 2. - Data From Methanation Pilot Plant - Run 14, Unit 6

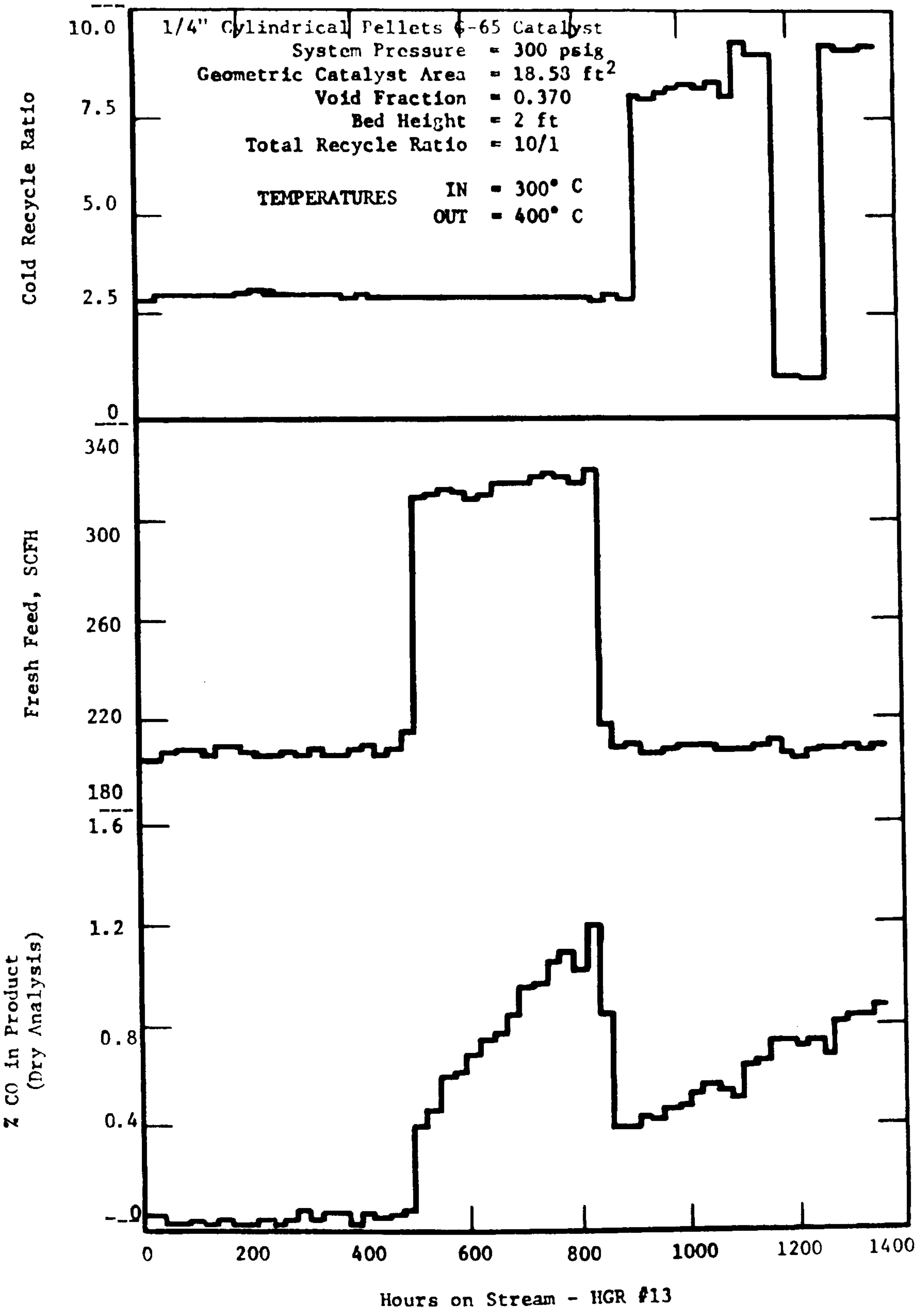

FIGURE 3: - Data From Methanation Pilot Plant - Run 13. Unit 6

parallel plates are 3/16" thick with a 3/16" spacing between plates. The plates are cut into 2 foot long grid assemblies which will be stacked in the reactor. A flow sheet is shown in Figure 4. At present, an eductor is installed to circulate the hot recycle gas while cold recycle gas passes through a recriprocating compressor. The eductor is not very efficient or flexible so a centrifugal compressor has been designed and built for this application and should be installed before the first run.

A clean-up methanation reactor is used to reduce CO concentration in the effluent from the HGR to below 0.1 percent CO. This reactor is a simple packed bed and no recycle is needed because the CO concentration in the inlet will always be below a few percent. The bed is 1 foot in diameter by 2.5 ft. long. It will be filled initially with Girdler Modified G-87 catalyst. There is provision for removal of water before this reactor if desired.

SYNTHANE Tube Wall Reactor (TWR)

This is an isothermal reactor using the heat extraction method to control the heat of reaction. It can operate with no recycle gas. Raney nickel catalyst is applied to the inside wall of 2-inch tubes in a heat exchanger bundle. Heat of reaction is transferred through the tube wall to boiling Dowtherm A on the shell side. The boiling Dowtherm generates high pressure steam. Reaction temperature is fairly high, about 390° C. This is about the upper temperature limit of the Dowtherm.

We have operated a reactor with 7 externally coated 2 inch diam. tubes in a bundle, 27" long, with baffles in the gas space and, more recently, a single internally coated tube which is 2 inches in diameter by 14 feet long. Coating the inside surface of a tube required an especially designed spray gun and a wire that can be fed down the long barrel. Raney nickel is brittle and can't be extruded into a wire form so we use Raney nickel powder held together in a wire by a plastic binder (20%). Measured catalyst life has been in excess of 4 months with a high productivity of 177 mscf/lb catalyst. The higher operating temperature contributes to the increased productivity. In smaller bench-scale reactors, catalyst life has been over 6 months.

The SYNTHANE 75 ton/day pilot plant also has a TWR. The design was developed with the help of a mathematical model [8]. The bundle contains 22 tubes, 2 inch in diameter and 20 ft long in a 2-pass arrangement so the gas passes through 11 tubes in parallel. The TWR is also designed to methanate 1/8 of the gasifier output. It, too, is followed by a clean-up methanator. A flow sheet is shown in figure 5. A recycle compressor is included but probably will not be needed.

SYNTHANE Hybrid Reactor

We have recently developed a "hybrid reactor" which uses a combination of dilution and heat extraction for heat removal. X-shaped inserts are coated with Raney nickel catalyst and placed in the uncoated tube wall reactor.

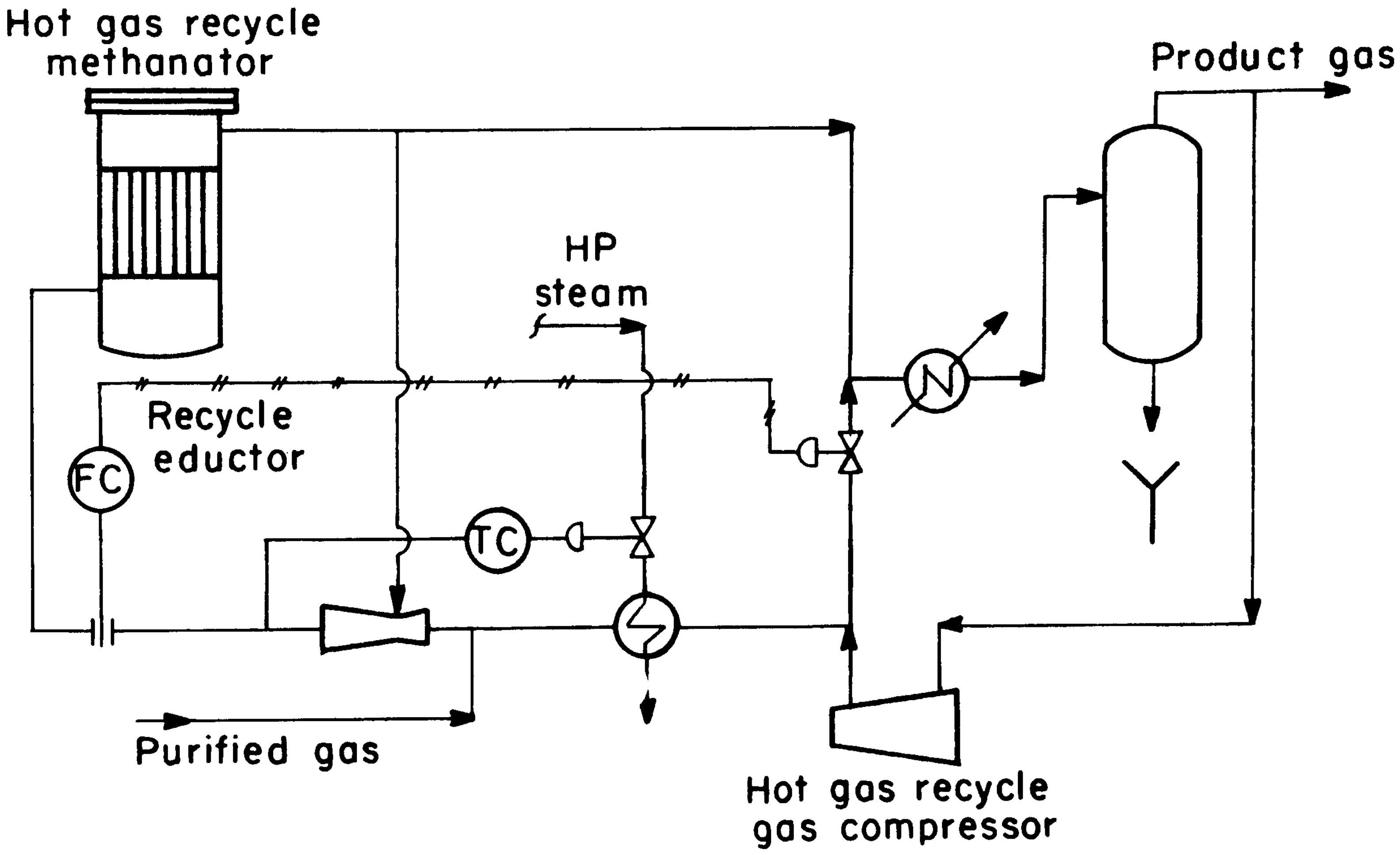

Figure 4 – HGR methanator . (Prototype)

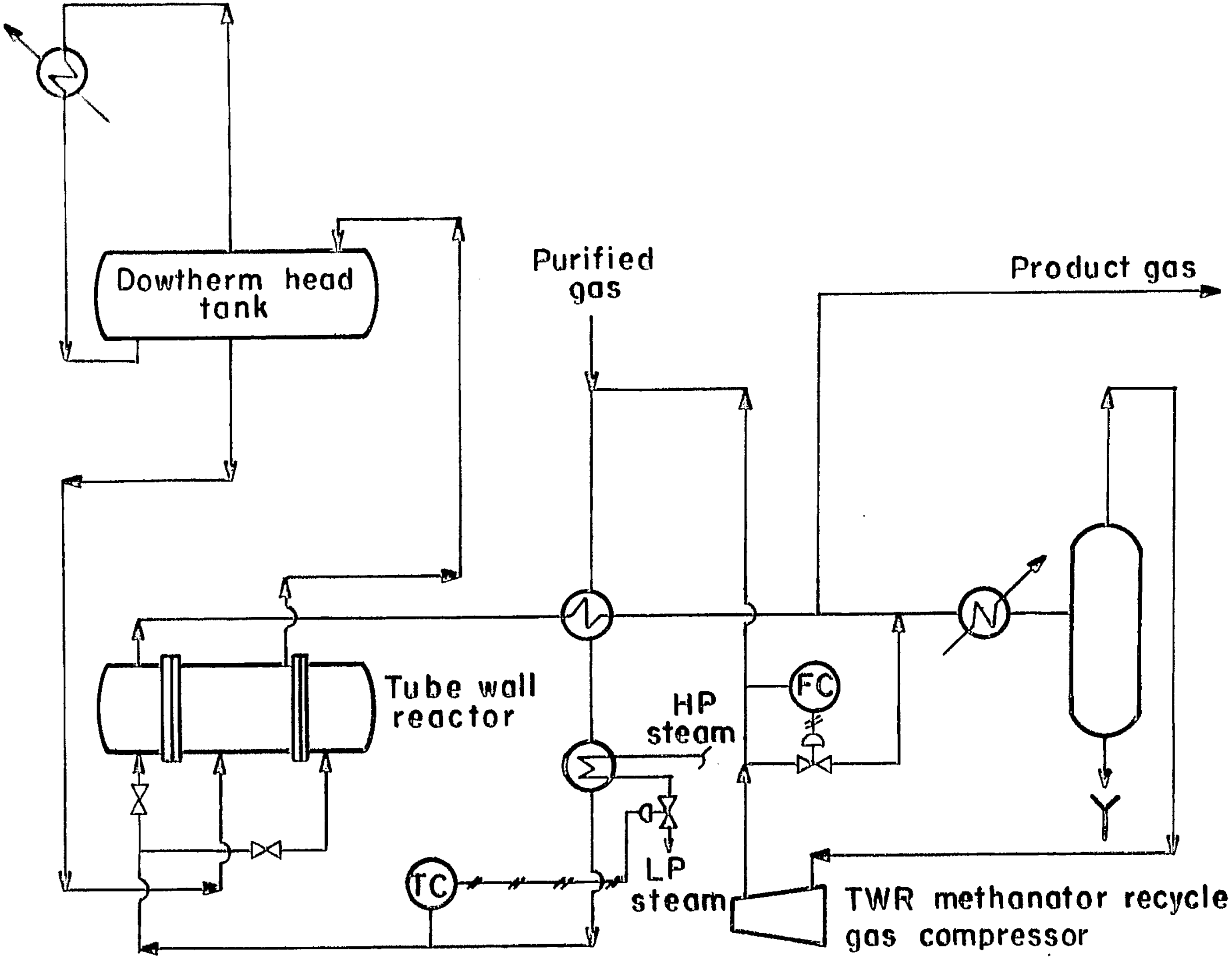

Figure 5 — TWR methanator . (Prototype)

The inlet temperature is 300° C and the Dowtherm temperature is also 300° C. Recycle is added to control the maximum temperature or "hot spot" at 400° C. With this system, about 65 percent of the heat is removed by the Dowtherm and the remainder by the sensible heat of the gas. Recycle can be reduced from the normal 10/1 down to about 8.5/1. The principal advantage is that the X-shaped inserts can be easily replaced. These inserts have a surface area about 15 percent greater than the TWR and area can be increased even further by using inserts with more fins.

Conoco Methanation - Westfield Demonstration

Commercial scale methanation was recently demonstrated by Continental Oil Company along with 16 other American companies in a $6 million demonstration project at the Westfield Coal Gasification plant in Scotland [9]. A methanation system was added to an existing Lurgi gasifier. The Rectisol purification system was used for purification prior to methanation. A "fixed-bed, gas recycle, adiabatic methanation reactor" was used. The product was fed into the local gas grid. Experimental details and flow sheets are not available.

IGT Split Feed Recycle Reactor

A split feed recycle reactor is being developed by the Institute of Gas Technology (IGT) [10]. In this system, two or more packed bed adiabatic reactors are used in series with addition of fresh feed at the inlet and between beds. The product gas, consisting primarily of methane, from the first stage acts as the diluent for the second stage. In this way the overall recycle ratio and pressure drop can be significantly reduced. Each stage becomes progressively larger to accomodate the increased flow. Addition of fresh feed and cold recycle between stages also cools the product from the previous stage which reduces the requirements for heat exchange equipment.

The reactors in IGT's HYGAS pilot plant are 15.7 and 31.4 ft^3 in volume and are packed with a Harshaw pelleted nickel-on-kieselguhr catalyst. CO concentration before each stage is about 4 percent with inlet temperatures of 288° C (550° F) and exit temperatures of 482° C (900° F). Overall recycle ratio is below 1.5/1. Relatively low space velocities of 3200-4400 are used with an essentially sulfur free feed gas. This system has been successfully operated for over 500 hrs with no evidence of catalyst deactivation. Carbon monoxide conversion has been complete.

Lurgi Methanation

Lurgi has operated two semicommercial pilot plants to demonstrate methanation [11]. In Schwechat, Austria, synthesis gas from naptha was methanated. The other demonstration was on a sidestream from the SASOL Fischer-Tropsch plant in Sasolburg, South Africa. This plant produces a synthesis gas from coal in Lurgi gasifiers. In both cases a BASF catalyst was used in a fixed bed recycle methanator followed by a clean-up methanator. Based on the pilot plant experience, a catalyst life of 16,000 hrs is expected. Lurgi flowsheets for a commercial plant show a split feed recycle system with two or three beds in series and all recycle introduced before the first bed.

CCI Methanation

Catalysts and Chemicals Inc. (CCI) in conjunction with El Paso Natural Gas Company and, later, Western Gasification Company and COGAS Development Co., operated a methanation pilot plant from 1971 to 1974. It used the split feed recycle system with two primary beds of 1 to 5 ft^3 in volume followed by a final methanator. The feed was a syngas made by reforming. They tested a CCI catalyst for 4000 hours and extrapolate a catalyst life of over 2 years.

CO_2 Acceptor Process Methanation

A methanation system was recently installed at the CO_2 Acceptor Process pilot plant in Rapid City, S. D. The heat extraction method is used by packing heat exchanger tubes with catalyst. Boiling Dowtherm on the shell side removes the heat and is used to raise high pressure steam. No results are available at present.

Chem Systems Liquid Phase Methanation

A three-phase fluidized bed is used with gas bubbling up through a fluid such as a mineral oil (C_{15}-C_{21}) with catalyst suspended in the oil [12]. The oil absorbs the heat of reaction and is cooled externally in a heat exchanger where high pressure steam is generated. Commercial methanation catalysts from 1/16 to 1/4 inch are used. No recycle gas is needed. Chem Systems has operated bench scale units and a PDU (4.5" O.D. X 84"). The PDU has been run for 580 hours in one test and a catalyst life of 8000 hrs. has been extrapolated. A pilot plant with a 2' diameter by 15' long reactor has been built and will probably be installed in the HYGAS or CO_2-Acceptor Process pilot plant. It is designed to handle a feed of 2 MM SCFD of feed gas at 1000 psig.

BCR Fluidized Bed Methanation

Bituminous Coal Research (BCR) has developed a fluidized bed methanation reactor. Preliminary results of tests on a 6" I.D. X 10 ft reaction zone PEDU have been reported [13]. Heat is removed by cooling coils containing Dowtherm G. Recycle gas can be provided. The bed contains about 1 ft^3 of catalyst and is designed to operate with up to 6000 scfh of feed gas produced by natural gas reforming. Actual space velocities of 1200 to 3200 have been used at about 1000 psig. Average catalyst size is 230 mesh. Useful conversion has been from 50 to 93 percent. Steady state attrition and

and catalyst life data are not yet available. The fluidized bed methanation in the Bi-Gas pilot plant represents a scale-up by about a factor of 50.

RMProcess

The Ralph M. Parsons Co. has developed a unique methanation system [6]. Shift and methanation are accomplished simultaneously in a series of six adiabatic fixed bed reactors operating at very high temperatures. The syngas feed is split between the first three reactors and steam is added to prevent carbon deposition and for the shift reaction. Inlet temperatures to the reactors are about 900°, 1000°, 1000°, 1000°, 600°, 500° F. Exit temperatures can exceed 1400° F. One of the principal advantages is that 1500 psi steam can be raised between beds, about 1/3 of which is used in the process. A pilot plant has been operated but test details have not yet been presented.

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