

TABLE 11-4 (Cont'd)
 PERFORMANCE OF GASIFICATION TECHNOLOGIES VS. CRITERIA

CRITERIA AND SUBCRITERIA	EXPLANATION	WESTINGHOUSE	EXXON	SHELL	U-GAS
8.0 GASIFIER INTEGRABILITY					
8.1 Feed Preparation	No. of operations	3	6	5	3
8.2 Raw Gas Handling	No. of operations	3	3	4	3
8.3 Residue Disposal	No. of operations	2	4	2	2
9.0 THROUGHPUT					
9.1 Vessel Capacity	Per Gasifier.	1450 TPD	2800 (?) TPD	900 - 1100 TPD	1000 TPD
10.0 PROCESS TECHNIQUES					
10.1 Equip't Available	Standard Vessels.	Yes	Yes	Yes	Yes
11.0 MATERIALS OF CONSTRUCTION					
11.1 Availability	None exotic.	Yes	Yes	Yes	Yes
11.2 Gasifier Shell Material		C Steel	C Steel	C Steel	C Steel
11.3 Waste Heat Recovery System	Expected life.	No comm'l demo.	No comm'l demo.	No comm'l demo.	No comm'l demo.
12.0 COMPLEXITY					
12.1 Gasifier Stages		Single stage.	Single stage.	Single stage.	Single stage.
12.2 Gasification Area Steps Required	No. of steps	6	7	6	6
12.3 Area Recycles	Gas, liquid, and/or solid.	1 recycle.	2 recycles.	2 recycles.	1 recycle.
12.4 Mechanical	Index.	0	0	0.5	0

11-13

TABLE 11-4 (Cont'd)

PERFORMANCE OF GASIFICATION TECHNOLOGIES VS. CRITERIA

CRITERIA AND SUBCRITERIA	EXPLANATION	WESTINGHOUSE	EXXON	SHELL	U-GAS
13.0 SEVERITY					
13.1 Temperature	deg F	1700-1850 Exit	1200-1300	2550-2700 Exit	1750-1900
13.2 Pressure	psig	450-600	500	450	450
14.0 CONTROLLABILITY					
14.1 Control System	Index.	1.0	1.0	1.0	1.0
14.2 Turndown	% of full rate.	50%	50%	50%	50%
14.3 Response	Index.	1.1	1.1	0.9	1.1
15.0 RELIABILITY					
15.1 Standby Requirements	Active/total.	8/9	4/5	6/7	8/9
15.2 Consequence of Failures	Risk involved.	Low	Low	Low	Low
15.3 Maintenance Extent	Index.	0.9	0.9	1.0	0.9
16.0 ENVIRONMENTAL CONSIDERATIONS					
16.1 Solid Effluents	Extra steps.	None.	One step.	None.	None.
16.2 Liquid Effluents	Extra steps.	None.	None.	None.	None.
16.3 Gaseous Effluents	Extra steps.	None.	None.	None.	None.

CRITERIA

EXPLANATION (CONTD.)

- 11.3 WASTE HEAT RECOVERY SYSTEM - The materials of construction requirements for waste heat recovery should be less severe with the lower outlet temperatures. In order of increasing severity; Lurgi and BGC/Lurgi; Exxon; Westinghouse and U-GAS; and GKT, Texaco and Shell.
- 12.2 GASIFICATION AREA STEPS REQUIRED - GKT, Texaco, and Shell are the least complex; Exxon is the most complex due to catalyst recycle requirements.
- 12.3 AREA RECYCLES - Westinghouse recycles fines and gas, U-GAS recycles only fines. Exxon recycles fines, gas and catalyst. Shell recycles only gas.
- 12.4 MECHANICAL - Westinghouse, Exxon and U-GAS are the simplest gasifiers. GKT, Shell and Texaco must manage slag. Lurgi requires moving grate(s). BGC/Lurgi has a stirrer and slag handling parts.
- 14.2 TURNDOWN - The fluidized-bed processes (Westinghouse, Exxon and U-Gas) are limited to about 50% turndown. Texaco's turndown is limited by heat balance. The other processes provide wide ranges of turndowns.
- 14.3 RESPONSE - Based upon process stability at varying load conditions, the fluidized bed processes are the most stable, with U-GAS slightly less because of minor concerns about the central jet. Fixed bed gasifiers are stable but somewhat unresponsive. The entrained bed processes are the least stable because their short residence time eliminates all but after-the-fact control.
- 15.1 STANDBY REQUIREMENTS - Westinghouse and U-GAS were judged to require the least extent of idle parallel equipment with Exxon close to the same level. Next were the fixed bed gasifiers, while the entrained bed gasifiers require major sparing.
- 15.2 CONSEQUENCE OF FAILURE - Based on the extent of significant damage that would result from a major upset in operation, the fluid bed processes would expect relatively minor damage. BGC/Lurgi would have the slag complications. The entrained bed gasifiers would have the most consequences because of slag and because an upset could result in

CRITERIA

EXPLANATION

- 1.1 COAL TYPES - GKT, Westinghouse, Shell, and U-GAS have demonstrated all types; Exxon should not have limits but has only been demonstrated with a few U.S. coals; Lurgi cannot readily accept caking coals; BGC/Lurgi has not been demonstrated with low rank coals. Texaco cannot tolerate the moisture content of lignite.
- 1.2 PLANT FINES UTILIZATION - Lurgi cannot use $\frac{1}{4}$ inch material; BGC/Lurgi can accept a greater amount of the fines than Lurgi but not all.
- 1.5 DRYING - In order of more demanding drying: Lurgi and BGC/Lurgi; Westinghouse and U-GAS; Texaco; Exxon; GKT and Shell.
- 3.1 PLANT COLD GAS EFFICIENCY - The U-GAS plant cold gas efficiency of 62% for Eastern coal was based on a design without ash deposit control. Deposit control would result in an efficiency of about 60%.
- 4.1 GASIFIER FINES - The fluidized bed processes (Westinghouse, Exxon, and U-Gas) lose minor amounts of fines which escape the cyclone(s). GKT produces a large quantity of fines that are not recycled.
- 5.2 STEAM - The Texaco slurry feed system cancels the need for steam injection. GKT requires only low-pressure steam.
- 7.1 NUMBER OF PROCESS BLOCKS - See Block Diagrams.
- 8.1 FEED PREPARATION. See Block Diagrams.
- 8.3 RESIDUE DISPOSAL - GKT, Texaco, BGC/Lurgi, and Shell should have the most ease in solids disposal because they operate in the slagging ash mode; then Westinghouse and U-GAS with agglomerated ash. Lurgi (due to dust) and Exxon (due to residual catalyst contamination on ash) should have the most difficulty in residue disposal.
- 11.2 GASIFIER SHELL/LINING LIFE - The non-slagging processes are less severe on the gasifier shell/lining than the slagging processes.

CRITERIA

EXPLANATION (CONTD.)

potential mixing of oxygen with syngas in downstream equipment.

- 15.3 MAINTENANCE EXTENT - Fluidized beds would require minimum maintenance; Lurgi has moving parts; BGC/Lurgi also has slag to increase routine maintenance needs; the high temperature entrained bed gasifiers would need the most maintenance.
- 16.1 SOLIDS EFFLUENTS - Lurgi's ash is dusty; Exxon's ash is contaminated with catalyst.
- 16.2 LIQUID EFFLUENTS - The fixed bed processes produce significant quantities of liquids. Exxon has the potential for catalyst carryover into aqueous effluents.

REVIEW OF SELECTED SHIFT AND METHANATION
PROCESSES FOR SNG PRODUCTION

FINAL REPORT

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JULY 1985

217

REVIEW OF SELECTED SHIFT AND METHANATION
PROCESSES FOR SNG PRODUCTION

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REVIEW OF SELECTED SHIFT AND METHANATION
PROCESSES FOR SNG PRODUCTION

TABLE OF CONTENTS

1. Introduction and Summary
2. Conventional Shift and Methanation Process
3. Combined Shift and Methanation Process
4. Direct Methanation Process
5. Comflux Process
6. Comparison of Performance/Design Parameters

1.0 INTRODUCTION AND SUMMARY

Kellogg Rust Synfuels, Inc. (KRSI) has assembled background information for use in evaluating technologies for downstream gas processing, specifically Shift and Methanation, as part of work with the GRI/Advisors Planning and Strategy (GAPS) Committee under GRI Contract No. 5082-222-0754.

The GAPS Committee chose four representative technologies for evaluation. These were:

- Conventional Shift And Methanation Multiple, adiabatic fixed-bed reactors; Shift and Methanation in two stages.
- Combined Shift and Methanation Multiple, adiabatic fixed-bed reactors in series and/or series - parallel; Shift and Methanation in one stage.
- CRC Direct Methanation Multiple, adiabatic fixed-bed reactors; higher outlet temperatures; Shift and Methanation in one stage.
- Comflux Fluid-bed process with internal cooling; Shift and Methanation in one stage.

KRSI proceeded to prepare a "Status Summary" report for each of the four technologies mentioned above. Their directions were to summarize pertinent, recent information within a concise report for each process. Each of the Status Summary reports is divided into the following sections, as applicable:

- General Information
- Catalyst and Process Development
- Feedstocks Tested
- Process Description
- Performance Data
- By-Product and Environment
- Commercial Plans
- Advantages and Limitations
- Techno-Economic Evaluations
- References

The Status Summary reports appear in Sections 2.0 through 5.0 for the Conventional Shift and Methanation, Combined Shift and Methanation, CRC Direct Methanation and Comflux processes, respectively. These documents comprise a body of background information for use in further work.

STATUS SUMMARY

CONVENTIONAL METHANATION

- 1.0 GENERAL INFORMATION
- 2.0 CATALYST AND PROCESS DEVELOPMENT
- 3.0 FEEDSTOCKS TESTED
- 4.0 PROCESS DESCRIPTION
- 5.0 PERFORMANCE DATA
- 6.0 BY-PRODUCT AND ENVIRONMENT
- 7.0 COMMERCIAL PLANS
- 8.0 ADVANTAGES AND LIMITATIONS
- 9.0 TECHNO-ECONOMIC EVALUATIONS
- 10.0 REFERENCES

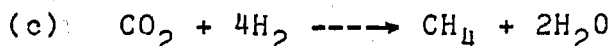
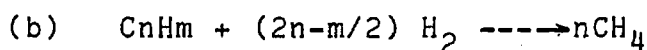
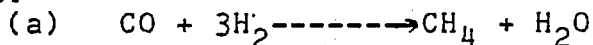
1.0 GENERAL INFORMATION

Developers: The conventional methanation process has been developed by several firms, either in conjunction with their coal gasification technology, e.g., Lurgi, Conoco (Cono-Meth), or as a stand-alone application, e.g., catalyst vendors such as Haldor Topsoe, BASF, etc. Several engineering firms have the capability to design the process which can use any of the catalysts from the recommended by the catalyst vendors.

Reactor Type: The conventional methanation process uses multiple adiabatic fixed-bed reactors.

Feed Gas: The feed gas hydrogen content is adjusted slightly above the stoichiometric reaction requirement to convert the feed carbon (CO and heavier hydrocarbons) to CH_4 . The feed gas must contain less than 0.02 ppmv H_2S equivalent sulfur.

Principal Reactions:



Catalyst Type: Major constituent of the catalyst is NiO on an Al_2O_3 support. The catalyst is poisoned by³ sulfur. Several grades (characterized by range of operating temperatures) of the catalyst are available. Different grades may be employed at the same time depending upon the reactor system chosen.

Operating Conditions: The catalyst can be operated between 0-1500 psig pressure, and depending upon the type, between 450°F (inlet) and 900°F (outlet). In general, high pressure and low temperature favor the methanation reactions.

Products: The product gas from conventional methanation process, after compression and drying, will meet the gas interchangeability standards for pipeline quality gas.

Application: Conventional methanation is better suited for coal gasifiers producing raw gas with high H_2/CO ratio. Units upstream of the methanation step must include shift, acid gas removal and sulfur guard beds. Whereas C_2-C_4 range hydrocarbons will be methanated, the feed gas should be essentially free of C_5^+ hydrocarbons.

Status: Process is commercial and is offered by many engineering companies. This process is installed in the Great Plains coal gasification plant.

2.0 CATALYST AND PROCESS DEVELOPMENT

Catalyst:

The methanation catalysts are used for promoting the reaction of hydrogen with carbon oxides. It is also used, though to lesser extent, to hydrogenate olefins and traces of oxygen. They are nickel oxide catalysts prepared on active, stable supports.

Various types of methanation catalysts were developed and studied in the first half of the century. Nickel methanation catalysts did not achieve substantial commercial acceptance until the late 1950's, when they were incorporated into the process schemes of several hydrogen and ammonia synthesis gas plants to remove CO. Their usage achieved world-wide acceptance in the 1960's when essentially all new ammonia and hydrogen plants incorporated methanation catalysts in their process design.

The methanation catalysts employed for SNG manufacture are essentially an extension of these nickel catalysts characterized by a much higher nickel content. They operate over a wider temperature rise to achieve high carbon oxide conversion per pass. They are also characterized by high activity and thermal stability. The high activity is required to obtain the low residual carbon oxide concentration while high thermal stability is required (in addition to obtaining high CO conversion) to withstand excessive temperature rises that can result from an operational upset.

Of the several methanation catalysts offered by the various catalyst vendors, the ones offered by United Catalyst Inc. (UCI) are representative of the types available for application in the bulk methanation process for production of SNG. Table 1 and 2 show the principal characteristics of these catalysts.

Process:

Development of the conventional methanation process can be traced to its original application to hydrogenating small quantities of carbon dioxide in NH_3 and H_2 plants, followed by methanation of synthesis gas³ produced from naphtha reforming in the British Gas Corporation's CRG methanation process for SNG Production (24 Units totaling 609 MM scfd SNG capacity).

Cono-Meth offered by Conoco Inc. was developed at a demonstration plant operated with syngas generated by a Lurgi dry-bottom gasifier at BGC's Westfield facility in Scotland during 1974. Other process licensors include Lurgi, Parsons, Haldor Topsoe (Trempe methanation), etc. The process design is also available from any of the several A/E companies in conjunction with catalyst vendors.

3.0 FEEDSTOCKS TESTED

Synthesis gas streams found in NH_3 , H_2 and Olefins plants have been successfully methanated commercially. In relation to SNG production, methanation of gas from naphtha reforming has also been demonstrated commercially.

Bench scale and pilot plant work has been carried out by several catalyst vendors to study catalyst activity and life over long durations (6 months) using simulated synthesis gas.

As mentioned previously, at BGC's facility in Westfield, Scotland, a demo unit was operated in conjunction with Lurgi gasifiers producing 2.1 MM scfd SNG (979 Btu/Scf) over a period of two months (2).

The first U.S. commercial scale "Coal-to-SNG" facility, i.e., the Great Plains Project using North Dakota lignite was recently brought on-stream. It employs conventional methanation process designed by Lurgi.

TABLE 1

Methanation Catalysts for SNG

Catalysts

1. C150-4-03
2. C150-5-01/G115
3. C150-6-01

(Prior developmental catalysts — C150-1-1, C150-1-03 and G87.)

OPERATING RANGE

Catalysts Type	C150-6-01	G115/C150-5-01	C150-4-03
Form	Rings	Tablets	Tablets
Size*	5/8" x 1/4" x 5/16"	1/4" x 1/4"	1/4" x 1/4"
Operating Range			
Temperature, °C	450-850	230-650	230-500
Pressure, ata	0-100	0-100	0-100
Carbon Monoxide, %	10-50	3-25	0.1-10
Steam, %	20-70	10-60	5-60

*Note: Other sizes available

Source: Ref. 8

TABLE 2
METHANATION CATALYST
TYPICAL CHEMICAL AND PHYSICAL PROPERTIES

I. Catalyst Type, Form and Size

Catalyst Type	C150-4-03
Form	Tablets
Size	1/4" x 1/4" 3/16" x 3/16"

II. Chemical Composition

Weight Percent

1. Composition (dry basis)

NiO	75 ± 5
Al ₂ O ₃	22 ± 2
Na	<0.05
S	<0.05
C (graphite)	2 - 3
Cl	<0.02
CoO	<0.01
Fe ₂ O ₃	<0.10
SiO ₂	<0.10

2. Other Major Constituents (as received) Weight Percent

H ₂ O	<5.0
CO ₂	<3.0

3. LOI to Constant Weight at:

1000°F	<8.0
--------	------

III. Physical Properties

A. Bulk Density, lbs./cu. ft.	58 ± 5
B. Surface Area, m ² /g	225 ± 25
C. Pore Volume, cc/g	0.45 - 0.55

* Loss On Ignition

Source: Ref. 8

4.0 PROCESS DESCRIPTION

A conventional methanation process consists of multiple reactors and a recycle gas system. The recycle gas is used to limit the temperature rise across a reactor. The feed and recycle gas streams are split and fed in various proportions depending upon catalyst used in the reactor beds and to meet the SNG product gas specifications. In general, the recycle gas flow can be minimized by going to higher numbers of reactors. Thus economic optimization will establish exactly how many reactors, the ratio of recycle gas to feed gas and how the gas streams are split among the various reactors. A simplified process flow diagram (Figure 1) shows the typical arrangement of the equipment.

The main characteristics of the conventional methanation process are:

- Shifted Feed gas with a H_2/CO ratio greater than stoichiometric ratio of 3.0.
- Feed gas containing less than 0.02 ppmv H_2S equivalent total sulfur.
- Reactor inlet temperature of at least $450^\circ F$.
- Last reactor, operating at much lower outlet temperature ($600^\circ F$) to produce a gas containing less than 0.1 mol% CO concentration after dehydration.

Several other schemes have been proposed as modification to the basic process described above, and are discussed below.

Wet Methanation (Ref.6): Instead of using recycle gas, use of steam to limit the temperature rise in a reactor bed. Principal advantages are: simplicity (no splitting of feed among reactors) and conditions suppressing carbon deposition reactions. However, study has shown wet methanation does not have favorable economics over use of recycle gas methanation.

Methanation in presence of CO_2 (Ref.2): CO_2 is used as a heat sink by leaking higher amounts from the upstream acid gas removal unit. Study has shown this approach is not economical since it would require a downstream acid gas removal and trim methanation units. Optimally, CO_2 leakage from the AGR system should be no higher than allowed by the product specifications.

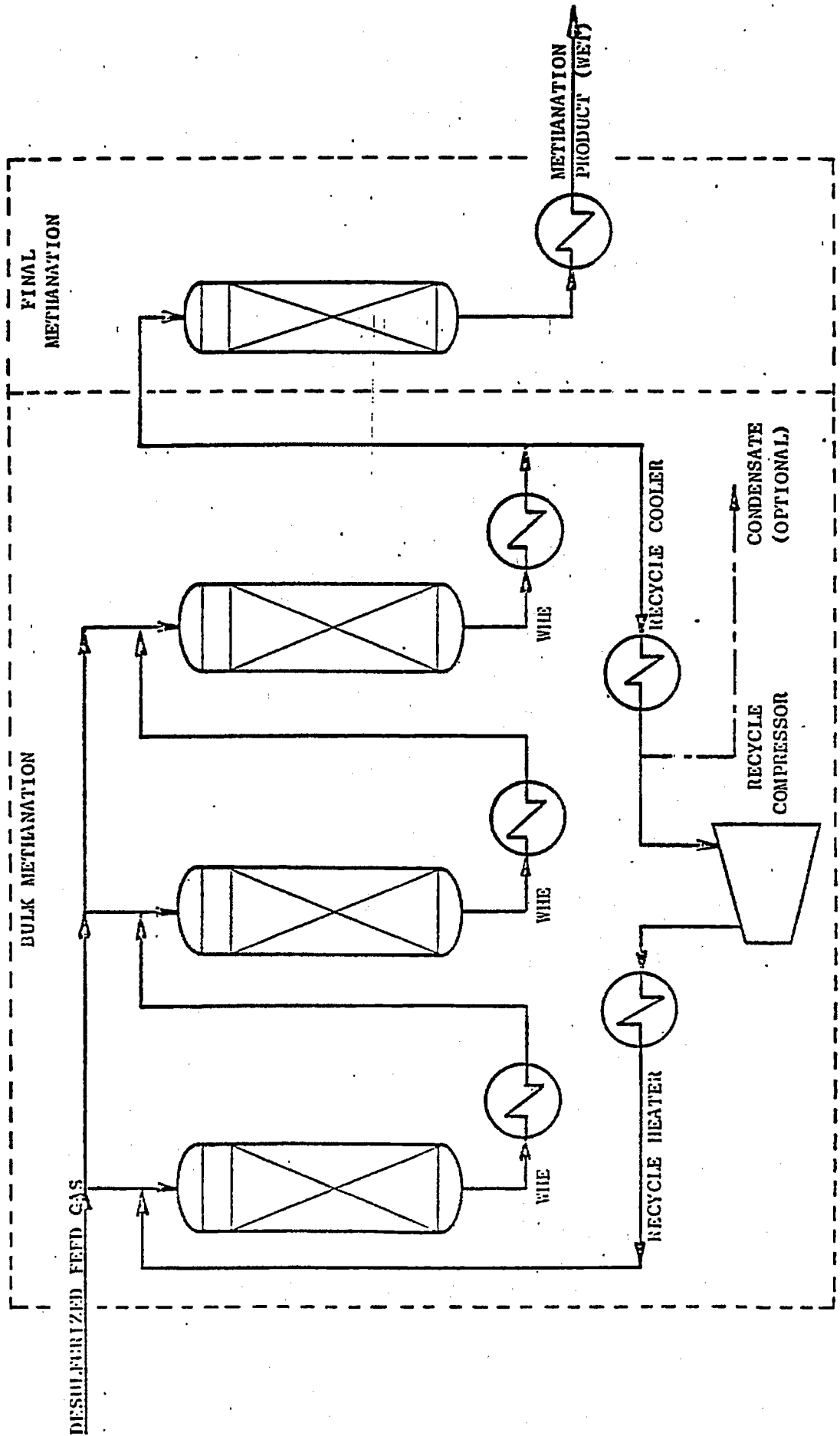
Other schemes involve use of various operating conditions. The conclusions from these studies indicate that the economics of the bulk methanation process can be improved by:

- Use of methanation catalyst operating with higher temperature rise (Reactor outlet temperatures presently limited to $950^\circ F$).
- Use of warm or hot gas recycle as used by Lurgi to maximize recovery of high level steam.

Figure 1

CONO-METHTM METHANATION PROCESS FLOW DIAGRAM

Source: Ref. 7



Use of reactors other than adiabatic reactor, such as boiling water reactor with catalyst in tubes and liquid phase methanation have been proposed. The former is licensed by Haldor Topsoe as IRMA methanation process while the latter is under development by Chem Systems Inc.

5.0 PERFORMANCE DATA

Laboratory scale performance data on the UCI-SNG methanation catalysts are shown in Tables 3 through 6 and Figures 2 through 4. Simulated synthesis gas was used in these tests.

Results of semi-commercial tests conducted jointly by Lurgi-Sasol using coal gasification synthesis gas are shown in Table 7 and Figure 5. The feed gas contained a rather large amount of CO_2 which was removed after methanation to give 972 Btu/SCF gas.² The advantage of retaining CO_2 during the methanation was said to be that the amount of unreacted hydrogen could be decreased. The preferred catalyst was supplied by BASF. After 4000 hours of operation, the catalyst retained good activity indicating expected life of the catalyst to be 16,000 hours. No carbon was detected in catalyst after 4000 hours. Steam was injected into the process to avoid carbon deposition (7).

6.0 BYPRODUCT AND ENVIRONMENT

The byproduct of the methanation reaction is water. Since the feed gas has no sulfur, the condensate from the process requires no special treatment and can be reused as process water makeup.

7.0 COMMERCIAL PLANS

Conventional methanation has been successfully demonstrated at semi-commercial scales using coal derived synthesis gas, e.g., by BGC at Westfield, Scotland and Lurgi at Sasol, South Africa.

The conventional methanation process is employed at the Great Plains project in North Dakota, U.S.A. This is the first commercial scale coal-to-SNG facility in U.S.A.

TABLE 3

Life Studies of Different Methanation Catalysts

1. C150-6-01 — C150-6-01 is basically a ceramic methanation catalyst. This was demonstrated by Parsons in their process development work.
2. G115/C150-5-01 pilot plant tests in laboratory units alternating between high and low CO gases with temperature varying from 600 to 1300°F, (316° to 704°C).

G115 Test Conditions — Run 6-36

	Feed Gases		Temperature °F — 600-1300
	1	2	
% H ₂	50.0	45.0	Pressure, psig — 300
% CO	15.0	28.0	Space Velocity — 6000
% CO ₂	25.0	19.0	(v/v/hr)
% CH ₄	10.0	8.0	
S/G	0.8	0.8	

	Gas 1				Gas 2			
	Initial		End of Run (30 days)		Initial		End of Run (30 days)	
	In	Out	In	Out	In	Out	In	Out
H ₂	54.9	44.0	41.1	28.1	55.5	44.8	42.0	35.7
CO	15.4	5.8	14.3	2.0	23.4	5.3	27.7	6.2
CO ₂	23.9	29.1	26.7	38.3	14.7	28.1	15.3	35.8
CH ₄	5.8	14.1	17.9	31.6	6.4	21.8	5.0	22.7

S/G = Steam to Dry Gas Ratio

FIG. 2

% of Bed Used for Reaction versus Time on Stream -- G115

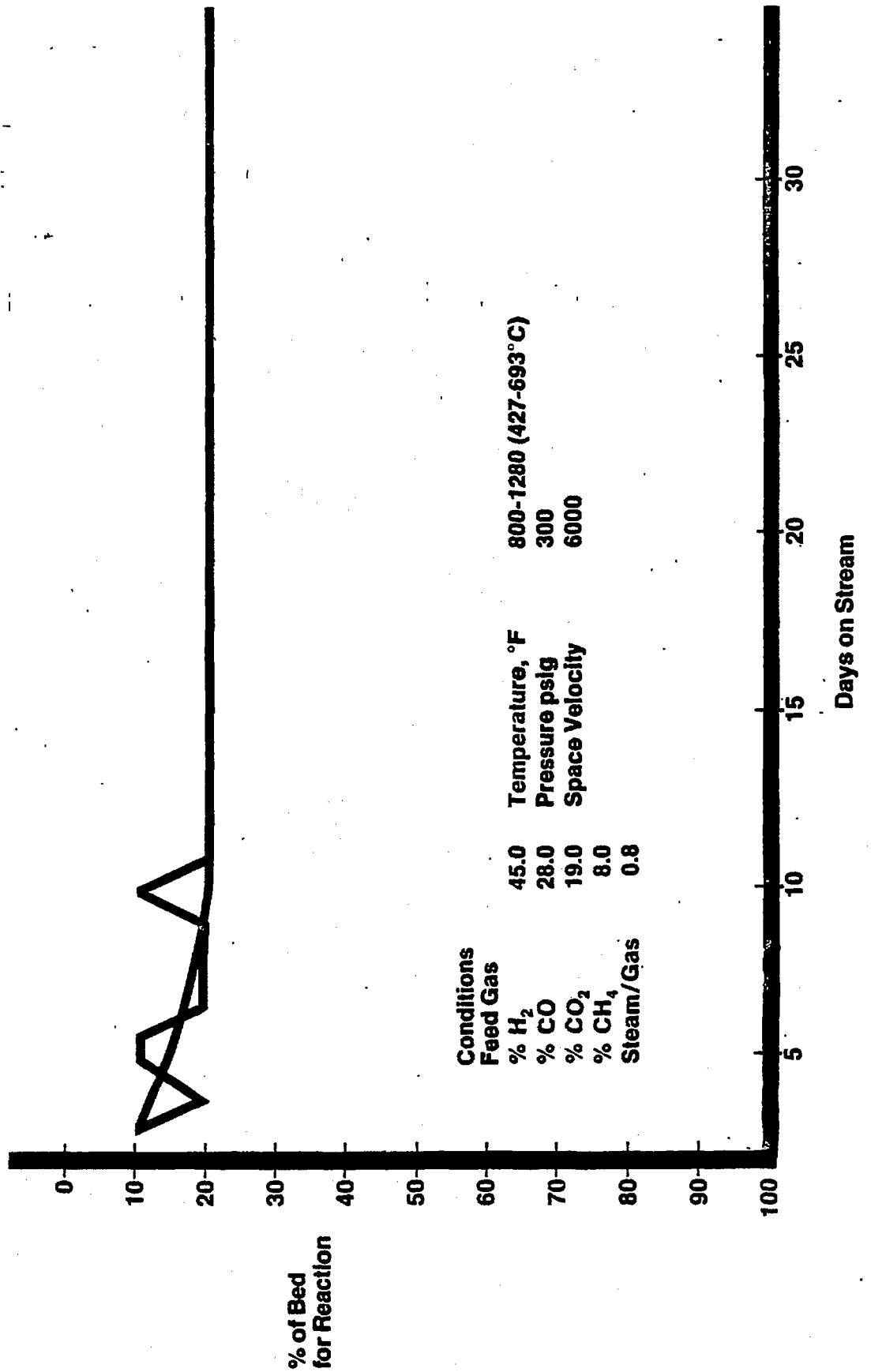


TABLE 4

Activity Evaluation and Life

C1504-03

- El Paso and other participants sponsored a 2 year pilot plant, \$0.75 million program at UCI in Louisville.

Process development unit with fixed bed adiabatic reactors with product gas recycle to control ΔT

- Life Test Conditions

Feed Gas		Temperature, °F
% H ₂	22.0-25.0	— 500-850
% CO	4.5-5.5	— 350
% CO ₂	4.0-6.0	— 18,000-20,000
% CH ₄	65.0-70.0	(v/v/hr)
S/G	0.40-0.45	

S/G = Steam to Dry Gas Ratio

METHANATION PILOT PLANT (EL PASO/UCI)

FIG. 3

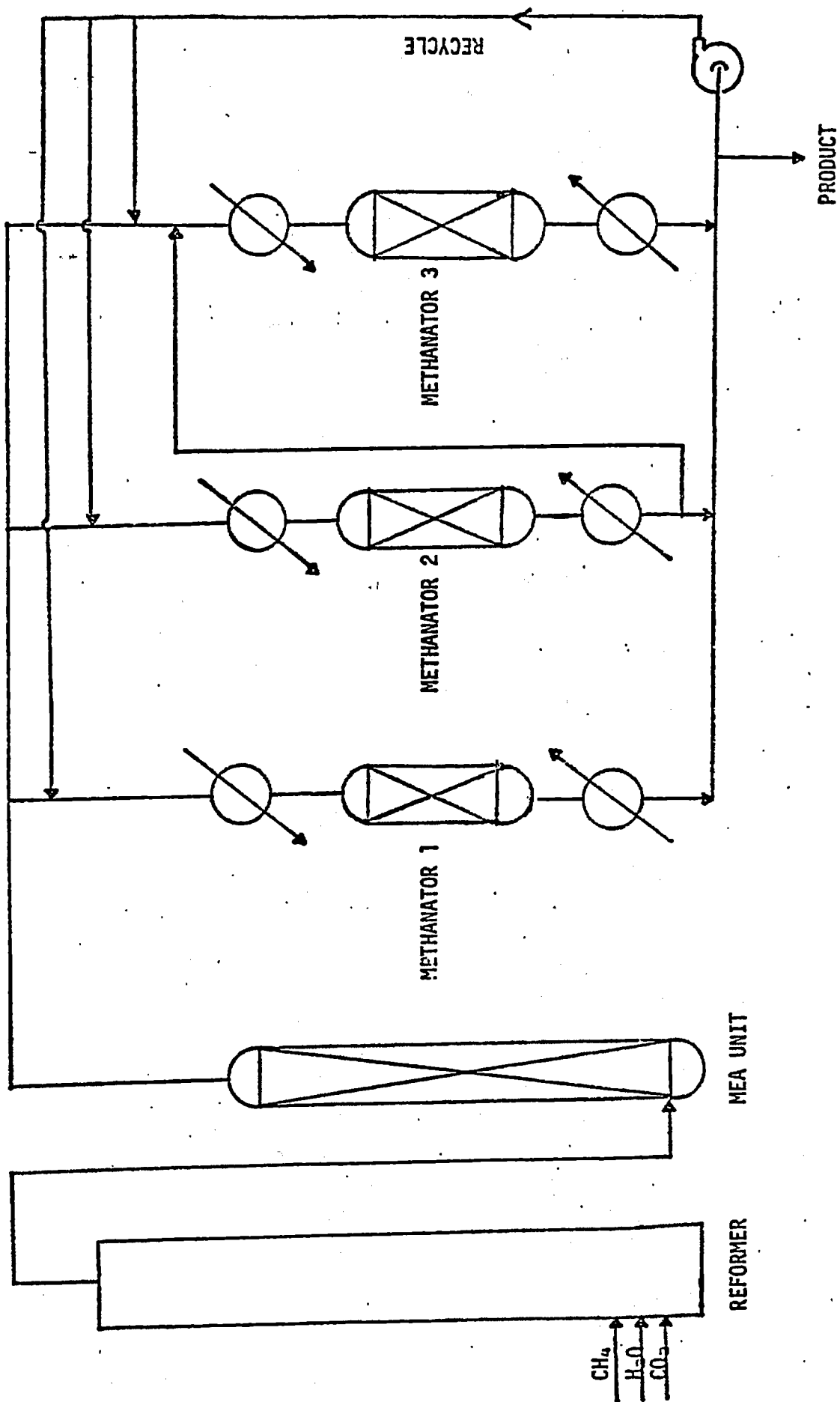


TABLE 5

3. C150-4-03 — Process Development Unit — Adiabatic Fixed Bed
 — Reactor with Recycle to control ΔT (pictures)

Most crucial catalyst because of high activity of high activity for low temperature operation and long life

Life Test Conditions

Feed Gas
 % H₂ 22.0-25.0 Temperature, °F — 500-850
 % CO 4.5-5.5 Pressure, psig — 350
 % CO₂ 4.0-6.0 Space Velocity, — 18,000-20,000
 % CH₄ 65.0-70.0 v/v/hr
 S/G 0.40-0.45

S/G = Steam to Dry Gas Ratio **Test 1**
 4000 hours (six months)

Operating conditions and gas compositions at end of life test 1—4,000 hr

	Primary methanators		Secondary methanators	
	Bed 1 — C150-1-01 ¼ in. by ¼ in.		Bed 3 — C150-1-01 ¼ in. by ¼ in.	
	Inlet	Exit	Inlet	Exit
Temperature, °F	570-575	850-860	530-535	840-850
Pressure, psig	340-345	340-345	340-345	340-345
Dry-gas space velocity, v/v/hr	12,000-15,000	12,000-15,000	12,000-15,000	4,000-6,000
Wet-gas space velocity, v/v/hr	18,000-20,000	18,000-20,000	18,000-20,000	4,000-6,000
Reactor gas composition:				
% CO	4.0-5.0	0.15-0.20	4.0-5.0	0.10-0.15
% CO ₂	4.0-5.0	5.0-6.0	4.0-5.0	5.0-6.0
% H ₂	20.0-25.0	10.0-15.0	20.0-25.0	10.0-15.0
% CH ₄	60.0-70.0	80.0-85.0	60.0-70.0	80.0-85.0
Steam/gas ratio	0.35-0.45	0.55-0.65	0.35-0.45	0.55-0.65

Discharged-catalyst analysis from life test 1

	Bed 1 (C150-01-01)		Bed 2 (C150-1-03)		Bed 3 (C150-1-01)	
	Used		Used		Used	
	New	Top Bottom	New	Top Bottom	New	Top Bottom
Nickel, wt %	47.5	77.6	47.0	77.7	47.5	53.8
% Reduction	50.0	85	165	80	90	60
Nickel crystallite size A	180	nil	0.01	nil	0.02	nil
Delta S, wt % added	nil	nil	nil	nil	nil	nil
Delta C1, wt % added	0.24	0.30	nil	nil	0.50	0.21
Delta C, wt % added	28	114	250	133	280	211
Surface area, (m ² /gm)	28	114	250	132	280	211

TABLE 6

Operating conditions and gas compositions at end of life test 2 — 1,000 hr

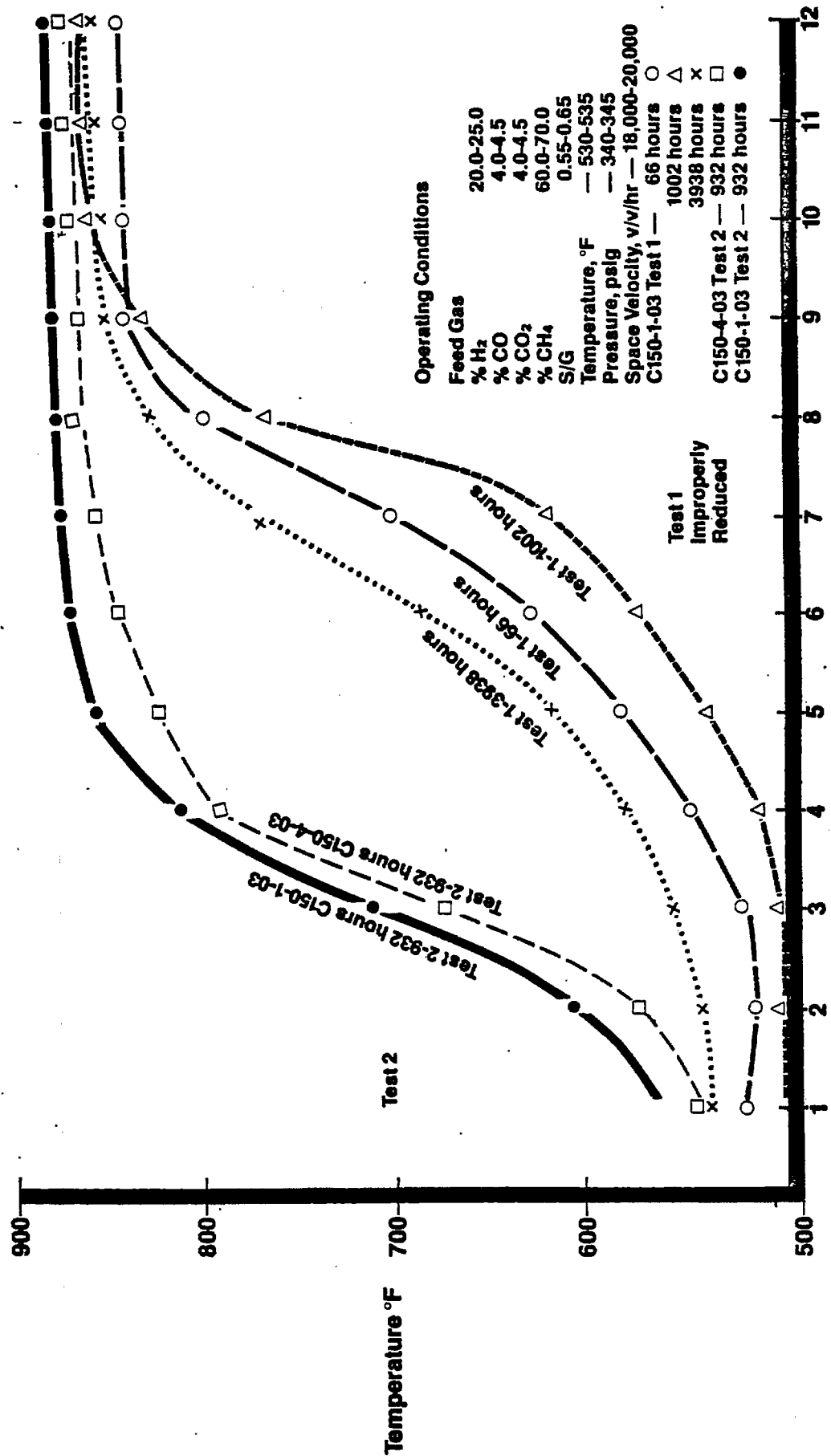
	Primary methanators		Secondary methanators	
	Bed 1 — C150-1-03 ¼ in. by ¼ in.		Bed 3 — C150-4-03 ¼ in by ¼ in.	
	Inlet	Exit	Inlet	Exit
Temperature, °F	530-535	850-855	525-530	845-830
Pressure, psig	350-355	350-355
Dry-gas space velocity, v/v/hr	12,000-15,000	12,000-15,000	5,000-7,000
Wet-gas space velocity, v/v/hr	18,000-20,000	18,000-20,000	5,000-7,000
Reactor gas composition:				
% CO	4.5-5.5	0.05-0.15	4.5-5.5	0.05-0.10
% CO ₂	4.0-6.0	5.0-7.0	4.0-6.0	5.0-7.0
% H ₂	22.0-25.0	8.0-12.0	22.0-25.0	8.0-12.0
% CH ₄	65.0-70.0	80.0-85.0	65.0-70.0	80.0-85.0
Steam/gas ratio	0.40-0.45	0.5-0.6	0.40-0.45	0.5-0.6

Discharged-catalyst analysis from life test 2 and thermal-stability tests

	Bed 1 (C150-01-03)		Bed 2 (C150-4-03)		Bed 3 (C150-4-03)	
	Used		Used		Used	
	New	Top Bottom	New	Top Bottom	New	Top Bottom
Nickel, wt %	41.2	50.7 51.0	55.6	65.0 66.8	55.6	65.6 65.9
Reduced Ni, wt %	42.2 42.9	53.1 56.8	50.9 48.8
% Reduction	83.3 84.2	81.7 85.0	77.6 74.1
Nickel crystallite size A	115 100	115 115	80 85
Delta S, wt % added	0.07 nil	0.04 nil	nil nil
Delta C1, wt % added	nil nil	nil nil	nil nil
Delta C, wt % added	nil nil	nil nil	nil nil
Surface area, (m ² /gm)	250	139 132	250	77.0 69.0	250	105 109

FIG. 4

Temperature vs. Bed Depth as Function of Time
 C150-4-03 & C150-1-03 Catalyst



237

TABLE 7 Lurgi-Sasol Methanation Pilot Plant: Gas Analyses and Process Conditions

	Synthesis gas	Main Methanator D-2		Final Methanator D-3	
		Reactor Inlet	Reactor Outlet	Reactor Inlet	Reactor Outlet
Temperature (°C):	gas				
Gas flow rate, wet (N-m ³ /hr):	270	300	450	260	315
	18.2	96.0	89.6	8.2	7.9
Gas composition (vol %)					
CO ₂	13.0	19.3	21.5	21.5	21.3
CO	15.5	4.3	0.4	0.4	0.05
H ₂	60.1	21.3	7.7	7.7	0.7
CH ₄	10.3	53.3	68.4	68.4	75.9
C ₂ ⁺	0.2	0.1	0.05	0.05	0.05
N ₂ /Ar	0.9	1.7	2.0	2.0	2.0
H ₂ O (v/v dry gas)	0.0	0.37	0.50	0.04	0.08

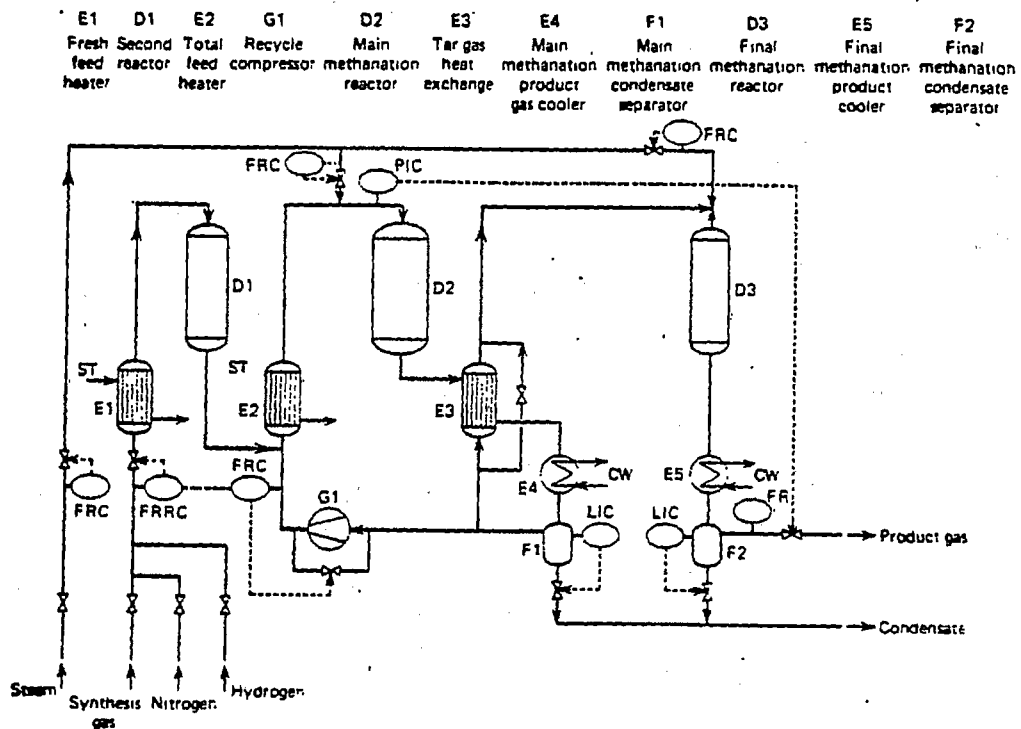


FIG. 5 Flowsheet of the Lurgi-Sasol methanation pilot plant

Source: Ref 7

8.0 ADVANTAGES AND LIMITATIONS

Advantages

- o Offers use of demonstrated catalyst.
- o The process is equally applicable to any gasification technology since it requires pretreatment of feed. Raw gases containing high H_2/CO and steam/dry gas ratios generally have an advantage in using conventional methanation since shift is minimized.
- o The product of conventional methanation does not require any further treatment such as acid gas removal. Only drying and compression are needed to produce pipeline quality gas.
- o The process does not produce undesirables such as COS and sour water.
- o Hydrocarbons in raw feed gas are upgraded to lighter products by the raw gas shift.
- o Light hydrocarbons (C_2-C_4) are either hydrogenated or hydrocracked to methane in methanation.
- o Large quantity of high level steam is produced as a product.

Limitations

- o Sulfur in the feed gas must be removed before feeding to methanation reactors, to avoid catalyst poisoning.
- o Some processes may require addition of steam to avoid carbon deposition.
- o Heavier hydrocarbons (C_5^+) will however have a tendency to deposit carbon.

9.0 TECHNO/ECONOMIC EVALUATIONS

Tables 8 and 9 show the contribution of gas cost for conventional methanation process in coal-to-SNG facilities using Westinghouse and Lurgi gasifiers.

TABLE 8

CALCULATION OF CONTRIBUTION TO GAS COST
CONVENTIONAL SHIFT/METHANATION SYSTEM
WESTINGHOUSE GASIFIERS

Coal Type	N. Dakota lignite		
Evaluator	Kellogg Rust Synfuels, Inc. (9)		
Project Report No.	Contract No. 5082-222-0754(6440-07)		
Date Published	1985		
Plant Capacity	250 Billion Btu/day SNG		
Feed to Methanators	84,264 Lb moles/hr		
Methane Produced	18,240 lb moles/hr		
CAPITAL COSTS :	\$ MM (Mid-1982)		
Installed Equipment	85.0		
Contingency @ 15%	12.8		

DFCI	97.8		
Home-Office costs @ 12%	11.7		

TFCI	109.5		
Initial Catalyst Charge	19.5		

Total Plant Investment	129.0		
OPERATING COSTS :	\$/hr		
Produced	-----		
Steam Credit(1500 psig)	-1,250,665 #/hr	@ \$ 5.50/ 1000 lb	-6878.7
Steam Credit(600 psig)	-837,120 #/hr	@ \$ 5.50/ 1000 lb	-4604.2
Consumed	-----		
Steam(1500 psig)	117,280 #/hr	@ \$ 5.50/ 1000 lb	645.0
Process Steam(600 psig)	368,962 #/hr	@ \$ 5.50/ 1000 lb	2029.3
Electricity	1,670 Kw	@ \$ 0.05/ Kwh	83.5
Cooling water	9,030 Gpm	@ \$ 0.10/ 1000 Ga	54.2
Catalyst & Chemical	average hourly charge		575.3

TOTAL	-8095.5		
Total Operating Cost, \$ MM/yr at 100 % Stream factor =	-70.9		
CONTRIBUTION TO GAS COSTS :	Specific Cost,	Charge Rate,	Contribution,
	\$/MM Btu-Yr	Year	\$/MM Btu
Capital Related	1.57	0.089	0.14
Operating	-0.86	1.000	-0.86

Total Credit	-0.72		

TABLE 9

CALCULATION OF CONTRIBUTION TO GAS COST
CONVENTIONAL SHIFT/METHANATION SYSTEM
LURGI GASIFIERS

Coal Type	N. Dakota lignite
Evaluator	Kellogg Rust Synfuels, Inc. (10)
Project Report No.	Contract No. 5082-222-0754(6440-16)
Date Published	1985
Plant Capacity	250 Billion Btu/day SNG
Feed to Methanators	71,850 Lb moles/hr
Methane Produced	15,234 Lb moles/hr

CAPITAL COSTS : \$ MM (Mid-1982)

Installed Equipment(*)	104.0
Contingency @ 15%	15.6

DFCI	119.6
Home-Office costs @ 12%	14.4

TFCI	134.0
Initial Catalyst Charge	12.5

Total Plant Investment	146.5

OPERATING COSTS :

Produced				\$/hr

Steam Credit(1500 psig)	-1,099,198 #/hr	@ \$ 5.50/	1000 lb	-6045.6
Steam Credit(600 psig)	-459,363 #/hr	@ \$ 5.50/	1000 lb	-2526.5
Steam Credit(60 psig)	-676,515 #/hr	@ \$ 3.85/	1000 lb	-2604.6
Consumed				

Steam(1500 psig)	166,493 #/hr	@ \$ 5.50/	1000 lb	915.7
Steam(100 psig)	184,864 #/hr	@ \$ 3.95/	1000 lb	730.2
Electricity	2,147 Kw	@ \$ 0.05/	Kwh	107.4
Cooling water	9,167 Gpm	@ \$ 0.10/	1000 Ga	55.0
Catalyst & Chemical		average hourly charge		365.3

TOTAL				-9003.1
Total Operating Cost, \$ MM/yr at 100 % Stream factor =				-78.9

CONTRIBUTION TO GAS COSTS :

	Specific Cost, \$/MM Btu-Yr	Charge Rate, Year	Contribution, \$/MM Btu
Capital Related	1.78	0.089	0.16
Operating	-0.96	1.000	-0.96

Total Credit			-0.80

(*) Includes shifted gas cooling & bypass gas cooling.

10.0 REFERENCES

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STATUS SUMMARY

COMBINED SHIFT METHANATION

- 1.0 GENERAL INFORMATION
- 2.0 CATALYST AND PROCESS DEVELOPMENT
- 3.0 PROCESS DESCRIPTION
- 4.0 ADVANTAGES AND LIMITATIONS
- 5.0 TECHNO-ECONOMIC EVALUATION
- 6.0 REFERENCES

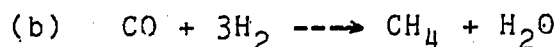
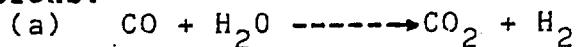
1.0 GENERAL INFORMATION

Developers: The combined shift and methanation process has been developed by several companies, either in conjunction with their coal gasification technology, viz., Conoco (SUPER-METH); British Gas Corporation (HICOM), Bituminous Coal Research Fluidized Bed Process, and Koppers or as a stand-alone application by engineering companies and catalyst vendors, e.g., R.M. Parson's (RM Process) and United Catalyst Inc. Most engineering companies have the capabilities to design the process which use any of the catalyst from the recommended by the catalyst vendors.

Reactor Type: Multiple adiabatic, fixed-bed reactors in series and/or series-parallel arrangement are used.

Feed Gas: The process can handle a wide range of feed gases having H_2/CO ratios in the range from 0.4 to 2.4. Typically, when the feed H_2/CO ratio is less than 1.0, water and/or steam addition is required to increase its hydrogen content. Also, the catalyst cannot tolerate more than 0.02 ppmv H_2S equivalent sulfur. However, the RM Process has been operated with gases containing up to 5 ppm H_2S .

Principal Reactions:



Catalyst Type:

Major constituents of the catalyst are NiO and Al_2O_3 . The catalyst is poisoned by sulfur. Several grades (characterized by range of operating temperatures) of the catalyst are available. Different grades may be used in the same design depending on the reactor system.

Operating Conditions:

The catalyst can be operated between 0 and 1500 psig, and depending upon the type, between $450^\circ F$ (inlet) and $1550^\circ F$ (outlet).

- Products:** The product gas from the combined-shift-methanation process, after CO₂ removal, compression and drying will meet the gas interchangeability standards and higher heating value for pipeline gas. Other byproducts include process condensate and CO₂.
- Application:** The combined shift methanation is better suited for coal gasifiers producing raw gas with H₂/CO ratio less than or equal to 1.0. Units upstream of the process must include H₂S removal and sulfur guard beds. The feed gas should also be free of C₅⁺ hydrocarbons.
- Status:** According to the catalyst developers and process licensors, the catalysts available for the combined shift-methanation process have been extensively tested on a pilot plant scale. However, due to the current excess world deliverability of natural gas, all the plans for the commercialization of these coal-to-SNG processes have been delayed with one exception, the HICOM Process.

2.0 CATALYST AND PROCESS DEVELOPMENT

Catalyst

The use of nickel-based methanation catalyst in ammonia, hydrogen, town gas and SNG from naphtha plants has been widely practiced since 1960's.

In the early 70's, these nickel-based catalysts were improved to operate over a wider temperature rise and a higher initial carbon monoxide concentration. Because the carbon monoxide to methane reaction is highly exothermic, these new catalysts have a much higher thermal stability. Moreover, the nickel content of these new catalysts was increased to improve the selectivity of the carbon monoxide-to-methane reaction. The new methanation catalysts for SNG synthesis can operate between 550°F and 1550°F. The conventional methanation catalysts cannot tolerate temperatures above 950°F.

Process

The development of combined shift methanation processes can be traced to its application in town gas and naphtha-based SNG synthesis projects in the 60's. Typical processes are the CRG (Catalytic Rich Gas), FBH (Fluidized Bed Hydrogenation), GRH (Gas Recycle Hydrogenation) processes licensed and developed by British Gas Corporation; the Gasyntan process developed and licensed by Lurgi Kohle & Mineraloel-technik GmbH and BASF, and the MRG (Methane Rich Gas) process developed by JGC Corporation.

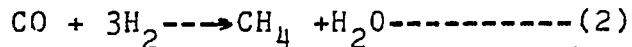
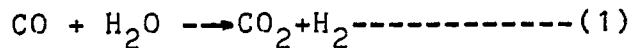
In the 70's, interest in coal-based SNG plants prompted the development of methanation catalyst, with higher selectivity and thermal stability. Process licensors and engineering companies in conjunction with catalyst vendors began developing different combined-shift methanation processes:

- RM Process by R. M. Parsons.
- HICOM Process by British Gas Corporation.
- Koppers-ICI Process by Heinrich Koppers Co. and Imperial Chemicals.
- SUPER-METH Process by Conoco Coal Development Company.
- Fluidized Bed Methanation Process by Bituminous Coal Research, Inc.

3.0 PROCESS DESCRIPTION

Reaction Chemistry

The combined shift methanation process is based on the two reactions:



In reaction 1, steam (water) is consumed while in reaction 2, steam (water) is produced. The combined shift methanation process thus minimizes the consumption of steam. These reactions are catalyzed by nickel-based catalyst and can withstand a high temperature.

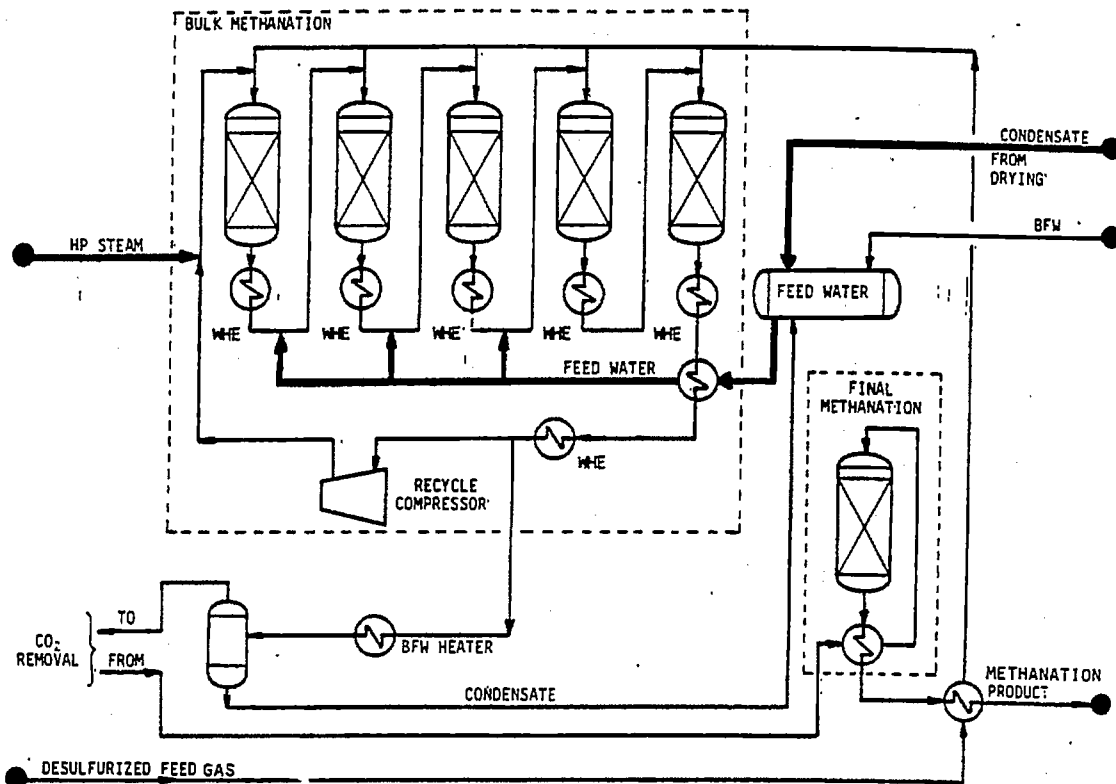
Process

There are different variations of the combined shift methanation process, each one being optimized to suit the feed gas composition. The SUPER-METH and HICOM processes are designed for raw gas from a BGC/Lurgi gasifier while the Koppers/ICI process was designed for raw gas from a GKT gasifier. The RM Process, however, can be tailored to suit any feed gas composition. Simplified process flow diagrams for these processes are shown in Figures 3-1 to 3-4. The BCR's Fluidized Bed Methanator is shown in Figure 3-5.

All these combined shift methanation processes have the following characteristics:

- Steam injection and/or water addition is required to provide additional hydrogen in the CO-rich feed gas (via the shift reaction) and suppress carbon formation in the reactors.
- Feed gas should contain less than 0.02 ppmv H₂S equivalent total sulfur. The RM Process has been operated with gases containing up to 5 PPM H₂S.
- High pressure steam generation between catalytic reactor stages.
- CO₂ removal is required after the bulk methanation reactors.
- Trim methanation is required in most cases after the CO₂ removal to meet pipeline gas standards.

In addition, recycle gas was used in the SUPER-METH and HICOM processes to limit the temperature rise in the reactors.



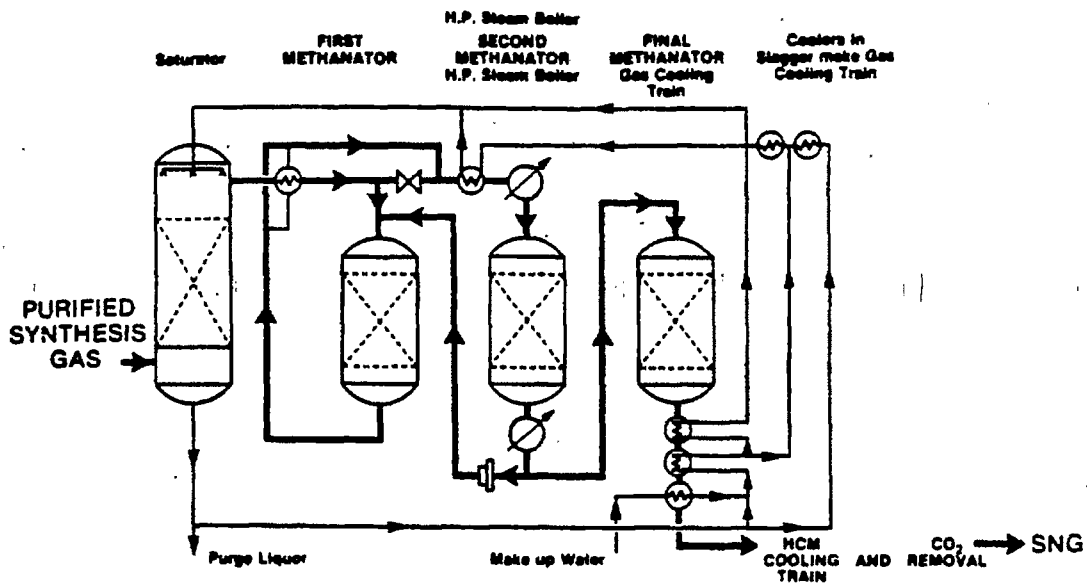
Typical Composition of Feed Gas to
SUPER-METH Process Units

	Mol%
Hydrogen	28.8
Carbon Monoxide	60.9
Carbon Dioxide	2.4
Methane	7.0
CnHm	0.3
Nitrogen	0.6
Water	0.0

	100.0

FIG. 3-1 SUPER-METH PROCESS

Source: Ref. 3



Typical Gas Compositions from a HICOM Pilot Test

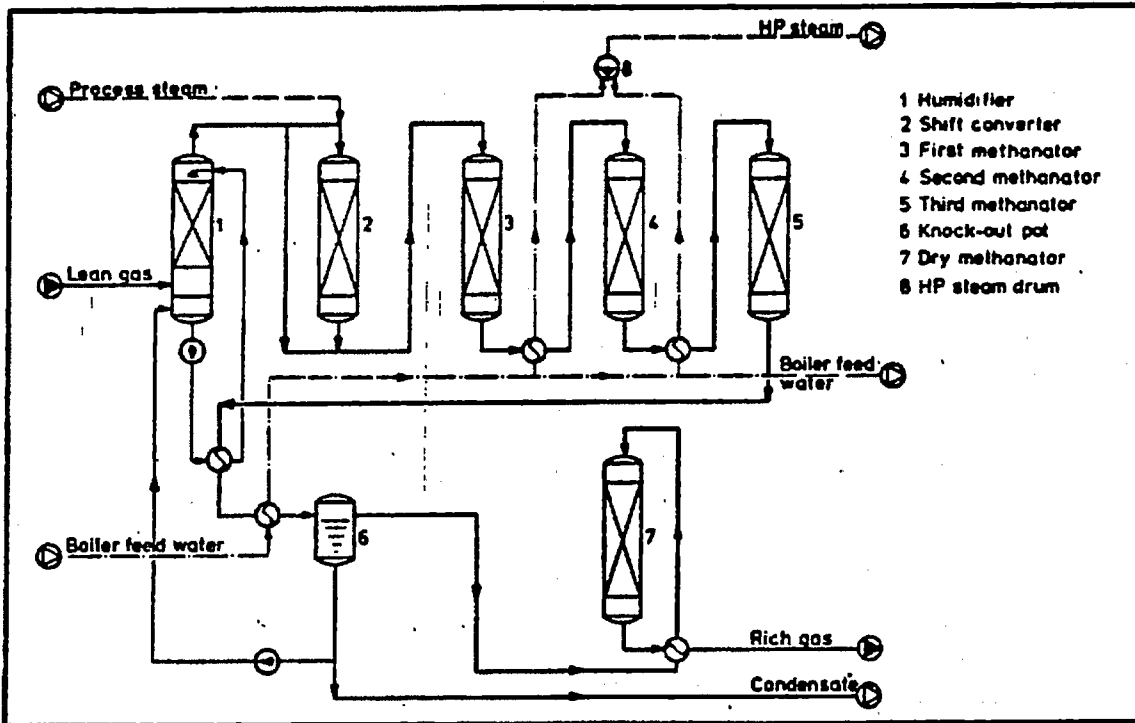
Component	Feed to HICOM Reactor % mol	Product from HICOM reactor % mol
CO	12.6	1.1
CO ₂	43.0	53.1
H ₂	11.7	5.5
CH ₄	31.7	39.3
N ₂	1.0	1.1

Range of Operating Conditions

Inlet Temperature, °C	230 - 320
Pressure, bar	25 - 70
Maximum Temperature, °C	460 - 640
Total Test Time, h	15,000

FIG. 3-2 HICOM PROCESS

Source: Ref. 4 & 5



Raw Coal to the Plant		
Moisture	8.00	% weight
Ash	19.06	-
C	55.89	-
H	4.16	-
S	0.72	-
N	1.06	-
O	11.11	-
Total	100.00	-

SNG Exit Plant		
CO ₂	0.43	% Vol
CO	0.43	-
H ₂	1.39	-
N ₂ -Argon	2.60	-
CH ₄	95.15	-
Total	100.00	-

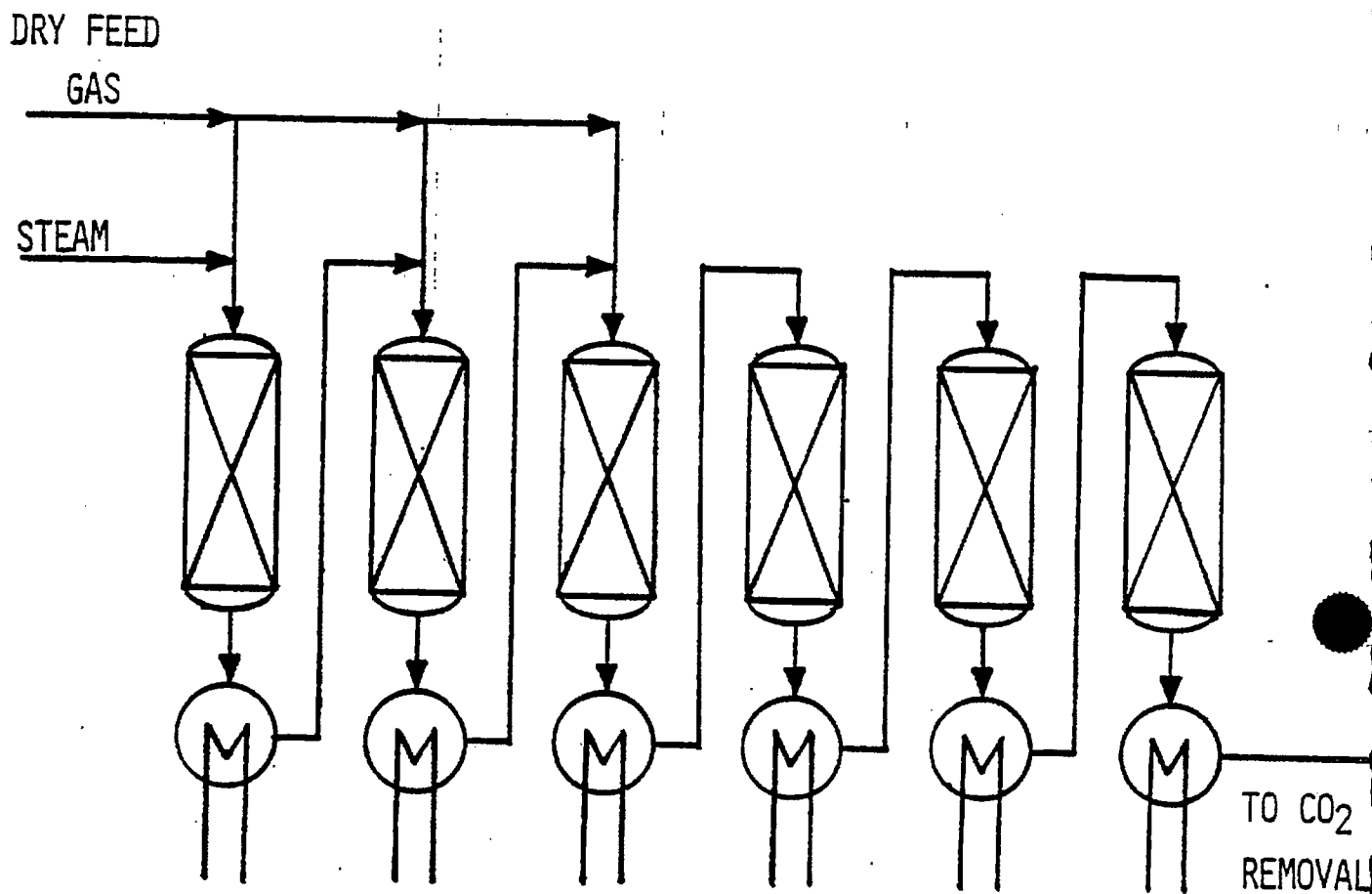
Calorific Value		
Net	5300	kcal/kg = 9540 BTU/lb
Gross	5575	kcal/kg = 10025 - -

Calorific Value		
Net	8190	kcal/Nm ³ = 876 BTU/scf
Gross	9115	kcal/Nm ³ = 975 - -

Gas Analysis Conversion-Methanation					
	Entrance		Exit		
CO ₂	9.95	% Vol	65.58	% Vol	
CO	56.87	-	0.15	-	
H ₂	32.47	-	0.48	-	
N ₂ -Argon	0.61	-	0.90	-	
CH ₄	0.10	-	32.89	-	
Total	100.00	-	100.00	-	

FIG. 3-3 KOPPERS-ICI PROCESS

Source: Ref. 1



Reactor No.:	Feed		Outlet					
	1	1	2	3	4	5	6	
Composition (vol %)								
H ₂	49.80	54.53	48.07	43.09	36.90	22.86	9.29	
CO	49.80	13.97	18.46	20.63	15.25	5.64	.87	
CO ₂	0.10	25.80	24.04	23.64	29.21	39.90	46.84	
CH ₄	0.30	5.70	9.43	12.64	18.64	31.60	43.00	
Steam/gas	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
Pressure (psia)	1.20	0.88	0.56	0.43	0.50	0.65	0.83	
Temperature (°F)	397	387	372	357	342	327	312	
	900	1424	1434	1423	1322	1119	881	

FIG. 3-4 RM PROCESS

Source: Ref. 2

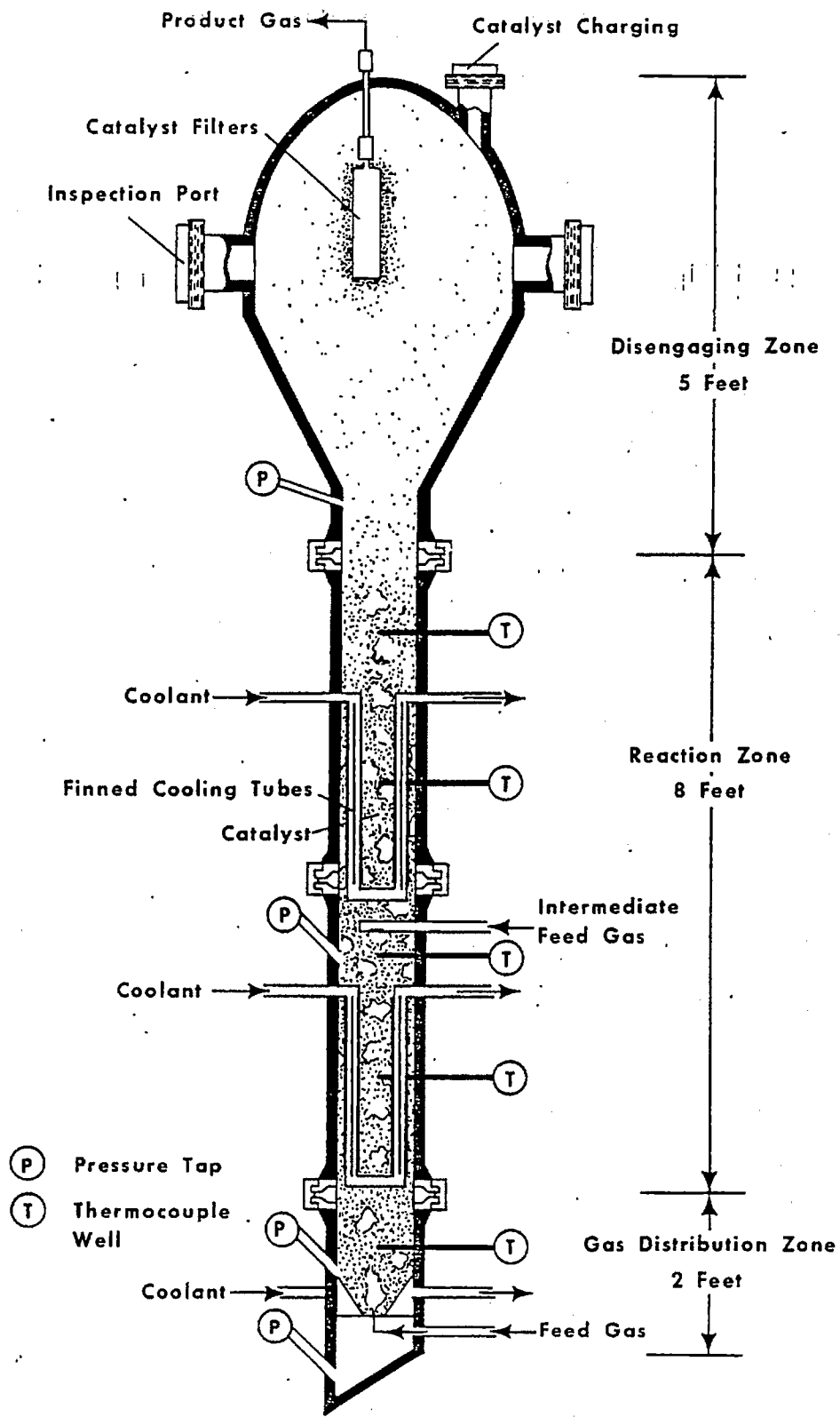


FIGURE 3-5
FLUIDIZED-BED METHANATOR

4.0 ADVANTAGES AND LIMITATIONS

Advantages

- Less shifting of the quenched raw gas is required to achieve a stoichiometric ratio of H_2/CO of 1; hence a separate shift stage is not required.
- The quenched raw gas is desulfurized before the combined shift methanation process. Therefore, a more concentrated H_2S acid gas stream can be obtained since the H_2S/CO_2 ratio is higher than in the conventional methanation process.
- The CO_2 removal unit cost is lower because the total gas volume to be processed is much less in the combined shift methanation case as compared to the conventional methanation process.
- Higher allowable temperature rise in the reactors results in greater amount of steam being recovered at high pressure. The combined-shift methanation process is a net producer of high pressure steam.

Limitations

- Heavier Hydrocarbons in the feed gas will cause deactivation of catalyst.
- Except for the RM Process, other processes cannot tolerate more than 0.02 ppmv H_2S equivalent sulfur.
- Steam injection is required to provide additional hydrogen in the CO-rich feed gas.

5.0 TECHNO-ECONOMIC EVALUATION

In 1981, KRSI completed a techno-economic evaluation of a 250 billion Btu/day SNG plant from Pittsburgh #8 coal using both Westinghouse (now KRW) and IGT U-Gas gasifiers. KRSI designed the combined/shift methanation area with catalyst specifications from Katalco. A simplified process flow diagram is shown in Figure 5-1. A summary of the material balance and economic data is shown in Tables 5-1 and 5-2 respectively.

TABLE 5-1
 DESIGN DATA FOR A COMBINED SHIFT-METHANATION SYSTEM
 IN A 250 BILLION BTU/DAY COAL-TO-SNG PLANT

	SYNGAS	STEAM	SNG PRODUCT	LOW-BTU FUEL GAS	CO2 VENT	NET CONDENSATE
	Mol %	Mol %	Mol %	Mol %	Mol %	Mol %
CO	53.75		42 ppm	0.01		
CO2	7.74		2.65	93.81	82.31	
H2	27.25		0.75	0.00		
CH4	10.70		94.82	5.72	0.49	
N2 & Ar	0.49		1.55	0.01		
H2O	0.07	100.00	0.22	0.45	17.20	100.00
	100.00	100.00	100.00	100.00	100.00	100.00
TOTAL #/HR	1934730	1099744	490820	673236	1079996	790422
MPH	92670	61046	29093	15919	27409	43876

Source: Ref.5

TABLE 5-2

CALCULATION OF CONTRIBUTION TO GAS COST
COMBINED SHIFT/METHANATION SYSTEM
WESTINGHOUSE GASIFIERS

Coal Type	Pittsburgh #8
Evaluator	Kellogg Rust Synfuels, Inc. (6)
Project Report No.	FE-2778-45
Date Published	July 1981
Plant Capacity	250 Billion Btu/day SNG
Feed to Shift/Meth.	92,670 Lb moles/hr
Methane Produced	18,332 Lb moles/hr

\$ MM (Mid-1982)

Installed Equipment	23.8
Contingency @ 15%	3.6

Direct Facility	
Constr Investment	27.4
Home-Office costs @ 12%	3.3

Total Facility	
Constr Investment	30.7

Royalties	0.0
Initial Catalyst Charge	21.6

Total Plant Investment	52.3
------------------------	------

OPERATING COSTS:

Produced			\$/hr

Steam(800 psig, sat.)	-1,047,200 #/hr	@ \$ 5.50/ 1000 lb	-5759.6
Steam(50 psig, sat.)	-591,400 #/hr	@ \$ 3.85/ 1000 lb	-2276.9
Consumed			

Cooling water	4,662 Gpm	@ \$0.10/ 1000 Gal	28.0
Catalyst & Chemical		average hourly charge	627.9

TOTAL			-7380.7

Total Operating Cost, \$ MM/yr at 100 % Stream factor =	-64.7
---	-------

	Specific Cost, \$/MM Btu-Yr	Charge Rate, Year	Contribution, \$/MM Btu
Capital Related	0.64	0.089	0.06
Operating	-0.79	1.000	-0.79

Total			-0.73

6.0 REFERENCES

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STATUS SUMMARY

CRC DIRECT METHANATION

- 1.0 GENERAL INFORMATION
- 2.0 CATALYST AND PROCESS DEVELOPMENT
- 3.0 OPERATING CONDITIONS TESTED
- 4.0 PROCESS DESCRIPTION
- 5.0 PERFORMANCE DATA
- 6.0 BYPRODUCT AND ENVIRONMENT
- 7.0 ADVANTAGES & LIMITATIONS
- 8.0 COMMERCIAL DESIGN DATA
- 9.0 REFERENCES

1.0 GENERAL INFORMATION

Developer: Catalytic Research Corporation
Palisades Park, New Jersey
Under contract by Gas Research Institute,
Chicago, Illinois.

Reactor Type: The direct methanation process uses multiple adiabatic fixed-bed reactors. The catalysts used are the GRI Series C-500 which are sulfur-tolerant and are immune to the deposition of carbon from low water/high carbon content feed gases.

Reaction: $2 \text{CO} + 2 \text{H}_2 \rightarrow \text{CH}_4 + \text{CO}_2$

Operating Conditions:

The catalysts will promote the direct methanation for a wide range of feed gas compositions (H_2/CO ratio from 0.4 to 2.4). Operating pressures between 200 and 1000 psig and temperatures between 600 and 1250°F have been tested.

Application: Direct methanation process can be applied to synthesis gas from coal gasification or heavy oil partial oxidation with low H_2/CO ratios.

2.0 PROCESS DEVELOPMENT

In 1974, Catalysis Research Corporation began developing a sulfur-resistant methanation catalyst. This catalyst development program, from 1974 - 1978, led to two patented catalyst formulations:

- A cerium-molybdenum catalyst, designated as GRI Series 200 (GRI-C-284); and
- A cerium-molybdenum-aluminum catalyst, designated as GRI Series 300 (GRI-C-318)

In 1979, a new family of transition-element oxysulfide catalysts was developed. These catalysts promote the direct methanation reaction with higher activity and selectivity than the GRI-C-200 and 300 series. A patent covering this new catalyst formulation was issued to GRI and designated as the GRI-C-400 and 500 series.

In 1981, a series of novel catalyst formulations was discovered. These formulations show significant improvement over the GRI-C-500 series catalyst. These high activity catalysts, designated as GRI-C-600 series, can achieve over 80% CO conversion rate.

Concurrent with the development of new catalyst formulations by CRC, GRI contracted other research organizations to advance and guide the direct methanation technology toward practical application in future coal gasification plants.

Until 1983, SRI International was responsible for characterizing the properties of successful catalyst formulations developed by CRC. The studies were intended to define the bulk and surface properties that affect the specific methanation activity, thermal stability, and deactivation resistance.

Institute of Gas Technology (IGT) was responsible for evaluating the performance of the catalyst formulations prepared by CRC. The catalysts were subject to different simulated synthesis gases from leading gasifier types. The effects of temperature, pressure, feed composition, and trace constituents concentration on catalyst performance were measured and used to develop process design data for various processing sequences.

During 1981-1983, C F Braun & Co, developed several conceptual process designs from the design data collected by IGT and from the process sequences recommended by CRC. First-pass economic evaluations were performed based on these conceptual process designs.

3.0 OPERATING CONDITIONS TESTED

Bench scale work has been carried out on the direct methanation catalysts to provide design data. Synthetic blends simulating quenched gases from the Lurgi, BGC/Lurgi, Westinghouse, and Hygas processes were tested.

Feed Gas H ₂ /CO ratio	0.1 - 3.0
H ₂ O concentration in feed gas	0 - 40 mole %
Pressures	200 - 1000 psig
Temperature	600 - 1250 ^o F
Space Velocities	1000 - 16,000 SCF/hr/ft ³

Sulfur

(H₂S, COS, CS₂, CH₃SH, C₂H₅SH, C₃H₇SH, and C₄H₄S)

Up to 3 mole %

Higher hydrocarbons

(C₂H₆, C₃H₈, C₄H₁₀, C₆H₆)

Up to 2 mole %

C₆H₅OH

Up to 0.05 mole %

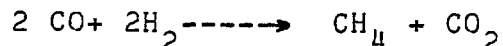
NH₃

Up to 0.3 mole %

4.0 PROCESS DESCRIPTION

Reaction Chemistry

The direct methanation process is based upon the direct production of methane and carbon dioxide via the reaction:



This reaction is catalyzed by high activity transition metal compounds rather than the conventional nickel catalysts. These direct methanation catalysts are not poisoned by the presence of sulfur compounds and they resist deposition of carbon deposits at low H_2/CO ratios ($\text{H}_2/\text{CO} < 2$) even with low water content in the feed gas.

Process

Figure 4-1 describes a process scheme typical of a direct methanation system. Quenched raw gas is first preheated and then enters a series of adiabatic catalytic reactors with heat recovery steam generators between reactors.

The methane content is increased to about 36% in the effluent from the last methanator. Depending on feed composition, the COS content of the gas may increase in the middle of the reactor train as a result of the reverse COS hydrolysis reaction. A COS hydrolysis reactor might also be required to reduce the COS content to about 10 ppm. The gas leaving the direct methanation system is then fed to an acid gas removal system where all of the H_2S and COS, and about 99.5% of the CO_2 is removed. Zinc oxide sulfur polishing units are required to further purify the gas after acid gas removal to a sulfur content less than 0.1 ppmv before the gas enters a trim methanator. The trim methanator is a fixed-bed catalytic reactor using a conventional nickel catalyst and operated adiabatically on a once-through basis.

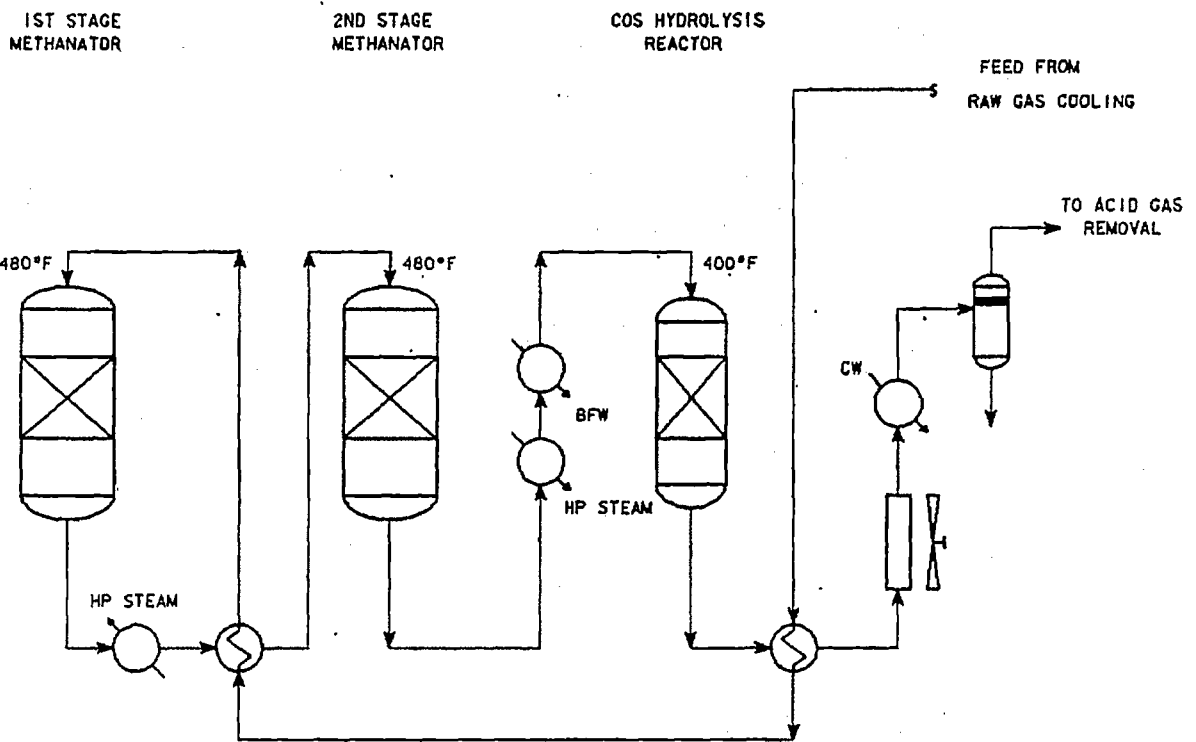


FIGURE 4-1

DIRECT METHANATION SYSTEM

5.0 PERFORMANCE DATA

The kinetic data obtained from bench scale catalyst testing were correlated into kinetic expressions. The following rate equations apply to performance at 950°F.

$$r_{\text{CH}_4} = \frac{22.67 P_{\text{CO}} P_{\text{H}_2}^{0.5}}{(1.0 + 0.085 P_{\text{CO}_2})^{1.15}} \quad (4)$$

$$r_{\text{H}_2\text{O}} = 0.296 P_{\text{CO}_2} P_{\text{H}_2} \left(1.0 - \frac{P_{\text{CO}} P_{\text{H}_2\text{O}}}{0.2208 P_{\text{CO}_2} P_{\text{H}_2}} \right) \quad (5)$$

Where,

r_{CH_4} = rate of methane production per hour per unit volume of reactor, m^3 (NTP)/hr/ m^3

$r_{\text{H}_2\text{O}}$ = rate of water production per hour per unit volume of reactor, m^3 (NTP)/hr/ m^3 .

p_i = partial pressure of species i ($i = \text{CO}, \text{H}_2, \text{CO}_2, \text{H}_2\text{O}$) at any point in the reactor, atm (1 atm = 0.1013 MPa).

(Source: Ref. 2)

Table 5-1 shows sample test results of the GRI-C-529 catalysts conducted by the SRI International.

TABLE 5-1
 RATE OF PRODUCT FORMATION DURING DIRECT METHANATION
 CATALYZED BY GRI C-529*

Space Velocity (hr ⁻¹)	Rate of CO Consumption r _{CO} (cm ³ · min ⁻¹ · g ⁻¹)	Rate of Product Formation (cm ³ · min ⁻¹ · g ⁻¹)	
		r _{CH₄}	r _{CO₂}
2700	4.6	2.3 ± 0.1	2.3 ± 0.1
4800	6.6	3.2 ± 0.2	3.6 ± 0.2
12000	9.5	4.6 ± 0.2	4.8 ± 0.2

*

Pressure 14.33 atm (200 psig)
 Temperature 783 K (510°C)
 Space velocity 4800 hr⁻¹
 Feed gas composition (vol%)
 39 CO
 44 H₂
 17 CH₄
 0.25 H₂S (2500 ppm)

Source: Ref. 4

6.0 BYPRODUCT AND ENVIRONMENT

The byproducts of the direct methanation reaction are CO_2 and water. Since the feed gas is not desulfurized, process condensate would have to be treated in a sour water stripper to remove dissolved H_2S , COS , and CO_2 before it can be used as process/boiler feed water make-up.

The production of COS from H_2S and CO_2 may also pose an additional concern in some of the acid gas removal processes. However, this is dependent on the feed gas composition, depending on which there may even be a reduction in the COS content of the product gas leaving the direct methanation reactor.

7.0 ADVANTAGES & LIMITATIONS

Advantages

- The sulfur tolerance of direct methanation catalyst permits acid gas removal after methanation from a much smaller volume of gas with a higher CO_2 partial pressure. In a conventional system, if beginning with equal molal quantities of carbon monoxide and hydrogen, the removal of acid gases after shift conversion requires removal of one mole of CO_2 from five moles of gas, since the shift reaction is:



With direct methanation, again with a 1:1 H_2/CO ratio, one mole of CO_2 must be removed from two moles of gas:



Thus, the partial pressure of CO_2 would be 2-1/2 times as great after direct methanation relative to that after conventional shift conversion. Therefore, a physical solvent process, which typically requires lower energy as compared to a chemical solvent process, can be used.

- By limiting or eliminating shift conversion and by not requiring steam in direct methanation to avoid carbon deposition, the process steam demand would be significantly reduced.
- Operation of the direct methanation catalyst at temperatures higher than normal for conventional methanation would allow the recovery of more high quality steam. This, along with the previous item, would lead to the reductions of capacity and cost of the coal-fired steam generation systems.

Limitations

- The H_2/CO ratio in the feed gas determines the processing sequence necessary prior to methanation.
- The formation of COS, in certain cases, via reverse COS hydrolysis reaction, might cause a problem in subsequent acid gas removal step.
- Methanation reactors must process a large volume of feed gas because CO_2 and H_2S are not removed prior to methanation.

8.0 COMMERCIAL DESIGN DATA

A summary of the design data for a Direct Methanation system of a 238 Billion Btu/day coal-to-SNG plant is shown in FIGURE 8-1. The feed gas is from the gasification of Illinois #6 coal in BGC/Lurgi gasifiers. Table 8-1 shows the contribution of gas cost for direct methanation process in a coal-to-SNG facility using Lurgi gasifiers.

9.0 REFERENCES

1. Meyer, H. S., et al., "Direct Methanation - A New Method of Converting Synthesis Gas to SNG", paper presented at ACS Meeting, Division of Fuel Chemistry, Las Vegas, Nevada, March 28 - April 2, 1982.
2. Happel, J., et al., "Methanation Kinetics with Transition Element Catalysts", paper presented at 1938 International Gas Research Conference, London, June 1983.
3. C. F. Braun & Co, "Evaluation of the Catalysis Research Corporation Methanation Process in the British Gas/Lurgi Slagging Gasifier Process," pp 23, in Fossil Fuel Gasification Technical Evaluation Services - Final Report 1983, "GRI-81/0174, prepared for Gas Research Institute, May 1983.
4. SRI International "Basic Studies of New Coal Conversion Catalysts - Annual Report 1981," pp 16., GRI-81/0078, prepared for Gas Research Institute, February 1982.
5. Happel, J. and M. A. Hnatow, "Sulfur Resistant Molybdenum Catalysts for Methanation", U.S. Patent 4,151,191, April 24, 1979.
6. Happel, J. and M. A. Hnatow, "Alumina-Containing Methanation Catalysts", U.S. Patent 4,260,553, April 7, 1981.
7. Happel, J. and M. A. Hnatow, "Process for Making High Activity Transition Metal Catalysts", U.S. Patent 4,320,030, March 16, 1982.
8. Happel, J. et al., "Methods of Making High Activity Transition Metal Catalysts", U.S. Patent 4,491,639, January 1, 1985.
9. Kellogg Rust Synfuels Inc., "Design and Economics of a Lignite-to-SNG Facility Using Lurgi Gasifiers and Direct Methanation Process", for Gas Research Institute, to be published, 1985, GRI Contract 5082-222-0754.

TABLE 8-1

CALCULATION OF CONTRIBUTION TO GAS COST
DIRECT METHANATION SYSTEM
LURGI GASIFIERS

Coal Type	N. Dakota lignite
Evaluator	Kellogg Rust Synfuels, Inc. (9)
Project Report No.	Contract No. 5082-222-0754(6440-25)
Date Published	1985
Plant Capacity	250 Billion Btu/day SNG
Feed to Methanators	108,042 Lb moles/hr.
Methane produced	12,175 Lb moles/hr.

CAPITAL COSTS : \$ MM (Mid-1982)

Installed Equipment(*)	90.0
Contingency @ 15%	13.5
DFCI	103.5
Home-Office costs @ 12%	12.4
TFCI	115.9
Initial Catalyst Charge	11.1
Total Plant Investment	127.0

OPERATING COSTS :

				\$/hr
Produced				

Steam Credit(1500 psig)	-1,271,704 #/hr	@ \$ 5.50/ 1000 lb		-6994.4
Steam Credit(600 psig)	-248,910 #/hr	@ \$ 5.50/ 1000 lb		-1369.0
Steam Credit(60 psig)	-724,499 #/hr	@ \$ 3.85/ 1000 lb		-2789.3
Consumed				

Steam(1500 psig)	112,577 #/hr	@ \$ 5.50/ 1000 lb		619.2
Steam(100 psig)	53,220 #/hr	@ \$ 3.95/ 1000 lb		210.2
Electricity	1,118 Kw	@ \$ 0.05/ Kwh		55.9
Cooling water	8,142 Gpm	@ \$ 0.10/ 1000 Ga		48.9
Catalyst & Chemical		average hourly charge		565.1
TOTAL				-9653.4

Total Operating Cost, \$ MM/yr at 100 % Stream factor = -84.6

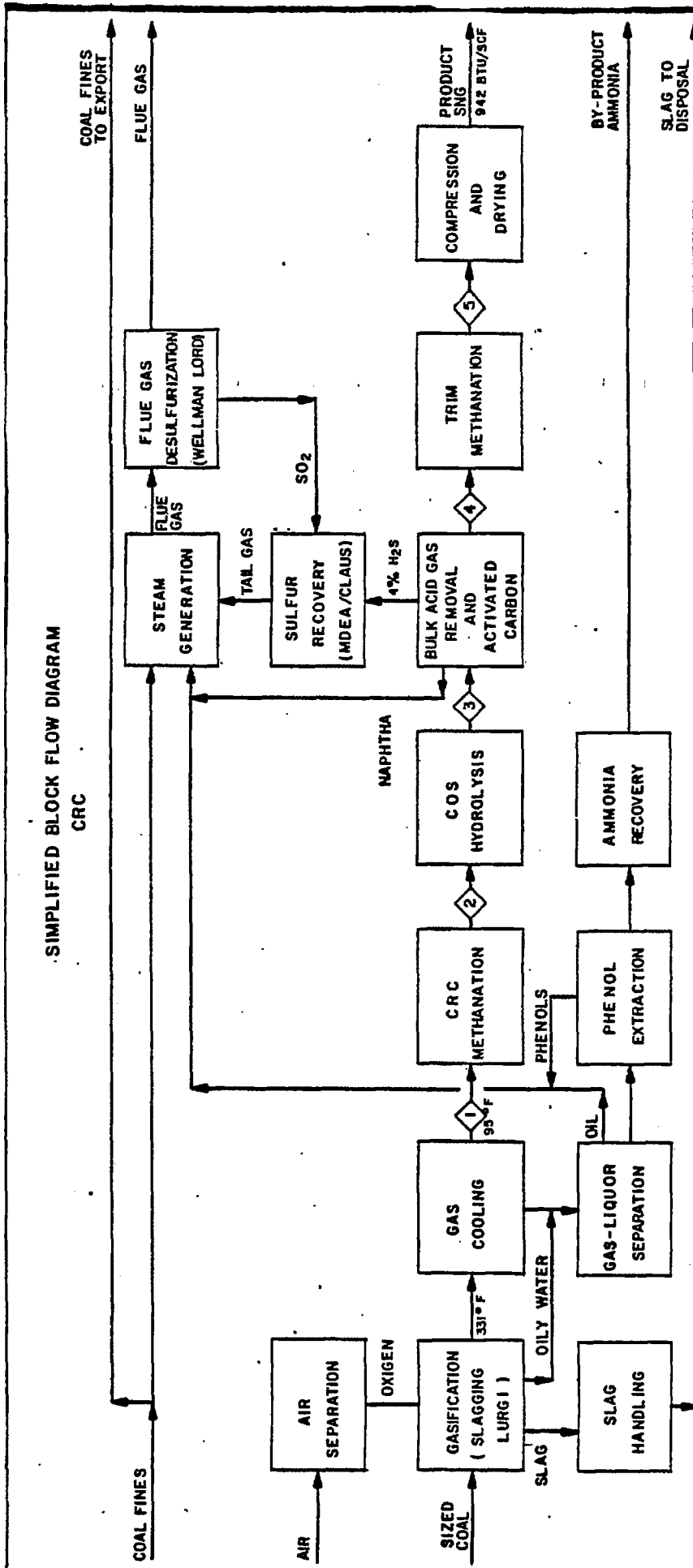
CONTRIBUTION TO GAS COSTS :

	Specific Cost, \$/MM Btu-Yr	Charge Rate, Year	Contribution, \$/MM Btu
Capital Related	1.55	0.089	0.14
Operating	-1.03	1.000	-1.03
Total Credit			-0.89

(*) Includes raw gas cooling and trim methanation.

FIG. 8-1

Source: Ref. 3



NOTE:
MATERIAL BALANCE IS BASED ON 100% PLANT
CAPACITY FOR A PLANT PRODUCING
236 BILLION BTU/DAY OF SNG.

STREAM NUMBER	IDENTIFICATION	1	2	3	4	5
COMPONENT	RAW GAS TO CRC METHANATION					
H		23,702.5	4,872.8	4,872.8	4,859.2	1,423.1
CO		53,997.8	1,239.1	1,239.1	1,236.5	20.0
CO ₂		5,944.1	40,872.6	40,909.4	31	170.3
CH ₄		5,620.8	23,517.9	23,517.9	23,460.0	25,430.8
C ₂ +		465.4	465.4	465.4	461.8	
H ₂ / COS		1,783.2 / 104.4	1,850.1 / 37.5	1,886.9 / 0.7		
N ₂ / Ar		656.0	656.0	656.0	656.0	656.0
C ₆ +	(MW=127)	117.7	117.7	117.7		
TOTAL, C		92,391.9	73,629.1	73,665.9	30	27,700.2
H ₂ O		220.5	4,901.6	36,833.0	30,831.6	2,751.0
TOTAL WET		92,612.4	78,530.7	110,498.9	30,831.6	30,451.2

STATUS SUMMARY

COMFLUX

- 1.0 GENERAL INFORMATION
- 2.0 PROCESS DEVELOPMENT
- 3.0 PROCESS DESCRIPTION
- 4.0 PERFORMANCE DATA
- 5.0 ADVANTAGES AND LIMITATIONS
- 6.0 REFERENCES

1.0 GENERAL INFORMATION

Developer: Thyssengas GmbH, Duisburg and
Didier Engineering GmbH, Essen
Federal Republic of Germany

Licensors: Thyssengas GmbH, Duisburg
Federal Republic of Germany

Sponsor: Government of Federal Republic of Germany

Type: The Comflux process is a catalytic (nickel catalyst), pressurized fluid-bed process to convert CO-rich gas into Substitute Natural Gas (SNG) in a single-stage, i.e. shift conversion and methanation in one step. The reaction heat is recovered to superheated HP-steam.

2.0 PROCESS DEVELOPMENT

The Comflux process was developed in three stages.

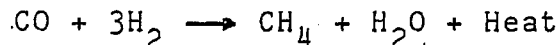
The first stage of the development was performed between 1976 and 1981 in a semi-technical test plant on the premises of Ruhrchemie AG in Oberhausen. A 1.30 ft. diameter (0.4 meter) and 26 ft. high (8.0 meter) reactor was operated for more than 7000 hours to produce up to 12300 ft³/hr SNG.

After establishing the process concept in the semi-technical test plant, design of a pilot plant was started in 1979 for second stage development. A reactor with I.D. of 3.3 ft. (1.0 meter) and 36 ft. tall with an anticipated capacity of 8800 ft³/hr was constructed at the same site. Start-up of the pilot plant took place in 1981. The plant was operated for a cumulative on-stream time of 8000 hours by end of 1984. Test results are reported in Section 4.0 of this report. West Germany's Federal Government funded more than half of the pilot plant's expenses, estimated at \$25 million.

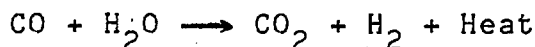
The third stage of the development will be the construction of a full scale demonstration plant with a 9.8 ft. (3.0 meter) to 15 ft. (4.5 meter) ID reactor having a capacity to produce 1.41 to 4.24 MM ft³/hr of SNG. Due to the changes in the energy market over the past few years, Thyseengas has not completed this stage yet.

3.0 PROCESS DESCRIPTION

The Comflux process is a catalytic (nickel catalyst) pressurized fluid-bed process to convert CO-rich gasification gases into Substitute Natural Gas (SNG) in a single step. Most gases produced from coal inherently contain much less hydrogen than required for a methanation reaction:



Hence, part of the carbon monoxide must be reacted with water to form additional hydrogen using the water-gas shift reaction:



The Comflux process performs both these reactions simultaneously in a single reactor with complete CO conversion. The water formed in the methanation reaction is available for water-gas shift reaction. Thus, a gas with a H_2/CO ratio of less than 3 can be methanated without adding water.

A schematic diagram of the Comflux fluidized bed reactor is shown in Figure 3-1 and a simplified process flow diagram is shown in Figure 3-2. The desulfurized feed gas is preheated against the product gas to the reaction initiation temperature and then fed into the reactor. The gas fluidizes the powdery catalyst, and both methanation and water-gas shift reactions take place simultaneously in the fluidized bed. The axial temperature gradient in the fluidized bed is extremely small, and the reactor is operated under high loads almost isothermally. Hot catalyst particles cool down sufficiently fast by mixing with colder particles and by contact with integrated heat exchangers, so that the high heat of the methanation reaction causes no superheating of the bed. The reaction heat is utilized to generate high pressure superheated steam. The product gas with less than 0.1% (vol) CO, is then cooled and the process water is condensed. If the feed gas has H_2/CO ratio of less than 3.0, the CO_2 formed with the reaction, must be removed to meet the pipeline quality specifications. The resulting product gas is SNG with a heating value of 926 - 1016 BTU/SCF and chemical properties identical to natural gas.

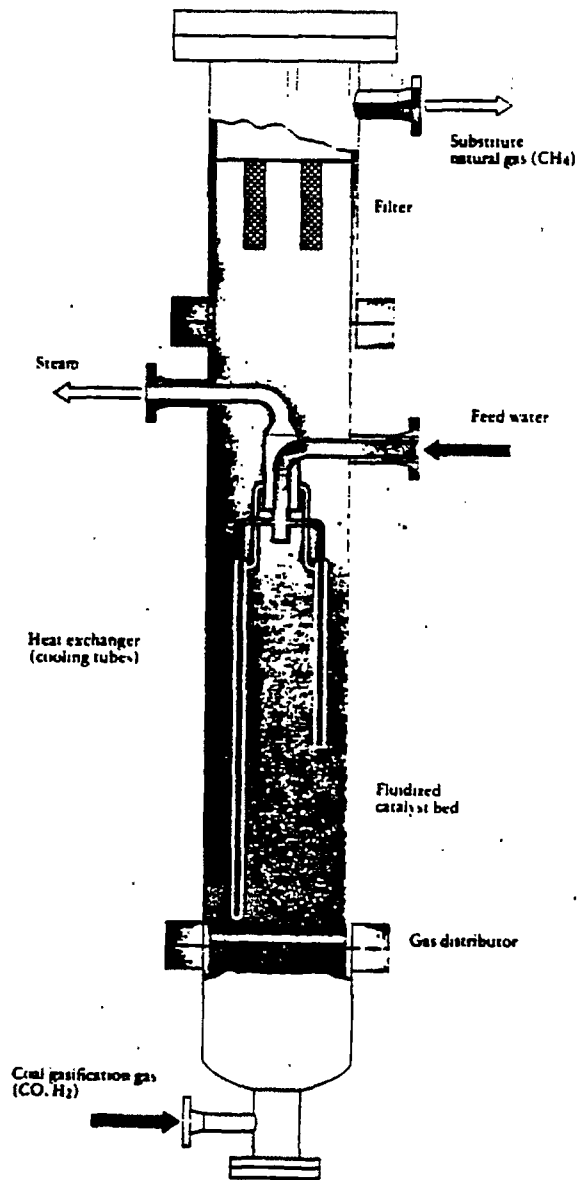


Figure 3-1
COMFLUX FLUIDIZED BED REACTOR

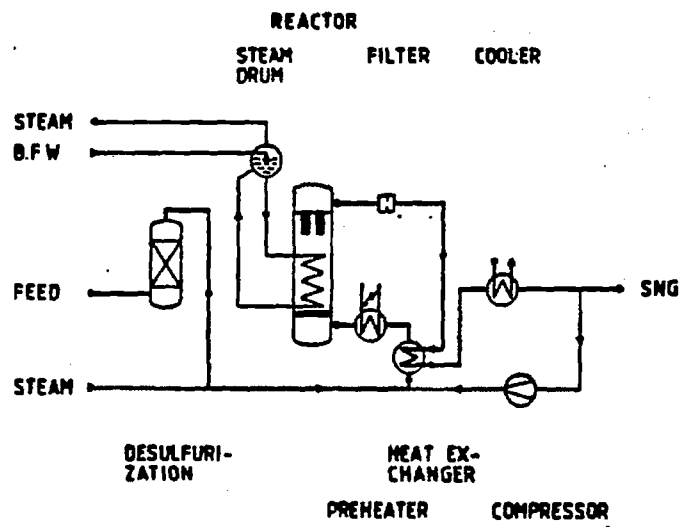


Figure 3-2
SIMPLIFIED PROCESS FLOW DIAGRAM

4.0 PERFORMANCE DATA

Semi-Technical Test Plant Operating Conditions:

Output Capacity:	3500 - 12300 FT ³ /HR
Pressure	290 - 870 PSI
Temperature	752 - 932 ^o F
H ₂ /CO Ratio	1.8 - 3 Vol/Vol
Recycle/Feed Ratio	0 - 0.5 Vol/Vol
Gas Velocity	0.16 - 0.82 FT/SEC
SNG Production, Vol %:	
Methane	86 - 96
Hydrogen	2 - 8
Carbon Dioxide	2 - 6
Gross Heating Value:	926 - 1016 BTU/SCF

Pilot Plant Operation Data

Reactor Diameter	3.28 ft. (internal)
Reactor Height	36.0 ft.
Pressure	190 - 870 PSI
Fluidized Bed Temperature	840 - 1020 ^o F
Feed Gas	112,000 - 400,000 SCF/hr
H ₂ /CO Ratio	2.0 - 3.0 Vol/Vol.
Recycle Gas Ratio	0 - 0.3 Vol./Vol.
Gas velocity	0.16 - 1.0 ft/sec.
SNG Production	45,000 - 112,000 SCF/hr
Steam Production	1.0 - 5.2 t/hr.
Steam Temperature	700 - 890 ^o F
Fluidized Bed Height	6.4 - 12.9 ft.
Catalyst Charge	0.8 - 1.6 tons
Catalyst Particle Size Distribution	10 - 400 microns

5.0 ADVANTAGES AND LIMITATIONS

Advantages

The process performs both water-gas shift reaction and methanation reaction simultaneously and produces pipeline quality gas in a single fluidized bed reactor.

The shift and methanation reactions can be combined even with a H_2/CO ratio of two without adding steam. With small amounts of steam, SNG can be produced from gases with a H_2/CO ratio as low as 1.5.

Conversion of heat of reaction into super-heated high pressure steam with minimal loss.

Operation of the reactor without or with only a small amount of recycle (recycle ratio 0 to 0.5 vol/vol).

The process will have fewer reactors and other associated equipment than a conventional multistage fixed-bed methanation process with a separate shift-conversion. This would probably mean less capital investment.

The process will have lower utility requirements than a conventional shift and methanation scheme which would be reflected in the final gas cost.

Limitations

Loss of catalyst by attrition

Feed gas has to be desulfurized before feeding into the reactor.

Scaleup of the process to define fluidization behavior, erosion of bed internals and heat recovery must be demonstrated.

6.0 REFERENCES

1. Lommerzheim Werner, and Flockenhaus Claus," One stage Combined Shift-Conversion and Partial Methanation Process for Upgrading Synthesis Gas to Pipeline Quality", paper presented at the Tenth Synthetic Pipeline Gas Symposium, October 30 to November 1, 1978, Chicago, Illinois.
2. "Development Project Substitute Natural Gas by the Comflux Process", published by Thyssengas GmbH, Duisburg, West Germany, 1982.
3. "West Germany: Confidence for Comflux", Chemical Engineering, November 16, 1981, PP. 45 - 47.
4. "Thyssengas nearing completion of coal gas pilot in West Germany", Synfuels, September 18, 1981, P. 4.
5. Flockenhaus Claus, and Werner Lommerzheim, "One Stage Shift - Conversion and Partial Methanation Process for Upgrading Synthesis Gas", paper presented at the Ninth Synthetic Pipeline Gas Symposium, October 31 to November 2, 1977, Chicago, Illinois.
6. Lommerzheim, Werner, "The Pilot Development Stage of the COMFLUX - Process for Methanization of Coal Gas", paper presented at EPRI/KFA Conference on Coal Gasification and Synthetic Fuels for Power Generation, San Francisco, Ca., April 1985.

COMPARISON OF PERFORMANCE/DESIGN PARAMETERS

The GRI/Advisors Planning and Strategy (GAPS) Committee was established to develop a plan for guiding research in the areas of fossil fuel gasification and downstream gas processing. As part of the work, the committee has developed a procedure for evaluating Shift and Methanation processes by setting up performance criteria to evaluate processes. This allows the identification of specific advantages and disadvantages of various processes and to establish research goals for process improvement and new process development. The "Musts" in Shift/Methanation technology are shown in Table 6-1. The technical criteria and standards developed for Shift/Methanation technology appear in Table 6-2. A brief description and explanation of the same is provided where appropriate. Table 6-3 summarizes the performance of the four (Conventional Shift and Methanation, Combined Shift and Methanation, CRC Direct Methanation and Comflux) processes. All the data in Table 6-3 are extracted from the respective Status Summary reports and from the public sources. It should be noted that these data are based on current publicly available resources; as more data are developed or made available to the public by the licensors, this table could be updated. Footnotes at the end of the table are provided for additional clarification.

TABLE 6-1

'MUSTS' IN SHIFT/METHANATION
TECHNOLOGY SELECTION

The shift/methanation technology being considered must:

1. Be developed such that the basic concept is confirmed.
2. Be able to treat gas from at least one gasifier.
3. Be capable of producing a product gas, after CO₂ and water removal, is interchangeable with the pipeline gas.
4. Be capable of producing a product gas having a higher heating value (HHV) greater than 950 BTU/SCF after CO₂ and water removal.
5. Require no exotic materials of construction.
6. Involve no solvent or process reagent which is regarded as highly toxic or highly carcinogenic.

TABLE 6-2

TECHNICAL CRITERIA AND STANDARDS FOR SHIFT/METHANATION TECHNOLOGY

CRITERION	DESCRIPTION	STANDARD	EXPLANATION
1.0 FEED GAS PROCESSING CAPABILITY			
1.1 Sulfur (Equivalent H ₂ S)	Range of concentrations in inlet gas, volume %.	0.2 to 1.3	Process should be capable to treating raw gas from variety of gasifiers and coals without reduced conversion or selectivity.
1.2 C ₂ - C ₄ Gases		Up to 1.2	
1.3 C ₅ + Hydrocarbons		Up to 0.2	
1.4 Other Contaminants		Up to 50 ppm of NH ₃ or HCN	
1.5 (H ₂ /CO) Ratio		0.4 to 2.5	
1.6 Water		Up to 40	
1.7 CO ₂		Up to 35	
2.0 CONVERSION CAPABILITY			
2.1 CO	Percent of feed converted; capability to meet interchangeability spec's for SNG.	> 99.9	Product SNG must have less than 0.1 % CO and have HHV > 950 Btu/SCF after removal of acid gases and moisture.
2.2 H ₂		> 95	
2.3 HHV of Product, Btu/SCF		> 950	
2.4 C ₃ + Gases		> 95	
3.0 PROCESS EFFICIENCY			
3.1 Energy Recovery	% of shift/methanation heat of reaction recovered for use.	High	As BFW heating or steam generation.
3.2 Quality of Energy Recovered	Index, 500 psig sat'd steam = 1.0	1.0	
3.3 Energy Consumption	Utilities/HHV of feed gas	Low	Convert all to Btu/hr, HHV.
4.0 WASTE PRODUCT PRODUCTION			
4.1 Sour Water		Minimum	
4.2 Other		None	
5.0 REACTOR DESIGN CONSIDERATIONS			
5.1 Operating Pressure		400 psig	Letdown or compression not desired. Higher pressure favors CH ₄ formation, close approach to equilibrium.
5.2 Pressure Drop		Minimum	
5.3 Space Velocity	Gas SCFH/total catalyst volume	> 5000 /hr	
5.4 Approach to Equilibrium	At outlet	< 50 deg F	
5.5 Temperature Rise	As adiabatic temperature rise for each reaction stage.	> 400 deg F	Adiabatic temperature rise is equivalent to fractional conversion per stage.

TABLE 6-2
(continued)
TECHNICAL CRITERIA AND STANDARDS FOR SHIFT/METHANATION TECHNOLOGY

CRITERION	DESCRIPTION	STANDARD	EXPLANATION
6.0 CATALYST PROPERTIES			
6.1 Type/Constituents	To methane formation	Non-noble > 2 years	Less-expensive catalysts preferred.
6.2 Life/Cycle Time		Yes	
6.3 Regenerability		High	Overall reaction should not leave excess hydrogen or form higher hydrocarbons.
6.4 Selectivity		None	
6.5 Carbon Deposition	Catalyst should be non-corrosive non-flammable, non-phosphoric and dust-free.	High	Index vs. Conventional S/M Process.
6.6 Safety in Handling			
6.7 Spent Catalyst Disposition	Special handling requirements	None	Recycled catalyst preferred.
6.8 Deactivation Temperature	Minimum deterioration temperature	> 950 deg F	Sintering or loss of activity.
6.9 Reaction Ignition Temperature		< 500 deg F	
6.10 Storage/Activation Requirements	Special requirements or practices	None	
6.11 Mechanical Durability	Crush strength, psi	High	Index vs. Conventional S/M Process.
7.0 IMPACT ON SNG PLANT DESIGN			
7.1 Number of Blocks	Index vs. Conventional S/M	13	Standard for Conventional S/M Process.
7.2 Complexity	Index vs. Conventional S/M	< 1.0	Of units in balance of plant.
7.3 Utilities & Reagents			Of units in balance of plant.
7.4 Flexibility: Gasifiers	Ability to accommodate alternate choices of other process steps.	At least one	Maximum flexibility desired.
7.5 Flexibility: Balance of Plant	Number of extrapolations of key parameters for other areas	More	Prefer that process does not call for unproven designs.
7.6 Design Viability		None	
8.0 INTEGRABILITY			
8.1 Feed Pretreatment	Steps to prepare raw gas for feeding to S/M unit.	5	Steps are particulate removal, steam addition, shift, sulfur removal, CO2 removal.
8.2 Product Gas Treatment	Extra steps required for SNG after S/M unit, other than drying & compression.	None	Steps are sulfur removal, CO2 removal, shift, and trim methanation.

TABLE 6-2
(continued)
TECHNICAL CRITERIA AND STANDARDS FOR SHIFT/METHANATION TECHNOLOGY

CRITERION	DESCRIPTION	STANDARD	EXPLANATION
9.0 PROCESS TECHNIQUES			
9.1	Equipment Availability	Minimal Extrapolation	Use of equipment which is readily available or requires minimal extrapolation from proven ranges.
10.0 MATERIALS OF CONSTRUCTION			
10.1	Availability	Std'd Mat'ls	Materials of construction available at reasonable cost.
11.0 COMPLEXITY			
11.1	Gas Recycles	None	
11.2	Feed Gas Splits	None	
11.3	Reactors in Series	Less than 5	Minimum number preferred.
11.4	Mechanical Complexity	< 1.0	Special internals, mechanical devices or moving parts.
12.0 CONTROLLABILITY			
12.1	Control System	> 1.0	Use existing control methods.
12.2	Turndown Capability	To 50 %	
13.0 RELIABILITY			
13.1	Standby Requirements	None	
13.2	Consequence of Failure	Minimum	Likelihood of damage to other units due to failure in shift/methanation.
13.3	Maintenance Extent	< 1.0	Standard for Conventional S/M Process.
13.4	Overdesign Requirement	Minimum	
14.0 ENVIRONMENTAL CONSIDERATIONS			
14.1	Solid Effluents	None	
14.2	Liquid Effluents	None	
14.3	Gaseous Effluents	None	e.g., avoid carbonyl formation.

TABLE 6-3

PERFORMANCE OF SHIFT/METHANATION TECHNOLOGIES VS. CRITERIA

CRITERION	EXPLANATION	CONVENTIONAL SHIFT/METHANATION	COMBINED SHIFT/METHANATION	DIRECT METHANATION	COMFLUX METHANATION
1.0 FEED GAS PROCESSING CAPABILITY					
1.1 Sulfur (Equivalent H ₂ S)	Range of concentrations in feed gas, vol%	< 0.2 ppm for methanation, no limit for shift.	< 0.2 ppmv	No upper limit; minimum req't may exist.	< 0.2 ppmv
1.2 C ₂ - C ₄ Gases		> 1.2 vol %	> 1.2 vol %	> 1.2 vol %	> 1.2 vol %
1.3 C ₅ + Hydrocarbons		< 0.2 vol %	< 0.2 vol %	0 to 3 vol %	< 0.2 vol %
1.4 Other Contaminants		50 ppm of NH ₃ or HCN	50 ppm of NH ₃ or HCN	50 ppm of NH ₃ or HCN	50 ppm of NH ₃ or HCN
1.5 (H ₂ /CO) Ratio		3.0, shift req'd	0.4 to 2.5	0.4 to 2.5	If < 1.5, shift required.
1.6 Water		No limitation.	No limitation.	10 vol % maximum	No limitation.
1.7 CO ₂		1 to 2 % for meth	No limitation.	No limitation.	1 to 3 %
2.0 CONVERSION CAPABILITY					
2.1 CO	Percent of feed converted; capability to meet interchangability spec's for SNG.	> 99.9	< 99.9, trim methanation req'd	< 99.9, trim methanation req'd	> 99.9
2.2 H ₂		> 95.0	< 95.0, trim methanation req'd	< 95.0, trim methanation req'd	> 95.0
2.3 HHV of Product, Btu/SCF		> 950 Btu/SCF	> 950 Btu/SCF	> 950 Btu/SCF	> 950 Btu/SCF
2.4 C ₃ + Gases		> 95 %	Not announced	No conversion	Not announced
3.0 PROCESS EFFICIENCY					
3.1 Energy Recovery	% of heat of reaction re-covered.	Index = 1.0	Index = 0.9	Index = 1.2	Index = 1.1
3.2 Quality of Energy Recovered		Index = 1.0	Index = 1.05	Index = 1.1	Index = 1.2
3.3 Energy Consumption		Index = 1.0	Index = 0.9	Index = 0.8	Index = 0.7
4.0 WASTE PRODUCT PRODUCTION					
4.1 Sour Water		Index = 1.0	Index = 0.8	Index = 0.8	Index = 0.8
Other		None	None	COS	None

TABLE 6-3 (CONT'D)

PERFORMANCE OF SHIFT/METHANATION TECHNOLOGIES VS. CRITERIA

CRITERION	EXPLANATION	CONVENTIONAL SHIFT/METHANATION	COMBINED SHIFT/METHANATION	DIRECT METHANATION	COMFLUX METHANATION
5.0 REACTOR DESIGN CONSIDERATIONS					
5.1 Operating Pressure		No limitation	No limitation	No limitation	No limitation
5.2 Pressure Drop	No. of beds.	5 fixed beds	5 fixed beds	3 fixed beds	1 fluid bed
5.3 Space Velocity	Gas SCFH/cat- alyst volume.	> 5000 /hr	> 5000 /hr	4000 - 10000 /hr	Not announced
5.4 Approach to Equilibrium		< 50 deg F	< 50 deg F	> 50 deg F	< 50 deg F
5.5 Temperature Rise Tolerance	Adiabatic temp. rise for each stage.	450 - 500 deg F	700 - 800 deg F	700 - 800 deg F	> 800 deg F (Isothermal bed)
6.0 CATALYST PROPERTIES					
6.1 Type/Constituents	Type	Nickel/Alumina	Nickel/Alumina	Molybdenum	Nickel
6.2 Life/Cycle Time		3 years	2 years ?	2 years ?	2 years ?
6.3 Regenerability		Non-regenerable	Non-regenerable	Non-regenerable	Non-regenerable
6.4 Selectivity	To methane formation.	Index = 1.0	Index = 1.0	Index = 0.7	Index = 1.0
6.5 Carbon Deposition		Steam addition req'd for shift	Steam add'n req'd	No deposition	Steam add'n req'd
6.6 Safety in Handling		Index = 1.0	Index = 1.0	Index = 1.0	Index = 0.9
6.7 Spent Catalyst Disposition		No extra steps	No extra steps	No extra steps	No extra steps
6.8 Deactivation Temperature	Deterioration temperature.	950 deg F	950 F SUPER-METH 1400 F RM Process	1250 + deg F	Unknown
6.9 Reaction Ignition Temperature		500 - 550 deg F	450 - 850 deg F	480 deg F	750 - 900 deg F
6.10 Storage/Activation Requirements		No special req'ts	No special req'ts	No special req'ts	No special req'ts
6.11 Mechanical Durability	Crush strength, th. PSI	Index = 1.0	Index = 0.9	Index = 0.8	Index = 1.1

TABLE 6-3 (CONT'D)

PERFORMANCE OF SHIFT/METHANATION TECHNOLOGIES VS. CRITERIA

CRITERION	EXPLANATION	CONVENTIONAL SHIFT/METHANATION	COMBINED SHIFT/METHANATION	DIRECT METHANATION	COMFLUX METHANATION
7.0 IMPACT ON SNG PLANT DESIGN					
7.1 Number of Blocks	Total SNG plant blocks	13 blocks	15 blocks	14 blocks	13 blocks
7.2 Complexity		Index = 1.0	Index = 1.2	Index = 1.0	Index = 1.1
7.3 Utilities & Reagents		Index = 1.0	Index = 0.6	Index = 0.5	Index = 0.5
7.4 Flexibility: Gasifiers		Index = 1.0	Index = 0.9	Index = 0.8	Index = 0.8
7.5 Flexibility: Balance of Plant		Index = 1.0	Index = 1.0	Index = 1.0	Index = 1.0
7.6 Design Viability	Extrapolation	None required	None required	None required	None required
8.0 INTEGRABILITY					
8.1 Feed Pretreatment	Steps req'd.	5 steps	3 steps	1 step	3 steps
8.2 Product Gas Treatment	Other than drying&compr.	None required	2 steps	3 steps	1 step
9.0 PROCESS TECHNIQUES					
9.1 Equipment Availability	Extrapolation	None required	None required	None required	Will require extrapolation
10.0 MATERIALS OF CONSTRUCTION					
10.1 Availability	Std'd Mat'ls	Std'd Mat'ls	High Temp Mat'ls	High Temp Mat'ls	Std'd Mat'ls
11.0 COMPLEXITY					
11.1 Gas Recycles		Required for meth	None required	None required	May be required
11.2 Feed Gas Splits		One or two	One or two	Possibly one	None required
11.3 Reactors in Series	No. of stages.	Four reactors	Five reactors	Three reactors	One reactor
11.4 Mechanical Complexity		Index = 1.0	Index = 1.0	Index = 1.0	Index = 1.5

TABLE 6-3(CONT'D)

PERFORMANCE OF SHIFT/METHANATION TECHNOLOGIES VS. CRITERIA

CRITERION	EXPLANATION	CONVENTIONAL SHIFT/METHANATION	COMBINED SHIFT/METHANATION	DIRECT METHANATION	COMFLUX METHANATION
12.0 CONTROLLABILITY					
12.1 Control System		Index = 1.0	Index = 1.0	Index = 1.0	Index = 0.6
12.2 Turndown Capability	% of full rate	To 50 %	To 50 %	To 50 %	To 75 % ?
13.0 RELIABILITY					
13.1 Standby Requirements	Spares	No extra spares	No extra spares	No extra spares	No extra spares
13.2 Consequence of Failure	Risk involved	Index = 1.0	Index = 1.0	Index = 1.0	Index = 1.0
13.3 Maintenance Extent		Index = 1.0	Index = 0.9	Index = 1.0	Index = 1.2
13.4 Overdesign Requirement	To accommodate variations in feed gas comp or rate.	Index = 1.0	Index = 1.2	Index = 1.2	Index = 1.1
14.0 ENVIRONMENTAL CONSIDERATIONS					
14.1 Solid Effluents	Extra steps.	None	None	None	Catalyst dust ?
14.2 Liquid Effluents	Extra steps.	None	None	None	None
14.3 Gaseous Effluents	Extra steps.	None	None	None	None

FOOTNOTES

<u>CRITERIA</u>	<u>EXPLANATION</u>
1.1	SULFUR IN FEED GAS - The UCI version of combined S/M Process cannot accept sulfur in the feed gas; the RMP Process can accept up to 5 PPMV sulfur in the feed gas.
1.3	C5+ HYDROCARBONS IN FEED GAS - Presence of C5+ hydrocarbons in the feed gas will have a tendency to deposit carbon in the conventional, combined and Comflux processes.
1.5	H ₂ /CO RATIO IN FEED GAS - The combined and direct methanation processes can accept any range of H ₂ /CO ratio.
1.7	CO ₂ IN FEED - The Comflux process calls for upstream CO ₂ removal, while the conventional process requires CO ₂ removal prior to the methanation step.
2.1	CO CONVERSION CAPABILITY - The Direct Methanation and Combined shift and methanation processes cannot produce pipeline quality SNG because excess steam and/or CO ₂ in the effluent gas artificially dilute the outlet CO content and thus trim methanation is required.
2.2	H ₂ CONVERSION CAPABILITY - Just as for CO, unconverted H ₂ remains in the exit gases of the Direct and Combined Methanation processes.
3.1	ENERGY RECOVERY - When steam is added to the process gas, energy recovery is reduced due to the requirement of condensing the extra steam, resulting in loss of a portion of the recoverable heat to the cooling medium.

CRITERIA EXPLANATION

- 3.3 ENERGY CONSUMPTION - Primary considerations are steam addition to the process and multiple reaction stages, which cause added loss of heat during interstage cooling. The Conventional process requires recycle gas compression, steam addition at shift and at least 4 reactor stages. The Combined process requires steam addition and at least 5 reactor stages. Direct Methanation requires at least 3 reactor stages but does not need steam addition. Comflux Methanation may not need either steam addition or gas recycle and uses a single fluid-bed reactor.
- 4.1 SOUR WATER PRODUCTION - The Conventional process requires steam addition at shift; subsequent condensation of that steam causes an extra sour water load.
- 5.5 TEMPERATURE RISE - The temperature rise allowed by a catalyst is proportional to the fractional conversion in an exothermic reaction. Therefore, the higher the temperature rise, the greater the fractional conversion and fewer reaction stages are required for a given total conversion.
- 6.5 CARBON DEPOSITION - Steam addition is required to avoid carbon deposition in the Combined process and in the shift step of the Conventional process. Since the Comflux Methanation process uses a similar catalyst as the Combined process, a similar requirement is expected there. Direct Methanation does not require steam addition.
- 6.11 MECHANICAL DURABILITY - The catalyst in the Comflux process was judged superior since it must operate in a fluid bed. The Conventional process catalyst was then judged better in strength than the Combined process catalyst and the Direct Methanation catalyst.

CRITERIA

EXPLANATION

7.2 COMPLEXITY - The Direct Methanation and the Conventional processes were judged to be about the same in balance-of-plant complexity. The Comflux process was seen as more complex while splitting of the acid gas removal units caused the Combined process to be even more complex.

7.4 FLEXIBILITY: GASIFIERS - The Conventional process was judged to be most flexible since the feed to the methanation reactors is practically the same for any and all gasification processes. Direct Methanation and Comflux processes may require adjustment of gas depending upon the gasifier.

8.1 FEED PRETREATMENT - The feed pretreatment steps considered were as follows:

- a. Particulate removal
- b. Steam addition
- c. Shift conversion
- d. Sulfur removal
- e. CO₂ removal

Direct Methanation	Step a, c
Comflux Methanation	Steps a, b, d & e
Combined Process	Steps a, b & d
Conventional Process	Steps a,b,c,d,e

8.2 PRODUCT GAS TREATMENT - The product gas treatment steps (other than drying and compression) considered were as follows:

- a. Sulfur removal
- b. CO₂ removal
- c. Trim methanation

Conventional Process	None required
Comflux Methanation	Step b, c
Combined Process	Steps b & c
Direct Methanation	Steps a, b & c

<u>CRITERIA</u>	<u>EXPLANATION</u>
9.1	EQUIPMENT AVAILABILITY - The scaleup of the waste-heat recovery and fluid-bed systems of the Comflux process may present difficulties; existing equipment designs can be used for the other processes.
11.4	MECHANICAL COMPLEXITY - Comflux process may require internals for heat recovery and for gas distribution.
12.1	CONTROL SYSTEM - Operation of the fluid-bed and waste heat recovery systems of the Comflux process may require more complex control techniques as compared to the fixed-bed processes.
12.2	TURNDOWN CAPABILITY - Because of the minimum fluidization velocity requirement associated with the Comflux process, turndown could be a problem.
13.3	MAINTENANCE EXTENT - The Comflux process employs a fluidized bed and as such is judged to require more routine maintenance than do the fixed bed processes.
13.4	OVERDESIGN REQUIREMENTS - The Conventional process was judged most capable to respond favorably to variations in the feed gas composition, and thus it requires minimum overdesign of equipment.
14.1	SOLID EFFLUENTS - The Comflux process is expected to generate solid waste in the form of catalyst carryover due to attrition in the fluid bed.

**REVIEW OF SELECTED ACID GAS REMOVAL
PROCESSES FOR SNG PRODUCTION**

FINAL REPORT

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REVIEW OF SELECTED ACID GAS
REMOVAL PROCESSES
FOR SNG PRODUCTION

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REVIEW OF SELECTED ACID GAS
REMOVAL PROCESSES
FOR SNG PRODUCTION

TABLE OF CONTENTS

1. Introduction and Summary
2. List of Acid Gas Removal Processes
3. Selexol Process
4. Rectisol Process
5. Benfield Process
6. CNG Process
7. Ryan-Holmes Process
8. Comparisons of Performance/Design Parameters

INTRODUCTION AND SUMMARY

Kellogg Rust Synfuels, Inc. (KRSI) has assembled background information for use in evaluating technologies for downstream gas processing, specifically acid gas removal, as part of work with the GRI/Advisors Planning and Strategy (GAP) Committee under GRI Contract No. 5082-222-0754. Using pertinent references and in-house information, KRSI developed a list of 29 technologies for acid gas removal. The listing has been tabulated in Section 2.0. For each process, the name and location of the developer, a capsule description of process, typical operating conditions, number of units built or in operation and other comments are included. The listing has also been identified for the type of process (absorption, adsorption, or cryogenic distillation), type of solvent (chemical or physical), mode of operation (selective and/or non-selective) and major contaminants removed (H_2S , CO_2 , oil).

The GAPS Committee chose five representative technologies for further evaluation. These were:

- Selexol Absorption, physical solvent, selective and non-selective, CO_2 and H_2S .
- Rectisol Absorption, physical solvent, selective and non-selective, CO_2 and H_2S .
- Benfield Absorption, chemical solvent, non-selective, CO_2 and H_2S .
- CNG Absorption, physical solvent, selective CO_2 and H_2S .
- Ryan-Holmes Cryogenic distillation, selective CO_2 , H_2S and C_2 .

KRSI proceeded to prepare a "Status Summary" report for each of the five technologies mentioned above. Their directions were to summarize pertinent, recent information within a concise report for each process. Each of the Status Summary reports is divided into the following sections, as applicable.

- General Information
- Process Development
- Solvent Characteristics
- Process Description
- Commercial Design Data
- Advantages and Disadvantages
- Commercial Installations
- References

The Status Summary reports appear in Section 3.0 through 7.0 for the Selexol, Rectisol, Benfield, CNG and Ryan-Holmes processes, respectively. With the list of processes, these documents comprised a body of background information for use in further work. The Ryan-Holmes process was later deleted from the evaluation, for the reason it has not yet been applied or proven to process synthesis gas from coal gasification units.