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**ASPEN Simulation of the SNG
Production Process in an Indirect
Coal-Liquefaction Plant**

Jennifer E. Bistline
Toby B. Shafer

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CHEMICAL TECHNOLOGY DIVISION

MASTER

ASPEN SIMULATION OF THE SNG PRODUCTION PROCESS
IN AN INDIRECT COAL-LIQUEFACTION PLANT

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ABSTRACT

The synthetic natural gas (SNG) production process (methanation, CO-shift, and hydrogen removal) in an indirect coal-liquefaction plant was simulated using the Advanced System for Process Engineering (ASPEN). The simulation of the methanation unit agreed to within 12% of Fluor's design for converting carbon monoxide and carbon dioxide.

A parametric study examined the effect of four important operating parameters on product composition, process thermal efficiency, and outlet temperature from the second methanation reactor. The molar split of gas feed to the CO-shift unit before methanation was varied from 0.2 to 0.6; variations of molar recycle ratio (0.01 - 0.67), molar steam-to-feed ratio (0.04 - 0.19), and feed temperature (478 - 533 K, 400-500°F) to the first methanation reactor were also studied.

A 50%-lower split improved thermal efficiency by 6%, but the mole % hydrogen and carbon monoxide in the product SNG required to meet pipeline-quality standards and temperature constraints were not met. Increasing the steam-to-feed ratio from 0.04 to 0.19 improved product quality but decreased thermal efficiency by 8%. By decreasing the feed temperature from 533 to 477 K (500 to 400°F), product specifications and temperature constraints were met with no effect on thermal efficiency. However, it may be impractical to operate the reactor at 477 K (400°F) because the kinetics are too slow. Increasing the recycle ratio from 0.4 to 0.67 had no effect on thermal efficiency, and temperature constraints and product specifications were met. The SNG production process should be optimized at recycle ratios above 0.67.

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1. SUMMARY

Tri-State Synfuels Company is considering building an indirect coal-liquefaction plant to convert coal to gasoline, synthetic natural gas (SNG), and chemicals. As they are seeking loan guarantees from the Synthetic Fuels Corporation, Oak Ridge National Laboratory (ORNL) was asked to assist in evaluating the process.

ORNL has already used Advanced System for Process Engineering (ASPEN) to simulate many sections of the indirect coal-liquefaction plant. The objective of this project was to simulate the SNG production process in the plant and to determine the effect of operating conditions on process thermal efficiency and product composition. The SNG production process includes three units: the methanation unit, the carbon-monoxide-shift unit, and the pressure-swing absorption unit. Carbon monoxide and carbon dioxide are converted to methane (SNG) in the methanation unit; carbon monoxide and water are converted to carbon dioxide and hydrogen in the CO-shift unit; and hydrogen is removed in the pressure-swing absorption unit.

The methanation unit was first simulated and compared with results obtained by Fluor (8). Seventy-eight percent of the carbon dioxide and 99% of the carbon monoxide were converted to methane in the ASPEN simulation, whereas Fluor obtained 88% conversion of carbon dioxide and 99.9% conversion of carbon monoxide in their analysis. Agreement was within 12% for conversion of carbon dioxide and 1% for carbon monoxide.

The operating conditions for the first methanation reactor varied in a parametric study were: molar recycle ratio (0.01 - 0.67), feed temperature (478 - 533 K, 400 - 500°F), and molar ratio of steam to feed (0.04 - 0.19). The fraction of purge gas sent to the CO-shift unit (the split) before being fed to the methanation unit was also varied from 0.2 to 0.6. The base case was defined using a recycle ratio of 0.25, a steam-to-feed ratio of 0.04, a reactor feed temperature of 533 K (500°F), and a split of 0.4.

Lowering the split from 0.4 to 0.2 improved thermal efficiency by 6%; but a low split resulted in an outlet temperature above 755 K (900°F) at which temperature the nickel catalyst started to lose efficiency, and product specifications were not met. Increasing the steam-to-feed ratio from 0.04 to 0.19 improved product quality, decreased thermal efficiency by 8%, and lowered the outlet temperature from the second methanation unit to 744 K (880°F).

Decreasing the feed temperature to 477 K (400 °F) had no effect on thermal efficiency but improved product quality and lowered the outlet temperature from the second reactor to below 755 K (900°F). Slow reaction kinetics may make it impractical for the methanation reactor to operate with a feed temperature of 477 K (400°F).

Increasing the molar recycle ratio from 0.4 to 0.67 had no effect on thermal efficiency, but both improved product quality so that it met the mole % hydrogen and carbon monoxide specifications for pipeline-grade synthetic natural gas and lowered the second reactor outlet temperature to 747 K (886°F). The SNG production process should be optimized at high (≥ 0.67) recycle ratios.

The first methanation reactor was modeled as a stoichiometric reactor. Based on calculations of equilibrium constants, equilibrium was not reached in the reactor. The model was also checked by manual calculation.

A modified design of the SNG production process was also considered. Although this design was not successfully simulated, work on this design should not be continued because anticipated savings in thermal energy would be offset by increased energy requirements for compressors.

2. INTRODUCTION

2.1 Background

The Tri-State Synfuels Company is planning to build a 9.07×10^6 kg coal/day (10,000 ST/D) indirect coal-liquefaction plant to produce gasoline, synthetic natural gas (SNG), and chemicals from coal. As shown in Fig. 1, the plant proposed by Fluor Engineers and Constructors, Inc., (8) uses Lurgi Mark-IV gasifiers to gasify the coal, producing carbon monoxide and hydrogen. This synthesis gas is fed to a Rectisol gas-purification unit, then to a methanol synthesis unit. The methanol produced is converted to gasoline in fixed-bed reactors using the Mobil methanol-to-gasoline (MTG) process. Purge gas from the methanol synthesis unit, along with two smaller gas streams, is converted to methane (SNG) in the SNG production unit.

Because Tri-State is seeking loan guarantees from the Synthetic Fuels Corp. to finance the liquefaction plant, ORNL was asked to assist in evaluating the proposed process designs. ASPEN (Advanced System for Process Engineering) computer simulations are being developed at ORNL to provide design data for an economic evaluation which will be compared with Fluor's estimates. Also, accurate simulations of the process units are being used to study process sensitivity to changes in design and operating conditions. Detailed simulations of the methanol synthesis and Mobil MTG units were made by Chien and Luther (2) and Barker (5). The SNG production process is the most important process, with respect to thermal efficiency and overall economics, which has not been analyzed (5).

2.2 Objectives

The objectives of this project were to simulate the SNG production process proposed by Fluor in detail, using ASPEN, and to determine the

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DATE 4-19-82	DRAWN BY TBS	FILE NO. CEPS-X-352	FIG. 1
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effect of varying operating conditions on the process thermal efficiency and product composition. The specific goals were to:

1. Conduct a rigorous heat- and mass-balance simulation of the individual unit operations in the SNG production process design.
2. Evaluate the effect on the process thermal efficiency and product composition of varying the following operating conditions:
 - a) the molar fraction of the methanol-synthesis purge gas sent to the CO-shift unit before entering the methanation unit;
 - b) the temperature of the feed to the first of two methanation reactors;
 - c) the molar recycle ratio to the first methanation reactor;
 - d) the molar ratio of steam to the first methanation reactor to overall feed to the SNG production process.
3. Evaluate a modified design of the SNG production process.

3. SNG Production Process

3.1 Feed and Product-Stream Specifications

The feed to the SNG production process consists of three streams, both a purge gas and an off-gas stream from the methanol synthesis unit, and a purge-gas stream from the naphtha hydrotreater. The methanol-synthesis purge-gas stream, at 316 K and 7.86×10^3 kPa (103°F, 1140 psia), represents 94 mol % of the total feed to the SNG production process with a flow rate of 5678 kg-mol/h (12,519 lb-mol/h). The purge gas withdrawn from the recycle stream of the methanol reactor contains mostly hydrogen and methane, along with carbon monoxide, carbon dioxide, and some organics. The off-gas stream, at 314 K and 345 kPa (105°F, 50 psia), which consists mostly of methane and carbon dioxide, is produced at a rate of 349 kg-mole/h (770.2 lb-mole/h) during the expansion of the methanol product stream. The flow rate of the naphtha-hydrotreater purge gas, which is approximately 80% hydrogen and 20% methane, at 316 K and 4433 kPa (103°F, 643 psia), is 9.9 kg-mole/h (21.7 lb-mole/h). The compositions of the feed streams are given in Table 1.

The saturated steam input to the carbon monoxide-shift reactor is at 566 K and 7722 kPa (559°F, 1120 psia), whereas the saturated steam added to the first methanation reactor is at 589 K and 1.07×10^4 kPa (600°F, 1550 psia). All the boiler feed water used to generate steam is available at 389 K (240°F) and at the desired pressure for the steam generated.

Table 1. Composition and Flow Rates of SNG
Production Process Feeds (5)

Component	Methanol-Synthesis Purge Gas (mole %)	Methanol-Synthesis Off-Gas (mole %)	Naphtha-Hydrotreater Purge Gas (mole %)
H ₂	0.30	0.07	0.82
CO	0.16	0.07	0.00
CO ₂	0.04	0.16	0.00
CH ₄	0.46	0.58	0.17
C ₂ H ₆	0.01	0.05	8.1×10^{-3}
CH ₃ OH	8.4×10^{-3}	0.06	0.00
H ₂ O	1.5×10^{-5}	1.9×10^{-4}	1.4×10^{-3}
N ₂	0.02	9.5×10^{-3}	6.0×10^{-4}
<u>Flow Rates</u>			
kg-mole/h	5678	349	9.9
(lb-mole/h)	(12,519)	(770)	(21.7)

The required product streams from the SNG production process are: (1) a 159 kg-mole/h (350 lb-mole/h) stream of approximately 98% pure hydrogen for use in the naphtha hydrotreater; and (2) a stream of SNG with carbon dioxide. The SNG stream may contain no more than 5 mole % hydrogen and 0.5% carbon monoxide to meet pipeline-quality standards (5).

3.2 Flowsheet and Description of the SNG Process

The SNG production process in the indirect coal-liquefaction plant proposed by Fluor Engineers and Constructors, Inc., consists of three units: carbon monoxide shift, pressure-swing absorption (PSA), and methanation (8), as shown simplified in Fig. 2 and in detail in Figs. 3 and 4. The stream numbers that follow refer to Figs. 3 and 4 and the stream numbers used in the ASPEN simulation. Purge gas from the methanol synthesis unit (stream 1) is split into two streams. One stream (33) is fed directly into the methanation unit; the other stream (2) is sent to the carbon-monoxide-shift unit where carbon monoxide and water react to form carbon dioxide and hydrogen:

Before this product stream (24) is fed into the methanation unit, hydrogen is removed in the pressure-swing absorption unit:

3.2.1 Methanation Unit

The gas stream (30) from the pressure-swing absorption unit and the off-gas stream from the methanol-synthesis unit (stream 31) are mixed and compressed to 7860 kPa (1140 psia) by three compressors with inter-stage coolers. This stream (41) is mixed with the purge gas (stream 34) from methanol synthesis and preheated. The resulting stream (45) is then mixed with the recycle stream (54) from the first reactor steam (stream 48) and purge gas from the naphtha hydrotreater (stream 44) before being fed into the first reactor. Steam is added to prevent carbon formation and to control temperature by diluting the reactants in the first reactor. Methane is formed in the first reactor by the four exothermic reactions listed in Table 2.

Table 2. Heats of Reaction for Methanation Reactions

Reaction	ΔH°_{298} (J/g-mol) [Btu/lb-mol]		
$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	-49,271	[-88,632]	(2)
$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	-39,414	[-70,901]	(3)
$\text{CH}_3\text{OH} + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	-27,627	[-49,697]	(4)
$\text{C}_2\text{H}_6 + \text{H}_2 \rightarrow 2\text{CH}_4$	-7,771	[-13,979]	(5)

A nickel catalyst which degrades at temperatures above 755 K (900°F) is used (4).

The reactor effluent (stream 50) is cooled by exchanging heat with the purge gas from the naphtha hydrotreater (stream 43) before being split into two streams. One stream (44) is recycled back into the first reactor, while the other (stream 55) is cooled by generating steam and then fed into the second reactor. The effluent from the second reactor (stream 57) is cooled by preheating the feed (stream 46) and generating steam. Water is removed in a series of four knockout drums with inter-stage coolers. The resulting product stream (69) is at 308 K and 7102 kPa (95°F, 1030 psia).

3.2.2 CO-Shift Unit

Part of the purge-gas stream from the methanol synthesis unit (stream 1) is sent into the CO-shift unit. This stream (2) is preheated from 313 to 589 K (103 to 600°F) by exchanging heat with the CO-shift reactor effluent (stream 7). In the CO-shift reactor, carbon dioxide and hydrogen are formed. The reactor effluent (stream 7) is cooled by generating steam and preheating the feed (stream 3). Water is removed in a series of knockout drums with interstage coolers. Carbon dioxide is removed from the cooled stream (24A) in a Rectisol unit before being sent to the PSA unit.

3.2.3 Pressure-Swing Absorption (PSA) Unit

The gas stream entering the PSA unit (24) is split into two streams. One stream (27) is mixed with the purge gas from the methanol-synthesis unit and is sent directly to the methanation unit. The other stream (28) is fed into a separator where 159 kg-mole/h (350 lb-mole/h) of hydrogen is removed by molecular sieves. The remaining gas stream (30) is at 345 kPa (50 psia) and is mixed with the off-gas from the methanol-synthesis unit (stream 31) before being sent to the methanation unit.

4. ASPEN MODEL OF THE SNG PRODUCTION PROCESS

ASPEN (1), a computer simulator developed at the Massachusetts Institute of Technology Energy Laboratory for fossil-energy-conversion processes, uses a modular flowsheet system to simulate complex processes. Blocks are specified to represent reactors, heat exchangers, and other unit operations; the inlet and outlet streams are used to connect the blocks which establish the flowsheet. The conditions of the feed and key streams, as well as operating conditions for process units, must be given as input to the program. The ASPEN-simulation output includes a mass and energy balance over each process unit, plus the temperature, pressure, flow rate, composition, and phase of all streams.

In modeling the SNG production process on ASPEN, several modifications were made to the process operating units to accommodate limitations in ASPEN and to simplify the computational requirements.

Iterative loops were used to converge the operating conditions of a two-sided heat exchanger. The number of iterative loops was reduced by using two one-sided heat exchanger-blocks in the simulations. The heat duty to achieve the stream outlet conditions required in one heat exchanger block, was supplied to the other heat-exchanger block. Therefore, in a two-sided heat exchanger, the second-stream-outlet conditions were directly calculated from the heat duty required to obtain the desired outlet conditions of the first stream. All heat-exchanger outlet-stream temperatures were checked to ensure that no crossover of stream temperatures had occurred. A minimum 11-K (20°F) temperature difference between streams was assumed for countercurrent operation in all heat exchangers.

In simulating heat exchangers in which steam was generated from boiler feed water, a steam-generation block written by Barker (5) was used. Heat-duty information from one-sided heat exchanger blocks was given to the steam-generation block. This block calculated the amount of steam at a desired temperature and pressure that could be generated from boiler feed water of a specified temperature and pressure, if heat duties are given.

The second modification to the process flowsheet was the addition of mixer blocks which combined multiple streams of different pressure, temperature, and composition into one stream. Since most operation blocks in ASPEN accept only one feed, for which the temperature, pressure, composition, flow rate, and phase must be known, mixer blocks were inserted before all operation blocks having more than one feed.

Splitter or separator blocks were inserted to divide one stream into two substreams. Simple splitters were used to separate a stream into substreams of the same composition and pressure; separator blocks were used to simulate the process equipment necessary to remove pure carbon dioxide or pure hydrogen from streams. For example, the pressure-swing absorption unit was modeled as a separator block which produced outlet streams of different composition, pressure, and flow rate.

Initially both methanation reactors and the CO-shift reactor were modeled as adiabatic equilibrium reactors. However, the resulting simulation outlet temperature from the first methanation reactor was about 844 K (1060°F); the catalyst in the reactor begins to degenerate at approximately 755 K (900°F) (4). The first methanation reactor was modeled as adiabatic and stoichiometric for temperature control. The conversions for reactions (2) and (3) in Table 2 were constant and equal. A temperature design-specification loop was used around the reactor to converge on the conversion, resulting in an outlet temperature of 728 K (850°F). This temperature was chosen to maximize conversion in the first reactor, while giving a 27-K (50°F) safety interval between the reactor temperature and the temperature at which the catalyst loses efficiency (755 K, 900°F).

A design specification block was also used to determine the flow rate of steam (stream 5) into the carbon-monoxide-shift reactor. This block set the molar steam flow rate at three times the molar flow rate of carbon monoxide in the feed stream (stream 4) to the shift reactor (5). The CO-shift reactor and the second methanation reactor were modeled as adiabatic, equilibrium reactors.

The ASPEN block flowsheet used to simulate the SNG production process is shown in Figs. 5 and 6. A 69-kPa (10 psi) pressure drop across all heat exchangers and reactors was assumed, and the pressure of the stream from the pressure-swing absorber (stream 30) was set at 345 kPa (50 psia). No pressure drop was assumed in mixers, splitters, or flash blocks (where condensed water is separated from the gas stream). In addition, assumed stream temperatures are given in Table 3.

Due to an unresolved problem in the overall ASPEN simulation of the SNG production process, the simulation was divided into two sections. The CO-shift and PSA-unit simulation was run; the resulting product streams (streams 32 and 34) were read as input to the separate methanation unit simulation as feeds. Samples of the required data for ASPEN simulations for both the CO-shift and PSA unit, and the methanation unit are given in Appendix 10.1

5. SIMULATION RESULTS AND DISCUSSION

5.1 Comparison of ASPEN Methanation-Unit Simulation with Fluor's Design

To determine whether the ASPEN simulation of the methanation unit predicted reasonable product compositions, the simulated product (stream 69) was compared with that obtained by Fluor. The feeds and product for the ASPEN simulation and the Fluor design are shown in Table 4; the percentage of carbon monoxide and carbon dioxide converted to methane is given in Table 5 for both the ASPEN simulation and Fluor's results.

Table 3. Stream Temperatures Specified in ASPEN
Simulation of the SNG Production Process

Stream No.	Temperature	
	(K)	(°F)
3	433	320
4	589	600
9	444	340
17	400	260
22	311	100
36	333	140
37	311	100
39	333	140
40	311	100
44*	533	500
47*	533	500
53*	533	500
56	533	500
59	422	300
62	394	250
65	366	200
68	308	95

* Varied for temperature parametric study.

Table 4. Feed and Product Comparison

Component	Feed		Product	
	ASPEN kg-mole/h (lb-mole/h)	Fluor kg-mole/h (lb-mole/h)	ASPEN kg-mole/h (lb-mole/h)	Fluor kg-mole/h (lb-mole/h)
H ₂	695 (1532)	695 (1531)	75 (164.8)	15 (32)
N ₂	68 (149)	68 (149)	68 (149)	68 (149)
CO	74 (164)	75 (165)	0.7 (1.6)	0.05 (0.1)
CO ₂	123 (272)	124 (273)	28 (61)	15 (33)
CH ₄	648 (1429)	648 (1428)	846 (1865)	862 (1900)
H ₂ O	252 (556)	252 (556)	1.1 (2.5)	0.8 (1.7)
C ₂ H ₆	11 (25)	11 (24)	0.1 (0.2)	0.0 (0.0)
CH ₃ OH	6 (14)	6 (14)	0.0 (0.0)	0.0 (0.0)
Total	1877 (4141)	1879 (4140)	1019 (2244)	961 (2116)

Table 5. Percentage Conversion of Carbon Monoxide and Carbon Dioxide to Methane

	ASPEN	Fluor
% conversion* of CO	99.0	99.9
% conversion* of CO ₂	78	88

*
conversion = $\frac{\text{moles in} - \text{moles out}}{\text{moles in}}$

Although the ASPEN simulation of the methanation unit predicts lower conversion of carbon monoxide and carbon dioxide than Fluor's, the conversions agree to within 12%. For the ASPEN simulation, a molar recycle ratio of 0.25 and pressure of 9410 kPa (1365 psia) were used for the first methanation reactor; the second methanation reactor pressure was set at 9100 kPa (1320 psia). An inlet feed temperature of 533 K (500°F) was used for both reactors. No information is available on the reactor temperatures and pressures or types of reactors Fluor used in their analysis. The agreement between the Fluor and ASPEN results is sufficient to show that the ASPEN simulation models the methanation unit as well as Fluor's design, although the agreement could be improved by adjusting the reactor operating conditions.

5.2 Parametric Study of the SNG Process

The purpose of the parametric study was to determine the effect of operating conditions on product composition, thermal efficiency of the process, and outlet temperature from the second methanation reactor. Thermal efficiency is defined as the sum of the enthalpies of the product streams plus the enthalpy of steam generated divided by the sum of the enthalpies of feed streams, boiler feed water, and the steam fed to the reactors, plus the work required to run the compressors, if a 0.72 compressor efficiency is assumed (see Appendices 10.2 and 10.3). The composition of the feed streams (1, 32, and 42) are based on work done by Barker (5) on the methanol synthesis unit and are given in Table 1.

The operating conditions that were varied were: the molar ratio of steam added to the first methanation reactor to the total SNG unit feed (stream 18/streams 1, 32, and 42), the split to the CO-shift and methanation units (streams 2 and 33), the feed temperature (stream 49), and molar recycle ratio (stream 52/stream 55) of the first methanation reactor. The split between the CO-shift and methanation units is defined as the molar fraction of the purge gas (stream 1) from the methanol-synthesis unit which is fed to the CO-shift unit. The operating conditions used for the base case are given in Table 6.

Table 6. Base-Case Operating Conditions

Steam/Feed (stream 18/streams 1, 32, 42)	Split to CO-Shift Unit	Feed Temperature to First Reactor	Recycle Ratio (stream 52/stream 55)
0.19	0.4	533 K (500°F)	0.25

5.2.1 Steam-to-Feed Ratio in Methanation Reactor

Steam (stream 48) is added to the first methanation reactor to prevent carbon deposition and to absorb sensible heat so a higher conversion of carbon monoxide and carbon dioxide to methane can be obtained for a given temperature rise in the reactor.

The effect of the steam-to-feed ratio on process thermal efficiency, outlet temperature of the second reactor, conversion in the first reactor, and percentage hydrogen and carbon monoxide in the product was determined for molar steam-to-feed ratios of 0.04 and 0.19. The higher steam ratio is used in Fluor's design. The base-case conditions given in Table 6 were used for all other process conditions and the results are given in Table 7.

Table 7. Effect of Steam-to-Feed Ratio on Operating Conditions

Steam/Feed (stream 48/streams 1, 32, and 42)	Reactions (2) and (3), Conversion in First Methanation Reactor	Outlet Temperature Second Reactor	Thermal Efficiency	Product (stream 69) (mole %)	
				H ₂	CO
0.04	0.313	797 K (975°F)	0.79	6.17	0.53
0.19	0.366	744 K (880°F)	0.73	5.7	0.17

A higher steam-to-feed ratio resulted in a higher stoichiometric conversion in the first reactor because the steam absorbed some of the heat of reaction; therefore, more carbon monoxide and carbon dioxide reacted for the same temperature rise across the reactor. Accordingly, less carbon monoxide and carbon dioxide reacted in the second reactor, and this outlet temperature was lower. The temperature of the outlet stream (57) from the second reactor was higher than the catalyst can tolerate in the case where the lower steam-to-feed ratio was used. The product stream (69) contained less carbon monoxide and hydrogen when more steam was added because the additional steam changed the equilibrium conversion. The hydrogen product specification (<5 mole % hydrogen) was not met in either case; however, when the higher (0.19) steam-to-feed ratio was used, the carbon monoxide specification (<0.5 mole %) was met.

The disadvantage of adding more steam was that the thermal efficiency decreased from 0.79 to 0.73. Because lower steam-to-feed ratios resulted in higher thermal efficiencies, the other parametric studies used the lower ratio to determine whether product specifications and operating constraints could be met by varying other operating conditions.

5.2.2 Split Between CO-Shift and Methanation Units

When higher mole-fraction splits of the purge gas (stream 1) from the methanol synthesis to the CO-shift unit were used, more hydrogen was produced, more carbon monoxide reacted, and more carbon dioxide was removed in the CO-shift unit. For base-case conditions (Table 6) at all other process variables, the split was varied from 0.2 to 0.6, as shown in Table 8.

Table 8. Effect of Split on Operating Conditions

Split to CO-Shift	Reactions (2) and (3), Conversion in First Methanation Reactor	Outlet Temperature of Second Methanation Reactor	Thermal Efficiency	Product Composition (mole %)	
				H ₂	CO
0.2	0.253	809 K (996°F)	0.84	5.5	1.0
0.4	0.313	797 K (975°F)	0.79	6.17	0.53
0.5	0.358	789 K (961°F)	0.77	6.6	0.33
0.6	0.406	777 K (939°F)	0.74	7.34	0.14

When a lower split was used, there was more carbon dioxide and carbon monoxide in the methanation reactor-I feed (stream 49), which had to be converted to methane to reach equilibrium. The temperature constraint in the first reactor required that the carbon monoxide and carbon dioxide be converted to methane in the second reactor, which resulted in a higher outlet temperature from that reactor. As the split increased, the amount of hydrogen in the methanation reactor-I feed increased, and the amount of carbon monoxide decreased. For splits between 0.5 and 0.6, the concentration of carbon monoxide in the product stream met product specification. For all splits tested, there was more hydrogen than is allowable in pipeline SNG. As the split was increased, the thermal efficiency decreased because more steam was added to the CO-shift reactor and less steam was generated in the methanation unit. At base-case conditions (Table 6) for all process conditions except the split, neither the desired mole % hydrogen and carbon monoxide in the product nor the second reactor outlet temperature limit could be achieved.

5.2.3 Temperature of Feed to Methanation Unit

The temperature of the feed to the first methanation reactor (streams 44, 47, and 53) was varied from 478 to 533 K (400 to 500°F), as shown in Table 9, to determine whether product specifications and operating constraints

could be met with the other process parameters set at the base-case values given in Table 6.

Table 9. Effect of Feed Temperature to First Methanation Reactor

Temperature of Feed to First Reactor	Reactions (2) and (3), Conversion in First Methanation Reactor	Outlet Temperature of Second Methanation Reactor	Thermal Efficiency	Product Composition (mole %)	
				H ₂	CO
478 K (400°F)	0.410	752 K (894°F)	0.79	4.20	0.24
505 K (450°F)	0.362	775 K (934°F)	0.79	5.10	0.36
533 K (500°F)	0.313	797 K (975°F)	0.79	6.17	0.53

At a lower feed temperature, more carbon monoxide and carbon dioxide were converted to methane in the first reactor, reducing the stoichiometric conversion required in the second reactor to reach equilibrium. The second reactor outlet temperature was lower, so equilibrium produced a smaller fraction of hydrogen and carbon monoxide in the product stream. At a feed temperature of 478 K (400°F) the outlet temperature was less than 755 K (900°F), the maximum that can be tolerated by the catalyst (4). The hydrogen product specification was met at the feed temperature of 478 K (400°F), and the carbon monoxide product specification was met at temperatures lower than 505 K (450°F). The disadvantage of using lower feed temperature is that the residence time in the first methanation reactor increases due to slower reaction kinetics.

5.2.4 Recycle Ratio to Methanation Reactor

The molar recycle ratio (stream 52/stream 55) was varied between 0.0101 and 0.67 to determine whether product specifications could be met with a split of 0.4, a feed temperature of 533 K (500°F), and a steam-to-feed ratio of 0.04. These results are given in Table 10.

Table 10. Effect of Recycle Ratio on Operating Conditions

Recycle Ratio	Reactions (2) and (3), Conversion in First Methanation Reactor	Outlet Temperature of Second Methanation Reactor	Thermal Efficiency	Product Composition (mole %)	
				H ₂	CO
0.0101	0.301	821 K (1018°F)	0.79	7.39	0.78
0.053	0.313	813 K (1004°F)	0.79	6.98	0.686
0.25	0.313	797 K (975°F)	0.79	6.6	0.33
0.67	0.352	748 K (886°F)	0.79	4.05	0.219
2.03	1.0	-	-	-	-

Increasing the recycle ratio decreased the molar concentration of carbon monoxide and carbon dioxide in the feed to the first reactor, causing a higher conversion in the first reactor and a lower effluent temperature from the second reactor. Because the outlet temperature was lower, the mole fractions of carbon monoxide and carbon dioxide were also lower. Both product specifications were met when a recycle ratio of 0.67 was used. Increasing the recycle from 0.67 to 2.03 produced complete conversion in the first reactor and the simulation aborted. To use a high recycle ratio in the simulation, the outlet temperature of the first methanation reactor must be specified to be lower than 728 K (850°F).

Based on this parametric study, it is best to operate at recycle ratios above 0.67, with the lower steam-to-feed ratio (0.04) and the lowest split for which product specifications can be achieved.

5.3 Design of Methanation Reactor

The two methanation reactors were originally modeled as equilibrium adiabatic reactors. This model was not acceptable because the catalyst degrades at 755 K (900°F); and with the feed given in Table 4, the temperature of the effluent from the first reactor (stream 50) was higher than 811 K (1000°F). To solve this problem an adiabatic stoichiometric reactor was used to model the first methanation reactor. A simulation design specification set the outlet temperature of the first methanation reactor; and the conversion of reactions (2) and (3) in Table 2 (set equal), which would yield this outlet temperature, was calculated by an iterative method. An outlet temperature of 727 K (850°F) was chosen because this is below the temperature at which the catalyst loses efficiency by a 28 K (50°F) safety margin (4).

A reactor can operate like either the stoichiometric model or the equilibrium model, depending on the reaction kinetics and residence time. When the reactor is designed, the kinetics of the methanation reactions will be used to calculate the mean residence time needed to reach the conversion associated with the desired outlet temperature. There are many kinetic models in the literature for the production of methane from carbon monoxide and carbon dioxide (3). The necessary reactor size to give a mean residence time can be approximated by:

$$V = \tau u \quad (6)$$

where τ is the mean residence time, u the volumetric flow rate, and V the reactor volume.

The methanation reaction kinetics are fast enough so that the residence time needed to approach equilibrium corresponds to a reactor volume which can be accommodated in the methanation plant (3, 4). To design a reactor from the equilibrium model, the mean residence time needed to approach equilibrium is calculated from kinetic rate equations; the reactor size can be approximated by Eq. (6).

The difference between the design of a reactor based on the stoichiometric model and that of the equilibrium model is that the size of the stoichiometric reactor is smaller than that of the equilibrium reactor. The size difference depends on the reaction kinetics and the desired outlet temperature from the stoichiometric reactor. To improve the ASPEN simulation of the methanation unit, the reactors should be modeled with reaction kinetics to determine the mean residence time and the size of reactors. This modification requires that a user-written model for the kinetics be included in the simulation.

In the ASPEN simulation of the methanation unit, it was assumed that equilibrium is not reached in the stoichiometric reactor. Equilibrium constants were calculated from the Gibbs free energy of reaction ($\Delta G_{\text{reaction}}$). These constants were compared with the ratio of partial pressures of the products to the partial pressures of the reactants in the effluent from the equilibrium reactor (stream 57). These two constants were of the same order of magnitude. In the stoichiometric reactor the ratios of partial pressures in the effluent (stream 50) were between two and four orders of magnitude lower than the theoretical equilibrium constant, as shown in Table 11. Therefore equilibrium was not reached in the first reactor. Equilibrium conversions are compared with obtained conversions in Appendix 10.6.

Table 11. Equilibrium Constants of the Methanation-Reactor-I Effluent

Temp. of Feed	Split	Steam/ Feed	Recycle	$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$		$\text{CH}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	
				$K_{p\text{theo}}$	$K_{p\text{ASPEN}}$	$K_{p\text{theo}}$	$K_{p\text{ASPEN}}$
533 K (500°F)	0.4	0.04	0.25	1049	3.97×10^{-2}	131	6.3×10^{-2}
533 K (500°F)	0.4	0.19	0.25	1049	0.181	131	1.02
533 K (500°F)	0.67	0.04	0.25	1049	0.131	131	0.45

To further validate the simulation of the methanation unit, a manual calculation of the mass and energy balances was done to check the ASPEN model of the stoichiometric methanation reactor. The calculation gave an outlet temperature from the first reactor of 722.6 K (841°F), while the ASPEN simulation predicted 723.2 K (842°F) (see Appendix 10.5). Therefore the ASPEN simulation correctly models the stoichiometric reactor.

In methanation reactors there is the possibility of carbon formation, which could cause deactivation of the nickel catalyst and plugging of the reactor. Carbon deposition is not likely due to the reaction kinetics in reactors operating at the conditions used in the ASPEN simulations. Streeter (7) constructed a ternary phase diagram which illustrates the hydrogen-to-carbon-to-oxygen ratios for which carbon deposition is thermodynamically possible at 7102 kPa and 755 K (1030 psia, 900°F). This ternary phase diagram with the feed compositions used in the simulation is shown in Fig. 7. A sample calculation for determining this ternary ratio is shown in Appendix 10.4. Ternary phase diagrams can be constructed for different temperatures and pressures by the methods described by White *et al.* (9). Although it is thermodynamically possible to have carbon deposition, Streeter found no carbon deposition during steady-state operation using feeds with carbon-to-hydrogen-to-oxygen ratios similar to those of interest in this study. However, Streeter observed some deposition during startup operations. Hottel and Howard (4) report that carbon deposition occurs only at temperatures above 728 or 755 K (850 or 900°F). One design criterion of the ASPEN simulation was that temperatures in the reactors be below 755 K (900°F) to preclude carbon deposition.

6. MODIFIED DESIGN OF THE SNG PRODUCTION PROCESS

In the original SNG production design, the effluent from the CO-shift reactor was cooled, dried, and fed to the methanation unit where it was heated. Barker (5) proposed the design modification to save energy, shown

○ Compositions of feed to methanation reactors I and II

• Streeter data points

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AT
OAK RIDGE NATIONAL LABORATORY

CARBON DEPOSITION DIAGRAM FOR TOTAL
EQUILIBRIUM AT 755 K (900°F)
AND 6977 kPa (1015 psia) (9)

DATE
4-19-82

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FIG.
7

simplified in Fig. 8, in which effluent from the CO-shift reactor was sent directly into the methanation unit. In this design, hydrogen was removed after methanation, and no steam was added to the first methanation reactor. A detailed flow design is shown in Fig. 9.

The only difference between the methanation unit of the original and modified designs was that the modified design had an additional heat exchanger which cooled the effluent from the first reactor by preheating the feed to the CO-shift reactor.

In the modified CO-shift unit, the reactor effluent was cooled to the temperature of the feed to the first methanation reactor. The series of knockout drums with interstage coolers was eliminated, and no steam was generated from heat exchange in the coolers.

In the modified pressure-swing absorption unit, hydrogen was removed from the product stream, and the pressure of the product stream was reduced to 345 kPa (50 psia). The product-gas stream was recompressed to 7102 kPa (1030 psia) by a series of three compressors with interstage coolers.

The modified design was not successfully simulated. During one of the ASPEN calculations used in the model of the second methanation reactions, the execution aborted due to calculational problems, and the error could not be corrected.

The original motivation for considering this design modification was to save thermal energy. In the modified design, the effluent from the CO-shift reactor would not be cooled, dried, and then heated. Energy savings would be less than first thought because the gas stream exiting the PSA unit was at 344 kPa (50 psia). In the original SNG production process, only about 544 kg-mole/h (1200 lb-mole/h) was fed to the PSA unit, while 4082 to 4536 kg-mole/h (9000 - 10,000 lb-mole/h) was fed to the PSA unit in the modified design. Most of the energy that would be saved in not heating the gas feed stream in the methanation unit would be used in compressing the product stream from the PSA unit to the required pipeline pressure of 7101 kPa (1030 psia). For this reason, work on the ASPEN simulation of the modified design should not be continued.

7. CONCLUSIONS

1. The simulation of the methanation unit agrees within 12% of Fluor's estimate for product conversion.

2. The methanation unit should be optimized primarily by increasing the recycle ratio (≥ 0.67), which gives mole percentage in the product of hydrogen and carbon monoxide less than 5 and 0.5, respectively, reactor temperature control, and high process thermal efficiency (0.79).

Purge Gas from Methanol Synthesis

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

SIMPLIFIED FLOWSHEET OF
MODIFIED SNG PRODUCTION PROCESS

DATE
4-19-82

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TBS

FILE NO.
CEPS-X-352

FIG.
8

3. Product quality and temperature control can be achieved by increasing the steam-to-feed ratio from 0.04 to 0.19 or by decreasing feed temperature below 533 K (500°F). However, increasing steam usage lowers process thermal efficiency, and decreasing feed temperature lowers reaction rates.

4. A lower (50%) split to the CO-shift unit improves thermal efficiency by 6%.

5. Due to kinetic restraints, carbon formation should not occur in the methanation reactors at the operating conditions under consideration, although thermodynamically, carbon formation is possible.

8. RECOMMENDATIONS

1. Improve the simulation of the methanation reactors with a model incorporating the reactor kinetics.

2. Define the optimum operating ranges for steam-to-feed ratio, inlet temperature, and split to the CO-shift unit in the first methanation reactor.

3. Optimize the SNG production process at higher (≥ 0.67) recycle ratios.

9. ACKNOWLEDGMENT

We thank our consultants R.E. Barker, J.H. Clinton, and P.J. Johnson for the many hours they spent helping us on this project.

This appendix contains the listing for simulation of the CO-shift and PSA units, and the listing for the methanation simulation.

NEW

GLOBAL DATA

IN-UNITS ENG

HISTORY MSG-LEVEL PROPERTIES=2

RUN-CONTROL MAX-TIME= 100.

FLWSHEET

FLOW SHEET

```
BLOCK      MSSPLIT IN=1MSGAS OUT=2COSIN 33MSGAS1
           COHEAT3 IN=2COSIN OUT= 3COSF1 CQQ1
           COHEAT1 IN=3COSF1 OUT=4COSF2 CQQ2
           COMIXER1 IN=4COSF2 5COSTMIN OUT=6COSF3
           COREACT IN=6COSF3 OUT= 7COSE1 CORLIQ
           COCOOL1 IN=7COSE1 CQQ2 OUT= 8COSE2
           COCOCL2 IN=8COSE2 OUT=9COSE3 CQQ3
           COSEP1 IN=9COSE3 OUT=13COSE4 12COSEPW
           COCOOL3 IN=13COSE4 CQQ1 OUT=14COSE5
           COSEP2 IN=14COSE5 OUT=16COSE6 15COSEPW
           COCOCL4 IN=16COSE6 OUT=17COSE7 CQQ4
```

```

COSEP3 IN=17COSE7 OUT=21COSE8 20COSEPW
COCOOL5 IN=21COSE8 OUT=22COSE9
COSEP4 IN=22COSE9 OUT=24ACOS 23COSEPW
COBOIL1 IN=10COBFW1 COQ3 OUT=11COSTM1
COBOIL2 IN=18COBFW2 COQ4 OUT=19COSTM2
COMIXER2 IN=12COSEPW 15COSEPW 20COSEPW 23COSEPW &
          OUT=25COCON
SEPCO2 IN=24ACOS OUT=24BCO2 24COSOUT
SPTPSA IN=24COSOUT OUT=26SPTCCM 28SPTSEP
COMPSA IN=26SPTCCM OUT=27COMGAS COW1
SEPPSA IN=28SPTSEP OUT=29SEPH2 30SEPGAS
MIXPSO IN=30SEPGAS 31MSOGAS OUT=32PSOGAS
MIXER IN=33MSGAS1 27COMGAS OUT=34MSGAS2

```

```

*****
;
;
;
      PHYSICAL PROPERTY DATA
;
;
;
*****

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;
;
;
COMPONENTS H2 H2/N2 N2/H2O H2O/CO CO/CC2 CO2
            CH4 CH4/CH4O CH4O/C2H6 C2H6
;

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;
;
;
PROPERTIES SYSOP3 GLOBAL/SYSOP12
;
;
;
*****

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;
;
      STREAM DATA
;
;
;
*****

```

```

STREAM 1MSGAS TEMP=103. PRES=1140. &
          MOLE-FLOW=12519. V-FRAC=1.
          MOLE-FRAC H2 .30/N2 .02/ H2O 1.5D-5/CO .16/ &
                      CO2 .04 /CH4 .46 /CH4O 8.4D-3/C2H6 .01
STREAM 5COSTMIN TEMP=559. PRES=1120. &
          MOLE-FLOW=1. V-FRAC=1.
          MOLE-FRAC H2O 1.
STREAM 10COBFW1 TEMP=240. PRES=90. &
          MOLE-FLOW=1. V-FRAC=0.
          MOLE-FRAC H2O 1.
STREAM 18COBFW2 TEMP=240. PRES=40. &
          MOLE-FLOW=1. V-FRAC=0.
          MOLE-FRAC H2O 1.
STREAM 31MSOGAS TEMP=105. PRES=50. MOLE-FLOW=770.15 &
          V-FRAC=1.
          MOLE-FRAC H2 .066/N2 9.48D-3/H2O 1.9D-4/ &
                      CO .072/CO2 .162/CH4 .577/CH4O .062/ &
                      C2H6 .051

```

```

;
;
;
DEF-STREAMS HEAT COQ1 COQ2 COQ3 COQ4
DEF-STREAMS WORK COW1
;

```

```

; *****
;
;      UNIT OPERATIONS BLOCK SPECIFICATIONS
;
; *****
;
BLOCK MSSPLIT FSPLIT
      FRAC 2COSIN .4
BLOCK COHEAT3 HEATER
      PARAM TEMP=320. PRES=-10.
BLOCK COHEAT1 HEATER
      PARAM TEMP=600. PRES=-10.
BLOCK COMIXER1 MIXER
BLOCK COREACT REQUIL
      PARAM NR=1 PRES=-10. Q=0 TEST=750. NPK=1
      STOI 1 CO2 -1 O/H2 -1 C/CO 1 O/H2O 1 0
BLOCK COCOOL1 HEATER
      PARAM PRES=-10.
BLOCK COCOOL2 HEATER
      PARAM TEMP=340. PRES=-10.
BLOCK COSEP1 FLASH2
BLOCK COCOOL3 HEATER
      PARAM PRES=-10.

BLOCK COSEP2 FLASH2
BLOCK COCOOL4 HEATER
      PARAM TEMP=260. PRES=-10.
BLOCK COSEP3 FLASH2
BLOCK COCOOL5 HEATER
      PARAM TEMP=100. PRES=-10.
BLOCK COSEP4 FLASH2
BLOCK COBOIL1 USER
      DESC 'STEAM GENERATOR'
      PROPERTIES SYSOP12
      SUBROUTINE BOILER USRRFT
      PARAM NINT=100 NREAL=10 NIW=100 NW=400
      REAL 90. 0.0
BLOCK COBOIL2 USER
      DESC 'STEAM GENERATOR'
      PROPERTIES SYSOP12
      SUBROUTINE BOILER USRRFT
      PARAM NINT=100 NREAL=10 NIW=100 NW=400
      REAL 40. 0.0
BLOCK COMIXER2 MIXER
BLOCK SPTPSA FSPLIT
      MOLE-FLOW 28SPTSEP 700. 1
      DEF-KEY ID = 1 COMP=H2

```



```

BLOCK COMPSA COMPR
      PARAM TYPE=3 PRES=1140. GFLAG=1
BLOCK SEPPSA SEP2
      FLASH-SPECS 29SEPH2 PRES=1060.
      FLASH-SPECS 30SEPGAS PRES=50.
      MOLE STRM= 29SEPH2 COMP=F2 FLOW=350.
BLOCK SEPCO2 SEP2
      FRAC SUBS=MIXED STREAM=24COSOUT COMP=CO2 FRAC=.02
BLOCK MIXPSO MIXER
BLOCK MIXER MIXER

FORTRAN STMFLOW
      DEFINE F1 MOLE-FLOW STREAM=5CCSTMIN COMP=H2O
      DEFINE F2 MOLE-FLOW STREAM=4CCSF2 COMP=CO
F      F1=3*F2
      EXECUTE BEFORE COMIXER1
SIMULATE
//

```

```
//ZZZWIT JOB (15884,IC25),'BIN B--BISTLINE',TIME=2,MSGLEVEL=(0,0)
// EXEC ASPEN,USER='T.ZZZ15884',RUNID='MITWIT',USTRG=SPDA,
//   REGION.RUN=1900K,PARM.LKED='LET,MAP,SIZE=(600000,65000)',
//   REGION.LKED=670K,REGION.GC=1900K
//RUN.SYSIN DD *
NEW
```

```

:
:
: TITLE 'METHANATION SIMULATION - BY J.E. BISTLINE AND T.B. SHAFER'
: DESCRIPTION "THIS PROGRAM SIMULATES THE METHANATION
:               PROCESS FOR UPGRADING THE PURGE GAS FROM
:               METHANOL SYNTHESIS TO PIPELINE GRADE SNG."
```

```

: *****
:
:   GLOBAL DATA
:
: *****
```

```

: IN-UNITS ENG
:
: HISTORY MSG-LEVEL PROPERTIES=2
:
: RUN-CONTROL MAX-TIME=100.
:
: SIM-OPTIONS RESTART-FLAG=0
```

```

: *****
:
:   FLOWSHEET
:
: *****
```

FLOWSHEET

```

  BLOCK COMP1 IN=32PSOGAS OUT=35MOGAS1 W1
    COOL1A IN=35MOGAS1 OUT=36MOGAS2 Q1A
    COOL1B IN=36MOGAS2 OUT=37MOGAS3 Q1B
    COMP2 IN=37MOGAS3 OUT=38MOGAS4 W2
    COOL2A IN=38MOGAS4 OUT=39MOGAS5 Q2A
    COOL2B IN=39MOGAS5 OUT=40MOGAS6 Q2B
    COMP3 IN=40MOGAS6 OUT=41MOGAS7 W3
    MIXER1 IN=41MOGAS7 34MSGAS OUT=45R1FEED
```

```

  BLOCK HEAT3 IN=45R1FEED Q3 OUT=46R1FEED
    HEAT4 IN=46R1FEED OUT=47R1FEED Q4
    MIXER2 IN=47R1FEED 48STEAM 54RECY3 44NHGAS OUT=49R1FEED
    CH4RX1 IN=49R1FEED OUT=50R1FEED
```

```

BLOCK COOL5 IN=50R1EF1 Q5 OUT=51R1EF2
      SPLIT1 IN=51R1EF2 OUT=55R1EF3 52RECY1
      COOL6 IN=52RECY1 OUT=53RECY2 Q6
      COMP5 IN=53RECY2 OUT=54RECY3 W5
BLOCK COMP4 IN=42NHGAS OUT=43NHGAS1 W4
      HEAT5 IN=43NHGAS1 OUT=44NHGAS Q5

BLOCK COOL7 IN=55R1EF3 OUT=56R1EF4 Q7
      CH4RX2 IN=56R1EF4 OUT=57R2EF1 LRX2EFL
      COOL4 IN=57R2EF1 Q4 OUT=58R2EF2
      COOL8 IN=58R2EF2 OUT=59R2EF3 Q8
BLOCK KO1 IN=59R2EF3 OUT=60KO1V1 61KO1B
      COOL3 IN=60KO1V1 OUT=62KO1V2 Q3
      KO2 IN=62KO1V2 OUT=63KO2V1 64KO2B
      COOL9 IN=63KO2V1 OUT=65KO2V2 Q9
      KO3 IN=65KO2V2 OUT=66KO3V1 67KO3B
      COOL10 IN=66KO3V1 OUT=68KO3V2 Q10
      KO4 IN=68KO3V2 OUT=69PROD 70KO4B
      MIXER3 IN=61KO1B 64KO2B 67KO3B 70KO4B OUT=71BYPROD
BLOCK QMIXER IN= Q6 Q7 Q8 OUT= CTOTAL
      BFWSTEAM IN= 72BFW QTOTAL OUT= 73STEAM

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      PHYSICAL PROPERTY DATA

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```

COMPONENTS H2 H2/N2 N2/H2O H2O/CO CO/CC2 CO2
            CH4 CH4/CH4O CH4O/C2H6 C2H6

```

```

PROPERTIES SYSOP3 GLOBAL/SYSOP12

```

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*****

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```

      STREAM DATA

```

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*****

```

```

STREAM 34MSGAS TEMP=105.4 PRES=1140. MOLE-FLOW=10810. V-FRAC=1.
      MOLE-FRAC H2 .349/N2 .020/H2O 4.45E-4/CO .1170/
      CO2 2.90D-2/ CH4 .4662/CH4O 7.8D-3/C2H6 1.01D-2
STREAM 42NHGAS TEMP=105. PRES=643. MCIE-FLOW=35.0 V-FRAC=1.
      MOLE-FRAC H2 .817/N2 5.99D-4/CH4 .173/
      C2H6 8.06D-3/H2O 1.43E-3
STREAM 32PSOGAS TEMP=102. PRES=50. MCIE-FLOW=1941.22 V-FRAC=1.
      MOLE-FRAC H2 .206/N2 .020/CO .043/CO2 .067/
      CH4 .604/C2H6 .028/CH4O .029/
      H2O 1.19D-3
STREAM 54RECY3 TEMP=500 PRES=1100 MCIE-FLOW=600 V-FRAC=1
      MOLE-FRAC H2 .15/N2 .05/H2O .3/CH4 .5

```

STREAM 48 STEAM TEMP=600.59 PRES=1550. MOLE-FLOW=555.1
MOLE-FRAC H2O 1.

STREAM 72 BFW TEMP=240. PRES=550. MOLE-FLOW=1. V-FRAC=0.
MOLE-FRAC H2O 1.

STREAM Q3

STREAM-ATTR HEAT DUTY=.19E7

DEF-STREAMS HEAT Q1A Q1B Q2A Q2B Q3 Q4 Q5 Q6 Q7 Q8 Q9 Q10 QTOTAL

DEF-STREAMS WORK W1 W2 W3 W4 W5

UNIT OPERATIONS BLOCK SPECIFICATIONS

3 COMPRESSORS AND 4 COOLERS ARE USED TO INCREASE
THE PRESSURE OF THE OFF GAS FROM METHANOL SYNTHESIS
TO THE PRESSURE OF THE PURGE GAS FROM METHANOL SYNTHESIS

BLOCK COMP1 COMPR

PARAM TYPE=3 PRES=151.

BLOCK COOL1A HEATER

PARAM TEMP=140. PRES=-10.

BLOCK COOL1B HEATER

PARAM TEMP=100. PRES=-10.

BLOCK COMP2 COMPR

PARAM TYPE=3 PRES=396.

BLOCK COOL2A HEATER

PARAM TEMP=140. PRES=-10.

BLOCK COOL2B HEATER

PARAM TEMP=100. PRES=-10.

BLOCK COMP3 COMPR

PARAM TYPE=3 PRES=1140.

THE PURGE GAS AND OFF GAS FROM METHANOL SYNTHESIS
ARE MIXED

BLOCK MIXER1 MIXER

PARAM PRES=1140.

THE TEMPERATURE OF THE GAS STREAM IS INCREASED BY
EXCHANGING HEAT WITH THE EFFLUENT FROM THE FIRST
KNOCKOUT DRUM AND EFFLUENT FROM THE SECOND REACTOR

BLOCK HEAT3 HEATER
PARAM PRES=-10.

BLOCK HEAT4 HEATER
PARAM TEMP=500. PRES=-10.

THE TEMPERATURE AND PRESSURE OF THE NAPHTHA
PURGE GAS STREAM IS INCREASED TO THAT OF THE
GAS STREAM

BLOCK COMP4 COMPR
PARAM TYPE=3 PRES=1130.

BLOCK HEAT5 HEATER
PARAM TEMP=500 PRES=-10.

THE TWO GAS STREAMS ARE MIXED WITH STEAM AND
RECYCLE FROM THE FIRST REACTOR

BLOCK MIXER2 MIXER
PARAM PRES=1120.

THE METHANATION REACTION IS ADIABATIC.
THE METHANATION REACTIONS ARE

BLOCK CH4RX1 RSTOIC
PARAM PRES=-10. Q=0 TEST=600 NPK=1
STOICH 1 MIXED CO -1 / H2 -3 / CH4 1 / H2O 1
STOICH 2 MIXED CO2 -1 / H2 -4 / CH4 1 / H2O 2
CONV 2 MIXED CO2 .85
CONV 1 MIXED CO .85
BLOCK-OPTIONS HMB-RESULTS=2

THE REACTOR EFFLUENT IS COOLED BY EXCHANGING HEAT
THE NAPHTHA PURGE GAS. PART OF THIS STREAM IS
RECYCLED BACK TO THE FIRST REACTOR. THE RECYCLE
IS COOLED BY GENERATING STEAM AND IS THEN COMPRESSED.

```

BLOCK COOL5 HEATER
      PARAM PRES=-10.
BLOCK SPLIT1 SSPLIT
      FRAC MIXED 55R1EF3 .8
BLOCK COOL6 HEATER
      PARAM PRES=-10 TEMP=500
BLOCK COMP5 COMPR
      PARAM TYPE=3 PRES=1120.

```

THE REACTOR EFFLUENT IS COOLED BY
GENERATING STEAM BEFORE ENTERING THE
SECOND REACTOR

BLOCK COOL7 HEATER
PARAM TEMP=500 PRES=-10

THE SECOND REACTOR IS ADIABATIC

```
BLOCK CH4RX2 REQUIL
PARAM NR=4 PRES=1080. Q=0 TEST=600. NPK=1
STOI 1 CO -1 0/H2 -3 0/CH4 1 0/ H2O 1 0
STOI 2 CO2 -1 0/H2 -4 0/ CH4 1 0/ H2O 2 0
STOI 3 C2H6 -1 0/ H2 -1 0/CH4 2 0
STOI 4 CH4O -1 0/H2 -1 0/CH4 1 0/ H2O 1 0
```

THE REACTOR EFFLUENT IS COOLED BY EXCHANGING
HEAT WITH THE FEED GAS STREAM AND BY GENERATING STEAM

```
BLOCK COOL4 HEATER
      PARAM PRES=-10
BLOCK COOL8 HEATER
      PARAM TEMP=300 PRES=-10
```

THE HEAT GENERATED IN COOLING THE REACTOR EFFLUENTS AND RECYCLE STREAM (Q6, Q7, AND Q8) IS USED TO GENERATE STEAM (550 PSIA).

```
BLOCK QMIKER MIXER
BLOCK BFWSTEAM USER
DESC 'STEAM GENERATOR'
PROPERTIES SYSOP12
SUBROUTINE BOILER USRRPT
PARAM NINT=100 NREAL=10 NIW=100 NW=400
REAL 550.
```


10.2 Simulation Data

The flow rates and enthalpies of the streams used to calculate the thermal efficiency of the methanation-unit simulation which used Fluor's feed are tabulated in Table 13; descriptions of the streams are given in Table 12. A stream-to-feed ratio of 0.19, feed temperature of 533 K (500°F), and recycle ratio of 0.25 were used. Enthalpies are based on pure components at 298 K (77°F) and 101.3 kPa (14.7 psia).

Table 12. Description of Streams

Stream	Description
SCO ₂	feed used in Fluor's design of methanation unit
34MSGAS	feed to methanation unit from CO-shift unit
32PSOGAS	feed to methanation unit from PSA unit
42NHGAS	feed to methanation unit from naphtha hydrotreater
31MSOGAS	feed to SNG unit
1MSGAS	feed to SNG unit
48STEAM	steam feed to first methanation reactor
5COSTMIN	steam feed to CO-shift reactor
10COBFW1	boiler feed water to CO-shift unit
18COBFW2	boiler feed water to CO-shift unit
72BFW	boiler feed water to methanation unit
11COSTM1	steam generated in CO-shift unit
19COSTM2	steam generated in CO-shift unit
73STEAM	steam generated in methanation unit
24BCO ₂	CO ₂ product from CO-shift unit
29SEPH2	hydrogen product from PSA unit
69PROD	SNG product from methanation unit
COW1	compressor work in CO-shift unit
W1	compressor work in methanation unit
W2	compressor work in methanation unit
W3	compressor work in methanation unit
W4	compressor work in methanation unit
W5	compressor work in methanation unit

Table 13. Flow Rates and Enthalpies of Streams Used to Calculate Thermal Efficiency for Fluor Comparison

Stream	Flow Rate (lb-mole/h)	Enthalpy (Btu/lb-mole)
CSO2	100	-1.37×10^5
34MSGAS	3,103	-2.48×10^4
32PSOGAS	3,478	-3.21×10^4
42NHGAS	35	-5.82×10^3
48STEAM	55,511	-1.02×10^6
W1	-	6.78×10^5
W2	-	7.25×10^5
W3	-	7.36×10^5
W4	-	4.79×10^4
W5	-	7.33×10^4
72BFW	2,446	-1.20×10^5
69PROD	2,245	-3.19×10^4
73STEAM	2,447	-1.01×10^5

Conditions of each simulation run for the parametric study are listed in Table 14, and compositions of the product (stream 69) are listed in Table 15. Composition of the reactor effluent (streams 50 and 57) used to calculate equilibrium constants are given in Table 16.

Table 14. Conditions of Each Run

Run No.	Temperature of Feed to First Reactor	Split	Recycle	Steam-to-Feed Ratio
1	500	0.6	0.25	0.04
2	500	0.4	0.25	0.04
3	500	0.2	0.25	0.04
4	500	0.5	0.25	0.04
5	400	0.4	0.25	0.04
6	450	0.4	0.25	0.04
7	500	0.4	2.03	0.04
8	500	0.4	0.67	0.04
9	500	0.4	0.053	0.04
10	500	0.4	0.25	0.19
11	500	0.4	0.0101	0.04

Table 15. Product Compositions (lb-mole/h)

Run	H ₂	N ₂	H ₂ O	CO	CO ₂	CH ₄	CH ₄ O	C ₂ H ₆
1	582	251	10.8	16.1	256	7783	2.62×10^{-4}	1.58
2	537	255	11.4	46.3	582	7847	4.10×10^{-4}	2.38
3	475	257	12.1	90.8	985	7853	5.01×10^{-4}	3.14
4	578	254	11.1	28.5	380	7838	3.43×10^{-3}	1.98
5	359	255	11.3	20.4	557	7899	2.16×10^{-3}	1.88
6	443	255	11.36	31.25	570	7874	3.02×10^{-4}	2.12
7	-	-	-	-	-	-	-	-
8	346	255	11.3	18.7	552	7908	2.03×10^{-4}	1.83
9	613	255	11.5	60.2	588	7829	5.03×10^{-4}	2.56
10	493	255	11.4	14.5	594	7867	2.38×10^{-4}	1.22
11	650	255	11.5	68.7	593	7813	5.5×10^{-4}	2.66

Table 16. Composition of Reactor Effluent

	Run No. <u>2</u>	<u>2</u>	<u>10</u>	<u>8</u>
Recycle ratio	0.25	0.25	0.25	0.25
Feed Temperature (°F)	500	500	500	500
Steam/feed ratio	0.04	0.04	0.19	0.04
Split	0.4	0.4	0.4	0.67
Methanation Reactor No.	1	2	1	1
Stream No.	50	57	50	50
Reactor outlet pressure (atm)	74.8	73.5	74.8	74.8
Composition (lb-mole/h)				
H ₂	2603	537	2193	2396
N ₂	319	255	319	425
H ₂ O	1716	1728	4139	2708
CO	1075	46	980	1180
CO ₂	354	583	322	388
CH ₄	8588	7848	8714	11,790
CH ₄ O	176	4.7x10 ⁻³	176	235
C ₂ H ₆	<u>205</u>	<u>2</u>	<u>205</u>	<u>273</u>
Total	15,035	11,000	17,048	19,397

10.3 Thermal Efficiency Calculations

The thermal efficiency is defined as:

$$\eta = \frac{\Sigma \Delta H_{\text{product}} + \Delta H_{\text{steam produced}}}{\Sigma \Delta H_{\text{feed}} + \Delta H_{\text{steam inputed}} + \epsilon W_{\text{compressor}}} \quad (7)$$

A sample calculation is given below for run 2 (see Table 14). To obtain the given energies, the stream enthalpies (Btu/lb-mole) were multiplied by their respective flow rates (lb-mole/h).

Energy In			Energy Out		
Stream	ΔH : kJ/h	(Btu/h)	Stream	ΔH : kJ/h	(Btu/h)
1MSGAS	-4.0×10^8	(-3.8×10^8)	69PROD	-3.78×10^8	(-3.58×10^8)
31MSOGAS	-4.6×10^4	(-4.35×10^7)	29SEPH2	6.89×10^4	(6.53×10^4)
42NHGAS	-1.33×10^5	(-1.26×10^5)	11COSTM1	-1.62×10^8	(-1.54×10^8)
5COSTMIN	-2.58×10^8	(-2.45×10^8)	19COSTM2	-3.32×10^7	(-3.15×10^7)
48STEAM	-5.96×10^9	(-5.65×10^7)	73STEAM	-7.30×10^8	(-6.92×10^8)
10COBFW1	-1.91×10^8	(-1.81×10^8)	24BCO2	-1.61×10^8	(-1.53×10^8)
18COBFW2	-3.88×10^7	(-3.68×10^7)	Total	-1.47×10^9	(-1.39×10^9)
72BFW	-8.69×10^8	(-8.24×10^8)			
COW1	3.96×10^5	(3.75×10^5)			
W1	3.98×10^6	(3.77×10^6)			
W2	3.97×10^6	(3.76×10^6)			
W3	3.78×10^6	(3.58×10^6)			
W4	2.25×10^4	(2.13×10^4)			
W5	2.32×10^5	(2.20×10^5)			
Total	-1.86×10^9	(-1.76×10^9)			

$$\eta = \frac{\text{out}}{\text{in}} = 0.79$$

10.4 Calculation for Carbon-Deposition Analysis

A sample calculation for determining the fraction of carbon, hydrogen, and oxygen in the feed to the first reactor (stream 49) is given below for run 2 (see Table 14).

<u>Component</u>	<u>Moles</u>	<u>Moles H</u>	<u>Moles C</u>	<u>Moles O</u>
H ₂	4713	9.43x10 ³	-	-
H ₂ O	905	1.81x10 ³	-	905
CO	1564	-	1564	1564
CO ₂	514	-	514	1028
CH ₄	7938	3.18x10 ⁴	7938	-
CH ₄ O	176	7.04x10 ²	176	176
C ₂ H ₆	205	1.23x10 ³	410	-
Total		4.5x10 ⁴	1.06x10 ⁴	3.50x10 ³
Fraction		0.761	0.179	0.059

10.5 Calculation to Check First-Methanation-Reactor Model

The stoichiometric methanation-reactor mass and energy balances were checked for run 2 (Table 14). For the conversion given by the simulation, the outlet temperature from the reactor was calculated as:

$$\begin{aligned} \sum C_{p_i} M_i (T_o - T_i) + \sum C_{p_i} M_{r_i} (25 - T_i) + M_{Co,r} \Delta H_{Co,r} \\ + M_{CO_2,r} \Delta H_{CO_2,r} + \sum C_{p_i} M_{p_i} (T_o - 25) = 0 \end{aligned} \quad (8)$$

where

C_{p_i} = heat capacity of component i

M_i = mass of component i unreacted

T_o = outlet temperature

T_i = inlet temperature

$M_{r,i}$ = mass of component i reacted

$M_{p,i}$ = mass of component i produced

$\Delta H_{CO,r}$ = heat of reaction of $CO + 3H_2 \rightarrow CH_4 + H_2O$

$\Delta H_{CO_2,r}$ = heat of reaction of $CO_2 + 4H_2O \rightarrow CH_4 + 2H_2O$

First the material in the reactor effluent was summarized as shown in Table 17.

Table 17. Material in Reactor

<u>Component</u>	<u>Moles Unreacted</u>	<u>Moles Reacted</u>	<u>Moles Formed</u>
H ₂	2603	2110	-
N ₂	319	-	-
H ₂ O	906	-	810
CO	1075	489	-
CO ₂	354	161	-
CH ₄	7938	-	650
CH ₄ O	176	-	-
C ₂ H ₆	205	-	-

Heat capacities were calculated from three-term empirical equations (6) at 626 K (668°F). The heat capacities are shown in Table 18.

Table 18. Heat Capacities of Components

Component	C_p (cal/g-mol-K or Btu/lb-°F)
H ₂	7.04
N ₂	7.36
H ₂ O	8.84
CO	7.38
CO ₂	11.36
CH ₄	12.99
CH ₄ O	16.90
C ₂ H ₆	21.83

The inlet temperature to the first reactor was 533 K (500°F). The calculations used to obtain the outlet temperature are shown below:

$$\begin{aligned}
 \sum C_{p_i} M_i &= 2603(7.04) + 319(7.36) + 906(8.84) + 1075(7.38) \\
 &\quad + 354(11.36) + 7938(12.99) + 176(16.90) + 205(21.83) \\
 &= 1.51 \times 10^5 \text{ Btu/°F} \quad (9)
 \end{aligned}$$

$$\begin{aligned}
 \sum C_{p_i} M_{r_i} (25 - T_i) &= [2110(7.04) + 489(7.38) + 161(11.36)](25 - 500) \\
 &= -9.64 \times 10^6 \text{ Btu} \quad (10)
 \end{aligned}$$

$$M_{\text{CO},r} \Delta H_{\text{CO},r} = -88,632(489) = -4.33 \times 10^7 \text{ Btu} \quad (11)$$

$$M_{\text{CO}_2,r} \Delta H_{\text{CO}_2,r} = -70,901(161) = -1.14 \times 10^7 \text{ Btu} \quad (12)$$

$$\sum C_{p_i} M_{p_i} = 810(8.84) + 650(12.99) = 1.56 \times 10^4 \text{ Btu} \quad (13)$$

Substituting these numbers into Eq. (8) gives:

$$T_o = 841^\circ\text{F}$$

This is in close agreement with the ASPEN simulation result of 842°F.

10.6 Equilibrium Calculations

To determine whether equilibrium was reached in the first methanation reactor (a stoichiometric conversion reactor), the theoretical equilibrium constant was compared with the equilibrium constant calculated from the reactor-effluent composition. The calculated equilibrium constant should be one or more orders of magnitude lower than the theoretical to ensure that conversion in the reactor has not passed the equilibrium conversion. One order of magnitude was chosen as an acceptable difference since the theoretical constant and the constant calculated from the second methanation reactor (an equilibrium reactor) effluent composition were of the same order of magnitude.

The theoretical equilibrium constant was calculated using:

$$\ln K_p = - \frac{\Delta G}{RT} \quad (14)$$

The Gibbs energy of reaction ($\Delta G_{\text{reaction}}$) for the two important methanation reactions are given in Table 19.

Table 19. $\Delta G_{\text{reaction}}$ (Kcal/g-mol) for Methanation Reactions

	$\Delta G_{\text{reaction}}$	
	800 K (985°F)	725 K (850°F)
R1: $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	-5.58	-10.02
R2: $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-3.23	- 7.02

Equilibrium constants for reactor effluents were calculated from the following equations for the reactions shown in Table 19:

$$\text{R1: } \ln K_p = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} p^{-2} \quad (15)$$

$$\text{R2: } \ln K_p = \frac{[\text{CH}_4][\text{H}_2\text{O}]^2}{[\text{CO}_2][\text{H}_2]^4} p^{-2} \quad (16)$$

Data for calculating the equilibrium constant K_p from reactor-effluent composition are presented in Table 17. A sample calculation of K_p for reaction R1 in the second methanation reactor with data from run 2 is:

$$K_p = \frac{[CH_4][H_2O]}{[CO][H_2]^3} p^{-2} = \frac{(7848/11,000)(1728/11,000)}{(46/11,000)(537/11,000)^3} (73.5)^{-2}$$

$$= 42.6$$

In Table 20 theoretical equilibrium constants are compared with the calculated constants for the second methanation reactor

Table 20. Comparison of Equilibrium Constants at 800°K (975°F)

	R1	R2
$K_{p\text{theoretical}}$	33.5	7.63
$K_{p\text{ASPEN}}$ (run 7)	42.6	11.6

The theoretical equilibrium constants are of the same order of magnitude as the constants calculated from the ASPEN results for the equilibrium reactor.

The comparison between the equilibrium constant calculated from the Gibbs free energy with that calculated from the first-reactor effluent composition is shown in Table 21.

Table 21. Comparison of Equilibrium Constants at 725 K (850°F)

Run	Reactor 1		Reactor 2	
	$K_{p\text{theoretical}}$	$K_{p\text{ASPEN}}$	$K_{p\text{theoretical}}$	$K_{p\text{ASPEN}}$
2	1049	3.97×10^{-2}	131	6.3×10^{-2}
10	1049	0.181	131	1.02
8	1049	0.131	131	0.45

The ASPEN equilibrium constants are at least two orders of magnitude lower than those calculated from the Gibbs energy.

10.7 Location of Original Data

The original calculations for this project are on file at the MIT School of Chemical Engineering Practice, Bldg. 1505, ORNL.

10.8 Nomenclature

$C_{p,i}$	heat capacity of component i , cal/gmol
K_p	equilibrium constant
M_i	mass of component i unreacted, kg (lb)
$M_{p,i}$	mass of component i formed, kg (lb)
$M_{CO,r}$	mass of CO reacted, kg (lb)
$M_{CO_2,r}$	mass of CO ₂ reacted, kg (lb)
P	pressure, Pa (psia)
R	universal gas constant
T_i	inlet temperature, K
T_o	outlet temperature, K
u	flow rate, kg-mol/h (lb-mol/h)
V	volume, m ³ (ft ³)
W	compressor work, J (Btu)
ΔG	Gibbs energy, J/kg-mol (Btu/lb-mol)
ΔH	enthalpy, J/kg-mol (Btu/lb-mol)
$\Delta H_{CO,r}$	heat of reaction for $CO + 3H_2 \rightarrow CH_4 + H_2O$, J/kg-mol (Btu/lb-mol)
$\Delta H_{CO_2,r}$	heat of reaction for $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$, J/kg-mol (Btu/lb-mol)
η	thermal efficiency
$[x]$	mole fraction of x
τ	mean residence time, h

10.9 Literature References

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