

**DIRECT METHANE CONVERSION
PROCESS EVALUATIONS**

**PRESENTED AT THE INDIRECT LIQUEFACTION
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Section 1

INTRODUCTION

Methane rich gas is formed as a byproduct during coal gasification and Fischer Tropsch synthesis. Methane is also the primary constituent of both natural gas and the associated gas resulting from crude oil production. These gases have little value unless they can be moved to large scale consumers via pipeline, as liquefied gas or by other means of transportation. The conversion of methane to a transportable liquid hydrocarbon fuel would open new markets and is a goal which is being actively pursued around the world.

There are currently two commercially viable approaches for methane conversion to liquid hydrocarbons:

- o The methane to gasoline route via methanol synthesis proven in New Zealand starting in 1985.
- o The Fischer-Tropsch route proven in South Africa and in a plant in Texas. The latter was shut down in 1957 for economic reasons.

Both of these processes start with the production of synthesis gas; a high temperature, endothermic and costly operation. Much exploratory work is currently being carried out on concepts for direct conversion of methane to a liquid hydrocarbon fuel without initial methane reforming to synthesis gas. A few of these concepts, while still developmental, have reached the stage where a preliminary engineering and economic evaluation is possible.

1.1 OBJECTIVE

The objective of this study is to compare direct methane conversion technologies, using the same rigorous methods used by Bechtel in previous studies (Reference 1) for the assessment of conventional technology.

Three of the most promising of these new developments, selected in a screening study, have been subjected to evaluation. Since the key issue is how these new technologies compare with conventional technology, costs of syngas based processes from reference 1 have been adjusted to the same basis to provide this comparison.

1.2 CASES STUDIED

A brief description and block flow sketch for each of the three direct conversion cases selected in the screening study and three more conventional synthesis gas based cases, used for comparison in this study, follows:

Oxidative Coupling (Figure 1.1)

Desulfurized methane-rich gas is contacted at 1,472°F (800°C) and 55 psia with a reducible metal oxide catalyst in a circulating fluid-bed riser reactor. The catalyst is reoxidized in a separate oxidizer using air. A sketch of the reactor/oxidizer is given in Figure 1.2. Methane and other light paraffins undergo oxidative dehydrogenation with the reactor catalyst to produce free radicals and water. The radicals combine to form light olefins which are oligomerized to gasoline in a second reaction step over ZSM-5 catalyst in fixed bed reactors. Byproduct CO₂ and water are removed between the two reaction steps. Conversion in the first step is limited to 25 percent to maintain 78% selectivity, thus unconverted gases are recycled between reactors. Since the second reaction step operates at 440 psia, there is a large compression requirement and an expander on the recycle gas return recovers part of this energy. Heat recovery produces steam to supplement the expander in driving the recycle compressor. The large amount of recycle moderates the temperature risen in the second step permitting the use of fixed-bed reactors. The design is based primarily on ARCO data (Reference 2).

FIGURE 1.1
OXIDATIVE COUPLING

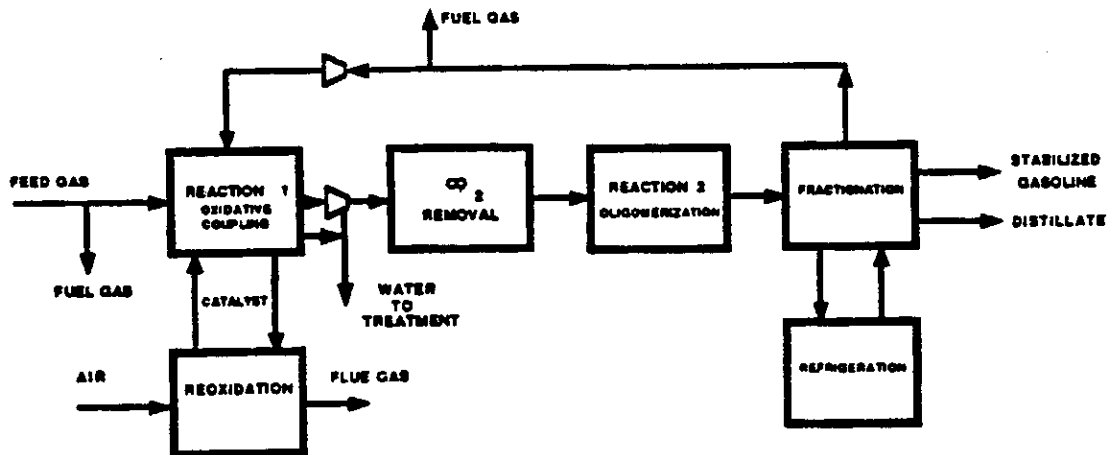
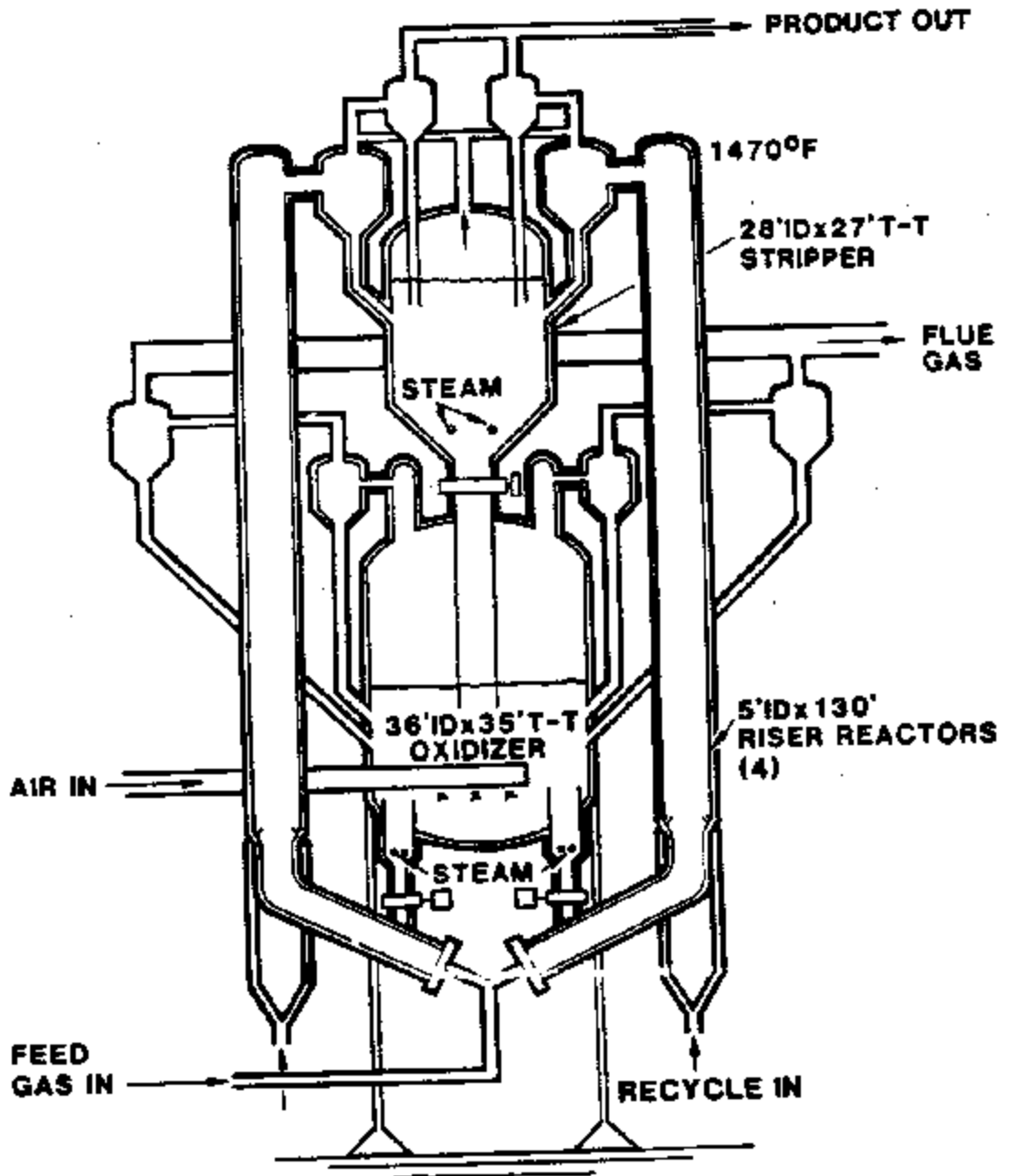


FIGURE 1.2

OXIDATIVE COUPLING REACTOR



Partial Oxidation (Figure 1.3)

At elevated pressure (60 atmospheres), methane is selectively oxidized with 99.5 percent oxygen to produce methanol and formaldehyde in a 4 to 1 ratio. A low conversion per pass (5.5 percent) is used to obtain 80% selectivity. Temperature rises from 750°F at the inlet to 930°F at the outlet. The reaction product is expanded to 45 atm. pressure and fed directly to a fixed bed ZSM-5 oligomerization reactor where gasoline and byproduct water are produced. Light components are recovered in a refrigerated lean oil system and recycled to the oxidation step. Paraffins heavier than methane react more rapidly and promote the reaction of methane. Steam is generated from the heat of reaction in a tubular reactor and used to supplement expander power and drive the recycle gas and oxygen plant compressors. Carbon dioxide removal is required since CO₂ is the major byproduct in the oxidation step. The yield versus selectivity relationship used for design is shown as Curve 2 in Figure 1.4. This curve is based primarily on the data of Gesser (Reference 3). While others have had difficulty reproducing this data, a great deal of research is underway on improving partial oxidation selectivity to methanol and the relationship used provides a reasonable target.

FIGURE 1.3
PARTIAL OXIDATION

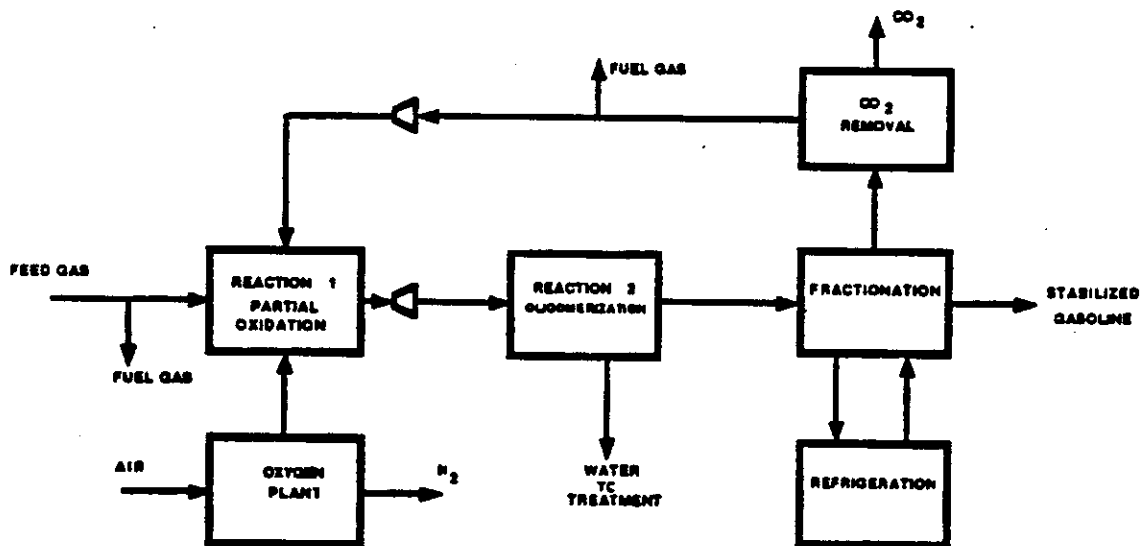
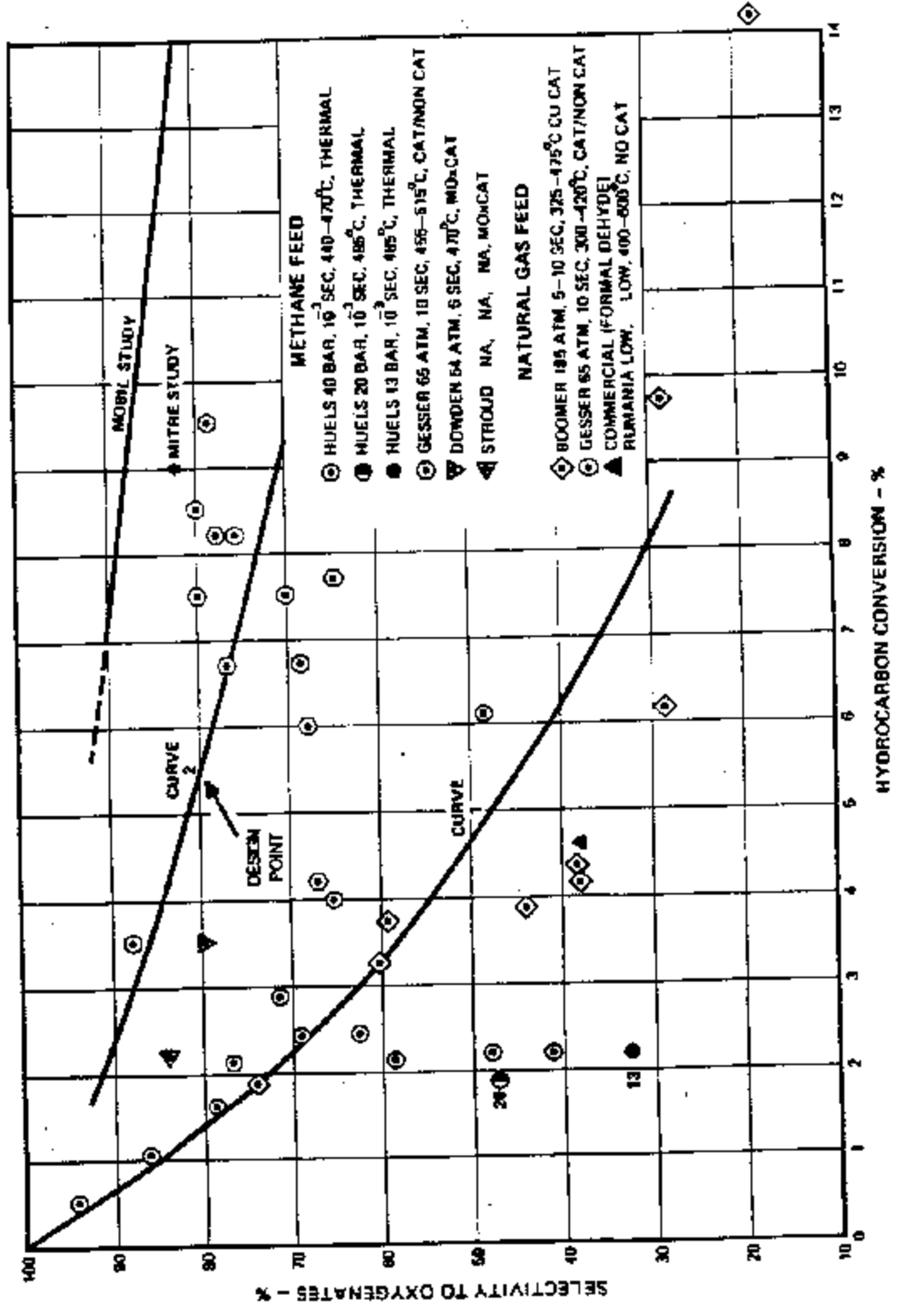


FIGURE 1.4

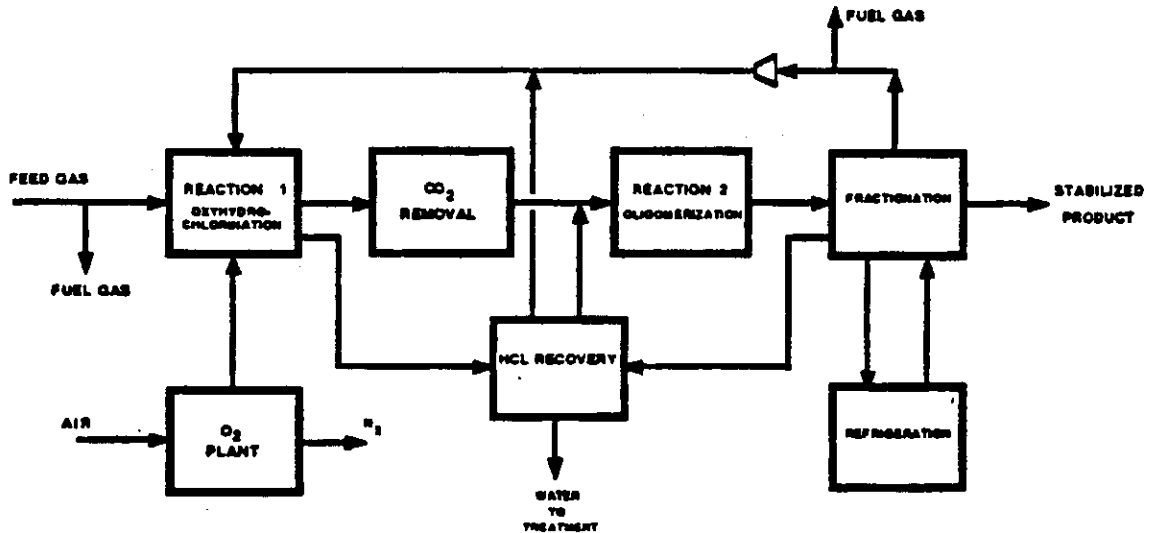
SELECTIVE PARTIAL OXIDATION
NATURAL GAS AND METHANE



Oxyhydrochlorination (Figure 1.5)

Methane-rich gas is reacted with oxygen and hydrogen chloride in a fluid bed reactor at 230 psia and 650°F over catalyst made of CuCl, KCl, and LaCl₂. The reactants are cooled and condensed. Water containing unreacted hydrogen chloride and byproduct formic acid is removed and the HCl is recovered for recycle by means of azeotropic distillation. The products of the oxyhydrochlorination step are primarily chloromethane and dichloromethane in a 4 to 1 ratio. Selectivity to CO₂ is 3%. Conversion of methane is limited to 25 percent to maintain this selectivity. Paraffins heavier than methane are assumed to give 50 percent conversion and to yield the corresponding chlorinated product. The chlorinated hydrocarbons are dried, heated and fed to a radial fixed bed reactor where they are oligomerized to gasoline. Hydrogen chloride byproduct along with unconverted methane and other light hydrocarbons are recovered by low temperature distillation and recycled to the first reactor. Heat recovery produces steam to drive the recycle and oxygen plant compressors. A purge of recycle gas is taken to remove nitrogen. Carbon dioxide is removed by an amine system prior to oligomerization. HCl is scrubbed from the purge gas so that the purge gas can be used for fuel. The HCl-water solution is sent to the azeotropic distillation section for recycle. Recovered water is treated and used for makeup. The design is based on research being conducted at the Department of Energy's Pittsburgh Energy Technology Center (PETC), Reference 4.

FIGURE 1.5
OXYHYDROCHLORINATION

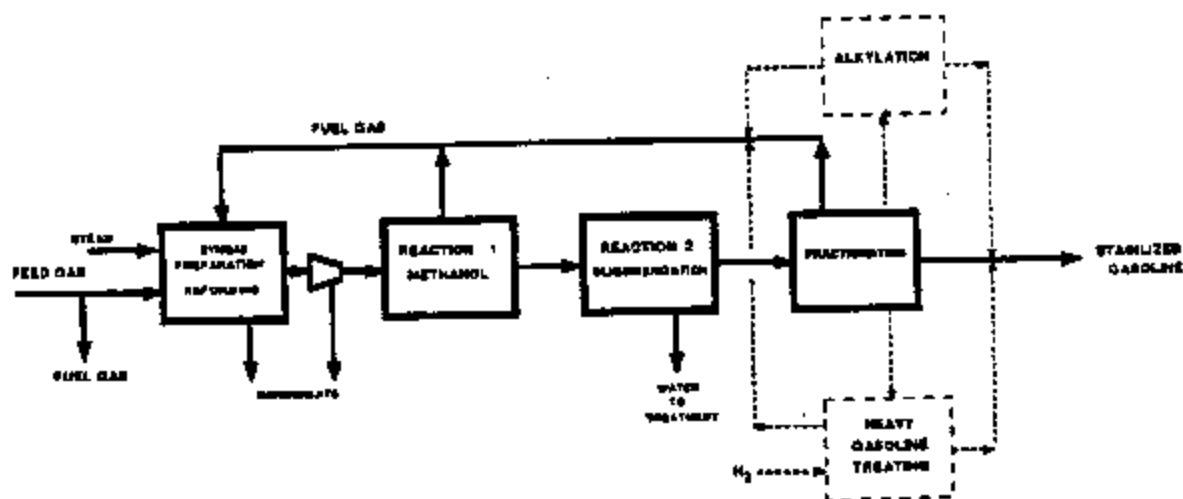


Fixed-Bed and Fluid-Bed MTG (Figure 1.6)

A conventional methanol plant, using ICI technology, produces crude methanol which is stored as a liquid. In the fixed-bed design, crude methanol is vaporized and fed to an oligomerization section consisting of a dimethylether reactor followed by five parallel fixed-bed reactors containing ZSM-5 catalyst. Outlet conditions are 775 °F and 260 psia. Reactor effluent gas from the product separator is recycled for temperature control. The methanol is completely converted to hydrocarbon product and a byproduct water stream containing about 2500 ppm of oxygenates. The water is treated and reused for cooling tower makeup. The hydrocarbons are recovered in a fractionation section where gasoline recovery is approximately 86% by weight. The remainder of the hydrocarbon product is used as fuel gas, supplementing the hydrogen rich purge gas from methanol synthesis. The reactors are periodically cycled out of service for regeneration. The overall process is that described in Reference 4 except that Heavy Gasoline treatment (for durence control) is omitted.

The fluid-bed scheme also starts with conventional crude methanol synthesis, but uses a single fluid-bed MTG reactor with internal steam generation coils for the second step. The reactor operates at 55 psia and 765 °F. Since independent heat removal is provided, the large recycle gas requirement of the fixed-bed system is eliminated. This removes a considerable amount of costly equipment. The yield of C3 and C4 components is higher than in the fixed-bed case. This results in larger fractionators and the addition of a gasoline alkylation unit, but overall gasoline recovery increases to 88 Wt% and product quality increases about two octane numbers to 94-95 research clear. A further description of the fluid bed process may be found in Reference 6.

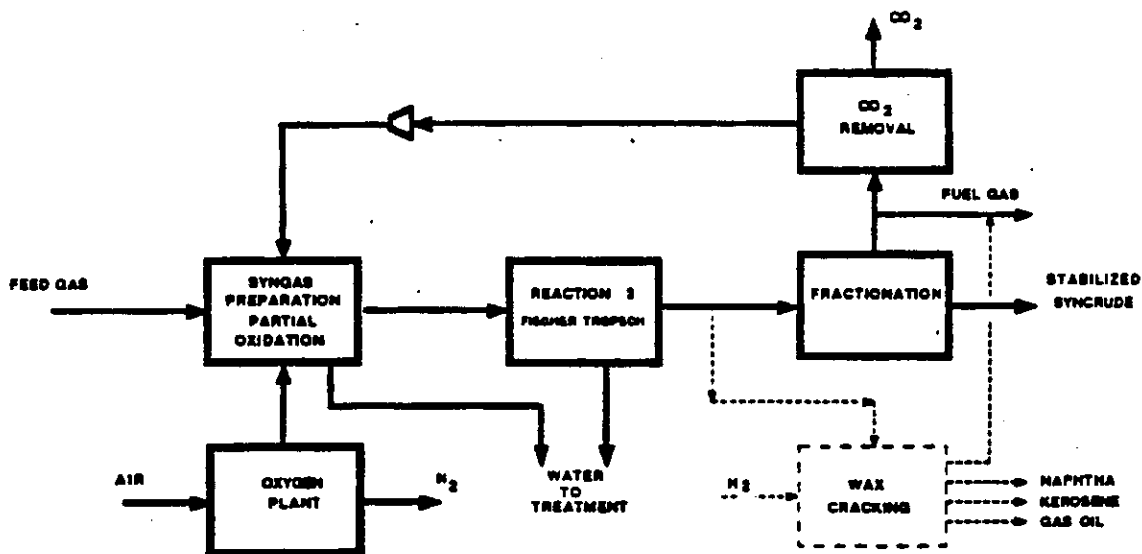
FIGURE 1.6
METHANOL TO GASOLINE



Fischer-Tropsch (Figure 1.7)

Synthesis gas is produced in a non-catalytic partial oxidation (POX) gasifier operating at 2600 °F and pressure sufficient that compression of synthesis gas is not required. After heat recovery and water removal, synthesis gas is admitted directly to the Fischer-Tropsch synthesis loop. Fourteen tubular fixed-bed reactors are used with steam generation in the shell. These are patterned after the ARGE reactors at SASOL (South Africa) but have 3.3 times the capacity. Conditions are 400 °F and 250 psig. CO conversion per pass is 60%, with an ultimate conversion of 89%. Selectivity to C5 and heavier is 84% and the Schulz-Flory parameter is 0.9. A stabilized waxy syncrude is produced for shipment. Wax cracking, shown as optional in the diagram, has not been included in this study. Excess tail gas from the fractionation section, over and above that required for fuel balance, is recycled back to the POX converter. CO₂ Removal on the recycle stream prevents buildup of CO₂ in the system. Conditions and yields are based on information provided by Gulf-Badger (7). Similar data have also been given by Shell (8).

FIGURE 1.7
FISCHER TROPSCH VIA POX



1.3 STUDY BASIS

1.3.1 Technical Parameters

The basis for comparison is a self-sufficient grass-roots facility producing 14,500 BPSD of a stabilized hydrocarbon product loaded onto tankers for shipment. The feed gas is a typical high methane gas containing sufficient sulfur to require removal by zinc oxide beds if a steam reformer were used. The gas contains minor quantities of CO₂ and N₂. Table 1.1 summarizes feed gas composition and conditions. The composition is typical of a lean natural gas. The primary difference if this were byproduct gas from coal gasification or Fischer Tropsch would be the presence of some light olefins. Natural gas was selected as feed gas for this study since it is easy to define in terms of composition and cost.

The plants are, in each case, self-sufficient in power. Since all of the processes under consideration generate substantial quantities of steam from byproduct heat, the plants use high pressure steam for the turbine drivers. For reliability, a gas turbine drive is used for the backup electric power generator. In general, compressors are not spared but pumps are. The primary cooling medium is cooling water with an inlet temperature of 85°F and an average outlet temperature of 120°F. The only materials entering the plant are feed gas, raw cooling water of river water quality, air and the catalysts and chemicals required to operate the plant. Table 1.2 summarizes design parameters, including utilities.

Offsites provided include raw water treating and condensate polishing, waste water treatment, cooling water system, steam boiler and power plant, relief and blowdown, air supply, nitrogen supply, interconnecting piping, electrical distribution, buildings and product storage. No intermediate storage is provided, but the facilities include 30 days final product storage and a marine terminal for shipping out the product and receiving supplies. A natural harbor is assumed with no particular dredging or siting problems.

In each case studied, conversion must be limited in the first step in order to obtain good selectivity. The final step is oligomerization to gasoline over ZSM-5 catalyst. The gasoline is stabilized and the lighter components are recirculated back to the first step reactor or purged to the fuel gas system. The gasoline will be blended into a large gasoline pool so heavy gasoline treatment for durene removal is not required. The product in each case is an excellent gasoline with a clear research octane of 92-100. Any distillate produced will also be of excellent quality.

The oligomerization step is modeled on known ZSM-5 technology but differs in certain important respects:

- o In the case of oxidative coupling the olefin content of the feed to oligomerization is predominantly ethylene. Oligomerization of C₃ and higher olefins to gasoline and distillates is standard MOGD¹ technology, but ethylene is known to be more difficult to react. Yields and conditions are inferred from both MOGD and methanol to gasoline (MTG) experience and the product is expected to resemble olefinic MOGD gasoline plus a small quantity of distillate.

¹Mobil Olefins to Gasoline and Distillate

- o In the oxyhydrochlorination case, the feed to oligomerization is a 4:1 mixture of monochloro and dichloromethane. Preliminary PETC data indicates that such a mixture can be oligomerized over ZSM-5 without undue carbon deposition but the stoichiometry is such that production of light gases and paraffins is suppressed, favoring aromatics production. MTG fixed bed yields were, therefore, adjusted to achieve carbon and hydrogen balances. This resulted in a reduction by a factor of 0.4 in the C₄ minus yields and a denser, more aromatic gasoline product.
- o A very similar situation exists in the partial oxidation case where the feed consists of methanol and formaldehyde in a 4:1 ratio. The same adjustment to MTG yields was applied to account for the deficiency of hydrogen relative to carbon in the feed. The similarity between this case and the oligomerization of chloromethanes was noted by Kuo (Reference 9, page V-4). No data, however, are available to support the adjustment.
- o In all three cases the feed to the oligomerization step is quite dilute in the active components due to the presence of unconverted methane from the first step. In actuality, however, the concentration of reacting species is not too different from fixed bed MTG where the practice is to use an internal recycle loop for the control of temperature rise. It is assumed that concentration effects can be accounted for by maintaining similar partial pressures. Space velocity has been assumed to be the same as Fixed Bed MTG on a carbon atom basis (i.e., 0.05 atoms C/hr/unit weight of catalyst).

Since selectivity, conversion and space velocity are generally not well-defined in these processes, an attempt has been made to provide realistic estimates which err, if anything, in being favorable to the process under evaluation. Key assumptions are identified as a guide to future researchers and, in particular, the effect of improving the selectivity-conversion relationship is reviewed in a semi quantitative manner.

1.3.2 Cost Parameters

While each facility is self-sufficient, as would be expected in a remote location, the cost estimates assume on-site construction at a Gulf Coast, U.S. location. Gulf Coast construction is familiar to cost estimators everywhere, most of whom have developed location factors for other sites around the world using this as a standard. In many areas of the world, wage rates, productivity, shipping and other factors cancel out to give location factors close to 1.0. Typically, the range is between 0.6 and 2.0. In certain high cost areas such as Alaska, creative construction methods, such as barge mounting and modularization, can be used to reduce the location factor.

Capital costs presented in this report are mid-1988 costs for the main process plants, offsites and support facilities. No escalation beyond mid-1988 is included. The infrastructure to support the facility is assumed to exist, though this may not always be the case in reality. The cost of production and transport of feed gas and water are built into the delivery price used for these materials.

Table 1.1

DIRECT METHANE CONVERSION PROCESS EVALUATIONS

FEED GAS

Feed Gas Composition	
CH ₄ - Mol %	95.5
C ₂ H ₆	2
C ₃ H ₈	1
N ₂	0.5
CO ₂	1
LHV - Btu/SCF	923.7
HHV - Btu/SCF	1024.8
H ₂ S - ppmv	30
Conditions @ B/L	
Pressure - psia	460
Temperature - °F	80

Table 1.2

DIRECT METHANE CONVERSION PROCESS EVALUATIONS

DESIGN BASIS SUMMARY

Production - BPSD	14,500
Specifications	
Volatility	Stabilized 10# RVP
Durene Removal	Not Required
Byproduct Disposition	Fuel Gas, Recycle or Waste Disposal
Utilities Basis	
Water Source	River Water
Cooling Medium (Primary)	Cooling Water
Temp. in - °F	85
Max. Temp. out - °F	120
Steam System	
Water Quality	Demineralized and Polished
Pressure Levels	As dictated by the process
Condenser Pressure - "Hg	3
Drivers	Steam with GT Backup for Power
Blowdowns	Effluent Disposal
Capital Cost Basis	
Location Factors	U.S. Gulf Coast
Construction	Stick Built (On site construction)
Timing	2nd Quarter 1988
Exclusions	No Infrastructure Cost, w/o Escalation, w/o Sales Tax

Process plant costs are based on major equipment definition. Bulk materials (piping, instrumentation, etc.) and labor requirements are factored from major equipment costs using Bechtel historical records. An \$18 per manhour wage rate is used, corresponding to Gulf Coast union agreements. Combining major equipment, bulk materials and labor gives the direct field cost for these plants.

Direct costs for standard process plants (such as oxygen) and for offsite plants are estimated from historical records of cost versus capacity and/or other definition provided. Offsite plants for which capacities are identified include:

- o Raw water treatment
- o Demineralization
- o Cooling water circulation
- o Electric power generation and distribution
- o Steam generation (boiler plant)
- o Product storage

Other offsites are prorated directly based on the relative cost of the process facilities unless an obvious reason exists why this procedure should be modified.

Indirect construction costs include such items as the field office, construction equipment, tools and construction supplies and are normally factored from the direct labor cost. An allowance of 10% is then made for the contractor's home office engineering costs and fee. The total thus arrived at is the total plant cost, exclusive of owner's cost and a contingency allowance. This is sometimes referred to as the "contractor's cost."

Owner's costs include items such as license fees/royalties, spare parts inventory, organization and startup costs, the owner's engineering costs, working capital, allowance for funds during construction and land costs. These costs can vary between 10 and 30 percent of the total plant cost. For this study, owner's costs have been estimated using factors given in Table 1.3 and average out at about 10% of the total plant cost.

A contingency allowance has been applied to the total investment. This varies between cases, as discussed later. It should be emphasized that the plant costs in this study do not necessarily cover all of the cost factors that could be encountered in a given installation at a specific site. They are aimed primarily at providing a realistic comparison between processes and should be quite adequate for that purpose.

Table 1.3

BASIS FOR OWNER'S COSTS

License Fees and Royalties	at	1% of Plant Cost
Spare Parts Inventory	at	3 months of Maintenance Materials
Organization and Startup Costs	at	3 months fixed O&M Costs 3 months variable costs excl. gas 1 month feed gas 1% of Plant Cost
Owner's Management Cost	at	10% of Contractors Home Office Cost
Working Capital	at	3 months of Labor Costs 2 months of Other Consumables Contingency of 25% on above 2 items 30 days Product Storage @ \$40/Bbl
Land Costs - 200 acres	at	\$100 per acre

No allowance has been made for interest on funds required during construction (AFDC). This is built into the capital recovery factor in the estimation of production cost.

Section 2

SUMMARY OF RESULTS

2.0 The primary conclusion from this study is that direct methane conversion technology has the potential for a significant economic breakthrough provided improvements in selectivity and conversion are achieved. The direct conversion technologies considered in this study have yet to achieve this potential. The best of the three (oxyhydrochlorination) is competitive with synthesis gas based processing only when no differential contingency allowance is made.

Potential improvements in each of the cases have been identified and the ultimate potential of direct conversion technology has been examined by looking at a process with ideal selectivity and improved conversion. It is shown that breakthrough economics (i.e. competitive with gasoline from \$20/barrel crude oil) can be achieved if good selectivity can be achieved in a relatively uncomplicated process environment.

2.1 COMPARATIVE ECONOMICS (INCLUDING MTG AND F-T)

2.1.1 Capital Cost Comparison

Estimates of plant cost and total investment for the three direct conversion technologies, in a plant producing 14,500 BPSD of liquid hydrocarbon product, are summarized in Table 2.1, (2nd Q, 1988 basis). The breakdown, at the direct cost level, between the process plants and the offsite facilities is shown, along with provisions for construction distributables, home office engineering, owner's costs and a contingency allowance. Previous Bechtel studies (1) of related synthesis gas based technologies have been adjusted to the basis for the present study and are shown for comparison. Oxyhydrochlorination is clearly the best of the direct conversion technologies, despite the need for special materials of construction. Comparing results without the addition of a contingency allowance, Oxidative Coupling is competitive with Fixed-Bed Methanol-to-Gasoline (MTG); Oxyhydrochlorination, with Fluid-Bed MTG. Adding in a reasonable contingency, none of the new direct conversion technologies shows any significant advantage.

A more detailed breakdown of the relative cost percentages accounted for by each process plant is depicted in the bar chart, Figure 2.1. This chart is useful in showing that while the expensive synthesis gas preparation step has been eliminated, it has been replaced by increases in the cost of the two main reaction steps and, in several cases, by the addition of oxygen plants. The refrigeration plants, shown for all the direct conversion cases, are required by the low conversions in these processes and the large amount of methane that must be recovered and recycled.

A similar breakdown for the offsite plants is given in Figure 2.2. Costing of the utility plants is based on the utility requirements listed in Table 2.2.

Table 2.1
CAPITAL COST COMPARISON
GAS TO LIQUID PROCESSES
SMH - Mid 1988
14500 BPSD

	Oxidative Coupling	Partial Oxidation	Oxyhydro- chlorin ation	Fixed- Bed MTG	Fluid- Bed MTG	Fischer- Tropsch (POX)
Direct Costs						
Process Plants	273.2	346.9	218.4	261.1	220.5	240.0
Offsites	208.2	273.5	204.1	208.3	203.6	216.9
Total Direct Costs	481.4	620.4	422.4	469.4	424.1	456.9
Distributable Costs	77.0	82.7	58.0	89.2	81.4	78.3
Home Office Costs	55.8	70.3	48.0	55.9	50.6	53.5
Total Plant Cost	614.2	773.4	528.4	614.4	556.1	588.7
Catalyst and Chemicals	3.9	2.2	4.5	10.6	10.8	4.2
Owner's Costs	65.4	68.4	63.3	57.6	54.6	53.9
Total w/o Contingency	683.5	844.0	596.1	682.6	621.4	646.8
Contingency	136.7	168.8	119.2	0.0	31.1	64.7
Total Investment	820.2	1012.8	715.4	682.6	652.5	711.5
% Contingency	20	20	20	0	5	10

Table 2.2
UTILITY REQUIREMENTS SUMMARY
GAS TO LIQUIDS PROCESSES
14500 BPSD

	Oxidative Coupling	Partial Oxidation	Oxyhydro- chlorin ation	Fixed- Bed MTG	Fluid- Bed MTG	Fischer- Tropsch (POX)
Electric Power - KW						
Normal	6170	19000	11814	7032	7413	5150
Connected	12000	25000	18000	13000	13300	12000
Cooling Requirements						
Duty - MMbtu/Hr	2400	3475	2292	2269	2069	2707
CW Flow - gpm	220650	328700	187600	181500	165500	237000
Delta T - Deg F	21.8	21.1	24.4	25.0	25.0	22.8
Water Reqts - gpm						
Raw Water	6425	7851	5793	5350	5410	6388
Deminerlizer Makeup	664	175	99	766	841	1445
Steam Production - MLb/Hr						
Byproduct Steam	1257	1892	1199	1268	1143	2502
Auxiliary Steam	140	272	376	0	0	70
Boiler Duty -MMbtu/Hr Abs	600	1000	650	120	120	550
Effl to Treatment - gpm	(549)	902	575	672	653	524
Fuel Gas - MMbtu/Hr - LHV						
Requirements	358	1027	861	2930	2860	248
Production	259	662	682	2486	2648	248
Feed to Fuel	97	365	178	453	212	0
Feed Gas - MMbtu/Hr - LHV	5315	6257	5213	5113	5001	5390
Oxygen - TPD	air 4970	5626	3236	0	0	4907

() indicates effluent does not require biotreatment

PROCESS PLANT COST BREAKDOWN

GAS TO LIQUID HYDROCARBON PROCESSES

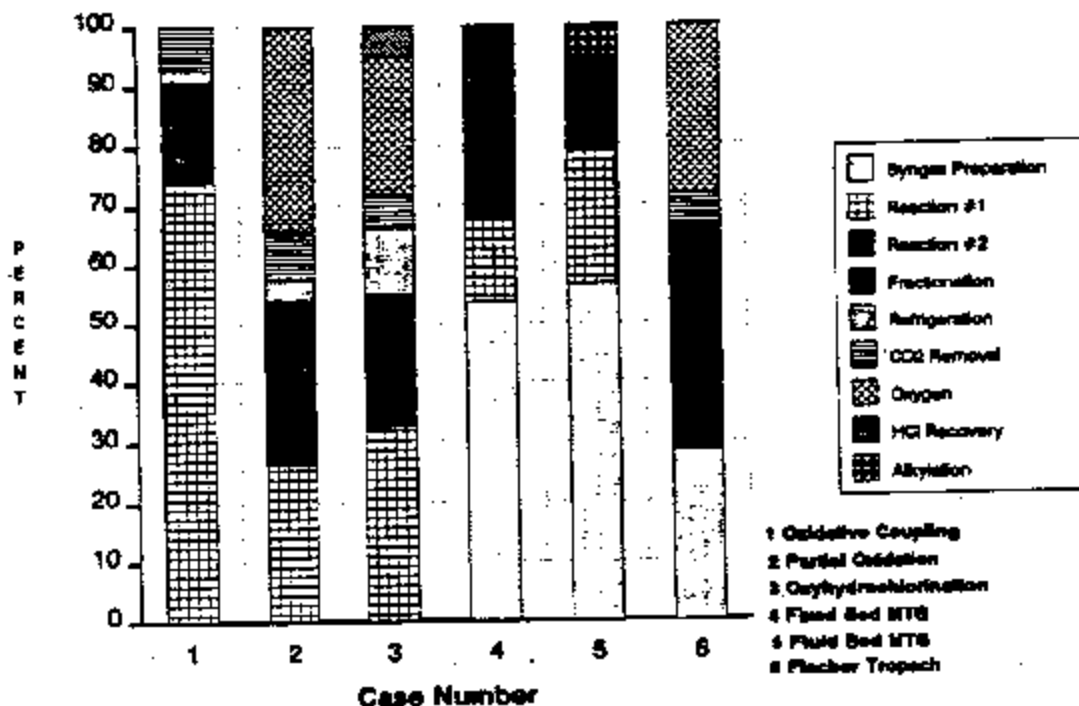


Figure 2.1

OFFSITES COST BREAKDOWN

GAS TO LIQUID HYDROCARBON PROCESSES

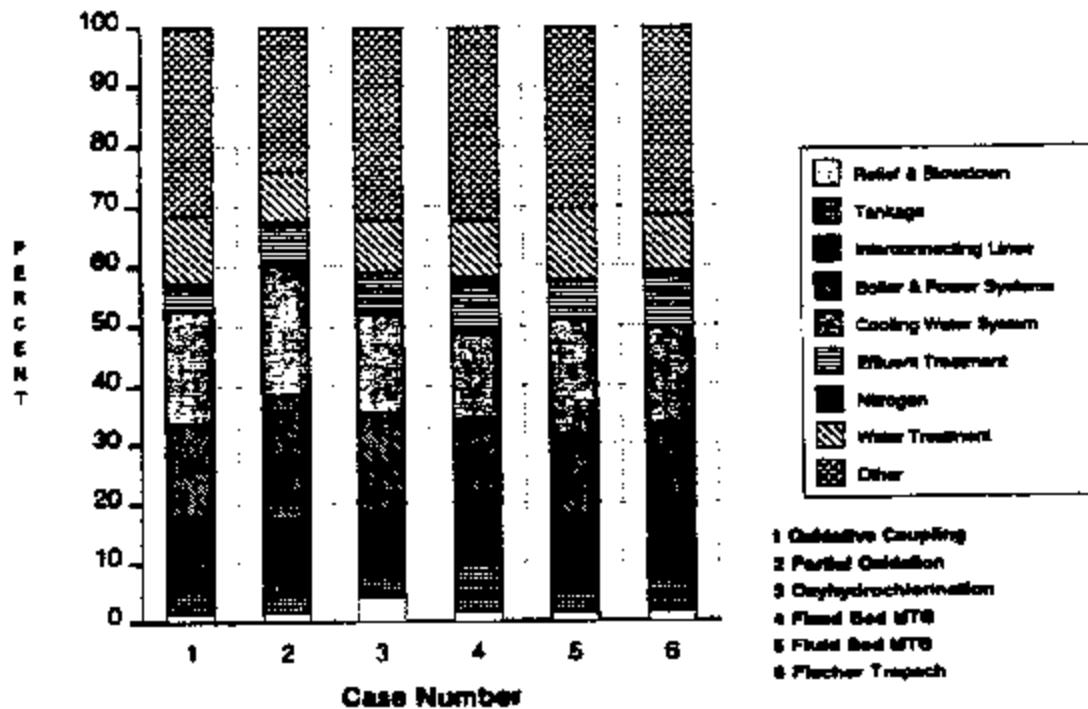


Figure 2.2

The contingency allowances shown in Table 2.1 are intended to account for engineering uncertainties and lack of complete definition from the process side. This is somewhat different than the usual application of a contingency allowance by a cost engineer, which would also include site factors and procurement factors. Any design which is costed from a process flow diagram and equipment list is likely to suffer from a lack of complete definition leading to an underestimation of the actual cost. In any brand new technology this effect may be exaggerated. (There are also possibilities for optimization of both process plants and utilities, but generally the negative factors prevail). Unfortunately, the contingency allowance can be so large as to mask possible improvements, so the economic comparisons in this study are made both with and without contingency.

2.1.2 Operating Cost Comparison

Operating costs for the three direct conversion technologies and the three reference synthesis gas based technologies are compared in Tables 2.3 and 2.3A. (The former does not include the capital cost contingency, the latter does.) The primary differences identified are in the variable operating costs and in maintenance. Labor and administrative costs for these cases are judged to be about equal since the degree of complexity and number of plants are roughly equivalent. Total staffing is 245 persons and the wage rate averages out at \$20.80 per hour.

Differences have been identified in the percentage applied to the capital cost in estimating annual maintenance cost. Oxyhydrochlorination is penalized because of the corrosive conditions and Oxidative Coupling because of the elevated temperature. Total annual maintenance as a percentage of plant cost is as follows:

Oxidative Coupling	4%
Partial Oxidation	3.5%
Oxyhydrochlorination	5%
Synthesis Gas Based Processes	3%

The maintenance labor component has been kept constant with the difference being applied to maintenance material and subcontract maintenance costs (Maint Matl + S/C in Tables 2.3 and 2.3A).

The important variable cost components are the cost of catalyst and chemicals and the cost of the feed gas. No credit is given for byproduct nitrogen produced (in excess of internal demand) since the facility is considered to be remote from any market for nitrogen.

Table 2.3
OPERATING COST SUMMARY
GAS TO LIQUIDS PROCESSING
\$MM/yr

	W/O Contingency					
	Oxidative Coupling	Partial Oxidation	Oxyhydro- chlorin ation	Fixed- Bed MTG	Fluid- Bed MTG	Fischer- Tropsch (POX)
Operating Costs Excluding Cost of Gas						
Fixed Costs						
Operating Labor	2.91	2.91	2.91	2.91	2.91	2.91
Maintenance Labor	5.19	5.19	5.19	5.19	5.19	5.19
Maint Matl + S/C	19.38	21.88	21.23	13.24	11.49	12.47
Administrative	2.50	2.50	2.50	2.50	2.50	2.50
Total Fixed Costs	29.98	32.49	31.84	23.85	22.10	23.08
Variable Costs						
Catalyst & Chemicals	15.76	7.94	13.83	8.82	9.00	4.23
Raw Water	0.12	0.15	0.11	0.10	0.10	0.12
Total Variable Costs	15.88	8.09	13.94	8.92	9.10	4.35
Total Cost excl Gas	45.86	40.57	45.77	32.77	31.20	27.43
Gas @ \$0.50/MM Btu	23.67	28.96	23.59	24.34	22.80	23.57
Total Operating Cost	69.54	69.53	69.36	57.11	54.00	51.00

Table 2.3A
OPERATING COST SUMMARY
GAS TO LIQUIDS PROCESSING
\$MM/yr

	With Contingency					
	Oxidative Coupling	Partial Oxidation	Oxyhydro- chlorin ation	Fixed- Bed MTG	Fluid- Bed MTG	Fischer- Tropsch (POX)
Operating Costs Excluding Cost of Gas						
Fixed Costs						
Operating Labor	2.91	2.91	2.91	2.91	2.91	2.91
Maintenance Labor	5.19	5.19	5.19	5.19	5.19	5.19
Maint Matl + S/C	24.29	27.29	26.51	13.24	12.32	14.24
Administrative	2.50	2.50	2.50	2.50	2.50	2.50
Total Fixed Costs	34.90	37.90	37.12	23.85	22.93	24.84
Variable Costs						
Catalyst & Chemicals	15.76	7.94	13.83	8.82	9.00	4.23
Raw Water	0.12	0.15	0.11	0.10	0.10	0.12
Total Variable Costs	15.88	8.09	13.94	8.92	9.10	4.35
Total Cost excl Gas	50.78	45.99	51.06	32.77	32.03	29.19
Gas @ \$0.50/MM Btu	23.67	28.96	23.59	24.34	22.80	23.57
Total Operating Cost	74.45	74.95	74.65	57.11	54.83	52.77

2.1.3 Production Cost vs. Cost of Gas

In estimating production costs, the annual capital recovery factor is taken at 20% on the total investment. It has been found that this corresponds to a 12% internal rate of return on a 20 year project life, with equity financing, without inflation and using U.S. tax law. Investment is distributed over a three year period prior to the start of operation and allowance is made for operation at 50 % of design capacity for the first 6 months. At a 25/75 debt to equity ratio and 10% interest on debt, the corresponding internal rate of return is 15%. Production cost (in \$/bbl) is the sum of the annual operating and capital recovery costs divided by the annual production in barrels.

Production costs are shown as a function of gas cost in \$/MMBtu (HHV) in Figures 2.3 (w/o contingency) and 2.3A (with contingency). In either case, the direct conversion cases fall above the best of the conventional synthesis gas cases (Fluid-Bed MTG) and, in the order of increasing cost, rank as follows:

- o Oxyhydrochlorination
- o Oxidative Coupling
- o Partial Oxidation

When the contingency allowance is removed, Oxyhydrochlorination compares favorably with Fixed-Bed MTG.

The slope of the lines in Figures 2.3 and 2.3A is an indication of gas consumption per unit of production, in other words the thermal efficiency. The intercept at zero gas cost (extrapolated) is composed of two contributions; that due to capital recovery and that due to operating costs exclusive of gas cost. These are summarized below for each of the six cases shown in Figure 2.3A:

	<u>\$/Bbl Production Cost at Zero Gas Cost</u>		
	<u>With Contingency</u>		<u>Total</u>
	<u>Operating Cost</u>	<u>Capital Recovery</u>	
Partial Oxidation	9.65	42.53	52.18
Oxidative Coupling	10.66	34.44	45.10
Oxyhydrochlorination	10.72	30.04	40.76
Fischer-Tropsch	6.13	29.87	36.00
Fixed-Bed MTG	6.88	28.66	35.54
Fluid-Bed MTG	6.72	27.40	34.12

The strong influence of capital cost recovery is apparent in these numbers, but the maintenance cost allowance is also evident in the increased operating cost for the three direct conversion processes..

Some significant differences are expected in the quality of the hydrocarbon product. The Fischer-Tropsch product, for example, has a broad range molecular weight distribution and might properly be called a synthetic crude. The heavier cuts are amenable to hydrocracking, producing a good diesel fraction, but the gasoline is paraffinic and of low octane. The Fixed-Bed MTG process produces an excellent gasoline, 92 - 93 RON unleaded. The Fluid-Bed product is several octane numbers higher.

PRODUCTION COST COMPARISON
GAS TO LIQUID HYDROCARBON PROCESSES

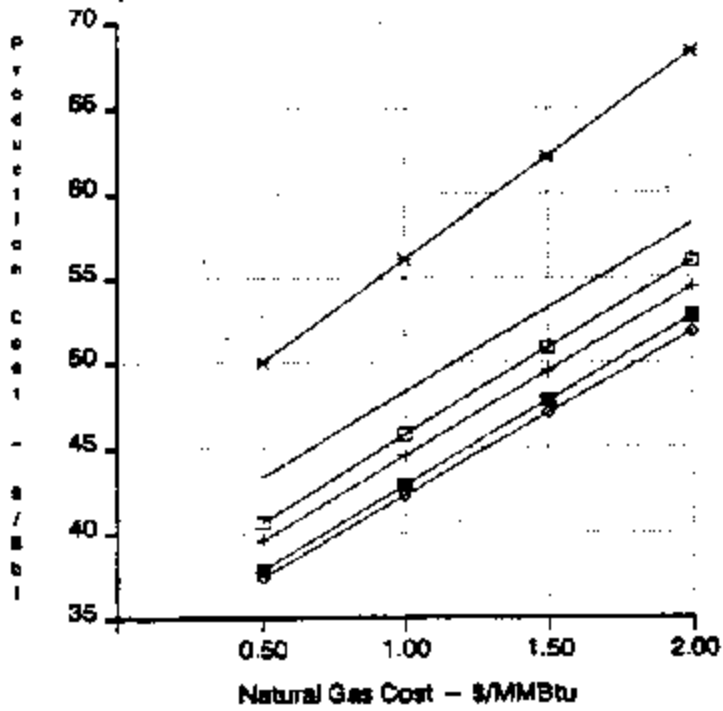
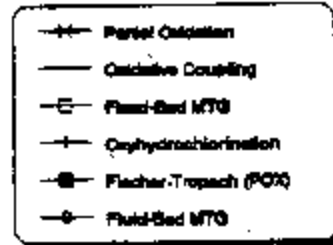


Figure 2.3



W/O Contingency

PRODUCTION COST COMPARISON
GAS TO LIQUID HYDROCARBON PROCESSES

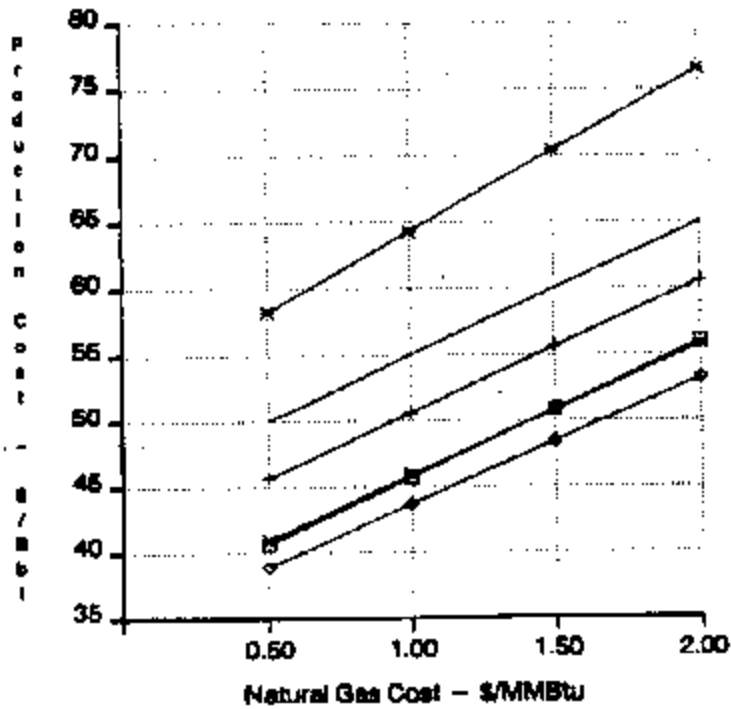
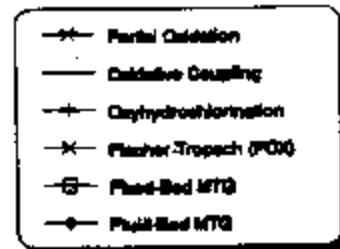


Figure 2.3A



With Contingency

The exact nature of the product produced by the direct conversion processes is unknown but the quality is expected to be good. The Oxidative Coupling process (using olefin oligomerization), should produce a mixture of good quality gasoline and diesel. Since the feed is predominantly ethylene, the exact ratio of gasoline to diesel is unknown. The product from the Partial Oxidation and Oxyhydrochlorination cases is produced by oligomerization of a hydrogen deficient intermediate (in the first case from a mixture of methanol and formaldehyde; in the second, from a mixture of mono and dichloromethane). To achieve an elemental balance in this study, it was necessary to adjust the typical MTG product distribution in the direction of increased C6 to C10 aromatics and lower light ends and paraffins. The product should be of very high octane but is more dense than the MTG product. Production of 14,500 BPSD of product thus requires about 14% more feed gas. (The possibility exists that durene content of the product will be higher in these two cases. Assuming that the gasoline will be blended into a large pool at a distribution center, this has been neglected in this study. Some care may be required in processing, storing and transporting the product to avoid precipitation of durene. Heated containers may be required. Exactly the same situation exists in the case of Fischer-Tropsch syncrude. The durene content of the product from the Oxidative Coupling and MTG cases should not give special handling problems except, perhaps, under arctic conditions for the Fixed- and Fluid-Bed MTG products.)

While it is true that hydrocarbons are sold on a volumetric basis, the heating value of a fuel is also of prime importance. Figures 2.4 and 2.4A show production costs in \$/MMBtu (HHV) of product as a function of gas cost. On this basis, both Partial Oxidation and Oxyhydrochlorination economics are improved and the latter becomes competitive with conventional technologies even with a 20% contingency allowance on the capital investment. The slope of these lines is equal to the reciprocal of the thermal efficiency (HHV basis), as defined in Section 2.2.1.

2.1.4 Key Parameters Affecting Capital Cost

Each of the direct conversion cases operates at low conversion in the primary reaction step. If conversion could be increased without a penalty in selectivity, there would be savings in the size of compressors and exchangers and reduced utilities consumption. Rough estimates have been made of the savings that would result from increases in conversion which are significant, but not large enough to completely change the design of the plant. These differ from case to case and are summarized below:

<u>Process</u>	<u>Conversion Increased</u>		<u>Cost Decreased</u>
	<u>From</u>	<u>To</u>	<u>To</u>
Oxidative Coupling	25%	35%	89.5%
Partial Oxidation	5.5%	10%	85.5%
Oxyhydrochlorination	25%	50%	91%

Selectivity is also of considerable importance, particularly where the alternative is carbon dioxide production. Selectivity affects not only gas consumption but the whole energy balance and the amount of heat dissipated to the environment. The favorable result for the Oxyhydrochlorination case, despite severe materials of construction restrictions, is attributable to the high selectivity. The point is developed further in Section 2.3.

PRODUCTION COST COMPARISON

GAS TO LIQUID HYDROCARBON PROCESSES

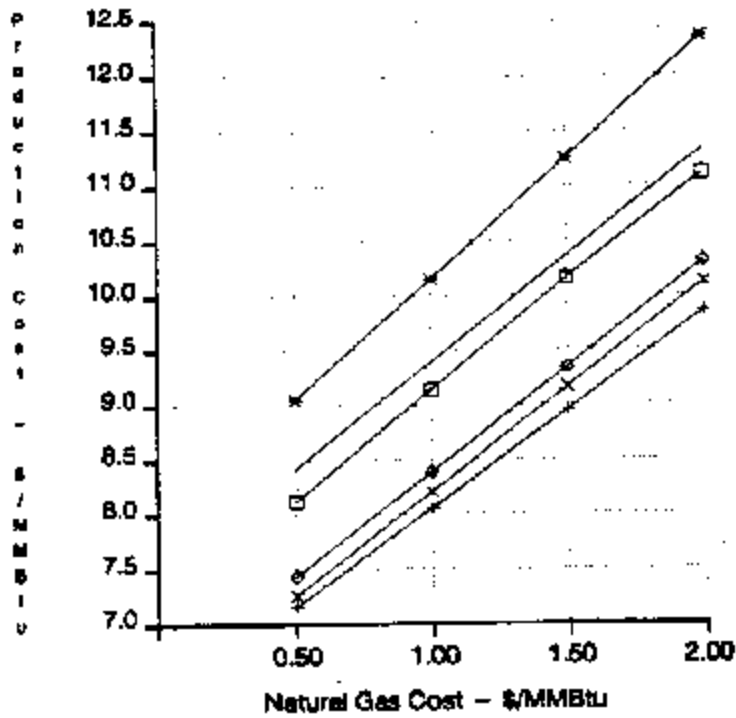
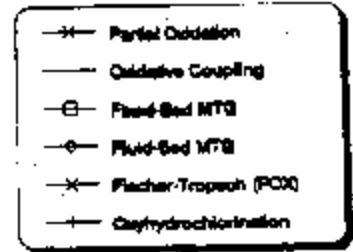


Figure 2.4



W/O Contingency

PRODUCTION COST COMPARISON

GAS TO LIQUID HYDROCARBON PROCESSES

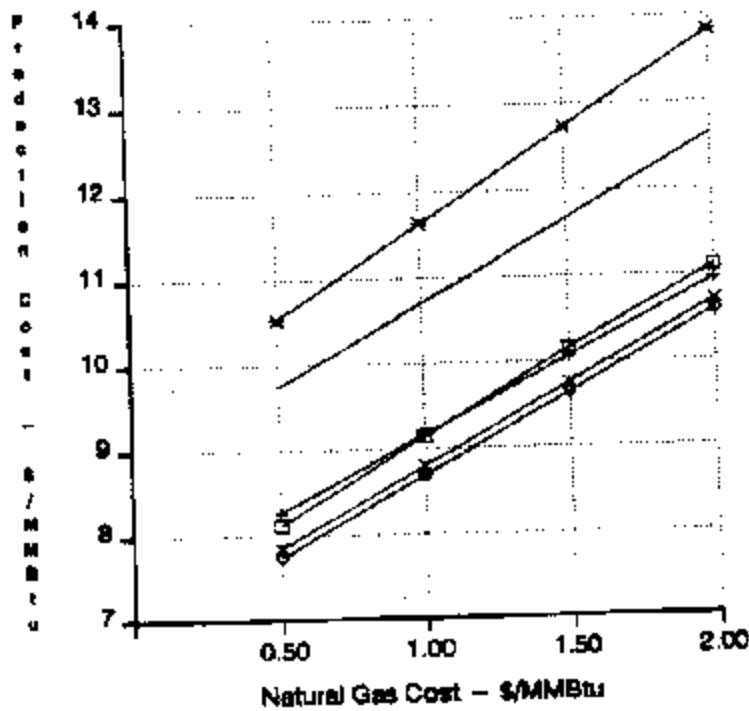
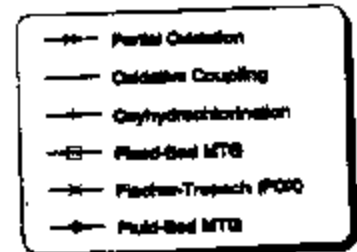


Figure 2.4A



With Contingency

An analysis has also been made of the effect of materials of construction on the cost of the Oxyhydrochlorination case. It is estimated that a 15% overall savings could be effected if special materials could be replaced with carbon steel throughout.

Figure 2.5 shows the breakdown in identified major equipment costs by type of equipment for the three direct conversion cases plus conventional Fixed-Bed MTG. Of particular note is the high cost of compression in the Oxidative Coupling and Partial Oxidation cases. Vessel costs represent a high percentage of the total for all the direct conversion cases, taking the place of the high furnace cost in the MTG case. (Precautions are necessary in the interpretation of Figure 2.5 since the equipment requirements for standard plants are not identified. An Oxygen Plant, for example, is a standard plant which is high in compressor and exchanger costs. The percentage of the total cost for which the equipment breakdown can be identified is noted on the diagram in each case.)

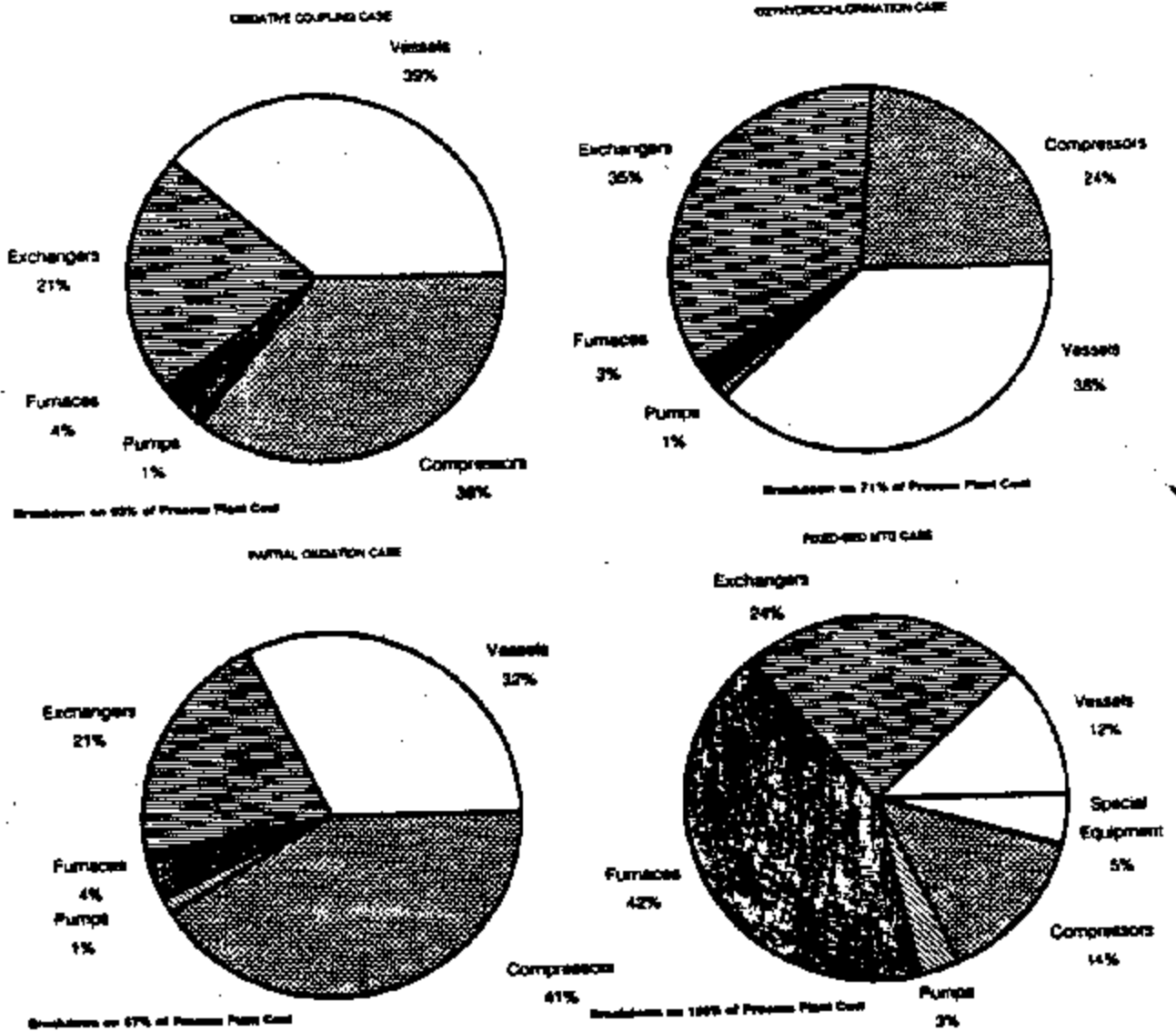
A review has been made of the very large compression costs in the Partial Oxidation and Oxidative Coupling cases. It is concluded that further optimization of both cases may be possible but would require redesign efforts beyond the scope of this study. The original concept for Partial Oxidation was that linking the two reaction steps in a single circuit without intermediate condensation (similar to Topsoc's TIGas design - Reference 10) would reduce process steps and save money. The problem is that the pressure levels for the two reactions may be too far apart. Unless the pressure level in the partial oxidation reactor can be reduced or conversion per pass increased, it might be better to recover the oxygenates by condensation from the recycle gas before feeding them to the second step, as in the conventional MTG process.

In the Oxidative Coupling case, the initial step runs at a much lower pressure level than the oligomerization step. Intermediate condensation is not feasible, but it still may be possible to reduce compression requirements by design optimization. The oligomerization reactor pressure level has been set by product separation requirements and may be higher than that required for olefin conversion. If this is true, compression requirement can be reduced at the expense of a more costly absorber system. Alternative oligomerization reactor designs which reduce pressure drop may also be feasible. The radial reactor, used in the Oxyhydrochlorination case, might also have been used here to reduce pressure drop.

Vessel costs are strongly dependent on operating conditions such as pressure, temperature, and space velocity. The high pressure (65 atm.) in the Partial Oxidation reactors, the high temperature (1600 °F) in the Oxidative Coupling reactors and the corrosive conditions in the Oxyhydrochlorination reactors all contribute to the high vessel costs indicated in Figure 2.5. It will be important to define space velocity requirements more accurately as these reactors are scaled-up.

The high reaction temperature in the Oxidative Coupling case permits very efficient use of the energy released by the reaction and leads to improved thermal efficiency (see Section 2.3.1, last paragraph). On the other hand, it also leads to high exchanger costs. The large catalyst circulation requirement does not have a major effect on the cost of the reactor as long as there is enough recycle gas to provide transport. (This is the reason why the increment in conversion per pass was limited to 10% for this case when estimating capital cost savings.) Catalyst circulation does have significant side effects on thermal efficiency and indirectly on capital cost by virtue of catalyst stripping steam requirements and the carryover of reactive materials from the reactor to the regenerator and inerts from the regenerator to the reactor. Even with

Figure 2.5
MAJOR EQUIPMENT COST BREAKDOWN



considerably better stripping than in a cat cracker, it is estimated that this carryover results in a 2% increase in gas consumption. Both this and the stripping steam requirement lead to higher heat loads. (Catalyst circulation is defined by stoichiometry and the oxygen carrying capacity of the catalyst. It is strongly influenced by the selectivity of the reaction.)

Feed gas composition is also a significant factor in the design of the direct conversion processes. Inerts present in the feed gas must be removed by purging to the fuel gas system. The quantity of purge and the level of inerts buildup in the recycle is determined by engineering judgement, since a true optimization is beyond the scope of a preliminary evaluation. In general, a reasonable balance is achieved between fuel supply and demand at 0.5% nitrogen in the feed gas. Fuel balance problems could exist at higher levels than this. Of the other components, CO₂ is not a real problem since it is removed along with CO₂ produced in the process. Hydrocarbons other than methane are assumed to convert more readily than methane. They should thus be beneficial.

2.2 TECHNICAL REVIEW

2.2.1 Thermal Efficiency

The facilities in this study are self-sufficient in terms of fuel requirement and produce no export steam or power. This is accomplished, where necessary, by recycling byproduct light hydrocarbons back to the first step for further reaction, taking only enough purge gas to balance fuel requirements. Since all plants are thus in balance, the thermal efficiency can be expressed as the heating value of the product as a percentage of the heating value of the total gas (feed plus fuel) to the plant. Normally the lower heating value is used, although a case can be made for using the higher heating value since most of the water produced by reaction is condensed and leaves as a liquid.

Table 2.4 summarizes estimates of thermal efficiency for the three direct conversion cases and compares them to estimates made previously for conventional synthesis gas based technologies when using a similar high methane feed gas. (Feed gas composition is a particularly significant factor in establishing the thermal efficiency of processes using methanol as an intermediate. Higher hydrocarbons in the feed gas result in a synthesis gas which is closer to the stoichiometric composition for methanol and CO₂ in the gas is, in effect, a reactant for the production of methanol.)

Thermal efficiencies obtained in this study for the direct conversion processes compare favorably with those for conventional processing, but are somewhat lower than those reported in earlier studies by Mobil (Ref.9) and Mitre (Ref.11). This is attributed to the more detailed accounting of inefficiencies, to the use of a more realistic feed gas and, in the case of Partial Oxidation, to a less optimistic interpretation of the literature data on conversion vs. selectivity.

In assessing performance, it should be recognized that the ultimate thermal efficiency for a methane conversion process producing liquid hydrocarbons and water is about 76% (LHV basis). This point will be developed further in Section 2.3. There is a similar limit for processes which proceed via synthesis gas, since the excess hydrogen produced is burned to supply heat for the reforming reaction.

Table 2.4
THERMAL EFFICIENCY COMPARISON
GAS TO LIQUIDS PROCESSING

	Oxidative Coupling	Partial Oxidation	Oxyhydro- chlorin- ation	Fixed- Bed MTG	Fluid- Bed MTG	Fischer- Tropsch (POX)
Feed + Fuel - MBtu/Hr						
HHV	6005	7347	5984	6175	5784	5980
LHV	5412	6622	5391	5566	5213	5390
Product						
HHV - MBtu/Hr	3106	3341	3341	3024	3030	3150
LHV - MBtu/Hr	2913	3155	3155	2846	2850	2958
Density - Lb/Bbl	255.5	287.1	287.1	252.2	250.6	259.0
@tu/Lb - HHV	20121	19261	19261	19846	20072	20130
@tu/Lb - LHV	18871	18189	18189	18678	18824	18903
MBtu/Bbl - HHV	5141	5530	5530	5005	5030	5214
MBtu/Bbl - LHV	4822	5222	5222	4713	4717	4896
Efficiency - HHV Basis - %	51.7	45.5	55.8	49.0	52.5	52.7
Efficiency - LHV Basis - %	53.8	47.6	58.5	51.1	54.7	54.9

2.2.2 Technology Status

All of the direct conversion processes considered in this study must be considered highly developmental at this time, though it is understood that ARCO has completed the design of a demonstration unit for their Oxidative Coupling technology and undoubtedly has unpublished information on which to base their design. A large scale demonstration is required for both the Oxidative Coupling and Oxyhydrochlorination reactors owing to difficulties in establishing backmixing effects when scaling up fluid-bed processes. Where tubular reactors provide for reaction with simultaneous heat and mass transfer, pilot plant scale-up studies will also be required. Wall effects may be significant in the small-scale test units used to date. The erratic yield/conversion data reported in the literature for the Partial Oxidation process may be a consequence of catalytic wall effects.

Typically, fluid-bed reactions are demonstrated in vessels several feet in diameter with capacities of 50 to 200 BPD. Tubular reactors require tests on one commercial size tube, whereas adiabatic fixed bed reactors have been successfully scaled-up from properly done bench scale tests.

The designs provided in this study should not be considered definitive. There is a distinct possibility that further optimization is possible. Before any additional design effort is expended, however, further definition of the process steps should be available. The primary need, in these low conversion processes, is to demonstrate both steps in an operation involving recycle. In all cases, the level of information available on the second step reaction is unsatisfactory and recourse has been made to extrapolations from MTG experience. The fate of light ends recirculated with the unconverted methane back to the first step reactor is not well defined. These effects can be simulated separately, but eventually there is a need to pilot the entire process in a true recycle mode.

Certain design factors in each of the direct conversion cases are not well defined. Assumptions have been made which will require additional test data for confirmation. These include:

- Materials of construction and non-ideal separation data in the Oxyhydrochlorination case,
- Catalyst reaction time and regeneration rate in the Oxidative Coupling case,
- Contact time and catalytic wall effects in the Partial Oxidation reactor

The results of this study also indicate that further bench scale development is required to improve on selectivity and conversion. This is probably the most pressing requirement and will be developed further in the next Section.

2.3 DIRECTIONS FOR FUTURE RESEARCH

The economical conversion of methane and other light hydrocarbon gases to liquid fuels is not an easy task for several reasons:

- o Methane, in particular, is a very stable compound and is difficult to activate. Once activation occurs, it is easy to overconvert.
- o Stoichiometry leads to large usages of reactants and intermediates such as oxygen, HCl and the Oxidative Coupling catalyst.
- o Heats of reaction are substantial.

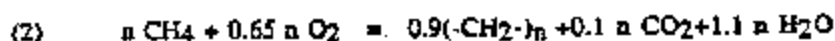
In order to put direct conversion processes on a more consistent basis and assess the ultimate economic potential, the stoichiometry and thermodynamics of the reactions have been reviewed and actual results related to the model reactions as a function of selectivity.

2.3.1 Thermodynamics of Model Reactions

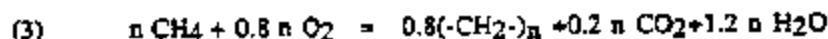
Direct methane to liquid processes can be characterized as either oxidative or reductive. In the reductive processes, hydrogen is produced as a byproduct, the reaction is endothermic and equilibrium is unfavorable, although above 1600 °F aromatics formation becomes possible. In the oxidative processes, excess hydrogen is oxidized creating a favorable equilibrium situation. By considering the hydrocarbon product as an oligomer of -CH₂- groups and oxygen as the oxidant, the overall reaction can be written:



If 10% of the methane reacts to CO₂, the overall reaction is:



If 20% of the methane reacts to CO₂, the overall reaction is:

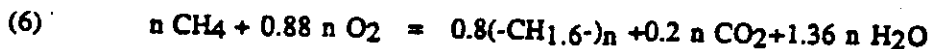
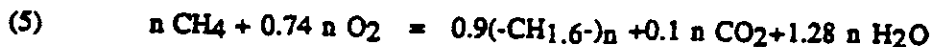
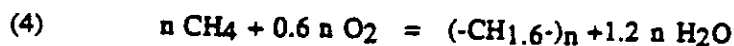


Some key thermodynamic and stoichiometric constants for these reactions are as follows (reactants are treated as gases and hydrocarbon product as a liquid):

Selectivity to CO ₂ -%	0	10	20
Heat Release-Btu/lb Oxygen			
LHV Basis	5179	5245	5286
HHV Basis	6362	6246	6174
Efficiency-%			
LHV Basis	76.0	68.4	60.8
HHV Basis	73.4	66.1	58.7
lb O ₂ /lb Product	1.14	1.65	2.28
To Produce 14,500 BPSD @ a density of 252 lb/bbl:			
Heat Release-MMBtu/hr			
LHV Basis	899	1316	1836
HHV Basis	1105	1567	2144
TPD Oxygen	2084	3010	4168
gpm Water Byproduct	391	478	587

The relative constancy of the heat release per ton of oxygen consumed is worth noting, as it simplifies making estimates for differing stoichiometry.

In the Partial Oxidation and Oxychlorination cases the hydrogen to carbon ratio of the hydrocarbon product reduces from 2 to 1.6 because the feed gas has been overoxidized in the first step. Stoichiometry requires that Equations (1), (2) and (3) now become:



The thermodynamic and stoichiometric constants are revised as follows:

Selectivity to CO ₂ -%	0	10	20
Heat Release-Btu/lb Oxygen			
LHV Basis	5225	5271	5582
HHV Basis	6409	6294	6216
Thermal efficiency %			
LHV Basis	70.9	63.8	56.7
HHV Basis	67.9	61.1	54.3
lb O ₂ /lb Product	1.41	1.93	2.58
To Produce 14,500 BPSD @ a density of 287 lb/bbl:			
Heat Release-MMBtu/hr			
LHV Basis	1277	1765	2501
HHV Basis	1566	2108	2785
TPD Oxygen	2933	4019	5376
gpm Water Byproduct	550	743	980

When the above predictions are checked against the utility consumptions and oxygen demand in Table 2.2, using actual CO₂ selectivities, there is a reasonably good correspondence. This is shown in Table 2.5. For the cases which do not involve steam reforming, the heat release estimates account for 75 to 85% of the cooling water duty. Oxygen requirements and byproduct water production rates are in rough agreement, with differences being explainable by differences assumed in the H/C ratio of the product. Estimates for the conventional synthesis gas based processes are also shown, including a typical steam reformer Fischer-Tropsch operation.

The carbon selectivity to product is closely related to the thermal efficiency for all these cases. Very roughly the thermal efficiency is about 75% of the carbon selectivity. A comparison has been made of actual thermal efficiency as a percentage of values predicted from the above stoichiometry. Results were as follows:

Oxidative Coupling	91%
Partial Oxidation	84%
Oxyhydrochlorination	85%

These estimates measure the actual efficiency of the process design. It is believed that the higher ratio for Oxidative Coupling is indicative of the effectiveness of energy recovery at the high temperatures employed in the process.

Table 2.5
Carbon Selectivity vs Performance in Methane Conversion Processes

	Oxidative Coupling	Partial Oxidation	Oxyhydrogenation	Fixed Bed MTG	Fluid Bed MTG	Fischer Tropsch (Ref)	Fischer Tropsch (POX)
C Atom Distribution ¹ - %							
CO ₂ Byproduct	21.1	18.2	2.0	2.2	2.3	2.7	19.3
Other Byproducts	0.0	negl.	0.4	negl.	negl.	0.7	1.4
CO ₂ in Fuel Gases							
Byproduct Fuel - 1st Step	5.9	10.1	12.6	12.7	13.3	9.1	0.0
Byproduct Fuel - 2nd Step	N/A	N/A	N/A	9.6	9.8	20.5	10.9
Net Gas Fired	1.79	5.51	3.4	8.17	4.07	5.1	0.0
Net Product	71.3	66.2	81.3	67.9	70.3	61.9	88.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Effective CO ₂ Conversion %	22.4	20.3	2.6	2.5	2.9	3.9	21.7
Other Oxygenates %	0.0	negl.	0.5	negl.	negl.	1.0	1.5
Predicted O ₂ Consumption-TPD	4520	5530	3240	N/A	N/A	N/A	4880
Actual O ₂ - TPD Note 1	4870	5626	3236	N/A	N/A	N/A	4907
Predicted Efficiency - LHV %	58.97	56.56	69.07	73.87	73.77	73.04	59.53
Actual Efficiency - LHV %	53.82	47.84	58.52	51.13	54.67	49.61	54.66
Efficiency Ratio in %	91.27	84.23	84.73	69.22	74.11	68.20	92.19
Predicted CW Duty - MMBtu/Hr	2338	2820	1720	1200	1206	1300	2400
Actual CW Duty - MMBtu/Hr	2800	3475	2292	2269	2059	1908	2707
Ratio Therm Eff/Carbon Select	0.755	0.720	0.720	0.759	0.775	0.804	0.802

Note 1. In Oxidative Coupling case this is equivalent oxygen transferred by the catalyst.

2.3.2 Effect of Selectivity on Cost

The significance of the previous Section is that it enables some rough estimates to be made of the effect of selectivity on cost of the plant. If the selectivity of the Partial Oxidation process can be made to approach 100%, then the various portions of the plant would reduce in size substantially, as follows:

- o The Oxygen plant, by a factor of 0.4,
- o CO₂ Removal eliminated,
- o The rest of the process plants, by a factor of 0.88 due to product density reduction,
- o Total compressor load by a factor of 0.6,
- o Total heat release and cooling water load by a factor of 0.4,
- o The reactor would be simpler due to the reduced heat load.

It is estimated that the total plant cost would reduce from \$773MM to \$525MM, a factor of 0.68, under conditions of ideal selectivity. It is probable that the plant would remain close to fuel balance. If no CO₂ were produced, but the methanol to formaldehyde ratio stayed at 4:1, the resulting cost becomes \$593MM, a cost reduction factor of 0.767.

The Oxyhydrochlorination case is already operating at high selectivity (only 3% CO₂) except for the monochloro to dichloromethane ratio of 4:1. The effect of this ratio is to increase the size of the whole facility by 14% owing to the increased density of the product. There is an additional 24% increase in capacity of the hydrochloric acid recovery and oxygen plants. Offsites are also affected. At optimum selectivity, it is estimated that the cost reduction factor is 0.812.

Some significant effects would also occur in the Oxidative Coupling process if selectivity were improved to 100%:

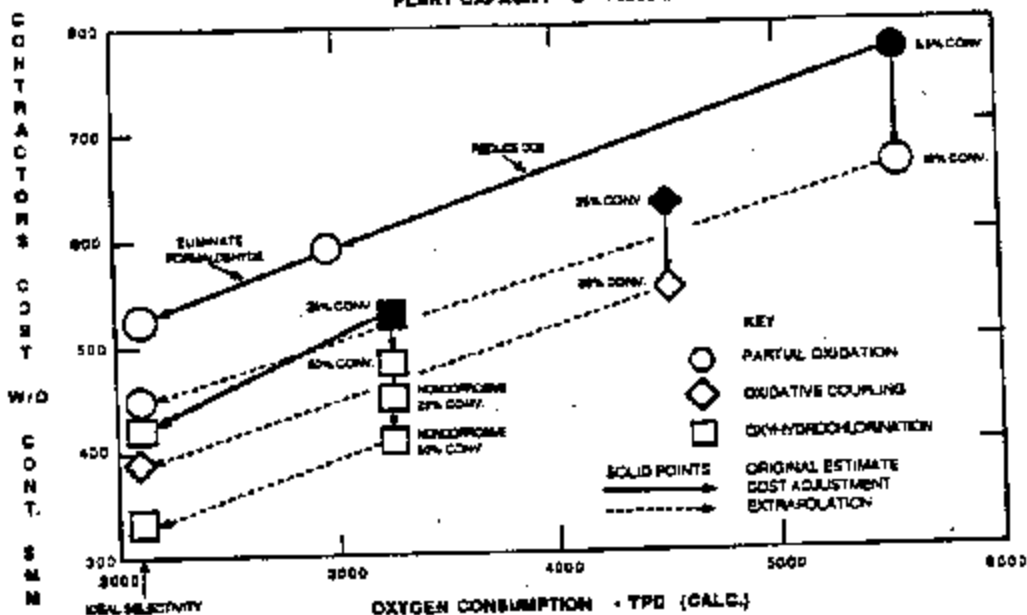
- o A reduction in catalyst circulation by a factor of 0.46
- o A reduction in air flow to the regenerator by a similar factor, reducing regenerator size and air compressor horsepower.
- o A similar reduction in cooling water duty.

A simple analysis is not possible for Oxidative Coupling, since the reactor design and the heat balance around the system would have to be completely revised. A substantial cost reduction is probable.

2.3.3 The Ideal Process

Various cost reduction factors have been estimated previously in this study and these can be put together to get some idea of what an ideal direct reduction process would look like. The following table summarizes the situation, assuming that effects can be combined:

FIGURE 2.8
 CAPITAL COST OF DIRECT METHANE CONVERSION PROCESSES
 EFFECT OF SELECTIVITY
 AS MEASURED BY OXYGEN CONSUMPTION
 PLANT CAPACITY = 14500 BPSD



<u>Process</u>	<u>Study Basis Cost*</u>	<u>Factors</u>	<u>Ultimate Cost</u>
	<u>\$MM</u>		<u>\$MM</u>
Oxidative Coupling	614	.895	550 @ 22%CO ₂
Partial Oxidation**	773	.855x.68	449 @ 0%CO ₂
Oxyhydrochlorination**	528	.91x.812x.85	332 @ 0%CO ₂

* w/o contingency and owner's costs.

** 100% to methanol or monochloromethane in these cases.

The first factor in each case is the correction for increased conversion/pass given in Section 2.1.4, the second is the ideal selectivity correction from the previous section, the third (in the case of Oxyhydrochlorination) is that for non-corrosive reactants. The results provide a rough indication of the cost of a process with ideal selectivity, improved conversion per pass and no corrosion resistant materials required.

There will also be a substantial reduction in cost of the Oxidative Coupling process if selectivity can be improved. While a redesign of the Oxidative Coupling reactor is beyond the scope of this study, a rough estimate is possible assuming that the effect is similar to that in the Partial Oxidation case. The resulting estimate for Oxidative Coupling is a plant cost of \$385 MM.

Figure 2.6 depicts the above effects in graphical form, using the theoretical oxygen consumption as a measure of selectivity. Cost corrections which have actually been estimated are shown as solid lines, extrapolations as dotted lines. The intercepts at 2084 TPD oxygen consumption correspond to the costs of processes with ideal selectivity. A rough pattern can be seen indicating that selectivity and conversion/pass dominate the cost effects, despite significant differences between processes.

It is concluded that a cost in the neighborhood of \$300MM - \$350 MM may be feasible for the ideal direct reduction process. Full advantage has not been taken of complete elimination of recycle, of the possibility of a single-step reaction or of further process and utilities optimization. On the other hand, 100% selectivity is probably an unreachable goal. It should be noted that all of the above costs are plant costs without contingency and do not include owners costs.

If plant costs can be reduced to this level then a delivery cost of under \$30/barrel is considered achievable.

2.3.4 Comparison With Synthesis Gas-Based Processes

In a screening study, possible improvements in synthesis gas based technology were reviewed. It was concluded that a reduction to 77% of the cost of the conventional Fixed-Bed MTG process (as used in New Zealand) may be possible by a combination of Fluid-Bed MTG with improved technology for producing synthesis gas. This would reduce plant cost to the level of \$473 MM. Low temperature methanol synthesis technology has the potential to reduce this still further.

It is recommended that both direct conversion and improved synthesis gas technology continue to be pursued, neither having a clearcut advantage at this time. It does appear that a direct conversion process achieving high selectivity without penalty will be superior to processes using the synthesis gas route. The problem is that high selectivity at reasonable conversion per pass appears to be a difficult goal for the direct conversion processes.

2.4 CONCLUSIONS

The three direct conversion processes evaluated in this study have the potential to compete favorably with conventional technology provided improvements can be made in the selectivity and conversion per pass. This may not be easy to accomplish because of the inherent non-selectivity of free radical reactions.

Of the three technologies studied, Oxyhydrochlorination, followed by oligomerization of methyl chloride to gasoline, showed the lowest cost and best economics. Oxidative Coupling to olefins, followed by oligomerization of olefins, was a close second and Partial Oxidation to methanol, followed by MTG, was a distant third. It is considered significant that this ranking is in the same order as selectivity:

- o Oxyhydrochlorination has by far the lowest conversion to carbon dioxide (3%), but overchlorinates 20% of the methane molecules to methylene dichloride, i.e. a dichloro to monochloro ratio of 1/4. The dichloro to monochloro ratio can be decreased only at the expense of reduced conversion per pass. This is already only 25%.
- o Oxidative Coupling, at 25% conversion per pass, has a 22% selectivity to carbon oxides (the assumption is that carbon monoxide will equilibrate to carbon dioxide).
- o Partial oxidation, at 5.5% conversion per pass, has both a 20% conversion to carbon oxides and a hydrogen deficient intermediate product, i.e. the formaldehyde to methanol ratio is 1/4.

It is concluded that selectivity is important not only in terms of feed gas consumption and its effect on operating cost, but also in terms of the capital cost of the project. Poor selectivity increases heat release, oxygen consumption and CO₂ removal, all of which increase capital cost.

Other factors found to have a significant effect on capital cost were conversion per pass (doubling conversion per pass was found to reduce capital cost about 10 to 15%) and the materials of construction required due to corrosive reagents in the Oxychlorination case (15% effect on overall capital cost). Not specifically evaluated, but also judged important were the high operating pressure in the Partial Oxidation case and the high temperature in the Oxidative Coupling case. Operating conditions were judged to be significant from a maintenance standpoint as well. Higher maintenance factors than normal were applied in developing operating costs where operating conditions were severe.

In comparing direct conversion processes with conventional MTG or Fischer-Tropsch technology via synthesis gas, the key cost factors were as follows:

Process	No Contingency Basis	
	Capital Investment \$MM	Production Cost in \$/bbl
Oxidative Coupling	684	43
Partial Oxidation	844	50
Oxyhydrochlorination	596	40
Fixed-Bed MTG	683	41
Fluid-Bed MTG	621	37
Fischer-Tropsch (High MW)	647	38

@ 14500 BPSD for \$0.50/MMBtu Feed Gas

With Allowance for Contingency

<u>Process</u>	<u>Capital Investment \$MM</u>	<u>Production Cost in \$/bbl</u>
	<u>@ 14500 BPSD for \$0.50/MMBtu Feed Gas</u>	
Oxidative Coupling @(20%)	820	50
Partial Oxidation @(20%)	1013	58
Oxyhydrochlorination @(20%)	715	46
Fixed-Bed MTG @(0%)	683	41
Fluid-Bed MTG @(5%)	653	39
Fischer-Tropsch @(10%)	712	41

If production costs are compared in \$/MMBtu, then the Partial Oxidation and Oxyhydrochlorination cases improve their relative standing and Oxyhydrochlorination has the lowest cost of all on a non-contingency basis.

An analysis of capital cost indicates that the large cost of the synthesis gas preparation step in conventional technology is being supplanted, in direct conversion, by large reaction sections with high compression costs and large oxygen plants. The key issue in oxidative direct conversion is the reaction stoichiometry. For every mole of methane reacted, 1/2 mole of oxygen must react. This is roughly 4 moles of oxygen per mole of product. Even with perfect selectivity, 2084 TPD of oxygen are required to produce 14500 BPSD of product. Heat release is almost directly related to oxygen consumption at about 6300 Btu per pound of oxygen. In the same regard, production of methyl chloride requires one mol of HCl per mole of methane, thus 4750 TPD of HCl must be recirculated. A loss in selectivity affects these numbers directly.

Thermal efficiency (LHV basis) is somewhat improved over the synthesis gas based processes:

Oxidative Coupling	54%
Partial Oxidation	48%
Oxyhydrochlorination	59%
Fixed-Bed MTG	51%
Fluid-Bed MTG	55%
Fischer-Tropsch	55%

The synthesis gas based processes all have a limit on thermal efficiency because of the large amount of fuel required to produce synthesis gas. As a result, carbon selectivity is never above about 70%. Direct conversion processes have the capability of quite high carbon selectivities, in fact the Oxychlorination case has a carbon selectivity of 81% and this does translate into a higher thermal efficiency as shown above. It appears then that direct conversion processes have the greater potential for improved thermal efficiency. Analysis of an ideal direct conversion process shows that it may be possible, ultimately, to reduce the capital cost by 50%.

Recommendations for further research can be summarized as follows:

1. Develop catalysts and conditions which lead to improved selectivity without sacrificing conversion/pass. This can lead to significant reductions in the cost of process plants and offsites.
2. If recommendation No. 1 can be implemented in a non-corrosive environment at moderate temperature and pressure so much the better.

3. Look at the possibility of a single step process where the intermediates are removed faster than they can overconvert. Remember that 8 to 10 moles of an intermediate such as methanol must be handled per mole of gasoline produced. The ratio is even higher for a distillate.
4. If a two-step process is required, try to match operating pressures and temperatures between steps.
5. Capital cost is more significant in the economics than operating cost when the feed gas is low in value, so the design does not need to maximize thermal efficiency.
6. If the process is carried out in a remote location (the basis for this study), then it is required that the plant be in energy balance as there is no market for export power or steam. There will always be byproduct fuel produced to supply internal energy demands. A selective, low temperature process where energy recovery is not practised could show the lowest capital cost. Thermal efficiency would still be adequate if a very high selectivity were achieved.
7. All of the direct conversion cases covered in this study require further test work to define conditions, yields and conversion in a true recycle operation. It has been assumed in this study that byproduct light hydrocarbons can be recycled, producing additional product.
8. Improvements are being made in methanol production which offer the possibility of higher efficiency and lower cost in the the synthesis gas production step. These could also lead to improved economics in gasoline production. It is concluded that both direct conversion and improvements in synthesis gas technology should be actively pursued.

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