

DIRECT CONVERSION OF METHANE TO C₂'s AND LIQUID FUELS

DOE Contract No. DE-AC22-87PC79817

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by

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by B. K. Warren and J. L. Matherne**

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OBJECTIVE: The objective of this program is to discover and evaluate novel catalytic systems for the conversion of methane or byproduct light hydrocarbon gases through intermediate light gases rich in C₂'s to liquid hydrocarbon fuels, and to evaluate different conceptualized schemes for this.

ABSTRACT

TECHNICAL APPROACH: For Task 1, the approach is to test several specific classes of potential catalysts for the conversion of methane selectively to C₂ products rich in ethylene. The conversion of C₂'s to fuels will be evaluated briefly during the last six weeks of the contract. Task 2 involves development and economic evaluation of conceptual processes for converting methane to C₂'s and C₂'s to fuels.

ACCOMPLISHMENTS: Catalyst and screening facilities have been installed, and several classes of materials have been evaluated as catalysts for the oxidative conversion of methane to C₂'s. Selectivities of over 60% and C₂ yields of over 25% were obtained using one type of catalyst, which showed high (>10) ethylene to ethane ratios. Several ways to retard or reverse catalyst deactivation with certain types of catalysts were discovered. Engineering evaluations of the economics of both a Comparison Case (methane → synthesis gas → methanol → olefins → fuels) and a hypothetical Case 1 (methane to ethylene) were completed.

DIRECT CONVERSION OF METHANE TO C₂'S AND LIQUID FUELS

TECHNICAL APPROACH:

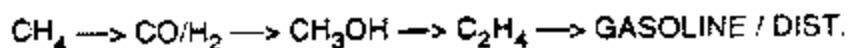
Transportation fuels can be generated by direct and indirect (through synthesis gas) liquefaction of coal. The production of light gases and methane in these processes represents a significant economic inefficiency. Although methane is useful as a fuel, it is expensive to transport, so often it is more economical to burn methane rather than transport it.

Conversion of byproduct gases from Fischer-Tropsch or Lurgi Dry Bottom Gasifier processes, principally methane, to liquid fuels in a simple, energy-efficient, economical reaction process is an important chemical challenge. Such a process would provide a significant increase in the value of coal. If sufficiently selective and economically attractive, this technology could also be applied to our large natural gas reserves for the production of liquid fuels. It would offer a feasible and economic approach to reducing our dependence on foreign petroleum sources. One route from methane to liquid fuels would be through light hydrocarbon gases rich in ethylene. Production of ethylene from methane is a useful goal in its own right. These light hydrocarbons may then, ideally, with little or no separation of products, be converted over molecular sieve catalysts to gasoline and distillates. This project's goal is to discover economically attractive catalysts and process conditions to convert methane to ethylene. The conversion of light hydrocarbon gases rich in ethylene to liquid hydrocarbon fuels will be examined only briefly. Union Carbide Corporation (UCC) predicts that this process would be more practical and economical than a single step process or other alternatives.

Our approach to accomplishing the objectives of Task 1, the discovery of catalytic systems for converting methane to liquid fuels, is to test several specific classes of potential catalysts for the conversion of methane selectively to C₂ products rich in ethylene. In the last six weeks of the two year period for this project, the conversion of methane to C₂'s will be integrated with the conversion of C₂'s to fuels with little or no separation between steps, and the use of byproduct gas mixtures typical of Fischer-Tropsch or Lurgi Dry Bottom Gasifier processes, (principally methane) will be demonstrated.

Task 2 is the engineering evaluation of alternative processes for the conversion of methane to liquid hydrocarbon fuels and assistance to the R&D catalysis program. R&D and engineering will work closely together on conceptual processes for converting methane to liquid fuels, as well as on the details of catalyst design and testing, physical chemistry concepts, and reactor and process design.

Technology exists for converting methane to liquid fuels. C_2H_4 indicates light hydrocarbon gases rich in ethylene.



This project proposes to avoid the reforming step which is required in existing technology to convert methane to liquid fuels because it is capital intensive.

It has long been known that methane could be pyrolytically converted to C_2+ hydrocarbons. The direct conversion, in one step, of methane to liquid fuels,



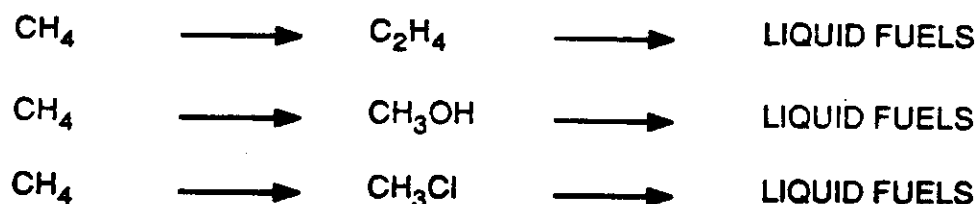
has been accomplished thermally, but is very inefficient. The carbon-hydrogen bond energy of methane is much higher (104 kcal/mol) than the carbon-hydrogen bond energy of ethane (98 kcal/mol) or most other hydrocarbons (85-98 kcal/mol). Under conditions suitable for removal of the first hydrogen from methane, other hydrocarbons will react preferentially. Thus one would expect significant conversions of hydrocarbons other than methane to less useful, hydrogen-deficient, polymeric materials, such as coke and heavier aromatics and tars, before much of the methane is reacted. The direct conversion of methane is highly endothermic. Temperatures of over 800 °C are required to effect practical conversions. The extreme temperatures required make it expensive to generate and transfer the required heat to the reaction. The operation of such processes is uneconomical, and materials problems are encountered.

Although the direct, thermal conversion of methane to hydrocarbons is extremely endothermic, the process becomes exothermic with an oxidative reaction, where water, rather than hydrogen, is co-produced. A two-step process from methane to liquid hydrocarbon fuels either with minimal or no separations between steps would approach the economics of a hypothetical single step process, and with optimization of the first step, it is estimated that a two-step process would be more practical and economical than a single step process for reasons discussed below.

Under oxidative conditions, complete combustion is expected to compete with methane activation. Therefore good yields of gasoline and distillates appropriate for jet and diesel fuels directly from methane in one step are not expected to be achievable, even with a multifunctional catalyst. However, it seems more likely one could successfully activate only the first hydrogen of methane to form either methanol or the coupled product, ethane, under conditions where the product is rapidly removed from the catalytic

reaction area. It would therefore be likely that an economically attractive process to produce either ethane or methanol could be achievable. This is illustrated by the pioneering work at UCC in the synthesis of ethylene via oxidative coupling of methane over metal oxide catalysts [1].

To understand why UCC prefers the production of liquid fuels through C_2 intermediates, the following reaction sequences may be compared.



The technical challenge in developing any of the non-chloride routes shown above from methane to liquid hydrocarbon fuels is in the first step, the conversion of methane to either methanol or ethylene. The conversion of methanol to gasoline has been commercialized [2]. The conversion of olefins to a gasoline / distillate mixture has been demonstrated in refinery-scale equipment [2].

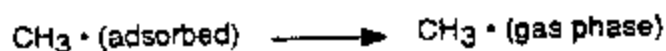
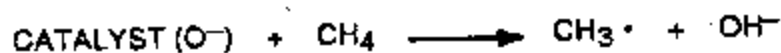
UCC believes that a methane to ethylene process is more technically feasible than a methane to methanol process from both chemistry and engineering considerations. High selectivities to methanol from methane have been reported only at low productivities, and it has been suggested [3] that some major studies in this area have been dropped due to unattractive economics, cumbersome quenching equipment, and explosion hazards. Among the better results reported, Iwamoto [4] reported an 85.6% selectivity with 11.2% conversion of methane (12.7% formaldehyde) at 550°C using a V_2O_5/SiO_2 catalyst, and a 98.5% selectivity to methanol at 1.1% conversion with a WO_3/SiO_2 catalyst. The yields here are below 10%. Yields of 20-30% have been reported for the conversion of methane to C_2 hydrocarbons.

Stoichiometric conversion of methane to methyl chloride is known technology. Chlorine has been used in the commercial practice of this reaction, but it is too expensive a reagent to consider for direct stoichiometric use in the conversion of methane to liquid fuels. Although Union Carbide made public very little of its work in oxychlorination [5,6], oxychlorination, requiring hydrogen chloride rather than chlorine, was thoroughly explored for the selective conversion of several hydrocarbons to chlorides. Methane was converted to chlorinated methanes on a plant scale using this technology.

Although the steps in routes from methane to liquid hydrocarbon fuels through methyl chloride may be closer to the development stage than the direct conversion of methane to ethylene or methanol, the stoichiometric use of halide compounds to facilitate

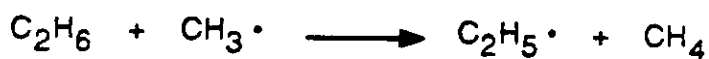
selective abstraction of hydrogen from hydrocarbons will present serious corrosion and recovery problems, and special materials of construction would be required. Handling of the chlorides and disposal of chloride wastes, especially those containing organic chlorides (some of which are either carcinogens or hazardous) would present environmental problems which will add significant investment and operating costs. The costs for ancillary equipment to recycle the corrosive chlorides will also add to investment and operating costs. For these reasons, Union Carbide favors an approach which avoids the recycle of large amounts of halides. In reported economic studies of various routes from methane to liquid hydrocarbon fuels, these problems and associated investments are not quantitatively taken into account.

Many catalysts have been reported for the conversion of methane to C₂ products in the last few years. Product distributions are similar for a variety of very dissimilar catalysts, which encourages the belief that the chemistry leading to the observed product distributions is dictated by gas-phase rather than catalyst chemistry. Lunsford [7-11] and coworkers have elegantly and convincingly demonstrated that methyl radicals are most likely intermediates in the conversion of methane to ethane. Methyl radicals are produced by abstraction of hydrogen from methane by the catalyst followed by release of the methyl radical into the gas phase where it couples to form ethane. The methyl radical may or may not be actually adsorbed on the catalyst surface.



Kimble and Kolts [12] have demonstrated that the conversion of ethane to ethylene in the presence of oxygen is not enhanced in the presence of catalyst, indicating that at least for their Li/CaO catalyst under conditions used, ethane is converted to ethylene primarily (if not exclusively) in the gas phase.

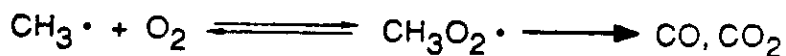
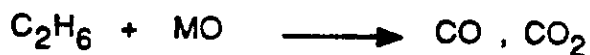
Reactions which have been proposed to be involved in the conversion of ethane to ethylene are illustrated below.



Lunsford [7] suggests that below 700 °C, ethylene may be formed by reaction of ethane with catalyst surface O²⁻ or by reaction of ethane in the gas phase with oxygen. The gas phase reaction with oxygen leads to a chain of other reactions which generate more methyl radicals.

In addition to oxidative dehydrogenation of ethane, where surface or gaseous oxygen abstracts hydrogen from ethane to produce an ethyl radical, at temperatures above 700 °C, ethane may be converted to ethylene in the absence of oxygen through a series of thermal reactions which include carbon-carbon bond breaking. Under conditions reported by Sofranko [13], thermal and oxidative dehydrogenation routes to ethylene were found to have rates of the same order of magnitude.

It is currently thought that carbon oxides are produced primarily from oxidation of ethylene at higher methane conversions [14] and from oxidation of methyl radical at low methane conversions [7]. Carbon monoxide and carbon dioxide have been proposed to be formed by the following reactions.



The relative contribution of each of these reactions is unknown, but in some systems, selectivity drops as surface area of the catalyst increases [15-17]. This indicates that after the methyl radical is produced and released into the gas phase, collisions with and subsequent oxidation on the catalyst surface might be responsible for formation of at least some of the carbon oxides. Recent unpublished work by J. R. H. Ross indicates that the rate to carbon oxides depends on the concentration of ethane or ethylene, rather than on the concentration of methane. He has also proposed that the rate limiting step in the formation of carbon oxides may be the formation of a particular type of oxygen species on the catalyst surface which is responsible for the formation of the carbon oxides. These findings have not been taken into account in recent kinetic models which predict a mechanistic barrier to the C₂ yield possible for methane coupling.

Important goals in studying methane coupling are:

- a low temperature reaction (450 - 700 °C),
- high C₂ yields (selectivity x conversion > 30%),
- a higher selectivity or a lower carbon dioxide to carbon monoxide ratio at a given yield,
- a high ethylene to ethane ratio, and
- a stable catalyst system.

It will also be very important to have a process which can operate under moderate pressure (100-400 psig) rather than at near-atmospheric pressure.

ACCOMPLISHMENTS:

Task 1

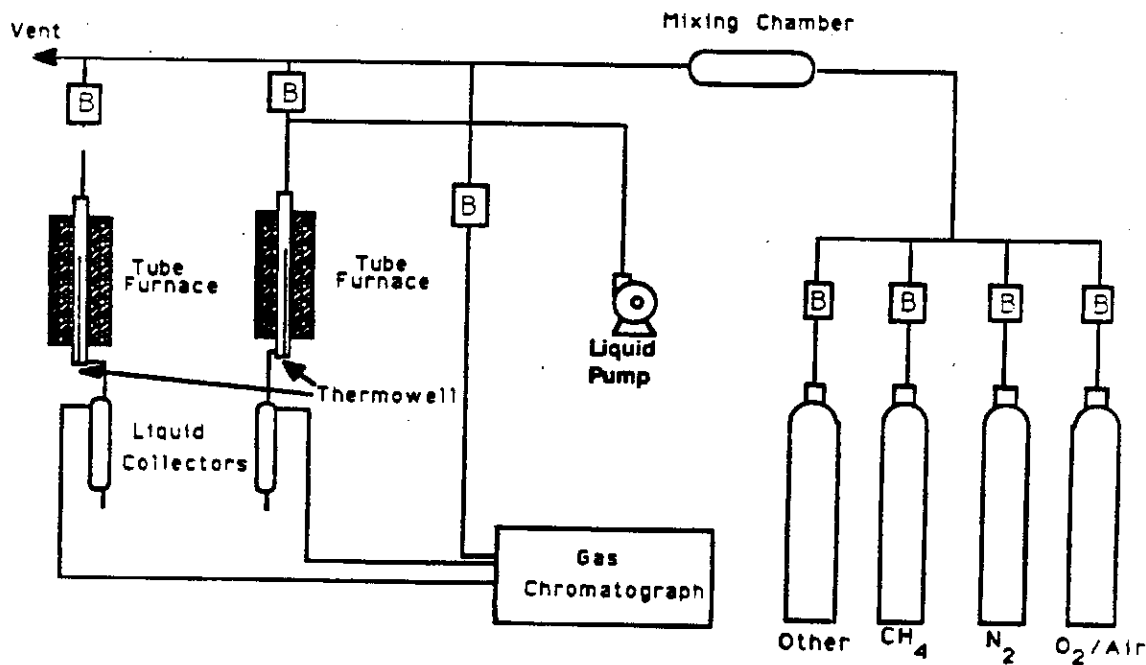
Union Carbide Corporation (UCC) has completed the first year of a two year, cost-shared contract to study the direct conversion of methane or byproduct light hydrocarbon gases through intermediate light gases rich in C₂'s (mainly ethylene) to liquid hydrocarbon fuels. For Task 1 work, literature results were translated into common units and the references and individual runs were put into a computer database which allows searching and sorting. Literature and Union Carbide proprietary catalysts from earlier work were used to test the reactor systems and to verify differences among catalysts. Control studies were completed, and a designed set of experiments was conducted to determine the effect of the uncatalyzed gas-phase reaction under different process

conditions so that conditions for operating could be chosen where the homogeneous reaction would not interfere with tests of catalyst efficiency.

Reactors were constructed and tested in a variety of materials and designs. The void volume of the reactor was minimized, and quartz was chosen as the reactor material of preference for laboratory work. Quartz chips were used to reduce the void volume prior to the catalyst bed. Catalyst mesh size and mass diffusion studies were completed to allow the choice of catalyst test conditions outside of ranges where mass diffusion would be important. The trends and effects of important process variables on the selectivity and activity of methane coupling were studied for a variety of catalysts. Supports were characterized and tested to choose those appropriate for supported catalysts.

The major activity of Task 1 has been catalyst design, preparation, and testing. Catalyst promoter - support interactions have been studied. The effect of different catalyst preparation procedures on catalyst activity, selectivity, and stability has been studied for a few catalysts.

Four laboratory reactors were constructed and each is capable of continuous, unattended operation. A drawing of one of the reactor systems is shown below.



Each dual-reactor unit consists of a variety of gases fed through mass flow meters to a mixing chamber. The gases are metered into the reactors, pass through cooled drop-pots (which remove water), and gases are analyzed on-stream using column switching. Steam or volatilized liquids may be added to one reactor in each laboratory.

The experimental conditions used for catalyst screening varied, but typically a methane to oxygen ratio of 2 [28% methane and 14% oxygen (72% air) or 10% methane and 5% oxygen] was used with nitrogen as diluent. Temperatures were commonly 600 - 850 °C, pressures 5 - 15 psig, and from 0.1 to 30 grams of catalyst were used. Space velocities varied from 500 to 30,000 Hr⁻¹.

The following results illustrate the products produced by the non-catalyzed, thermal homogeneous reaction under different process conditions at 850 °C. The void volume of the reactor was 25.1cc.

UNCATALYZED GAS-PHASE OXIDATION OF METHANE

P (Psig)	CH ₄ /O ₂ Molar	R.T. (sec.)	CH ₄ Conv. %	O ₂ Conv. %	C ₂ Sel. %	C ₂ Yield %	=/ Molar
5	2	4.8	35.4	81.2	25.3	8.6	4.1
15	2	14.3	38.3	94.4	15.3	5.7	10.4
5	15	4.9	3.14	28.7	58.6	1.8	1.4
15	14	4.8	4.4	54.3	53.1	2.4	2.1

R.T. is the residence time, and =/ is the ethylene to ethane ratio. High selectivities and high ethylene to ethane ratios can be obtained from the uncatalyzed oxidation of methane. The C₂ yield of 8.6% is as high as any C₂ yield in the literature for the homogeneous oxidation, and it is thought that the uncatalyzed reaction will not be economically practical because higher C₂ yields will be difficult or impossible to obtain.

The list of catalysts on the next page shows the general types of catalysts of interest and the number of catalysts of each type tested. One hundred and sixty four catalysts were tested in three major classes. There were 17 significantly different types of catalysts tested. Metal oxide catalysts of interest include promoted hole-defect catalysts and catalysts containing rare earth oxides. Certain promoted metal oxide catalysts have resulted in yields to C₂'s of 20 to 26% with ethylene to ethane ratios of 3 to 20. J. R. H. Ross has reported C₂ yields of 20 to 25% to be in the range of commercial interest [18]. Some simple rare earth oxide mixtures have been tested, but some of the more interesting materials, including some proprietary materials, have not yet been tested.

CATALYST DESIGN AND TESTING

(164 catalysts)

Metal Oxide Catalysts

Promoted Metal Oxide Catalysts	4 types	95 catalysts
Rare Earth Oxides - Mixtures and Promoted REO's	2 types	8 catalysts

Metals in Unusual Oxidation States

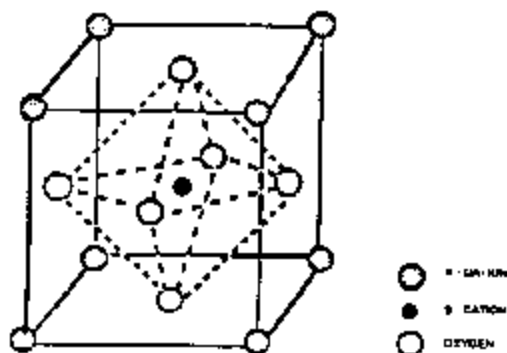
Perovskites	5 types	25 catalysts
Metals in Molecular Sieves		7 catalysts
Other Structures		9 catalysts

Other Novel Catalysts and Process Ideas

Solid Base Catalysts	0	
Certain Other Novel Catalyst Systems	4 types	20 catalysts

Catalysts with metals in unusual oxidation or coordination states, e.g., stabilized in rigid oxide frameworks such as a perovskite or a molecular sieve, have been made and tested. A perovskite is a low-surface area mixed metal oxide with an ABO_3 structure (or $AA'BO_3$ or $ABB'O_3$). The A and B atoms have a defined size relationship and the sum of the oxidation states of the cations must equal six. Small amounts of an A' or B' atom with multiple oxidation states can be substituted so that the cation is stabilized in a higher and possibly more reactive oxidation state. The idea is to trap metals in unusual (high energy) oxidation or coordination states so that activity and selectivity are altered. This can be accomplished using any rigid, stable framework. Perovskites are of particular interest because they have low surface areas (high surface areas are reported to favor low selectivities), and because they are stable and easy to make.

PEROVSKITE



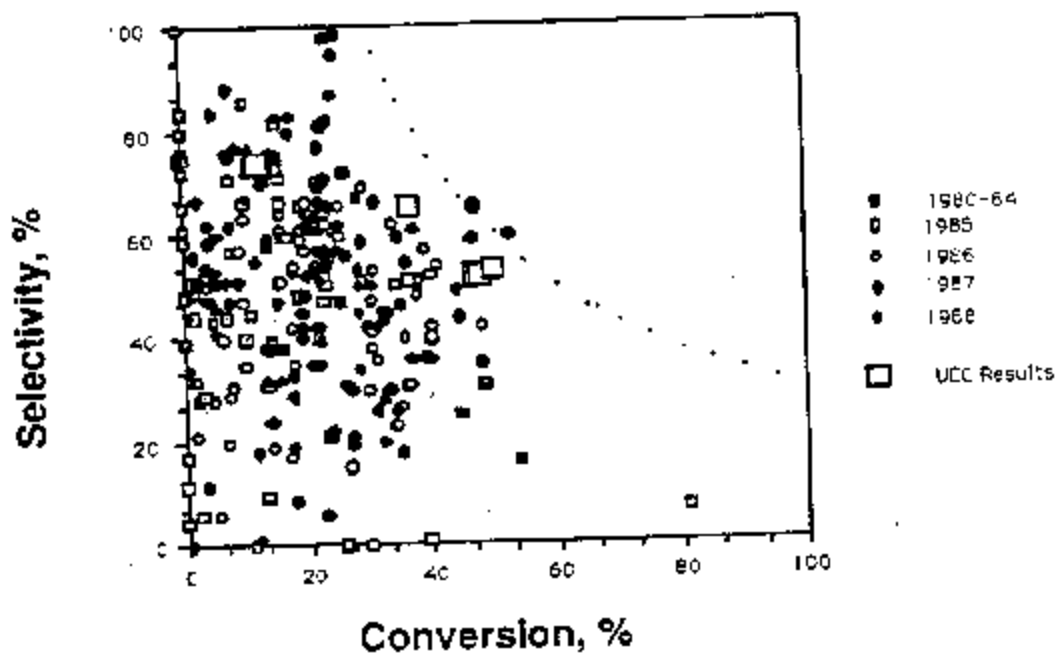
Low to average selectivities and high activities have been obtained using perovskites. Molecular sieves with metals in the framework have not been stable under reaction conditions. One specific complex mixed metal oxide has provided C_2 yields of 17% in initial results. This unexplored class of compounds has a very interesting structure which has not been used previously for any catalytic reactions. The well defined structure will allow the exploration of some mechanistic concepts, and compounds of this structure might provide improved selectivities and activities.

Under "Other Novel Catalysts and Process Ideas," solid base catalysts have not yet been explored. These are materials which might abstract a proton rather than a hydrogen atom from methane. Electron transfer might follow, but the mechanism might be different from that typically observed in methane coupling, providing different selectivities.

Certain other novel catalysts systems have been tested which promise either low-temperature catalysts or reaction systems which do not proceed by the commonly accepted mechanism discussed above.

A modified Jon McCarty plot is shown below with the best results from 166 references. The squares on this plot represent results from Union Carbide.

LITERATURE AND UCC RESULTS



Further economic evaluations with realistic examples will determine what area on such a plot is actually commercially viable, but without this input, the area of C_2 yield above

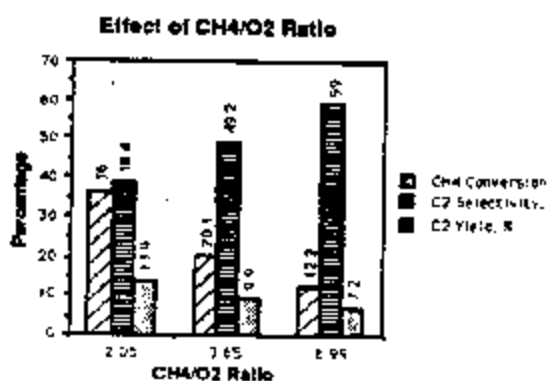
30% (indicated by a dotted line) is considered interesting. C₂ selectivities as high as 74%, C₂ yields as high as 26%, and ethylene to ethane ratios of 5 to 20 have been obtained with one class of promoted metal oxide catalysts. Representative results are shown in the following table where =/- is the ethylene to ethane ratio.

SPECIFIC CATALYST RESULTS

Catalyst	T (°C)	GHSV (Hr ⁻¹)	CH ₄ Conv. %	C ₂ Sel. %	C ₂ Yield %	=/- molar
UCC-A:SC1MM6	760	2087	12	74	9	1.4
UCC-A:D1Y6	700	2341	37	65	23	6.0
UCC-A:BC4MM6	800	2087	50	53	26	6.8
UCC-A:B4Y6	750	878	48	52	24	15
UCC-A:S1Y6	750	1171	47	52	24	17
UCC-MO:13	800	3000	39	43	17	1.8
UCC-G:B4Y3	650	682	32	32	10	0.8

The first five examples in the table correspond to the squares on the plot of literature and UCC results. The UCC-MO:13 catalyst is one of the complex mixed metal oxides from the unexplored class of compounds with the unique structure. The UCC G:B4Y3 catalyst is one of "Certain Other Novel Catalyst Systems" which might lead to a low temperature catalyst.

The following plot (for UCC-MO:13) shows behavior typical for many classes of catalysts tested. The selectivity can be raised at the expense of C₂ yield and methane conversion, so there will be some flexibility in the choice of operating conditions should selectivity or conversion turn out to be more important.



The following data indicates that for a UCC-A (promoted metal oxide) catalyst, two of the components show low methane conversions and C₂ yields, and the metal oxide shows low methane conversions, low C₂ yields, and low C₂ selectivities, but the catalyst made from both promoters and the metal oxide results in high activities, C₂ selectivities, C₂ yields, and ethylene to ethane ratios.

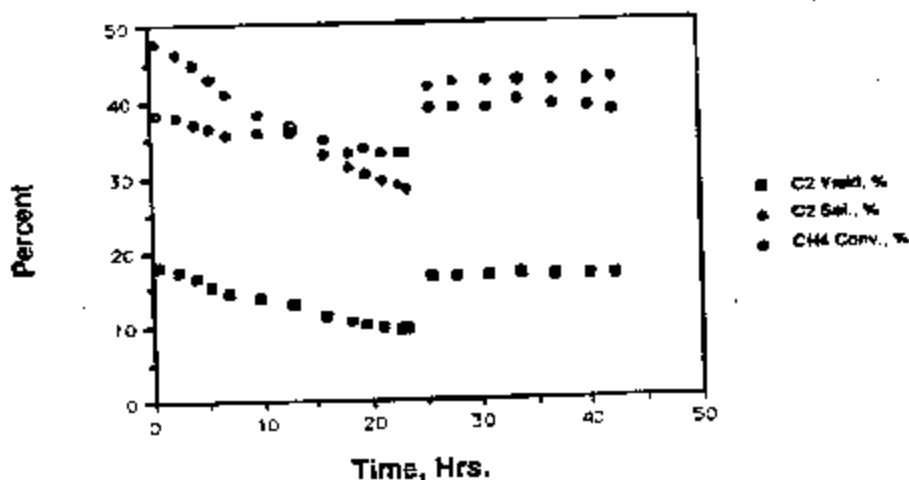
PROMOTER / SUPPORT INTERACTIONS

	T°C	CH ₄ C	Sel	Yield	$\frac{C_2}{C_1}$
Two Components	750	2	49	0.8	0.2
	800	4	53	2	1
Metal Oxide	750	4	26	1	0.7
	800	11	31	3	1
UCC-A:B4Y6	750	48	52	24	15

For these catalysts, two mechanisms of catalyst deactivation were defined, and it was possible to design catalysts to avoid the first type of deactivation. A way to retard and/or reverse the second type of deactivation was discovered. The following plot shows a catalyst which was reactivated after 24 hours of operation. The resulting catalyst was stable and showed no signs of deactivating. During the period after the catalyst was reactivated, the ethylene to ethane ratio was 10.

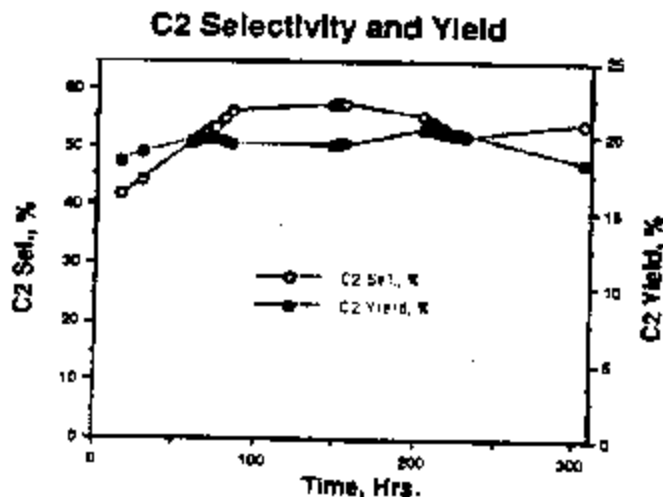
CATALYST DEACTIVATION / REACTIVATION

Results for UCC-A:B4T3



These UCC-A catalysts have long lifetimes if operated under the proper process conditions. In the following plot, changes in C₂ yields and selectivities are the result of changes in one process variable. This catalyst operated for over 330 hours with a final C₂ yield (not shown) of over 20%.

CATALYST LIFETIME



With respect to Task 1, the terms of the contract have been met or exceeded.

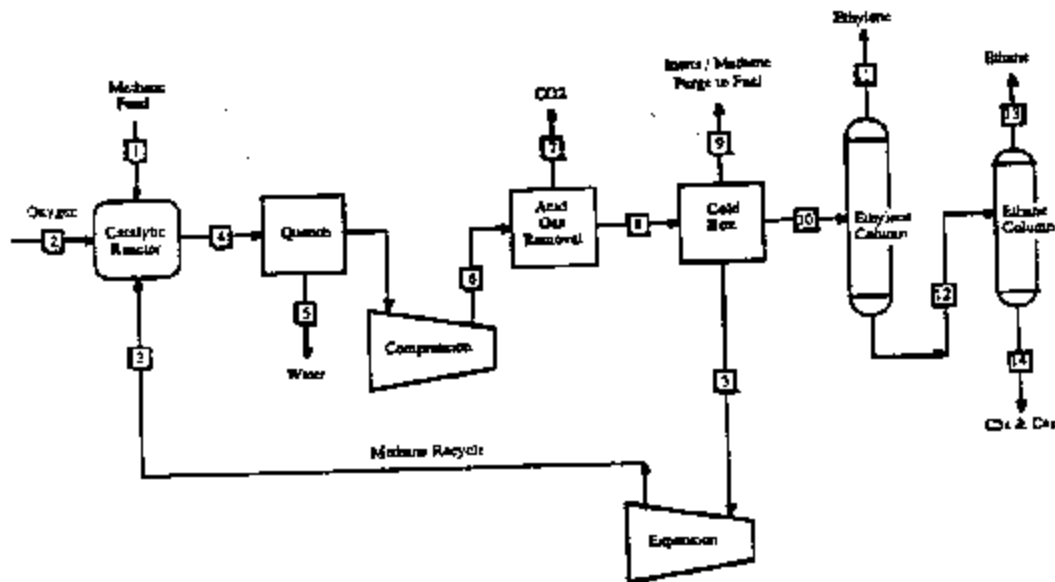
Task 2

Within Task 2, Case 1, a first-pass economic analysis of a process for oxidatively coupling methane to form heavier hydrocarbons, predominantly ethylene and ethane, has been completed. This analysis is based on a detailed heat and material balance of a hypothetical oxidative coupling process, and includes both investment and operating cost estimates. The hypothetical case is based on selectivities in a Phillips patent example [19]. The selectivities used are those reported in the patent, except small amounts of CO and higher hydrocarbons were added to determine the cost of separating these, since, although unreported, they might be expected. The oxygen conversion was increased to 100% and the pressure was raised. Higher conversions usually result in lower selectivities, and it is generally assumed, without adequate data to support the assumption, that higher pressures will result in lower selectivities. To counteract this, the methane to oxygen ratio for our example was changed from 4.4:1 to 9:1, which is known (see above) to increase the selectivity. This would add cost to the separations and require a larger recycle. Case 1 has not been demonstrated in the laboratory. The results of the evaluation will be used for the sensitivity studies, which are in progress. These will be used to direct laboratory efforts toward most economical results.

The results of this initial analysis indicate that a commercial-scale Methane Coupling Unit could produce ethylene at a variable cost of \$0.0588 per pound. The ISBL (inside battery limits) investment for this 1.0 billion pound per year unit would be \$311MM. The result is a Return on Investment of 24 percent (after tax). This is encouraging, since results are considered achievable, and there is room for improvement of the process design.

The Simplified Block Diagram for Case 1 is shown below.

Methane Coupling Diagram Simplified Block Diagram



The Methane Coupling model consists of 40 blocks connected by 50 streams. The Simplified Block Diagram shows only the major streams and processing steps, with each "block" comprising one or more blocks.

The following table presents a summary of the Material Balance for Case 1 that was generated using the model. The Material Balance is expressed in terms of thousands of pounds per hour for a unit producing one billion pounds per year of ethylene.

Methane Coupling Material Balance - Case 1

<u>Stream:</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
	<u>CH₄</u> <u>Feed</u>	<u>O₂</u> <u>Feed</u>	<u>CH₄</u> <u>Recycle</u>	<u>Rx</u> <u>Product</u>	<u>Quench</u> <u>Water</u>	<u>Comp</u> <u>Dischg</u>	<u>CO₂</u> <u>Purge</u>
N ₂	2.6	6.5	80.6	89.7		89.7	
O ₂		285.8	0.8	0.9		0.9	
CO			0.8	0.9		0.9	
CO ₂	1.1			51.1		51.1	51.1
CH ₄	371.6		922.2	1003.7		1003.7	
C ₂ H ₄			12.5	133.5		133.5	
C ₂ H ₆	3.7		1.8	110.0		110.0	
C ₃ H ₆				11.7		11.7	
C ₃ H ₈				7.4		7.4	
C ₄ H ₈				0.5		0.5	
H ₂ O				280.7	280.7		
Total	379.0	292.3	1018.7	1690.1	280.7	1409.4	51.1
<u>Stream</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>
	<u>Cold Box</u> <u>Feed</u>	<u>Inert</u> <u>Purge</u>	<u>C₂H₄ RC</u> <u>Feed</u>	<u>C₂H₄ RC</u> <u>Make</u>	<u>C₂H₄ RC</u> <u>Tails</u>	<u>C₂H₆ RC</u> <u>Make</u>	<u>C₂H₆ RC</u> <u>Tails</u>
N ₂	89.7	9.1					
O ₂	0.9	0.1					
CO	0.9	0.1					
CO ₂							
CH ₄	1003.7	81.4					
C ₂ H ₄	133.5	0.1	120.9	119.8	1.1	1.1	
C ₂ H ₆	110.0		108.1	0.1	108.0	107.8	0.2
C ₃ H ₆	11.7		11.7		11.7	1.3	10.4
C ₃ H ₈	7.4		7.4		7.4	0.1	7.3
C ₄ H ₈	0.5		0.5		0.5		0.5
H ₂ O							
Total	1358.3	90.8	248.6	119.9	128.7	110.3	18.4

The Catalytic Reactor block is a non-rigorous representation of the conversion of a specified amount of raw material into products via a few simple stoichiometric equations. Reaction mechanisms and the effects of temperature and pressure on the reaction rates are not considered. An overall heat balance is performed, however, as the utilization of the heat released by this reaction has a significant impact on the overall process economics. For this Case 3, the assumed operating conditions and selectivities to products are as follows:

- * Methane - to - oxygen ratio = 9/1
- * Pressure = 150 psig
- * Temperature = 725 °C
- * Oxygen purity = 97.5 mole %
- * Selectivity =
 - 47.3 % ethylene
 - 38.1 % ethane
 - 6.1 % CO₂
 - 1.0 % CO
 - 4.6 % propylene
 - 2.8 % propane
 - 0.2 % butene

The feed to the Catalytic Reactor is a mixture of three process streams: the fresh methane feed (stream 1), the oxygen feed (stream 2), and the methane recycle (stream 3). Nearly all of the oxygen that is fed to the reactor is converted. But this corresponds to only a 22.4 % conversion of methane per pass due to the high ratio of methane to oxygen in the feed. Therefore, unreacted methane is the major constituent in the reactor product (stream 4).

In the Quench step, a fixed temperature-pressure flash is performed which calculates rigorously the amount of water that will condense out of the reactor product stream when it is cooled to 45 °C (with cooling water). The remainder of water is assumed to be removed via a regenerable fixed-bed drying system. Stream 5 is the water removed via the combination of these two operations.

The Compression step is a rigorous calculation of the amount of power required to deliver the quenched reactor outlet stream to the pressure needed by the downstream processing blocks. In this case the pressure that is needed is set by the Cold Box, which operates at 530 psig. This operation would actually be carried out in three equal stages separated by intercoolers to limit the discharge temperature from each. For Case 1, the power required for this compression step is 27,000 HP per stage -- 81,000 HP total. Stream 6 is the discharge from the third stage.

The Acid Gas Removal step is a non-rigorous representation of an amine absorption

system, similar to those used to sweeten natural gas. This is standard technology, and this process presents no unique requirements. Stream 7 is the carbon dioxide that is removed in this step.

The Cold Box and Expander steps are a rigorous treatment of the cryogenic distillation operations by which the unreacted methane is separated from the ethylene, ethane, and heavier products; and by which a purge stream is taken to remove inerts that enter the process via the raw materials. Cold Box designs are proprietary, but it can be revealed that the unit consists of a series of partial condensers in which ethylene, ethane, and heavier components are removed as the liquid product (stream 10), and in which a methane-rich stream is taken as the vapor product. Stream 3 is the methane recycle, which goes back to the reactor block. A purge (stream 9) is taken to remove inerts from the cycle.

The Ethylene Column block is a rigorous representation of the distillation column which produces refined (99.85 %) ethylene (stream 11) from the crude product stream taken from the Cold Box (stream 10).

Finally, the Ethane Column block is a rigorous representation of the distillation column which produces ethane at a 98 % purity (stream 13) from the Ethylene Column tails product (stream 12). Stream 14 is the remaining propylene, propane, and butene, which can either be sold as a mixture or further refined as individual products.

The investment cost estimate for the ISBL (inside battery limits) portion of the unit was obtained by sizing and costing 65 of the largest Major Equipment items using standard factors. Only one-third of the total number of Major Equipment items that would ultimately be required were identified, but these accounted for two-thirds of the total Major Equipment cost. The bulk material and labor, and the other investment quantities were estimated by applying standard factors to the adjusted total number of Major Equipment items and cost. Results are summarized on the next page.

Methane Coupling Investment Summary

Reaction and Quench System	\$81MM	+/-40%
Compression System	\$84MM	
Gas Pretreating System	\$14MM	
Cold Box and Expander System	\$52MM	
Refining System	\$18MM	
Refrigeration System	\$63MM	
Total ISBL (Inside Battery Limits) Investment	\$311MM	
+/- 40%		
Oxygen Plant (3,500 tons/day)	\$64MM	
OSBL (Outside Battery Limits)	\$78MM	
<u>Total Fixed Investment</u>	<u>\$453MM</u>	<u>+/- 40%</u>

The operating cost estimate includes raw material requirements, by-product credits, and utilities. The raw material and co-product credits come directly from the yield assumptions. The utilities were estimated by first tabulating the heating, cooling, and shaft-work inputs and outputs from the model, and by then applying a manual heat-integration technique to reduce the amount of energy that must be imported via utilities.

It was assumed that the waste-heat from the Reaction System could be used to generate high-pressure steam, which would then pass through condensing turbines to help drive the Compression and Refrigeration Systems. For Case 1, it was found that this waste heat alone was sufficient to provide the 116,000 HP needed to drive these systems. Therefore, the major utility requirements for the Base Case are the fuel gas required to preheat the raw materials to the reactor operating temperature, and the electricity required to operate the oxygen plant.

The balance sheet on the next page summarizes both the investment and operating cost breakdown for the Methane Coupling process.

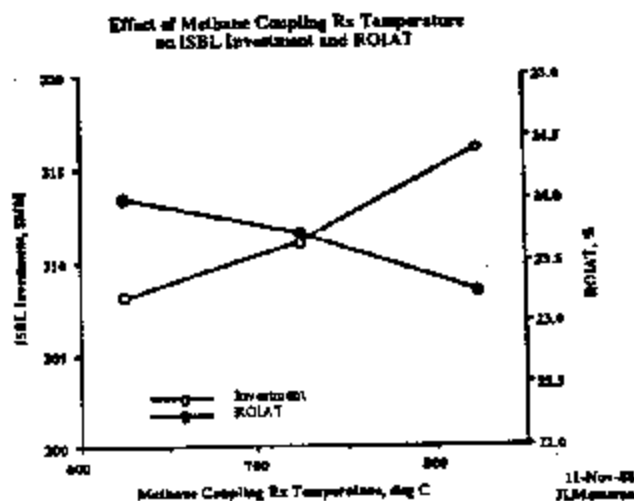
Methane Coupling Economics

	<u>Price</u> <u>\$/Unit</u>	<u>Volume</u> <u>Units/Yr</u>	<u>Value</u> <u>\$MM/Yr</u>
Investment			
ISBL		1000	311
Oxygen Plant		3508	64
OSBL			78
Total Fixed Investment			453
Working Capital			15
Total Utilized Investment			468
Ethylene Sales	\$0.320	1000	320
Variable Cost			
Methane, Lb	\$0.043	3161	136
By-Product Credit			
Fuel Gas, MMBTU	\$1.800	15	-26
Ethane, Lb	\$0.055	920	-51
Propylene, Lb	\$0.205	87	-18
Other Hydrocarbons, Lb	\$0.072	65	-5
Total By-Product Sales			-99
Utilities, MMBTU	\$1.800	12	22
Catalyst & Chemicals			1
Total Variable Cost			59
Fixed Cost			40
Total Cash Cost			98
Operating Income			222
Depreciation (10%)			45
NIAT (37% Tax Rate)			111
ROIAT			24%

The results of this initial analysis indicate that a commercial-scale unit could produce ethylene at a variable cost of \$0.0588 per pound. The ISBL (inside battery limits) investment for this 1.0 billion pound per year unit would be \$311MM. This results in a Return on Investment of 24 percent (after tax).

Sensitivity studies around Case 1 have been initiated. The first consider the effect

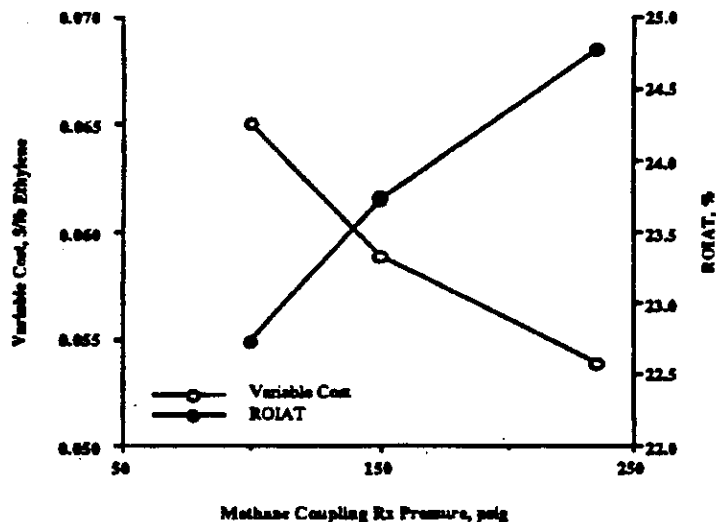
of the reactor temperature and pressure on the base case profitability, independent of any effect that these might have on the reacted product mix. The following graph summarizes the results for temperature.



As the reactor temperature increases within the range of 625-825 °C, so does the ISBL investment. This is due to the higher cost of construction for the reactor vessel at higher temperatures. It was found that the effect of reactor operating temperature on operating cost was negligible. Higher investment without a concurrent decrease in operating costs causes the Return on Investment after tax (ROIAT) to decrease accordingly. Therefore, all things being equal, the economics favor a lower reactor operating temperature.

The following figure shows that as the reactor operating pressure increases within the range of 80-240 psig, the variable cost per pound of ethylene decreases.

Effect of Methane Coupling Rx Pressure on Variable Cost and ROIAT



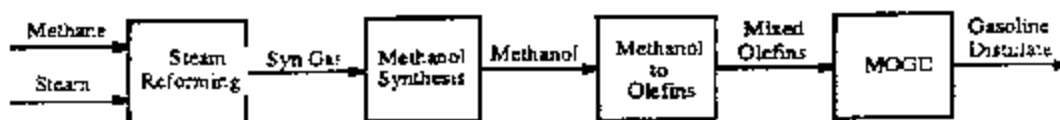
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This is due entirely to the lower compression costs that higher reactor operating pressure affords. It was found that higher reactor pressure decreases the compression system investment, but this is offset by higher reaction system investment, so that, overall, the effect of reactor operating pressure on total investment is negligible. Lower operating costs without a concurrent increase in investment causes the ROIAT to increase accordingly. Therefore, all things being equal, the economics favor a higher reactor operating pressure. Raw material costs are based on late 1988 dollars for Case 1.

The economics of a Comparison Case based on demonstrated technology have been calculated. This case consists of the conversion of methane through synthesis gas to methanol, the conversion of methanol to a mixture of light olefins, and the conversion of this mixture to liquid fuels. This case will be used to establish a benchmark against which to compare emerging technology for the direct conversion of methane to ethylene and liquid fuels. It will be compared with results from Case 2, the conversion of methane to fuels through intermediate light gases rich in C₂'s (Case 1 integrated with Mobil Olefins to Gasoline and Distillate, not yet done).

In the Comparison Case, synthesis gas production is accomplished by steam reforming of natural gas and ICI's low pressure methanol process is used to convert the synthesis gas to methanol. Methanol is then converted to olefins via the Methanol to Olefins (MTO) process and the final conversion of olefins to liquid fuels is accomplished using the Mobil Olefins to Gasoline and Distillate (MOGD) process. The block diagram of this is shown below.

Methane Coupling Comparison Case Block Diagram



The Comparison Case is based upon a total production of 3320 metric tons per day of methanol in two parallel operating units followed by single train MTO and MOGD facilities which produce 10,700 barrels per day of gasoline and distillate. The process sequence for the conversion of methane to methanol is based upon SRI International's [20] formulation of an integrated process to produce synthesis gas from methane by steam reforming of natural gas followed by ICI's low pressure process for the conversion of synthesis gas to methanol. The crude methanol product contains 18.3 wt% water and can be fed directly to the process for converting methanol to olefins. Mobil's Olefins to Gasoline and Distillate (MOGD) process is used to convert olefins to liquid fuels with a distillate to gasoline ratio of six to one. Raw material costs are based on early 1988 dollars for the Comparison Case. This will be updated later when this case is compared with Case 2, the conversion of methane to fuels through intermediate light gases rich in C₂'s (Case 1 integrated with Mobil Olefins to Gasoline and Distillate).

Methane to Distillate Comparison Case Economics

	<u>Base Case</u>			<u>Hypothetical Case</u>		
	<u>Price</u>	<u>Volume</u>	<u>Value</u>	<u>Price</u>	<u>Volume</u>	<u>Value</u>
	<u>\$/Unit</u>	<u>Units/Yr</u>	<u>\$MM/Yr</u>	<u>\$/Unit</u>	<u>Units/Yr</u>	<u>\$MM/Yr</u>
Investment						
ISBL, bbl/day		10700			16100	
Methane to Methanol			249			255
Methanol to Olefins			44			60
Olefins to Gasoline & Distillate			30			41
Total ISBL			323			356
OSBL			132			149
Total Fixed Investment			455			505
Working Capital			49			60
Total Utilized Investment			504			565
Sales						
Gasoline & Distillate, gal	\$1.71	147.63	252	\$1.320	222.13	293
Variable Cost						
Methane, Lb	\$0.039	1491	59	\$0.039	2042	80
Other Raw Materials,			6			6
Utilities, MMBTU	\$1.650	2	4	\$1.650	4	6
Total Variable Cost			69			92
Fixed Cost						
Assigned Overhead			11			13
Total Cash Cost			118			147
Operating Income						
Depreciation (10%)			46			51
Local T&I			9			10
NIAT (37% Tax Rate)			50			54
ROIAT			10%			10%

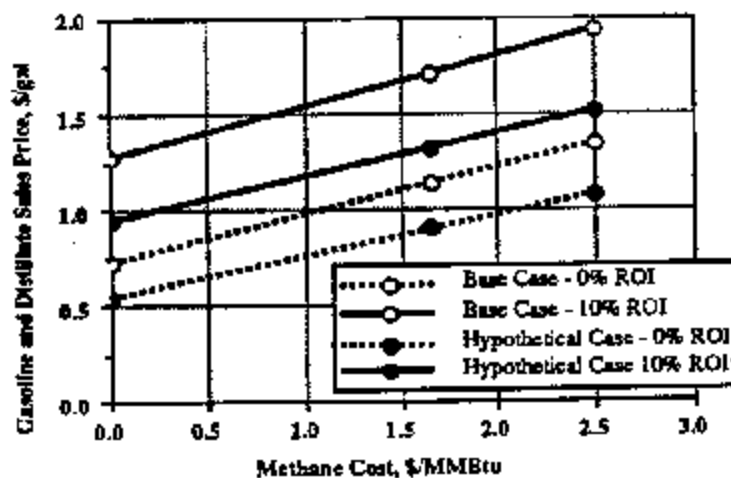
The total fixed investment is \$455MM and a sales price of \$1.71/gallon of gasoline and distillate products will be required in order to generate a ten percent after tax return on

investment based upon a natural gas cost of \$1.65/MMBTU. Even if the methane were free and a zero percent return on investment were acceptable, the required liquid fuels sales price of \$0.72/gallon would still exceed the present price of about \$0.50-0.60/gallon. Clearly, existing technology for the conversion of methane to liquid fuels is not competitive with the current oil based route in the present pricing environment.

There are some indications in the literature that further improvements may be achievable by reducing the consumption of methane and/or by decreasing the total fixed investment for the conversion of methane to methanol. For example, Lurgi's [21] low pressure methanol process claims a methane consumption which is about 14% lower than in the present analysis and Korchnak [22] has reported a 25% reduction in investment using a "Catalytic Partial Oxidation and Methanol Synthesis" scheme instead of the conventional "Steam Reforming and Methanol Synthesis" process. Assuming that both of these improvements could be achieved simultaneously, the total fixed investment required for the production of 16,100 barrels per day of gasoline and distillate is \$504.6 MM and an average sales price of \$1.32/gallon will generate an after tax return on investment of ten percent.

The impact of methane cost on the required sales cost of gasoline and distillate for the Comparison Case and the Hypothetical Case - that assuming the improvements described above - is illustrated by the following graph.

Impact of Methane Cost on the Required Sales Price for Gasoline and Distillates



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GLCulp/JLMathern

In summary, for Task 1, continuous, unattended operation capabilities have been installed in four reactors in two laboratories. One reactor is capable of pulsed, sequential reactions. Eleven classes of compounds were tested (164 catalysts plus pure components and supports). Yields per pass of several different types of catalysts compete with better literature results. One catalyst system gives ethylene to ethane ratios of 3 to 20 with C₂ yields of 20-26%. Selectivities of up to 74% have been achieved at lower methane conversions. A stable catalyst system showed a C₂ yield of 20% with a 56% selectivity to C₂'s after 330 hours. Within Task 2, an economic evaluation of the Comparison Case (methane → synthesis gas → methanol → olefins → fuels) has been completed. A similar case was completed which incorporated some optimistic assumptions. Economics for a hypothetical Case 1 (methane to ethylene) were completed. Sensitivity studies have been started.

Plans are to continue work according to the contract plan by making and screening novel catalyst systems within the categories proposed and described (to a limited extent) above, by pursuing the better leads with fundamental and process studies, by completing sensitivity studies on Case 1, by doing economic studies of laboratory catalyst systems which are the most promising, and by completing the economic evaluation of Case 2, the conversion of methane through C₂'s to fuels.

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