DIRECT CONVERSION OF METHANE TO C_2's AND LIQUID FUELS -- PROCESS ECONOMICS

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by

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TITLE: Direct Conversion of Methane to C2's and Liquid Fuels - Process Economics

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<u>Objective:</u> The objective of this work is to evaluate, from an engineering perspective, the economics for different conceptualized schemes for the conversion of methane through intermediate light gases rich in C2's to liquid hydrocarbon fuels, and to provide economic direct on to the chemistry program through sensitivity studies of key process variables.

<u>Technical Approach:</u> The economic sensitivities of important process variables were evaluated for actual and hypothetical catalyst systems. The economics of producing gasoline and distillates using methane coupling were evaluated and compared to the economics of producing gasoline and distillates from methane through synthesis gas, methanol, and olefins.

<u>Significant Accomplishments:</u> This report describes the final results of the engineering portion of Union Carbide's two-year contract. Economic results from studies r   ial and hypr hetical cases for the conversion of methane to C2's will be presented. E   nomics for the best process configuration were based on laboratory results using a BaCO- $_2$O$_3$/ethyl chloride catalyst with a methane / oxygen feed ratio of 7/1, a reactor temperature of 725 °C, a methane conversion of 18.4%, and a selectivity to C2's of 76.7%. It was assumed that the ethylene / ethane production ratio would be 3/1, that co-product ethane would be cracked to ethylene, and that the reactor pressure was 50 psig. Important process variables studied included selectivity to C2's, methane conversion, reactor diluents, methane / oxygen feed ratio, co-feed versus sequential mode, fixed-bed versus fluidized-bed reactors, ethylene / ethane production ratio, the fate of co-product ethane (crack versus sell), reactor pressure, and reactor temperature. For both nitrogen and steam dilution cases, the economics improve with increasing methane / oxygen feed ratio, which increases selectivity to C2's at the expense of lower methane conversion. The methane dilution case is favored economically over any of the nitrogen and steam dilution cases, due to the higher selectivity to C2's.

The economics of producing gasoline and distillates from methane via olefins from this oxidative coupling process are essentially equivalent to the economics of producing liquid fuels from methane via synthesis gas, methanol, and olefins. This result is viewed as encouraging given the early stage of development of oxidative coupling catalysis, since future improvements should confer superior economics to the oxidative coupling process.

Direct Conversion of Methane to C_2's and Liquid Fuels - Process Economics

Introduction

This paper describes the most significant final results of the engineering portion of Union Carbide's two-year contract. The objective of this work has been to evaluate, from an engineering perspective, the economics for different conceptualized schemes for conversion of methane through intermediate light gases rich in C_2's to liquid hydrocarbon fuels, and to provide economic direction to the chemistry program through sensitivity studies of key process variables. The following topics will be addressed:

1. Sensitivity of the Methane Coupling economics to:

   - reactor diluent
   - co-feed versus sequential feed
   - methane-to-oxygen feed ratio

   for making ethylene on a demonstrated catalyst.

2. Economics of producing gasoline and distillate fuels via:

   - Methane Coupling
   - synthesis gas and methanol.

3. Sensitivity of the Methane Coupling economics to:

   - methane conversion
   - selectivity to C_2's

   for making ethylene on a hypothetical catalyst.

Summary

The major findings of this engineering / economic evaluation are:

1. The preferred Methane Coupling configuration is:

   - Methane diluent
   - Co-feed mode
   - High methane-to-oxygen feed ratio (7/1)
     - low methane conversion (18%)
     - high selectivity to C_2's (77%)

   for making ethylene on a demonstrated catalyst.

   Yield-to-C_2's is not a good general predictor of economics.

2. Equivalent economics for producing gasoline and distillate fuels via:

   - Methane Coupling
   - synthesis gas and methanol

   This is viewed as an encouraging result given the early stage of development of Methane Coupling catalysis.

3. For a hypothetical Methane Coupling catalyst operating at current conditions, high selectivity to C_2's is more important than high methane conversion.

   Future catalyst improvements should confer superior economics to the Methane Coupling Process.

Discussion

Methane Coupling Process Simplified Block Diagram

Figure 1 summarizes the process arrangement that has been used for the Methane Coupling sensitivity studies. It depicts not only the integration of this process with the MOGD (Mobil Olefins to Gasoline and Distillates) process for producing gasoline and distillate fuels, but also the optional Refining System which would be required to produce high-purity ethylene.

In the Catalytic Reactor System, fresh and recycle methane and any diluent are contacted with either air or oxygen supplied externally to conduct the oxidative coupling reaction. Both fixed-bed and fluidized-bed reactor systems have been evaluated.

The fixed-bed reactor system consists of a series of shell-and-tube heat exchangers, the tubes packed with a supported catalyst. It has been assumed that stainless steel tubes would provide sufficient corrosion resistance. The large exothermic heat of reaction dominates the reactor design by requiring that a large heat transfer area be provided. In the fixed bed reactor system the reaction heat is removed as superheated 600 psig steam, which is generated on the shell sides of the reactors. This is accomplished by spraying in a mist of hot 600 psig condensate which vaporizes instantly and superheats rapidly to near the process-side temperature. This superheated steam is used to drive condensing turbines in the Compression and Refrigeration portions of the process.

Alternately, a dilute-phase co-current down-flow reactor design has been used as the model for the fluidized-bed reactor system in this evaluation. The advantage of this system over more conventional fluidized-bed designs is the large catalyst-to-process flow ratios and the short contact times that are made possible. All of the reactor system vessels are constructed of refractory-lined steel, which confers both temperature and corrosion/erosion resistance. In this system, the large exothermic heat of reaction is removed by spraying hot condensate directly onto the circulating catalyst solids, generating low-pressure superheated steam. This superheated steam is used to drive condensing turbines in the Compression and Refrigeration portions of the process.

Whether fixed-bed or fluidized-bed, the reactor feed is brought up to the reactor operating temperature by first cross-exchanging with the hot reactor product stream, followed by additional heating with a direct gas-fired heater. Only a portion of the methane that is fed is converted on each pass, but typically with a fairly high selectivity to ethylene and ethane. The balance of the methane that is converted forms carbon monoxide and dioxide, and C_3

and heavier hydrocarbons.

The reactor product gas is cooled first in the feed cross-exchanger, and then is further cooled in a second exchanger to produce hot condensate. The cooled reactor product gas then enters the Quench portion of the process. This is a large water-cooled partial condenser which cools the gas down to ambient temperature, and removes most of the water of reaction as a liquid. From there, the product gas enters the Compression System.

The Compression System consists of four stages of centrifugal compression. The first stage operates at a suction pressure of about 16 psig, and handles only the Steam Cracker System product gas. The Catalytic Reactor product mixes with the Steam Cracker product at the second stage, which operates at a suction pressure of 40 psig. Water is condensed out of the process stream at each of the compressor intercoolers. The discharge pressure from the fourth stage of the Compression System is 300 psig.

The compressed product gas then enters the Acid Gas Removal System, which consists of a standard amine-scrubbing system for removal of carbon dioxide from the product gas. This is followed by a molecular sieve dryer system which removes the last traces of moisture from the product gas. The compressed, scrubbed, and dried product gas then is ready for processing in the Cold Box System.

The Cold Box feed first enters a series of refrigerated partial condensers, which remove successively larger portions of the stream as liquid. The last of these partial condensers operates at a temperature of less than -95°C (-140°F). These liquid fractions are richer in C_2 and heavier hydrocarbons than the remaining vapor, and are fed to a Methane Column for removal of the light components. The vapor that is left after the final partial condenser then is combined with the vapor off the top of the Methane Column for further processing in a series of centrifugal expanders. Separators following each of these expanders collect liquids which are rich in C_2's and heavier hydrocarbons. These liquids are recycled to the Methane Column. A portion of the remaining vapor is removed as a purge from the process, while the rest is recycled back to the Catalytic Reactor System. The purge gas is then expanded down to 5 psig before it is released from the process. Both the purge and recycle gas streams are heated back up to ambient temperature by cross-exchanging with the gas entering the Cold Box System. This cross-exchanging reduces the load on the Refrigeration System (not shown in Figure 1).

The bottoms product from the Methane Column in the Cold Box System consists of C_2 and heavier hydrocarbons. This can be fed directly to the MOGD System where the ethylene, propylene, and a substantial portion of the C_4's are converted to gasoline and distillate

fuels. Ethane passes through the MOGD System unconverted.

Alternately, the bottoms product from the Methane Column in the Cold Box System can be fed to a two-column Refining System for making high-purity ethylene. The De-ethanizer separates the C_3 and heavier hydrocarbons from the ethylene and ethane. The overhead make stream from the De-ethanizer is fed to the Ethylene Column. This column employs a vapor recompression system to reduce the refrigeration load on the column condenser. High purity ethylene (99.85% by volume) is produced as the overhead product, while the bottoms product is ethane containing less than 1% ethylene.

Ethane rejected by either the MOGD System or the Ethylene Column is returned to a conventional Steam Cracker System. About 55% of the ethane that enters the cracking furnaces is converted, with an 85% selectively to ethylene. The rest of the ethane that is converted forms hydrogen, methane, carbon monoxide and dioxide, propylene and heavier hydrocarbons. The cracked gas exits the furnaces directly into transfer line exchangers which cool the gas and produce dilution steam for the furnaces.

The furnace gas then enters a Quench section where it is further cooled by direct contact with cold water in a large column. The quenched gas then enters the Compression System, where it is combined with the product from the Catalytic Reaction System.

Methane Coupling Case Descriptions

Table 1 summarizes the four Methane Coupling reactor diluent cases that have been evaluated. It was assumed that the maximum amount of oxygen that can be present in the reactor feed is about 10-11% by volume, determined by the explosive limits for the mixture. However, the oxidative coupling reaction consumes only two moles of methane per mole of oxygen. The methane conversion per pass is thereby limited to less than 25%, if only methane and oxygen are reacted with an initial oxygen concentration of 10-11%. Therefore, the incentive for adding a diluent is to allow the methane conversion per pass to be increased above what would be possible by feeding methane and oxygen alone.

The Nitrogen Diluent case is the logical starting point for these sensitivity studies since most of the laboratory studies on Methane Coupling are conducted in nitrogen. The catalyst performance which is reflected in Table 1 for the Nitrogen Diluent case is based on actual Union Carbide laboratory results with a $BaCO_3$ on alumina catalyst with ECl added as a promoter at atmospheric pressure. It has been assumed that the reactor pressure can be increased to 50 psig without major impact on the catalyst selectivity. The ratio of methane

to oxygen in the feed for this case is 2, which was the mid-point of the range studied. The selectivity to C_2's is only 50% for this case, but the methane conversion is 45%, giving a yield to C_2's of 22%. This performance is competitive with any other oxidative coupling catalyst described in the literature. The reactor type is the fixed-bed system described in the previous discussion of the Simplified Block Diagram. An advantage of the Nitrogen Diluent case is that the oxygen can be added to the process in the form of air. This eliminates the need for an Air Separation system, which is both a high investment and a high operating cost item.

The Methane Diluent case described in Table 1 covers the case wherein only methane and oxygen are fed to the catalytic reactor at an initial oxygen concentration of 10-11%. Since the methane is in vast excess to its requirements in the reaction, this excess methane essentially becomes the diluent. The catalyst performance for this case is based on actual Union Carbide laboratory results from the same $BaCO_3$ catalyst that was used for the Nitrogen Diluent case. Again, it has been assumed that the atmospheric pressure laboratory results could be translated to 50 psig. The reactor type is fixed-bed. The methane-to-oxygen feed ratio is 7. Note that while the conversion per pass for this case is lower than that for the nitrogen diluent case, the selectivity to C_2's is higher. However, the overall effect is a yield-to-C_2's of only 14%.

The Steam Diluent case considers an alternative to nitrogen as a diluent in the Methane Coupling Process. The catalyst performance for this case has been assumed to be identical to that for the Nitrogen Diluent case for lack of better information. The primary incentive of steam versus nitrogen as a diluent is that almost all of the steam will condense in the Quench step following the Catalytic Reactor, and will not have to be handled in the downstream Compression and Separation Systems. There is some precedent for using steam as a diluent also, since most hydrocarbon cracking operations use steam as a diluent to limit coke formation on the furnace tubes.

For the Nitrogen, Methane and Steam Dilution cases, all of the reactants are mixed at the inlet to the fixed-bed catalytic reactor and enter all at the same time, which is referred to as the Co-feed system.

In the Sequential Feed system, the methane and oxygen are introduced to the reactor separately, rather than together. This allows the methane conversion per pass to be increased without a diluent, avoiding the explosive mixture limitations of the Co-feed cases. To do this, the catalyst is oxidized with air in one step, and then reduced in a separate step via the coupling reaction by contacting it with methane. The conversion per pass in this system is limited only by the relative proportions of methane and catalyst present and by the methane residence time in this second reaction zone. The catalyst

performance data depicted in Table 1 for the Sequential Feed case is based on literature results[1,2] for an Arco catalyst system. A 24% methane conversion per pass and 62% selectivity to C_2's have been assumed, giving a 15% yield. Note that this case makes much more heavy C_4's+ hydrocarbons than the Co-feed cases. The fluidized-bed reactor design has been assumed for this case, allowing the sequential reaction to be carried out by feeding the methane and air separately but continuously to different points in the catalyst cycle. A fixed-bed Sequential Feed process is felt to be impractical.

The oxygen conversion in the Catalytic Reactor has been assumed to be 100% for all cases, versus actual laboratory oxygen conversions of 75 to 95%. It has been assumed that half of the hydrogen and carbon monoxide that enter the Reactor via the methane recycle stream are converted to water and carbon dioxide, respectively. All of the ethane and ethylene that is recycled to the Reactor is assumed to be burned to carbon dioxide. Therefore, C_2 recycle is minimized.

All of these cases assume that the ratio of ethylene to ethane in the Catalytic Reactor product is about 3/1. Laboratory studies indicate that using ECl as a promoter can produce this relatively high ratio versus the more typical ethylene to ethane ratio of 1/1 that has been reported in the literature without a promoter. Sensitivity studies indicate that achieving this relatively high ratio is important economically, but that still higher ratios become less so. The economic significance of the ethylene to ethane ratio should not be ignored, even though assuming about the same ratio for each of these cases eliminates this variable from this sensitivity analysis.

Methane Coupling Investment Costs

Table 2 summarizes the results of the investment estimates that have been prepared for the four Methane Coupling cases. In each case, facilities are included to produce refined ethylene, but not gasoline and distillate fuel via the MOGD Process. The inherent assumption is that the process that is best for producing ethylene will also be the best for making liquid fuels

All the ISBL (Inside Battery Limits) investment figures are of ±25% quality. They have been built-up from discrete, individual equipment sizes and costs, and have only been grouped into process systems to facilitate comparisons among the cases. They are based on 1989 US Gulf Coast non-union construction costs, and include a 15% contingency. The OSBL (Outside Battery Limits) investment has been estimated as 40% of the combined ISBL plus Air Separation investment.

The Nitrogen Diluent case has by far th ighest investment cost of the group. Compared to the other cases, this case is more costly in the Compression, Acid Gas Removal, Cold Box and Refrigeration Systems. These systems are all involved in maintaining the large nitrogen diluent cycle, and in separating the excess nitrogen from the unreacted methane. Therefore, while using nitrogen as a diluent may be logical for laboratory s dies, a Nitrogen Diluent full-scale facility is impractical due to the high investment c st.

The _ethane and Steam Diluent and the Sequential Feed cases all have about the same investment cost, well within the ±25% investment estimate accuracy.

The cost of the Catalytic Reactor System is most closely related to the amount of heat released in the reaction step. The heat released by the oxidative coupling reaction is much less than that for the non-selective burning reaction. Therefore, the Methane Diluent case has the lowest Catalytic Reactor investment, since it has the highest selectivity to C_2's, and hence the lowest amount of carbon monoxide and dioxide formed via the burning reaction.

Note that whether a case allows feeding air versus oxygen is not a significant distinguishing feature among these cases. This is because the Air Compression Systems for delivering air to the Catalytic Reactor are almost equal in cost to the Air Separation Systems.

Methane Coupling Economics

Table 3 summarizes the economics of the four Methane Coupling cases. Consistent with the investment estimates, these economics have been cast on the basis of producing ethylene for sales.

The Total Fixed Investment for each case is from Table 2. The Working Capital is an estimate of the value of the inventory and accounts receivable that would be involved in a Methane Coupling operation. The Total Utilized Investment is the sum of the Total Fixed Investment and the Working Capital.

All of the Operating Costs in Table 3 have been expressed in terms of $MM (millions of dollars) for a unit producing one billion pounds oer year of ethylene. Methane is by far the largest Operating Cost component. It has been assumed for this analysis that methane is being purchased at the 1989 average US Gulf Coast Intrastate Delivered price of $2.15 per MMBtu, or 5.1¢/lb. The Methane Diluent case has the lowest methane usage due to its high selectivity to C_2's.

The By-Product Credits are the sum of the values of the C_3 and heavier co-products, plus the fuel value of the lights purge stream. The Nitrogen Diluent case has a lower By-Product Credit than the others since the fuel value of its lights purge stream is extremely low. On the other hand, the economics of the Sequential Feed case is most sensitive to the By-Product Credits, because of the large amount of C_4 and heavier materials produced in this process.

The Utilities requirements for the Methane Coupling cases are mostly the fuel to fire the Catalytic Reactor preheaters, plus the electrical power to drive the Compression, Refrigeration, and Air Separation or Air Compression Systems. However, it has been found that the fuel requirements can usually be satisfied by the inerts purge stream from the Cold Box. Likewise, credit has been taken for the steam that is produced in the Catalytic Reactor Systems, which is used in turbine drivers and offsets the electrical requirements.

The Steam Diluent case is distinguished by its high utility cost, since most of the steam generated in the Catalytic Reactor System must be used as diluent, rather than as motive steam in turbines elsewhere in the process. On the other hand, the Sequential Feed case is distinguished by its low utility cost. The absence of a diluent that characterizes this case causes the Compression and Refrigeration System operating costs to be low. Also, air is used to oxidize the catalyst, which eliminates the high operating cost for the Air Separation System.

The Fixed Costs are mostly the cost of maintenance, which is assumed to be an annual percentage of the Total Fixed Investment. Operating labor is also included.

The Total Cash Cost is the sum of the Variable and Fixed Operating Costs. This represents the net cost of producing the product, and does not include any ex-plant costs such as distribution, or any marketing, sales, or technical staff support costs.

The ROIAT (Return on Investment After Tax) for each case is based on a 1989 average sales price of $0.22/lb for ethylene. ROIAT is the ratio of the NIAT (Net Income After Tax) to the Total Utilized Investment. NIAT is sales income minus cash cost, depreciation, and taxes.

ROIAT can be thought of as the first year's "interest rate" that the facility investment would return to the owners, assuming capacity operation. In this light, the returns from the Nitrogen and Steam Diluent cases are clearly unacceptable. The Methane Diluent case and the Sequential Feed cases are approximately equal on an ROIAT basis, both generating an acceptable return.

These returns are all likely to decrease over the next few months as the price of ethylene returns to more historical levels. As this happens, however, the cases should retain their current relative economic ranking, with the Methane Diluent and Sequential Feed Cases being clearly superior to either the Nitrogen or Steam Diluent cases.

Referring back to Table 1, note that the yield-to-C_2's for both the Methane Diluent and the Sequential Feed cases are *lower* than the yields for the Nitrogen and Steam Diluent cases. *But Table 3 shows that the Methane Diluent and the Sequential Feed cases have better economics.*

The key to understanding this apparently contradictory result is to note that the cases with the lower cash costs have the better economics, and that methane cost is the largest single component of the cash cost. The low methane cost in the Methane Diluent case is due to its high selectivity to C_2's. The Sequential Feed case has not only high selectivity to C_2's, but also high by-product credits and low utility costs. The benefits of higher methane conversion and yield-to-C_2's that characterize the Nitrogen and Steam Diluent cases are more than offset by the costs of their lower selectivity to C_2's. Therefore: *yield-to-C_2's is not a good general predictor of economics.*

While the Methane Diluent and Sequential Feed cases are economically equivalent, other factors tip the balance of this overall analysis in favor of the Methane Diluent case. These non-economic factors in favor of the Methane Diluent case are:

- The Methane Diluent case is based on actual laboratory catalyst results, while the Sequential Feed case is based solely on literature catalyst results.

- The Sequential Feed case requires a fluidized-bed reactor design, which is inherently more risky from an engineering standpoint than the fixed-bed reactor design which the Methane Diluent case allows.

- The low cash cost for the Sequential Feed case is due in part its high co-product credits, based on the presumption of a ready customer for the heavy C_4's+ hydrocarbons stream. No such presumption is necessary for the Methane Diluent case.

Therefore, the Methane Diluent case will be used as the preferred model for the Methane Coupling Technology for the balance of this analysis.

Results of Methane Coupling Sensitivity Studies

The sensitivity of the Methane Coupling economics to the methane-to-oxygen ratio in the feed to the Catalytic Reactor System is shown in Figure 2. For each of the three graphs in Figure 2, the methane-to-oxygen ratio is the horizontal axis. Moving from left to right, from a low methane-to-oxygen ratio to a high one causes the methane conversion per pass to decrease but the selectivity to C_2's to increase. This effect for the Co-feed cases has been quantified on the same $BaCO_3$ catalyst system as has been used elsewhere in this study. The effect of increasing methane conversion on the Sequential Feed catalyst has been estimated via the literature sources. For this case the methane-to-oxygen feed ratio is the ratio of these components in the two feed streams, and is not indicative of the composition of any particular stream in the process.

The graph in the upper left corner of Figure 2 indicates that the TFI (Total Fixed Investment) for the cases vary substantially with methane-to-oxygen ratio. Starting at a ratio of 1, the TFI for both the Steam and Nitrogen Diluent systems decrease dramatically with increasing methane-to-oxygen ratio. This is due to the high cost of supplying or recycling the large amounts of diluent needed to produce such a low methane-to-oxygen ratio. The Nitrogen Diluent case cannot be extended beyond a methane-to-oxygen ratio of about 4 and still have air fed directly to the process. As the methane-to-oxygen ratio is increased beyond 4 in the Steam Diluent case, both the process itself and its TFI approach that of the Methane Diluent case. The Sequential Feed case TFI reaches a minimum at a methane-to-oxygen feed ratio of about 5. Beyond this point, the benefits of higher selectivity to C_2's are overwhelmed by the accompanying cost of lower methane conversion.

The graph in the upper right corner of Figure 2 shows how the Cash Cost of ethylene varies with changes in methane-to-oxygen ratio. The strong sensitivity of the cash cost to selectivity to C_2's discourage operation of any of the cases at a low methane-to-oxygen feed ratio, in spite of the high methane conversion that would result.

The large graph at the bottom of Figure 2 shows how the overall ROIAT for the cases vary with methane-to-oxygen ratio. This graph shows that the economics for the Methane Diluent case is essentially equal to the best of the Sequential Feed cases. This graph also underscores the earlier conclusion that across much of the range of conditions that has been studied, selectivity to C_2's is more important economically than methane conversion.

Note that each diluent system has been presented at its mid-point methane-to-oxygen ratio in Tables 1, 2, and 3. That is, the results indicated for the Nitrogen and Steam Diluent

cases in Tables 1, 2, and 3 correspond to a methane-to-oxygen ratio of 2, the Methane Diluent case is at a methane to oxygen ratio of 7, and the Sequential Feed case is at a ratio of 5.

Synthesis Gas / Methanol Process Simplified Block Diagram

The existing technology for producing liquid fuels from methane goes through synthesis gas and methanol as intermediates. The economics of producing liquid fuel by this route have been determined for direct comparison with the Methane Coupling technology.

Figure 3 is the Simplified Block Diagram for this Synthesis Gas / Methanol Process.

Methane is first converted to synthesis gas in the Steam Reforming section of the process. The process information for this portion of the process is per SRI's formulation of an integrated methanol process[3]. A large excess of water is used in this system, which is recovered for recycle by condensing it away from the synthesis gas in a heat-integrated quench step.

The synthesis gas is then compressed for delivery to the Methanol Synthesis section of the process. This section is patterned after ICI's low-pressure process by SRI[3]. The methanol is condensed away from the unreacted synthesis gas in the second quench step. The methanol goes on to the MTO (Methanol to olefins) section, while the unreacted synthesis gas is recycled to the Methanol Synthesis section.

UOP's MTO process[4] makes both DME (dimethyl ether) and mixed olefins. The unreacted methanol is recovered in a third quench step. The DME is removed in a water absorber, and is recycled back to the the Methanol Column. The water of reaction is removed by the Methanol Column as the bottoms product, and the make is a mixture of methanol, DME, and water, which is recycled to the MTO reactor. The DME is recycled to extinction by converting it to additional product. The DME Absorber overhead stream contains the mixed olefins product.

The MOGD system[5] produces gasoline and distillate fuels at a ratio of six to one. A small amount of light hydrocarbons are removed as a purge to fuel.

Gasoline and Distillate Economics

Table 4 summarizes the economics of making gasoline and distillate fuels via Methane Coupling versus the Synthesis Gas and Methanol route. The Methane Coupling facility does not include the Refining System equipment that would be needed to produce high-purity ethylene, but rather is integrated with the MOGD process per the Methane Coupling Simplified Block Diagram. Both cases are cast on the basis of 1989 US Gulf Coast construction and operating costs, with methane purchased at the Intrastate Delivered price of $2.15/MMBtu (5.1¢/lb).

The two routes are similar in that most of the Total Fixed Investment is in the methane conversion portion of the processes. The MTO investment is a relatively small component of the Synthesis Gas and Methanol route ISBL investment, and the MOGD investment is a relatively small component of the Total Fixed Investment for both routes. Overall, the investment costs for the two routes are about equal: the difference between them is well within the ±25% investment estimate accuracy.

But the Operating Cost advantage that is shown for the Synthesis Gas and Methanol route is thought to be real. The selectivity to C_2's for the Methane Coupling route is only about 77%, versus nearly 100% for the competition. This difference in methane efficiency translates directly into a slight but real cash cost advantage for the Synthesis Gas and Methanol route.

Therefore, this route has a slightly lower Required Sales Price to produce a 10% ROIAT: $1.94/gallon versus $2.09/gallon via Methane Coupling. This difference is slight when compared to the current wholesale price of liquid fuels of less than $0.60/gallon. But a low-cost source of methane (such as at a remote location) would make the cost of producing liquid fuels via either of these processes more competitive overall. This would also diminish the impact of the lower methane usage for the Synthesis Gas and Methanol route. Therefore these two technologies are essentially equivalent economically.

This result is viewed as encouraging, given the early state of development of oxidative coupling catalysis. The Synthesis Gas and Methanol route has had the benefit of many years of development and commercial practice. The economics of this route are not likely to be improved significantly by further research. In contrast, Methane Coupling is a comparatively young technology with no current commercial applications. Therefore, it is reasonable to expect that further research might incrementally improve the performance of the current catalyst systems, or lead to the discovery of novel catalyst systems with greatly improved performance.

Hypothetical Catalyst Performance Economics

Figure 4 summarizes the economics of hypothetical or future catalyst systems as a function of the methane conversion and selectivity to C_2's using the current technology as the starting point. The current technology is represented by the Methane Diluent case, which has been shown earlier to be the best of the Methane Coupling systems that have been considered.

The graph in the upper left corner of Figure 4 shows how the TFI (Total Fixed Investment) could be reduced from that required for the current technology. If catalyst improvements could be made that would allow the methane conversion to be increased while retaining the current or higher selectivity to C_2's, then the TFI could be reduced from the current $530MM to less than $400MM.

The graph in the upper right corner of Figure 4 shows how the Cash Cost to ethylene could be reduced below that for the current technology. The strong effect of selectivity to C_2's on the Cash Cost is evident. Even at today's conversion per pass of only 18%, increasing the selectivity to C_2's to 85% would have almost as great an effect on the Cash Cost to ethylene as would increasing the conversion to 55% at 77% selectivity. Overall, catalyst improvements have the potential for reducing the cash cost from the current 13.7 ¢/lb to less than 11.5 ¢/lb.

The large graph at the bottom of Figure 4 shows how the ROIAT for a Methane Coupling facility could be improved over that for current technology. The horizontal dashed line at an ROIAT of 25% represents the minimum return that Methane Coupling would have to offer to attract investment. Any new process must have compelling economics versus the alternatives to justify taking on the associated technical and financial risk. Note that even a methane conversion of 55% does not bring the return up to the economic threshold if the selectivity is 77%. On the other hand, if the selectivity to C_2's could be improved to 85%, then a conversion per pass of 37% or more would generate sufficient return versus the alternatives to attract attention.

This goal is regarded as attainable long-term. Therefore, given sufficient time and resources, *future catalyst improvements should confer superior economics to the Methane Coupling Process.*

In order to assure a substantial economic incentive in its favor, the most conservative Methane Coupling catalyst performance target would be 55% methane conversion and 85% selectivity to C_2's at current operating conditions.

Conclusions

The major findings of this engineering / economic evaluation are:

1. The preferred Methane Coup: configuration is:

   - Methane Diluent (versus Nitrogen or Steam)
   - Co-feed mode (versus Sequential Feed)
   - High methane to oxygen ratio (7/1), which gives
     - Low conversion (18%) but
     - High selectivity (77% to C_2's). which is the key to success.

   These results are for making ethylene on a __demonstrated__ catalyst. This conclusion is reached in spite of the fact that the other cases that were considered offered a higher yield-to-C_2's. Therefore:

   Yield-to-C_2's is not a good general predictor of economics.

2. Equivalent economics for producing gasoline and distillate fuels via:

   - Current Methane Coupling
   - synthesis gas and methanol

   This is viewed as an encouraging result given the early stage of development of Methane Coupling catalysis.

   However, neither technology produces liquid fuels at anywhere near their current US wholesale price using methane purchased at the current US Gulf Coast price.

3. For a __hypothetical__ Methane Coupling catalyst operating at current conditions, high selectivity to C_2's is more important than high methane conversion. Further:

   Future catalyst improvements should confer superior economics to the Methane Coupling Process.

ASSUMPTIONS

Investment Estimate Basis: 1989 US Gulf Coast

Outside Battery Limits (OSBL) Investment:

    40% of (Inside Battery Limits (ISBL) + Oxygen Plant Investment)

Working Capital: 10% of Sales + 20% of (Raw Materials + Utilities Costs)

Ethylene Value: 32 ¢/lb (used to compare among oxidative coupling cases)

Propylene Value: 21 ¢/lb (used to compare among oxidative coupling cases)

Propane Value: 21.6 ¢/gallon (5.11 ¢/lb)

Crude C$_4$'s Value: 25 ¢/gallon (5.13 ¢/lb)

Methane (Fuel Gas) Price: $2.15 / MMBtu (5.13 ¢/lb)

Electricity Cost: $43.00 / Mkhw

Period Costs:

    Operating Labor: $325M per operating position

    Maintenance: 4% of total Fixed Investment

    Laboratory: 20% of Operating Labor

    Location Overhead: 50% of (Maintenance + Operating Labor)

Depreciation: 10% of Total Fixed Investment

Taxes: 37% of (Operating Income - Depreciation)

Listed Major Equipment:	Total major equipment cost based on heat and material balance quantities
Unlisted Major Equipment:	12.5% of Listed Major Equipment
Direct Material:	89% of (Listed + Unlisted Major Equipment)
Indirect Material:	22% of (Listed + Unlisted Major Equipment)
Direct Labor:	63.7% of (Listed + Unlisted Major Equipment) (based on 1989 US Gulf Coast non-union construction)
Indirect Labor:	49.4% of Direct Labor
Subcontracts:	15% of (Listed + Unlisted Major Equipment)
Site Administration:	15.8% of Direct Labor
On-Site Cost:	Sum of Listed Major Equipment and all the above
Engineering:	27.6% of On-site Cost
Contingencies:	15% of (On-site Cost + Engineering)
Total Installed Cost:	On-site Cost + Engineering + Contingencies = 5.47 * Listed Major Equipment

The methane raw material is assumed to be of the following composition:

Methane: 99.0 mole %
Ethane: 0.5 mole %
Nitrogen: 0.4 mole %
Carbon Dioxide: 0.1 mole %

Oxygen produced by an Air Separation Unit is assumed to be of the following composition:

Oxygen   97.5 mole %
Nitrogen   2.5 mole %

The oxygen conversion per pass in the oxidative coupling reaction has been assumed to be 100% in all cases.

References

1. C. A. Jones, J. J. Leonard and J. A. Sofranko, *J. Catal.*, **103**, 311 (1987).

2. J. A. Sofranko, J. J. Leonard, C. A. Jones, A. M. Gaffney and H. P. Withers, *ACS: Petrol. Div. Preprints*, **32**, 770 (1987).

3. SRI International, PEP Report No. 148, "Costs of Synthesis Gases and Methanol", February, 1983.

4. Kaiser, S. W., US Patent No. 4499327, to Union Carbide Corporation, February 12, 1985.

5. Owen, H. et al, US Patent No. 4456779, to Mobil Oil Corporation June 26, 1984.

Figure 1

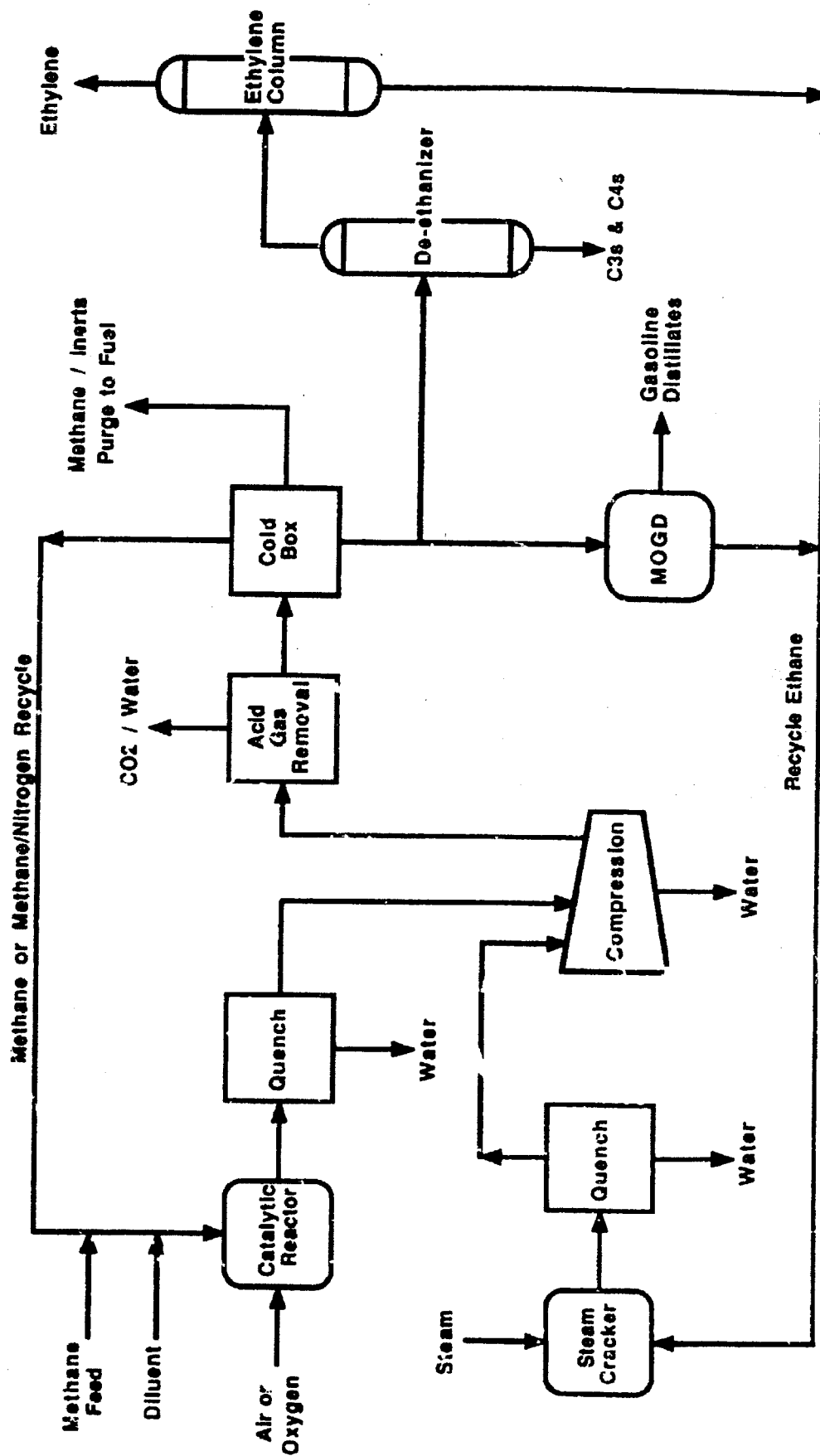## Methane Coupling Process   Simplified Block Diagram

15 Nov 89
JLMatherne

Table 1

Methane Coupling Case Descriptions

Using Nitrogen or Steam as a diluent gives high Yield-to-C_2's.

Diluent	Nitrogen	Methane	Steam	None
Feed System		Co-feed		Sequential
Catalyst		UCC $BaCO_3/Al_2O_3/ECl$		Arco $Mn/Na/P/SiO_2$
Reactor				
Type		Fixed-Bed		Fluidized-Bed
Temperature, °C		750		850
Pressure, psig		50		50
GHSV, hr^{-1}		2133		1200
CH_4				
Conversion, %	45	18	45	24
Selectivity to:				
C_2H_4, %	39	58	39	48
C_2H_6, %	11	19	11	14
C_3H_6, %	2.2	4.3	2.2	4.6
C_3H_8, %	0.7	1.7	0.7	1.5
C_4's +, %	0.2	--	0.2	10
CO, %	15	3	15	11
CO_2, %	32	14	32	11
C_2 Yield, %	22	14	22	15

Table 2

Methane Coupling Investment Costs

Nitrogen Diluent has the highest investment cost.

| Diluent	Nitrogen	Methane	Steam	None
Feed System		Co-feed		Sequential
Catalyst		UCC $BaCO_3/Al_2O_3/ECl$		Arco $Mn/Na/P/SiO_2$
System				
Catalytic Reactor	116	72	113	95
Steam Cracker	25	28	25	26
Compression	149	81	48	77
Acid Gas Removal	31	14	13	14
Cold Box	49	45	26	51
Refining	31	31	31	31
Refrigeration	39	45	38	49
Acetylene Hydrogenation	1	1	1	1
Air Compression	66	--	--	36
Total ISBL	510	315	295	380
Air Separation	--	62	105	--
OSBL	200	153	160	150
Total Fixed Investment	710	530	560	530

All Figures are $MM ±25% for a 1,000 MMppy Unit.

Table 3

Methane Coupling Economics

Yield-to-C_2's is not a good general predictor of economics.

Diluent	Nitrogen	Methane	Steam	None
Feed System		Co-feed		Sequential
Catalyst		UCC $BaCO_3/Al_2O_3/ECl$		Arco $Mn/Na/P/SiO_2$
Total Fixed Investment	710	530	560	530
Working Capital	65	60	70	60
Total Utilized Investment	775	590	630	590
Operating Costs				
Methane	146	112	132	124
By-Product Credits	(12)	(44)	(22)	(50)
Utilities	24	29	56	14
Variable Cost	159	97	166	90
Fixed Cost	53	40	42	41
Total Cash Cost	212	137	209	130
ROIAT, %	3	14	6	15

All Costs are $MM/yr for a 1,000 MMppy Unit.
ROIAT is based on ethylene sales at $0.32/lb

Figure 2

Results of Methane Coupling Sensitivity Studies

TFI

Cash Cost

ROIAT
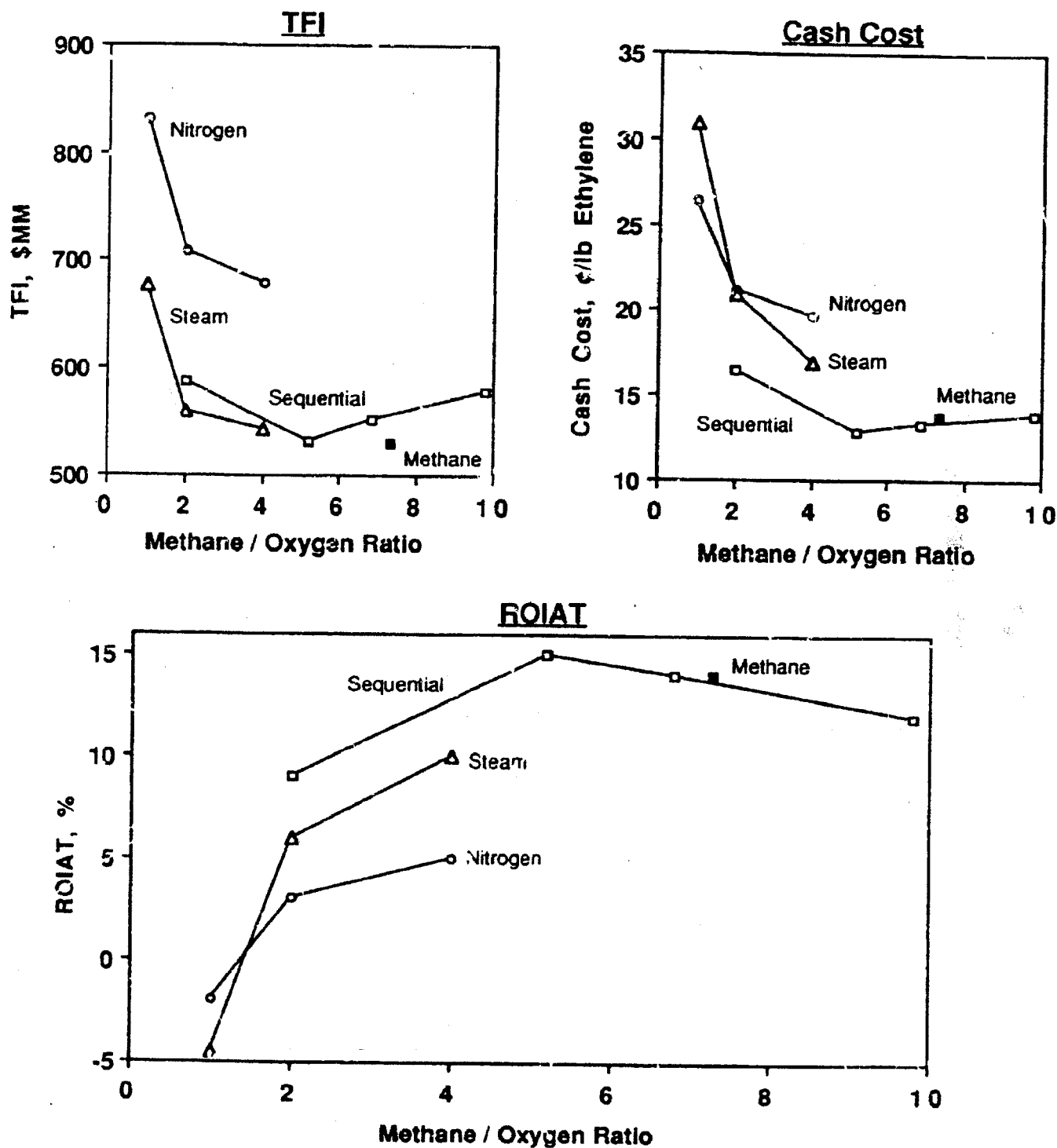
Selectivity to C2's is more important than methane conversion

Figure 3

Synthesis Gas / Methanol Process   Simplified Block Diagram
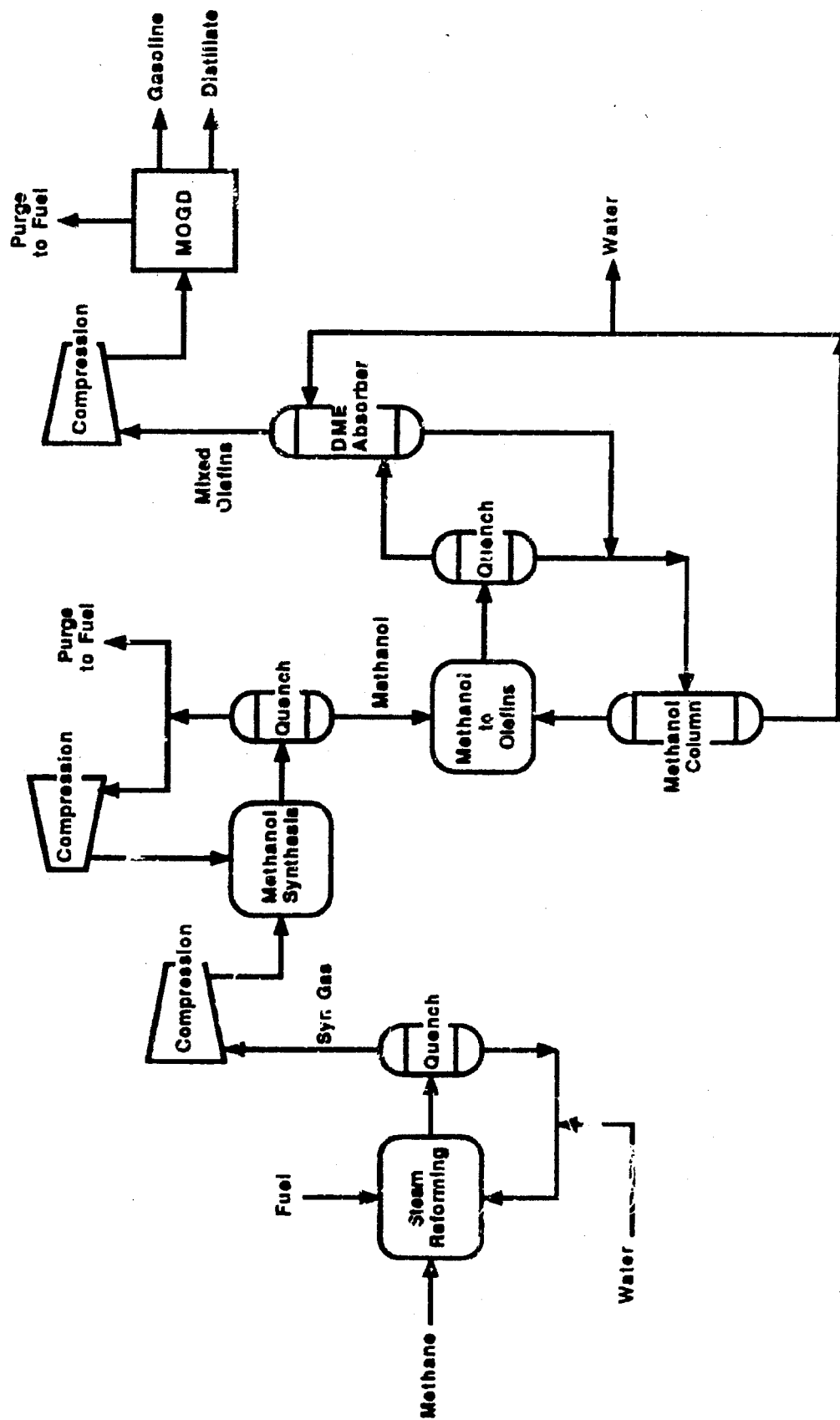
Table 4

Gasoline & Distillate Economics

*The two routes are equivalent.*

	Methane Coupling	Synthesis Gas & Methanol
ISBL Investment	285	314
Air Separation Unit	61	--
MOGD	40	35
OSBL Investment	154	141
Total Fixed Investment	**540**	**490**
Working Capital	50	46
Total Utilized Investment	**590**	**536**
<u>Operating Costs</u>		
Methane	101	60
By-Product Credits	(26)	(2)
Utilities	23	28
Variable Cost	**98**	**88**
Fixed Cost	38	40
Total Cash Cost	**136**	**128**
Required Sales Price $/gal Product	**$2.09**	**$1.94**

All Costs are $MM/yr for a 10,600 bpd Unit
   (1,000 MMppy olefins)
Required Sales Price generates a 10% ROIAT

Figure 4

Hypothetical Catalyst Performance Economics
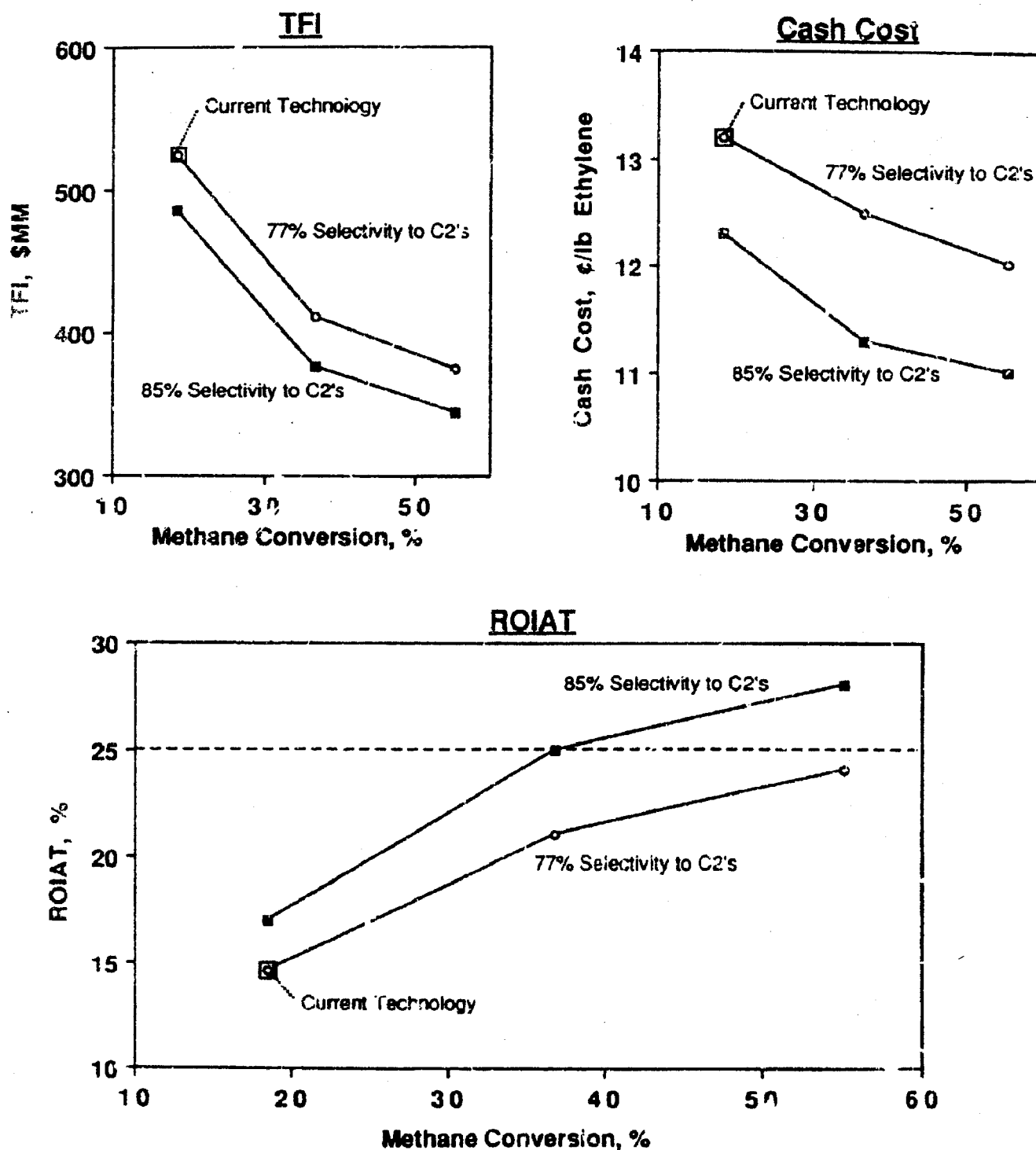
Catalyst improvements promise to confer superior economics