

DIRECT METHANE CONVERSION - AN ASSESSMENT

David Gray and Glen Tomlinson
The MITRE Corporation
McLean, VA

and

John Shen
U.S. Department of Energy
Washington, D.C.

Worldwide proven reserves of natural gas are estimated to be approximately 3500 trillion cubic feet of which the U.S. has approximately 6 percent⁽¹⁾. Gas production and consumption worldwide are about 63 trillion cubic feet annually. In 1985 the U.S. produced about 27 percent of this (i.e., about 17 trillion cubic feet)⁽¹⁾. In terms of energy, natural gas consumption represents about half of the total petroleum consumed and natural gas reserves are being discovered at twice the rate of petroleum. This trend indicates the increasingly important role that gas will play in the future energy supplies of the world.

Large quantities of this natural gas are located in remote areas, isolated from centers of commerce and population. No distribution network exists for its transportation. In fact, gas associated with petroleum is often flared rather than utilized. Transportation costs of remote natural gas are a relatively expensive part of the final delivered price. Therefore, most natural gas is consumed in the country where it is produced. Liquefied natural gas (LNG) terminals and vessels can bring remote gas to market. In 1985, 30 percent (1.7 trillion cubic feet) of natural gas traded internationally was transported as LNG and this percentage is growing⁽²⁾. For shorter distances, remote gas can be compressed (CNG) and transported using tankers with pressurized containers. Alternatively, depending on the economic conditions, on-land and subsea pipelines can be constructed to transport the remote gas.

A potentially attractive option, currently being practiced in New Zealand, is to convert the gas on-site to readily transportable liquids like methanol or liquid hydrocarbons. These liquids can then be transported using conventional tankers. The New Zealand plant produces 14,500 barrels per day of gasoline, which are shipped to a refinery for blending into the New Zealand gasoline pool⁽³⁾. The option of on-site conversion of gas to liquids not only allows for easier transportation but also produces a more valuable energy commodity, i.e. a liquid transportation fuel in the case of higher hydrocarbons, or a petrochemical feedstock, gasoline additive or turbine fuel in the case of methanol. In a world where requirements for liquid transportation fuels are paramount, natural gas will increasingly be used to fulfill this role.

Methane, the major constituent of natural gas, is also a by-product of Fischer-Tropsch and other synthesis processes for the production of liquid fuels and chemicals from synthesis gas. This methane must be reformed back to synthesis gas if only liquid products are required; this process is both thermally inefficient and expensive. Thus, alternative processes for converting this methane by-product into liquids will also be a benefit to indirect liquefaction technology.

Conventional transformation of natural gas to methanol and liquid hydrocarbons involves the reforming of the natural gas to synthesis gas followed by catalytic synthesis to produce methanol. If hydrocarbons are required, the methanol can be

further processed using Mobil's Methanol-to-Gasoline (MTG) technology to produce high octane gasoline⁽⁴⁾. This conventional process is a complex processing sequence involving the highly endothermic steam reforming reaction followed by exothermic methanol synthesis.

If it were possible to convert methane directly to methanol or higher hydrocarbons with high conversion and selectivity, both the steam reforming and methanol synthesis steps could be eliminated. This direct conversion approach has the potential for considerable savings in cost if technically sound processes can be developed. Interest in direct methane or natural gas conversion has recently intensified worldwide. Several approaches to this are being researched at oil companies and in programs funded by the Department of Energy or the Gas Research Institute. The more technically advanced processes are those that operate in the temperature range 600-800°C.

This paper assesses the technical potential of some of these high temperature direct methane conversion approaches being researched by various groups. These new approaches are then compared to the conventional technology for converting methane to gasoline by utilizing steam reforming, methanol synthesis and Mobil's Methanol-to-Gasoline (MTG) technology⁽⁵⁾. The direct methane conversion approaches analyzed in this report are Oxidative Coupling, Partial Oxidation, and Oxyhydrochlorination. Computer simulation has been used to model the technical performance of conceptual commercial plants that utilize these direct methane conversion approaches. In addition, the conventional technology has been simulated with the same size plant to provide a baseline to which the new approaches could be compared. These analyses were based on the thermodynamics of the reactions and the reported yields and selectivities for each process. Results are reported on the basis of the efficiency of the lower heating value (LHV) of the product. LHV of the product is the heating value of the product divided by the heating value of the reactant. Sensitivity studies have been conducted for some of the new approaches to identify the levels of performance necessary for these direct conversion techniques to be technically as efficient as the baseline conventional technology.

Data on Oxidative Coupling have been obtained from open literature sources that document the results from Atlantic Richfield (ARCO)⁽⁶⁻⁸⁾. Partial oxidation data have been obtained from published results of H. Gesser et al. of the University of Manitoba⁽⁹⁻¹⁴⁾. Preliminary results of the Oxyhydrochlorination of methane have been obtained from the Pittsburgh Energy Technology Center (PETC)⁽¹⁵⁾.

In the analysis of Oxidative Coupling, the system used was the redox mode. In this approach, methane is contacted with a solid oxidant, in this case manganese oxide on silica. This oxidant provides lattice oxygen for the oxidative coupling of the methane and the manganese is reduced to a lower oxidation state. The solid is then transferred to a regeneration reactor where it is reoxidized. The reoxidized solid is then transferred back to the oxidative coupling reactor where it reacts again with the methane. The products from the oxidative coupling reactor, which are predominantly C₂+ olefins, are then sent to a ZSM-5 polymerization reactor where they undergo oligomerization to form gasoline.

For analysis of Partial Oxidation, methane is reacted with pure oxygen at pressures of 65 bar in a glass-lined, non-catalytic reactor to produce methanol and carbon oxides. The methanol is then sent to an MTG unit, as in the baseline case, to give high octane gasoline as a final product.

In Oxyhydrochlorination, methane is reacted with oxygen and hydrogen chloride over a copper chloride catalyst⁽¹⁶⁾. The analysis assumes a process in which the

products formed are cooled to remove water and hydrogen chloride, and the methyl chlorides produced are sent to a ZSM-5 reactor where they undergo polymerization to form gasoline and liberate hydrogen chloride. The first stage data used gave a 25 percent conversion of methane per pass and a selectivity to mono- and dimethyl chlorides of 81 percent with a molar ratio of mono- to dichloride of approximately 4 to 1. Complete oligomerization of the mono- and dichlorides was assumed to occur over the second stage ZSM-5 reactor to give a stoichiometric mixture of C₈ hydrocarbons and toluene.

Table I summarizes the known process parameters and calculated conversion efficiencies for the new direct methane conversion approaches and the baseline technology considered in this analysis. Using the preliminary data available, the computer simulations of the new approaches all show overall system efficiencies that are not greatly different from the conventional technology. Using ARCO data for the 15 percent Mn/SiO₂ system that gave a methane conversion per pass of 26 percent for a C₂+ selectivity of 60 percent, an LHV product efficiency of 56 percent was obtained for the Oxidative Coupling approach. ARCO showed that promotion of this system with sodium pyrophosphate increased C₂+ selectivity to about 70 percent. Our analysis shows that LHV product efficiency increases to 64 percent at this higher selectivity level. For Partial Oxidation, using the best available data⁽⁹⁻¹⁴⁾, an overall product efficiency of 59 percent was obtained. It was assumed that a product selectivity to methanol of 83 percent was obtained at a per pass methane conversion of 8 percent. For Oxyhydrochlorination, using the assumptions mentioned above, the overall product efficiency was estimated to be 65 percent.

Oxidative Coupling looks promising provided that the selectivity to CO and CO₂ can be maintained at a level of about 25 percent. The design of a practical high pressure redox reactor system needs to be addressed. The excess waste heat from the system, which is of good quality, also needs to be effectively utilized. If this can be done with the current selectivities, then the overall system efficiency including the potentially recoverable heat would be around 70 percent.

Partial Oxidation would appear to be a potentially attractive alternative, based on our estimates of efficiency, provided that high methanol selectivities can be achieved. However, the results from the University of Manitoba are considerably better than have been achieved elsewhere; they may be a function of the particular reactor dimensions used in the experiments. This requires further investigation.

Based on efficiency, Oxyhydrochlorination looks very attractive. However, this analysis has assumed very favorable polymerization potential for the methyl chlorides over ZSM-5, which has yet to be demonstrated in practice. Of greater potential concern for this technology, however, is the severe materials corrosion problems that exist with the handling and recovery of wet hydrogen chloride.

To further evaluate the process potential of these new technologies, additional research and development is needed together with economic analyses to quantify the expected cost savings associated with the elimination of steam reforming and methanol synthesis.

Acknowledgement:

This work was funded by Sandia National Laboratories, which is supported by the U.S. Department of Energy under Contract DE-AC04-76DP00789.

References:

1. Oil and Gas Journal, December 30, 1985, p. 66.
2. Leibson, I., S. T. Davenport and M. H. Muenzier, "Costs to Transport Natural Gas," Hydrocarbon Processing, April 1987, p. 47.
3. Fox, Joseph M., "The Fixed-Bed Methanol-to-Gasoline Process Proposed for New Zealand," paper presented at the Australian Institute of Petroleum, Coal Gasification Conference, Adelaide, March 2, 1982.
4. Haggin, J., "Methane-to-Gasoline Plant Adds to New Zealand Liquid Fuel Resources," Chemical and Engineering News, June 22, 1987, p. 22.
5. Kuo, J. C. W., Gasification and Indirect Liquefaction. Chapter 5 from The Science and Technology of Coal and Coal Utilization, edited by B. R. Cooper and W. A. Ellingson, Plenum Publishing Corp., 1984.
6. Jones, A. C., J. J. Leonard and J. A. Sofranko, "The Oxidative Conversion of Methane to Higher Hydrocarbons Over Alkali-Promoted Mn/SiO₂," Journal of Catalysis, 103, 311-319, 1987.
7. Jones, A. C., J. J. Leonard and J. A. Sofranko, "Fuels for the Future: Remote Gas Conversion," Energy and Fuels 1, 12-16, 1987.
8. Sofranko, J. A., J. J. Leonard and C. A. Jones, "The Oxidative Conversion of Methane to Higher Hydrocarbons," Journal of Catalysis, 103, 302-310, 1987.
9. Gesser, H. D. and N. Hunter, "The Direct Conversion of Methane to Methanol by Controlled Oxidation," Chemical Reviews 85 (4), August 1985, p. 235.
10. Gesser, H. D., N. R. Hunter, L. A. Morton, P. S. Yarlagadda and D. P. C. Fung, "The Direct Conversion of Methane to Methanol by a High Pressure Partial Oxidation Reaction," American Chemical Society, Division of Fuel Chemistry, Preprints 32 (3), 255, 1987.
11. Hunter, N. R., et al., "The Direct Conversion of Methane to Methanol," Proceedings of the VI International Symposium on Alcohol Fuels Technology, Ottawa, May 21-25, C-14, Vol. 11-147, 1984.
12. Hunter, N. R., et al., "The Direct Conversion of Natural Gas to Methanol by Controlled Oxidation at High Pressure," Proceedings of the 35th Canadian Chemical Engineering Conference Category, Oct. 6-9, 1985.
13. Hunter, N. R., et al., "The Direct Conversion of Natural Gas to Alcohols," presented at the VII International Symposium on Alcohol Fuels, Paris, Oct. 20-23, 1986.
14. Yarlagadda, P. S., et al., "Direct Catalytic Conversion of Methane to Higher Hydrocarbons," Fuel Science and Technology Int. 5(2), 169-183, 1987.
15. Taylor, C. E. and R. P. Noceti, "Conversion of Methane to Gasoline-Range Hydrocarbons," American Chemical Society, Division of Fuel Chemistry, Preprints 32 (3), 307, 1987.
16. Pieters, W. J. M., E. J. Carlson, E. Gates and W. C. Conner, U.S. Patent, 4,123,389 (1978).

TABLE 1
SUMMARY OF DIRECT METHANE CONVERSION APPROACHES
FOR PRODUCTION OF GASOLINE

	3	2	2	2
	BASELINE TECHNOLOGY	OXIDATIVE COUPLING	PARTIAL OXIDATION	OXHYDRO-CHLORINATION
<u>Number of Stages</u>	3	2	2	2
<u>Stage 1</u>	Steam Reforming	Oxidative Coupling	Partial Oxidation	Oxyhydrochlorination
Catalyst	Nickel	Mn/SiO ₂	None	CuCl/KCl on Silica
Temperature (°C)	800-900	815	458	340
Pressure (Bar)	7-20	35	65	15
CH ₄ Conversion Per Pass	---	26	8	25
Overall CH ₄ Conversion & Selectivity	90	99	95	93
	---	50% to C ₂ ⁺	83% to CH ₃ OH	77% to CH ₃ Cl
<u>Stage 2</u>	Methanol Synthesis	Olefin Oligomerization	Methanol-to-Gasoline	Methyl Chloride Oligomerization
Catalyst	Cu/Zn	ZSM-5	ZSM-5	ZSM-5
Temperature (°C)	250-300	370	320	400
Pressure (Bar)	80-100	27	22	12
<u>Stage 3</u>	Methanol-to-Gasoline	None	None	None
Catalyst	ZSM-5			
Temperature (°C)	320			
Pressure (Bar)	22			
Overall LHV Efficiency *	59	56	59	65