BNL-66589

*Symposium in Catalysis on "Syngas Conversion to Fuels and Chemicals"*
**Division of Petroleum Chemistry**
**Spring ACS Meeting, Anaheim, CA**
**March 21-25, 1999**

# DEVELOPMENT OF ATOM-ECONOMICAL CATALYTIC PATHWAYS FOR CONVERSIONS OF SYNGAS TO ENERGY LIQUIDS

*D. Mahajan*, J.E. Wegrzyn and T. Lee*
Building 815, Department of Applied Science, Brookhaven National Laboratory, Upton, New York 11973
*M. Gurevich*
Office of Heavy Vehicles Technologies, U.S. Department of Energy, Washington, D.C. 20585

(Key words: catalysis, syngas conversion, oxygenated fuels, methanol, dimethyl ether)
FAX: 516-344-7905

## INTRODUCTION

The subject of catalytic syngas conversions to fuels and chemicals is well studied (1-3). But globally, the recent focus is on development of technologies that offer an economical route to desired products (4). Economical transport of natural gas from remote locations and within clathrate hydrates is of continuing interest at Brookhaven National Laboratory (BNL). Under this project, a Liquid Phase Low Temperature (LPLT) concept is being applied to attain highly efficient transformations of natural-gas derived syngas to specific products. Furthermore, a more precise term "Atom Economy" has been recently introduced by Trost to describe development of highly efficient homogeneously catalyzed synthesis of organic molecules (5). Taken from reference 5, the term "Atom Economy" is defined as maximizing the number of atoms of all raw materials that end up in the product with any other reactant required on in catalytic amount. For application to methane transformations that may involve one or more steps, atom economy of each of these steps is critical. We, therefore, consider atom-economy synonymous with overall energy efficiency of a process. This paper describes potential liquid products from catalytic

*Tel.: (516) 344-4985; Fax: (516) 344-7905; E-mail: dmahajan@bnl.gov

syngas conversions, i.e. gas to liquids (GTL) technologies and process considerations that are necessary for economical transport of natural gas. As such, the present study defines an atom-economical standard to directly compare competing GTL technologies.

## NATURAL GAS CONVERSIONS

We consider options to promote natural gas usage that meet the following set-forth criteria: 1) fits well in the present distribution infrastructure, 2) safe based on public perception, 3) is in harmony with the environment, and 4) favorable process economics.

Equations 1-13, shown collectively in Figure 1, represent available options to harness energy from natural gas for various applications. The overall energy delivery efficiency is defined as:

$$\mathcal{E}_{Eff} = E_T - (E_I + E_{TF} + E_{TP} + E_{EC}) \,/\, E_T \qquad (14)$$

where

$E_T$ = total stored energy in natural gas at the well site.

$E_I$ = energy required for exploration, drilling, and refining i.e., total energy that is required to bring natural gas to the surface.

$E_{TF}$ = energy required to physically or chemically transform methane and make it transportable.

$E_{TP}$ = energy needed to transport.

$E_{EC}$ = energy for environmental compliance.

The delivery efficiency ($\mathcal{E}_{Eff}$) refers to the stored energy in natural gas. The following discussion sets forth the direction for the present study:

1. The most exothermic process is to burn natural gas at the well site. Natural gas combustion energy is 20,551 BTU/lb (Equation 1). Due to a mismatch between source location and need, remote gaseous natural gas is first liquefied and then transported in refrigerated tankers. Minimizing energy input that is required to transport gas is the goal.

2. Natural gas transport either as compressed natural gas (CNG) or liquefied natural gas (LNG) is known. Here, LNG is the preferred option with delivered energy efficiency ($E_{eff}$) of ~80%. As shown in Equation 2, this serves as the baseline because this physical transformation only requires energy of liquefaction ($E_L$). Here, $E_L$ equals the $E_{TF}$ term in Equation 14. The delivery efficiency is about 16,500 BTU/lb.

3. Other options to transport natural gas as "other liquids" are considered. In conversion of natural gas to energy liquids (GTL), the total energy required for chemical transformation ($E_{CT}$) determines delivery efficiency. With the available data, direct methane to methanol is considered a viable process (Equation 3). This route is under development (6, 7).

4. In the second GTL option, the conventional two-step process offers a variety of clean fuel product options. Here, the $E_{CT}$ term includes:

$$E_{TF} = E_{CT} = E_{SP} + E_{ST} \qquad (15)$$

where $E_{SP}$ relates to syngas production Step I and $E_{ST}$ relates to Step II in which syngas is converted to liquids. Here, five product options are considered in two broad categories. These are: a) hydrocarbon products (Equation 9) and b) oxygenated products (Equations 10-13). Equations 10-12 should be viewed in the context of MeOH as a feedstock because both dimethyl ether (DME) and methyl formate (MF) can be derived from methanol. Because of recent interest in dimethyl ether (DME), this product is considered separately. The basis of this paper thus considers F-T liquids, MeOH, DME as viable options to LNG. Two guidelines are considered critical:

1. Any envisioned natural gas-based costs must include preserving options that allow natural gas use as a feedstock at the point of delivery.

2. It is to be noted that all five reactions (Equations 9-13) are exothermic. But the overall

GTL transformation is a net energy user and overall process efficiency is dependent on energy required for chemical transformations $E_{ST}$. Since both **C** and **H** atoms in natural gas are energy carriers, maximizing transport of these atoms will minimize fuel value loss of the delivered product. It is this aspect that the term "Atom Economy" relates to.

From the overall discussion, it is clear that minimizing $E_I$, $E_{TF}$, $E_{TP}$, $E_{BC}$ terms i.e. total energy input will maximize $E_{eff}$. In this paper, the emphasis is on minimizing $E_{TF}$ that, in turn, relates to the $E_{TP}$ and $E_{BC}$ terms in Equation 14.

**THE LIQUID STATE OPTIONS**

Realizing that transporting (the $E_{TP}$ term) natural gas as a liquid is safer and less expensive, the ongoing BNL R & D effort is directed to minimize the $E_{TF}$ term. The emphasis is on atom economy of catalytic transformations and this formed the basis for developing novel catalysts to attain these goals. In addition to ongoing work at BNL related to GTL, other promising systems under development are also considered. These are:

- Direct methane to methanol conversion using Catalytica technology (6). Another option is still under development (7).
- The Syntroleum approach that uses air for partial oxidation of methane to produce syngas (Step I or Equation 4). The effect of eliminating an $O_2$-separation plant but increased operating pressure (to accommodate $N_2$ in syngas) during F-T synthesis.
- The BNL approach utilizing the LPLT concept for methanol production.
- DME synthesis with upcoming technologies including that based on the BNL LPLT concept.
- The BNL one-pot synthesis of methyl formate.

An earlier costing study (8) that took the "cradle to grave" approach in calculating overall energy efficiency for various transformations is relevant. Specifically reviewed in the present study are emerging atom-economical GTL technologies that emphasize safety and environmental impact and cost advantages of various options to transport natural gas from remote locations. With presently popular LNG option of delivery efficiency ~ 80% as a baseline, conversion of natural gas to clean liquid fuels in skid-mounted, product flexible, and economical GTL plants at the well-site is the goal.

**LITERATURE CITED**


(1) Hutchings, G.J. and Scurrell, M.S. (eds.), Synfuels, Elsevier; Catal. Today, 6(3) (1990).

(2) Hindermann, J.P., Hutchings, G.J., and Kiennemann, A., Catal. Rev.- Sci. Eng. 35 (1), 1 (1993).

(3) Dry, M.E., J. Organomet. Chem. 372, 117 (1989).

(4) Remote Gas Strategies, pp. 4,5 and 13,14, April 1998.

(5) Trost, B.M., Angew. Chem. Int. Ed. Engl. 34, 259 (1995).

(6) Periana, R.A., Taube, D.J., Gamble, S., Taube, H., Satoh, T., and Fujii, H., Science, 280, 560 (1998).

(7) Lin, M., Hogan, T., Sen, A., J. Am. Chem. Soc., 119, 6048 (1997).

(8) Stodolsky, F. and Santini, D.J., CHEMTECH, 54, October 1993.


Work at Brookhaven is supported under US DOE Contract No. DE-AC02-CH10886.

# Figure 1: The Reaction Scheme

**Well-Site Usage:** $CH_{4(g)} + 2O_2 \rightarrow CO_2 + 2H_2O$ (1)

**Physical Transformation:** $CH_{4(g)} + E_L \rightarrow CH_{4(\ell)}$ (2)

**Chemical Transformation:** $CH_{4(g)} + E_{CT} \rightarrow$ Energy Liquid (3)

**Step I: Syngas Production**

$CH_{4(g)} + E_{SP} \rightarrow CO + nH_2$ (4)

1. *Steam Reforming:* $CH_{4(g)} + H_2O \rightarrow CO + 3H_2$ (5)

2. *Partial Oxidation:*

   i. With Oxygen:

   $CH_{4(g)} + \frac{1}{2} O_2 \rightarrow CO + 2H_2$ (6)

   ii. With Air:

   $CH_{4(g)} + \frac{1}{2} O_2 \text{ (Air)} \rightarrow CO + 2H_2 + (N_2)$ (7)

**Step II: Syngas Transformations**

$x\,CO + yH_2 + E_{ST} \rightarrow$ Hydrocarbons
$\rightarrow$ Oxygenates (8)

***1. Hydrocarbon Synthesis (F-T process)***

$nCO + 2nH_2 \rightarrow (\text{-}CH_2\text{-})_n + nH_2O$ (9)

***2. Methanol Synthesis***

$CO + 2H_2 \rightarrow CH_3OH$ (10)

***3. Dimethyl Ether Synthesis***

$2CO + 4\,H_2 \rightarrow (CH_3)_2O + H_2O$ (11)

***4. Methyl Formate Synthesis***

$2CO + 2H_2 \rightarrow CH_3OCHO$ (12)

***5. Higher Alcohols Synthesis***

$nCO + 2n\,H_2 \rightarrow C_nH_{2n+1}OH + (n\text{-}1)\,H_2O$ (13)