ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 106 (2005) 301–304

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Natural gas conversion to liquid fuels in a zone reactor

Ashley Breed [a], Michael F. Doherty [b], Sagar Gadewar [a], Phil Grosso [a],
Ivan M. Lorkovic [a], Eric W. McFarland [a,b,*],
Michael J. Weiss [a]

[a] Gas Reaction Technologies, Inc., 861 Ward Drive, Santa Barbara, CA 93111, USA
[b] Department of Chemical Engineering, University of California,
Santa Barbara, CA 93106, USA

Abstract

A process for conversion of natural gas to liquid fuels is described. The process can be conducted in a “zone reactor” in which oxygen or air is first contacted with solid metal bromide, producing bromine and metal oxide. The bromine passes into a second zone, in which it reacts with natural gas, producing alkyl bromides and hydrogen bromide. The products of the second zone pass into a third zone, in which they react with metal oxide, producing metal bromide and liquid product. At the end of the cycle the oxygen feed and product streams are switched and the flow reversed. The advantages of the process including safety and capital cost reduction are presented and results discussed.

Keywords: Natural gas; Zone reactor; Fuels; Gas to liquids

1. Introduction

Development of natural gas conversion strategies has been dominated by gas-to-liquids processes involving a three-step process including syngas generation, Fischer–Tropsch (FT) synthesis and product refining. Less commonly, there are processes under development that involve methanol synthesis as an intermediate with subsequent conversion employing methanol-to-olefins (MTO) and methanol-to-gasoline (MTG) processes to the desired products [1–4]. Potentially simpler strategies including direct partial oxidation of natural gas have also been pursued: reactor and process technology have improved carbon efficiencies of these technologies. Capital and operating costs have been optimized to the extent possible, although not to the extent necessary for wide-scale commercialization to take place at current pricing of natural gas and products.

We recently demonstrated a two step process chemistry for partial oxidation of alkanes by oxygen [5–7]. In the current embodiment, natural gas (here represented by methane) is first brominated using Br_2 (Eq. (1)):

$$n\mathrm{CH_4} + n\mathrm{Br_2} \rightarrow n\mathrm{CH_3Br} + n\mathrm{HBr} \quad (1)$$

$$n\mathrm{CH_3Br} + n\mathrm{HBr} + n\mathrm{MO} \rightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H_2O} + n\mathrm{MBr_2} \quad (2)$$

$$n\mathrm{MBr_2} + (n/2)\mathrm{O_2} \rightarrow n\mathrm{MO} + n\mathrm{Br_2} \quad (3)$$

$$\mathrm{Sum}: n\mathrm{CH_4} + (n/2)\mathrm{O_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H_2O} \quad (4)$$

The brominated intermediates were further converted either to unsaturated hydrocarbons by reaction with a metal oxide solid reactant (Eq. (2)). The metal oxide served to remove HBr, and to direct the output to specific partial oxidation products dependent upon the metal oxide composition and reaction conditions. Complete recovery of bromine and regeneration of the metal oxide was accomplished by reaction of the spent solid with O_2 (Eq. (3)).

---

* Corresponding author. Tel.: +1 805 893 4343; fax: +1 805 893 4731.
E-mail address: mcfar@engineering.ucsb.edu (E.W. McFarland).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.08.001

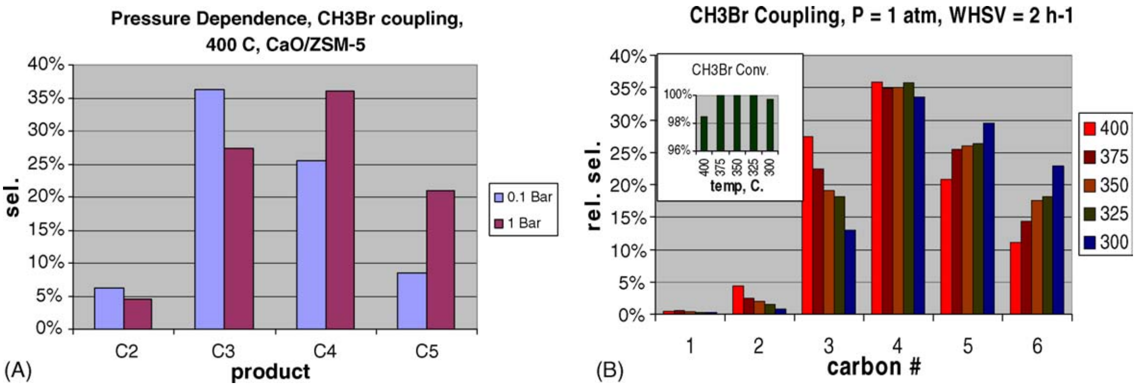

Fig. 1. (A) Pressure dependence of product selectivity from methyl bromide coupling at 400 °C over a CaO/ZSM-5 combination. (B) Temperature dependence of methyl bromide coupling over CaO/ZSM-5 at 1 atm total pressure and a WHSV of 2 h^{-1}.

2. Process chemistry

We have demonstrated that the methyl bromide coupling chemistry described above follows many of the same trends as, and produces product similar to, the methanol-to-gasoline chemistry. Using the same CaO–ZSM-5 cataloreactant described in previous work [6], increasing pressure from 0.1 to 1 bar at a constant temperature of 400 °C shifts the product distribution towards higher hydrocarbons (Fig. 1) (higher carbon numbers, and aromatics not shown). Likewise, decreasing the coupling temperature can also produce a heavier product distribution. Residence time has a somewhat less obvious effect, as disproportionation reactions such as Eq. (5) occur at longer bed residence times, leading to an increase in the aromatic content at the longer residence times. A comparison of results at 100 s residence time to MTG literature results obtained using a methanol feed and similar conditions suggests the product distribution from methyl bromide can be similar to that seen in methanol-to-gasoline processes (Fig. 2):

$$4C_7H_{14}\,(\text{olefin}) \rightarrow 3C_7H_{16}\,(\text{paraffin}) + C_7H_8\,(\text{aromatic}) \tag{5}$$

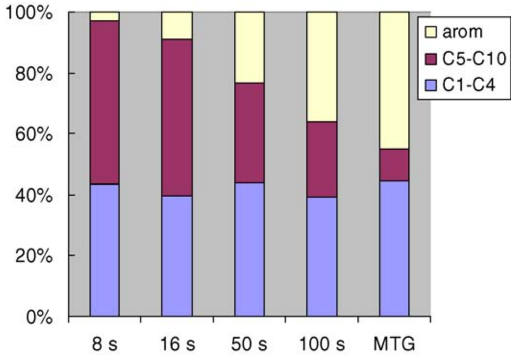

Fig. 2. Hydrocarbon product distribution dependence on residence time at 400 °C, 3 bar with comparison to methanol-to-gasoline results at 371 °C, 1 atm [1].

3. Zone reactor

This process chemistry can be implemented in a conventional reactor scheme where the gas-phase bromination reaction is run in a plug flow reactor followed by a packed bed or fluidized bed reactor containing the cataloreactant. Separations may be done before and/or after the second reactor depending on the desired product mix and the ease with which the species can be separated. The alkylbromide intermediates have many separation advantages. However, since the process involves both a mobile gas-phase reactant and a solid, regenerable, cataloreactant, a major cost saving advantage is possible to simplify the overall process and limit the bromine inventory to a single ‘‘zone reactor,’’ shown in Fig. 3.

The bromine source in the zone reactor is derived from simultaneous regeneration of spent cataloreactant (in the form of a metal bromide) in oxygen at approximately 350–450 °C, releasing bromine and regenerating the metal oxide cataloreactant MO in the regeneration zone. The methane feed and recycle mixture are contacted with the bromine in the bromination zone where alkyl bromide intermediates are produced at a temperature of approximately 450 °C. The intermediate products move into the solid reactant zone maintained at approximately 350–450 °C containing initially the solid metal oxide cataloreactant which simultaneously forms products and neutralizes the HBr, converting the metal oxide to a solid-product metal bromide. Following exhaustion of the metal oxide bed forming the metal bromide, the oxygen feed and product streams are switched. The flow is reversed, with the oxygen now introduced into the spent cataloreactant metal bromide and the alkylbromides directed over the regenerated bed now containing metal oxide.

The bromination and regeneration reactors can be run adiabatically. Heat is generated in the exothermic metathesis reaction. The metathesis and regeneration temperatures are typically within approximately 75 °C of each other to minimize the need for temperature cycling.

Cataloreactants have been developed that have similar reaction and regeneration temperatures (which avoids

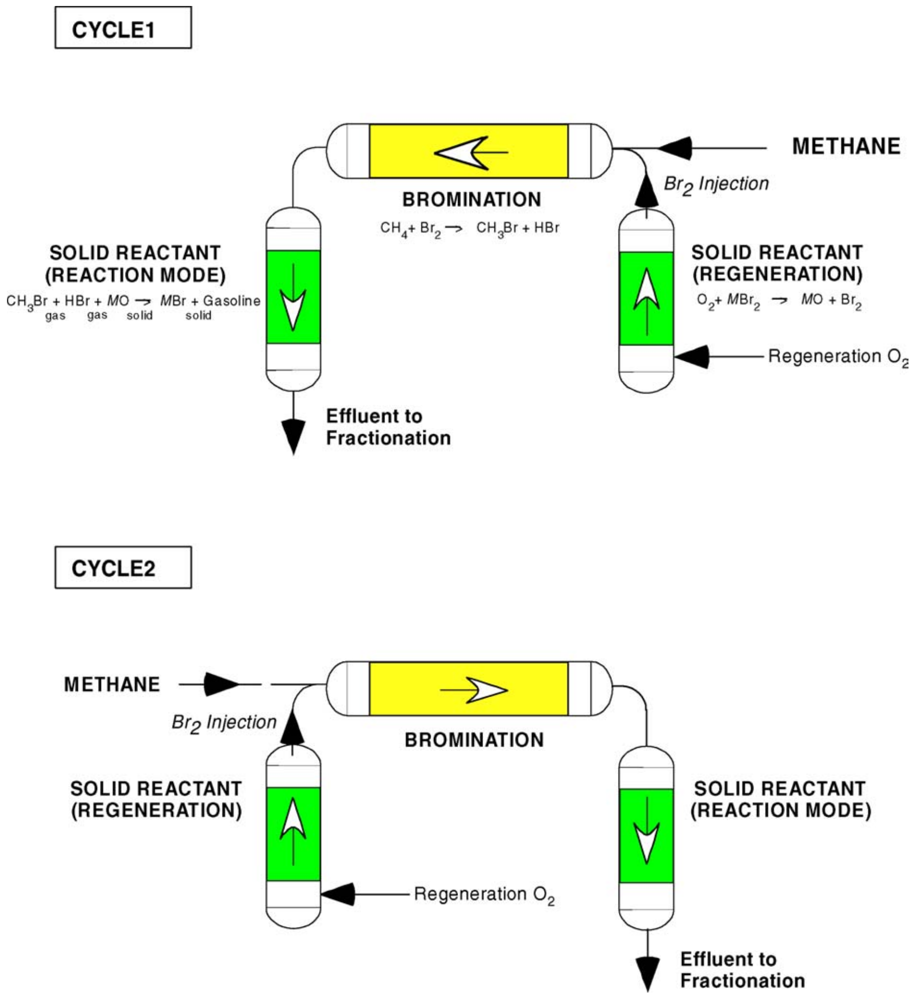

Fig. 3. In the “zone reactor” scheme, bromine is liberated in the “regeneration zone” from the solid product (MBr_2) reacting with oxygen. The bromine liberated in the regeneration zone reacts with methane in the “bromination zone” and the intermediates then react with the solid reactant (MO) to form products in the “solid reactant zone”. In the second cycle, the flow direction is reversed (bottom). No bromine leaves the system and the reactor system can be operated under nearly isothermal conditions.

excessive temperature cycling) and that are stable, chemically and mechanically over multiple regeneration cycles. Major advantages of the cataloreactant chemistry are:

- Simple two step process—no syngas intermediate.
- No extreme temperatures or pressures required.
- Insensitive to common gas impurities (sulfur, carbon dioxide, nitrogen, water).
- Cataloreactant materials are inexpensive and robust on regeneration.
- Regeneration accomplished with air, no oxygen plant required.
- Flexible product distribution control from light olefins and alcohols to jet fuel or gasoline.

Methane conversion to gasoline using the cataloreactant process in a zone reactor has a significant projected capital cost reduction compared to alternative GRT process schemes, and competing GTL technologies. The use of the zone reactor simplifies the process, eliminating several systems and reducing the size and cost of others. The main benefits are:

- Simplified process with few unit operations.
- Reduced pressure and temperature requirements.
- Improved feedstock utilization.

Table 1
Performance expectations for scale-up of GRT zone reactor GTL process

	Flare gas application with no recycle	GTL fuels application with recycle
Single pass methane conversion (%)	70	40
Methane requirement (std ft^3 CH_4/bbl fuels)	12310	8475
O_2 requirement (std ft^3/bbl fuel)	7575	8214
CO_2 production (std ft^3/bbl fuels)	1951	1303
Net heat generation (MMBTU/bbl fuel)	2.936	1.463

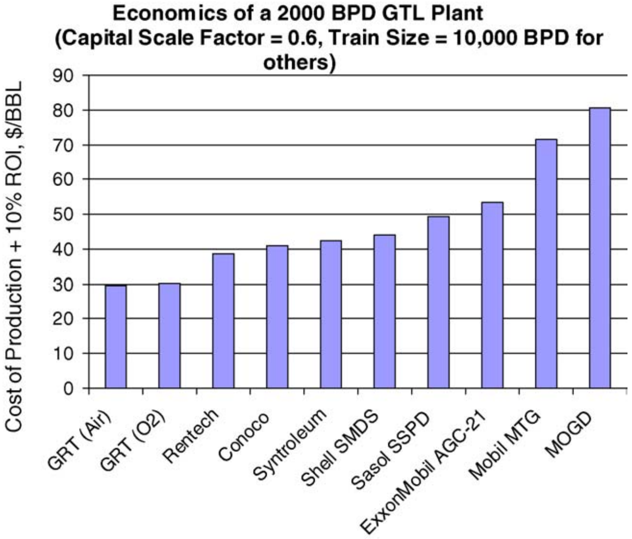

Fig. 4. Comparative economics of 2000 BPD GTL Plants. Data adapted from literature sources.

- Direct production of gasoline.
- Reduced separation costs.
- Can use air or oxygen.
- No need to move the solid (energy and capital cost reduction).
- Corrosion resistant metallurgy is limited to a single vessel (reactor cost reduction).
- No need for storage or handling of bromine outside the reactor (safety improvement).

4. Process economics

In order to refine our estimates of process economics, we have tested the process chemistry and zone reactor concept in a ~1 gal/day unit as shown in Fig. 5. Many similarities exist between the GRT cataloreactant process scale-up and the MTG process commercialized by Mobil in New Zealand. The significant cost advantage of the GRT process is that neither syngas nor high value methanol is needed as a feedstock. Comparative economics for competing GTL processes are shown in Fig. 4.

Initial engineering studies and increasingly large laboratory reactors show that the zone reactor can be scaled up. To date the conventional and zone reactor operation at scales of up to approximately 1 gal/day has yielded the performance expectations shown in Table 1.

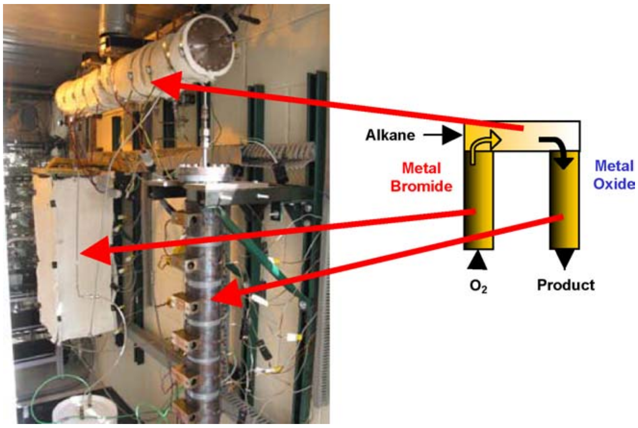

Fig. 5. 1 gal/day zone reactor unit.

The GRT gas-to-liquids process can be implemented competitively at small-scales (up to 4000 BPD) in refineries or gas plants and also stranded gas sites (Fig. 4). One planned implementation is to use the zone reactor to convert associated gas at the well head to oil soluble products that can be reinserted into the crude stream and sent to the refinery.

5. Conclusions

A bromine-mediated chemistry for the conversion of natural gas into liquid fuels has been described. The chemistry has been implemented in a ‘‘zone reactor,’’ with a number of advantages leading to projections of reduced capital and operating costs relative to existing technologies.

References

[1] C.D. Chang, A.J. Silvestri, J. Catal. 47 (1977) 249.
[2] C.D. Chang, W.H. Lang, A.J. Silvestri, US Patent 3,998,898 (1976).
[3] C.D. Chang, W.H. Lang, US Patent 3,899,544 (1975).
[4] S.A. Butter, A.T. Jurewicz, W.W. Kaeding, US Patent 3,894,107 (1975).
[5] X.-P. Zhou, A. Yilmaz, G.A. Yilmaz, I.M. Lorkovic, L.E. Laverman, M.J. Weiss, J.H. Sherman, E.W. Mcfarland, G.D. Stucky, P.C. Ford, Chem. Commun. (2003) 2294.
[6] I. Lorkovic, M. Noy, M. Weiss, J. Sherman, E.W. McFarland, G.D. Stucky, P.C. Ford, Chem. Commun. (2004) 566.
[7] I. Lorkovic, M.L. Noy, W.A. Schenck, C. Belon, M. Weiss, S. Sun, J.H. Sherman, E.W. McFarland, G.D. Stucky, P.C. Ford, Catal. Today 98 (2004) 589.