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Natural gas conversion to liquid fuels in a zone reactor

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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)):

$$nCH_4 + nBr_2 \rightarrow nCH_3Br + nHBr \tag{1}$$

$$nCH_3Br + nHBr + nMO \rightarrow C_nH_{2n} + nH_2O + nMBr_2 \tag{2}$$

$$nMBr_2 + (n/2)O_2 \rightarrow nMO + nBr_2 \tag{3}$$

$$\text{Sum}: nCH_4 + (n/2)O_2 \rightarrow C_nH_{2n} + nH_2O \tag{4}$$

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)).

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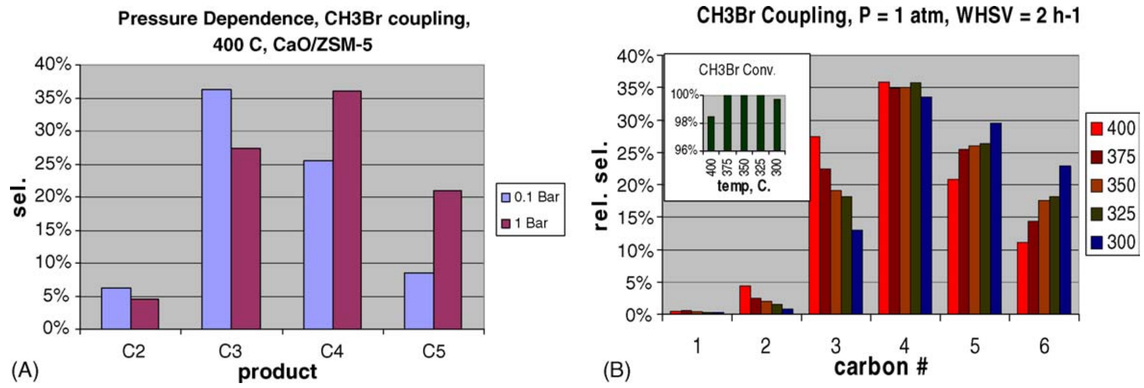

Fig. 1. (A) Pressure dependence of product selectivity from methyl bromide coupling at 400 °C over a CaO/ZSM-5 combination. (B) Temperature dependence of methyl bromide coupling over CaO/ZSM-5 at 1 atm total pressure and a WHSV of 2 h^{-1}.

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):

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

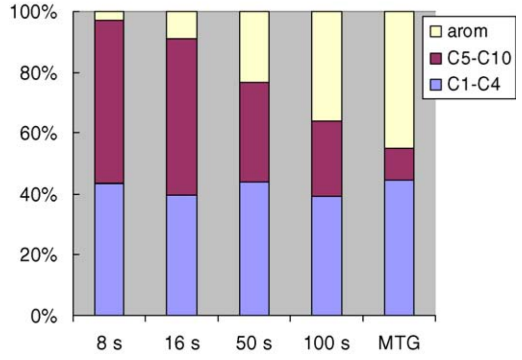

Fig. 2. Hydrocarbon product distribution dependence on residence time at 400 °C, 3 bar with comparison to methanol-to-gasoline results at 371 °C, 1 atm [1].

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