Challenges and Progress in the Conversion of Natural Gas to Fuels and Chemicals

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Low heteroatom and high hydrogen contents make natural gas an attractive feedstock for the synthesis of fuels and chemicals currently derived from petroleum. This keynote lecture describes recent progress in concept demonstrations and technological applications as well as in the fundamental understanding of the kinetic and thermodynamic constraints prevalent in direct and indirect methane conversion routes to fuels and chemicals. These recent advances combine catalyst improvements with the design and implementation of novel chemical reactors and separation schemes. These topics are discussed also in the context of their thermal efficiency and of their impact on potential strategies to minimize CO_2 formation and the economic viability of CO_2 sequestration.

Gas conversion processes will produce predominately liquid fuels in remote locations, because the prevalent economies of scale and the required field depletion rates will require large process throughputs. These throughputs are too large for chemical markets, with the possible exception of the ethylene and methanol markets. Depletion strategies based on methane conversion to liquid fuels will ultimately be replaced by the direct use of natural gas as a fuel, as pipelines and liquefied natural gas facilities develop together with the local economies and the required distribution infrastructures. Concurrent production of commodity and intermediate chemicals in large natural gas conversion complexes will increase economic incentives for first-of-a-kind technologies and possibly lead to their earlier deployment. The significant market penetration of wax, lubricants, and linear α-olefins from initial coal and gas conversion deployments by Sasol attests to the potential for co-production of chemicals, but also to their significant impact on relatively small chemical markets. The use of natural gas for chemicals syntheses will continue, using both remote and local fields, well beyond the remote gas-to-liquids commercialization time window, because natural gas provides clean and economical routes to methanol and ammonia, as well as to other chemicals currently derived from crude oil.

The conversion of natural gas to useful products is discussed here in the context of a methane refinery, possibly located far from markets, and designed to produce fuels, chemicals, and intermediates currently derived from crude oil. Process simplicity, minimal cycling of process and reaction conditions, and high conversions per pass lead to higher practical thermal efficiencies and lower capital costs for both direct and indirect processes for converting natural gas to fuels and chemicals. Direct conversion routes, however, provide paths to only a few desired products, and the high reactivity of these products typically requires their kinetic protection or selective extraction, both of which increase process complexity and costs. Indirect routes via synthesis gas provide broader options for final products or intermediates. They require less toxic and expensive oxidants than indirect functionalization routes involving bisulfate or halogenated methane derivatives. Direct paths involve C-H bond activation and the conversion of the resulting CH_x or CH_yO species to desired products within a single vessel. Pyrolysis, oxidative coupling, selective oxidation (to methanol or formaldehyde), partial oxidation (to synthesis gas; H_2/CO) and reforming with either steam or carbon dioxide are direct (one-step) methane conversion routes. Direct processes can produce only a few products (H_2/CO, acetylene, ethylene, benzene, methanol, formaldehyde). In many cases, these reaction products are much more reactive than the CH_4 reactant, either because of their weaker C-H bonds or their unsaturated character. Thus, they progress along reaction paths that ultimately lead to thermodynamically more stable carbon or CO_2 products. Only H_2/CO mixtures, useful only as intermediates to more useful products, reach equilibrium yields without significant formation of carbon or CO_2, and only as a result of the thermodynamic preference for H_2 and CO at conditions used for partial oxidation and reforming reactions.

High product yields in most direct routes therefore require continuous removal of desired products from the reaction zone or the thermodynamic or kinetic protection of these products against subsequent reactions. These approaches increase process complexity and second-law inefficiencies. In general, maximum attainable yields depend on the thermodynamic tendency of a given product to oxidize to CO_2 or to dehydrogenate to solid carbon. Weaker C-H bonds in products tend to favor their activation at lower reaction temperatures in the absence of thermodynamic or kinetic protection. Thus, low temperatures actually disfavor desired products in such cases, because subsequent reactions of such desired products have much lower activation energies that CH_4 activation steps leading to the desired initial products.

Direct paths become indirect when desired products are made via the initial formation of chemically-protected intermediates, which must be subsequently converted to the desired products. In such cases, the first step forms a protected form of methane, which resists further conversion to CO_2 or carbon because of its low reactivity, while a second step in a downstream vessel "de-protects" this intermediate and forms the desired products in higher yields than by the corresponding direct routes. For example, synthesis gas (H_2/CO) is in effect a thermodynamically protected, but quite reactive, form of “activated” methane, useful to form a broad range of hydrocarbons and oxygenates. High-temperature CH_4 reactions with H_2O, CO_2, or even O_2 form minor amounts of CO_2 because of thermodynamic constraints imposed by high reaction temperatures at typical reactant stoichiometries.

Synthesis gas conversion processes are significantly more advanced in development than direct processes and than other two-step conversion schemes using methane bisulfate or halogen derivatives. Indirect gas conversion processes via synthesis gas are currently practiced for methanol synthesis and for hydrocarbon formation via the Fischer-Tropsch synthesis. Diesel-range hydrocarbons (via Fischer-Tropsch synthesis) and gasoline (via methanol to gasoline) can be produced with thermal efficiencies as high as 80% of their respective theoretical values (78% and 75%). These indirect processes have continuously evolved with advances in synthesis gas generation, in the design and deployment of three-phase bubble columns for synthesis gas conversion, and in the development of improved catalytic materials for the selective synthesis of paraffins, intermediate size α-olefins, and higher alcohols. Small modular gas conversion plants using catalytic partial oxidation in monolith reactors and CO hydrogenation in bubble columns may also create future opportunities for combining H_2 and power generation and the synthesis of commodity petrochemicals, and even of liquid fuels, in smaller scales than for remote fuels-based gas to liquid plants.

Clean diesel products and intermediate range α-olefins can be efficiently produced via Fischer-Tropsch synthesis pathways, but lighter olefins, such as ethene and propene, and gasoline-type hydrocarbons require an additional process step, in which methanol derived from synthesis gas reacts on shape-selective catalysts.

Attractive routes for the synthesis of oxygenates with C-C bonds will require new approaches involving bifunctional dehydrogenation-condensation pathways. Multifunctional reactors combining membrane separations with chemical reactions and cyclic reactors for temporal separation of reactants and products hold significant promise for increasing the efficiency of synthesis gas generation and direct conversion steps, but their ultimate impact on capital costs and thermal efficiencies remain unclear.

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