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Catalytic conversion of natural gas and methane to synthesis gas and beyond: A collection of published research (2009–2015)

1. Introduction

This article serves as the introduction and overview to the *Journal of Natural Gas Science and Engineering's* virtual special issue (VSI) concerning *Catalytic Conversion of Natural Gas and Methane to Synthesis Gas and Beyond*, compiled in July 2015. The compilation includes 41 articles addressing diverse topics related to the conversion of natural gas and methane feedstock to synthesis gas ("syngas"), from which hydrogen and/or more valuable liquid hydrocarbons involving more complex, higher-carbon-number molecules can be derived. These articles were published by *Journal of Natural Gas Science and Engineering* during the period from 2009 to July, 2015. These conversion processes typically involve catalysts and the characterization and performance of various catalysts is addressed by some of the manuscripts. Each article included in the compilation represents a stand-alone analysis and research on a relevant topic that has passed the journal's rigorous peer-review editorial system.

Collectively, the published articles compiled in this virtual special issue provide a useful synthesis of progress made in recent years in several diverse research areas pertaining to research techniques, analytical tools, technologies, catalysts and optimization algorithms involved in natural gas to liquid (GTL) conversion processes. Cost and efficiency implications plus other commercial and environmental issues are also addressed by some of the articles.

The articles compiled in this JNGSE virtual special issue are organized into six distinct categories:

1. Introduction to this JNGSE virtual special issue and summary of compiled GTL articles (i.e., this article)
2. Potential applications for GTL technologies in natural-gas-resource-rich areas
3. Methane conversion to synthesis gas ("Syngas")
4. Characterization and performance of catalysts used in gas conversion processes
5. Hydrogen production and extraction from synthesis gas
6. Optimization algorithms and methodologies applied to gas conversion

Note that published articles relating to hydrocarbon liquid conversions are not included in this compilation as they are addressed in another recent JNGSE virtual special issue focused specifically on hydrocarbon conversions to methanol, other oxygenates, gasoline components, olefins and other valuable and complex petrochemical products. JNGSE has recently published the other VSI with the title "Conversion of Natural Gas and Gas Liquids to Methanol, Other Oxygenates, Gasoline Components, Olefins and Other Petrochemicals: A Collection of Published Research (2010–2015)" (Wood, 2015) that also addresses conversion of hydrocarbons to liquids via a range of mainly catalytic processes, many utilizing some form of Fischer-Tropsch (F-T) synthesis to produce their high-value liquid products. F-T also features in many of the techniques discussed in the gas conversion manuscripts included in this VSI. Readers interested more generally in F-T processes and catalysts will find manuscripts of interest in this VSI and the one focusing on a wide range of hydrocarbon liquid products.

The brief summaries of the articles included in this virtual special issue now follow, organized into the categories described above.

2. Potential applications for GTL technologies in natural-gas-resource-rich areas

The three articles in this section review the opportunities, technologies and attractiveness of gas-to-liquid solutions more generally to monetize remote and stranded gas resources and to displace, with gas-derived liquid products, imports of expensive oil-refinery-derived liquid transportation fuels, lubricants and, in some cases, petrochemicals.

Stanley (2009) examined the potential uptake of GTL conversion technologies as a sustainable gas utilization options to avoid flaring of associated gas, and to reduce Nigeria's dependence on imported refined petroleum products. The key GTL processes and products are outlined, together with the capital cost and technology barriers that need to be overcome in order for GTL technologies to be successfully deployed in Nigeria on a commercial basis. The conclusion reached is that he vast array of marketable products that it is possible to generate using GTL technologies offer realizable and sustainable alternative energy sources for countries such as Nigeria, which have enormous untapped gas resource yet growing demand for transportation fuels.

Velasco et al. (2010) reviewed the natural gas industry and resources in Bolivia. Despite holding substantial gas resources and reserves, accompanied by significant production, including some exports by pipeline to Brazil, Bolivia experiences shortages of diesel and other liquid transportation fuels, which it must import at high cost. Its diesel shortage cannot be solved using conventional refining processes due the light nature of the crude oil produced in Bolivia and the configuration of its refineries. The Bolivian internal diesel market, in 2010, was estimated to be some 23,600 bpd

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against its refinery diesel production of some 11,200 bpd. This led to the conclusion that GTL processes offer potentially promising solutions to Bolivia's diesel problems, with additional benefits of creating local jobs and industrial development, and reducing Bolivia's dependency on expensive petroleum product imports.

Wood et al. (2012) reviewed the various GTL technologies associated with the commercial plants in operation, development and planning, and the range of market opportunities for GTL products. Scaling-up technologies by the large scale technology providers has proved to be more costly and technically challenging than initial plans suggested. As well as large-scale plants suited to large gas resource-holding countries, small-scale niche markets exist to avoid gas flaring (onshore and offshore) and to meet small-scale, transportation-fuel requirements of land-locked regions such as in the Caspian region and Bolivia. Although Fischer-Tropsch (F-T) technologies dominate the industry other technologies to produce methanol, dimethyl ether (DME), gasoline and a range of petrochemicals are the subject of much recent research. Some generic capital cost, operating costs, schedule and capacity assumptions for a 50,000 barrels/day F-T plant are presented. The high costs, complex technologies, dominated by patented processes, and the risk exposure to fluctuating gas and oil prices are highlighted in the challenges that need to be overcome for GTL sector to prosper.

3. Methane conversion to synthesis gas ("syngas")

Sadooghi and Rauch (2013) developed a mathematical model simulating synthesis gas production by methane steam reforming a fixed-bed, catalyst-filled reactor. The pseudo-heterogeneous model represents diffusion phenomena inside the reactor tube. Heat and mass transfer equations are coupled with detailed reaction mechanisms and solved for both the flow phase and within the catalyst pellets. The model is used to evaluate the effects on methane conversion and hydrogen yields within a temperature range from 873 to 1073 (K). The results provide temperature and concentration distributions along the reactor's axial and radial coordinates, and reveal strong radial temperature gradients particularly close to the entrance of the reactor. Also the water-gas shift reaction rate is shown to reverse its direction at a finite axial position along the reactor.

Talkhoncheh and Haghighi (2015) considered syngas production via dry reforming of methane over Ni-based nanocatalyst involving various supports of clinoptilolite (NH_4NO_3), ceria (CeO_2) and alumina (Al_2O_3). The nanocatalysts were prepared by the impregnation method and used for CO_2 (dry) reforming of CH_4 into synthesis gas. The physico-chemical properties of the samples were characterized by XRD, FESEM, EDX, BET and FTIR analyses. XRD analysis is showed that the interaction between NiO and CeO_2 results in good dispersion of NiO. Based on the BET analysis, Ni/Al_2O_3 nanocatalyst has the highest specific surface area in comparison to the other nanocatalysts studied. FESEM images illustrate that, all the samples have nanoscale morphology. EDX analysis demonstrates the homogenous dispersion of Ni on Ni/Al_2O_3 and Ni/CeO_2 nanocatalysts. The activity and stability of the synthesized nanocatalysts for CO_2 reforming of CH_4 were tested over a temperature range of 550–850 °C. Ni/Al_2O_3 nanocatalyst demonstrates much higher conversions (93% CH_4 and 96% CO_2 at 850 °C) and yields (90% H_2 and 93% CO). Also, the activity of Ni/Al_2O_3 remained stable for 1440 min. Among the prepared samples, Ni/Al_2O_3 nanocatalyst has the best performance due to its preferential physicochemical properties. On the other hand, Ni/Clinoptilolite, as an inexpensive and economical nanocatalyst, has relatively good activity, but its H_2 and CO yields as well as H_2/CO molar ratio are lower than that of the Ni/Al_2O_3 nanocatalyst.

Chein et al. (2015) conducted thermodynamic analysis of dry reforming of CO_2 with CH_4 (DRM) at high pressures. The thermodynamic equilibrium of DRM was studied using the Gibbs-free-energy minimization at elevated pressures. CH_4 and CO_2 conversions, carbon formation, H_2 yield, H_2/CO ratio and H_2O formation were used to characterize the DRM performance using the reaction temperature as the primary variable. The result shows that DRM is unfavorable at high pressure. CO_2 and CH_4 conversions decrease while carbon and H_2O formation increase as the pressure increases. By increasing CO_2/CH_4 ratio in the reaction, CH_4 conversion is enhanced, carbon formation is suppressed, but CO_2 conversion is lower due to excess CO_2 supply. The simulation results indicated that the introduction of inert gas into the system would not produce a significant beneficial effect on the DRM performance. The performances of combined DRM and partial oxidation of methane (POM) and combined DRM and methane-steam reforming (MSR) were also studied to suppress the carbon formation. It was found that carbon formation could be reduced by introducing oxygen. However, the resulting H_2/CO ratio is less than unity. Introducing H_2O into the reaction system can eliminate carbon formation when amount of H_2O is large. However, the system must be operated at high temperature to produce high CH_4 and CO_2 conversions.

Meng et al. (2015) investigated the effect of a Ce promoter on the structure and catalytic performance of Ni/Al_2O_3 catalyst for CO methanation in a slurry-bed reactor, i.e., to produce a CH_4-rich synthetic gas. The catalysts were prepared by the wet impregnation method. The effect of the impregnation sequence of Ni and Ce, and the calcination temperature on catalyst structure and catalytic methanation was investigated using BET, XRD, TEM, TPR and XPS. The results showed that Ni–Ce/Al_2O_3 catalyst samples prepared by co-impregnation of Ni and Ce possessed larger specific surface area, higher Ni species dispersion, smaller Ni particle size, lower reduction temperature, and higher catalytic activity for catalytic methanation of CO than Ni/Al_2O_3 catalyst samples, or Ce/Ni/Al_2O_3 catalyst samples (i.e., impregnated first with Ni and then with Ce), or Ni/Ce/Al_2O_3 catalyst samples (i.e., impregnated first with Ce and then with Ni). With an increase in calcination temperature, the interaction between the Ni species and the g-Al_2O_3 support strengthened. The Ni–Ce/Al_2O_3 catalyst calcined at 350 °C, obtained a moderate interaction and exhibited the optimum catalytic activity under the reaction conditions of 280 °C and 1.0 MPa, with CO conversion and CH_4 selectivity reaching 95.4% and 90.7%, respectively, and C_2 to C_4 selectivity being approximately 1%. Further increase in calcination temperature decreased the catalyst reducibility and catalytic performance.

Behroozsarand and Pour (2014) compare models for synthesis gas production via CO_2 (dry reforming) of natural gas in a micro reactor. Specifically, the Langmuir-Hinshelwood kinetic (LHK) and microkinetic (MK) models are evaluated using a two-dimensional numerical model for single micro channel involving a rhodium catalyst. Micro-channel wall temperature, pressure, CH_4/CO_2 ratio, H, CO, and steam concentrations in the feed gas stream are calculated in order to evaluate micro-channel performance. The results show that increasing wall temperature in LHK model, CO concentration and pressure in MK model have positive effects on the methane conversion within the micro reactor. Also, decreasing CH_4/CO_2 ratio and steam concentration in the LHK model, and wall temperature, CH_4/CO_2, hydrogen composition in the MK model shows similar benefits. From the results it is concluded that the LHK model is more suitable than the MK model evaluated for predicting DR process behavior, because it provides more rational and appropriate responses.

Farniaei et al. (2014) simulated the use of a tri-reforming process to provide the energy source for driving the highly-endothermic methane dry reforming (DR) process in a multi-tubular recuperative thermally coupled reactor (TCTDR). The TCTDR modeled was