

DIRECT CONVERSION OF METHANE TO HYDROGEN AND ELEMENTAL CARBON

OVERVIEW

In a recent paper in Science in November of 2017, Upham¹ et. al., describe a catalytic process that employs a molten metal catalyst system to convert methane directly into hydrogen and elemental carbon. The reaction is very clean and occurs in 1 step with little or no product gas cleanup required, Equation 1, below.

For certain applications this process should favorably compete with the standard hydrogen production process of steam methane reforming (SMR). In the SMR process methane is reacted with water to produce carbon monoxide and hydrogen, Equation 2. The next step, the water gas reaction, is used to convert the carbon monoxide through reaction with water to hydrogen and carbon dioxide, Equation 3. The article also provides a good historical background to the SMR process.

THE DIRECT REACTION:

The direct conversion of methane to hydrogen and carbon



The reaction is endothermic so external heat has to be applied to get any reasonable conversion. In fact, the reaction is conducted at 1000C and involves the use of a combination of Ni and a low melting metal (relative to 1000C) as the Ni carrying medium. Supporting metals tested included Bi, Au, Pb, Ga, In & Sn, all as melts.

The SMR reaction



The SMR reaction is very endothermic and a considerable energy input is required to push the reaction along compared to Reaction 1. This reaction is usually conducted in the 500C-900C range. It can be seen the direct reaction, Reaction 1, is more energy efficient per mol of hydrogen produced compared to Reaction 2, 37 kJ/mol vs >65 kJ/mol.

The SMR reaction is an energy and CAPEX hog accounting for most of the energy required to drive the process; CAPEX is typically stated at >60% of the total plant cost as noted by Shell's Pearl plant in Qatar. But wait, there's more, the water gas shift reaction is required to convert the CO formed in reaction 2 to maximize the hydrogen product.

¹ D C Upham, et. Al., Science, 358, 917-921 (2017)
<http://science.sciencemag.org/content/358/6365/917>

The water gas shift reaction



The water gas shift reaction, unlike the other two processes, is exothermic, so cooling, rather than heating, is required. The water gas shift reaction, in practice, is usually conducted in 2 steps, in separate reactors, the first runs around 350C and the second around 250C. As these temperatures are considerably lower than temperature of the SMR reactor, active cooling of the output from the SMR reactor and the first water gas shift reactor is required. The processes are highly optimized, so as much heat as possible is recaptured for use in the process. A comprehensive review of these hydrogen production processes is given in a recent monograph². Not much more will be said about these 2 processes.

The molten metal reactor system for the direct conversion of methane

The authors found that a 27% Ni – 73% Bi alloy exhibited the best reactivity for the process, equation 1. When operated at a temperature of 1065C a 95% conversion of the methane was observed. The reaction is very clean with the gaseous hydrogen easily separating from the reactor. The solid carbon product floated on the top of the metal melt. The initial carbon product contained a small amount of Ni + Bi (<4atom%) which could be removed by submersion of the carbon in the molten metal bath.

The reactor

The reactor system is shown in Figure 1, on the next page. The figure shows Pt as the active metal catalyst but most of the work was done with Ni as it was more active than Pt. The rate data for all the systems studied are given in Figure S-12. The boiling point for Bi is 1564C with a low vapor pressure at 1000C.

So...CONSEQUENCES?

Hydrogen from the Direct Methane to Hydrogen Process

The hydrogen from the subject process is extremely clean but may have some unreacted methane (a who cares?). (If the hydrogen is used for either ammonia syntheses or as a PEM fuel, the presence of methane is a "who cares".) Another virtue of this process is that it is a single "pot" process which should scale with the volume of the reactor, a cubic function³. Where could this technology be of use? See Appendix for clues.

² K Liu, C Song, & V Subramani, Hydrogen and Syngas Production and Purification Technologies, AIChE Wiley, Hoboken NJ (2010)

³ Another, hydrocarbon free process for hydrogen production is water electrolysis which produces both hydrogen and oxygen. The best electrolyzers run with about a 68% efficiency and scale with electrode area, a square function.

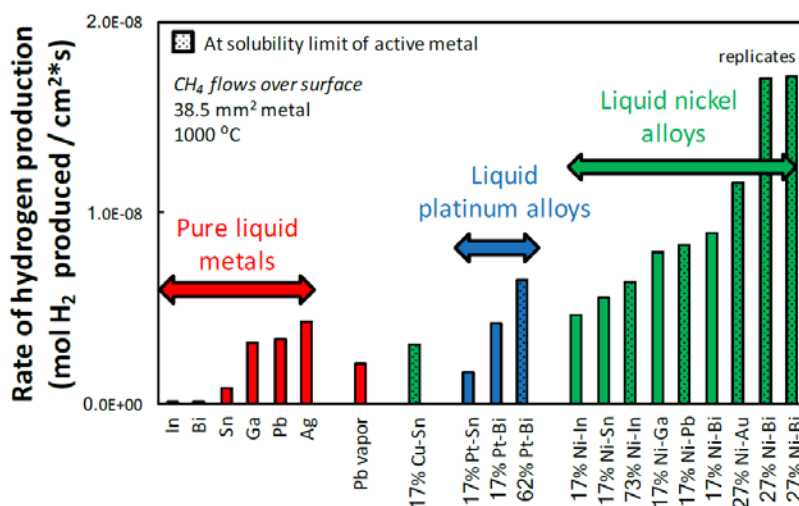


Fig. S12. Graphical comparison of activity reported in Table 1 for methane pyrolysis at 1000 °C, over 38.5 mm² of molten metal. The same reactor volume was used in all cases, including for Pb vapor. All compositions are molar percent.

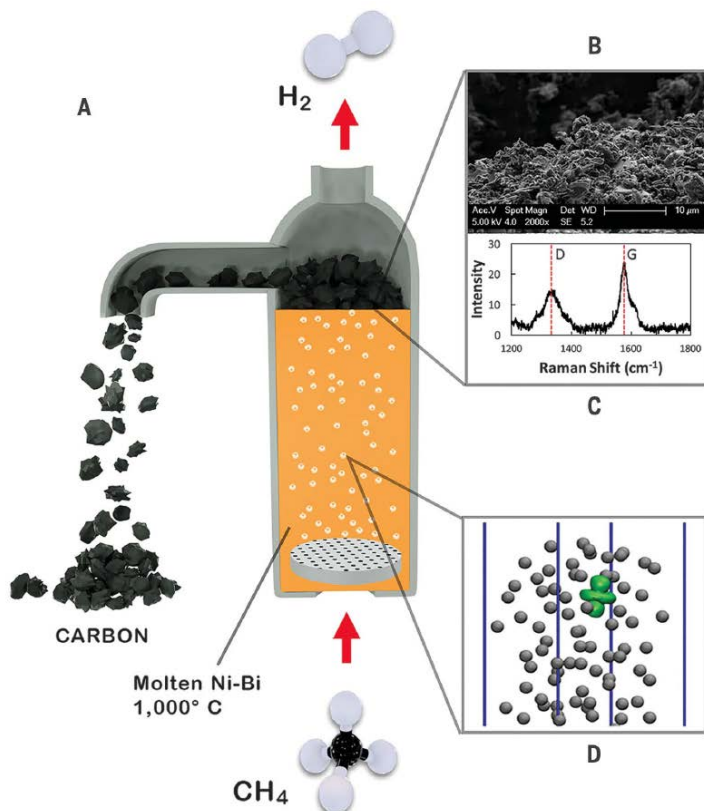


Fig. 1. Hydrogen production with a Ni-Bi molten catalyst. (A) Reactor for CH₄ conversion to H₂ and carbon in a molten-metal bubble column with continuous carbon removal. (B) Scanning electron microscopy image of the surface carbon produced. (C) Raman spectrum of surface carbon. The dashed line labeled "D" is at 1350 cm⁻¹, and the dashed line labeled "G" is at 1582 cm⁻¹. (D) Ab initio molecular dynamics simulation showing an orbital (green) of a Pt atom dissolved in molten Bi (gray) alloy.

Hydrogen the from Water Gas Shift Reaction

Hydrogen is also a major industrial chemical commodity. It is used for the production of ammonia by reaction with nitrogen, the Haber-Bosch process. It is also the fuel for PEM fuel cells. In both cases, residual CO or CO₂ in the product gas stream from the Water Gas Shift reaction must be removed before usage in either process. Both of these carbon oxides are catalyst poisons. The removal of CO and CO₂ is typically accomplished with a methanation step. Methane does not interfere with either ammonia synthesis or PEM fuel cell operation.

Syngas

Syngas is an important chemical commodity and will remain as such irrespective of any development of the direct process discussed here. Syngas is the feedstock for gas-to-liquids (GTL) processes, aka Fischer-Tropsch, which is the foundation of many chemical plants world-wide. The production of syn gas employs only the SMR reaction and dispenses with a global use the water gas shift reaction except for polishing the SMR reaction for any hydrogen balance required.

The largest practitioner of this chemistry is Shell at their Pearl Plant in Qatar. Qatar has natural gas but no liquid petroleum resources. Shell has built the GTL plant with a stated capacity of (I recall) of 180,000 bpd⁴. This plant had an original budget around \$18 billion, final figure was in the \$21-\$22 billion range. The plant has yet to operate at full capacity. However, there are many other GTL plants in operation around the world.

Is There a Market Potential for the Direct Methane to Hydrogen Process?

(Important background information is contained in Appendix A.) The US already has 2 extensive energy infrastructure networks in place, the electric grid and the natural gas pipeline grid. So, what if we set suitably sized (market determined) direct methane to hydrogen processing units along the major transportation corridors to produce the fuel hydrogen onsite. What could these service centers look like?

The hydrogen coming off the reactors would be fairly clean and dry but at low pressure (not too much above atmosphere pressure). The working pressure for hydrogen fueling stations for vehicle usage is typically 70 MPa (10,000 psi). The product hydrogen would have to be compressed to this level with, most likely, 2 stage compressors, not inexpensive. It would have to be stored in (very) high pressure storage tanks again not cheap. Finally, the byproduct carbon would have to be stored before pickup. This approach would obviate the need to develop a 3rd infrastructure of hydrogen distribution pipelines, probably a pipe dream, pun intended.

As an aside here, no fuel cell company ever has showed a profit notwithstanding the many many millions of dollars of investment. About 2-3 years ago, I actually thought that there were two fuel cell companies which could have made it to the profitable

⁴ Bpd = barrels per day

side of the balance sheet. Alas, they did not make it, one is still struggling and the other was acquired by a Korean conglomerate. (BTW: Fuel cells were first described by Grove in England in the **1840s!**)

The Carbon Product

The carbon co-product has value and could be sold as a fungible commodity to offset some of the expense for the hydrogen service station costs. Graphitic carbon and the byproduct carbon are mostly graphitic in nature and have many uses. For example, the carbon can find uses as: electrodes in aluminum production; as the carbon black filler for tires; and, as a soil amendment in agriculture⁵. Also consider its use as the anode component for Li-ion batteries if its structure qualifies. It is fairly pure carbon and may be more suitable than the current sources of anode carbon which are mined out of the ground.

Food for thought CARB...

Appendix A: A Potential Use of the Methane to Hydrogen Process

CARB⁶ has for several decades pushed the deployment of fuel cell vehicles as the cure for all CA's air pollution woes. This quest has been called, at times, the pursuit of perfection at the detriment of the merely "good". There has been progress in fuel cell vehicles (FCV) over these decades of this chase for perfection.

Yes, FCVs are now being offered by several manufacturers but all the FCVs have the same Achilles heel...the lack of a hydrogen fuel infrastructure. This situation presents itself as the ultimate chicken vs egg conundrum. We can't sell the (very expensive!) FCVs because they have virtually nowhere to fuel up. We can't build the hydrogen fuel infrastructure because we don't have any customers. So, where to now?

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This process is very reminiscent of the Molten Metal Technology⁷ of the late 1990s which purported to use molten nickel to destroy hazardous waste materials. Had a lot of fanfare, high visibility, a high revenue raise. The technology did not work and the company had a spectacular fail. The rise and fall of MMT is reviewed in reference 7, a case study from the School of Management at Boston University.

⁵ David M. Filiberto and John L. Gaunt, Practicality of Biochar Additions to Enhance Soil and Crop Productivity, *Agriculture* **2013**, 3, 715-725; doi:10.3390/agriculture3040715

⁶ CARB = California Air Resources Board, the national leader in combatting air pollution from mobile sources...vehicles.

⁷ [webuser.bus.umich.edu/ajhoffs/teaching_cases/MMT%20\(A\)%20Case.pdf](http://webuser.bus.umich.edu/ajhoffs/teaching_cases/MMT%20(A)%20Case.pdf)