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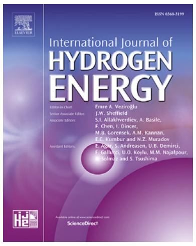

Hydrogen production using methane: Techno-economics of decarbonizing fuels and chemicals

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ABSTRACT

In the near-to-medium future, hydrogen production will continue to rely on reforming of widely available and relatively low-cost fossil resources. A techno-economic framework is described that compares the current best practice steam methane reforming (SMR) with potential pathways for low-CO_2 hydrogen production; (i) Electrolysis coupled to sustainable renewable electricity sources; (ii) Reforming of hydrocarbons coupled with carbon capture and sequestration (CCS) and; (iii) Thermal dissociation of hydrocarbons into hydrogen and carbon (pyrolysis). For methane pyrolysis, a process based on a catalytic molten Ni-Bi alloy is described and used for comparative cost estimates. In the absence of a price on carbon, SMR has the lowest cost of hydrogen production. For low-CO_2 hydrogen production, methane pyrolysis is significantly more economical than electrochemical-based processes using commercial renewable power sources. At a carbon price exceeding \$21 t^{-1} CO_2 equivalent, pyrolysis may represent the most cost-effective means of producing low-CO_2 hydrogen and competes favorably to SMR with carbon capture and sequestration. The current cost disparity between renewable and fossil-based hydrogen production suggests that if hydrogen is to fulfil an expanding role in a low CO_2 future, then large-scale production of hydrogen from methane pyrolysis is the most cost-effective means during the transition period while infrastructure and end-use applications are deployed.

Introduction

Fossil hydrocarbons possess enormous stored chemical potential from prehistoric photosynthetic processes. Humanity has globally prospered because of their widespread availability and relatively low cost. At present we combust approximately 10 trillion kilograms of carbon in low cost fossil fuels annually. Their use, however, is ultimately limited by the fact that they are a finite resource. In the shorter term, before the prices increase due to depletion, the risk of unacceptable environmental consequences from increased atmospheric CO_2 may drive society towards alternatives to ensure sustained human

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prosperity [1]. The immense challenge of shifting away from carbon dioxide intensive processes to more sustainable alternatives will require many massive projects and investments spanning decades and generations [2].

Of the fossil resources, methane in natural gas provides the most energy per unit mass of carbon dioxide produced and is potentially the largest fossil reserve (if hydrates are included) [3]. Substitution of coal by methane would achieve significant emissions reductions. However, for the long term moving to fuels that produce no CO_2 is highly desirable. Hydrogen, burns cleanly producing only water and can be used in fuel cells; it has long been a candidate for a major future fuel. Today, 96% of global hydrogen is produced by fossil fuel reforming technologies (Eqs. (1) and (2)) and is predominately used in the production of ammonia-based fertilizers for agriculture [2]. The remaining 4% is produced by electrolysis that splits water with electricity that could potentially be CO_2 free (Eq. (3)).

The most common hydrocarbon based hydrogen production technology is steam methane reforming (SMR) which satisfies approximately 48% of global demand. SMR produces stoichiometric amounts of process-based CO_2 from the combination of steam reforming and the water-gas shift reactions and additional combustion-based CO_2 when supplying the heat required to drive the overall endothermic reaction [4].

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad \Delta H^0 = 165\ kJ\ mol^{-1},\quad \Delta G^0 = 114\ kJ\ mol^{-1} \tag{1}$$

$$C + 2H_2O \rightarrow CO_2 + 2\,H_2 \quad \Delta H^0 = 90\ kJ\ mol^{-1},\quad \Delta G^0 = 63\ kJ\ mol^{-1} \tag{2}$$

$$2H_2O \rightarrow O_2 + 2H_2 \quad \Delta H^0 = 572\ kJ\ mol^{-1},\quad \Delta G^0 = 47\ kJ\ mol^{-1} \tag{3}$$

A typical SMR hydrogen plant produces approximately 9–10 tonnes of CO_2 equivalent (t CO_2e) per tonne of hydrogen [5]. By contrast, if hydrogen were to be produced by coal gasification (currently 18% of global H_2 production), the CO_2 emissions per tonne of hydrogen product would double compared to SMR. Put simply, hydrogen produced from fossil hydrocarbons using today's fossil-based technology has diminished value as a fuel in a carbon constrained world.

Alternate processes for hydrogen production from non-fossil resources are commercially available for small markets, but to be economically competitive for large-scale applications the technologies need to compete with technologies that utilize low-cost and abundant hydrocarbons [6]. In the most ambitious vision, all the hydrogen required would be liberated from water using sustainable energy sources and utilized in fuel cells or burned in hydrogen-based thermal engines [7]. At present, renewable energy-based processes for hydrogen production (electrolysis of water coupled with photovoltaic cells or wind turbines, photo-catalysis, photo-biological water decomposition, etc.) cannot produce hydrogen at a price or scale that is competitive with fossil fuels [8]. As such, the use of fossil hydrocarbons such as methane for power, heat and electricity production is likely to continue until they become less economically competitive than alternatives like hydrogen [8].

Low-cost methane can be used to produce hydrogen without producing carbon dioxide by pyrolysis (Eq. (4)) which produces hydrogen and solid carbon [9]. Previous attempts at commercializing pyrolysis technologies for hydrogen production have been limited by the need to use a solid catalyst, which rapidly deactivates, decreasing hydrogen yields. However, for production of more valuable solid carbon products (e.g. carbon black) pyrolysis has been used commercially [10,11].

$$CH_4 \leftrightarrow C_S + 2H_2 \quad \Delta H^0 = 75.6\ kJ\ mol^{-1},\quad \Delta G^0 = 50.8\ kJ\ mol^{-1} \tag{4}$$

Numerous studies concerning future hydrogen demand have been published [12–14]. We are interested in the production of large-volumes of low-cost hydrogen with very low associated CO_2 emissions, which would increase the rate of adoption of power generation using hydrogen as well as hydrogen vehicles. Applying rigorous economic analyses to proof-of-concept research and development technologies can provide critical guidance on future resource allocation, research and development priorities and technology projections. Accordingly, in this study we develop a conceptual design for a novel methane pyrolysis process and describe a techno-economic framework for comparing low-carbon hydrogen production options using the dominant pathways actively discussed in literature [8]. The pathways are: (i) Electrolysis coupled to sustainable electricity sources; (ii) Reforming of hydrocarbons coupled with carbon capture and sequestration (CCS) and; (iii) Thermal dissociation of hydrocarbons into hydrogen and carbon (pyrolysis). These comparisons can help us to address the following questions and in doing so guide research, development and demonstration priorities:

(i) What are the comparative economics of hydrogen production from water electrolysis, SMR, SMR with CCS, and methane pyrolysis?
(ii) How does a price on carbon (i.e. \$ t^{-1} CO_2e) influence the overall relative economics?
(iii) What innovations might make methane pyrolysis compete directly with SMR without a carbon price?

Current commercial hydrogen production

Steam methane reforming

Current costs and carbon emissions

In conventional SMR, methane is reacted with steam using a catalyst at relatively high temperature, 650–1000 °C, and a pressure of 5–40 bar to produce carbon monoxide and hydrogen. Additional hydrogen is produced by reacting carbon monoxide with water in the water-gas shift reaction [15]. The final stage of the process separates high-purity hydrogen (99.99%) from CO_2 using pressure swing adsorption. The CO_2 generated exits in two streams, a diluted stream (stack gases with CO_2 concentration 5–10% vol.) and a concentrated stream (approximately 50% by vol. after PSA) [16]. Approximately 9.5 t CO_2e t^{-1} H_2 are produced, 60% of which is generated from the process chemistry, while the remaining 40% is the product of the combustion of the additional flue gas required by the steam reformer [17]. The pure CO_2 stream is readily amenable for low-cost CCS if appropriate geological storage reservoirs are located nearby. If carbon dioxide

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