



CO₂ mitigation costs of catalytic methane decomposition

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ABSTRACT

Catalytic methane decomposition (CMD) is promising for producing hydrogen without direct CO₂ emissions. We estimate the CO₂ mitigation costs associated with CMD for hydrogen production and subsequent power generation in a fuel cell. The overall CO₂ emissions and economic viability are evaluated based on four scenarios: whether the by-product carbon can be sold or must be discarded into landfill; whether the catalyst can be recycled or not. CO₂ emission savings and the associated costs of CMD concept are compared to the combined-cycle gas turbine (CCGT) power plant with and without carbon capture and storage (CCS). The results illustrate that the profitability of the concept as well as the ensuing CO₂ abatement costs strongly depend on the ability to separate the catalysts from the carbon generated during the CMD. The life-cycle CO₂ emissions per unit of electricity output of a CCGT plant with CCS are marginally higher than those generated in the CMD with perfect separation and regeneration of the catalysts. The levelized costs of electricity generation (LCOE) of CMD without selling the by-product are also higher than for CCGT with CCS. In contrast, the CMD can be highly profitable assuming selling the by-product carbon at current prices.

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1. Introduction

The generation of affordable and environmentally friendly electricity while limiting greenhouse gas emissions is a major contemporary challenge. Hydrogen fuel cells are a power generation technology that may contribute to achieve this goal, as they offer high efficiency and hydrogen is considered a promising energy carrier [1]. Hydrogen is already widely used in the chemical and oil industry for the production of many valuable products, such as ammonia and methanol, and it has great potential for additional applications, especially for use in fuel cell electric vehicles [1–3].

The production of large amounts of hydrogen from renewable

sources is a long-term goal [4]. Water electrolysis using renewable energy, biomass reforming and photo-electrolysis are among the technologies considered to achieve this goal. However, costs must be considerably reduced before the hydrogen obtained from these processes becomes economically competitive [1,5]. Currently, hydrogen is produced mainly from fossil fuels. Their availability, relatively low cost and the existing infrastructure for delivery and distribution lead to substantial cost advantages in comparison to the use of alternative renewable sources for hydrogen production. Unfortunately, the production of hydrogen from fossil fuels invariably results in significant carbon dioxide (CO₂) emissions. It has been estimated that a steam methane reforming (SMR) hydrogen plant vents about 13 gCO₂/gH₂ into the atmosphere [6,7].

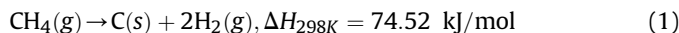
An intermediate solution towards renewable hydrogen generation is the production from fossil fuels without direct CO₂ emissions. One option is to utilize CO₂ capture and storage (CCS) technologies. However, this approach is highly-energy intensive and costly [7]. Another interesting alternative is hydrogen production via the catalytic decomposition of hydrocarbons [5,8].

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Catalytic methane decomposition (CMD) allows the production of pure hydrogen and solid carbon from natural gas without direct emissions of CO₂ and other greenhouse gases (GHG) [9,10].



With its strong C–H bond (440 kJ/mol), methane is the most inactive hydrocarbon and its decomposition requires elevated process temperatures above 1473 K in order to obtain reasonable hydrogen yield [8]. By using an appropriate catalyst, this temperature can be significantly decreased. Substantial progress has been realized in developing efficient catalysts for CMD. The literature mainly reports on two types of catalysts, namely supported-metal (predominant iron group metals) [11–13] and carbon-based (disordered/amorphous forms of carbon) catalysts [12,13]. Each catalyst type results in a different morphology of the produced carbon. Carbonaceous catalysts just generate amorphous carbon while metal-based catalysts induce the formation of valuable carbon nanomaterials (CNMs), which are mainly multi-walled carbon nanotubes. Due to the richness and diversity of their properties including mechanical, electronic, thermal and chemical characteristics, CNMs are of great interest for several large markets [12].

Despite the potentials of CMD, finding an effective catalyst regeneration strategy is a challenging issue [13]. Any catalyst will eventually become deactivated as a result of encapsulating carbon formation and/or as a result of space limitation in the reactor. For instance, when applying metal-based catalysts, methane decomposes at the gas/metal interface of the catalyst, producing carbon which dissolves and diffuses through the catalyst particle to the metal/support interface. Catalyst deactivation occurs when the rate of carbon diffusion through the metal particle is slower than the rate of carbon formation at the surface. Under these circumstances, excess carbon builds up at the gas side of the metal particle, forming a layer of graphitic carbon. The encapsulation of the metal particle leads to a loss in catalytic activity due to the gradual decrease in active surface area [14]. Deactivation also occurs because of space limitations in the reactor due to the formation of carbon filaments [15]. During the nucleation phase of the filament formation, carbon precipitates in the form of graphite at the metal/support interface and the metal particle detaches from the support by the formation of a carbon filament with the metal particle on its tip. The filament grows and the metal surface remains active, since the carbon deposited is removed from the surface by diffusion through the particle [16]. Though this mode of carbon accumulation allows the catalyst to maintain its activity for an extended period of time without deactivation, the generated carbon filaments will block the reactor which hinders the reaction further happening.

The CMD process was firstly industrialized by UOP in 1966 as the HYPRO process [17]. The process uses a circulating fluidized bed reactor (FBR) operating at 1250 K and atmospheric pressure. The carbon material deposited on the catalyst surface is burned off in a regenerator column in order to reactivate the catalyst and supply the energy required in the reactor [18]. However, the combustion still leads to the release of substantial CO₂, diminishing the environmental sustainability of this process. In addition, this procedure also hinders the utilization of carbon as a valuable by-product. Therefore, a suitable catalyst regeneration strategy that enables a valorization of the produced carbon filaments is a key aspect to make CMD economically and environmentally competitive to conventional hydrogen production processes. A few researchers evaluated the possibility of catalyst regeneration by removal of the deposited carbon via attrition. Jang and Cha investigated the effect of a fluidized bed reactor on the CMD process using iron supported on alumina [19]. They observed carbon attrition from the catalyst

surface during fluidization. Moreover, the methane conversion rate was maintained via the attrition of the deposited carbon. Based on this finding, Ammendola et al. [20] developed a model for CMD in a fluidized bed reactor taking the reactivation of the catalyst by means of carbon attrition into account. Their calculations indicate that carbon attrition is possible and plays a key role in the regeneration of the external catalyst surface. Currently, CMD has not yet been widely implemented in large-scale industrial applications, primarily due to technological barriers associated with the use of the catalysts and the disposal of the deposited carbons. Nevertheless, the increasing demand for CO₂-free hydrogen production and, more generally, the need for CO₂ emission reductions are such that a large-scale continuous production process based on CMD is becoming more attractive.

Despite the importance and potential applicability of CMD, a systematic process design and an integrated investigation of the technical, ecological and economic aspects is lacking in the existing literature. Based on experimental process data, Rodat et al. [21] calculated the production cost of non-catalytic solar thermal methane decomposition as 3.5 €/kg H₂. Comparing with some other hydrogen production technologies, it was stated that this process is not economically competitive [22,23]. Furthermore, Machammer et al. [24] analyzed the electricity-assisted thermal methane pyrolysis process based on the estimated product cost structure and carbon footprint finding that pyrolysis has favorable cost and carbon footprint. Postels et al. [25] performed a prospective life-cycle assessment of CMD based on a liquid-metal technology. By extrapolating lab data, they showed that CMD has the potential to reduce CO₂-equivalent (CO_{2eq}) greenhouse gas emissions for hydrogen production even compared to water electrolysis using wind power at the cost of doubling or tripling fossil resource depletion.

In this article, we focus on developing a large-scale process model of CMD. In order to close the gap in the existing literature, we estimate the potential profitability of this technology for hydrogen use in fuel cells, and assess the ensuing CO₂ emission reduction costs as a metric for environmental feasibility. We consider two types of catalysts, namely metal- and carbon-based in the process design, in addition to non-catalytic thermal decomposition (TD). Furthermore, since power plants aim at both profit maximization and CO₂ emissions minimization, we consider the ratio of the profits (from electricity generation and where applicable carbon sales) over the CO₂ emissions as the objective function.

In this analysis of CMD, we focus on the production of hydrogen from natural gas for use in a fuel cell. Given the emphasis of the selected CMD process on electricity production, we compare our estimates of the CO₂ emission reduction costs primarily to gas plants, both stand-alone and with combined CCS technology. This choice is motivated by the need to consider power plants that are operated in a similar way with respect to the merit order curve, dispatchability, and load response strategy [26]. The metric utilized herein for calculation of CO₂ abatement costs accounts for CO₂ emissions of the different technologies and the associated cost of electricity per unit of power output normalized over the lifetime of the technology. Note that in the comparison of abatement costs we take the conservative approximation that no revenue is achieved from the sale of carbon and all emissions are allocated to the production of electricity. In other places, we estimate the profits from selling the carbon using the optimistic assumption of current market prices and thus ignoring the effect of the production rate on the market price. Note that the objective function used in the optimization is thus different than the metrics used in the subsequent analysis.

Obviously, the production and use of hydrogen and the

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