Energy Conversion and Management 126 (2016) 923–934

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Thermo-catalytic decomposition of methane: The effect of reaction parameters on process design and the utilization possibilities of the produced carbon

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ARTICLE INFO

Article history:
Received 6 July 2016
Received in revised form 19 August 2016
Accepted 20 August 2016

Keywords:
Carbon capture
Hydrogen production
Methane decomposition
Natural gas
Process design

ABSTRACT

The study presents a path for selecting the reaction and reactor parameters of a process applying thermo-catalytic decomposition of methane (TDM). Temperature and catalyst are the main reaction parameters affecting the type of TDM carbon and defining the reaction's theoretical heat requirement. Secondly, the reaction parameters affect the reactor design including the selection of reactor type and heating source as well as the reactor dimensioning. The reactor dimensioning is discussed by highlighting the methane residence time requirement at different reaction conditions. Finally, the economic value of the TDM products is analyzed. According to the analyses, the reaction temperature and catalyst have a significant effect on reactor design and on the value and utilization possibilities of the TDM carbon. The prices of carbon products vary greatly as does the global demand of those. The utilization possibilities of carbon highly affect the overall viability of the TDM process and therefore should be carefully considered during process design.

1. Introduction

Tackling the global climate change requires the reduction of CO_2 emissions into the atmosphere. The International Energy Agency (IEA) has created several climate scenarios and analyzed which technologies could be utilized to achieve the CO_2 emission reductions required in each scenario. In the most ambitious scenario of IEA, the 2 °C scenario, the increase in the average global temperature will be limited to 2 °C [1]. The most recent target is to limit the increase in the average global temperature to 1.5 °C, which was the outcome of the Paris Climate Change Conference in 2015 [2]. The means to reduce CO_2 emissions include switching fossil fuels to carbon neutral fuels and energy efficiency improvements. Besides those, IEA has stated that carbon capture and storage (CCS) has a critical role in the reduction of CO_2 emissions [3]. IEA presumes in the 2 °C scenario that CCS technologies will to be implemented gradually from 2020 onward. The CCS technologies are based on the capture of CO_2 in a gaseous form and transportation to a storage site. However, the capture, transportation and storage of CO_2 requires considerable investments on infrastructure, and therefore the implementation of this technology is a time-consuming process. Thus, new solutions for the near-future CO_2 emission mitigation are urgently needed.

Thermo-catalytic decomposition of methane (TDM) could be applied to natural gas utilization with a benefit that it produces less CO_2 emissions than the conventional technologies. TDM is an endothermic reaction in which methane, which is the main component of natural gas, is thermally converted to solid carbon, gaseous hydrogen, and traces of higher hydrocarbons. Thus, instead of capturing gaseous CO_2, the carbon could be captured in a solid form. Dufour et al. have conducted several life cycle analyses [4–6] for processes where TDM has been applied to hydrogen production. They have compared the TDM process with the currently most common technology for hydrogen production, steam methane reforming (SMR), both with and without coupling CCS to the SMR process. The result of their analyses was that TDM was more environmentally-friendly process than SMR even when the SMR process was coupled to CO_2 capture and storage. Dufour et al. have also analyzed a theoretical case of autocatalytic TDM process where the product carbon would catalyze the TDM reaction and consequently the reaction temperature would be lower than in the non-catalytic thermal process. Consequently, this would result in a further reduction in environmental impact. However, so far the experimental observations of autocatalysis are limited to short periods at the beginning of the reaction [7].

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http://dx.doi.org/10.1016/j.enconman.2016.08.060
0196-8904/

Currently, natural gas is considered the cleanest fuel among the fossil fuels, but if the limits on CO_2 emissions become tighter, emission reductions are needed also in the utilization of natural gas [8]. The current global hydrogen production is approximately 7.2 EJ and nearly half of that is produced from natural gas with SMR, as stated by IEA [9]. Moreover, IEA has stated in the same report that hydrogen, when produced with low CO_2 emissions, could significantly contribute to the CO_2 emission reduction targets in the energy sector. IEA also estimates an increase in natural gas demand from the current 3.4 trillion m^3 to 5.4 trillion m^3 until 2040 [10].

TDM has been proposed to be applied to hydrogen production (potentially without CO_2 emissions) [11] to fulfill the demand of chemical industry or to be further utilized to produce electricity either by a steam-power cycle [12] or fuel cells [13]. Muradov [14] has analyzed the potential of TDM in hydrogen production and presented the benefits of TDM over SMR. Muradov and Veziroğlu [15] have conducted an economic analysis for TDM by studying the effect of the product carbon price on the hydrogen production cost. They have also presented typical prices of different carbon products, and number of these carbon products are valuable enough to make the TDM process economically more feasible than SMR. Keipi et al. [12] have previously published a techno-economic analysis of a commercial-scale TDM application. In that study, the conclusion was that the market value of the product carbon, which depends on its quality, is the main factor affecting the economic feasibility of the TDM processes when assuming a moderate cost of CO_2 emission allowances.

Different TDM reactor concepts have been investigated and presented in the literature, such as plasma-assisted TDM process [16,17], implementing TDM in a molten metal reactor [18–24] and a cyclic reactor that consists of separate heating and decomposition units which is known as the thermal black process introduced already at the 1920s [25]. Furthermore, various heating sources have been proposed to conduct the TDM reaction: an electric arc, partial combustion of feedstock methane, regenerative heat supply with cyclic heating and decomposition steps, and heat supply with heating elements outside the reactor [12,26]. Despite the numerous technical alternatives presented in the literature to conduct the TDM reaction, there is a lack of comprehensive analysis on the selection of TDM reaction and reactor parameters. The focus in this article is to highlight the different aspects that need to be taken into account when designing a TDM reactor. The selection of the TDM reaction and reactor parameters and the effect of those to the overall process design are analyzed. Altogether, this article presents a path illustrated in Fig. 1 along which the TDM reactor design can be conducted as a part of the overall process design.

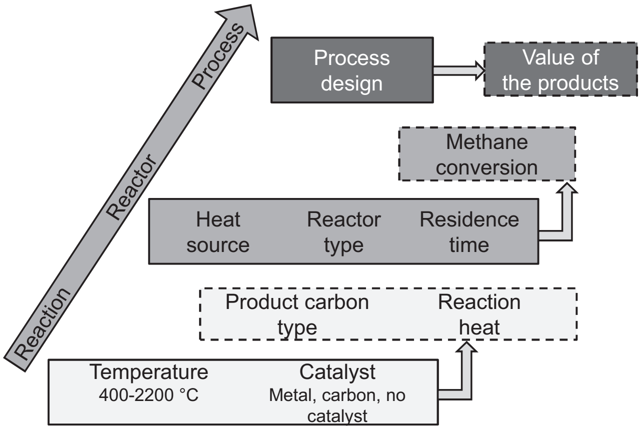

Fig. 1. The path for selecting the reaction, reactor and process parameters when applying TDM. The parameters that can be selected are inside the solid lines and inside the dashed lines are the consequent parameters.

2. Reaction parameters

The primary parameters in the TDM reaction are the reaction temperature and the catalyst. The selection of a catalyst and temperature are linked together and the mutual dependence of these two parameters is illustrated here by reviewing the experimental studies of TDM presented in the literature. Furthermore, these experimental studies can be applied to predict the type of product carbon even in a full-scale process.

2.1. Reaction equilibrium

In methane decomposition reaction, also known as methane decarburation, (direct) methane cracking or methane pyrolysis, methane is thermally decomposed to solid carbon, gaseous hydrogen, and traces of higher hydrocarbons. Eq. (1) presents the simplified reaction equation, that takes into account only the main products, carbon and hydrogen [11].

$$CH_4 \rightarrow C(s) + 2H_2 \quad \Delta H_r^0 = +74.9\ \mathrm{kJ\ mol^{-1}} \tag{1}$$

The reaction enthalpy ΔH_r^0 is defined at a reference temperature of 298.15 K [27]. The maximum methane conversion in a certain temperature can be calculated by considering the equilibrium composition of the gas mixture containing methane and hydrogen in that temperature. Villacampa et al. [28] have presented the following equation for the Gibbs energy of TDM reaction as a function of temperature:

$$\Delta G^0(T) = 89658.88 - 102.27T - 0.00428T^2 - 2499358.99T^{-1} \tag{2}$$

Eq. (2) is calculated by assuming the formation of graphite in TDM, and therefore it is an approximation. Furthermore, the Gibbs energy can be expressed in the means of equilibrium constant K_p:

$$\Delta G_R(T) = \Delta G^0(T) + R_u T \cdot \ln K_p \tag{3}$$

where R_u is the gas constant (8.314 J/mol K) and T is the reaction temperature (K). In the equilibrium state, the Gibbs energy is a minimum, i.e. $\Delta G_R(T)$ equals zero. For TDM reaction, the equilibrium constant depends on the partial pressures of methane ($P_{CH_4,eq.}$) and hydrogen ($P_{H_2,eq.}$) in the gas mixture as follows:

$$K_p(T) = \frac{(P_{H_2,eq.})^2}{P_{CH_4,eq.}} = \frac{(2 \cdot (P_{CH_4,0} - P_{CH_4,eq.}))^2}{P_{CH_4,eq.}} = \frac{4 \cdot P_{CH_4,0} \cdot a^2}{1 - a} \tag{4}$$

where $P_{CH_4,0}$ is the partial pressure of methane (atm) in the initial state and a is methane conversion (–). The methane conversion a is the proportion of the feedstock methane that dissociates according to Eq. (1) and its value varies from zero (no methane dissociation) to one (complete methane dissociation). Moreover, it is assumed in Eq. (4) that methane and hydrogen are the only gaseous components in the TDM reaction and the formed carbon is in its solid state. However, if desired, for example Snoeck et al. [29] have presented the thermodynamics of carbon filament formation in TDM more detailed.

Finally, Eqs. (2)–(4) were combined to present the methane conversion as a function of temperature in the equilibrium state. This is graphically presented later as a part of Section 3.2. In practice, this equilibrium curve states the maximum methane conversion that can be achieved at a certain temperature when the reaction time approaches infinity.