



# Exergy analysis of methane cracking thermally coupled with chemical looping combustion for hydrogen production



Zhe Wang<sup>a,b</sup>, Weiyu Fan<sup>a,\*</sup>, Guangqing Zhang<sup>b</sup>, Shuang Dong<sup>c</sup>

<sup>a</sup> State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao, Shandong 266580, China

<sup>b</sup> School of Mechanical, Materials and Mechatronic Engineering, University of Wollongong, NSW 2522, Australia

<sup>c</sup> Production Preparation Department, Sinopec Tianjin LNG Company Limited, TEDA, Tianjin 300457, China

## HIGHLIGHTS

- A novel MC–CLC process for H<sub>2</sub> production is proposed.
- Energy utilisation of three MC processes is analysed by exergy analysis.
- MC–CLC has the highest exergy efficiency compared with MC–CH<sub>4</sub> and MC–H<sub>2</sub>.
- MC–H<sub>2</sub> provides an advantage of absence of CO<sub>2</sub> generation.

## ARTICLE INFO

### Article history:

Received 8 October 2015

Received in revised form 26 December 2015

Accepted 22 January 2016

### Keywords:

Methane cracking

Exergy analysis

Chemical looping combustion

Hydrogen production

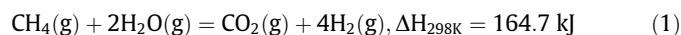
## ABSTRACT

This paper proposes a novel hydrogen production process by Methane Cracking thermally coupled with Chemical Looping Combustion (MC–CLC) which provides an advantage of inherent capture of CO<sub>2</sub>. The energy utilisation performance of the MC–CLC process is compared with that of conventional Methane Cracking with combusting CH<sub>4</sub> (MC–CH<sub>4</sub>) and Methane Cracking with combusting H<sub>2</sub> (MC–H<sub>2</sub>) using exergy analysis, with focus on exergy flows, destruction and efficiency. The three MC processes are simulated using Aspen Plus software with detailed heat integration. In these processes, the majority of the exergy destruction occurs in the combustors or CLC mostly due to the high irreversibility of combustion. The CO<sub>2</sub> capture unit has the lowest exergy efficiency in the MC–CH<sub>4</sub> process, leading to a lower overall exergy efficiency of the process. The combustor in the MC–H<sub>2</sub> process has a much higher exergy efficiency than that in the MC–CH<sub>4</sub> process or the CLC in the MC–CLC process. Although the use of H<sub>2</sub> as fuel decreases the H<sub>2</sub> production rate, the MC–H<sub>2</sub> process provides the advantage of an absence of CO<sub>2</sub> generation, and stores more chemical exergy in the solid carbon which can be utilised appropriately. The MC–CLC process obtains the highest exergy efficiency among the three models and this is primarily due to the absence of a CO<sub>2</sub> capture penalty and the CLC's higher fuel utilization efficiency than the conventional combustion process.

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## 1. Introduction

Hydrogen is considered an ideal fuel of the future because of its ability to reduce anthropogenic emissions of greenhouse gases, particularly carbon dioxide (CO<sub>2</sub>). At present, 80–85% of the world's total hydrogen is produced by steam methane reforming (SMR) [1–3]. Hydrogen can be separated from a gas mixture by a pressure swing adsorption (PSA) [4,5] or membrane [6] separator. The overall SMR reaction is given in Eq. (1).

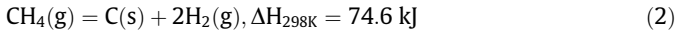


Due to the high endothermic characteristic of the reaction, a significant amount of energy is supplied by the combustion of additional CH<sub>4</sub> or the off-gas from the H<sub>2</sub> separation unit. The combustion process leads to a relatively low energy efficiency of SMR (60–75%) [1,7,8] and high CO<sub>2</sub> emissions.

Nowadays, it has been more and more important to develop low CO<sub>2</sub> emission economy due to the greenhouse gas concerns. However, a mature technology for economical storage of CO<sub>2</sub> has not been available yet. As a result, a good strategy to reduce CO<sub>2</sub> emission is to reduce or eliminate its generation. Compared to SMR, methane cracking (MC) is an attractive route for hydrogen production because of its simplicity and the absence of CO<sub>x</sub> by-product [9], as described by Eq. (2).

\* Corresponding author.

E-mail address: [fanwyu@upc.edu.cn](mailto:fanwyu@upc.edu.cn) (W. Fan).



The reaction is mildly endothermic and can proceed at a reasonable rate when the operating temperature is over 600 °C [9]. The hydrogen production via MC in Eq. (2) has been achieved using different techniques, such as solar radiation [10,11], plasma [12], molten metal bath [13], and thermal reactors without a catalyst [14] or with metal [15–18] or carbon [9,19–21] catalysts.

In the MC process, hydrogen is the only gaseous product in a mixture with unreacted methane. Hydrogen can be separated from unreacted methane easily by adsorption or membrane separation, which is much simpler than the complicated separation processes that deal with the CO and CO<sub>2</sub> in SMR. This is particularly important in the case of proton-exchange membrane fuel cell (PEMFC) applications, as the CO concentration in hydrogen streams fed into PEMFCs must be lower than 20 ppm to prevent the poisoning of the Pt-based electrocatalyst [22,23]. The filamentous solid carbon produced in the process is a commercially valuable material. It is useful in many applications, particularly in the adsorption and catalysis processes or as an option for storing carbon [11,24] or as the fuel of a direct carbon fuel cell (DCFC) [25].

Different reactors for continuous MC have been proposed, such as a set of parallel fixed-bed reactors alternating between different conditions or a fluidized bed/regenerator combination [26]. Muradov [27] proposed a circulating fluidized bed reactor for the MC process, mainly consisting of a methane cracker, a grinder, a heater and a gas separation unit. Methane is decomposed in the cracker over fine carbon particles at 850–950 °C and at a pressure of 10–20 atm. Necessary heat input to the cracker can be provided by combustion of a portion of methane or non-permeate gas. A CO<sub>2</sub> capture unit is also required to separate the CO<sub>2</sub> from the exhaust from the combustion. Alternatively, the heat needed by the methane cracking process can be produced by combustion of a portion of hydrogen produced in the process to avoid CO<sub>2</sub> emissions.

Three main CO<sub>2</sub> capture methods have been considered for chemical and power plant applications: post-combustion systems, oxy-fuel combustion, and pre-combustion systems [28]. Although most of the technologies can reduce CO<sub>2</sub> emissions, they also have a high energy penalty, leading to a reduction in the energy efficiency of the processes and an increase in the price of the energy. The energy consumed in the CO<sub>2</sub> separation processes can reduce the overall energy efficiency of SMR by 6% [7] and 5–20% in a power plant [29,30].

As a promising technology, the chemical looping combustion (CLC) process with inherent separation of CO<sub>2</sub> was firstly proposed in 1983 by Richter and Knoche [31]. The process is conducted based on the transfer of oxygen from air to fuel by means of a solid oxygen-carrier to avoid direct contact between the fuel and the air. Namely, a fuel is converted to CO<sub>2</sub> and/or H<sub>2</sub>O in the Fuel Reactor (FR) by reducing a metal oxide into corresponding metal, or from a high valency to a lower valency state; then in the Air Reactor (AR), the metal or lower valency oxide from the FR is oxidised by air into the original state. The heat released from the oxidation of the metal or lower valency oxide can be used as a thermal source for another process, e.g. methane cracking in this work. Previous studies identified oxides of Ni, Fe, Mn, Cu or Co as potential oxygen-carrier materials [32–36]. CO<sub>2</sub> and H<sub>2</sub>O are inherently separated from other components of the flue gases. After water condensation, a highly concentrated CO<sub>2</sub> stream ready for storage is obtained.

Proposals on the use of the CLC process for the production of H<sub>2</sub> have expanded greatly over the last 10 years. SMR integrated with CLC (SMR–CLC) was first proposed by Rydén and Lyngfelt [37]. In the SMR–CLC process, a CLC system is used to provide heat for the endothermic reforming reactions and capture CO<sub>2</sub> simultaneously. A process called auto-thermal Chemical-Looping Reforming (CLR) was initially proposed by Mattisson and Lyngfelt [38]. CLR is

based on the same basic principle as CLC, but the desired product in CLR is H<sub>2</sub> and CO rather than heat. The thermodynamics of SMR [1,4,7,8], SMR–CLC [8,39,40] and CLR [41–43] have been thoroughly studied by many researchers. However, studies on process simulation and thermodynamic analysis of the MC process are limited [25,27]. Methane Cracking thermally coupled with Chemical Looping Combustion (MC–CLC) has not been reported before. The objective of this study is to evaluate the MC–CLC process on its potential of energy saving by means of exergy analysis. The process is compared with conventional Methane Cracking with combusting CH<sub>4</sub> (MC–CH<sub>4</sub>) and Methane Cracking with combusting H<sub>2</sub> (MC–H<sub>2</sub>).

## 2. Methodology

The simulation of the three processes was conducted using Aspen Plus Software and using Peng–Robinson method to calculate thermodynamic properties. A stream class of MIXCIPSD was set up to allow the separation of gases from solids in the process simulation. The reactors in the three processes including methane cracker, combustor and CLC were simulated using the built-in RGibbs modules, with minimisation of the Gibbs free energy when the phase and chemical equilibrium in the reactors are achieved. Solid carbon is considered as one possible product in these reactors. It is found that no carbon formation occurs in the combustor and CLC in this study. The Aspen Plus simulation flow diagrams and the reactions taking place in each of the examined processes are described below.

### 2.1. Process description

Fig. 1 presents the schematic diagram of the three MC processes. The key device in the three processes is the cracker where

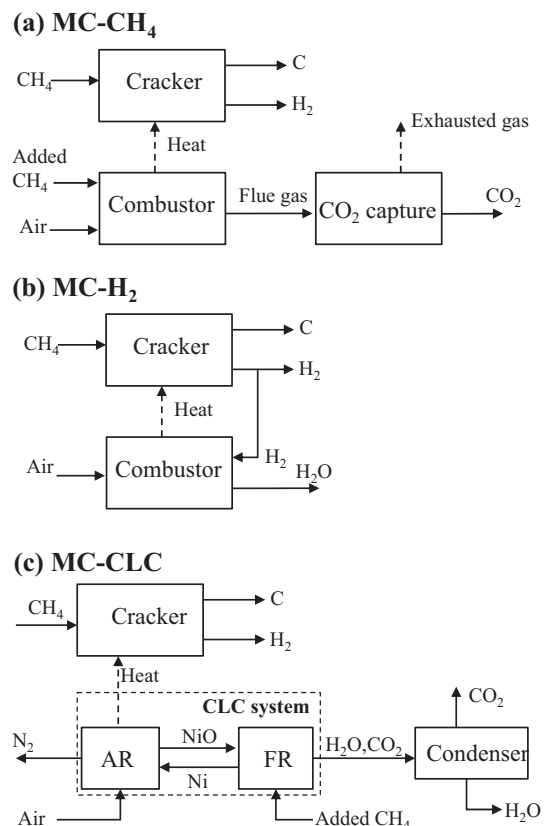


Fig. 1. Schematic diagram of (a) MC–CH<sub>4</sub>, (b) MC–H<sub>2</sub> and (c) MC–CLC process.

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