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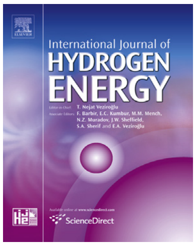

# Thermodynamic evaluation of hydrogen production from methane

Bhanu Kaini, Kanchan Mondal*

Department of Mechanical Engineering and Energy Processes, Southern Illinois University, Carbondale,
IL 62901, USA

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ABSTRACT

Exergetic and energetic analysis has been utilized to estimate the effect of process design and conditions on the hydrogen purity and yield, exergetic efficiencies and $CO_2$ avoided. Methane was chosen as a model compound for evaluating single stage separation. Simple steam reforming was considered as the base – case system. The other chemical processes that were considered were steam reforming with $CO_2$ capture with and without chemical looping of a reactive carbon dioxide removal agent, and steam gasification with both the Boudouard reaction catalyst and the reactive carbon dioxide removal agent with and without the solids regeneration. The information presented clearly demonstrates the differences in efficiencies between the various chemical looping processes for hydrogen generation. The incremental changes in efficiencies as a function of process parameters such as temperature, steam amount, chemical type and amount were estimated. Energy and exergy losses associated with generation of syngas, separation of hydrogen from $CO_x$ as well as exergetic loss associated with emissions are presented. The optimal conditions for each process by minimizing these losses are presented. The majority of the exergy destruction occurs due to the high irreversibility of chemical reactions. The results of this investigation demonstrate the utility of exergy analysis. The paper provides a procedure for the comparison of various technologies for the production of hydrogen from carbon based materials based on First and Second Law Analysis. In addition, two figures of merit, namely the comparative advantage factor and the sustainable advantage factor have been proposed to compare the various hydrogen production methods using carbonaceous fuels.

## Introduction

Hydrogen is an important raw material in the chemical industries such as in the manufacture of ammonia, methanol, etc.. The possibility of hydrogen as a future energy source in heating, electric power and transportation sectors will cause a huge increase in the hydrogen demand. Currently, the primary route for hydrogen production is the conversion of natural gas and other light hydrocarbons. Coal and petroleum coke may also serve as raw materials for hydrogen production in the future. The current developments in steam methane

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* Corresponding author. Tel.: +1 618 453 7059.
E-mail address: kmondal@siu.edu (K. Mondal).

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reforming (SMR) or for that matter, the production of hydrogen from carbonaceous sources are targeted towards improved $CO_2$ capture.

The first step of forming hydrogen from a carbonaceous material is gasification/reforming [1–7] followed by water gas shift reaction [8–10]. Reforming reactions are very endothermic and thermodynamically favored by high temperature and low pressure. On the other hand, the water gas shift reaction is favored by low temperature and is not pressure dependent. Due to the overall endothermic nature, gasification is generally conducted at high temperatures. Thermochemical conversion of carbonaceous raw materials to high yield hydrogen via the use of catalysts is gaining attention from several researchers [11–14].

The $CO_2$ generated, a greenhouse gas with a potential to contribute to global warming, is generally released to the atmosphere. With stringent environmental regulation already in place and the requirement for zero emissions in the future, it is important to develop means to capture/sequester $CO_2$ from the process. In the current context, *in situ* capture of $CO_2$ not only provides a chance to sequester the greenhouse gas, but also increases the conversion to and the purity of the hydrogen stream by removing the thermodynamic limitations at a given condition. Thus, separation of the carbon dioxide and hydrogen [15–20] needs to be achieved. Separation of $H_2$ from the carbon based gasification products also supports existing $H_2$ markets (such as refineries and power production) and makes hydrogen economy a distinct possibility. Given that a $CO_2$ acceptor is available, near zero CO content in the outlet gas may also be achieved. Existing technologies utilize the water gas shift reaction for the conversion of CO to $CO_2$. The carbon dioxide is then separated from hydrogen by absorption, adsorption, cryogenic separation, and membrane separation. The first attempt of using CaO in a "$CO_2$ acceptor process" was conducted by Curran et al. [21] and McCoy et al. [22]. In these studies, only 50% of CO and $CO_2$ was immobilized in the solids. However, later studies in a micro-autoclave [23,24], product gases consisting of primarily $H_2$ and $CH_4$ were obtained. Up to 84% purity hydrogen stream was reported by Lin et al. [16] in a pressurized bed reactor. The pressurized bed reactor provided higher rates of $CH_4$ decomposition resulting in the higher $H_2$ contents. A new method, Hydrogen Production by Reactions Integrated Gasification (HyPr-Ring), that combines the gas production and separation reactions in one reactor was suggested by Lin et al. [23]. In this process, the energy required for the endothermic reforming reactions were provided by the heat of $CO_2$ absorption. Wang and Takarada [25] reported that complete fixation of $CO_2$ with $Ca(OH)_2$ could be achieved for a Ca/C molar ratio of 0.6 (stoichiometry dictates the ratio to be 1) along with significantly enhanced decomposition of tar and char. Kuramoto et al. [26] also investigated $C–CaO–H_2O$ system, using subcritical steam (50–150 °C). They reported an increase in the $CH_4$ content due to the addition of $Ca(OH)_2$, along with the yields of hydrogen.

The overall conversion rates of CO to $CO_2$ are expected to be further enhanced by the inclusion of an oxygen donor in the reaction zone. The steam reforming rates of methane and other hydrocarbons released during coal pyrolysis may also be enhanced by the choice of a suitable oxygen donor that may double as a catalyst. Iron oxide is known to show WGS activity at high temperatures. However, iron oxide is found to oxidize hydrogen at a much faster rate (nearly 3–4 times) as compared to CO [27,28]. This would result in a reduction in the yield of hydrogen. Several studies on the reduction of iron oxide and various ores containing iron oxide have been conducted in the past [27–32]. Moon and Rhea [27] estimated that the reaction rate for $Fe_2O_3$ reduction with CO was 2–3 times slower than that with $H_2$. They estimated the value of the apparent activation energy for iron oxide reduction to be 14.6 kJ/mol in a carbon monoxide atmosphere. In a later work [28], they estimated the activation energy for the reduction reaction in CO to be 19.8 kJ/mol in pure CO stream, the value of which increased with reducing CO partial pressure in a $CO–H_2$ gas stream. The value of the activation energy was found to be 42.1 kJ/mol in a 100% hydrogen atmosphere. The effect of $Fe_2O_3$ on simultaneous coal gasification and $H_2$ separation have also been investigated by Mondal et al. [33]. In the past, Nikanorova and Antonova [34] reported an increase in hydrogen yield by 1.5 times due to the addition of iron oxide to lignite prior to gasification with a final purity of 60%. The addition of the iron oxide during atmospheric pressure mild gasification of shenmu bituminous coal was also found to significantly increase the hydrogen yield while decreasing the CO content [35]. Researchers [36–40] have also discussed the positive effects of the presence of iron oxide on the decomposition of coal and other hydrocarbons. In addition, Li et al. [41] reported that $Fe_2O_3–CaO$ mixtures were efficient in sulfur removal in IGCC processes through multiple desulfurization–regeneration cycles. Thus, selection of $Fe_2O_3$ and CaO as the oxygen transfer agent (OTA) and carbon capture agent (CCA), respectively, provides additional benefits in hydrogen production.

While significant experimental studies have been conducted on different systems for the production of high purity hydrogen, the processes have not been compared on an unbiased basis. Energy efficiency, economic and environmental aspects as regards to individual systems have been evaluated. Analyses such as those utilizing first and second laws of the thermodynamics, life cycle analysis, etc., can provide such an unbiased basis to a certain degree. Specifically, there is a lack of information that compares the various processes on the basis of exergetic or 2nd law efficiencies. Simpson et al. [42] evaluated SMR with subsequent WGS reaction model for hydrogen production using exergy analysis. The calculated thermal and exergy efficiencies were found to be lower than those in available literatures. Exergetic efficiency was reported to be 62.7%. As expected, the majority of exergy destruction was due to high irreversibility of chemical reactions and heat transfer. Rosen et al. [43] investigated the thermodynamic performance of an electrolysis process using energy and exergy analysis. They found that exergy loss associated with cooling water is negligible and most of the exergy losses occur in the heat engine for electricity generation required for the electrolysis. In addition, they identified the irreversibilities associated with the chemical reaction and heat transfer across large temperature differences. Adhikari et al. [44] performed thermodynamic analysis for steam reforming process of glycerol at different pressure (1–5 atm), temperature (600–1000 K) and water to glycerol ratio of 1:1–9:1. They found the best conditions occurred at