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Thermodynamic analysis of syngas production via tri-reforming of methane and carbon gasification using flue gas from coal-fired power plants

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ABSTRACT

Tri-reforming of methane (TRM) and carbon gasification (CG) for syngas production were analyzed in this study using flue gas from coal-fired power plants as feedstock based on the thermodynamic equilibrium theory. The obtained results suggested that for both TRM and CG, reaction temperature should be higher than 500 °C to obtain positive carbon dioxide conversion and higher yields of hydrogen and carbon monoxide. The results also indicated that both TRM and CG are unfavorable at high pressure. Conversions of carbon dioxide, methane and carbon decreased as the reaction pressure increased. In TRM with methane added into flue gas, carbon dioxide conversion, methane conversion, and hydrogen/carbon monoxide ratio were enhanced by increasing methane/carbon dioxide ratio. For CG with carbon added into the flue gas, negative carbon dioxide conversion was found for low carbon/carbon dioxide ratios. The hydrogen/carbon monoxide ratio was found to be less than unity at high temperatures because no hydrogen source was added. From carbon dioxide equivalent analysis, it was found that the reduced carbon dioxide equivalent can be enhanced with higher conversions of carbon dioxide and methane and lower methane yield. It was also found that TRM was more competitive in reducing carbon dioxide equivalent as compared with CG. From the energy balance analysis, higher energy input was required when the methane/carbon dioxide or carbon/carbon dioxide ratio was increased. Although thermo-neutral reaction could be achieved, low or negative carbon dioxide conversion was resulted. For air or water added in TRM, decreased carbon dioxide conversion was found due to more carbon dioxide production from methane oxidation or water-gas shift reaction. For air or water added in CG, carbon dioxide conversion was also found to decrease due to more carbon dioxide production from carbon oxidation or water-gas shift reaction. This study also indicated that the only way to achieve high carbon dioxide conversion is to increase the methane in TRM or carbon in CG. However, carbon formation and lower carbon conversion were possible with increased methane and carbon additions in TRM and CG, respectively.

1. Introduction

Rising CO_2 levels in the atmosphere have been a serious concern and threat to the environment. Mitigation of CO_2 is an important global warming and climate change issue. Fossil fuel based power stations contribute about 47% to the world CO_2 emissions (IPCC Report, 2015). There exists an urgent need to mitigate these emissions. Due to lack of reliable CO_2 capture and sequestration (CCS) technology with enough understanding of potential long-term impact and effects, utilization of CO_2 that converting CO_2 into useful products seems to be an alternative pathway. One of the most attractive approaches is the reforming of flue gases by reaction with methane in the presence of catalysts (Majewski and Wood, 2014; Antonio et al., 2014; Singha et al., 2016; Dwivedi et al., 2017). That is, the CO_2, H_2O, and O_2 contained in the flue gases react with added CH_4 to form syngas. This is known as the tri-reforming of methane (TRM) proposed by Song and Pan (2004). TRM combines three generally used methane reforming methods

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for syngas production. In TRM the following reactions are coupled and carried out in a single reactor.

Steam-methane reforming (SMR):

$$CH_4 + H_2O \leftrightarrow CO + 3H_2,\ \Delta H_{298\ K} = +206\ kJ/mol \quad (1)$$

Dry reforming of methane (DRM):

$$CH_4 + CO_2 \leftrightarrow CO + 2H_2,\ \Delta H_{298\ K} = +247\ kJ/mol \quad (2)$$

Partial oxidation of methane (POM):

$$CH_4 + 0.5O_2 \leftrightarrow CO + 2H_2,\ \Delta H_{298\ K} = -36\ kJ/mol \quad (3)$$

Besides CH_4, coal, biomass, or any other carbonaceous solid materials may also be used to perform CO_2 reduction in flue gas. This is actually known as carbon gasification (CG). The chemical reactions involved in CG are.

Carbon combustion (CC):

$$C + O_2 \leftrightarrow CO_2,\ \Delta H_{298\ K} = -393.5\ kJ/mol \quad (4)$$

Boudouard reaction (BR):

$$C + CO_2 \leftrightarrow 2CO,\ \Delta H_{298\ K} = +172.4\ kJ/mol \quad (5)$$

Water-gas reaction (WGR):

$$C + H_2O \leftrightarrow CO + H_2,\ \Delta H_{298\ K} = +131.3\ kJ/mol \quad (6)$$

Methanation reaction (MR):

$$C + 2H_2 \leftrightarrow CH_4,\ \Delta H_{298\ K} = -75\ kJ/mol \quad (7)$$

As shown in Eqs. (1)–(3), TRM combines the DRM and SMR endothermic reactions with the POM exothermic reaction. The heat released from POM is used as the heat supply for SMR and DRM, making the TRM more energy efficient (Solovev et al., 2012). In addition to energy efficiency, TRM offers several advantages for syngas production compared with the single reaction described in Eqs. (1)–(3). As shown in Eq. (2), CO_2 is directly used as the feedstock for DRM and CO_2 separation is not required. This implies that the flue gas from power plant combustion processes can be used directly as a CO_2 source for TRM (Qian et al., 2015; Minutillo and Perna, 2009; Halmann and Steinfeld, 2006). Moreover, H_2/CO of the produced synngas can be adjusted depending on the applications (Diez-Ramirez et al., 2016). For CG shown in Eqs. (4)–(7), heat released from carbon combustion is used as the heat supply for BR and WGR. Moreover, methane may be formed in CG due to MR, as shown in Eq. (7). Because of the exothermic reactions, thermoneutrality is possible for both TRM and CG.

TRM has been studied from both experimental measurements and numerical modeling aspects in the literature. Using thermodynamic analysis based on the Gibbs energy minimization, Zhang et al. (2014) found that high temperature and low pressure are favorable to achieve high H_2 production and CO_2 conversion in TRM using flue gas as feedstcok. The excessive additions of H_2O, O_2, and CO_2 resulted in lower H_2 yield and CO_2 conversion, while low concentrations of H_2O, O_2, and CO_2 resulted in more intense carbon formation. Extending from the model of Zhang et al. (2014), Dwivedi et al. (2017) proposed a model that coupled both tri-reforming and methanol production processes. They evaluated the performance of the process in terms of the profit generating and CO_2 valorization potential. A catalytic TRM model in a fixed bed reactor was established in the study of Chein et al. (2017). The operating condition and reactant composition effects on TRM performance were reported. Similar to the CO/CO_2 hydrogenation reaction, a challenging problem for TRM is to find an active and stable catalyst (Rostrup-Nielsen and Trimm, 1977; Ginsburg et al., 2005; Wang et al., 2018; Aramouni et al., 2018).

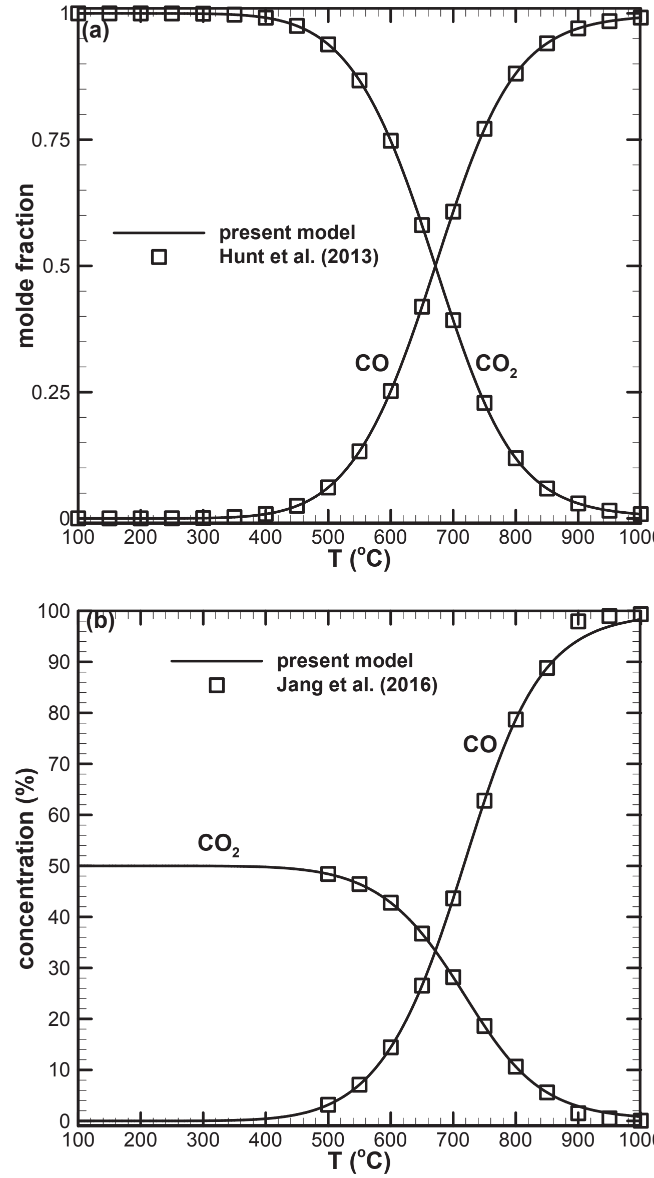

Fig. 1. Numerical model verification by comparing the results of Boudouard reaction ($C + CO_2 \leftrightarrow 2CO$) predicted from present model and those from the thermodynamic equilibrium theory. (a) mole fractions of CO and CO_2 as a function of reaction temperature. (b) Concentrations of CO and CO_2 as a function of reaction temperature.

Coal gasification in CO_2-rich gas mixture is recognized as a promising technology for pulverized coal-fired power plants to control CO_2 emissions (Cavaliere and Joannon, 2004; Ryzhkov et al., 2018). It enables diverse utilization of the produced syngas through chemical syntheses and also allows for a reduction of the negative impact of coal utilization on the environment. From the current