Solar fuels via chemical-looping reforming

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ABSTRACT

The potential of solar thermal chemical-looping reforming for efficient and sustainable co-production of synthesis gas and hydrogen is discussed. In an endothermic partial oxidation step, methane reacts with oxygen released from a metal oxide to produce hydrogen and carbon monoxide. In an exothermic second step, steam reacts with the reduced metal oxide to produce hydrogen. This review summarizes the process and chemical thermodynamic foundations of solar chemical-looping reforming and provides a synopsis of materials studies that reflect the state of knowledge in 2017. The challenges and opportunities for future research and development are discussed.

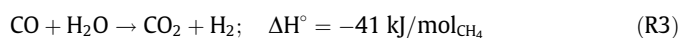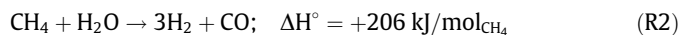© 2017 Published by Elsevier Ltd.

1. Introduction

The development of processes to produce sustainable alternatives to petroleum-derived fuels is imperative given the expanding global demand for liquid fuels. Hydrocarbon fuels are projected to be important for transportation in the foreseeable future even with an expanding market for electric vehicles. In 2015, transportation comprised 28% of total energy consumption in the U.S. with 92% supplied by petroleum (EIA, 2016a). Globally, energy consumption in the transportation sector is predicted to increase 1.4% annually to 163.5 EJ (155 quadrillion Btu) in 2040 (EIA, 2016b).

One approach to meet the growing demand for liquid fuels produced sustainably is to use solar energy to offset a portion of the energy required for Gas-to-Liquid (GTL) processes. GTL processes convert a mixture of hydrogen and carbon monoxide (termed synthesis gas or syngas) to liquid fuels, including high cetane diesel, high octane gasoline, and kerosene (jet fuel) (Wright et al., 2003; Wood et al., 2012). In conventional GTL, methane is partially oxidized via (R1) to ca. 2:1 H_2:CO syngas (Uhde, 1997; de Klerk, 2011; Wilhelm et al., 2001; Said et al., 2016).

$$CH_4 + 1/2O_2 \rightarrow 2H_2 + CO; \quad \Delta H^\circ = -36 \text{ kJ/mol}_{CH_4} \tag{R1}$$
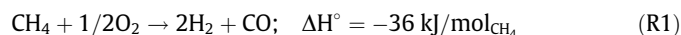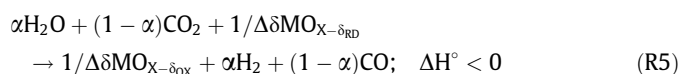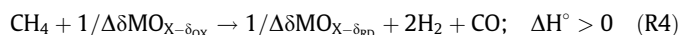
Reaction (R1) is implemented almost exclusively with high purity oxygen (Wilhelm et al., 2001; Said et al., 2016; Rostrup-Nielsen, 2002). Air separation is energy intensive and the oxygen plant can comprise up to 40% of the total cost of a syngas plant (Wilhelm

et al., 2001). Furthermore, safety measures must be implemented to mitigate the risk of explosion (Said et al., 2016). An auxiliary stream of ca. 3:1 H_2:CO syngas is obtained via methane steam reforming (R2) and converted by water-gas shift (R3) and pressure swing adsorption to high purity hydrogen.

$$CH_4 + H_2O \rightarrow 3H_2 + CO; \quad \Delta H^\circ = +206 \text{ kJ/mol}_{CH_4} \tag{R2}$$

$$CO + H_2O \rightarrow CO_2 + H_2; \quad \Delta H^\circ = -41 \text{ kJ/mol}_{CH_4} \tag{R3}$$

The hydrogen is used to tailor the H_2:CO ratio of the syngas stream to match the requirements for GTL processing.

Chemical-looping reforming (CLR) is a two-step thermochemical cycle to produce syngas and hydrogen (or carbon monoxide). In the endothermic partial oxidation step (R4), methane reacts with oxygen released from a metal oxide (MO_x) to produce syngas. In the exothermic oxidizer splitting step (R5), H_2O and/or CO_2 react with the reduced metal oxide to produce H_2 and/or CO.

$$CH_4 + 1/\Delta\delta MO_{X-\delta_{OX}} \rightarrow 1/\Delta\delta MO_{X-\delta_{RD}} + 2H_2 + CO; \quad \Delta H^\circ > 0 \tag{R4}$$

$$\alpha H_2O + (1-\alpha)CO_2 + 1/\Delta\delta MO_{X-\delta_{RD}}$$
$$\rightarrow 1/\Delta\delta MO_{X-\delta_{OX}} + \alpha H_2 + (1-\alpha)CO; \quad \Delta H^\circ < 0 \tag{R5}$$

In comparison to reduction of a metal oxide in an inert sweep gas or sub-atmospheric pressure, the introduction of methane in reaction (R4) lowers the thermodynamic barrier to split water (or carbon dioxide), such that the thermodynamics of CLR are those of methane reforming rather than the less favorable thermodynamics of thermolysis. The net products of CLR match those of steam and dry reforming for steam fractions of $\alpha = 1$ and $\alpha = 0$,

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Nomenclature

C	solar concentration ratio
F	loss coefficient
h	molar enthalpy ($J\,mol^{-1}$)
HHV	higher heating value ($J\,mol^{-1}$)
I	direct normal irradiance ($1000\,W\,m^{-2}$)
n_i	number of moles of species (mol)
$\dot{n}'_i$	mass specific molar species flow rate ($mol\,s^{-1}\,g^{-1}$)
P	pressure (bar)
p_{O_2}	oxygen partial pressure (bar)
P_∞	total pressure (1 bar)
Q	heat (J)
$\dot{Q}$	heat transfer rate (W)
R	ideal gas constant ($8.314\,J\,mol^{-1}\,K^{-1}$), CH_4:O_2 ratio (Figs. 3–7)
S_C	carbon selectivity
S_{CO}	carbon monoxide selectivity
S_{H_2}	hydrogen selectivity
t	time (s)
T	temperature (K)
$\dot{V}$	flow rate of gas per gram of oxygen carrier ($mL\,min^{-1}\,g^{-1}$)
W	work (J)
X_{CH_4}	methane conversion
X_{CO_2}	carbon dioxide conversion
X_{H_2O}	water conversion
y	mole fraction

Symbols

α	steam fraction used in (R5)
δ	nonstoichiometry
ΔP	pressure drop (bar)
$\Delta\delta$	change in nonstoichiometry

η	efficiency
σ	Stefan-Boltzmann constant ($W\,m^{-2}\,K^{-1}$)
[∗]	active site

Superscripts

∗	chemisorbed species

Subscripts

∞	ambient conditions (1 bar, 298 K)
1, 2, …	state
FC	fuel cell
GAS	energy associated with process gases
i	species
IN	inlet of the reactive bed, entering the system
LOSS	conduction/convection to ambient
OUT	outlet of the reactive bed, exiting the system
OX	oxidation, oxidizer
RAD	radiative emission
REACTOR	solar reactor, i.e. includes conduction, convection, and emission losses
REJECT	excess heat that is rejected to maintain isothermal operation
RD	reduction
SEP	separation
SOLAR	solar
S → E	solar-to-electric conversion

Abbreviations

CLR	chemical looping reforming
SCLR	solar chemical looping reforming
SSA	specific surface area ($m^2\,g^{-1}$)

respectively. Decoupling the partial oxidation and oxidizer splitting steps provides advantages over conventional reforming. Syngas produced via (R4) has a H_2:CO ratio of 2:1 compared to 3:1 and 1:1 for steam and dry reforming, respectively. The syngas from (R5) can be tuned via the steam fraction, α, to obtain any H_2:CO ratio. Operating with $\alpha = 1$ (i.e. water splitting) yields separate streams of syngas and high purity H_2. For CO_2 splitting, the energetic and economic costs of providing pure CO_2 will be high (Kim et al., 2011, 2012; Herron et al., 2015). This cost is one reason for a preference for water splitting. To prevent catalyst deactivation by carbon deposition, conventional reformers must operate with excess oxidizer (e.g.·H_2O:$CH_4 \geq 3$), which increases energy requirements and lowers process efficiency (Simakov et al., 2015). CLR does not require excess oxidizer because carbon deposition can be prevented by limiting the extent of reduction of the metal oxide (Otsuka et al., 1993, 1997, 1998; Cho et al., 2005). Conventionally, process heat for CLR is supplied by combusting up to 41% of the methane feedstock (Simakov et al., 2015), resulting in a 24% reduction in energy content compared to the feedstock.

Feedstock utilization and CO_2 emission can be improved by supplying process heat with concentrated solar energy, as illustrated in Fig. 1. Solar CLR (SCLR) is net endothermic. The chemical energy requirements for producing synthesis gas are identical to the energy required for solar steam methane reforming (SMR) or solar dry methane reforming (DMR). Solar energy is stored in the products and the syngas has a higher energy content than the methane feedstock. The energetic upgrade factor, U, given in Eq. (1), is the ratio of the total higher heating value (HHV) of the products (species i) to the heating value of the methane feedstock.

$$U = \frac{\sum_i n_{i,OUT}HHV_i}{n_{CH4,IN}HHV_{CH_4}} \quad (1)$$

With complete conversion of methane and oxidizer to syngas, the energetic upgrade factor is 128%. Combustion of the solar upgraded syngas emits 59% of the carbon per kilojoule that would be emitted in the combustion of syngas from conventional CLR.

Solar-to-chemical efficiency is commonly used to project commercial viability of a nascent solar thermochemical cycle such as SCLR. Efficiency has been used traditionally as a surrogate for cost, although the authors and the research community recognize that more complex factors including the value of competing technologies are important. The solar-to-chemical efficiency, given by Eq. (2), is defined as the net gain in the higher heating value (HHV) of the gases divided by the direct solar thermal power input to the reactor, Q_{SOLAR}, and the solar thermal power required to provide parasitic work, $W/\eta_{S \to E}$, including that required for separations, pumping, etc.

$$\eta = \frac{\sum_i (n_{i,OUT} - n_{i,IN})HHV_i}{Q_{SOLAR} + W/\eta_{S \to E}} \quad (2)$$

Based on reasonable assumptions for the parasitic energy requirements and operation of a concentrated solar thermochemical reactor, Krenzke et al. project an efficiency of SCLR of 54%. Key assumptions in this projection are complete conversion of reactants to syngas and hydrogen in (R4) and (R5) and operation at 1273 K and 1000 suns solar input (1 sun equals $1000\,W\,m^{-2}$ concentration). Consistent with the majority of studies included in this review, the projection assumes isothermal operation of the cycle at atmospheric pressure.