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A review of solar methane reforming systems

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ABSTRACT

Because of the increasing demand for energy and the associated rise in greenhouse gas emissions, there is much interest in the use of renewable sources such as solar energy in electricity and fuels generation. One problem with solar energy, however, is that it is difficult to economically convert the radiation into usable energy at the desired locations and times, both daily and seasonally. One method to overcome this space-time intermittency is through the production of chemical fuels. In particular, solar reforming is a promising method for producing chemical fuels by reforming and/or water/carbon dioxide splitting. In this paper, a review of solar reforming systems is presented, as well as a comparison between these systems and a discussion on areas for potential innovation including chemical looping and membrane reactors. Moreover, a brief overview of catalysis in the context of reforming is presented.

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Introduction

As the world's population, standards of living, and economy continue to grow, energy demand rises significantly, leading to higher emissions, especially in greenhouse gases. Much work has been done to expand the use of renewable energy sources (such as solar energy) to meet these demands while curtailing emissions. Solar energy has the potential to provide all the world's energy demands; however, converting solar radiation into useful energy forms at the desired times and locations and at a reasonable cost is challenging.

One method of converting solar radiation into usable energy is the production of chemical fuels. This, in essence, creates a means of relatively easy storage and transportation of the solar energy [1–3]. This conversion can be achieved

through a number of different ways including (i) thermochemical cycles for splitting water and carbon dioxide, (ii) solar cracking/gasification of solid fuels, and (iii) solar reforming of liquid and gaseous hydrocarbons [4–7]. Thermochemical cycles for water splitting involve using heat sources to dissociate water into hydrogen and oxygen. While most desirable, water splitting requires very high temperatures outside most solar collection technologies [8]. The temperature can potentially be lowered through the use of membranes to remove oxygen or hydrogen and shift the equilibrium towards further dissociation [9] or chemical looping processes using oxygen carriers [10–12]. Solar cracking involves using heat to decompose a hydrocarbon into hydrogen and carbon, and similar to water splitting, temperatures required for methane decomposition can also be very high unless a separation process is used [8,13]. Solar

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Nomenclature

Latin letters

ΔH°	standard enthalpy of reaction, kJ/mol
Q	heat input, W
\dot{n}	molar flow rate, mol/s

Greek letters

η	efficiency or conversion
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Subscripts

solar	solar input
fuel	fuel input
conv	fuel conversion
chem	chemical

reforming, on the other hand, can achieve significant conversion at relatively lower temperatures using catalysts to speed up the kinetics. Therefore, even though some CO₂ emissions are produced when using hydrocarbons, solar reforming is considered a promising method for converting solar radiation into chemical fuels [8,14], and hence is the focus of this review. It should be noted that in some reforming concepts such as chemical looping, the reforming system actually blurs the line between the different methods of converting solar radiation into chemical fuels, and the system can involve more than one method of conversion (i.e., reforming and water splitting). Therefore even though these systems are not strictly reforming systems, they will also be discussed.

Solar reforming is similar to traditional reforming except the solar energy is used to provide the high temperature heat source rather than burning extra fuel (or using nuclear heat). In most cases, a hydrocarbon fuel, such as natural gas, is reformed into syngas (a mixture of H₂ and CO) which has a higher heating value. With the additional step of water-gas shift, pure hydrogen can be produced after separating CO₂. A solar reforming system typically consists of two main parts: (i) a solar collector/concentrator and (ii) a chemical reactor [15]. The solar collector is (a) a trough, (b) a central receiver tower, or (c) a parabolic dish. The solar collector is used to raise the temperature of a heat transfer fluid that is used within the chemical reactor, or to directly heat the chemical reactor. The chemical reactor, of course, is where the catalyst-assisted reforming reactions occur.

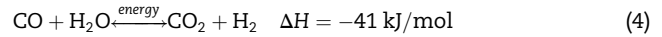
The most common reforming processes used in solar systems are steam or CO₂ (dry) reforming. The key reactions for the two processes (steam and dry reforming, respectively) are shown below for the case of methane [16]:



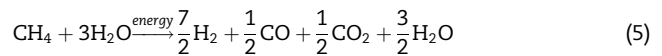
The enthalpy of reaction for steam reforming is approximately 23% of the enthalpy of combustion of methane, and hence the heating value of the syngas is 25% higher by the

same amount. Water vapor is typically used in the steam reforming reactions rather than liquid water. The enthalpy of reaction for dry reforming is approximately 28% of the enthalpy of combustion of methane, and the heating value of the syngas can be as much as 30% higher than the input methane.

Most often, the water-gas shift reaction occurs in conjunction with the reforming reactions. The water-gas shift reaction is shown below [16]:



For steam reforming, a steam methane ratio of 2:1 to 3:1 is required in order to obtain full conversion at reasonable temperatures, and to prevent coke formation (i.e., the thermal cracking of hydrocarbon occurring in parallel with steam reforming) [17]. With dry reforming, the process typically runs at a 1:1 ratio. Methane conversion (at equilibrium) for various temperatures and pressures for the two reactions is shown in Figs. 1 and 2, with steam to methane ratio of 3, and carbon dioxide to methane ratio of 1. For reference, the combined steam reforming and water-gas shift stoichiometric reaction for a 3:1 steam to methane ratio is shown below:



All equilibrium calculations are performed with an equilibrium reactor model (which calculates the outlet

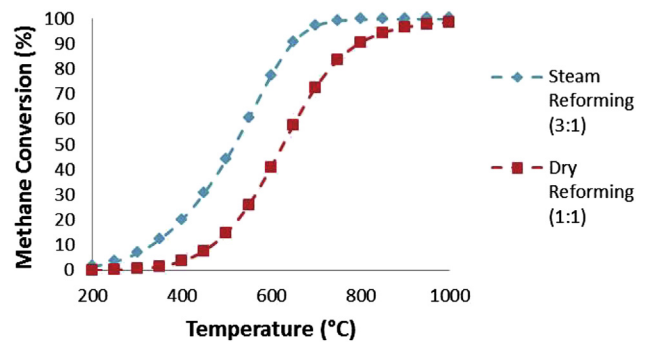


Fig. 1 – Temperature dependence of methane conversion at equilibrium for steam and dry reforming (Pressure = 1 atm).

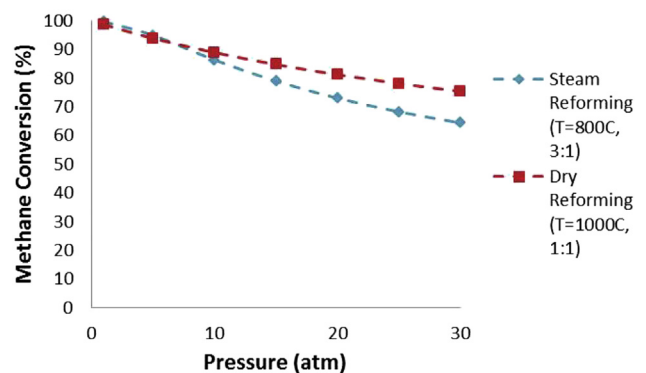


Fig. 2 – Pressure dependence of methane conversion at equilibrium for steam and dry reforming.

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