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ScienceDirect

Solar Energy 102 (2014) 45–55

SOLAR ENERGY

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Modeling and simulation of methane dry reforming in direct-contact bubble reactor

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Received 18 November 2013; received in revised form 5 January 2014; accepted 11 January 2014
Available online 1 February 2014

Communicated by: Associate editor Michael Epstein

Abstract

Modeling and simulation of the reforming behavior of a mixture of methane and carbon dioxide in a direct-contact bubble reactor (DCBR) was described. The endothermic catalytic reaction obeys the kinetics of the methane dry reforming in a direct-contact bubble reaction system containing an active catalyst, i.e., Ni–Al_2O_3 catalyst and molten salt mixture system. The reforming process was simulated, using commercial software for chemical kinetics, for a single reactor model, to examine a kinetic model based on the postulated heterogeneous reaction mechanism, in the temperature range 600–900 °C, at 1 atm. The simulated data were evaluated and validated with the measured data from a laboratory reformer. The catalyst activity in the DCBR was characterized using a catalyst–bubble contact model, in terms of the total-catalytic active surface area. We used the detailed simulation studies to identify the essential characteristics of the reaction mechanism in a DCBR.

Keywords: Methane dry reforming; Modeling; Simulation; Direct-contact bubble reactor; Hydrogen production; Solar reformer

1. Introduction

Solar energy is the most obvious alternative energy source, so the global directive on the development and use of abundant solar energy, which results in no or little pollution, is an important step toward the current urgent need to meet energy demands. However, solar energy is not a viable option unless the energy can be stored on a large scale (Dresselhaus and Thomas, 2001). Therefore, it is necessary to develop storage systems. The conversion of solar energy to chemical fuels is an attractive method of solar energy storage (Dell and Rand, 2001). Solar fuels such as hydrogen can be produced by upgrading fossil fuels, i.e. methane dry reforming.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^o_{@298K} = +247\ \text{kJ/mol} \tag{1}$$

Solar reforming of methane is considered to be a route to solar thermochemical processes because reforming is principally an endothermic reaction, and is an efficient way of storing solar energy (Steinfeld, 2005; Kodama, 2003; Agrafiotis et al., 2014). However, the intermittent nature of solar energy sources, which are affected by cloudiness, is a disadvantage compared with conventional resources (Powell and Edgar, 2012). One of the main drawbacks in solar methane reforming processes is the fluctuating incident solar radiation. Catalytic methane reforming with CO_2 requires stable operation under the fluctuations caused by cloud passage. Moreover, the solar chemical receiver reactor to which the concentrated solar radiation is directed requires thermal uniformity inside the reactor (Kodama et al., 2001).

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http://dx.doi.org/10.1016/j.solener.2014.01.010

Nomenclature

$\dot{s}_i$	molar surface rate of production of species *i* by surface kinetic reaction per unit surface area (mol/(cm^2 s))
$\dot{\omega}_i$	molar rate of production of species *i* by gas phase chemical reaction per unit volume (mol/(cm^3 s))
θ_i	site fraction of species, none
$[Y_i]$	molar concentration of species *i* (mol/cm^3)
Γ_{Ni}	site density of Ni (mol/cm^2)
υ'_{ij}	stoichiometric coefficient of reactant species *i* in reaction *j*, none
υ''_{ij}	stoichiometric coefficient of product species *i* in reaction *j*, none
k_{fj}	forward rate constant of the reaction *j*, depends on reaction
k_{rj}	reverse rate constant of reaction *j*, depends on reaction
r_j	rate of reaction *j* (mol/(cm^2 s))
$\mathbb{T}_{\text{CASA}}$	total catalytic active surface area available in a system (cm^2)
τ_{res}	residence time (s)
τ	time constant (s)
$t_{\text{res}}(\%)$	setting residence time to achieve (%) of equilibrium conversion (s)
MW_i	molecular weight of species *i* (g/mol)
$\dot{m}$	mass flow rate (kg/s)
ρ	gas density (kg/cm^3)
V	gas hold-up volume in reactor (cm^3)
y_{i}	mole fraction of species *i, none*
γ	sticking coefficient, none
L_o	average bubble travel distance in liquid (m)
D	reactor diameter (m)
ϑ_f	final velocity of rising bubbles in liquid (m/s)
ϑ_o	initial velocity of rising bubbles in liquid (m/s)
N	bubble generation rate (No. of Bubbles/s)
d_B	bubble diameter (m)
X_{CH_4}	methane conversion %, none
$X_{e-\text{CH}_4}$	equilibrium methane conversion % none
$f(\alpha)$	catalyst–bubble surface contact fraction, none
F	inlet gas feed volumetric flow rate (ml/min)

One effective solution for dealing with the intermittent nature of solar methane reforming is to use a direct-contact bubble reactor (DCBR) with a thermal fluid of high heat capacity as a heat transfer medium. The use of DCBRs for solar thermal energy storage schemes with high energy conversion capacities, high thermal efficiencies, and reliable operation under fluctuating incident solar radiation has been proposed (Al-Ali et al., 2012). DCBR collects solar energy as indirectly heated reactor using a thermal fluid (Agrafiotis et al., 2014) .Methane reforming in a direct-contact bubble reaction system is attractive in modern applications because of the high thermal efficiency and ideal heat transfer coefficient, compared with conventional methods using shell-and-tube heat exchangers.

Solar-aided reforming of methane-containing gaseous feedstocks for hydrogen and synthesis gas production has been extensively studied (Dahl et al., 2001, 2004; Kodama et al., 2009; Giaconia et al., 2008). Recently, work on solar methane reforming, aimed at catalyst and reactor development for conducting CO_2 reforming reactions (McNaughton, 2012), has been conducted at CSIRO in Australia. The concept of dry reforming of methane using a molten K_2CO_3/Na_2CO_3 system was proposed (Kodama et al., 2001). Various non-noble-metal catalysts such as Ni, Fe, Cu, and W supported on Al_2O_3 have been tested for activity and selectivity (Shimizu et al., 2001), and FeO has been investigated as a catalyst for H_2 production from CH_4 via redox reactions (Gokon et al., 2002). It was concluded that Ni/Al_2O_3 was the most active and selective catalyst.

The main aim of this study was to build a mathematical model for methane dry reforming reaction in a direct-contact bubble reaction system. The model depends on the physical, chemical, and conservation laws governing the processes within the internal boundaries of the system. These include the kinetic rates of the reactions, residence time, and the catalytic surface characteristics in terms of available active sites. By considering the mathematical theory, and comparing with statistical experimental data, i.e., CH_4 and CO_2 percentage conversions, a sufficiently accurate computational mathematical solution can be obtained in a practical form. In this paper, the focus is on modeling and simulating the endothermic reaction with respect to the kinetics of methane dry reforming in a direct-contact bubble reaction system containing a thermal fluid (molten salt) and an active catalyst, i.e., Ni/Al_2O_3.

2. Model formulation

In a DCBR (Fig. 1a), a mixed gas of methane and CO_2 is used as the reforming fluid, moving in counter flow for heat absorption by a thermal fluid, into which the mixed gas is dispersed as bubbles. The mixed gas stream is injected at the bottom of the vessel using an adequate distribution system, usually a perforated plate or a set of perforated pipes. During both formation and ascension of the bubbles through the thermal liquid, there is a natural mass flux from within the bubbles to their surfaces, which come into contact with the suspended catalyst surfaces. The catalytic activity in the direct decomposition of