INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 36 (2011) 466–472

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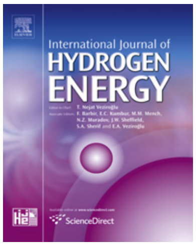

Hydrogen production by sorption enhanced steam reforming of propane: A thermodynamic investigation

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ARTICLE INFO

Article history:
Received 1 June 2010
Received in revised form
30 August 2010
Accepted 6 September 2010
Available online 8 October 2010

Keywords:
Hydrogen
Propane steam reforming
Sorption enhanced
Thermodynamic analysis

ABSTRACT

Thermodynamic features of hydrogen production by sorption enhanced steam reforming (SESR) of propane have been studied with the method of Gibbs free energy minimization and contrasted with propane steam reforming (SR). The effects of pressure (1–5 atm), temperature (700–1100 K) and water to propane ratio (WPR, 1–18) on equilibrium compositions and carbon formation are investigated. The results suggest that atmospheric pressure and a WPR of 12 are suitable for hydrogen production from both SR and SESR of propane. High WPR is favourable to inhibit carbon formation. The minimum WPR required to eliminate carbon production is 6 in both SR and SESR. The most favourable temperature for propane SR is approximately 950 K at which 1 mol of propane has the capacity to produce 9.1 mol of hydrogen. The optimum temperature for SESR is approximately 825 K, which is over 100 K lower than that for SR. Other key benefits include enhanced hydrogen production of nearly 10 mol (stoichiometric value) of hydrogen per mole of propane at 700 K, increased hydrogen purity (99% compared with 74% in SR) and no CO_2 or CO production with the only impurity being CH_4, all indicating a great potential of SESR of propane for hydrogen production.

1. Introduction

Increased fossil fuel consumption, coupled with both increasing awareness of environmental implications and diminishing natural resources, have provided the impetus to try and derive cleaner, quieter and more efficient sources of energy [1]. Utilizing hydrogen is one of the most promising approaches, with no emissions with the exception of water [2] and the capacity to be used in fuel cells [3]. One hydrogen source is steam reforming (SR) of hydrocarbons [4,5] and alcohols [6–8] among which propane is an attractive option as it is a primary constituent of liquefied petroleum gas (LPG) [9,10], produced in relative high amounts from natural gas and oil crude refining, it also has the benefit that it can be easily stored and distributed in a liquid state at 9 bar [11,12].

Catalyst development has been the principal focus of SR research of propane. Up to the present various catalysts were studied in propane SR, including noble metal-based [5,10,13–15] and nickel-based catalysts [16–18]. The direct utilization of the synthesis gas produced by SR for energy production, however, is a particular problem, with high CO_2 content negatively impacting upon efficiency of the proton

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doi:10.1016/j.ijhydene.2010.09.021

exchange membranes fuel cells (PEMFC) system and high CO content possessing a strong poisoning effects upon the catalyst of PEMFC [19]. In terms of fuel cell applications, a CO concentration of less than 10 ppm is required for low temperature PEMFC and alkaline fuel cells [20]. Separating the hydrogen from a hydrogen rich gas with impurities, however, is financially costly [21,22].

In order to solve these problems and enhance the hydrogen concentration in the product gas, the concept of sorption enhanced steam reforming (SESR) was proposed, which combines SR with in situ removal of CO_2 using a CO_2 sorbent [23–26]. The idea of SESR is based on Le Chatelier's principle, in which the reaction equilibrium will be shifted in favour of the reactant conversion, upon in situ removal of any of the products [24,27,28]. Such SESR approaches have been successfully applied in hydrogen production from biomass, methane, ethanol and glycerol [23–30]. To our knowledge, SESR has yet to be investigated for hydrogen production from propane. This work therefore seeks to understand, from a thermodynamic perspective, whether SESR can promote (and to what extent) the capacity of hydrogen production from propane SR. Theoretical analysis can provide a set of operating parameters to maximize the hydrogen production and/or propane conversion, through which, further experimental work can be guided.

In this study, we performed thermodynamic analysis of SESR of propane, where total Gibbs free energy minimization method was employed to calculate equilibrium compositions. The effects of process variables such as pressure, temperature and water to propane ratio (WPR) were studied and the carbon formation in SESR of propane was also illustrated. The promising potential for high purity hydrogen production by SESR of propane is for the first time shown here.

2. Methodology

The method of thermodynamic analysis by minimization of Gibbs free energy was introduced in our prior publications [7,31,32] and was also introduced in detail by other groups [28,33,34]. At low pressure and high temperature, the system can be considered as ideal [6,7].

The total Gibbs function for a system is given as follows:

$$G^t = \sum_{i=1}^{N} n_i \overline{G}_i = \sum_{i=1}^{N} n_i \overline{\mu}_i = \sum n_i G_i^0 + RT \sum n_i \ln \frac{\widehat{f}_i}{f_i^0} \tag{1}$$

For reaction equilibria in gas phase, $\hat{f}_i = \hat{\phi}_i \; y_i \; P$, $f_i^0 = P^0$, and since G_i^0 is set equal to zero for each chemical element in its standard state, $\Delta G^0 = \Delta G_{f_i}^0$ for each component is assumed. The minimum Gibbs free energy of each gaseous species and that of the total system can be expressed as Eqs. (2) and (3), with the Lagrange's undetermined multiplier method.

$$\Delta G_{f_i}^0 + RT \ln \frac{\widehat{\phi}_i y_i p}{p^0} + \sum_k \lambda_k a_{ik} = 0 \tag{2}$$

$$\sum_{i=1}^{N} n_i \left(\Delta G_{f_i}^0 + RT \ln \frac{\widehat{\phi}_i y_i p}{p^0} + \sum_k \lambda_k a_{ik} \right) = 0 \tag{3}$$

With the constraints of elemental balances:

$$\sum_{i=1}^{N} n_i a_{ik} = A_k \tag{4}$$

When solid is considered in the system, Eq. (5) is used in the calculations.

$$n_s \Delta G_{fs}^0 = 0 \tag{5}$$

The primary species involved in propane SR are C_3H_8, H_2O, H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6 and carbon (graphite). The most occurring products, including H_2, CO, CO_2, CH_4 and carbon [5,10,35], were discussed in this work. Calcium oxide (CaO) and calcium carbonate ($CaCO_3$) were also involved when CaO was used as a CO_2 sorbent. The thermodynamic equilibrium calculations were accomplished with the use of Outokumpu HSC Chemistry 4.0, a chemical reaction and equilibrium software, using the extensive thermochemical database delivered in the software package [36]. Gibbs module of this software is usually used to directly calculate product compositions at equilibrium employing the total Gibbs free energy minimization method. The initial amount of propane was assumed to be 1 mol with/without 3 mol of CaO in the system, therefore mole yield of each product presented in this study is based on per mole of propane. Thermodynamic analysis was carried out over the following variable ranges: pressure 1–5 atm, temperature 700–1100 K and WPR 1–18.

3. Results and discussion

Complete conversion of propane by the SR process was achieved for the range of pressure, temperature and WPR considered in this study, irrespective of the CO_2 sorbent CaO.

3.1. *Hydrogen production*

For both SR and SESR, the number of moles of hydrogen decreases with an increase in pressure as shown in Fig. 1 which depicts moles of hydrogen produced per mole of propane from SR and SESR of propane at selected pressures and WPR = 6. This is attributed to the overall reaction of propane SR, in which number of moles increases during the reaction (see Eq. (6)). Apparently, low pressure favours the reaction and high pressure has a detrimental effect on hydrogen production. We therefore selected atmospheric pressure (best one in terms of hydrogen production) throughout the following discussion. In addition to the effect of pressure, Fig. 1 provides the first indication that, in general, more hydrogen can be produced from SESR than SR at the same temperature and WPR.

$$C_3H_8 + 6H_2O \leftrightarrow 3CO_2 + 10H_2 \quad \Delta H_{298\ K} = 373.7\ \text{kJ/mol} \tag{6}$$

Fig. 2 illustrates moles of hydrogen produced per mole of propane as a function of WPR and temperature at atmospheric pressure. As seen from Fig. 2A, the number of moles of hydrogen increases with increasing temperature when WPR is less than 6 in SR. For a given WPR (>6), however, hydrogen production increases as temperature increases, before reaching a maximum at around 925–975 K and then begins to decrease slightly at higher temperatures. The greatest quantity of hydrogen (9.1 mol) is produced at 925 K with a WPR of 18.