



Thermodynamic analysis of acetic acid steam reforming for hydrogen production



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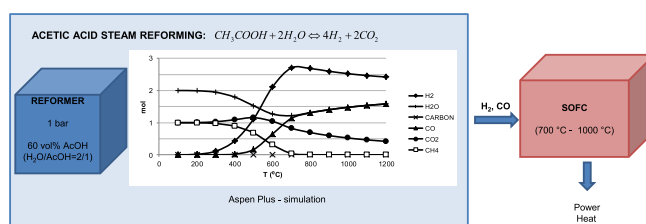
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HIGHLIGHTS

- H₂ for SOFC application can be obtained by acetic acid (AcOH) steam reforming.
- Steam reforming of high concentrated AcOH solution is simulated by Aspen Plus.
- Temperature and H₂O/AcOH ratio highly affect the equilibrium product distribution.
- Full conversion of AcOH to a H₂ and CO rich gas is achieved at high temperature.
- For a H₂O/AcOH ratio of 2/1 the optimal operation conditions are 700 °C and 1 bar.

GRAPHICAL ABSTRACT



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ABSTRACT

A thermodynamic analysis of hydrogen generation by acetic acid steam reforming has been carried out with respect to applications in solid oxide fuel cells. The effect of operating parameters on equilibrium composition has been examined focusing especially on hydrogen and carbon monoxide production, which are the fuels in this type of fuel cell. The temperature, steam to acetic acid ratio, and to a lesser extent pressure affect significantly the equilibrium product distribution due to their influence on steam reforming, thermal decomposition and water-gas shift reaction. The study shows that steam reforming of acetic acid with a steam to acetic acid ratio of 2 to 1 is thermodynamically feasible with hydrogen, carbon monoxide and water as the main products at the equilibrium at temperatures higher than 700 °C, and achieving CO/CO₂ ratios higher than 1. Thus, it can be concluded that within the operation temperature range of solid oxide fuel cells – between 700 °C and 1000 °C – the production of a gas rich in hydrogen and carbon monoxide is promoted.

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1. Introduction

Hydrogen (H₂) production processes are currently being investigated because H₂ is recognized as a clean fuel and energy carrier in fuel cells. The fuel cell technology is a promising alternative to

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traditional power generation systems for sustainable and efficient energy conversion. Among different types of fuel cells, the solid oxide fuel cell (SOFC) is gaining increasing attention because of the wide potential range of applications. One of the mayor advantages is their fuel flexibility due to the high operation temperature. SOFC can utilize a wide range of fuels by internal or external reforming for power generation [1]. It should be noted the tolerance of SOFC to carbon monoxide CO. While for other type of fuel cells, such as proton exchange membrane (PEM), CO acts as a poison, in SOFC it is a fuel. The SOFC offers the highest system efficiency of up to 60% by internal reforming of the fuel and gas recirculation [2], or over 80% combining heat and power generation [3] by using the waste heat.

Currently, the main process for H₂ production is steam reforming of fossil fuels, such as natural gas, naphtha, and coal. However, renewable sources like biomass have attracted much attention looking for CO₂ neutral energy balances. H₂ can be obtained from biomass by thermochemical processes, such as gasification to syngas or steam reforming of the bio-oil derived from a fast pyrolysis of the biomass. The conversion of bio-oil is one of the most promising routes, due to its higher energy yield compared to gasification [4] and the higher energy density of bio-oil than biomass. Bio-oil is a complex mixture of oxygenate compounds depending on biomass nature and pyrolysis conditions. One of the major components of bio-oil is acetic acid (AcOH) with up to 13 wt% [5], which is non-inflammable unlike methanol and ethanol. Hence, the widely available AcOH is a safe H₂ carrier, which can easily be stored, handled, and transported.

Steam reforming (SR) of AcOH as a model component of bio-oil for H₂ production has been investigated over different catalytic systems. It was shown that AcOH can be completely converted at a temperature of 700 °C with high H₂ selectivity [6–8]. Hence, AcOH can be used for internal reforming in SOFCs producing a H₂ rich gas mixture. The high operation temperature of 700–1000 °C [9] allows the direct conversion of the fuel into a H₂ and CO rich fuel in the electrochemical cell. Therefore, any external heat source for the endothermic SR as well as for fuel evaporation is not necessary. This enables a simple and efficient system design with reduced size and low costs [10].

Thermodynamic analyses of hydrocarbons, such as methane (CH₄), and of alcohols, such as ethanol or methanol, under SR conditions are widely investigated to identify operation conditions at which a H₂ rich fuel gas can be obtained [11–14]. However, literature dealing with the thermodynamic analysis of AcOH, or of the aqueous phase of bio-oil is scarce. Vagia et al. [15] studied the thermodynamics of AcOH SR at a temperature range between 130 °C and 1030 °C, steam to fuel ratio between 1 and 9 and at atmospheric pressure. They showed that SR of AcOH is thermodynamically feasible. AcOH can be fully converted at all operating conditions examined. As temperature is increased H₂ production grows till it reaches a maximum at 630 °C. The higher the steam to fuel ratio, the higher the H₂ yield is. The authors also ensure a carbon free operation at temperatures higher than 330 °C and steam to fuel ratios higher than 3.

The present thermodynamic analysis is aimed to examine optimal operation conditions for SOFC applications with internal reforming of AcOH. Therefore, the study focuses on high temperatures of up to 1200 °C. In order to achieve high fuel cell performance the water (H₂O) content in the fuel has to be minimized to avoid energy losses by evaporating the fuel and to optimize the system size [10]. Hence, the thermodynamic analysis for highly concentrated AcOH solutions of approximately 60 vol% was of especial interest in this study. In contrast to other studies, in this work the production of carbon monoxide (CO) is preferred over the generation of carbon dioxide (CO₂), since CO can be used as fuel in SOFCs, which provides more electricity output. The focus is put on

the influence of process parameters, such as temperature, feed composition, and pressure on the equilibrium product distribution of AcOH SR. Thermodynamically favorable operating conditions in terms of high H₂ yield, high CO/CO₂ ratio, high AcOH conversion, and minimal solid carbon deposition were determined.

2. Thermodynamic analysis

2.1. Simulation methodology

Generally, chemical equilibrium compositions are calculated based on the equilibrium constants of the reactions. However, for SR of AcOH this procedure is not useful, because a high number of simultaneous and consecutive reactions take place and the calculation becomes extremely complex. Therefore, the thermodynamic equilibrium of SR of AcOH was analyzed by the minimization of the Gibbs free energy using Aspen Plus software. This method helps to establish process models without tedious calculations for obtaining the equilibrium product distribution of a system. The simulation model was built using an equilibrium based reactor, which consists of Gibbs free energy (ΔG) minimization of the system subject to atom balance constraints (RGIBBS). This type of reactor is useful when reactions are not known or are high in number due to many components participating in the reactions. This model does not require reaction stoichiometry. RGIBBS can also determine phase equilibria, particularly for multiple liquid phases, only by the specification of the components present in the system and the type of streams (mole flow, mole fraction, mass flow, mass fraction, etc.) if adequate mixture thermodynamic models are selected. Temperature and pressure (or pressure and enthalpy) of the reactor and the steam to fuel ratio must also be specified.

In this analysis the formation of the following compounds was considered: H₂, CO, CO₂, CH₄, carbon, acetaldehyde, ethane, ethylene, and acetylene as products of SR of AcOH; and the possible unreacted reagents, H₂O and AcOH. All of them were found in vapor phase, except of carbon which was specified as a solid (in graphite form).

For a given isothermal and isobaric system, Gibbs free energy minimization method can be presented theoretically as follows [16]. The total free energy of the system is expressed in Eq. (1)

$$G = \sum_{i=1}^{NC} \sum_{j=1}^{NP} n_{ij} \mu_{ij} \quad (1)$$

where n_{ij} is the number of moles of component i in j phase; μ_{ij} is the chemical potential of component i in j phase, which is function of j phase composition, temperature and pressure; NP represents the number of phases; and NC the number of components.

The same Eq. (1) can be rewritten in terms of fugacity, f (Eqs. (2) and (3)):

$$G = \sum_{i=1}^{NC} \sum_{j=1}^{NP} \left(\mu_i^0 + RT \ln \frac{\hat{f}_i}{f_i^0} \right) \quad (2)$$

$$G = \sum_{i=1}^{NC} \sum_{j=1}^{NP} n_{ij} \left(\mu_i^0 + RT \ln \frac{\hat{f}_{ij}}{f_i^0} \right) \quad (3)$$

where μ_i^0 is the chemical potential of pure component i at a standard state; f_i^0 is the fugacity of the pure component i at a standard state; R represents the gas universal constant; and T is the temperature of the equilibrium.

The system was considered as a solid–gas system, and for the

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