Renewable and Sustainable Energy Reviews 30 (2014) 869–876

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Thermodynamic and economic analysis of hydrogen production integration in the Brazilian sugar and alcohol industry

Jose Luz Silveira [a,b,c,*], Celso Eduardo Tuna [a,b,c], Wendell de Queiroz Lamas [a,b,c], Marcio Evaristo da Silva [a,b,c], Valdisley Jose Martinelli [a,b,c]

[a] *Laboratory of Optimization of Energy Systems, Department of Energy, Faculty of Engineering at Guaratingueta, Sao Paulo State University, Guaratingueta 12516-410, Brazil*

[b] *Post-graduate Programme in Mechanical Engineering, Department of Mechanical Engineering, University of Taubate, Taubate, SP, Brazil*

[c] *Department of Basic and Environmental Sciences, School of Engineering at Lorena, University of Sao Paulo, Lorena, SP, Brazil*

A R T I C L E I N F O

Article history:
Received 16 May 2012
Received in revised form
5 September 2013
Accepted 19 October 2013
Available online 5 December 2013

Keywords:
DIR-MCFC
Electrical power generation
Ethanol steam reforming
Renewable energy
Technical analysis

A B S T R A C T

One of the biggest challenges today is to develop clean fuels, which do not emit pollutant and with viable implementation. One of the options currently under study is the hydrogen production process. In this context, this work aims to study the technical and economical aspects of the incorporation process of hydrogen producing by ethanol steam reforming in the sugar cane industry and MCFC (molten carbonate fuel cell) application on it to generate electric power. Therefore, it has been proposed a modification in the traditional process of sugar cane industry, in order to incorporate hydrogen production, besides the traditional products (sugar, ethylic, hydrated and anhydric alcohol). For this purpose, a detailed theoretical study of the ethanol production process, describing the considerations to incorporate the hydrogen production will be performed. After that, there will be a thermodynamic study for analysing the innovation of this production chain, as well as a study of economic engineering to allocate the costs of products of the new process, optimising it and considering the thermoeconomics as being as an analysis tool. This proposal aims to improve Brazil's position in the ranking of international biofuels, corroborating the nation to be a power in the hydrogen era.

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1. Introduction

Nowadays, economic and social reasons have spurred the use of ethanol as an alternative fuel and considered as one of the solutions for the environmental problems, such as increase of greenhouse effect, especially in the cities. Renewable fuels can be

* Corresponding author at: Sao Paulo State University, Department of Energy, Laboratory of Optimization of Energy Systems, Faculty of Engineering at Guaratingueta 333, Pedregulho, 12516-410 Guaratingueta, Brazil. Tel.: +55 12 3123 2836; fax: +55 12 3123 2835.
E-mail address: joseluz@feg.unesp.br (J.L. Silveira).

1364-0321/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.rser.2013.10.012

obtained from biomass such as sugar cane, contributing to carbon sequestration. According to [1], ethanol is less toxic than methanol, a subject to be considered to spur its studies.

Silveira et al. [2] and Vasudeva et al. [3] have shown that the most recent application of hydrogen is in fuel cell, an available alternative for electricity generation, especially in far places.

The hydrogen storage is not practical. A high pressure is required because the poor energy density by volume. Safety issues are important. According to [2], fuel cells are interesting devices for decentralized generation of energy where the chemical energy found on the fuel is converted to electricity (direct current in low voltage) as seen in a work carried out by [4]. Table 1 shows the main fuel technologies.

Hydrogen is the simplest, the lightest, and the most plentiful element in the universe. It is made up of one proton and one electron revolving around the proton. In its normal gaseous state, hydrogen is colourless, odourless, tasteless, non-toxic, and burns invisibly (in the case of air mixture). It should not be considered a "fuel", but instead, it should be considered as an energy transport mechanism. Currently, more hydrogen is made from natural gas through a process known as reforming.

Nowadays, fuel cells are one of the most promising energy generation technologies. Many of these devices need hydrogen and oxygen for electricity production through electrolytic process, contrary to water electrolysis. According to [7], hydrogen is not available as primary source; it is necessary to get it in some fuels such as fossil hydrocarbons, biomass, or water, by electrolysis, for example.

Reformers are reactors that produce mixtures containing hydrogen, carbon dioxide, and some other compounds, throughout the process called steam reforming, where superheated water and hydrocarbons react to produce a mixture with hydrogen, carbon monoxide, and carbon dioxide. This process is endothermic. Hydrogen can also be produced from a variety of other sources including water and biomass [6].

Other process used for hydrogen production are partial oxidation (this reaction is exothermic) and auto thermal reforming. In partial oxidation, air, which contains gases such as oxygen and nitrogen, is used.

This work aims to study the process incorporation of hydrogen producing by ethanol steam reforming in the sugar cane industry, according to Fig. 1. In this case, in addition to the production of sugar and ethanol, the Brazilian sugar cane industry would be able to produce biohydrogen, to be used, i.e., with fuel cells, or for sale.

Table 1
Main fuel cell technologies [5].

Fuel cell technologies	Electrolytes	Operation temperature ranges (°C)
AFC (alkaline)	KOH	50–200
PEMFC (proton exchange membrane)	Polymer membrane	50–90
PAFC (phosphoric acid)	H_3PO_4	180–210
MCFC (molten carbonate)	K_2CO_3/Li_2CO_3	600–750
SOFC (solid oxide)	ZrO_2/Y_2O_3	800–1200

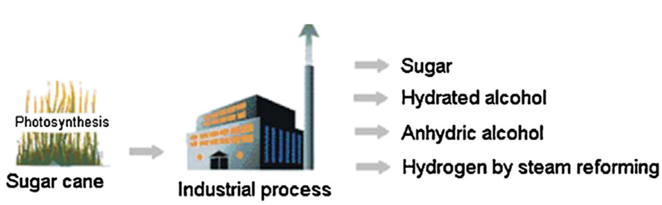

Fig. 1. New schematic of sugar cane industry [6].

2. Molten carbonate fuel cell

Selman [8] shows that molten carbonate fuel cells (MCFCs) are "the second generation" fuel cells. The first MCFC was developed by Broers and Ketelaar in the 1950s. This study is important because MCFC has high efficiency of generation using several fuels, contributing to low emission of pollutants.

According to [8], the MCFC has some issues:

The temperature of operation attains a range between 600 °C and 700 °C;

- It is generally used in nickel-based porous anode with chromium or aluminium and nickel oxide-based porous cathode doped with lithium.
- It is an alkaline carbonate electrolyte with $LiAlO_2$.

2.1. The electrochemical process

Silveira et al. [2] show that the reaction described in Eq. (1) occurs in the cathode. In this case, oxygen (O_2) reacts with carbon dioxide and electrons to produce carbonate ions (CO_3^2), according to [9].

$$1/2O_2 + CO_2 + 2e \rightarrow CO_3^2 \quad (1)$$

The carbonate ions cross over the electrolyte, from cathode to anode. On the anode, the reaction described in Eq. (2) occurs. The oxidation of hydrogen uses the carbonate ions to produce steam and carbon dioxide, according to [9].

$$H_2 + CO_3^2 \rightarrow H_2O + CO_2 + 2e^- \quad (2)$$

The electrochemical reaction is the oxidation of hydrogen, where transference of two electrons from anode to cathode occurs. Carbon dioxide can be transferred to cathode, where it is consumed.

On the anode, other fuel gases, such as carbon monoxide and methane, are used to produce hydrogen. Although the direct oxidation of carbon monoxide is possible, this act occurs at low velocity when compared with oxidation of hydrogen. However, the oxidation of carbon monoxide occurs, mainly through the reaction described in Eq. (3), called water gas shift reaction.

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

The direct electrochemical reaction from organic fuels, such as methane, methanol, ethane, ethanol etc, is very slow. Because of this, steam reforming, which can be carried out in separated reformer (external reforming) or inside the fuel cell (internal reforming), is suggested.

2.2. Internal reforming process

Silveira et al. [2] show that internal reforming process occurs in fuel cells, which operate at high temperature, near electrochemically active devices. Fig. 2 shows some configurations about internal reforming process.

3. Thermodynamic analysis of ethanol steam reforming

Several technologies for hydrogen production may be studied. Steam reforming is one of the most usual technologies installed in chemical industries. The reforming efficiency is obtained through studying of physical–chemical properties of the components, thermodynamic conditions (temperature and pressure of reaction,