Modeling and Design of a Bio-ethanol Steam Reforming Unit

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Abstract

Modeling for design purposes of a small bio-ethanol steam reforming unit for hydrogen production was performed, for a system composed of three reactors: a bio-ethanol steam reforming reactor (BSR), a water gas shift reactor (GSR) and a carbon monoxide preferential oxidation reactor (COPROX). Feeding streams of bio-ethanol and steam were considered for the BSR at 1 atm and pre-heated to 453 K. An oxygen stream at 1 atm and 403 K was adopted for the COPROX reactor. All reactors were at 1 atm, and no pressure drop was considered in this system since the aim of this work was for design purposes. The operational temperatures for the reactors were adopted following a previous author's work: 823 K for the BSR, 623 K for the GSR and 403 K for the COPROX reactor.

A sensitivity analysis regarding the amount of hydrogen produced was performed, varying steam to bio-ethanol ratio using Aspen Plus® software enhanced with FORTRAN routines, using the Peng-Robinson method for properties prediction. Results showed an asymptotic behavior of the system, leading to an operational optimum of 5.7 kmol of hydrogen per kmol of bio-ethanol. Also a pressure sensitivity analysis is discussed.

*Keywords: Process Modeling, Steam Reforming, Bio-ethanol, Hydrogen Production*

1   Introduction

1.1 Traditional industrial steam reforming process for hydrogen production

Steam reforming has been the predominant industrial route to obtain hydrogen from hydrocarbons since the 1930's, being methane from natural gas the most used raw material for bulk hydrogen production [1]. It is a catalytic process that involves reactions between methane from natural gas and steam, resulting in a mixture of hydrogen, carbon monoxide, carbon dioxide, water and many other gaseous products that held a 70% efficiency.

The traditional steam reforming process consists of three reaction stages: the reforming reaction, the water-gas shift reactions and the undesired residues removal process.

In the reforming stage, the methane catalytically reacts with steam fed into the furnace to produce hydrogen and carbon monoxide as shown in the reversible endothermic reactions (1) and (2). These reactions are carried out over metal-based catalysts (usually nickel), at temperatures of 973–1373 K and pressures ranging from 10 atm to 20 atm. The reforming reactions are endothermic and a heat must be provided by feeding natural gas to the reformer furnace.

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \qquad (1)$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad (2)$$
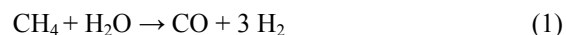
The water-gas shift reaction is fed with the gaseous products of the reforming furnace. The carbon monoxide reacts with water as described in reaction (3) in order to enhance the hydrogen production of the process. This reaction is slightly exothermic and sensitive to temperature, with the tendency to shift towards reactants as temperature increases.

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

In the industrial traditional steam methane reforming, the process is usually divided in two stages; first a high temperature water-gas shift reaction occurring at 623 K, carried out over iron oxide/chromium oxide catalyst and then a low temperature water-gas shift reaction, occurring at 473 K over copper on a support composed of aluminum oxide/zinc oxide.

The stage of undesirable residues removal depends on the H_2 purity required. For a high purity H_2 demand (99% volume), pressure swing adsorption (PSA) or amine scrubbing process may be considered [2].

Nomenclature

BSR	Bio-ethanol steam reformer
COPROX	Carbon monoxide preferential oxidation
GSR	Water-gas shift reactor
H	Enthalpy ($J.mol^{-1}$)
H^{ID}	Ideal gas enthalpy basis ($J.mol^{-1}$)
P	Pressure (atm)
P^{o}	Critical Pressure (atm)
PEMFC	Proton exchange membrane fuel cell
PSA	Pressure swing adsorption
r	Water to ethanol ratio
R	Universal gas constant ($8,314\ J.mol^{-1}.K^{-1}$)
S	Entropy ($J.mol^{-1}K^{-1}$)
T	Temperature (K)
V	Volume (L)
Z	Compressibility factor

1.2 Bio-ethanol as raw material

Although the steam methane reforming is a mature and well established process, recent attention is being given worldwide to develop steam reforming process using bio-ethanol as a feedstock to produce hydrogen. Special attention is being given to develop process to produce hydrogen for fuel cell uses [3, 4]. These researches are justified by the desire to reduce global anthropogenic carbon dioxide (CO_2) emissions once the vegetables used to produce bio-ethanol consumes the carbon dioxide produced, improving local (urban) air quality, and ensuring the security of energy supply from a sustainable source [5].

Currently, methanol-water mixture is the most common liquid feedstock considered for hydrogen production [6]. However, methanol itself has a high toxicity, low availability on ordinary basis and coal gas based production technology, which leads to emission problems. Bio-ethanol doesn't have any of these issues and has the advantage to has a mature industrial production. In many countries like Brazil and the United States it has also a very developed logistic distribution net, being found in almost any regular gas stations.

In Brazil, there is a particular interest in the development of processes to use such feedstock. The national program of bio-ethanol from sugar cane fermentation has a successful trajectory,

started in the 1970s, and during the 2007-2008 period, Brazil has produced 14.3 billion liters of bio-ethanol [7], being currently the world's second largest producer.

2 Bio-ethanol reforming process modeling

The bio-ethanol reforming process and the conventional industrial steam methane reforming process are very similar.
But as the purpose of the bio-ethanol reforming is to produce hydrogen to fuel cells, some particularities has to be observed.

For example, for low temperature fuel cell applications as PEMFC (proton exchange membrane fuel cells), the carbon monoxide is a poison for the fuel cell platinum catalyst in concentrations higher than 20 ppm. Therefore the water-gas shift reaction has to be set to maximize CO removal from the gaseous products of the reforming furnace.

For the same reason, a COPROX (Carbon monoxide preferential oxidation) reaction has to be considered after the water-gas shift reactor. It refers to the preferential oxidation of CO usually on an heterogeneous catalyst placed upon a ceramic support, such as platinum/iron and platinum/ruthenium, among others.

In this work, the modeling of a small bio-ethanol steam reforming unit for hydrogen production was developed using Aspen Plus® software. The model is schematically described in figure 1, ad it is composed of three reactors as follow: a bio-ethanol steam reforming reactor (BSR), a water-gas shift reactor (GSR) and a carbon monoxide preferential oxidation reactor (COPROX).
For the model building of the BSR, the following stages were considered: ethanol dehydrogenation reaction (4), acetaldehyde decomposition reaction (5) and methane steam reforming reaction (6).
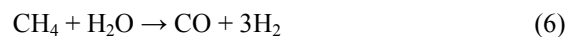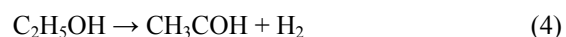
$$C_2H_5OH \rightarrow CH_3COH + H_2 \tag{4}$$

$$CH_3COH \rightarrow CH_4 + CO \tag{5}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{6}$$

Feeding streams of bio-ethanol and steam were considered for the BSR at 1 atm and pre-heated to 453 K. Due to these operational conditions, reaction (4) occurs very fast, and can be considered complete, and reactions (5) and (6) reach equilibrium in these conditions [8].
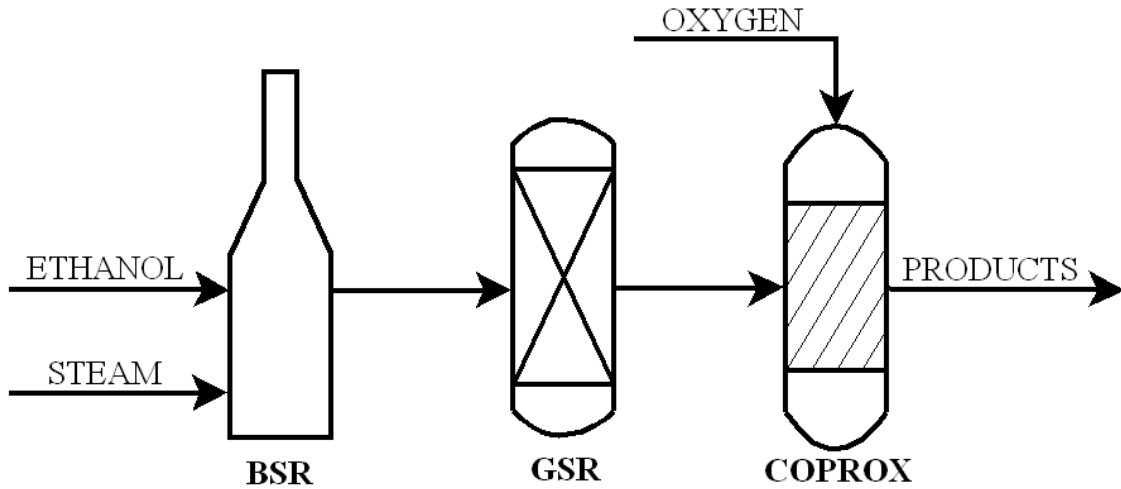
Fig. 1. Bio-ethanol model diagram

For the GSR, the reaction (3) is the only considered. It's the same as the traditional industrial steam methane reforming process.

Before feeding the COPROX reactor, the gaseous products leaving the GSR are mixed with oxygen at 1 atm and 403 K. Carbon monoxide reacts with oxygen (7), reducing its concentration to acceptable levels for the PEMFC, but a small quantity of hydrogen is also consumed in this stage (8).

$$2CO + O_2 \rightarrow 2CO_2 \tag{7}$$

$$2H_2 + O_2 \rightarrow 2H_2O \tag{8}$$

All reactors were modeled at 1 atm, and no pressure drop was considered in this system since the aim of this work was for design purposes. The operational temperatures for the reactors were adopted based on a previous experimental work of the authors [9] and other references [10, 11]: 823 K for the BSR, 623 K for the GSR and 403 K for the COPROX reactor.

A FORTRAN routine was implemented in the program to control the oxygen flow values, maintaining it compatible with CO production.

The Peng-Robinson equation state was adopted for properties prediction [12, 13]:

$$\frac{H - H^{ID}}{RT} = Z - 1 + \frac{1}{RT} \int_{\infty}^{V} \left[T \left(\frac{\partial P}{\partial T} \right) \Big|_{V} - P \right] dV \tag{9}$$

$$\frac{S - S_o^{ID}}{RT} = \ln Z - \ln \frac{P}{P^o} + \int_{\infty}^{V} \left[\frac{1}{R} \left(\frac{\partial P}{\partial T} \right) \Big|_{V} - \frac{1}{V} \right] dV \tag{10}$$

In the simulation, the ideal gas enthalpy basis of the software, H^{ID} is equal to the ideal gas enthalpy of formation at 298 K and 1 atm. The ideal gas enthalpy basis H^{ID} changes with temperature for each individual component in the calculations.

3   Simulation results

A sensitivity analysis regarding the amount of hydrogen produced by bio-ethanol feeding was performed, varying steam to bio-ethanol ratio r. The bio-ethanol flow was kept in 1 kmol/h, while the software simulated the hydrogen production scenarios for steam flows in kmol/h ranging r values from 2 to 20, at 1 atm. The simulation results are presented in the graphic of figure 2.
This performance analysis is based on the work of Francesconi et al. [14]. Their work was done in a similar system, although they modeled the process considering two water-gas shift reactors, a high temperature and a low temperature reactor, similarly to the traditional steam reforming process. In their work they used the HYSYS® simulator. As our purpose was the design of a small steam reforming unit, we decided to model only one water-gas shift reactor. This simplification had the objectives to reduce equipment investment and operational variables to control.
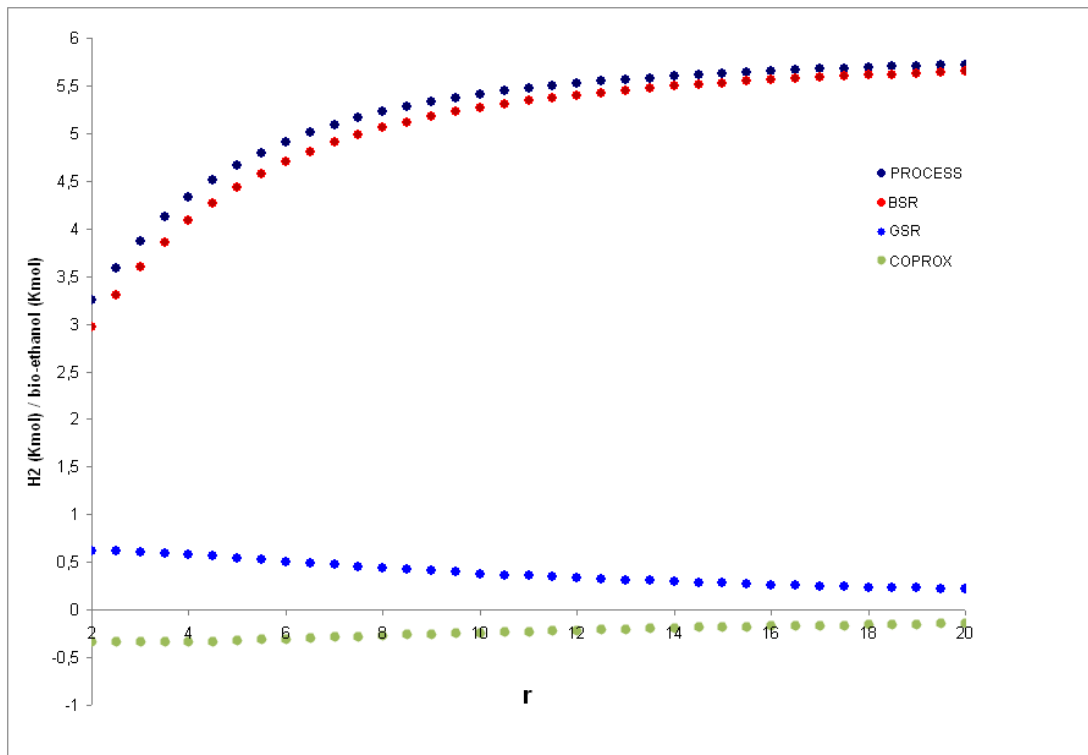
Fig.2. Molar hydrogen production per ethanol molar feeding variation according to water to ethanol molar ratio.

The graphic in figure 2 shows the molar hydrogen production per molar feeding of ethanol after each reaction stage of the process. It can be noticed an asymptotic behavior of the system, leading towards an operational stabilization.

A sensitivity analysis of pressure influence for the system is presented in figure 3. Pressures ranged from $1 - 7$ atm, varying r values and keeping all the other operational parameters constant.
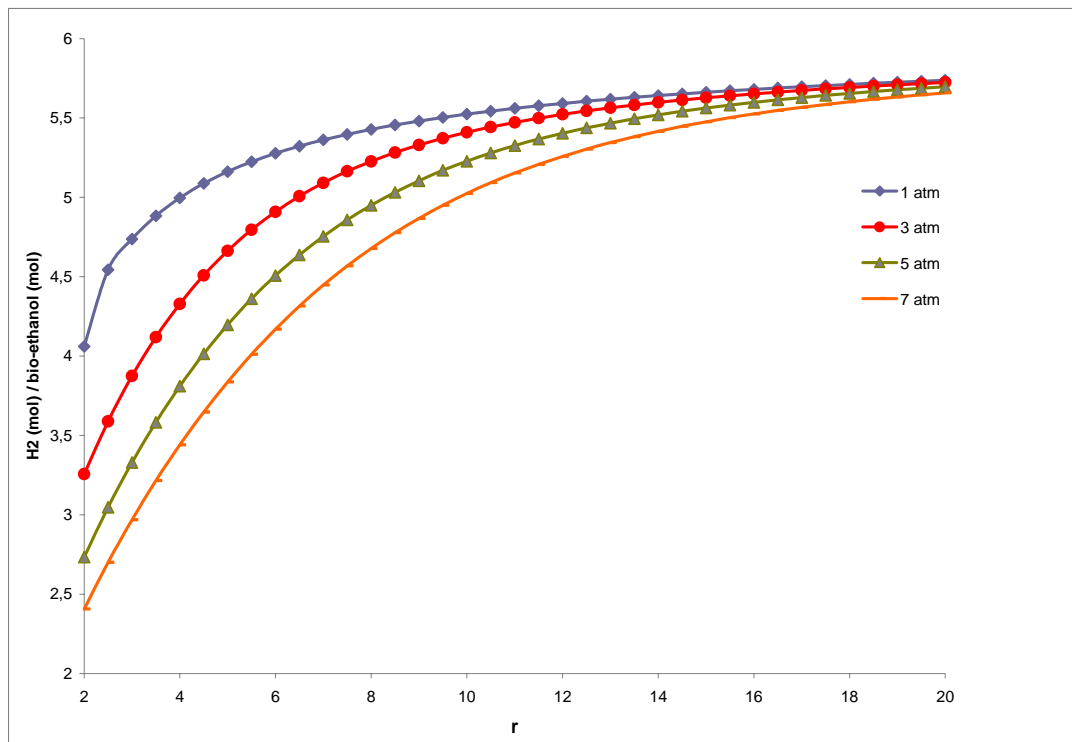

Fig.3. Pressure sensitivity analysis for the system.

4 Conclusions

A system for bio-ethanol reforming consisting of three reactors is modeled for design purposes, and sensitivities analysis regarding the molar production of hydrogen against ethanol molar feeding is made. An operational optimum of 5.7 kmol of hydrogen per kmol of bio-ethanol is achieved. These results in comparison to other reported data in similar system from the literature [14] showed that from a overall process point of view working with one or two water-gas shift reactors is indifferent, regarding hydrogen bulk production from bio-ethanol. This statement is valid for the simulation of operational conditions analyzed.

Also a pressure sensitivity analysis is performed, showing that pressure has a significant effect on the asymptotic behavior of the system. It can be inferred from analyzed conditions that pressure increase has a negative influence on the hydrogen production.

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