ABSTRACT - Bioethanol and hydrogen as a new source of energy are being strongly considered by industries and scientific community for causing less pollution and being cheaper when compared with fossil fuels. In this context, a new kind of engine, called fuel cells, that uses electro-chemistry, thermodynamics and transport phenomena (fluid mechanics, heat transfer and mass transfer) concepts to convert hydrogen in water, and generate electrical energy, has been designed and tested by researchers and big companies over the world. However, hydrogen is considered dangerous and expensive due to the storage requirements, which is usually made in spherical containers under high pressure. In order to overcome these drawbacks, on-board bioethanol reforming reactor (ESR), which converts bioethanol in hydrogen, is being integrated on board fuel cell systems to produce clean energy efficiently and safely. Moreover, the design of the control system for the reactor is fundamental once temperature and conversion profiles must be kept in profitable range front eventual disturbance. Therefore, a dynamic model is required in order to predict the behavior of the bioethanol steam reforming reactor when such disturbance takes place and to evaluate the controller parameters. This work has as purpose to develop a dynamic model for the ESR; to predict the dynamic behaviour front to usual industrial disturbance as well as to consider the pressure drop along the reactor; create a SIMULINK model that represents the process as a block diagram common used in process control loops, and to develop a Guide User Interface (GUI) in order the user can run the simulation outside the programming environment.

Keywords: Bioethanol, Hydrogen, Fuel Cells

INTRODUCTION

As an energy vector, hydrogen has a great potential for becoming a dominant fuel in a wide variety of application due to its high energy density, high heat capacity and non-pollutant products after oxidation processes (Ferold et al., 2012). Even though hydrogen can also be used in heat engines, fuel cells have been being considered the ideal processor system for producing electricity via hydrogen, which can be defined as a device in which converts electrochemical energy in heat and electricity while fuel is supplied (Ferold et al., 2012).

Some advantages of fuel cells when compared with the conventional heat engines, such as, higher efficiency (Holland et al., 2001) and conversion of chemical energy of hydrogen in electricity and heat without combustion processes (Bose et. al, 2003), are the motivation for many studies and publications about the design of Fuel Cells in a wide of residential and industrial environments. However, uncertainties are found about the development and economic feasibility of enabling technologies, such as use of renewable energy sources, advanced production processes, storage routine, safety and risk, and infrastructure (Ferold et al., 2012).

In terms of conversion of liquid fuels in useful power, internal combustion engine has achieved a maximum efficiency of 35% while fuel cells have achieved 85%. This is the main motive in which fuel cells have been being pointed out as a powerful alternative for energy production. Also, due to the lack of infrastructure as mentioned before, onboard processing system for producing hydrogen is being proposed as complement for the fuel cells system. In this way, many hydrogen sources has been studied, but renewable fuels has been focused by researchers, once the objective for fuel cell operation is guarantee a sustainable process (Degliuomini et al., 2012). In
this view. Bioethanol has become an ideal renewable fuel due to several motives, such as non-toxicity, high \( \text{H}/\text{C} \) ratio, net positive energetic balance, and cheap and ease production (Ferold et al., 2012).

In order to understand and design the fuel cell system, a dynamic model is required once it shows the interaction between process variables when such system are submitted to common industrial disturbances. Also, the dynamic model for the reactors involved in fuel cell power plants are important to predict the transient performance for the reactor, which has a strong impact on the efficiency of the fuel cell system (Degliuomini et al., 2012).

As this work focus on the bioethanol fuel cell systems, its main purpose is to develop a dynamic model for the Ethanol Steam Reforming Reactor to predict the effects of common industrial disturbances on its performance. Also, a fully implementation in MATLAB/SIMULINK, will be done for simulating the reactor performance, once it is one of the most used software's to design process control systems.

**PROCESS MODELING**

The main reactions occurring in Ethanol Steam Reforming Reactor (ESR) are provided by Souza (2013) following by the Eq. 1, 2, 3, and 4.

$$C_2H_5OH \rightarrow CH_4 + CO + H_2 \quad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (2)$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (3)$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad (4)$$

These reactions take place in a presence of Ni/Al/2O3 inside the ESR. In order to develop the governing equations for the reactor operation, the reaction rate expressions must be known. These expressions are provided by Souza (2013), which are shown by Eq. 5, 6, 7, 8, and 9.

$$r_1 = k_1 \cdot P \cdot y_{CO} \cdot y_{H_2O}$$

$$r_2 = \frac{k_2 \cdot P}{y_{H_2O} \cdot DEN^2} \left( y_{CO} \cdot y_{H_2O} - \frac{y_{CO} \cdot y_{H_2O}}{K_i} \right)$$

$$r_3 = \frac{k_3}{y_{H_2O} \cdot DEN^2} \left[ y_{CH_4} \cdot y_{H_2O} - \frac{y_{CH_4} \cdot y_{H_2O}}{K_i} \right]$$

$$r_4 = \frac{k_4}{y_{H_2O} \cdot DEN^2} \left[ y_{CH_4} \cdot y_{H_2O} - \frac{y_{CH_4} \cdot y_{H_2O}}{K_i} \right]$$

$$DEN = 1 + P \left( K_{CO} y_{CO} + K_{H_2} y_{H_2} + K_{CH} y_{CH} \right) \frac{K_{H_2O} y_{H_2O}}{y_{H_2O}}$$

In other to apply the material and energy balance in the ESR, some assumptions have been made in order to simplify the model and reduce the computational effort in solving the equations, which are:

1. ideal gas behavior;
2. pressure drop do not depend on time;
3. plug flow reactor;
4. constant overall heat transfer coefficient along the reactor jacket.

For a Plug Flow reactor, the dynamic energy and material balance given by Fogler (2004) are shown by the Eq. 10 and 11.

$$-\frac{1}{A_c} \frac{\partial F_j}{\partial z} + \sum j \cdot r_j = -\frac{\partial C_j}{\partial t} \quad (10)$$

$$U \frac{d(T_r - T)}{dt} = \frac{1}{A_c} \frac{\partial T}{\partial z} + \sum j \cdot r_j \cdot (-\Delta H_j) = \sum (C_j \cdot \frac{\partial T}{\partial t}) \quad (11)$$

These equations are partial differential equations (PDEs) in terms of time \( t \) and axial position \( z \), which solution may be difficult to obtain and they are not suitable for control design. In order to simplify these equations, a discretization in axial position \( z \) is required, which transforms the PDEs in Ordinary Differential Equations in terms of time for each element of volume comprised in \( \Delta z \). The mesh has been built considering the discretized points are evenly spaced by a distance \( \Delta z \). This procedure can be made knowing that a PFR is represented as an infinite series of Continuous Stirred Tanks Reactors (CSTRs). Such modeling is shown by Degliuomini (2012) and used in this work.

**Overall Material Balance**

Another assumption is made related with the overall material balance, which the accumulation of total mass inside the reactor is neglected. Therefore, a pseudo-steady state overall material balance discretized equation is shown by the Eq. 12.

$$F_{ri} = F_{ri-1} + 2 \cdot (r_i + r_{i+1} + r_{i+2}) \cdot W_{out,i} \quad (12)$$

**Momentum Equation (Pressure Drop)**

Assuming neglected effect of time in the pressure profile along the reactor, a pseudo-steady state for the Momentum Equation can be used to predict the pressure profile along the reactor. The Ergun’s equation has been considered in this work and it is shown by Eq. 13.
\[
\frac{dP}{dz} = \left( \frac{G(1 - \phi)}{\rho_0 g_s D_p \phi^3} \left[ \frac{150(1 - \phi) \mu}{D_p} + 1.75G \right] \right) \frac{P_i T_i F_i}{P_0 T_0 F_0} 
\]

(13)

Therefore, a discretized Ergun’s Equation is used for predicting the pressure in each element of reactor. Using backwards finite differences discretization, the discretized equation is shown by Eq. 14.

\[
P_i = P_{i-1} - \beta_0 \frac{P_0}{P_{i-1}} \frac{T_{i-1}}{T_0} F_i \Delta z
\]

(14)

Where

\[
\beta_0 = \frac{G(1 - \phi)}{\rho_0 g_s D_p \phi^3} \left[ \frac{150(1 - \phi) \mu}{D_p} + 1.75G \right]
\]

(15)

For simplicity, mass flux (G), porosity (\(\phi\)) and viscosity (\(\mu\)) are considered constant along the reactor.

**Component Material Balance**

The discretized component material balance is similar to that for a dynamic CSTR for each element of reactor, which is shown by Eq. 16 and 17.

\[
\frac{dy_j}{dt} = \frac{F_i y_{i,j-1} - F_i y_{i,j} + \sum_{k=1}^{4} v_{j,k} r_{i,k} w_{i,w,j}}{n_{i,i}}
\]

(16)

**Energy Balance**

\[
\frac{dT}{dt} = \frac{F_i c_p T_{i-1} - F_i c_p T_i - \sum_{k=1}^{4} r_{i,k} \Delta H_{r,k} w_{i,w,j}}{n_{i,i} c_p}
\]

(17)

Where

\[
Q_i = UA \Delta z (T_{in} - T_i)
\]

(18)

**RESULTS**

In order to simulate the conservation equation developed above, some process parameters for the ESR must be provided. The goal of this work is predict the dynamic behaviour of an Ethanol Steam Reforming Reactor that has industrial dimensions, once most of research in this field has been applied for small reactors. Therefore, the reactor dimensions proposed by Nummedal et al. (2004) have been used in this work. Such parameters are listed in the Table 1.
Disturbance in the Inlet Feed Flow Rate

The Fig. 4 and 5 show the dynamic behaviour of outlet temperature, ethanol and hydrogen compositions of the ESR, respectively, when the feed flow rate is increased from 1 mol/s to 1.2 mol/s and when it is decreased to 1 mol/s to 0.5 mol/s, in t=0s.

It can be observed that after increasing the feed flow rate, both outlet temperature and hydrogen composition decrease due to the decrease on the reactants residence time. Once it happens, the reactants spend less time into the reactor, hence, the conversion is diminished and the fluid is submitted to the heat transfer from the hot gases for less time and the temperature decreases.

These effects are inverted when feed flow rate is decreased.
Disturbance in the Inlet Temperature

The Fig. 7 and 8 show the dynamic behaviour of outlet temperature, hydrogen and ethanol compositions of the ESR, respectively, when the inlet temperature is increased from 982 K to 1200 K and when it is decreased from 982 K to 800 K, in t=0s.

After increasing the inlet temperature, an inverse response is observed for the exit temperature. As the overall ethanol steam reforming reactor is endothermic, based on the Le Chatelier’s principle, when the temperature increase the reaction dislocates to the endothermic way, which explain the increasing on the hydrogen composition and the first decreasing on the exit temperature. As the reactions have most effects at the beginning of the reactor, the heat losses due to the endothermic reactions has no longer effect on the temperature profile, and the heat transfer from the hot gases make the exit temperature increase.

Time delays are observed for all the cases; however, it is so small that cannot be observed in the previous graphs.

SIMULINK MODEL AND MATLAB GUIDE USER’S INTERFACE (GUI)

In industrial environment, the usage of interfaces for the equipment is important for control, simulation and training purposes; moreover, the coding may be extremely difficult to the user understand its usage. A SIMULINK interface provides good representation for process control design and, moreover, a good representation for the process once the block diagram shows the equipments and the signals for each stream within the process. The Fig. 8 shows the SIMULINK model developed in this work.

The block representing the ethanol steam reformer has been creating using an S-function coding, which enables the user to create its own block containing the solver and derivat. Also, the parameters for the model are directly inserted in the simulink model by masking the ethanol steam reformer block. The Fig. 9 shows the window at which the parameters are set up.
The main purpose of the GUI is plot the dynamic behaviour of outlet temperature and hydrogen composition once given the value of the disturbance in one of the inputs, which are inlet feed flow rate, pressure and/or temperature. Also, the number of discretized points can be given by the user depending on the time demand and precision of the results.

The initial conditions are set by the user and after clicking start, the SIMULINK starts the simulation without the user being in its platform.

CONCLUSION

Observing the results obtained in the simulations for each type of disturbances, the dynamic behaviour obtained for the ESR operation has followed the expected behaviour provided by chemical reactions engineering theory.

The steady state simulation have demonstrated that the ethanol is rapidly consumed near at the reactor entrance and the temperature drops down due to endothermic reaction effects, which is reduced some points fairly far from the entrance and the temperature increases due to the heat transfer from the hot gases in the jacket. Also,

Analyzing the dynamic simulation, the after step changes have been done on the inlet conditions the reactor behaviour has matched with what was expected by the theory. Once the inlet temperature is increased, both outlet temperature and hydrogen composition increase due to the Le Chatelier’s law, which endothermic are favored by the increase of the temperature.

Also, if the inlet flow rate is increase by a step change, the outlet temperature and hydrogen composition decrease due to the fact the residence time decrease and the reactants spend less time inside the reactional environment.

The MATLAB Guide User’s Interface can be considered an important step to make the simulation more realistic and suitable for process control analysis, once it can represent a real industrial interface.

The dynamic study for the bioethanol steam reforming reactor is important once it provides the hydrogen for the fuel cell and its operation can be quickly affected due to the fast response front disturbances in the reactor conditions.

The validation of the model has been done using data from other simulations; however, the authors are working on to find experimental data, which is being challenge due to the fact this technology is new.

NOMENCLATURE
\begin{itemize}
  \item $i$: inlet index
  \item $j$: node index
  \item $k$: component index
  \item $r$: reaction index
  \item $f_k$: reaction rate of reaction $k$ (mol/g s)
  \item $k_0$: rate constant of reaction $k$
  \item $K_k$: equilibrium constant of reaction $k$
  \item $K_j$: adsorption constant of component $j$
  \item $y_j$: molar composition of component $j$
  \item $P$: total pressure (Pa)
  \item $F_r$: total molar flow rate (mol/s)
  \item $T$: temperature (K)
  \item $\Delta z$: discretized element of space (m)
  \item $G$: mass flux (kg/m$^2$s)
  \item $L$: reactor length (m)
  \item $D_r$: reactor diameter (m)
  \item $D_p$: catalyst diameter (m)
  \item $U$: overall heat transfer coefficient (W/m$^2$K)
  \item $C_p$: mixture molar heat capacity (J/mol K)
  \item $\Delta H_{R,k}$: reaction heat of reaction $k$ (J/mol)
  \item $A_c$: reactor cross-sectional area (m$^2$
  \item $w_{cat}$: mass of catalyst (g)
  \item $T_a$: Hot Gases Temperature (K)

Greek Symbols
\begin{itemize}
  \item $\mu$: viscosity (Pa.s)
  \item $\Phi$: porosity
  \item $V_{j,k}$: stoichiometric coefficient of component $j$ in reaction $k$
  \item $\rho$: mixture density (kg/m$^3$)
  \item $\rho_c$: catalyst density (kg/m$^3$)
\end{itemize}

REFERENCES


