

Hydrogen production based on bio-ethanol and solar energy for feeding PEM fuel cells

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Abstract—This work focuses on the preliminary study of an integrated hybrid system to produce hydrogen from bio-ethanol using solar energy as an auxiliary power source. It is analyzed for mobile applications, particularly, for a system that can use an on-board bio-ethanol processor. The solar power is used for promoting the reforming reaction for hydrogen production to feed a PEM fuel cell. This new concept increases the fuel economy because it avoids burning a part of bio-ethanol for producing the reforming reaction. A dynamic model of this integrated system with the control structure is presented. It allows to test an energy management strategy (EMS) to best satisfy the power demand of the fuel cell. The simulation results are carried out to illustrate the applicability and effectiveness of this new proposed hybrid system.

I. INTRODUCTION

Alternative renewable energy technologies like solar and bio-fuels are receiving world-wide attention since the internal combustion engines, burning fossil fuels, must be replaced in the next future. Their low efficiency, high emissions that contribute to the global warming and depletion of natural resources have devastating consequences on the environment.

The fuel cell, feeded by hydrogen, represents an excellent alternative because they have higher efficiency with respect to internal combustion engines and its environmental friendliness, since water and heat are the only emissions. Transportation of liquid hydrocarbons is less dangerous and they can be transformed to hydrogen as soon as it is necessary. This represents an important improvement for the global economy, replacing the dependence on fossil fuels. On the other hand, among the Fuel Cells, the Proton Exchange Membrane (PEM-FC) is best suited to the requirements of portability of a mobile system and is capable of working at relatively low temperatures. In this work, an onboard hydrogen rich synthesis gas production from bio-ethanol is proposed. Some considerations taken into account for this proposal are, for instance, that bio-ethanol is one of the best candidates to be the fuel of tomorrow, since it does not have the toxicity of methanol, and a high H/C ratio. Applying an energy balance to bio-ethanol, a positive net value is achieved accounting the relationship between the obtained energy from its combustion respect to that required for its production. Usual methods of converting bio-ethanol

are catalytic partial oxidation and steam reforming. This last one is considered here because high concentrations of hydrogen can be obtained to feed the fuel cell stack

Therefore, in this work, a PEM-FC is chosen because it is capable of working at relatively low temperatures and high autonomy. It is must provide the power, being feeded with hydrogen, produced by reforming bio-ethanol. The PEM-FC requires hydrogen in high purity to work.

However, this kind of process requires external heating to complete the reforming reaction. A previous solution to this need was presented in [1], that was to burn a part of bio-ethanol, in a separate reactor and provide the heat from the obtained gases as it was shown. Here, it is proposed to introduce a solar system to provide power to a Bio-ethanol Processor System (BPS), so the oxidation of fresh ethanol is avoided, resulting in a better fuel economy. Previous works about hydrogen production using solar energy were presented. The hybridization between fuel cells and solar energy has been reported by [3]. They considered a photovoltaic cell as the main source of power, using the remaining power to operate an electrolyzer that produces hydrogen from water. The hydrogen was stored in a pressurized tank and consumed by a fuel cell when extra power is required by a load. Other authors, such as [2] have considered concentrated solar radiation as the energy source of high temperature process heat, to produce hydrogen by steam gasification of carbonaceous materials. Here, a new concept is introduced for hydrogen production and implies a more efficient use of the raw material, combining different renewable energy sources.

The hybrid integrated system proposed here must consider that the solar power depends on environment conditions. This implies that it has a natural variability, which can not be controlled. In addition, in case of automotive applications the power demand varies very sharply due to which it is necessary to include an energy storage system, such as batteries. In this context, an Energy Management Strategy (EMS) is required to tightly integrate the power systems, in order to cover the demands of the energy loads. The EMS is formulated as an algorithm able to handle at each sampling time which must be the source for power generation to fulfill the load requirements. A PhotoVoltaic (PV) cell can provide its maximum power depending on its architecture, but also on the temperature and insolation profile. In certain cases, the solar power that can be provided is null, or extremely low (at night or cloudy days). So, the ethanol burner must be present to generate the enough energy to produce the reforming reaction when the solar energy source

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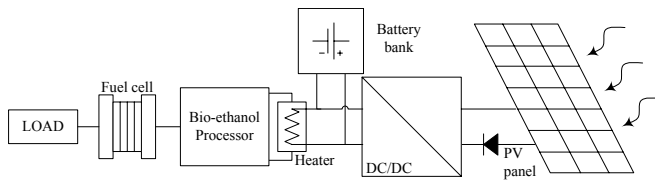


Fig. 1. Hybrid energy generation system

is not available. Besides, unexpected drops in the PV energy productions may occur, or demand increase of the BPS may surpass the availability of power. Therefore, quick start units are required to cover the energy lags or shortfalls.

In this scenario, to begin studying the proposed hybrid power generation system, a complete nonlinear dynamic model of the process is developed. The fuel processor is implemented through the use of a specific communication protocol between HYSYS and MATLAB. The reactors included in the bio-ethanol processor are modeled dynamically in the MATLAB environment as well as the solar power source. On the other hand, side reactions and by-products are considered in the reaction pathway. Since the anode of the fuel cell is sensitive to carbon monoxide, the hydrogen rich synthesis gas production must be done to ensure less than 10 ppm of CO to avoid catalyst poisoning.

The multivariable control of the BPS with PEMFC system is addressed by applying the emerging and well tested procedure named “minimum squared deviations (MSD)” strategy presented in [4].

In this work, the EMS is further explained in section IV. Mainly it is based on a series of operation modes oriented to improve the overall process efficiency.

Finally, a set of computer simulations shows preliminary results of the integrated system for variable load requirements. It allows to evaluate the potentiality of the proposed EMS using a complex hybrid nonlinear model.

II. SYSTEM DESCRIPTION

The modeling of the integrated energy generation and Bio-ethanol processor system is introduced in this section. The topology of the hybrid system under consideration in this paper is depicted in Fig. 1.

The solar module comprises several photovoltaic panels connected to the dc bus via a dc/dc converter which commands the current drained from the panel. The operation point of the PV cell and, consequently, its power generation are indirectly controlled by the panel. The dc bus collects the energy generated and delivers it to the fuel processor and, if necessary, to the battery bank. Its voltage is imposed by the battery bank which comprises lead-acid batteries connected in a series/parallel array. The lead-acid battery bank may be modeled as a voltage source connected in series with a resistance and a capacitance. For the models of the PV energy, the work presented by [8] is taken into account.

A. Bio-ethanol processor system

The Fuel Processor System (illustrated in Fig. 2) consists of a Bio-Ethanol Steam Reforming (ESR) plug flow reactor,

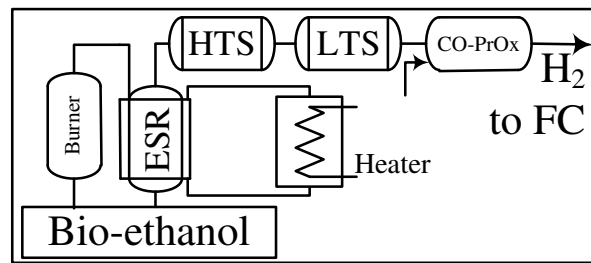
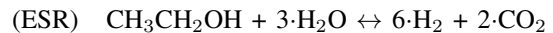


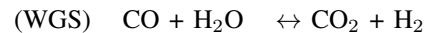
Fig. 2. Bio-ethanol processor system

where most of the conversion of ethanol to H_2 is made. Carbon monoxide, which poisons the fuel cell catalyst is produced in the ESR, so additional processing is needed to remove this substance. There are three reactors that configure the cleaning system; these are two Water Gas Shift (WGS), one of high temperature (fast) and the other of low temperature, that favors the equilibrium of the reaction to higher conversion rates of CO. The third is a Preferential Oxidation of Carbon monoxide (CO-PrOx) reactor, where oxidation of CO into CO_2 is made; also, the undesired oxidation of H_2 occurs, so the catalyst is selected to improve the conversion of CO.

Ethanol and vaporized water are mixed and then supplied to the ESR reactor, to produce ethanol decomposition:



The overall reaction is endothermic, and heat requirement, when solar power is not enough, is supplied by a burner, which is fed with ethanol and compressed air. The transfer of heat is achieved passing the hot gases through the jacket of the reformer. The produced reaction inside the WGS is:



This reaction produces heat and creates more hydrogen. Levels of CO are still high even after the two WGS reactors, so the final elimination is made in the CO-PrOx reactor, which produces the oxidation of CO. The WGS reaction takes place in this reactor too. Air is injected into the CO-PrOx to provide oxygen, the amount needed is about twice the stoichiometric relation to have a good selectivity and satisfy the requirements of the FC.

The plug flow reactors are modeled as 20 lined-up Continuous Stirred Tank Reactors (CSTR). The molar flow between two volumes is given by the orifice flow equation as a function of upstream pressure, and downstream pressure. Further details on the dynamic modeling, process constraints and normal behavior can be seen in [6].

B. Proton Exchange Membrane Fuel Cell

Proton exchange membrane fuel cells convert chemical energy directly into electrical energy. They are constituted by an anode, where the H_2 is injected, and a cathode, where the oxidant, normally air is injected. The electrodes are separated by a polymeric membrane that allows the proton exchange when it is properly humidified, but it is an excellent insulator

of electrons. Each cell generates an open-circuit voltage which is affected by a number of losses (activation, concentration and ohmic) that leads to a useful actual voltage. Transient behavior of manifold filling, membrane hydration, the air compressor and the heat management are included in the model. Interaction between processes are also included.

C. Photovoltaic cells

The electric energy generated by a PV cell depends on several parameters, mainly the effective area, determined by its configuration, and on variable environmental conditions such as insolation and temperature. This atmospheric conditions affects significantly the performance of the PV cells. Its electric behavior can be modeled by a nonlinear current source connected in series with the intrinsic cell series resistance. The current provided by this equivalent nonlinear source depends mainly on the actual insolation and the temperature because the reverse saturation current and the photocurrent depends on these atmospheric conditions. For example, according to a PV cell array presented in [9], the current provided for an insolation of 100 mW/cm² and a temperature of 25°C is 3.25 A. The mathematical description of the solar subsystem is the following:

$$\begin{aligned} \dot{v}_{PV} &= \frac{i_{PV}}{C} - \frac{i_O}{C}u \\ \dot{i}_O &= -\frac{v_b}{L} + \frac{v_{PV}}{L}u \\ i_{PV} &= n_p I_{ph} - n_p I_{rs} \left(\exp \left(\frac{q(v_{PV} + i_{PV} R_s)}{n_s A_c K T} \right) - 1 \right) \end{aligned}$$

where v_{PV} is the voltage level on the PV panel array terminals, i_O is the current injected into the dc bus, C and L are electrical parameters of the dc/dc converter, u is the control signal (duty cycle), i_{PV} is the current generated by the PV array, v_b is the voltage on the battery bank terminals, n_s is the number of PV cells connected in series, n_p is the number of series strings in parallel, K is the Boltzman constant, A_c is the cell deviation from the ideal p-n junction characteristic, q is the charge of an electron, I_{ph} is the photocurrent, I_{rs} is the reverse saturation current, and T is the temperature. The current from the photovoltaic subsystem is controlled in such a way that the optimal power for the environmental conditions is obtained when it is required, or otherwise if it is operating in power tracking mode.

D. Computational Model Implementation

The pressure requirements are satisfied with compressors and turbines modeled in HYSYS. Besides, it supports the important data bank information for the different components. In addition, the LNG tool in HYSYS, that solves material and heat balances for multi-stream exchangers and heat exchangers networks. On the other hand, the dynamic model of the reactors is developed in MATLAB, which integrates the differential equations. The communication interface is performed by the use of the spreadsheets in HYSYS and a specific library for doing the corresponding data transference and updating at scheduled sampling time between both programs.

E. Heat Integration

The heat integration in the model is performed by the LNG tool working in a pseudo dynamic mode. It is called by MATLAB for determining the instantaneous temperature values of the different cold and hot streams of the process. Therefore, it is assumed that the dynamic effect of the heat exchangers network is neglected. The minimum heat requirement of the system and the minimum heat to be evacuated can be computed for each operating point or with the system under different disturbances.

III. CONTROL STRUCTURE OF THE BPS

The main objectives of the BPS control are to maintain the H₂ level on the anode of the FC, because starvation can cause permanent damage, and overfeeding will lead to hydrogen waste. On the other hand, the CO level of the anode inlet stream must be low, and the temperatures of the reactors set and FC must be controlled to prevent damages and maintain the system efficiency.

A systematic and generalized procedure is applied to simultaneously solve the Optimal Sensor Location (OSL) and Control Structure Design (CSD) problems. The solution to these problems generates a control structure and a sensors network with the least amount of devices (hardware), minimizing the potential sources of process faults. In this work a brief analysis is presented, extended and unified from the proposals of [4].

In this section the generalized procedure for plant-wide control, called minimum square deviation (MSD), is presented. A direct connection with process synthesis area is assumed, which allows information feedback for future plant redesigns. Simultaneously, control objectives partially defined by this area can be incorporated effectively within the procedure.

The MSD methodology can be split in three groups acting sequentially:

- 1) Optimization and stabilization: In this stage, the operating point optimization from the original process is made (if necessary) considering, for instance, operational costs minimization. Simultaneously, it defines active constraints and minimal number of loops to guarantee process stability.
- 2) OSL: According to the availability of degrees of freedom from the previous stage, the OSL is executed using as evaluation index the sum of square deviations. In this manner, the controlled variables of the plant are defined (sensor location).
- 3) CSD: In this stage the control structure is determined according to the controlled variables defined previously. In this case the approach is different if dynamic information is available. The structure defined by the relative normalized gain array (RNGA) is preferred.

The first step for designing the control structure is the full plant stabilization. In this case, the primary control loops needed to stabilize the process are the pressure control of each reactor (ESR, HTS, LTS, CO-PrOx) by manipulating

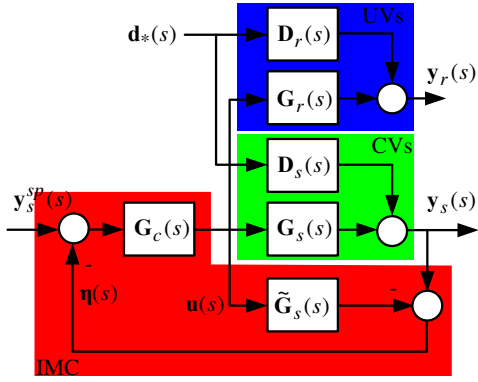


Fig. 3. Generalized IMC Structure

their corresponding exit flow, and the H_2 production to feed the anode of the fuel cell stack, determined by the current demand, with the fresh ethanol flow entering to the bioethanol steam reforming.

In accordance with the MSD strategy, and the process already stabilized, the next step is the System Identification (SI) stage. This procedure allows to obtain both a steady-state and dynamic linear models of the process for control design purposes. A model with fourteen outputs, six potential manipulated inputs and two disturbances inputs was identified. Any SI technique is useful to carry out the linearization. The SI experiment is based on exciting the inputs of the process with rich signals and collect the output data periodically with a suitable sample time, T_s . The inputs signals are selected as random steps whose amplitudes varying between $\pm 5\%$ (wide-range of linearization) from their nominal values and a period of 5 seconds (the steady-state is reached). The sample time is fixed to $T_s = 0.05$ s, this allows to collect about 100 samples per step change.

Basically, all the subspace state-space System Identification methods are based on system theory, numerical linear algebra and projections tools. The recorded data base is pre-processed by normalization to zero mean and unit variance for all variables before starting the SI procedure.

The data base obtained from the SI experiment was divided into two groups. One called the estimation data to develop the space-state linear model, and the second one called the validation data to test the accuracy of the model predictions. The order of the model was chosen according to a trade-off between the model size (amount of state) and the mean square prediction error. A very good approximation (either for stationary states and transients) is achieved with the reduced order model.

After the stabilization process the potential sensors location are 14 and the available manipulated variables are 6, then $14 - 6 = 8$ degrees of freedom exist. For analyzing which would be the best configuration it is very useful to adopt a full multivariable controller based on the internal model control (IMC) theory. It can be implemented as shown in Fig. 3, where, $G_s(s)$ is a transfer function matrix (TFM) containing the controlled variables (CVs) of the process

and $G_r(s)$ is a TFM representing the uncontrolled variables (UVs). Similarly, $D_s(s)$ and $D_r(s)$ represent the disturbance models for each part of the process. $G_c(s)$ represents the IMC controller designed based on the process model $\tilde{G}_s(s)$. The optimal selection of $G_s(s)$ (OSL), can be made by considering the Steady State (SS) ($s = 0$) error in the UVs when perfect control is supposed and both set points and disturbances changes are considered individually. Thus, the process outputs of UVs can be represented as

$$y_r = S_{sp}y_s^{sp} + S_d d_* \quad (1)$$

with $S_{sp} = G_r G_s^{-1}$ and $S_d = D_r - G_r G_s^{-1} D_s$. From (1) can be observed that the SS error only depends on the selected subprocess G_s . The SSD index can be stated as

$$\begin{aligned} SSD_{y_r} &= \sum_{i=1}^n \|e_{sp}(i)\|_2^2 + \sum_{j=1}^p \|e_d(j)\|_2^2 \\ &= \|\Lambda_2 S_{sp} \Lambda_1\|_F^2 + \|\Theta_2 S_d \Theta_1\|_F^2 \end{aligned}$$

where $e_{sp}(i)$ and $e_d(j)$ are the vector of deviations corresponding to the y_r outputs from their nominal operating point values when an unitary change happens in the i set point and j disturbance respectively. The vectors $y_{sp}^n(i)$ and $d_*(i)$ have an unitary entry at the location i and zero elsewhere. The diagonal weighing matrices Λ_1 , Λ_2 , Θ_1 and Θ_2 allow to include the process control objectives such as set point/disturbance magnitudes and the relative degree of importance among the overall outputs. Thus, the final problem can be stated as is shown in (2).

$$\min_{G_s} SSD_{y_r} \quad \text{subject to} \quad \det(G_s) \neq 0 \quad (2)$$

The OSL problem can be represented by a combinatorial one where the total amount of combination is $14!/(6!(14-6)!) = 3003$. In this case an exhaustive search can be implemented without computational problems. When the dimensionality grows some optimization/search tool is required, i.e. genetic algorithms. Therefore the best sensor location can be found. The solution suggests that the controlled variables should be the following ones,

- y_1 : ESR exit temperature
- y_2 : Burner exit temperature
- y_3 : CO-PrOx exit temperature
- y_4 : CO-PrOx molar ratio O_2/CO
- y_5 : Burner exit molar flow
- y_6 : Oxygen excess in the FC

In this context, to propose a decentralized plant-wide control policy, the RGA approach is accounted. The RGA allows to define the input-output pairing by using steady-state tools. In fact, accounting the OSL proposed earlier and the steady-state gains of the process from the SI the square process can be obtained. A suitable decentralized input-output pairing is obtained with the control loops shown in table I. The proposed control loops are implemented via unitary output feedback with PI (proportional/integral) structure.

TABLE I
VARIABLES PAIRING

| Controlled variable | Manipulated variable |
|---------------------|--------------------------|
| y_1 | Water to ESR inlet |
| y_2 | Exchanged heat |
| y_3 | Ethanol to burner |
| y_4 | Oxygen to burner |
| y_5 | Oxygen to CO-PrOx |
| y_6 | Compressor motor voltage |

IV. ENERGY MANAGEMENT STRATEGY

The capability of the hybrid electric generator system to satisfy the power demand depends on the atmospheric conditions. Such conditions and the role of the battery bank (either storing or supplying energy) will define different operation modes of the system. In a previous work the EMS for bio-ethanol processor system working onboard was presented at [5]. Basically, these operation modes are determined by the energy balance between the generation (solar and braking) and the total demand (load demand plus the required power to recharge the battery bank). A comprehensive energy management strategy is essential to efficiently manage the operation of the generation subsystems according to those modes. The three possible modes of generation here proposed are as follows.

- 1) When the minimal solar power production exceeds the load demand, the photovoltaic system operates at minimum power to satisfy the demand and recharge the battery with the remaining energy. If the maximum voltage for the battery is reached, the solar power is completely disconnected from the load, using only the draining of the storage system to satisfy the load demand. When the total power demand exceeds the minimum solar power, the control switches to Mode 2.
- 2) The solar subsystem is set for tracking the power reference. In modes 1 and 2, the battery bank demands the recharge current (I_{breq}) and it becomes part of the total demand. If the total power demand exceeds the maximum available generation of the photovoltaic array system, the operation is switched to mode 3.
- 3) The solar subsystem operates at maximum energy conversion point. To fully satisfy the load demand, the battery bank needs to revert its current flow, acting as power supplier depleting its stored energy. If the minimum voltage of the battery is reached, the burner reactor enters in operation, supplying the remaining heat, allowing the ESS to recharge, when it is possible.

To summarize, the energy management strategy is responsible of switching from one operation mode to another depending on the atmospheric conditions, the load demand, and the battery charge. Moreover, it is in charge of setting the reference values of the generation module and the battery current for each mode of operation.

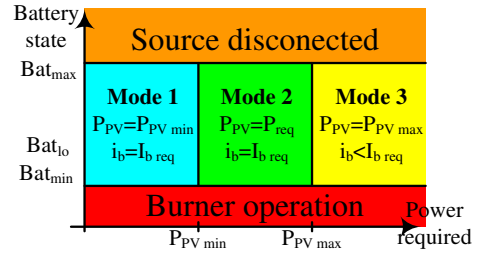


Fig. 4. Energy Management Strategy

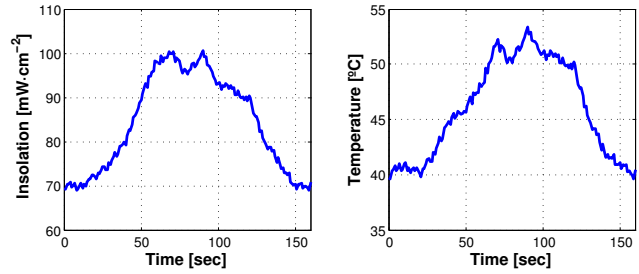


Fig. 5. Insolation and temperature profiles

A schematic description of the operation strategy is depicted in Fig. 4. Note that operation can be maintained as long as the energy available in the entire system is sufficient to satisfy the load requirements. Modes 1 and 2 take place under insolation regimes sufficient to supply the total power demand. On the other hand, under insufficient insolation regime, such as for mode 3, the PV controller tracks the maximum power operating point so that the system keeps the stored energy as much as possible.

V. SIMULATION RESULTS

The tests are done on the complete dynamic model system implemented in Matlab/simulink and HYSYS. Some assumptions have been taken into account: the current from the photovoltaic subsystem is controlled in such a way that the optimal power for the environmental conditions is obtained when it is required, or otherwise if it is operating in power tracking mode; the voltage of the DC bus is regulated in a constant voltage of 48 V; no losses are considered in the power converters and batteries; in the fuel processor, the pressures are perfectly controlled, and the heat integration is considered optimal.

The maximum power available depends on the temperature of the photovoltaic cell and the insolation provided by the sun, as described in section II-C. The considered profiles for this uncontrolled variables (considered as input disturbances) are presented in Fig. 5. Both seem to be similar because there is a direct relationship between them.

The results obtained from the simulation can be seen in Fig. 6. It shows the power required to fulfill the thermal conditions of the ESR, supplied by the PV cell. The heat required is the thermal necessity of the main reactor to keep the reaction efficiency and the equilibrium balance in favor of the products. The power from the solar subsystem is always

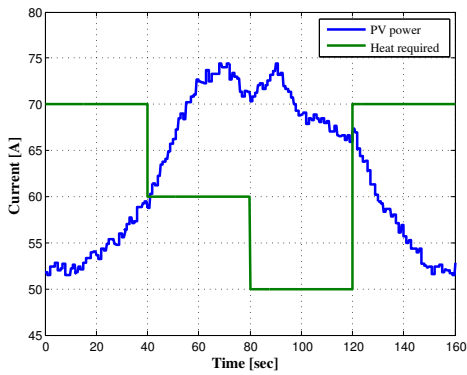


Fig. 6. Energy distribution

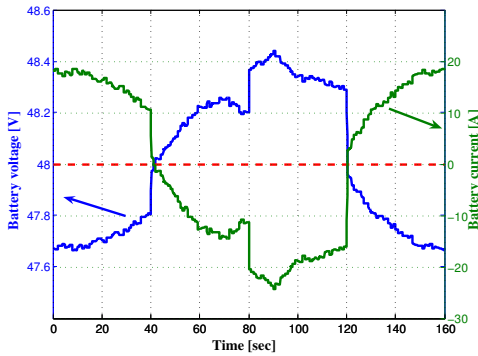


Fig. 7. Energy distribution

at a maximum, as determined by the management strategy. The power obtained from the PV array (directly determined by the sun conditions) is initially insufficient to fulfill the demand, requiring energy from the batteries. Then a sudden decrease in the load requires the solar cells to produce the maximum available for recharging the ESS. In the final part of the simulation the demand rises again over the maximum solar power available, depleting the charge from the batteries.

The Fig. 7 presents the state of the battery along the simulation. On the left axis is the voltage of the battery, which is related to the state of charge. The right axis shows the recharge (or discharge) current.

Under this configuration, the efficiency of the BPS based on the lower heating value of ethanol reaches 0.42 at the rated power of the FC. Such efficiency is the quotient between the obtained power from the FC and the enthalpy of the ethanol consumed. According to the assumptions adopted here, the BPS is working in the highest efficiency, so this determines a maximum bound for a real system. On the other hand, the net power obtained is nearly three times the power demanded to the solar+battery subsystem. The amount of hydrogen that can be obtained is 0.104 mole/sec consuming 0.02 mole/sec of ethanol, and demanding 3.19 kW for finish the reforming reaction. Considering this maximum efficiency operation, the result can be extrapolated for an entire hour. In this case, the plant will consume 72 moles of bio-ethanol, when the solar power is sufficient to fulfill the energy requirement of the ESR. Otherwise, if there is no solar power available and

the battery is depleted, then the burner reactor must supply the heat. In this case, the total consumption of ethanol rises to 85 moles under the same working conditions. In other words, the rate between the produced H_2 to the consumed bio-ethanol is 5.2 using PV and drastically reduced to 4.4 without solar energy.

VI. CONCLUSIONS AND FUTURE WORKS

A novel integrated system for obtaining power from bio-ethanol and solar energy sources was presented. A fuel processor reforms the ethanol to H_2 rich synthesis gas, and feeds a fuel cell, which converts the energy vector into useful power. The heat required by the plant is provided by electrical heating, through the operation of photovoltaic arrays. The efficiency of the system is significantly improved, in terms of hydrogen production to ethanol consumption. It is achieved since it is avoided to burn a part of the ethanol to fulfill the thermal requirements and accounting the power needed by the main reaction with solar power.

The new topology works properly and the energy management strategy is capable of keeping up to the requirements of the system, switching between energy sources, or using the battery when it is required. The power distribution maintains the subsystems operating in good efficiency zones, and keeps the battery charge in a safety zone. These preliminary results are very motivated to continue analyzing future works. They will include the inspection of new techniques for EMS and the development of a supervisory control designed for the plant-wide problem.

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