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Novel Biomass Upgrading Plant as a Renewable Source of Added-Value Chemicals

Tingxu Wang, Nouaamane Kezibri, Chakib Bouallou*

MINES ParisTech, PSL Research University, Centre for Energy Efficiency of Systems, 60 bd Saint Michel, Paris, France
chakib.bouallou@mines-paristech.fr

Global warming and energy crisis are the main issues humanity has to deal with in the forthcoming years. Biomass technology offers a suitable solution for energy production and can make significant greenhouse gas emissions savings compared to fossil fuels. However, further improvement regarding the decrease of CO_2 emissions to make full use of biogas can be achieved by converting the CO_2 contained in the biogas into bio-chemicals rather than being simply discharged into the atmosphere.

The aim of this work is to analyze the performance of a novel process for CO_2 and CO conversion into acetic acid (AA). Firstly, the biogas converts into bio-syngas through reforming and Water Gas Shift (WGS) steps with controlled H_2-to-CO_x ratio. From there, several applications can be taken under consideration as syngas is among the most widely used primary materials in the chemical industry. The main concept will provide a syngas with H_2-to-CO ratios well above the ones required for the AA synthesis. Excess hydrogen is used to provide energy to the system using a hydrogen-fueled SOFC (*Solid Oxide Fuel Cell*) coupled with heat recovery from exhaust air at the cathode to provide the necessary heat to the reformer. Thus, resulting in a self-sustainable system. Aspen Plus™ was used to create a steady state model of the global process. Afterwards, a parametric study was carried out to investigate the effects of some operating conditions on the overall performance. Effects of fuel utilization factor and current density on the SOFC performance were also evaluated.

1. Introduction

Biogas production through anaerobic digestion (AD) is an environmental friendly process utilizing the increasing amounts of organic, including industrial and municipal waste waters, agricultural, municipal, and food industrial wastes, as well as plant residues. However, because of the high concentration of CO_2 and other impurities, the efficiency of direct combustion is lower than conventional natural gas. It is an unreasonable method for using biogas resource and cleaner alternatives need to be found to improve biogas technology.

Biogas is a renewable energy with different components mainly CO_2 (20 - 44 %), CH_4 (50 - 75 %) and a small amount of H_2O, H_2S, NH_3. The latter can cause corrosion, toxicity, catalyst deactivation and reduction of heating value. To prevent damaging the units it is necessary to remove H_2S and NH_3 from the biogas. Purification of biogas by water scrubbing has the advantage of non-pollution and low cost, it has become a commonly used method in large and medium-sized biogas projects (Niesner et al., 2013).

Hydrogen demand is witnessing steady growth due to commercial processes such as oil refining, space transportation, chemical materials, etc. This increasing demand is a strong incentive to evaluate more H_2 generation technologies (Aboosadi et al., 2011). Methane steam reforming is the main industrial way to produce hydrogen rich syngas which is a mixture of H_2, CO and CO_2 (Ye et al., 2009). In recent years, about 50 % of H_2 is generated by methane-steam reforming and WGS reaction (Er-rbib et al., 2012).

On the other hand, Acetic acid is widely generated by chemical processes, such as Acetaldehyde oxidation, Ethylene oxidation, Oxidation fermentation and Methanol carbonylation. Bacteria catalytic acetic acid production has several advantages over conventional processes: lower energy required, greater resistance to poisoning and less pollutants emission in the process (Klasson et al., 1992). Most acetogenic bacteria can produce acetic acid directly from CO and H_2O but there is also known ways to generate acetic acid from CO or CO_2 with H_2 (Sim et al., 2007).

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The fuel cell (FC) is a promising technology. There are many types of FCs depending on the input fuel, electrolyte and oxidant. More and more attention is paid to solid oxide fuel cell (SOFC) among FCs. SOFC operating temperature is between 700 - 900°C. Additionally, syngas can be used to fuel the SOFC (Eguchi et al., 2012). Another advantage is the tolerance to CO. Carbon monoxide is poisonous for other FCs, such as Alkaline FC (AFC), Phosphoric Acid FC (PAFC) and Molten Carbonate FC (MCFC).

The aim of this paper is to evaluate a novel process layout converting CO_2 and CO into added-value chemicals and optimize operating parameters for each its component. The main idea behind this process is to convert Biogas to acetic acid and use a SOFC module to generate heat and power to achieve a self-sustaining system. The model which is developed using the commercial software Aspen Plus (AspenTech, 2018), sets the proper parameters and improves the process through sensitivity analysis. The effects of water flow rate, operating temperature and pressure, current density and fuel utilization factor are all considered influencing parameters.

2. Simulation methodology

Aspen Plus V8.8 software is used to simulate the processes. For biogas water scrubbing, absorption and stripping columns are modeled as Radfrac distillation blocks using nonrandom two-liquid (NRTL) property method. RadFrac is a rigorous model for simulating vapor-liquid fractionation. The Gibbs model is applied for simulating the steam reforming reactor. The REquil model is employed to simulate the WGS (Giwa et al., 2014). This model is used if reaction equations are known and thermodynamic equilibrium is reached. The syngas which is generated by steam reforming and WGS will produce acetic acid by bacterial catalytic reaction. Acetic acid generation is simulated by stoichiometry model.

SOFC module is not included in the Aspen Plus software. Aspen Custom Model (ACM) is used for coding SOFC model which is then imported to Aspen Plus environment. The final SOFC system is shown in Figure1.

The aim of this numerical approach is to find out the optimal parameters for each of the modeled units. Table 1 shows the specifications of Biogas used as input material. Sensitivity analysis is used to investigate the impact of some parameters, such as operating temperature, pressure, the water flow rate, current density and the fuel utilization factor of SOFC.

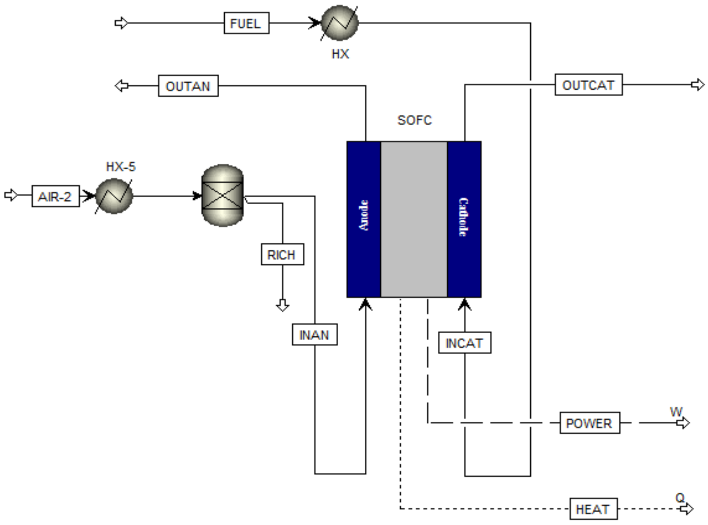


Figure 1: SOFC custom model imported to Aspen Plus environment

Table 1: Biogas used in the conversion process

Inlet Biogas specifications	
Temperature	25°C
Pressure	1 atm
Flow rate	20 kg/h
CH_4	57 %
CO_2	38 %
H_2O	4 %
H_2S	0.56 %
NH_3	0.44 %

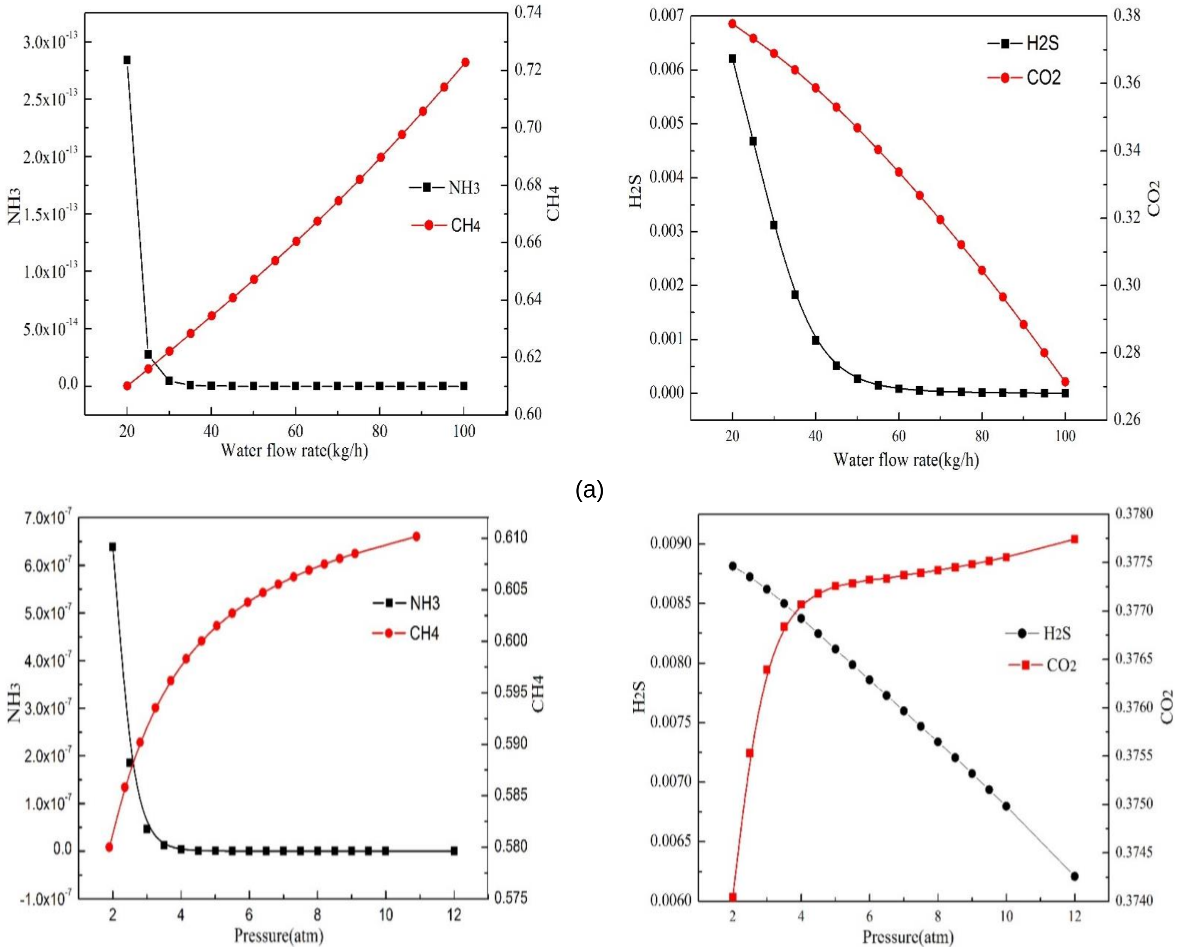
3. Results and discussion

3.1 Water pressure scrubbing

Feed biogas includes 0.91 % H_2S and 0.04 % NH_3 which should be removed before any further operation. Figure 2(a) shows the effects of water flow rate over H_2S, NH_3, CO_2 and CH_4 in the clean gas leaving the absorption column. It can be seen that pressure water scrubbing can be an effective measure to remove H_2S and NH_3 as their respective concentrations decrease rapidly compared to CH_4.

There is no NH_3 in the clean gas when the water flow rate is beyond 40 kg/h, and there is no significant decrease in H_2S concentration when the water flow rate is beyond 55 kg/h. At a water flow rate of 55 kg/h, H_2S concentration is below 10^{-3}. The higher the water flow rate, the more diluted gas are lost in water as shown in Figure 2(a). Therefore, the optimal water flow rate is about 50 kg/h.

Recovery of CO_2 is lower as it is more soluble in water than CH_4; CO_2 is not fully recovered in the intermediate flash vessel resulting in its loss. Figure 2(b) shows the effect of pressure over H_2S, NH_3, CO_2 and CH_4 in the clean gas leaving the absorption column. The H_2S solubility changes slightly so that higher pressure absorption column is required. Operating cost of the process is associated with power required for compression and make up of water lost in stripping column.



(a)

(b)

Figure 2: Biogas components concentration in the clean gas leaving water pressure scrubbing unit as a function of: (a) Water flow rate (kg/h), (b) Pressure (atm)

3.2 Synthesis gas production

Synthesis gas (syngas) which is the mixture of H_2 and CO can be precursor of long chain hydrocarbon production, such as Fischer-Tropsch process and syngas fermentation (Yang et al., 2014). The steam reforming and water gas shift are simulated using Aspen Plus tool. As can be noticed from the Figure 3(a), the mole fractions of methane, carbon dioxide and water present in the product decrease with the increase in reactor's temperature, while those of carbon monoxide and hydrogen increase with the increase in temperature. It can be observed that the more temperature of is increased, the more carbon monoxide is formed. This result means that increasing temperature favors the reforming reaction. From Figure 3(b), it can be observed that the mole fractions of water and carbon dioxide increase with increase in the feed water flow rate while that of methane is found to decrease. Additionally, as can be seen from these results, the mole fractions of hydrogen increased at first and decreased later with increasing in the volumetric flow rate of feed water.

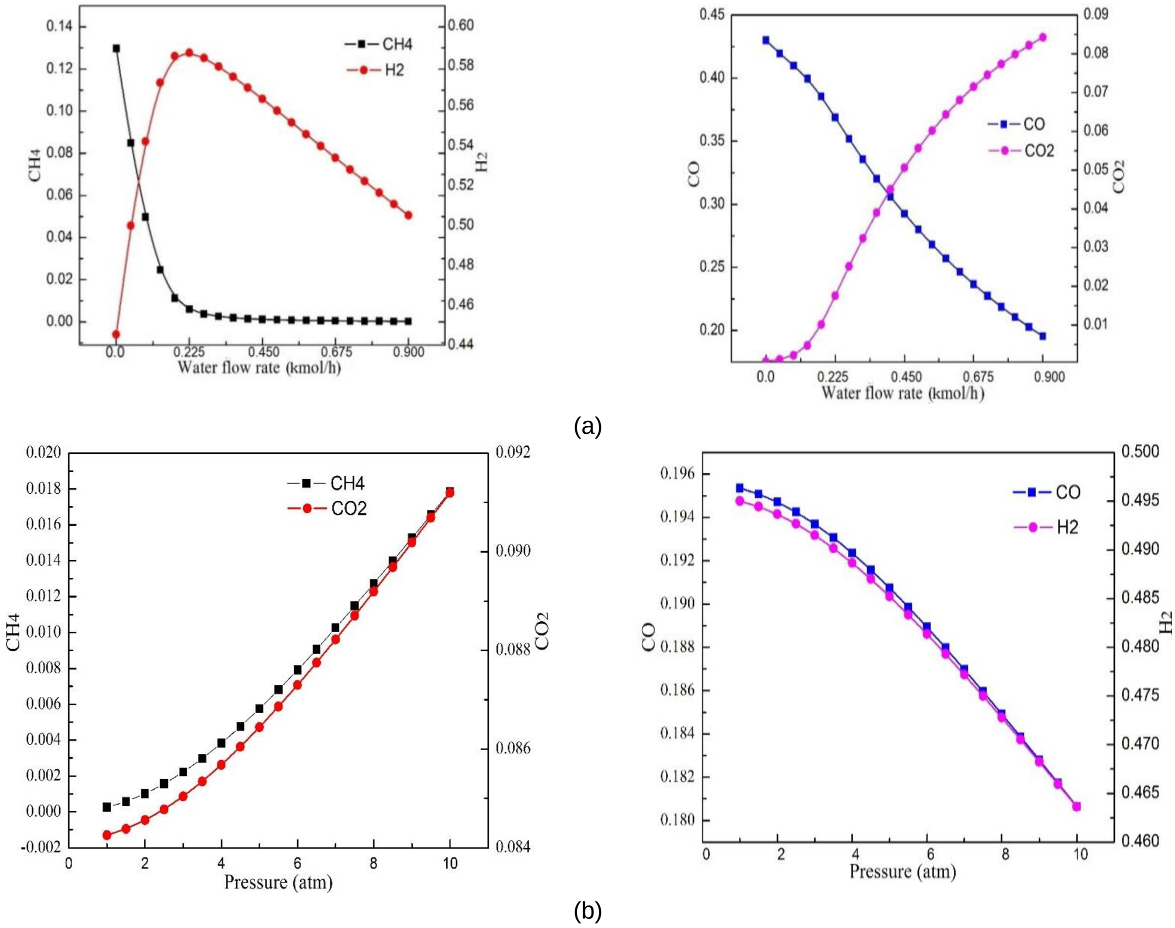
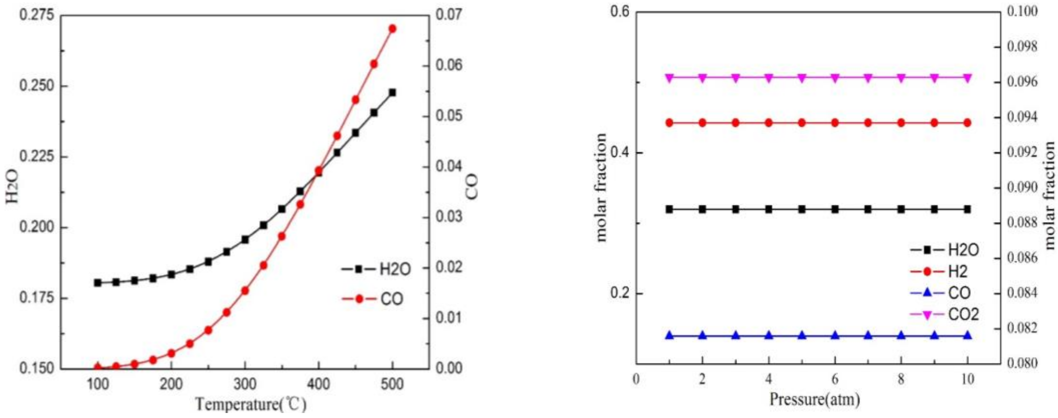


Figure 3: Biogas components concentration in the gas leaving steam reforming process unit at 740°C as a function of: (a) Water flow rate (kg/h), (b) Pressure (atm)

For the initial simulation of the WGS process, reaction temperature is set at 220°C while pressure is set to 1 atm. The low temperature WGS (LWGS) reactor follows the steam reformer. LWGS is used for further converting carbon monoxide into hydrogen. The reaction (1) occurring in the reactor is given by:

$$CO+H_2O \leftrightarrow CO_2+H_2 \qquad (1)$$

From the figure 4(a), it is observed that the mole fraction of CO increases meanwhile those of the products (hydrogen and carbon dioxide) decrease with the increase in reaction temperature. The simulation results have also revealed that low temperature is favorable to high conversion of the reactants in this process. According to Figure 4(b), mole fractions of the components are unchanged as the pressure is varied from 1 to 10 atm. There is no apparent influence on the reaction equilibrium when the pressure changes.



(a) (b)

Figure 4: Product composition as a function of (a) reactor temperature, (b) reactor pressure

3.3 Acetic acid production

Acetic acid can be produced by several anaerobic bacteria from H_2, CO_2 and CO, which produced from synthesis gas components. Several Bacteria can be used such as, Peptostreptococcus productus, Acetobacterium woodii, Clostridium thermoaceticum and Eubacterium woodii (Barik et al., 1987), which produce acetate following the reactions Eq(2) - Eq(4). Reactor's operating temperature and pressure are 25 °C and 1 atm, for the purpose of maintaining microbial catalytic activity.

The components of products from acetic acid reactor are $C_2H_4O_2$, H_2O and CO_2. Acetic acid is a colorless liquid and a widely used chemical raw material. Ordinary distillation method is mature, making it a simple process for separating acetic acid and water.

$$2CO+H_2 \rightarrow C_2H_4O_2 \qquad (2)$$

$$2CO_2+4H_2 \rightarrow C_2H_4O_2+H_2O \qquad (3)$$

$$4CO+2H_2O \rightarrow C_2H_4O_2+CO_2 \qquad (4)$$

The relationship between the minimum required reflux ratio and the number of theoretical stages is obtained by simply separating the DSTWU module from the simulated purity of 99.9 % (mass fraction). When reflux ratio is at a minimum value of 2.0, this later has less impact on reducing the number of plates. The number of theoretical stages is set to 44 when reflux ratio is 1.6. When the minimum number of stages is 18, the reflux ratio increment has less influence on significantly reducing the stages.

3.4 Hydrogen-fueled Solid Oxide Fuel Cell

The chemical reactions at cathode and anode sides as well as the overall reaction are given as follows:

$$O_2+4e^- \rightarrow 2O^{2-} \qquad (5)$$

$$H_2+ O^{2-} \rightarrow H_2O+2e^- \qquad (6)$$

$$H_2 + 0.5O_2 \rightarrow H_2O \quad -285.8 \text{ kJ/mol} \qquad (7)$$

With an increase of current density from 1,000 to 6,000 A/m^2, the ohmic, concentration and activation overpotentials are increased, so that the voltage of fuel cell is decreased. From Figure 5a, the fuel cell voltage is decreased from 0.8414 to 0.1334 V rapidly. The efficiency increase firstly and then decreases, the efficiency of fuel cell increases with current density increasing from 1,000 to 3,600 A/m^2 and it begins to decrease when current density increases from 3,600 to 6,000 A/m^2. There is a peak when the current density is up to 3,600 A/m^2. Actually, the current density cannot be up to 6,000 A/m^2 to make sure higher efficiency (Bo et al., 2009). Figure 5b shows effects on current density, cell potential and fuel efficiency. As the anode and cathode inlet gas composition does not change, under the assumption of same SOFC stack active surface, the current density is linear to U_f . It will reinforce the polarization of the fuel cell if the current density increases. The increase of U_f leads to the decrease of the hydrogen partial pressure and the increase of the steam partial pressure, which reduces the Nernst voltage. The actual voltage decreases as U_f increases due to the overpotential losses.

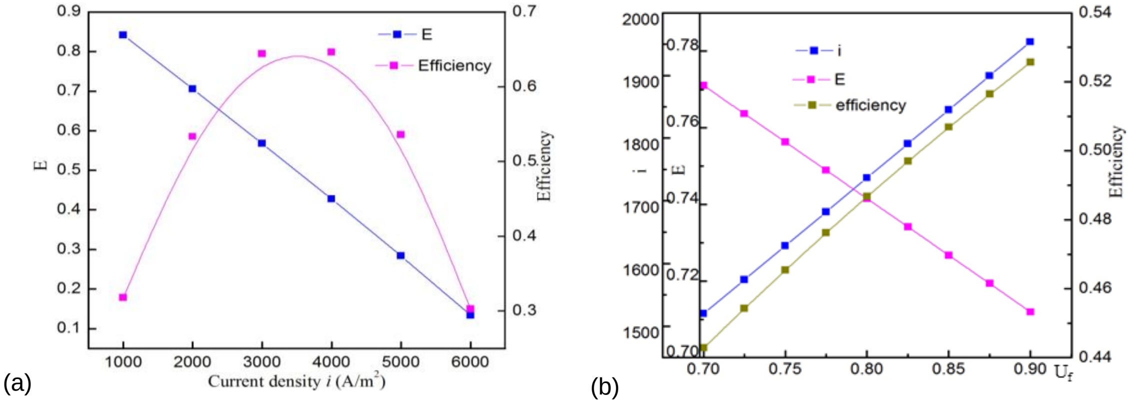


Figure 5: (a) Effects of current density (A/m^2) on cell potential and efficiency. (b) Effects of fuel utilization factor (U_f) on current density, cell potential and efficiency.

4. Conclusions

Instead of using Biogas are a mean to generate heat or energy for an industrial plant, it is preferred to convert it into chemical products. In this study, a simulation flow sheet has been developed for biogas conversion using Aspen Plus, developing the simulation model for each component of biogas conversion processes and handling the relationship among the different units. In the proposed concept, biogas will be cleaned firstly by the water pressure scrubbing process, then, the purified gas is reformed with steam to produce bio-syngas using a catalytic reforming reactor. To generate more hydrogen, the lower temperature water gas shift reactor is used after reforming step. H_2, CO_2 and CO will convert into acetic acid in the final step. Solid oxide fuel cells (SOFCs) are used for simultaneous power and heat generation. For this case, the novel processes are technically feasible, the optimal reaction temperature, pressure and water flow rate are respectively 740 °C, 1atm and 2.04 kmol/h in the reforming process. The SOFC model efficiency can reach to 64 % electrical efficiency when a current density of 3,600 A/m^2 is applied and with operating temperature of 900°C under atmospheric pressure.

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