

Valorization of CO₂ Emissions into Ethanol by an Innovative Process

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This study aims at assessing the possibility to produce value-added fuels from carbon dioxide (CO₂) and non-fossil hydrogen (H₂). Ethanol synthesis is an economically attractive route for CO₂ recycling. The proposed process includes three phases: [1] hydrogen generation by solar water splitting in the photo-electrocatalytic cells (PEC), [2] conversion of CO₂ to carbon monoxide (CO) by the reverse water-gas shift reaction (RWGS) using previously obtained H₂, and [3] ethanol synthesis from the synthesis gas (CO + H₂). A first simulation model of the process was carried out with Aspen Plus[®] software in order to investigate the quantitative and qualitative evolutions of the reaction products. Furthermore, a parametric study was conducted in order to specify the influence of the temperature, pressure, and reagents' ratio.

1. Introduction

Currently, the technologies of CO₂ sequestration (De Castro et al., 2010; Gonzalez-Garza et al., 2009) are the primary means for the mitigation of greenhouse gas accumulation. However, it does not meet world's expectations in terms of safety and costs: leakages that might occur through soil and injection pipes are serious environmental risks. Moreover, no one can be sure about the potential influences of buried CO₂ on the ecosystem in the long term.

Conversion of CO₂ instead of its sequestration is presently being explored as one potential alternative solution. Production of useful value-added chemicals, like ethanol from CO₂ and non-fossil hydrogen appears to be promising. However, currently hydrogen is fossil and comes from the two processes that emit CO₂ either expressly or by implication: steam reforming of natural gas and water electrolysis.

One method that has attracted more and more attention from scientists (Li and Zhang, 2010) is photo-electrocatalytic hydrogen production achieved from water splitting by sunlight is entirely carbon-free. Its strongest point is that both water and sunlight are abundant on Earth. Nature provides us with a fascinating example, which utilizes these two components in photosynthesis. Plants harvest the solar light in order to release oxygen by oxidizing water and reduce CO₂ to sugars.

In this article we introduce a potentially feasible process of ethanol production from CO₂ and photo-electrocatalytically generated hydrogen. This process could provide a solution to future energy and environmental challenges if successfully developed to be economically viable.

2. Process description

2.1 Photo-electrocatalytic hydrogen generation

Fujishima and Honda (1972) have discovered water splitting into hydrogen and oxygen by using light energy. The method focuses mainly on the development of a photo-electrocatalytic cell that includes two principal constituents: a photoanode for water oxidizing (Eq. 1) and a cathode for hydrogen reduction (Eq. 2).



Both electrodes are immersed in an aqueous electrolyte. Between them, a proton exchange membrane makes possible for hydrogen protons (H^+) to pass through to the cathode. Electrodes are connected by an electrical circuit, which allows transferring electrons from the photoanode to the cathode (Fig. 1). The photoanode is an essential element of PEC cells. It is covered with a photoactive semiconductor material, called photocatalyst, which is able to absorb the light and convert the energy of photons into electric current. Overall PEC process is represented by an endothermic uphill reaction involving both half-reactions (Eq. 1 and Eq. 2):



A minimum theoretical potential of 1.23 eV is needed for the reaction (Eq. 3) to proceed in PEC cell. Nevertheless, the key technical obstacle is the present-day absence of efficient, durable, and low-cost catalysts capable of producing the potential of 1.23 eV from sunlight.

Materials available for photo-electrocatalytic hydrogen production still offer very low efficiency: less than 5% of what is theoretically achievable, over 30% under optimized conditions, according to Li and Zhang (2010).

Another problem is the long-term stability of the materials for photocatalysts, which tend to degrade because of the side reactions and illumination that occur over a long period of time.

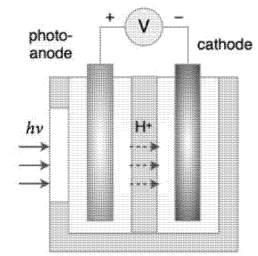
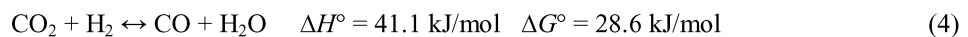


Figure 1: Schematic of PEC water splitting.

2.2 CO₂ conversion into CO

The well-known reverse water–gas shift reaction (RWGS), where CO₂ reacts with H₂, allows producing a mixture of CO and water vapor. The reaction is endothermic, thermodynamic equilibrium favors high conversion of CO₂ and H₂ at high temperatures.



Thermodynamic analysis shows that at atmospheric pressure substantial formation of CO and H₂O can only be obtained at temperatures above 850°C. However, the reaction can be conducted at lower temperatures in the presence of catalysts that enhance the reaction rate. Water has to be removed from the reactor with the help of a membrane during the reaction. In this case, the equilibrium conversion of CO₂ can be shifted further towards CO. A number of studies have been conducted to develop the efficient, stable, and low-cost RWGS catalysts for further commercialization.

Table 1: Performance of RWGS catalyst 6% Ru/ZrO₂-CeO wash coated on FeCrAlY foam (GHSV=330,000 h⁻¹, P=0.1 MPa).

		700°C	750°C	800°C
H ₂ /CO ₂ = 1	CO ₂ conversion, %	33.6	39.2	43.7
	Selectivity to CO, %	94.9	96.4	97.9
Equilibrium	CO ₂ conversion, %	44.0	48.0	49.3
	Selectivity to CO, %	99.2	99.8	100.0
H ₂ /CO ₂ = 1.5	CO ₂ conversion, %	41.7	48.1	53.2
	Selectivity to CO, %	91.7	94.1	96.1

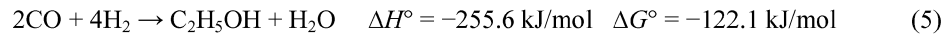
Hu et al. (2007) have investigated a monolith RWGS catalyst that was prepared by wash coating 6% Ru/CeO₂-ZrO₂ catalyst on FeCrAlY foam. Results shown in Table 1 indicate that increasing the hydrogen concentration results in increasing the CO₂ conversion beyond stoichiometric attainable at H₂/CO₂ ratio equal to 1 (Fig. 2).

Bustamante et al., 2004 have carried out the RWGS reaction in a quartz reactor and an Inconel[®] 600 reactor. The reaction took place on the surface of reactors.

Conversions attained in an Inconel[®] 600 reactor at 900°C and 0.101 MPa were approximately two orders of magnitude greater than those attained in the quartz reactor (50% and 28%, respectively).

2.3 Synthesis gas conversion into ethanol

Theoretically, ethanol can be obtained from synthesis gas (syngas), the mixture of CO and H₂, by its direct conversion (Eq. 5).



According to Spivey and Egbebi (2007), the reaction has to be carried out at temperatures below 350°C. A number of side reactions occur during this process by leading to various products: methane, paraffins and olefins C₂-C₅, ketones, aldehydes, ethers, and acetic acid.

Catalysts for ethanol production from syngas can be roughly divided into four groups: the rhodium-based, the molybdenum-based, the copper-based, and the Fischer-Tropsch catalysts. Egbebi and Spivey (2008) have reported the selectivities to ethanol while a rhodium-based catalyst is used for the reaction (Table 2).

Thermodynamically, methane is the most favored product. It is mainly formed by the following reaction:

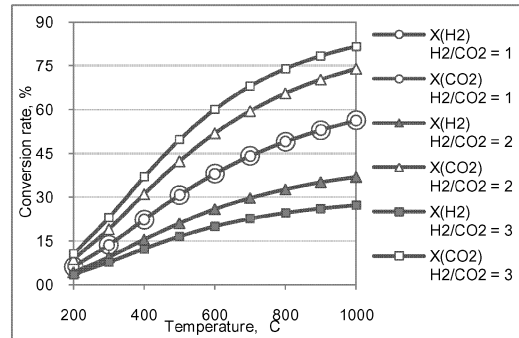
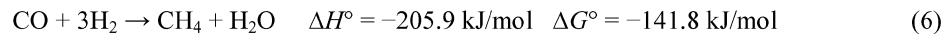


Figure 2: Change in conversion rate of H₂ and CO₂ with temperature and H₂/CO₂ ratio of the RWGS reaction at equilibrium (P = 0.1 MPa).

Table 2: Product selectivities at different H_2/CO ratio on Rh–Mn–Li/TiO₂ catalyst ($T=270^\circ\text{C}$, $P=20$ bar).

Reaction product	H_2/CO ratio		
	1.0	2.0	3.0
Methanol	3.3	3.4	3.4
Ethanol	3.5	4.3	4.8
Acetaldehyde	17.7	12.4	9.8
Methane	73.6	78.4	80.8

We have simulated the reaction of syngas conversion to ethanol in order to determine the equilibrium composition of product mixture. As shown on Figures 3, the methane prevails over all reaction products and completely blocks ethanol synthesis. Contrariwise, if an ethanol-selective catalyst could decline methane generation, ethanol would be presented (Fig. 4). Currently, ethanol selectivity on the catalysts is very low and methane formation is inevitable.

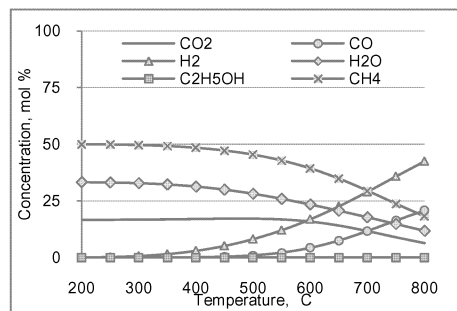


Figure 3: Actual equilibrium composition of the reaction of syngas conversion to ethanol ($H_2/CO=2$, $P=1.5$ MPa).

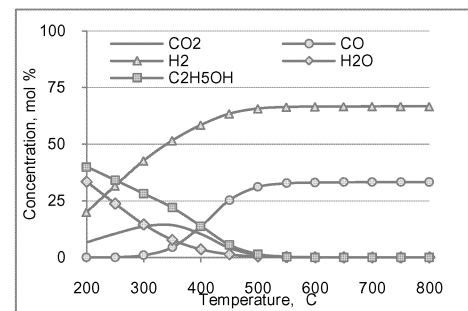


Figure 4: Equilibrium composition of the reaction of syngas conversion to ethanol with no methane formation ($H_2/CO=2$, $P=1.5$ MPa).

3. Process modeling

In order to obtain a rough estimation of the amount of consumed H_2 and CO_2 as well as produced ethanol, a simplified model of the process has been simulated with the help of Aspen Plus[®] software (Fig. 5). Operating conditions were chosen based on experimental results available in the literature cited above (Hu et al., 2007; Bustamante et al., 2004; Spivey and Egbibi, 2007).

The first step of PEC hydrogen production was not studied because of present absence of kinetic model for water splitting reaction. We have assumed that a potential water splitting plant could produce 20,000 tons of hydrogen per year. The second step of CO_2 conversion has been modeled in a series of three equilibrium reactors (600°C , 800°C , and 1000°C) with the intention of increasing overall yield of CO by maximizing conversion rate of CO_2 . The pressure has been fixed at 1.5 MPa while the inlet ratio H_2/CO_2 was equal to 1.

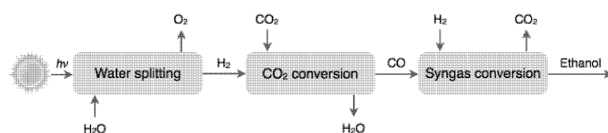


Figure 5: Schematic diagram of the proposed process.

The last step can be described as conversion of CO with H₂. An additional hydrogen is needed to carry out the reaction with H₂/CO ratio of 1. The temperature and pressure inside the reactor have been set at 200°C and 1.5 MPa, respectively. The methane formation has not been taken into account.

4. Results

The mass balance results of the modeled process are summarized in Table 3. Hydrogen reacts entirely whereas there is a half of converted CO₂. Several side reactions generate CO₂, which is not a positive issue in terms of its valorization. However, the unreacted CO₂ can be purified and recycled in the process as well as produced water.

Table 3: Mass balance obtained from the model in the Aspen Plus[®].

Component	Inlet, t/y		Outlet, t/y	
	Reacted	Unreacted	Produced	Recycled
Hydrogen	20,000	—	—	—
CO ₂	146,000	146,000	—	146,000
CO	—	—	1,000	—
Water	—	—	89,000	—
Ethanol	—	—	76,000	—
Total	312,000	312,000	312,000	312,000

As far as the energy balance is concerned, the second step of CO₂ conversion needs heat in order to carry out the endothermic reaction. On the contrary, the step of CO conversion is highly exothermic, thus it can provide this heat. The influence of reagent ratio, pressure, and temperature on H₂ and CO₂ conversion rates and ethanol yield are shown on Figure 6.

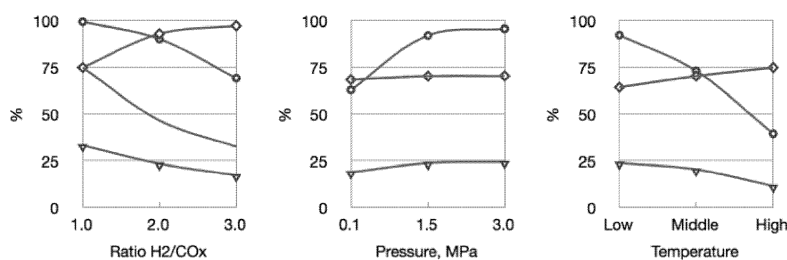


Figure 6: Influence of H₂/CO_x ratio, pressure and temperature for the CO₂ hydrogenation (— H₂ conversion rate; ♦ CO₂ conversion rate, x=2) and the ethanol synthesis (● H₂ conversion rate; ▼ ethanol yield, x=1).

During the CO₂ hydrogenation reaction, a higher H₂/CO₂ ratios and higher temperatures allow converting more CO₂. The pressure does not make a significant difference in conversion rates, neither of H₂ nor of CO₂. During the ethanol synthesis lower H₂/CO ratios and lower temperatures (~200°C) favor ethanol formation. Higher pressures enhance the conversion rate of H₂.

5. Conclusion

We have provided a brief description of the process that includes two main parts: the photo-electrocatalytic hydrogen production from water and sunlight, and the conversion of CO₂ to ethanol. The process is a first approach of recycling CO₂ into ethanol. The simulation allows obtaining promising results in terms of mass balance for the process. By supplying 20,000 tons of H₂ per year, it is theoretically possible to transform 146,000 tons of CO₂ and produce 76,000 tons of ethanol. The latter production capacity is comparable with those of existing bioethanol plants.

Current obstacles primarily include the absence of efficient and durable catalyst materials both for PEC cells and for the RWGS reaction, where the methane formation prevails. In long-term, it is highly hopeful that further research will overcome these difficulties and the process will be economically viable and could provide a solution to future energy and environmental challenges.

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