SASEC2015
Third Southern African Solar Energy Conference
11 – 13 May 2015
Kruger National Park, South Africa

EXPERIMENTAL APPARATUS FOR SOLAR ENERGY STORAGE VIA METHANE PRODUCTION

Rossi F.[a], Castellani B.*[b], Morini E.[a], Di Giovanna L.[b], Corsi N.[b], Giuliobello M.[b] and Nicolini A[a].
*Author for correspondence
[a]CIRIAF, University of Perugia, Perugia, Italy
[b]Consorzio IPASS Scarl, Perugia, Italy
E-mail: castellani@ipassnet.it

ABSTRACT

Renewable energy production from intermittent sources has seen a large expansion the last decade and has introduced new challenges in the energy system. Problems are related to the non-programmable electric power generated and the production peaks that especially characterize photovoltaic energy. In addition to these issues, the extensive and long-term task of reducing CO_2 emissions should be considered. The utilization of CO_2 as a feedstock for producing fuels not only contributes to alleviating global climate changes but also provides a new research field for energy development. An innovative process for solar energy storage via methane production seems to be a viable technology to tackle the above-mentioned issues. In this paper an experimental apparatus, formed by PV panels, a pressurized electrolyser and a Sabatier reactor is presented. The Sabatier reaction exothermically combines hydrogen and carbon dioxide to produce methane and water. The produced methane is a carbon neutral gas that fits in with the existing natural gas and allows to overcame issues related to the intermittence and non-programmability of solar power. The paper focuses on the description of the experimental apparatus and the results of a preliminary investigation. An economic evaluation was also carried out on the integration of methanation process with a traditional PV system.

INTRODUCTION

Environmental and economic sustainability of future energy system needs to overcome several challenges and technical aspects. Certain challenges, such as the shift from fossil to renewable energy sources and the reduction of anthropogenic CO_2 emissions, are already being addressed. However, intermittent energy provided by renewable sources has introduced new challenges in the energy sector [1].

While the existing electricity network results largely unchanged, solar and wind power have seen a large expansion during the last decade. This means that the current electrical energy system is un-optimized and in need of adjustments. The electricity transmission system needs to be adapted from the larger scale production sites used today to smaller local energy production sites. Energy storage solutions are being implemented to compensate for the fluctuations in intermittent energy production [2-3].

Other possibilities are addressed to solve resource depletion in the fossil fuelled economy such as hydrogen use as an energy carrier. Many challenges have been faced by research on hydrogen technologies, including production, storage and transportation infrastructure [4-6]. These challenges have not yet been overcome. However, many efforts were addressed to develop improved ways of producing H_2, such as electrolysis of water, direct photolytic water splitting, thermal-catalytic water splitting, and many others [7].

In addition to these issues, the reduction of CO_2 emissions should be considered to meet IPCC targets. [8].

Many strategies address these targets promoting energy efficient improvements and switching from fossil fuels toward less carbon intensive energy sources such as hydrogen and renewable energy.

This paper focuses and promotes another strategy: the exploitation of CO_2 as an economical, safe, and renewable carbon source for making materials and fuels [9-11].

The utilization of CO_2 as a feedstock for producing chemicals not only contributes to the mitigation of global climate changes caused by the increasing CO_2 emissions, but also provides a grand challenge in exploring new concepts and opportunities for energy development [12].

Given these considerations, and the increased urgency in addressing GHG emissions, it seems warranted to now encourage the application of CO_2 recycling via the Sabatier reaction.

Hydrogen and carbon dioxide are exothermically combined in Sabatier reaction. Methane and water are produced implying the possibility of renewably sourced methane. Methane is already an integral part of energy systems around the world, with huge amounts of infrastructure and expertise; it is easy to store and boasts an energy density around three times that of hydrogen.

A system, called Solargas, for the methane production by PV panels, a pressurized electrolyser and a Sabatier reactor has been analyzed. The efficiency of the Solargas system was evaluated as 7.24%, in terms of the ratio between the output energy (the energy content of the produced methane) and the input solar energy [13]. The system was compared to other biofuel production systems: it was obtained that the Solargas system efficiency is more than 8 times higher than the biogas production system efficiency (i.e. 0.45%) and the wood chip production system efficiency (i.e. 0.84%). Thus, Solargas has been defined as an effective solution for using PV panels in a programmable way [3].

This paper focuses on the energy characterisation of Sabatier reactor and aims at providing some information on the process performances and an evaluation to assess the economic feasibility of the plant.

PROCESS DESCRIPTION

The process analyzed in this work is based on the transformation of electrical energy to synthetic natural gas solar for solar energy storage via methane production.

The system is mainly composed by three stages as in Figure 1:

1. PV stage: this stage is constituted by photovoltaic panels that produce electrical energy from the solar source; it is connected to the subsequent electrolytic cell;
2. an electrolyser, directly supplied by the produced PV energy
3. a Sabatier reactor for the conversion of hydrogen into methane.

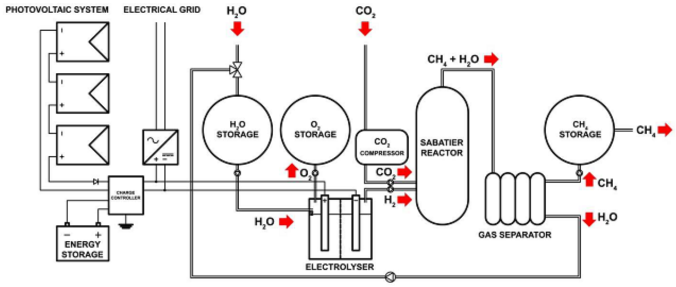

Figure 1 Scheme of the Solargas system.

The process uses an electrolyser and a Sabatier reaction.

First the electricity is used to split water in an electrolyser. An electrolyser splits water into hydrogen and oxygen by using electricity. Ideally 39 kWh of electricity and 8.9 kg of water are required to produce 1 kg of hydrogen at 25°C and 1 atm pressure [14]. Enthalpy is 286 kJ/molH_2 at 25°C and 1 atm pressure. In a real unit, there are losses and the efficiency of an electrolyser system ranges between 50 and 80% [14].

Electrolysers are categorized by the type of electrolyte used. The electrolyte can be a liquid (e.g. Alkaline electrolysers, the most common type in large applications where a large amount of hydrogen is produced) and a solid (e.g. Proton Exchange Membrane PEMs' electrolyte, which can operate in a variable power input mode and can generate hydrogen at pressures up to 20MPa with very little additional power consumption [15]).

PEM electrolysers are simpler than alkaline electrolizers.

PEMs' electrolyte is faster at adjusting its power consumption than the alkaline type and it also has benefits if the electrolyser is pressurized. When the pump and compressor efficiencies are assumed to be 50%, high-pressure electrolysis at 700 atm requires 5% less power [16]. The influence of the pressure on the electrolyser efficiency was found to be small. The electrolyser at high operating pressure was found to be safe, easy to maintain and flexible enough for all kinds of electrical power, referring in particular to intermittent renewable power sources [17].

In addition, the cost of an atmospheric electrolyser including a compressor is 30% lower than the cost of a high-pressure electrolyser to produce hydrogen at the same pressure [18]. The study suggests also that the use of atmospheric electrolysers is preferable to high-pressure ones for fluctuating energy sources for their better dynamic response.

In general, typical industrial electrolysers have electricity consumptions between 4 and 6.0 kWh/Nm^3, corresponding to an efficiency of 65-80% [15, 19].

Theoretical water consumption is of 1 liter of water per 1.24 Nm^3 of hydrogen. The actual use is 25% higher because of different losses: almost 12 kg of water per kg of hydrogen produced are used by current systems [20-22].

The resulting H_2 from electrolysis in the electrolyser is combined with CO_2 in the Sabatier reactor to produce CH_4.

The choice of a pressurized cell gives better efficiency to the entire chain and better integration with the subsequent Sabatier reactor (if the electrolyser pressure is the same of the Sabatier reactor one) [3].

The Sabatier reaction[23]:

$$CO_2 + 4\,H_2 = CH_4 + 2\,H_2O \qquad (1)$$

combines carbon dioxide and hydrogen. Methane and water are produced in the moderately exothermic (H°= -165 kJ/mol) reaction.

Lower operating temperatures, typically around 250-400°C, are desirable for higher CO_2 conversion and higher CH_4 selectivity. The generation of hot spots or the quenching of the reaction is a challenge in reactor design. They are avoided by removing heat produced by the exothermic reaction and maintaining a relatively low process temperature (around 350°C) [23].

The equilibrium of the reaction is highly dependent on the temperature and in particular a lower temperature favours H_2 conversion. At lower temperatures, the effect of the pressure will not have a large relative impact [24]. At higher temperatures instead a high pressure has a large effect on the conversion of H_2. The methanation of CO_2 is thermodynamically favorable ($\Delta G298K=-113.5$ kJ/mol). However, the reduction of the fully oxidized carbon to methane requires a catalyst to achieve acceptable rates and selectivities. It is an eight-electron process with significant kinetic limitations.

Nickel was the first catalyst used by Paul Sabatier in 1897. It is still commonly used. Further research has shown catalysts such as Ru, Rh and Co to be effective. However, Ru and Rh are both expensive noble metals so oxide supports (TiO_2, SiO_2, MgO and Al_2O_3) are used to both increase efficiency and minimise cost. Ru -TiO_2 results the most stable and active solution [25-27].

Supported nickel catalysts remain the most widely studied materials. The nature of support, usually oxides with high surface area, plays a crucial role in the interaction between nickel and support. It thus determines catalytic performances toward activity and selectivity for CO_2 methanation [28-29].

The conversion increases rapidly when the residence time is increased: nearly 90% at residence times greater than about 100 to 200 ms [30].

Several implementations of the process have been carried out: the three major types of reactors that have been considered are micro channel reactors, fluidized bed reactors and fixed bed reactors. Micro channel reactors are usually used in applications with a small reactant flow, and are currently only existing on a lab scale and are developed for space applications. Fluidized bed have been implemented for methanation reactors in a few cases. The most widely used reactor design for methanation processes is the fixed bed reactor where the active metal is coated onto the surface of a support.

The rate of heat release is very high. The reactor system is thus designed to be adiabatic with cooling after the reactor since internal cooling is not possible. The increasing temperature is kept under control by a recycling and water condensation step to control the temperature and achieve a high conversion of the H_2 and CO_2 to CH_4.

Some water is removed to lower the volume flow of the reactants. However removing water from the stream before a reactor requires heat. Some water is also needed in the reactant flow to avoid carbon formation during the reaction.

H_2 conversion is maximized when there is a minimum amount of water in the reaction, just enough water to avoid carbon formation is ideal. The produced CH_4 can be finally injected and stored in existing natural gas grids or used as a fuel for transportation.

EXPERIMENTAL SECTION

Preliminary experimental investigations are carried out in an experimental lab-scale apparatus, installed at Lab of Applied Physics in Terni – University of Perugia. The apparatus includes the following sections: hydrogen production section, CO_2-H_2 mixing section, a heating section, a reactor, a collecting section.

Hydrogen is produced by an electrolyzer supplied by Erredue Srl (G Series H03) and is then mixed with CO_2 according to the stoichiometric proportion (Equation 1). Gas flows are measured and controlled by calibrated flowmeters. CO_2 is provided is supplied directly by gas bottles through a pressure-reducing valve, that provides adjustment of the pressure to the gas injection line. CO_2 (99% purity) is provided by Air Liquide Italia Service.

Before entering the reactor, the gaseous in the heating section, constituted by a tube on which mineral insulated band heaters are mounted (Figure 2).

The reactor consists of a high-pressure cylindrical AISI 304 stainless steel vessel with a total internal volume of 2.8 l.

The reactor is provided with several ports for inserting temperature and pressure sensors and for gas inlet and outlet.

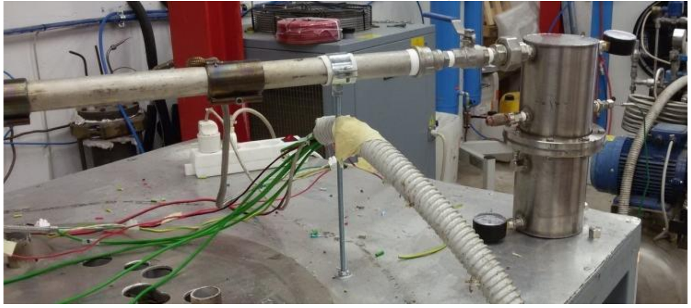

Figure 2 Heating system and methanation reactor.

The temperature sensors are mineral insulated type K thermocouples (accuracy class 1) and measure the temperature inside the vessel in the lower part and in the upper part.

The pressure sensor is a digital piezo-resistive manometer (Kobold - accuracy class 0.5). Voltage signals from pressure transducers and temperature sensors are collected by a software for data acquisition on a personal computer.

Preliminary tests were carried out using a Ni-based catalyst.

As regards the choice of the catalyst, it has to be considered that the development of novel catalyst with high activity and selectivity is still the key to improve Sabatier technologies, and is one of the main focuses in the academic community. On the basis of analysis of old and new literature investigations, we decided in the first step to use a Ni-based catalyst.

The Ni-based catalyst was prepared using a tape-casting process. The alloys mixtures are tape casted using the machinery in figure 3 and, after a phase of drying, 0,5 mm thick rubbery sheets (green tapes) are obtained.

Figure 3 Tape casting machine.

Ni-based catalyst is realized by stacking and rolling seven layers of green tape. The rolling is carried out to compact the components, improve the sintering process and prevent the separation of individual layers

The components are sintered in controlled atmosphere using the electric oven produced by FORNO MAB mod. HDM.

Ni-based catalyst used in the experimental campaign is shown in Figure 4.

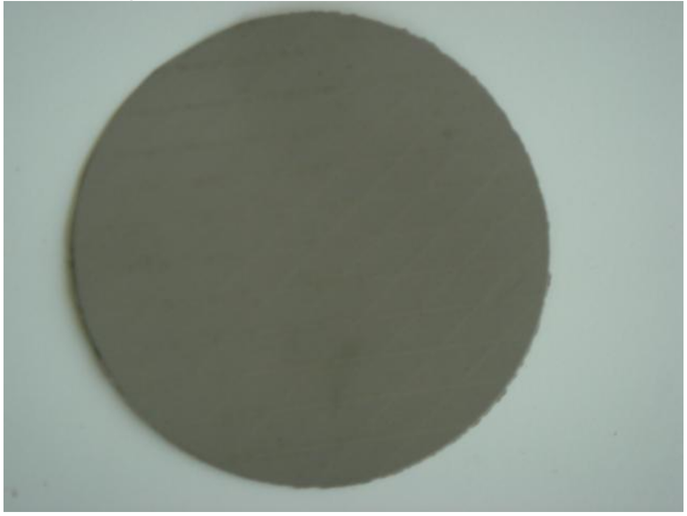

Figure 4 Ni-based catalyst.

Catalyst porous plate is mounted inside the reactor and gaseous mixture flows through it. The products of methanation were then sent to the cold trap, where gases were collected.

The reaction gases were analyzed by gas chromatograph analysis, that allowed to identify the composition of the reactor outlet gases.

The installation of the apparatus is shown in Fig. 5. The heating section is on the left part of the picture; the FT reactor is the cylinder on the right; behind on the wall there are flowmeters.

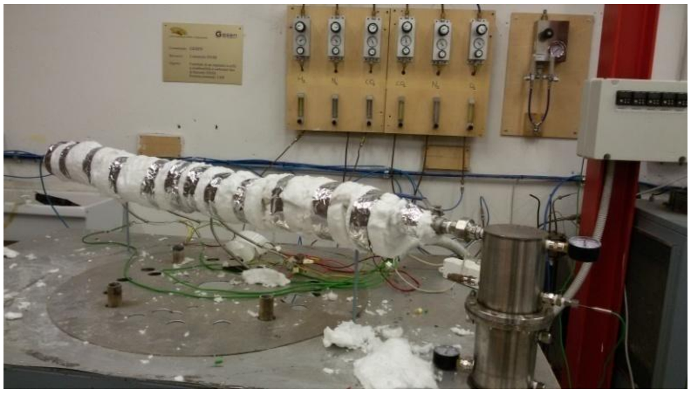

Figure 5 Experimental apparatus.

Experimental tests were carried out with internal temperature in the range of 300 and 350 °C and an internal pressure of 2 bar, using the stoichiometric H_2/CO_2 ratio of 4. When the internal pressure decreases gas is injected into the reactor to re-establish the correct pressure value.

Three different tests have been performed to evaluate methane production rates.

Figure 6 represents typical profiles of temperature vs. time for the three experimental runs. In the first 35 minutes the gas flow is heated and brought to the proper temperature (300 °C). Starting from t=35 min, temperature increases as a result of the exothermic process of methane formation. So, we can say that reaction starts at t=35 min and lasts for 25 minutes.

As regards the temperature values, our efforts in the reactor design were devoted to obtain a high level of temperature control. In fact, the temperature control is one of the most important factors deciding the performance of the methanation process. Temperature profiles reported in Fig. 6 show how our system for temperature control was able to remove reaction heat and bring back temperature to the initial values of ca. 300 °C in few minutes.

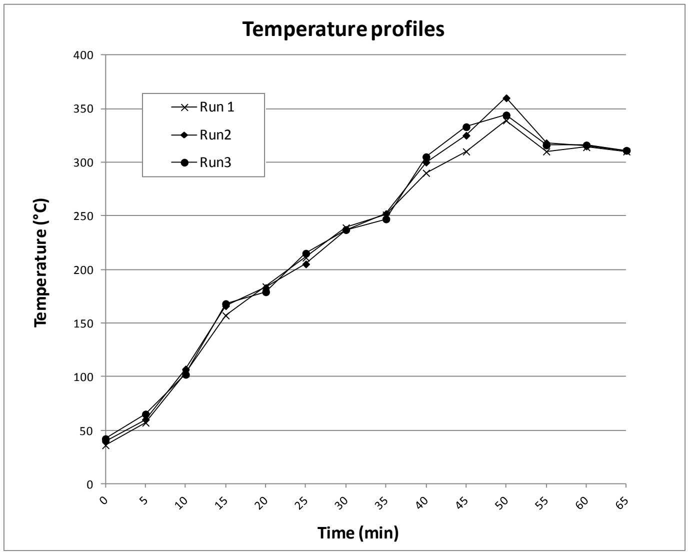

Figure 6 Temperature profiles.

The reaction gases were analyzed by gas chromatograph analysis, that allowed to identify the composition of the reactor outlet gases. The percentage in volume of methane for the three experimental runs is shown in Figure 7 as a function of time.

From Fig. 7 it is possible to observe that production of methane reaches 50% in volume after five minutes, while the maximum content of methane in the gaseous mixture is 81% (Run 2) after 23 minutes.

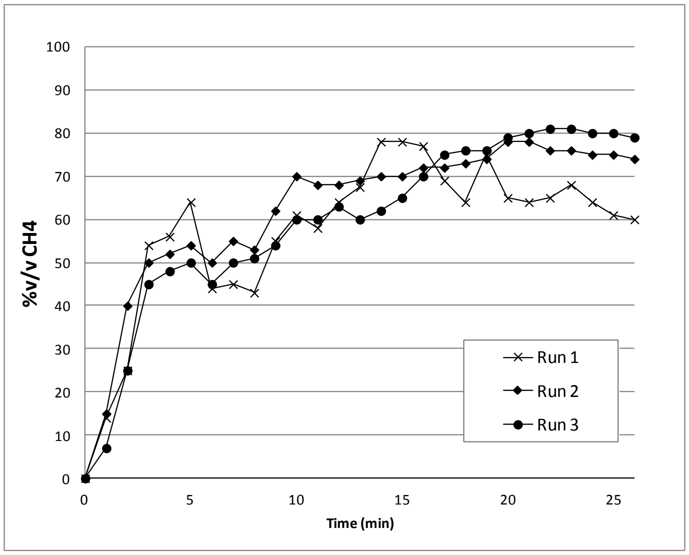

Figure 7 Methane content in outlet gas.

ECONOMIC EVALUATIONS

Economic evaluations were carried out considering energy production of a photovoltaic system of 832 KW, installed in Italy.

In Figure 8 data about daily energy production of PV system and hourly energy selling prices for June 2013 are provided.

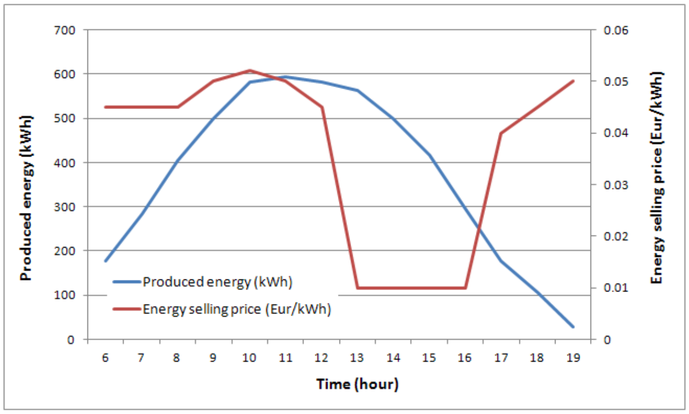

Figure 8 Energy production and selling prices.

Two scenarios are investigated:

a) All energy production is sold and injected into the the grid
b) when energy prices are low (from 1 to 4 pm), energy is not injected into the grid, but used to produce hydrogen and supply Solargas process. During the rest of day, the produced energy is injected into the grid.

For scenario b), the following assumptions were considered:

- electrolyzer's consumption equal to 4 kWh per 1 Nm^3 of produced hydrogen;
- overall efficiency of Sabatier process equal to 75%;
- CO_2 amount is calculated in accordance with stoichiometric ratio;
- selling price of methane equal to 0.77 Eur/Nm^3.

Results of calculation are shown in the following tables. Table 1 shows the energy production and the incomes in case of Scenario a), when all the produced PV energy is injected into the grid. Table 2 instead shows methane production and methane selling incomes for Scenario b), for hours 13-16, in which Solargas is used to produce methane. For the other hours of the day (6-12 and 17-19), results for Scenario b) are the same as in Scenario a) (Table 1).

Table 1 Results for Scenario a)

Scenario a)			
Hour of the day	Produced Energy (kWh)	Energy selling price (Eur/kWh)	Hourly income (Eur)
6	177.9	0.045	8.0
7	284.6	0.045	12.8
8	403.3	0.045	18.1
9	498.1	0.05	24.9
10	581.2	0.052	30.2
11	593.0	0.05	29.6
12	581.2	0.045	26.1
13	**563.4**	**0.01**	**5.6**
14	**498.1**	**0.01**	**5.0**
15	**415.1**	**0.01**	**4.1**
16	**296.5**	**0.01**	**3.0**
17	177.9	0.04	7.1
18	106.7	0.045	4.8
19	29.6	0.05	1.5
Total	5206.6		180.8

Table 2 Results for Scenario b)

Scenario b)				
Hour of the day	Produced H_2 (Nm3/h)	CO_2 used in the process (kg/h)	Produced methane (Nm3/h)	Methane hourly selling incomes (Eur)
13	140.8	507	211.3	162.7
14	124.5	448	186.8	143.8
15	103.8	373	155.7	119.9
16	74.1	267	111.2	85.6

Results show that the Solargas system allows to obtain economic benefits over a traditional PV system, since the daily income from Scenario a) is 180,8 Eur/day, while for Scenario b) is equal to 675,1 Eur/day. This value is obtained summing:

- methane selling incomes equal to 512,0 Eur obtained during hours 13-16 via Solargas process;
- PV energy selling incomes equal to 163,1 Eur obtained during hours 6-12 and 17-19 as shown in Table 1.

It is important to underline that in the evaluations CO_2 costs were not considered, as it was assumed that CO_2 is provided by other processes as waste material, such as power plants, refineries, cement kiln. Actually if CO_2 is purchased as a raw material, CO_2 costs are considerable and the process is not sustainable. In fact, in this case an increase of 30% in the management costs would occur.

CONCLUSION

The paper analyzed the system called Solargas for the methane production by PV panels, an electrolyser and a Sabatier reactor.

An experimental apparatus has been built at Terni Laboratories of Applied Physics of the University of Perugia. In the preliminary experimental investigation, a maximum CO_2/CH_4 conversion equal to 81% was obtained.

Economic evaluation were also carried out. Results show that the Solargas system allows to obtain economic benefits over a traditional PV system. The analyzed process could be very beneficial if coupled to CO_2-producing facilities.

REFERENCES

[1] Kjarstad, J.; Johnsson F. Fossil Fuels: Climate Change and Security of Supply. *Int. J. of Sustainable Water and Environmental Systems*, 2012, 4, pp. 79-87.

[2] Cotana, F.; Rossi F.; Nicolini A. Evaluation and Optimization of an Innovative Low-Cost Photovoltaic Solar Concentrator. *International Journal of Photoenergy 2011,* pp. 10.

[3] Cotana, F.; Rossi, F.; Nicolini, A.; Filipponi, M.; Pisello A.L. Energetic Analysis of Solar-Supplied Processes for Methane, Biogas and Wood Chip Production. *Advanced Materials Research 2013*, 772, pp 720-724.

[4] Rossi, F.; Nicolini, A. Experimental Investigation on a Novel Electrolyte Configuration for Cylindrical Molten Carbonate Fuel Cells. *Journal of Fuel Cell Science and Technology*, 2011, 8, pp. 1-9.

[5] Rossi, F.; Nicolini, A. A Cylindrical Small Size Molten Carbonate Fuel Cell: Experimental Investigation on Materials and Improving Performance Solutions. *Fuel Cells, 2009*, 9, pp. 170-177.

[6] Cotana, F.; Filipponi, M.; Castellani, B. A Cylindrical Molten Carbonate Fuel Cell Supplied with Landfill Biogas. *Applied Mechanics and Materials 2013*, 392, pp 512-516.

[7] Rossi, F.; Corsi, N.; Giuliobello, M.; Castellani, B. Sistemi innovativi di produzione di idrogeno da energie rinnovabili. Sistemi Innovativi di Produzione di Idrogeno da Energie Rinnovabili - *Progetto Nazionale FISR Vettore Idrogeno, 2009*, ISBN 978-88-904138-0-3.

[8] Hiraishi, T., Krug, T., Tanabe, K., Srivastava, N., Baasansuren, J., Fukuda, M. and Troxler, T.G. Supplementary Methods and Good Practice Guidance Arising from the Kyoto Protocol. Published: IPCC 2014, Switzerland Revised.

[9] Xu, X. D.; Moulijn, J.A. Mitigation of CO_2 by chemical conversion: plausible chemical reactions and promising products. *Energy Fuels*, 1996, 10, pp. 305–325.

[10] Yang, H.; Xu, Z.; Fan, M.; Gupta, R.; Slimane, R. B.; Bland, A. E.; Wright, I. Progress in carbon dioxide separation and capture: A review. *J. Environ. Sci*., 2008, 20, 14–27.

[11] Mikkelsen, M.; Jorgensen, M.; Krebs, F. C. The Teraton Challenge. A review of fixation and transformation of carbon dioxide. *Energy Environ*.Sci., 2010, 3, 43–81.

[12] Castellani, B.; Filipponi, M.; Nicolini, A.; Cotana, F.; Rossi, F. Carbon Dioxide Capture Using Gas Hydrate Technology, *Journal of Energy and Power Engineering 2013*, 7, pp. 883-890.

[13] Castellani, B.; Giuliobello, M.; Morini, E.; Filipponi, M.; Nicolini, A.; Di Giovanna, L.; Cotana, F.; Rossi, F. Methane production as solar energy storage: energy and process evaluations. *Proceedings of 14th CIRIAF National Congress Energy, Environment and Sustainable Development*. Perugia, Italy. April 4-5, 2014

[14] Harrison, K.; Levene, J.I. Electrolysis of water. In Solar Hydrogen Generation Toward a Renewable Energy Future, by Krishnan Rajeshwar, Robert McConnell and Stuart Licht, pp. 41-63. New York: Springer Science+Business Media, LLC, 2008.

[15] Barbir, F.PEM electrolysis for production of hydrogen from renewable energy sources. Journal of Solar Energy, 2005, 78, pp. 661-669.

[16] Roy, A.; Watson, S.; Infield, D. Comparison of electrical energy efficiency of atmospheric and high-pressure electrolysers, International Journal of Hydrogen Energy, 2006, 31, pp. 1964-1979.

[17] Onda, K.; Kyakuno, T.; Hattori, L.; Ito, K. Prediction of production power for high-pressure hydrogen by high-pressure water electrolysis. Journal of Power Sources, 2004, 32, pp. 64-70.

[18] Schug, C.A. Operational characteristics of high-pressure, high efficiency water-hydrogen electrolysis, International Journal of Hydrogen Energy, 1998, 23, pp.1113-1120.

[19] Mazloomi, K.; Sulaiman, N.; Moayedi, H. Electrical Efficiency of Electrolytic Hydrogen Production. Int. J. Electrochem. Sci., 2012, 7, pp. 3314 – 3326.

[20] Ivy, J. Summary of electrolytic hydrogen production, Milestone Completion Report, NREL/MP-560-36734, National Renewable Energy Laboratory; Golden, Colorado, September 2004.

[21] Contreras, A.; Posso, F.; Veziroglu, T. N. Modeling and simulation of the production of hydrogen using hydroelectricity in Venezuela, International Journal of Hydrogen Energy, 2007, 32, pp. 1219-1224.

[22] Spath, P. L.; Mann, M. K. Life cycle assessment of renewable hydrogen production via wind/electrolysis, Milestone Completion Report, National Renewable Energy Laboratory; Golden, Colorado, February 2004.

[23] Brooks, K.; Hu, J.; Zhu, H.; Kee, R. Methanation of carbon dioxide by hydrogen reduction using the Sabatier process in microchannel reactors. Chemical Engineering Science, 2007, 62, pp. 1161-1170.

[24] Turns, Stephen. An introduction to combustion Third edition. McGraw-Hill Education, 2011.

[25] Hoekman, S.; Broch, A.; Robbins, C.; Purcell, R. CO_2 recycling by reaction with renewably-generated hydrogen. International Journal of Greenhouse Gas Control, 2010, pp. 44-50.

[26] Mills, G. A.; Steffgen, F. W. Catalysis Reviews. Science and Engineering, 1974, 8, pp. 159-210.

[27] Mohseni, F., Magnusson, M., Gorling, M.; Alvfors, P., Biogas from renewable electricity – Increasing a climate neutral fuel supply. Applied Energy, 2012, 90, pp. 11- 16.

[28] Du, G., Lim, S., Yang, Y., Wang, C., Pfefferle, L., Haller, G. L. Methanation of carbon dioxide on Ni-incorporated MCM-41 catalysts: The influence of catalyst pretreatment and study of steady-state reaction. Journal of Catalysis, 2007, 249, 370.

[29] Weatherbee G.D.; C.H. Bartholomew. Hydrogenation of CO_2 on Group VIII Metals, IV. Specific Activities and Selectivities of Silica-Supported Co, Fe, and Ru. Journal of Catalysis, 1984,87, 352.

[30] VanderWiel, D.P.; Zilka-Marco, J.L.; Wang, Y.; Tonkovich, A.Y.; Wegeng R.S. Carbon Dioxide Conversions in Microreactors. In IMRET 4: Proceedings of the 4th International Conference on Microreaction Technology, AIChE Spring National Meeting, March 5–9, 2000 Atlanta, GA., pp. 187–193.