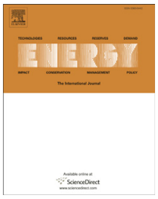
Energy 69 (2014) 497–505

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy



Optimal year-round operation for methane production from CO_2 and water using wind energy

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A R T I C L E I N F O

Article history:
Received 3 December 2013
Received in revised form
3 February 2014
Accepted 10 March 2014
Available online 13 April 2014

Keywords:
Energy
Wind power
Synthetic methane
Hydrogen
Electricity

A B S T R A C T

In this paper, we present the optimal year-round production of synthetic methane from water electrolysis using wind energy, and CO_2 from power plants. The plant consists of a wind farm, a system of electrolyzers which produces oxygen and hydrogen from water, a series of equipment used to purify and store the oxygen; and the purification of hydrogen using a deoxygenation reactor and its reaction with CO_2 to produce synthetic methane. We operate the plant over a year, considering monthly variability in wind velocity for constant methane production, and for variable methane production. We formulate the problem as a multiperiod NLP. The investment of a plant devoted to synthetic natural gas production is 375 M€ for a production cost of synthetic methane of 13.1 €/MMBTU, a price that is currently over the selling price of natural gas. If the plant operates at constant methane production rate, the investment and production costs are almost double, but we can obtain credit from the electricity produced; 2.9 kg of CO_2 per kg of CH_4 produced can be reused by this process.

1. Introduction

The increase in the demand for energy and current concerns on sustainability are pushing toward the development of technologies that use solar radiance, wind and biomass. While biomass is a carbon source and, thus, can be considered a source of chemicals, the use of wind and solar energy is typically related to the generation of electricity. One of the main features of renewable sources of energy is their variable nature across regions, restricting their use to their availability. Furthermore, renewable sources share another characteristic that constitutes a major challenge for process design: the day-long and year-long variability. Recently, Martín and Martín [1] optimized the year-long operation of a solar power facility determining the optimal operating conditions for the production of electricity, taking into account the variable solar radiation. The facility on its own cannot maintain the production level without combining energy sources. Vidal and Martín [2] coupled a solar plant and a biomass based polygeneration system to circumvent this disadvantage. Furthermore, by producing chemicals directly out of solar or wind energy, it is possible to somehow store that energy to be used in other processes.

Water electrolysis is the most environmental friendly option to produce hydrogen, as long as the energy for the electrolysis comes from renewable sources. The idea of using renewable energy can be traced back to 1923 and, although photovoltaic and wind energy have taken a head start and demonstration plants are already in operation [3], the first attempts back in the early 1900s considered the use of wind turbines [4]. The economical use of wind corresponds with those regions considered to be class 3 or higher, which means that the annual average wind velocity is 6.9 m/s at a height of 80 m. Around 13% of all stations worldwide belong to this group. So far, the production costs are still high. Based on this, global wind power potential for the year 2000 was estimated to be ~72 TW [5]. Thus, it has recently been estimated that the global potential for wind power is more than enough to supply the total current consumption of energy [6–8]. There is sufficient wind to supply all the world's energy needs. Fig. 1 shows the average wind velocity across Europe. Apart from the UK, the coast of Spain, France, Germany and Denmark represent interesting locations for the production of electricity from wind. Recently, hydrogen has been produced from wind energy to take advantage of the wind availability in certain regions, such as Canada [9] or Ireland [10].

The generation and emissions of CO_2 to the atmosphere due to human activities, particularly related to energy usage and consumption, is an important concern nowadays. CO_2 concentration in the atmosphere has recently increased to surpass 400 ppm [11]. Although biomass is a source of carbon for the production of

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http://dx.doi.org/10.1016/j.energy.2014.03.043
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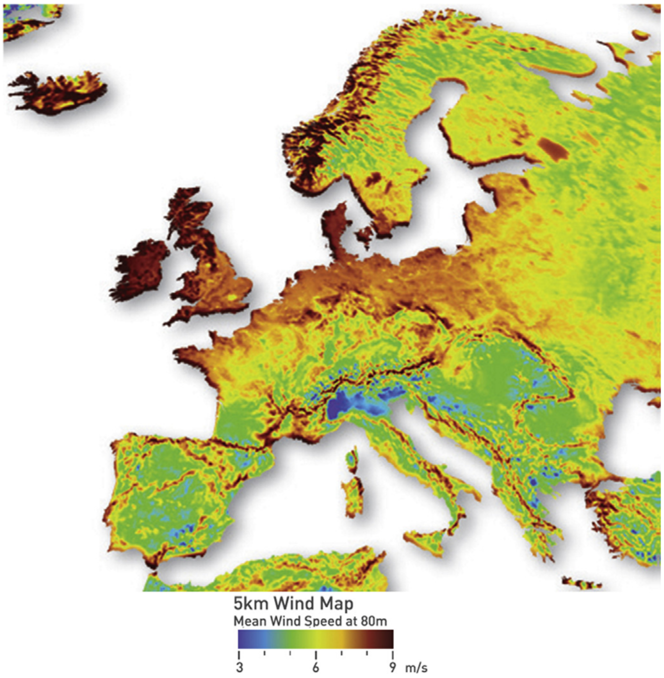

Fig. 1. Wind availability in Europe [15].

different chemicals, CO_2 can also be used. Nature captures CO_2 to produce hydrocarbons and biomass. However, this capturing process is slow compared to the requirements of the transport and energy sector. Because the CO_2 produced in the transport sector is difficult to handle (unless it comes from burning biofuels) when the source is fixed, carbon capture technologies have been proposed and are under development, such as PSA, amine solutions, etc. We can use the captured CO_2 as a source of chemicals while contributing to reduce emissions and providing further value out of it, such as for the production of methane [12–14].

In this paper we use hydrogen, produced from water electrolysis using wind energy, and CO_2 from power plants, to produce synthetic natural gas and evaluate the performance of such a plant and the economics along a year using mathematical optimization techniques. The paper is organized as follows: in Section 2, we describe the process. Next, in Section 3, we discuss the main modeling assumptions and solution procedures for the MINLP multiperiod problem which has been previously formulated. Subsequently, in Section 4 we present results divided into constant methane production along the year and variable methane production, ending with the economic evaluation of the latter option. Finally, in Section 5 we draw some conclusions.

2. Process description

The process consists of five stages: wind farm, electrolyzer, oxygen purification and storage, hydrogen purification, and the synthesis of methane.

The electricity is generated in the wind farm. Next, we have the electrolyzer, which breaks down the water into hydrogen and oxygen, operating at 80 °C. On the one hand, we have the line of oxygen, stream 3, which carries water vapor and traces of hydrogen. The water is condensed, D-1, and the resulting stream is dehydrated using a zeolite adsorber, D-2. Finally, the oxygen is compressed and stored. On the other hand, we have the stream of hydrogen, stream 2, which contains traces of oxygen and water vapor. Most of the water is separated by condensation. The presence of oxygen represents a challenge for further synthesizing stages and, thus, it is eliminated using deoxygenation reactor, R-2, where water is produced. Next, a zeolite, D-4, is used to dehydrate the stream. At this point, we mix the hydrogen with the CO_2. In order to avoid carbon deposition on the catalyst, a ratio of $H_2 - CO_2/CO + CO_2 \geq 3$ [16] is required. The gas phase is adjusted for the optimal operating conditions using a compressor, C-5, and a heat exchanger, E-7. Methane is produced based on a series of equilibria, which are the inverse of methane reforming, in reactor R-3. One important characteristic to reduce water consumption in this process consists of recycling the water produced together with the methane. Thus, water is condensed in exchanger E-8, separated, D-5, and recycled. The produced gas, which consists mainly of methane but which also contains CO_2 and unreacted H_2, must meet the composition constraints so that this gas product can be fed to the network that currently supplies natural gas. Fig. 2 shows the flowsheet for the plant.

3. Modeling

In this section we describe the main assumptions used while modeling the process for the production of synthetic methane using wind power and CO_2. We use mass and energy balances, design equations, thermodynamic equilibria and experimental data in order to develop models for all the units involved in the process. The list of species belong to the set: $i = \{\text{methane}, CO_2, CO, H_2, \text{water}\}$.

3.1. Wind turbine power

The power generated by the wind turbine as function of the wind velocity is computed using the correlation proposed by Masters [17]:

$$W = P_{\text{nominal}}\left[0.087 \cdot V - \frac{P_{\text{nominal}}}{D^2}\right] \tag{1}$$

where $P_{\text{nominal}} = 1500$ kW, $D = 86$ m and the typical turbine density is $4D \cdot 7D = 28D^2$ [15,16]. The mean wind velocity, V, is taken from the average monthly data. However, the formulation can also be applied for the everyday operation of a plant where the velocity is taken on an hourly basis.

3.2. Hydrogen production and purification

3.2.1. Electrolyzer

The reaction taking place in the electrolyzer is the breaking up of water. We use a solution of 25% of KOH as electrolyte. The reaction takes place at 80 °C and 100 kPa.

$$2H_2O \rightarrow 2H_2 + O_2 \tag{2}$$

The power required is 175,000 kJ/kg H_2 [18]. The water consumed at the electrolyzer is not only that used in the reaction, but also due to evaporation, since water vapor accompanies the gas phases saturating them. For the economic evaluation we consider that each electrolyzer generates 0.0124 kg H_2/s [19].

3.2.2. Water condensation

The gas phases that are comprised mainly of oxygen and hydrogen, respectively, are cooled down to 25 °C before compression. In this process the water condenses. An offline simulation of this stage using CHEMCAD and the thermodynamic model “electrolyte NRTL” was used to validate this separation stage. The water saturating the gases at 25 °C goes with the gas phase, while the rest