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Solar-Wind Hydrogen to Produce Nitrogen Fertilizers in the State of Ceara, Brazil

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Abstract: The mathematical model of the universal solar hydrogen energy system created by Veziroglu and Basar was extended for the feasibility study of producing ammonia as main component for the synthesis of nitrogen fertilizers in the State of Ceara, Brazil. The adapted model considers interrelationships of parameters such as population, energy demand, gross internal product per capita of the region where it is applied and makes long term estimates of the production of solar and wind hydrogen. Price of energy, necessary area of photovoltaic panels and wind turbines, capacity of desalination plant, capital investments, cost of operation and maintenance, environmental impacts and recently production of ammonia was also included in such model. In the present study it is investigated how the production of ammonia through solar and wind hydrogen can impact on the future market of nitrogen fertilizers of the federal State of Ceara in Brazil.

Key words: solar-wind hydrogen, ammonia, nitrogen fertilizers

1. Introduction

Chemical fertilizers, mechanization, breeding, genetic improvement, chemical pest control, processing and storage systems have contributed to vastly increase the productivity in the 20th century agriculture [1]. Without such advances and in special without nitrogen fertilizers agriculture would be able to support a little more than half of the current world population. Agriculture besides being an intensive user of fossil fuels is also one of the major emitters of greenhouse gases in the world and it contributes to nearly 14% of the whole emissions of such gas into the atmosphere [2].

Globally more than 100 million tons of nitrogen fertilizer is used every year and its production is very energy-consuming, accounting for 1.2% of global primary energy demand [3]. The basic component in the current industrial nitrogen fertilizer production is ammonia which uses nitrogen and hydrogen gases with the overall reaction being $N_2 + 3H_2 \rightarrow 2NH_3$ under the influence of an iron oxide catalyst in an environment of very high pressures ranging from 100 to 250 bar and moderate temperatures ranging from 350°C to 550°C [4, 5]. Although nitrogen purification is relatively simple and energy efficient, hydrogen generation is a very energy intense process. Currently, the hydrogen is most often derived from fossil fuels and nitrogen from air. Mostly based on the Haber-Bosch process of synthesis, in the world, about 72% of produced ammonia is originated from steam reforming of natural gas, 22% from coal gasification, 4% from fuel oil, 1%

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from naphtha, 1% from others [6]. Only 0.5% of the world's ammonia for fertilizer is based on hydrogen produced by water electrolysis. When natural gas is used it requires 28-40 GJ per ton of NH_3 emitting up to 2.3 ton of CO_2 per ton of NH_3. If coal is used the numbers are 16.7-165.9 GJ per ton of NH_3 and up to 16.7 ton of CO_2 per ton of NH_3, respectively [1].

The steady increase in the price of natural gas and coal, their depletion, particularly natural gas and concerns about greenhouse gas emissions, results in an interest in the technology of water electrolysis, mainly because renewable energy is a rapidly expanding and consequently more competitive, enabling the electrolysis process to produce ammonia [7]. In fact, in the past, ammonia has been produced from electrolytic hydrogen in countries where electricity was available at low cost, e.g., from hydropower in Norway, India, Egypt, Peru, and Canada. However, these plants were closed after the development of efficient technologies for using hydrocarbon feedstock [4]. At the present time, electrolytic hydrogen is more expensive than hydrogen obtained from fossil hydrocarbons, but in the long run the progressive depletion of fossil fuels is destined to make renewable hydrogen more convenient and this route has the advantage that the existing Haber-Bosch plants could be kept and utilized without major modifications [2].

The implications of producing renewable hydrogen for the ammonia synthesis with excess wind or solar power are vast: curtailed wind or solar power could be converted directly into ammonia which could be used as fertilizers for agriculture, or as bulk energy storage for grid applications. Ammonia that is synthesized using renewable energy would not be subject to fluctuations in the fossil-fuel markets: it would be stable over the long term like the renewable resources used to produce it. Stable fuel prices could also be a huge economic advantage for oil-dependent island communities [5]. Area which has no fossil energy resources and must, therefore, import all of its nitrogen fertilizer and at the same time having sufficient number of wind turbines and/or PV systems and whose power production capacity has now increased so much that the existing regional electrical grid cannot accept power from some turbines or PV systems during peak production, certainly will take advantage of such situation. As solar energy is available in all agriculturally relevant locations, it represents a prime candidate for a sustainable solution for powering a distributed system for nitrogen fertilizer solution [8]. If electricity were derived from wind or solar power, then ammonia could be synthesized as a carbon-free, carbon-neutral, liquid fuel or fertilizer.

The wind energy potential of the State of Ceara, in the northeast region of Brazil, is estimated in 35 GW which, if effectively used, corresponds to approximately 40% of the installed production capacity of electric energy in Brazil [9]. At the present year, the State of Ceara has about 1.4 GW wind farms in operation. Most of the installed and still to be installed wind farms in the State of Ceara are or will be in its coast. On the other hand, the State of Ceara has a significant potential to explore solar energy accounting that the average daily solar radiation in one square meter is about 5.7 kWh which is one of the highest in the Brazilian territory. At the year 2011 the State of Ceara launched a l MW private and commercial solar power plant in the city of Taua, 350 km far from its capital, Fortaleza, and by the end of year 2016, there was about 6 MW of PV systems installed.

Investments in the field of wind energy are directed to its coastal region and investments in the field of solar energy are directed to its interior region. It happens that the interior region of the State of Ceara is the region where agriculture activities takes place and most of the fertilizer needed is imported. The city of Taua locates just in the center of a region where fertilizers are needed, and which fertilizers are imported from other regions of Brazil or of international market. In terms of logistic, it could be interesting to see the feasibility of installing a renewable ammonia plant in the State of Ceara since there is plentiful availability of solar and wind energy and a relatively strong market for nitrogen fertilizers in Brazil as a whole.

The main objective of the present study was to realize a long-term techno-economic analysis of the eventual utilization of the photovoltaic and wind energy generated in the State of Ceara for the synthesis of ammonia. The mathematical model of universal solar hydrogen energy system created by Veziroglu and Basar [10] was adapted to the State of Ceara. Besides the calculation of different techno-economic and environmental parameters, estimates of consumption of ammonia in the State of Ceara and long-term comparison of the cost to produce ammonia with conventional fossil fuels ammonia were made.

2. Model Formulation

In the mid 70s, Veziroglu and Basar presented the mathematical model for the long-term calculation of technical, socioeconomic and environmental parameters related to the universal introduction of solar hydrogen as an alternative energy carrier instead of fossil fuels. After its first appearance the model was applied to many countries and regions as for example Libya, Pakistan, Egypt, Spain, United Arab Emirates, Brazil, Saudi Arabia and most recently to the State of Ceara, Brazil [11]. Basically in its original version, for a country or region of interest, the model interrelates parameters such as population, energy demand, energy production, gross national or domestic product, hydrogen production rates, fossil energy imports, world energy prices, air pollution, quality of life, environmental savings due to the higher utilization efficiency of hydrogen, by-product credit, agricultural income, income from hydrogen sale, photovoltaic cell area, total land area, water desalination plant capacity, capital investment, operation and maintenance costs, and total income from the system.

3. Data and Computation

The starting year in the simulation is 2000 and the period covered extends until the year 2100. Solar-wind generated hydrogen to produce ammonia in the State of Ceara is simulated to start in the year 2020. The initial data for the world and for the State of Ceara are shown in Table 1 [12].

Table 1 Initial data for the world and for Ceara (year 2000)

Variables description	Value for the world	Value for the State of Ceara
Population	6.1×10^9 Inhabitant	7.4×10^6 Inhabitant
Energy demand	208.07 EJ	0.13 EJ
Demand for nitrogen fertilizers		37.0×10^3 ton
Gross domestic product	45×10^{12} US$	11.5×10^9US$
Price of hydrogen	25.35 US$/GJ	25.35 US$/GJ
Price of natural gas	9.11 US$/GJ	9.11 US$/GJ
Price of ammonia	27.11 US$/GJ	27.11US$/GJ
Natural gas production	105.84 EJ	1.15 PJ
Imports of natural gas		0.69 PJ
Natural gas reserves	6.52×10^3 EJ	41.67 PJ
Pollution production	11.16×10^{12} kg	48.3×10^6 kg
Hydrogen energy production (year 2020)	3.2 EJ	2.75 TJ
Population growth doubling time	59 yr	40 yr
Energy demand growth doubling time	36 yr	12 yr
Energy consumption doubling time for improving quality of life	92 yr	17 yr
Gross domestic product doubling time	22 yr	10 yr
Gross product doubling time due to technological advances	57 yr	57 yr

Three different rates of hydrogen doubling time were chosen in order to show the effect of the hydrogen introduction on population, energy demand, gross production, pollution, ammonia production, etc.

$$\Theta_{hn} = 2.0 + 0.2(n-1) \quad (1)$$

$$\Theta_{hn} = 2.0 + 0.25(n-1) \quad (2)$$

$$\Theta_{hn} = \infty \quad (3)$$

The doubling times given by Eqs. (1) and (2) represent the respective fast and slow hydrogen introduction rates followed by the case where the doubling time equals to infinity corresponding to no hydrogen introduction instead of natural gas to produce ammonia.

It has been assumed that the solar-wind hydrogen for ammonia production will start at the year 2020 with the initial hydrogen production given as H_n = 2.75 TJ/year which corresponds to 2.42 tons of ammonia per day. The utilization efficiency ratio ηr (hydrogen utilization efficiency divided by fossil fuel utilization efficiency) is taken as 1.36. The conversion efficiency of the photovoltaic panels is taken as η_{pv} = 0.13 the efficiency of electrolyser is assumed as η_{el} = 0.75 until the year 2050 and η_{el} = 0.90 after that year, and the average annual insolation in the State of Ceara is assumed as S_{av} = 7.5 GJ/m^2/year. The environmental impact coefficient U and the ratio of pollution produced by hydrogen to that by fossil fuels ε are taken as 4.74 kg/GJ and 0.04, respectively [10]. The process of desalination of seawater will require 2.48 x 10^{-2} GJ of energy consumption per m³ of fresh water produced. Annual water consumption by electrolyser per GJ of hydrogen produced is 90×10^{-3} m³ of water per GJ of H_2. The annual demand for irrigation water per unit area is 5.66×10^5 m³/km²/year. The average annual agricultural income per unit area is assumed as 4.0×10^5 US$/km². The environmental damage cost per unit of fossil energy consumed is 12.52 US$/GJ. Credit for oxygen per GJ of hydrogen produced was taken as 3.50 US$/GJ. The capital required by electrolyser per GJ of hydrogen produced is given as 3.40 US$ /GJ. The cost of storage, compression and transmission of hydrogen has been taken as US$ 1.84 per GJ of hydrogen produced. Capital investment required for desalination plant per m³ of water 0.617 US$/m³ of fresh water. The annual cost of operation and maintenance per GJ of produced hydrogen required for electrolysis and storage, compression, and transmission, respectively, were taken as 0.68 US$/GJ and 0.4 US$/GJ, respectively. The annual O & M cost required for desalination plant per m³ of water is taken as 0.3 US$/m³ of fresh water. The annual capital required for the ammonia production plant is taken as 13.27 US$/GJ and the annual O & M cost required for the plant for production of ammonia is 0.07 US$/GJ of ammonia produced [12].

4. Results and Discussions

Sacramento et al. [11] developed studies about the introduction of a solar-wind hydrogen energy system for the State of Ceara and evaluated prospects for reducing emissions of fossil fuels pollutants. Using the same computational program of the present article, they presented long term evaluation of emissions of carbon dioxide, methane, sulphur oxide and nitrogen oxide of such State of when renewable hydrogen substitutes fossil fuels. Parameters such as population, energy demand, gross internal product, hydrogen and fossil fuels price, hydrogen energy production, fossil energy demand, import, and production, credit for by-product sale, environmental and economic aspects and quality of life indicator were also studied by such authors. Patricio et al. [12], using the same computational code of the present article, studied a wind hydrogen energy system aiming the gradual and long-term replacement of natural gas in the energy matrix of State of Ceara. Most of the results presented by the four above mentioned articles will be not reproduced or discussed here except those which are considered significant for analyses in the present article.

Although it was attributed three doubling times for introduction of hydrogen as seen in Eqs. (1) to (3) which characterize scenarios of fast, slow and no introduction of hydrogen in a region for the replacement of fossil fuels, it was observed for the present study that when applied there were no significant differences in the calculation of every parameters between the scenarios of fast and slow introduction of hydrogen when replacing natural gas for the synthesis of ammonia. This occurred due to the fact that the demand of nitrogen fertilizers in the State of Ceara is relatively not significant if it is put in terms of the energy demand of such State of because at the present time natural gas corresponds to only about 2% of the total energy demand of the State of Ceara and mainly it is used as fuel of automotive vehicles and in industry. Therefore, the doubling times of fast and slow introduction of hydrogen did not cause expressive differences between them. By this reason only two scenarios will be considered: the scenario of introduction and the scenario of no introduction of solar hydrogen for the synthesis of ammonia in the State of Ceara.

Fig. 1 presents annual solar energy resource of the State of Ceara [9]. It is observed that solar irradiation on such State of varies between 5.25 and 6.25 $kWh/m^2/day$.

There are regions where solar irradiation shows higher values than other regions, such as the central semi-arid and the Inhamuns regions, having the mean annual precipitation of less than 600 mm (± 240 mm standard deviation), reaching values as low as 200 mm during droughts [13]. This is one reason for the high value of solar irradiation on such region. The coastal region receives influence of the Intertropical Convergence Zone (ITCZ) and the south region of Ceara receives influences of cold fronts and upper tropospheric cyclonic vortex. That is also one reason why the coastal region of such State of receives a little lower solar irradiation than its interior and mountainous regions. Even so, it is a high level of solar irradiation when compared to other regions of the world.

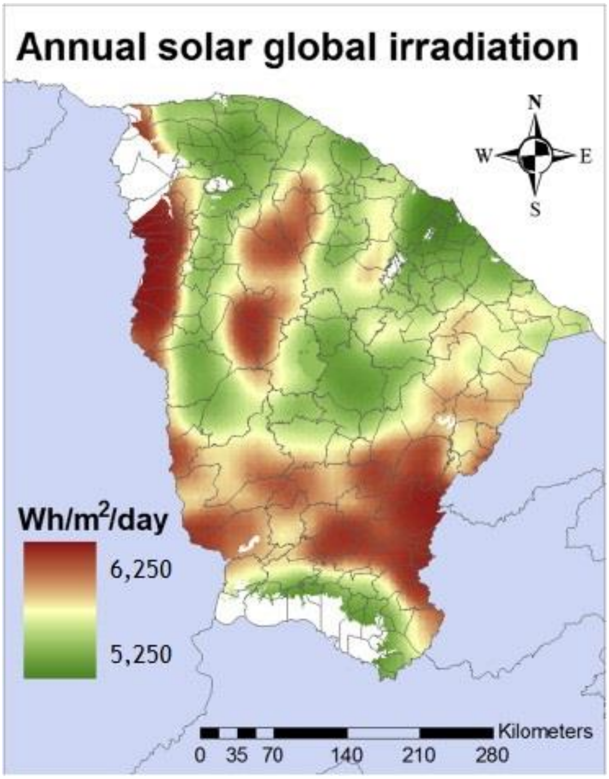

Fig. 1 Annual average daily solar radiation in the State of Ceara.

As can be observed in Fig. 2, the wind resource of the State of Ceara is strongly influenced by the trade winds in such State of, whose direction is predominately from East in this region. There is also a coupling during the day between the sea breeze and the trade winds that intensify the regime of coastal winds. The regions with higher values are seen in the coastal region, as well as locations in the mountainous regions, as for example, the Ibiapaba Mountain, located at the west of the State of Ceara. In the coastal region of such State of, at 50 m above the ground level the annual wind speed varies between 6.0 and 8.5 m/s.

Fig. 3 presents the projected demand of nitrogen fertilizers in the State of Ceara until the year 2100. In the year 2000 the consumption of fertilizer was about 37,000 tons. By the year 2100 it is expected the consumption of more than 400,000 tons of nitrogen fertilizers if Ceara continues in the trends of recent years. With the introduction of solar-wind hydrogen ammonia in 2020 the production will start with 800 tons and by the year 2057 the ammonia derived

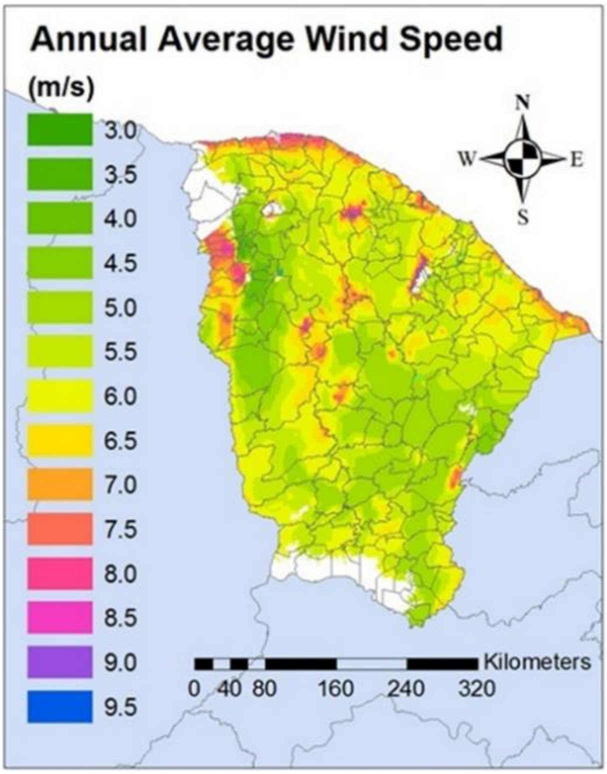

Fig. 2 Wind speed at 50 m above ground level at the State of Ceara.

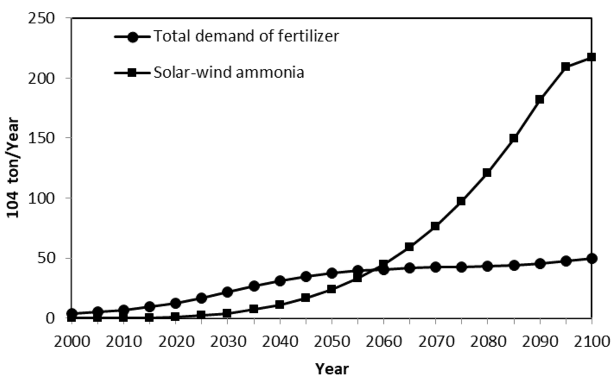

Fig. 3 Fertilizer demand and ammonia production of the State of Ceara, Brazil

nitrogen fertilizer production will be about 400,000 tons. If continued the production of solar-wind hydrogen derived nitrogen fertilizer will reach 2.2 million tons by the year 2100.

It is known that an all-electric ammonia plant based on solar-wind hydrogen will face a series of technical challenges. Although there is presently an abrupt reduction in the cost of renewable energy electricity turning it possible the green production of ammonia at least at economical point of view, its intermittency may cause poisoning catalyst due to the oxygen sensitivity of the Haber Bosch process which is still today the most developed process of producing ammonia. Other challenges are: the development of economical down-scaling to regional or local scales to avoid the need for transport networks, robustness and resilience to upsets or utility interruptions, intermittent operability from intermittent renewable resources, and technological simplicity [14]. After electricity prices and plant size, high load factors would be next important factor for ammonia plants. This is another reason why new opportunities for ammonia production based on solar and wind must be considered in best resources area and the State of Ceara is an example of them [15].

On the other hand, there is also problem of availability of water mainly due to the fact that the State of Ceara is located in a semi-arid region of the Brazilian northeast. The idea of the present proposal is to produce hydrogen derived from the desalinated seawater since the State of Ceara has a coastal extension of about 580 km. By the year 2060 the State of Ceara eventually will be producing about 400,000 tons of ammonia and this amount will need about 650,000 cubic meters of water with high degree of purity to feed electrolysers. As highlighted by Philibert [15], only the mechanical vapor compression process (MVC) can provide large-scale amount of water with sufficient degree of purity.

Fig. 4 presents the dimensionless pollution ratio as a function of time. It can be seen that if no solar-wind hydrogen is introduced for the production of ammonia, pollution would increase and at around the year 2060 will be 8 times the value of the pollution at the year 2000. The introduction of renewable energy hydrogen for the production of ammonia instead of natural gas would reduce the pollution ratio to about 0.5 after that year. The emissions of pollutants such as CO_2, NOx, SO_2 and CO will be 680,000, 520, 4 and 12 tons, respectively, if the production of ammonia still continue by natural gas. Others materials and emissions such wasted catalysts, ammonia itself, methanol and amines eventually will also be released to the environment [7].

Assuming 54 kWh per kg of hydrogen delivered at 30 bar and 234 kWh per ton of nitrogen delivered at 40 bar it results in about 10,200 kWh to produce a ton of ammonia [4, 14]. Hydrogen will consume 93.5%, nitrogen 0.7%, the Haber-Bosch will consume 5.5% and the mechanical vapor compression (MVC) for desalinating seawater will consume 0.3%, respectively, of such total [7].

Fig. 5 shows the price of ammonia per ton during the studied period. The official price of natural gas ammonia at the year 2000 was at the average of about US$ 200 per ton [16]. At that year, the present study shows that solar-wind produced ammonia would be about US$ 950 per ton. Around the year 2025 the price of fossil fuel derived ammonia will be practically equal to the price of each ton of solar-wind ammonia produced at such State of. At the end of the period studied here the price of fossil fuel derived ammonia will reach about US$ 500 per ton while the solar-wind ammonia produced at the State of Ceara will reach about US$ 300 per ton.

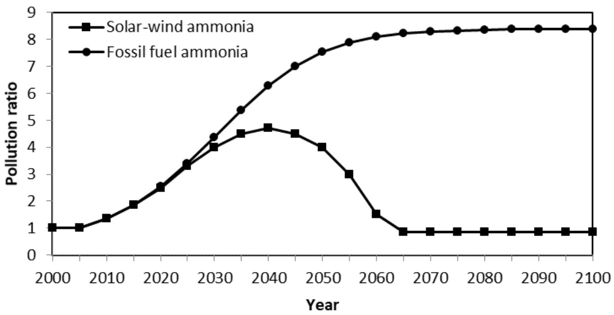

Fig. 4 Pollution ratio.

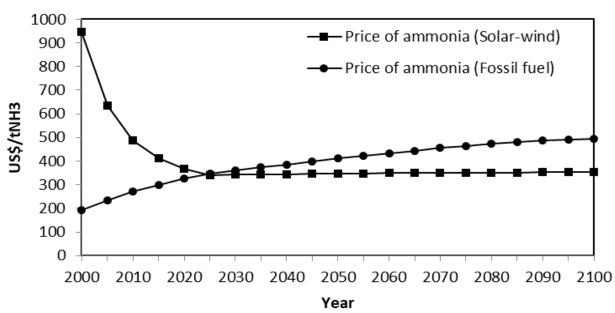

Fig. 5 Prices of ammonia.

5. Conclusions

The worldwide use of natural gas as feedstock to produce ammonia will put pressure on the price of nitrogen fertilizers because such fossil fuel is on route of total depletion. Although presently there are still many technological challenges to be tackled and relatively high cost, the solar-wind hydrogen to produce ammonia presents optimistic perspectives soon for regions where such renewable energy is abundant.

Results of the present study show the high potential of the state of Ceara, Brazil for producing solar-wind derived ammonia with the objective of supplying the market of nitrogen fertilizers in Brazil.

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