The challenge of Hydrogen production for the transition to a CO_2-free economy

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Abstract: The energy demand of the world is foreseen to be increased due to the improvements on the living standard of the developing countries and the development of the global economy. The increase in sustainability of the energy supply must be considered as a must to avoid spoiling natural resources for the next human generations and more dramatic effects such as the so-called global atmospheric warming. The utilization of CO_2-free energy sources, as in the case of renewables, is one of the most promising ways to attain such objectives. Nevertheless, the massive energy production with such energy sources are far from being practically feasible in the short-medium term and an innovative solution should be put into practice for the CO_2-free exploitation of the huge fossil fuel resources already available. This general assumption is also applicable to any energy carrier such as Hydrogen or electricity. In this case, an analysis is done of the Hydrogen production processes and the discussion of the need to develop a CO_2-free production scheme like methane cracking is shown.

Key words: Hydrogen, Low-Carbon, methane cracking

Introduction

One of the most important challenges of the humankind is how to cover the energy demand that is required to sustain its living standards and future development. The current energy system is mainly based on the utilization of fossil fuels by their oxidation, producing greenhouse gases that misbalance the on-going Carbon cycle in the atmosphere. Such a misbalance will produce disastrous climatic effects that put into risk not only the present landscape configuration (sea level, glacier, forest, and so on), but also the human environment as in the case of agriculture (draughts, temperature increase, ecosystem chance). The environmental concerns about climate changes and the limited availability in the future of fossil fuels force the transformation of the energy system from a scheme mainly based on the combustion of fossil fuels to one based on sustainable CO_2-free sources.

Hydrogen production processes

There is a wide range of processes to produce Hydrogen. Briefly, those methods are:

- Electrolysis: to split the water molecule by means of electricity. The primary energy could be a CO_2-free renewable energy such as PV, wind, solar thermal, and so on, as well as nuclear. Fossil fuel electricity production technologies based on coal, oil or natural gas such as coal-fired plants, Combined Cycle plants, could be used in combination with Carbon Capture and Sequestration (CCS) or Carbon Capture and Use (CCU). Among these methods, plasma-arc decomposition of natural gas can also be included.
- Hydrogen sulphide (H_2S) cracking by thermal catalytic methods or cyclical reactions.
- Thermochemical processes, with fossil fuels and water using direct thermal energy from thermal renewables or nuclear energy, such as coal gasification and fossil fuel reforming combined with CCS or CCU.
- Thermochemical cycles, based on oxide/metal oxide, or Sulphur cycles, proposed with thermal sources, either renewables (solar) or nuclear.
- Biochemical processes, with biomass as a Hydrogen source and water, as bio-photolysis, photo-fermentation, using solar energy in combination with bacteria, or biomass reforming and gasification.

Among these options, the technological portfolio of the energy scenarios considers for Hydrogen production the following technologies:

- Gas Steam Reforming, with/without CO_2 capture.
- Coal partial oxidation, with/without CO_2 capture.
- Biomass pyrolysis
- Solar high temperature thermolysis.
- Nuclear high temperature thermolysis.
- Water electrolysis, based on nuclear, wind or baseload electricity.

Presently, about 48% of the Hydrogen comes from natural gas steam reforming, 30% from naphta/oil reforming in the chemical industry and 18% from coal gasification. These figures imply that 96% of the Hydrogen production in the world comes from fossils, with a sensitive amount of CO_2 emissions. Only 4% of worldwide Hydrogen production is based on water electrolysis (Guerrero-Lemus & Martínez-Durant, 2010), that can be adapted to a CO_2-free production if it is produced with renewable sources. This fact is the consequence of the cost competitiveness of the production methods.

It is expected that the development of renewable technologies could bring water electrolysis from wind and solar, or thermochemical solar to a competitive market. Nevertheless, it is expected that fossil fuels will play a fundamental role in the future. For instance, the forecast for Hydrogen production of the European Commission (EUR 2038, 2006.) assumes that 30% of the Hydrogen production in 2050 will come from coal, and that will displace natural gas steam reforming as the main fossil source due to a more favourable raw material price. Among the CO_2-free sources, nuclear would be of the order of 15% and renewables around 60%.

The Hydrogen production methods based on CO_2-free technologies are the great hope for a future implementation of a sustainable Hydrogen economy. Anyhow, those technologies are into a development phase, and a transition phase will be required to transform a Hydrogen production market based on fossils with CO_2 emissions to a full renewable CO_2-free system, that will be able to drive a Hydrogen based economy, or with a substantial use of Hydrogen ad end-use energy.

As an additional technology under study for this transition, methane decarburation or methane cracking is a scientifically proven process that is based on the splitting of the methane into its atomic components (Carbon and Hydrogen), obtaining Hydrogen without CO_2 emissions. Table 1 shows a basic comparison between methane cracking and the most relevant Hydrogen production methods from fossil fuels. Either in coal gasification or natural gas steam reforming, the CO_2 emissions may avoid the full application of Carbon Capture and Sequestration, which is considered an adaption technology, as the risk of gas release may imply a final emission to the atmosphere. On the other hand, methane cracking does not produce CO_2, but Carbon aggregates that should be managed, either as a waste, or as a commodity for another purpose.

The development of methane cracking opens the path to exploit the huge known natural gas resources avoiding CO_2 emissions. The utilization of fossil fuels in many of the reference cases based on 'business as usual' establishes a stabilising atmospheric concentration of greenhouse gas emissions at around 650 ppm, resulting in a probable temperature rise of 3.5°C in the long term, well below the accepted 2°C target. Therefore a lot of effort should be done to provide the mechanisms and technologies that could avoid that situation.

Table 1. Comparison of fossil fuel based Hydrogen production processes

	Methane steam reforming	Coal gasification	Methane pyrolysis
Reaction	$CH_4+2H_2O=CO_2+4H_2$	$C+2H_2O=CO_2+2H_2$	$CH_4=C+2H_2$
Heat of reaction kJ $(mol\ C)^{-1}$	235.00	178.15	74.85
Heat of reaction kJ $(mol\ H_2)^{-1}$	63.25	89.08	37.43
Energy efficiency in transformation (%)	74	60	55
Energy efficiency with CCS (%)	54	43	55
CO_2 emission, mol CO_2 $(mol\ H_2)^{-1}$	0.34	0.83	0.05
CO_2 emission with CO_2-free energy source mol $CO_2 (mol\ H_2)^{-1}$	0.25	0.5	0
CO_2 production with CO_2-free energy source kg GJ^{-1}	61.1	150.9	0
Carbon production kg GJ^{-1}	0	0	24.8

One of the main problems to develop methane cracking is the stability of the strong C–H bond, what implies the need of very high temperatures. The Gibbs energy (Villacampa et al., 2003) for methane decarburation reaction equals zero at 819 K (°C), what implies that this reaction will theoretically take place above this temperature. Nevertheless, this energy threshold may be affected by other components that could be included in the reaction, as a catalyst or reaction media.

Several groups are working in the quest for a practical implementation of this reaction. They are basically based on the direct thermal cracking of methane (Rodat et al., 2011; Dahl et al., 2004; Steinberg, 1999; Hirsch, 2004) or in catalyst methane thermal cracking (Suelves, 2007; Villacampa et al., 2003; Muradov & Veziroglu, 2008). Both methods have found significant difficulties still unsolved due to the coke formation that either produces a blockage of the system, or de-activates the catalysts rapidly, which make the process very difficult to implement at an industrial scale.

Hydrogen production costs

Hydrogen cost in the future has some uncertainties that will depend on the technological development in the case of Hydrogen from renewables sources, and the price in the case of fossil fuels. On the other hand, there are a lot of components in the integral cost for Hydrogen delivery that will make a difference. Hydrogen cost depends on the cost of the production technology (which is comprised of capital investment, operation & maintenance and feedstock cost), and the cost of Hydrogen transportation.

Table 2 shows the average production cost of some Hydrogen production technologies. The most competitive means for Hydrogen production are based on coal gasification and steam methane reforming. Nevertheless, the implementation of these technologies should be implemented with Carbon Capture and Sequestration (CCS) to avoid environmental effects or the impact of the carbon taxes that would be charged to the CO_2 emission sources. The application of CCS increases the production cost more than 30% in some cases as a result of the large fraction of energy that should be used for carbon sequestration and its management.

Hydrogen production from methane cracking has been analysed by different authors, and in particular, into the SOLYCARB project (Rodat et al., 2011; Sattler, 2009). As a Hydrogen production process, its cost was estimated in the order of 3–4 \$ (kg $H_2)^{-1}$, which is clearly uncompetitive in comparison with existing fossil fuel technologies at the current state-of-the-art of the solar tower technology, which is able to reach the temperatures needed for direct thermal cracking (>1000ºC). Nevertheless, the potential target cost would be reduced if the heliostat and receiver cost is reduced, as it represents a substantial capital investment.

On the other hand, in a transition period, in which the solar technology should be developed to achieve sensitive cost reduction, the burning of the H_2 that is produced in the system may drive the methane decarburation reaction. In that case, the capital costs of the solar equipment disappear, and the H_2 production cost can be expected to be reduced as to be competitive with Steam Methane Reforming without Carbon Capture and Sequestration. In any case, the industrial development of this technology should be envisaged to achieve this goal.

Table 2. Cost of Hydrogen production technologies

Technology	Fuel	Prod. Cost ($ kg^{-1})	Referents
Central Steam Reforming	Natural gas	1.5	Guerrero-Lemus & Martínez-Durant, 2010; Pregger, 2009
Distrib. Steam Reforming	Natural gas	2.6	Guerrero-Lemus & Martínez-Durant 2010
Gasification	Coal	1.2	Guerrero-Lemus & Martínez-Durant 2010
Gasification with CCS	Coal	1.8	Guerrero-Lemus & Martínez-Durant, 2010; Pregger, 2009
Gasification	Biomass	1.4	Guerrero-Lemus & Martínez-Durant 2010
Distributed electrolysis	Grid electricity	6.8	Guerrero-Lemus & Martínez-Durant 2010
Central electrolysis	Wind	3.8	Guerrero-Lemus & Martínez-Durant 2010
Distributed electrolysis	Wind	7.3	Guerrero-Lemus & Martínez-Durant 2010
Thermochemical cycle	Nuclear	1.4	Guerrero-Lemus & Martínez-Durant 2010
Pyrolysis/Cracking	Natural gas + solar	3.0	Villacampa et al., 2003; Hirsch, 2004
Pyrolysis/Cracking	Natural gas + solar	3.6	Muradov & Veziroglu, 2008
Pyrolysis/Cracking	Natural gas + solar	4.5	Dahl et al.,2004
Steam Reforming	Natural gas + solar	2.2	EU project SOLREF…
FV electrolysis	Solar	9.1	Pregger, 2009
Solar thermoch. S cycles	Solar	5.3	Pregger, 2009
Sol. thermoch. Oxide/metal	Solar	8.3	Pregger, 2009

Conclusion

The transition to a low-Carbon Hydrogen production should follow a process in which fossil fuels are going to play a fundamental role to feed the market with Hydrogen to develop its utilization technology (fuel cell, mobile applications, hybrid fuel cell/internal combustion engine), providing its availability at a reasonable price. The technological development of production techniques based on sustainable, renewable energies (wind, solar, biomass) would make possible the gradual substitution of fossil-based by low-Carbon Hydrogen. In this transition, the environmental concerns regarding greenhouse gases emission to the atmosphere is a very important issue, which will lead to Hydrogen production scenarios in which either carbon capture and sequestration or decarburation could be applied as mitigation or adaptation measures to avoid CO_2 release.

On the other hand, Hydrogen is also envisaged as an energy carrier that could have an important role in reducing the environmental effect of fossil fuels. In particular, the transformation of natural gas or coal into Hydrogen is an alternative to reduce CO_2 release by combustion processes either in the transport sector or for electricity production. In that sense, the development of CO_2-free technologies to exploit fossil fuels is a must to make their utilization compatible with emission reductions. New innovative solutions should be put into practice. To attain this goal, methane cracking is a promising alternative.

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