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Exergy & Environmental Based Comparison of Hydrogen Production from Natural gas, Carbon and Nuclear energy

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Abstract

Hydrogen is an important energy carrier which could play a very significant role in the reduction of emissions of greenhouse gases. The route by which hydrogen is produced is the determining factor for its environmental performance. Hydrogen can be produced through methane reforming, coal gasification or through the electrolysis of water with the use of electricity. However, as these processes involve environmental and energy security concerns, it is of great importance to assess their environmental and energy performance. In this study, the environmental and exergy performance of auto thermal reforming of natural gas, coal gasification and thermochemical water-splitting are evaluated. It is noted that in the thermochemical water-splitting, decomposition reactions take place to produce H2, according to the method of sulphur-iodine. The increased temperature requirements are covered by a nuclear reactor H2-MIR. The calculations reveal that the exergy efficiency of CO2 sequestration reaches 70.3%; whereas the exergy efficiency of carbon gasification process to comes up to 35.8%.

Keywords: Exergy Analysis; LCA: Hydrogen production; Carbon Sequestration; Nuclear energy

1. Introduction

Concerns about security of energy supply, increased fuel prices, and the impact of emissions of carbon dioxide on global climate change has forced European Union (EU) to search for alternative energy sources. The impact of above factors on the energy sector is going to be intensified in the short and medium term as a result of increased energy demand (European Commission, 2003) and the continuing reliance on fossil fuels. Based on the abovementioned, EU, in order to improve the energy sustainability, has focused on the development of hydrogen energy sources to complement electricity and liquid fuels. It can be used in almost every sector where energy is required—transport, households and services, and in industry. Hydrogen can be produced by using three different energy-supply system classes, namely, fossil fuels (coal, petroleum, natural gas and as yet largely unused supplies such as shale oil, natural gas from geo-pressured locations, etc.), nuclear reactors including fission reactors and breeders, and renewable energy resources (including hydroelectric power, wind power systems, ocean thermal energy conversion systems including biomass production, photovoltaic energy conversion, solar thermal systems, etc.). The successful deployment of the hydrogen-including economy in Europe necessitates the identification of the promising production pathways, both on the large and small scale, that are likely to contribute to the successful penetration of hydrogen in the energy market in the short and medium term. In this context, this study aims to perform a comparative environmental impact study of three different hydrogen production methods. The goal is to provide useful and practical recommendations to policy makers in terms of research and development. Environmental impacts (global warming potential, GWP and acidification potential, AP) as well as exergy efficiencies of three different methods are compared. The method include: the production of hydrogen via natural gas steam reforming, coal gasification, thermochemical water-splitting and the sulphur-iodine method in a nuclear reactor. All three methods are catalytic and they take place at high temperatures.

2. Background : Hydrogen Production Methods under study

2.1. Steam reforming

Steam reforming is the most common method to produce hydrogen. In steam reforming, natural gas is first cleaned of impurities, mixed with steam and passed over an externally heated reactor, carbon monoxide (CO) and hydrogen (H2) are generated. After this step, a catalytic water - gas shift reaction converts the CO and water to hydrogen and carbon dioxide (CO2). The hydrogen gas is then purified. With this technology, it is possible to reach yields higher than 80% in large reformers (Royal Belgian Academy, 2006). The process (Fig.1) takes

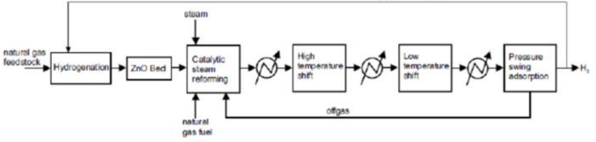

Figure 1. Hydrogen production via natural gas (Spath and Mann, 2001)

into consideration the following stages: Air separation unit, Pre-reform, Flue and adsorption of sulphur, Auto thermal reactor, Catalytic conversion of steam-water gas, CO_2 sequestration and Pressure-oscillation-adsorption unit.

2.2. Gasification

The most common method for hydrogen production from coal is carbon gasification with CO_2 sequestration. The by-products of the process are hydrogen and electricity. Hydrogen can be used directly as fuel or in combination with fuel cells, while the electricity is used entirely to meet the energy requirements of the CO_2 sequestration process. To be more specific, during the coal gasification process, coal is partially oxidized with steam and oxygen in a high-temperature and high-pressure reactor. The products are mainly CO and H_2, mixed with steam and CO_2 (syngas). To increase the hydrogen yield, the syngas undergoes a shift reaction. In order to recover elemental sulphur (or make sulphuric acid), the gas can be cleaned in conventional ways. If some of the syngas is used in a gas turbine, electricity can be generated. The major concern about coal gasification is the high carbon content of coal as the CO_2 emissions are higher compared to other feedstock options. In order to address this problem, CCS (Carbon Capture and Storage) technologies are being developed. The process of hydrogen production via gasification (Fig. 2) takes into consideration the following stages: Air separation unit, Carbon and water process, Gasification, Unit of heat recovery and particulate removal, COS-hydrolysis unit, Conversion reactors, H_2S recovery unit, CO2 sequestration, Unit of Pressure- Oscillation-Adsorption and the Cooling tower.

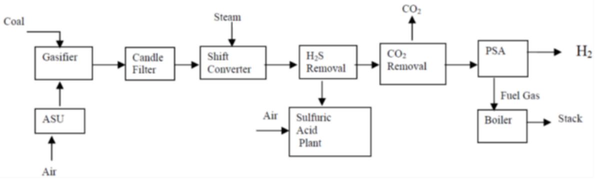

Figure 2. Hydrogen production via coal gasification (NETL,2006)

2.3. Hydrogen production from nuclear energy

Hydrogen can be produced by thermochemical water-splitting cycles that operate at temperatures of 500 0C or more using nuclear reactors (Marcus and Levin, 2002). Faster reaction rates and higher efficiencies can be achieved at higher temperatures. So far, more than 100 different high temperature water-splitting thermochemical reactions have been proposed (Brown *et al*, 2002). The process under study is considered to be the Sulphur-iodine (Fig. 3). The sulfur-iodine cycle requires a heat source capable of producing temperatures of 1000^0C. Since current light-water reactors operate at nominal 600 degrees, new generation high-temperature gas-cooled reactors must be used. Materials used for construction must be able to withstand high temperatures. Hydrogen production with the method of sulfur – iodine includes the following processes: i) Production and sulphuric acid separation with modern production of pure O_2 ii) Concentration and decomposition of sulphuric acid iii) Concentration of HI iv) Separation of HI and production of pure H_2

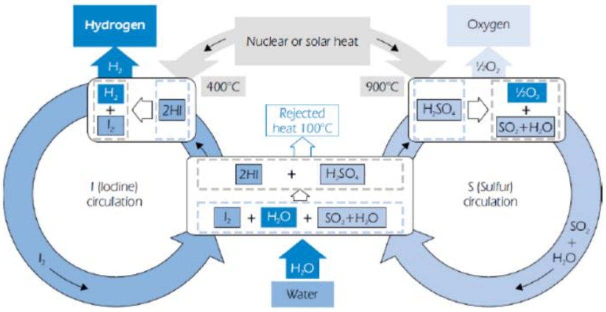

Figure 3. The concept of hydrogen production via sulphur – iodine method (IEA,2006)

3. Methods

Life Cycle Analysis and Exergy Analysis are employed for the purposes of this study. Life Cycle Assessment (LCA) is a tool that helps to evaluate the environmental performance of products and processes through the product's life- span from mining, its manufacture, use to its final disposal (Curran, 2006, ISO, 2006a, ISO, 2006b). LCA evaluates all stages of a product's life from the perspective that they are interdependent, meaning that one operation leads to the next. By including the impacts throughout the product life cycle, LCA provides a comprehensive view of the environmental aspects of the product or process and a more accurate picture of the true environmental trade- offs in product and process selection. LCA generally has four main phases: (i) goal and scope definition to specify intention, application and stakeholders, (ii) the life cycle inventory data collection phase on material and energy flows during the life cycle e during this phase, emissions and consumed resources are identified and quantified, (iii) life cycle impact assessment (LCIA), builds on the inventory results by assessing the environmental significance of each, and (iv) LCIA results are evaluated and recommendations to reduce environmental impacts of products are discussed. Exergy is defined as the maximum amount of work which can be produced by a system or a flow of matter or energy as it comes to equilibrium with a reference environment. Exergy measures the potential of the system or flow to cause change as a consequence of not being in stable equilibrium relative to the reference environment (Rosen and Dincer, 2001). Exergy analysis is an assessment tool based on exergy, in which exergy flows, balances, destructions and efficiencies are determined for an overall process or system and its subparts. Exergy analysis permits many of the shortcomings of energy analysis to be overcome. Exergy analysis is based on the second law of thermodynamics,

and is useful in identifying the causes, locations and magnitudes of process inefficiencies. Exergy analysis acknowledges that, although energy cannot be created or destroyed, it can be degraded in quality, eventually reaching a state in which it is in complete equilibrium with the surroundings and hence of no further use for performing tasks (Dincer and Rosen 2007).

4. Results

The total daily production of H_2 is estimated as 850,000 Nm3 H_2, which is equivalent to 85PJ/ year or 2700 MW. In this case, the exit pressure of the H_2 product is 60 bar and the energy efficiency of the plant reaches nH = 72%. The functional unit, also known as the production amount that represents the basis for the analysis, was chosen to be the net amount of hydrogen produced. The results of the LCA of the total production process take into consideration both auto thermal reforming of natural gas and CO_2 (case b) sequestration as well as absence of CO_2 sequestration (case a). Table 1 summarizes the abovementioned results. The results indicate that the two processes have approximately the same environmental impacts, except for the impact on earth's temperature as well as the impact on water and land contamination. This difference is attributed to the CO_2 sequestration unit.

Table 1. Comparative LCA of hydrogen production via steam reforming with (case b) and without (case a) CO_2 sequestration

Environmental Impacts	Case a	Case b	Units
Inventory Reduction	$1,07*10^{-1}$	$1,07*10^{-1}$	Kg Sb- eq.
Increase temperature of the earth	$8,44*10^{1}$	$1,96*10^{1}$	Kg CO2- eq.
Reduction of stratospheric ozone	$2,30*10^{-9}$	$2,30*10^{-9}$	Kg CFC- eq.
Pollution of coastal areas	$1,07*10^{2}$	$1,07*10^{2}$	Kg 1,4 DCB- eq.
Water Contamination	$4,36*10^{-3}$	$4,47*10^{-3}$	Kg 1,4 DCB- eq.
Land contamination	$3,43*10^{-4}$	$4,88*10^{-4}$	Kg 1,4 DCB- eq.
Acidification	$1,31*10^{-2}$	$1,34*10^{-2}$	Kg SO2- eq.
Eutrophication	$8,70*10^{-4}$	$8,81*10^{-4}$	Kg $PO3^{-4}$- eq.
Human diseases	$4,90*10^{1}$	$8,59*10^{-1}$	Kg 1,4 DB- eq.

The environmental impacts of hydrogen production via coal gasification are listed in Table 2. The results are also compared with those of Table 1 – regarding hydrogen production without CO_2 sequestration (case b). Hydrogen production from nuclear energy has many differences – compared to the other two methods. This is mainly attributed to the fact that through all stages – from mining to final production of hydrogen-, radioactive material is emitted. The stages (Fig. 4) of the above-mentioned process include:

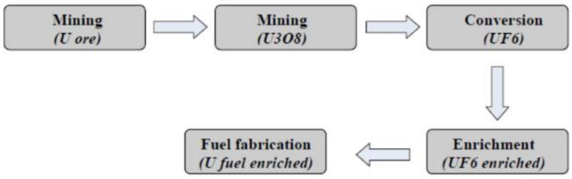

Figure 4. Uranium fuel cycle (Ozbilen *et al*, 2011)

Natural uranium mining: Natural uranium contains a small percentage of the active isotope U-235 (at a concentration of only 0.71%), while the largest percentage of it, includes the isotope U-238 which cannot be used as fuel. Industrial cleaning and production of U3O8: The extracted natural uranium is converted to peroxide of uranium (U3O8).Enrichment: UF6 that it is produced in the conversion process contains only 0.71% of the required isotope. At the stage of enrichment, the concentration of fuel in U-235 is increased to 3.25%.

Table 2. Comparative LCA of hydrogen production via steam reforming with (case b) and without (case a) CO_2 sequestration

Environmental Impacts	Case a	Case b	Units
Increase temperature of the earth	1,56	$4,9*10^{-1}$	eq.-kg CO_2
Acidification	$5,03*10^{-4}$	$3,19*10^{-4}$	eq.-kg SO_2
Eutrophication	$8,72*10^{-1}$	$9,43*10^{-1}$	eq.-kg PO^{3-}_4
Reduction of stratospheric ozone	$1,89*10^{-3}$	$2,7*10^{-3}$	eq.-kg CFC
Land contamination	$8,27*10^{-6}$	$6,55*10^{-7}$	eq.-kg1,4 DCB
Water contamination	$8,00*10^{-6}$	$1,19*10^{-5}$	eq.-kg1,4 DCB
Human diseases (water)	$1,11*10^{-2}$	$1,08*10^{-2}$	eq.-kg1,4 DCB
Human diseases (air)	$2,16*10^{-8}$	$3,21*10^{-8}$	eq.-kg1,4 DCB
Carcinogenesis	$2,02*10^{-8}$	$1,69*10^{-8}$	eq.-0,453 kg benzol
Inventory Reduction	$5,66*10^{-3}$	$5,53*10^{-3}$	eq.-Kg Sb
Water requirements	1,43	1,84	

Table 3 summarizes the emissions produced from the enrichment of 1 kg of uranium. Fuel Production: The H2-MHR reactors use fuel UCO powders in a quantity of uranium same as in the use of UO2. Then the fuel is shaped in pallets and it is placed into thin zirconium rods. Heat production in nuclear reactors: The produced fuel enters the reactor. The process is regulated to ensure stable decomposition rate of neutrons. H_2 production: The required heat from the reactor is used in the decomposition reaction of sulphuric acid. The produced H_2 exits the process at a pressure of 50 atm. Transport and storage of the produced fuel: U-238 is cooled before final soil deposition, in order to avoid conversion to plutonium. The final storage takes place in large geological reservoirs. Therefore, the entire waste fuel quantity of reactor (3.27 * 10-3 m3) must be used properly. Table 3 summarizes the LCA results of production of 1 TJ hydrogen. Exergy efficiencies are calculated as per below equation:

$$\Psi = \frac{\dot{m} * ex^{ch}}{\dot{E}x_{in}} \qquad (1)$$

where ex^{ch} is the chemical exergy of hydrogen and *Exin* is the rate of exergy input into the process. **Fig. 5**, depicts the calculated exergy efficiencies for the three hydrogen production methods under study

Table 3. Comparative LCA of hydrogen production via steam reforming with (case b) and without (case a) CO_2 sequestration

Env. Impacts	**Quantity**	**Units**
Inventory Reduction	9.75	Kg Sb- eq
Increase temperature of the earth	$2.46*10^3$	Kg CO_2- eq
Reduction of stratospheric ozone	$1.19*10^{-2}$	Kg CFC- eq
Contamination of coastal areas	$1.98*10^6$	Kg 1,4 DCB- eq
Water contamination	$6.67*10^2$	Kg 1,4 DCB- eq
Land contamination	$1.98*10^6$	Kg 1,4 DCB- eq
Acidification	$1.61*10^1$	Kg SO_2- eq
Radiation	$8.98*10^{-5}$	Inability to regulate life years
Eutrophication	$7.88*10^{-1}$	Kg PO^{3-}_4- eq
Human diseases	$3.88*10^3$	Kg 1,4 DCB- eq

5. Conclusions

In this study, a comparative assessment is performed to evaluate and compare environmental and technical performance of selected hydrogen production methods. Natural gas steam reforming, coal and nuclear based high temperature sulphur – iodine thermochemical cycle are compared based on their impacts to the environment as well as on their exergy efficiency. The results indicate that hydrogen production via natural gas and carbon emit greenhouse gases (CO_2, CH_4, and N_2O); therefore, the use of a CO2 sequestration unit is of great importance. Despite the fact that the operation of a nuclear plant does not emit CO_2, there is a significant Global Warming Potential contribution of using this option. In the nuclear plant, the nuclear fuel cycle (mining, fabrication and transportation) accounts approximately for 63% of the total CO_2 emissions; whereas materials, construction, operation and waste disposal contribute for 5%, 8%, 15%, and 9%, respectively. In terms of exergy efficiency the method of hydrogen production from natural gas has an advantage over the corresponding thermochemical process in a nuclear reactor using the sulfur-iodine method. However, the sulfur-iodine method is open to further improvements, particularly at the stage of decomposition of sulfuric acid. It is also noted that in the case of autothermical reformer, the efficiency of CO2 sequestration is 85% and the efficiency of the exergy process reaches 70.3%.

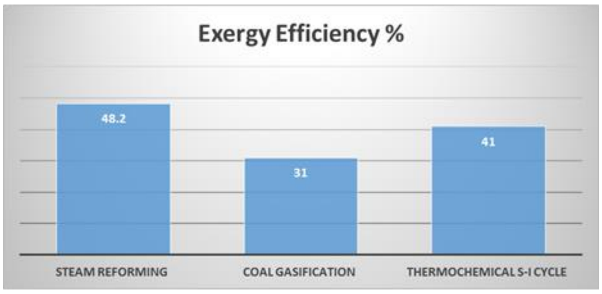

Figure 5. Calculated exergy efficiencies

Exergy efficiency of hydrogen production via carbon gasification process reaches 35.8%. Nonetheless this method does has a low score, in terms of environmental impacts. On the other hand, the autothermal steam reforming process and thermochemical water-splitting method with sulphur-iodine have an advantage in terms of exergy efficiency. The method that has both a good performance in terms of exergy efficiency and low environmental impacts is that of autothermal steam reforming of natural gas. The overall process of H2 production from natural gas outweighs the corresponding process using H2-MHR reactor in environmental exergy impac

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