Environmental Impact Comparison of Steam Methane Reformation and Thermochemical Processes of Hydrogen Production

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Abstract

This paper compares the environmental impact of various processes of hydrogen production, particularly steam methane reforming (SMR) and the copper-chlorine (Cu-Cl) and modified sulfur-iodine (S-I) thermochemical cycles. Natural gas is used as the energy source for each of the different methods. Also, an integrated Cu-Cl and SMR plant is examined to show the reduction of greenhouse gas emissions by modifying existing SMR plants with thermochemical processes. The analysis shows that the thermochemical Cu-Cl cycle out-performs the other conventional methods of hydrogen production, with lower fuel requirements and carbon dioxide emissions.

1 Introduction

Various methods and technologies currently exist for producing hydrogen. However, most of these are based on reforming of fossil fuels and thus emit carbon dioxide to the atmosphere [1-3]. Water electrolysis accounts for about 3 % of the world’s total hydrogen production. It is an environmentally friendly method, provided the source of electricity is clean. However, it is very energy intensive and it has relatively low efficiencies, especially when the efficiency of the generated electricity from a thermal power plant is taken into account. Thermochemical water splitting cycles are clean and more efficient alternatives to produce hydrogen, and they can be driven by various types of energy sources (i.e., nuclear, solar, geothermal or conventional fossil fuels). They can be linked with nuclear power plants for hydrogen production [4, 5]. Currently, active research around the world is being conducted for sulfur-iodine (S-I), copper-chlorine (Cu-Cl) and hydrogen sulfur cycles [6-11].

Unlike coal gasification and SMR (steam-methan reforming), thermochemical cycles use water as the feedstock for hydrogen, not fossil fuels. Thermochemical cycles can be linked to various types of energy sources, so they offer great flexibility and sustainability. The heat requirements of the Cu-Cl thermochemical cycle have been presented by Wang et al. [8, 9]. The cycle efficiency was found to be 46 % in Ref. [9]. The Cu-Cl cycle can operate at relatively low temperatures below 550 ^{o}C, whereas the S-I thermochemical cycle requires high temperature nuclear reactors with temperatures up to 900 ^{o}C.

This paper investigates the potential benefits of linking SMR and natural gas supplies with thermochemical cycles, in order to reduce greenhouse gas emissions and costs of conventional methods of hydrogen production. The paper specifically examines the feasibility of linking SMR with Cu-Cl and S-I thermochemical cycles and their potential comparisons, with respect to water and fuel requirements, as well as greenhouse gas emissions and cost comparisons.

2 Processes of Hydrogen Production

Hydrogen can be produced from a range of processes, i.e., reforming of fossil fuels, electrolysis, thermochemical water splitting, or biological hydrogen production. Currently, steam methane reforming (SMR) is the most widely used process to produce hydrogen, followed by other reforming methods such as coal gasification. Carbon-based methods emit large quantities of carbon dioxide, which motivates the need to develop alternative and sustainable methods of generating hydrogen. Thermochemical cycles, particularly the Cu-Cl and S-I cycles, are among the most promising large-scale alternatives.

Steam methane reforming consists of four main steps: desulfurization, catalytic reforming, CO conversion, and gas separation [2]. Figure 1 shows a schematic of an SMR plant. In the desulfurization step, sulfur-organic compounds in natural gas are converted to H_2S by a catalytic hydrogenation reaction. Then it is scrubbed by a ZnO bed to produce ZnS and H_2O. The removal of sulfur from natural gas is required because it poisons the catalyst used in the next step. In the catalytic reforming step, natural gas and steam react at a temperature of about 900 °C to produce hydrogen and CO through the following endothermic reaction:

$$CH_4 + H_2O \rightarrow 3H_2 + CO \qquad (1)$$

The products of the first step continue to the third step, where CO and steam react again in an exothermic reaction to produce more hydrogen as follows.

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (2)$$

This reaction is usually carried out in two sub-steps, to make sure all CO is converted to CO_2. The final step is a separation and purification step. Hydrogen is separated from the gas mixture, either by solvents that absorb the acid CO_2, or by adsorption beds that have molecular sieves of suitable pore size.

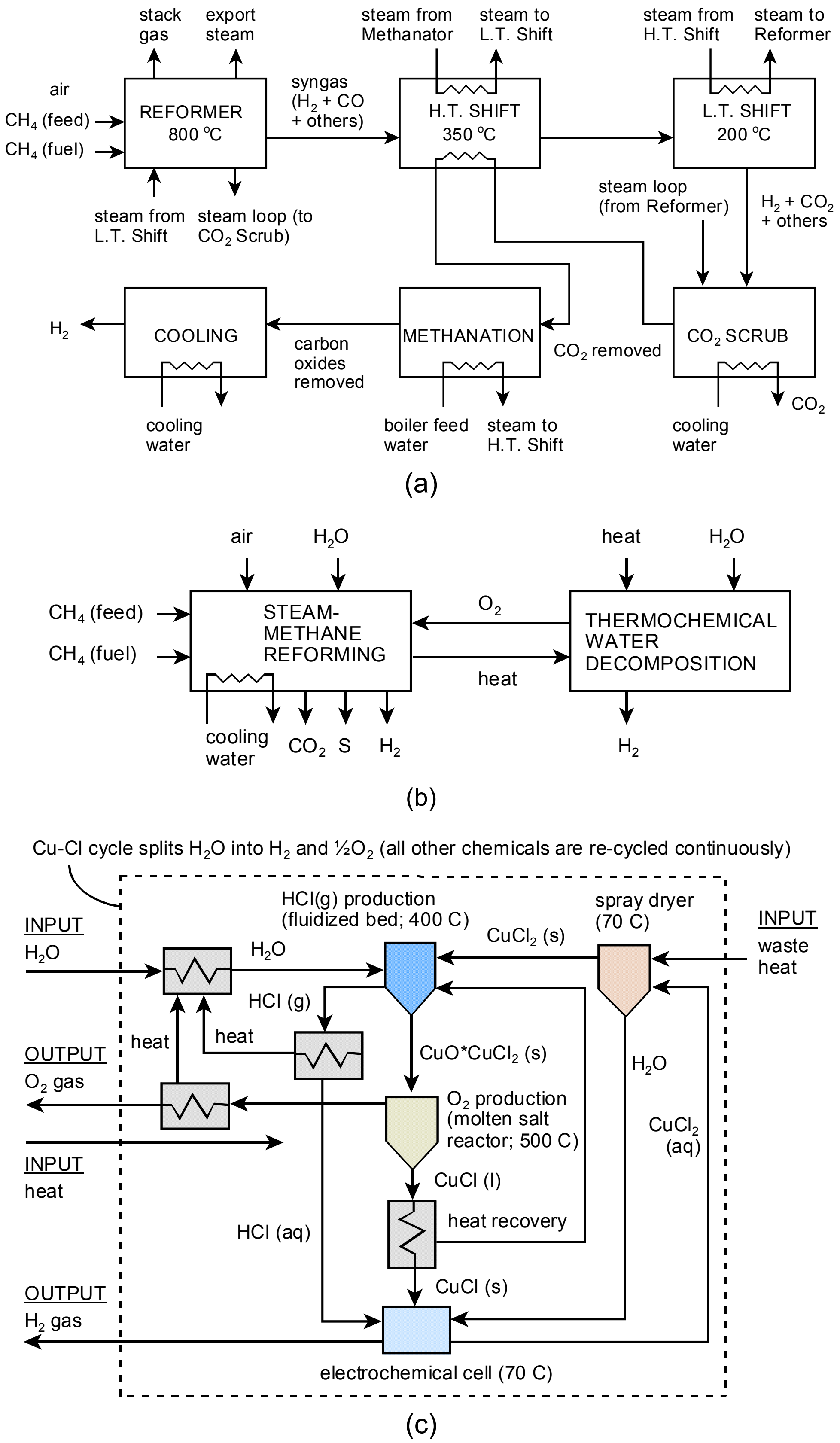

Figure 1: (a) SMR plant, (b) integrated SMR / Cu-Cl and (c) Cu-Cl cycle

Table 1: Steps and chemical reactions in the Cu-Cl cycle

Step	Reaction	Temp. Range (°C)	Feed/Output*	
1	$2CuCl(aq) + 2HCl(aq) \rightarrow H_2(g) + 2CuCl_2(aq)$	<100 (electrolysis)	Feed: Output:	Aqueous CuCl and HCl + V + Q H_2 + $CuCl_2$ (aq)
2	$CuCl_2(aq) \rightarrow CuCl_2(s)$	<100	Feed: Output:	Slurry containing HCl and $CuCl_2$ + Q Granular $CuCl_2$ + H_2O/HCl vapours
3	$2CuCl_2(s) + H_2O(g) \rightarrow CuO*CuCl_2(s) + 2HCl(g)$	400	Feed: Output:	Powder/granular $CuCl_2$ + $H_2O(g)$ + Q Powder/granular $CuO*CuCl_2$ + 2HCl (g)
4	$CuO*CuCl_2(s) \rightarrow 2CuCl(l) + 1/2O_2(g)$	500	Feed: Output:	Powder/granular CuO* $CuCl_2(s)$ + Q Molten CuCl salt + oxygen

* Q = thermal energy, V = electrical energy

The Cu-Cl cycle has been investigated by the Argonne National Laboratory [12] and Atomic Energy of Canada Limited [13] for hydrogen production with Super-Critical Water Reactors (SCWR). The cycle consists of five main steps (see Table 1 and Figure 1), wherein either a physical or chemical processes occurs in each step. Complete separation of hydrogen and oxygen from water is the net result. The first step in the cycle is the HCl and copper oxychloride (Cu_2OCl_2) production step, where HCl is produced within a fluidized bed reactor at about 400 °C. The products of this reaction move to the oxygen and hydrogen production steps. In the oxygen production step, copper oxychloride decomposes and releases oxygen at a temperature of 500 °C. The products of the oxygen step move to the electrochemical process, where copper is produced and subsequently used for the hydrogen production step.

The S-I cycle consists of three reactions; sulfuric acid decomposition reaction where oxygen is produced; a Bunsen reaction where the sulfuric and hydrioidic acids are produced by reacting iodine and sulfur dioxide; and finally the hydrogen production reaction where hydrogen is released from the hydrioidic acid. This cycle requires higher temperatures than the Cu-Cl cycle, typically over 900 °C. The efficiency of the cycle is similar to values reported for the Cu-Cl cycle [8].

Another process to be examined in this paper is integration of SMR with a thermochemical cycle (see Fig. 1). This is particularly advantageous to reduce CO_2 emissions, improve efficiency and potentially reduce costs of hydrogen production. There are a number of potential advantages of integrating SMR and thermochemical processes, such as reduced methane consumption, since the oxygen supply from the thermochemical cycle is not accompanied by nitrogen in air, which requires heating. There is potentially significant reduction of CO_2, NOx and other GHG emissions. Such potential benefits are examined numerically for comparison purposes.

3 Results and Discussion

To find the energy needs of SMR, the results of Rosen [8] will be used. For a SMR plant, about 67 % of the total natural gas is used in the reforming reaction, while 33 % is used to supply the heat requirements of the process. In the SMR processes, 1 mole of natural gas feed will supply 4 moles of hydrogen. By multiplying by the ratio of the fuel needed to the feed fuel, one obtains the required amount of natural gas as fuel to produce one mole of hydrogen. The results for these calculations are shown in Table 2. The total natural gas input is more than the required energy input because the analysis takes into account the natural gas needed for the reforming reaction.

Table 2: Summary of different process results

Process	Conventional SMR	Conventional Cu-Cl cycle	Cu-Cl with oxygen recovery	Modified S-I cycle
Maximum Temperature (°C)	900	530	530	900
Fuel requirement (mole CH_4 / mole H_2 produced)	0.12	0.26	0.25	1.70
Total natural gas input (mole CH_4 / mole H_2 produced)	0.37	0.26	0.25	1.70
Water consumption (mole H_2O / mole H_2 produced)	0.50	1.00	1.00	1.00
Carbon dioxide emissions (mole CO_2 / mole H_2 produced)	0.37	0.26	0.25	1.70

For the Cu-Cl thermochemical cycle, after considering heat recovery within the cycle, it was found that the cycle needs 149 kJ/mol H_2 [9]. The amount of thermal energy needed to supply reactions occurring at temperatures of around 530 °C from combusting one mole of natural gas with 140 % theoretical air was determined. Then the energy required to produce one mole of hydrogen can be found. Table 2 shows a summary of the results for the Cu-Cl cycle. From the table, the energy input to the cycle and the total natural gas requirements are equal, as the Cu-Cl cycle does not require any natural gas internally, unlike SMR. All of the produced hydrogen from the Cu-Cl cycle comes from splitting of water, as no hydrogen is produced from the natural gas, which explains why the water requirement for this cycle is higher than SMR.

For the Cu-Cl thermochemical cycle with internal oxygen recovery, upon splitting water in the Cu-Cl cycle, oxygen is also released along with hydrogen. For every mole of hydrogen produced by the Cu-Cl cycle, there is half of a mole of oxygen produced as well. If this amount of oxygen can be supplied to the combustion reaction with incoming outside air, it would reduce the amount of fuel needed to supply the heat requirements. This case has been analyzed and the results are shown in Table 2. It can be observed that the natural gas requirements and the carbon dioxide emissions have both been reduced by 5 % compared to the Cu-Cl cycle without any oxygen recovery. Considering the modified S-I Cycle, the same analysis has been performed as with the previous cases. This cycle is characterized by its high heat of reactions, especially at low temperatures. Again the case of heat recovery has been assumed and combustion occurs with 140 % theoretical air. The results are also shown in Table 2. It can be observed that the energy requirements for this cycle are high, due to the high heat of reactions.

4 Conclusions

This paper has found that the Cu-Cl cycle is the most attractive method for producing hydrogen in terms of fuel requirements, carbon dioxide emissions and cost. It has the lowest fuel requirements and carbon emissions, including about 40 % less natural gas than SMR, without considering oxygen recovery. Another promising method is to integrate the Cu-Cl cycle with existing SMR plants to operate in an integrated mode. The costs of producing hydrogen can be reduced and the overall performance of the plant can then be improved. The integrated process is a step towards more sustainable hydrogen production. The fuel requirements of the modified S-I cycle are higher, as well as the carbon dioxide emissions and costs. A sensitivity analysis has showed that the total cost of producing hydrogen was more sensitive to the fluctuations in natural gas price than changes in the carbon capture price. The sensitivity of the total cost to the fluctuations in fuel price is about 4 times the sensitivity of the total cost to the fluctuation in the carbon dioxide capture cost.

Acknowledgements

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