



Hydrogen Recovery in an Industrial Chlor-Alkali Plant Using Alkaline Fuel Cell and Hydrogen Boiler Techniques: Techno-Economic Assessment and Emission Estimation

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ABSTRACT

Some chemical processes, like the chlor-alkali industry, produce a considerable amount of hydrogen as by-product, which is wasted and vented to the atmosphere. Hydrogen waste can be recovered and utilized as a significant clean energy resource in the processes. This paper describes the thermodynamic analysis of hydrogen recovery at an industrial chlor-alkali plant by installation of hydrogen boiler and alkaline fuel cell. In addition, emission reduction potentials for the proposed systems were estimated. However, the goal of this work is to analyze the techno-economic feasibility and environmental benefits of using utilization systems of hydrogen waste. The results showed that hydrogen boiler scenario could produce 28 ton/hr steam at pressure of 25 bar and temperature of 245 °C, whereas the alkaline fuel cell system could produce 7.65 MW of electricity as well as 3.83 m³/h of deionized water based on the whole surplus hydrogen. In comparison, the alkaline fuel cell scenario has negative IRR (Internal Return Rate) and NPV (Net Present Value) due to cheap electricity and high cost of capital investment. However, regarding the steam price, the hydrogen boiler project has reasonable economic parameters in terms of IRR and NPV. Therefore, the hydrogen recovery scenario is proposed to install a hydrogen boiler as a feasible and economic idea for steam production in our case. Furthermore, in terms of emission reduction, hydrogen boiler and alkaline fuel cell techniques can significantly reduce greenhouse gas emission by 49300 and 58800 tons/year, respectively, whereas other pollutants can also be reduced by 141 and 95 tons/year in hydrogen boiler and alkaline fuel cell scenarios, respectively.

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1. INTRODUCTION

Hydrogen as a clean energy has many applications. Due to increasing demand for clean energy, the potential consumption of hydrogen becomes significant. Thus, its consumption by a diverse range of applications such as electronic industry, production of fine chemicals and pharmaceutical intermediates, metallurgy industry, food processing, float glass production, and scientific research is increasing year by year [1].

Hydrogen production is carried out in different ways. The most conventional way is the thermo-chemical production of gasoline, natural gas, propane, and methanol through reforming processes [2]. This production can also be renewably obtained by solar and wind power. The reformat hydrogen often requires an extremely precious purification process to minimize the concentration of impurities due to the reforming processes such as CO and H₂S, resulting in increasing the hydrogen production cost. In addition, if all the emissions from tailpipe to upstream (such as feedstock extraction and transport, fuel production, storage, transport,

and delivery) are considered, the hydrogen produced from reformat fuel will not be “zero emission”. On the other hand, the renewably derived hydrogen is a truly “zero-emission” fuel; however, the cost-consuming nature of renewable energy resources makes the produced hydrogen so expensive [3].

In this context, employing alternative hydrogen sources such as waste hydrogen from the chlor-alkali industry will be quite beneficial and cost-effective [3, 4].

Chlorine is industrially produced at so-called chlor-alkali plants, besides which sodium hydroxide and hydrogen are produced by brine electrolysis. This process is also one of the highest energy-consuming processes due to the high electricity utilization that becomes the critical issue to the process feasibility. Of course, attempts have been made to reduce the energy consumption of the chlor-alkali process using alternative sources of energy or by replacing the standard hydrogen-evolving cathode in membrane technology by an oxygen-depolarized cathode [5, 6]. Usually, chlorine and sodium hydroxide are considered as the only valuable products of this process and hydrogen is often discarded as a waste stream [1].

Given that chlorine production is one of the most energy-intensive industrial processes in the world, a significant reduction of energy demand in the chlor-alkali industry is

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highly desirable. Therefore, several approaches have investigated the viability of using hydrogen gas by-product as a fuel source on site of chlor-alkali process based on cleaner production and pollution prevention assessment [7-9].

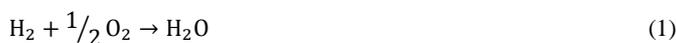
The hydrogen gas from chlor-alkali cells is normally used to produce hydrochloric acid burned as a fuel to produce steam using as a fuel to generate electricity or simply vented into the atmosphere.

In recent years, some fuel cell companies have made efforts to design electrochemical systems that can directly use waste hydrogen from chemical plants as an alternative fuel substitute for reformat hydrogen or electrolytic hydrogen. For example, Ballard Power Systems have recently entered the distributed power generation market using waste hydrogen from chemical plants [10, 11].

The world production of chlor-alkali plants in 2010 has been 53 million tons of chlorine, yielding 1.5 million ton or 16 billion Nm³ of hydrogen by-product. Highly efficient electrochemical systems can convert this quantity of hydrogen to around 2.7×10⁷ MWh (27 TWh) of electricity. At present, the vented fraction of hydrogen could be converted into 4×10⁶ MWh (4 TWh) of electricity [10].

AFC energy (AFCEN) has started the first 'KORE' system installation in AkzoNobel during 2014 with a total 500 kW electrical output funded through the European Fuel Cells and Hydrogen Joint Undertaking (FCH JU) [12, 13]. Furthermore, the European Project DEMCOPEM-2MW[14], led by AkzoNobel (NL), aims at demonstrating polymeric fuel cell technology scale-up, integrated in a chlorine production unit. The project objectives include high system efficiency (over 50 % electrical and 85 % total with cogeneration) and lifetime improvement. The resulting demonstration plant was installed in 2016 at the site of Ynnovate Sanzheng Fine Chemicals Co. Ltd. in Yingkou, Liaoning province, China. The high electricity prices (2 times higher than in Europe and even more rising) in most geographical areas along with the availability of waste hydrogen by currently chlor-alkali plants make the perspective use of this technology so attractive for this country[15].

In addition, steam production by using the surplus hydrogen in hydrogen boilers is another configuration that can be considered for hydrogen recovery. The hydrogen gas combustion is carried out according to Reaction (1):



In one chlor-alkali plant producing NaOH and Cl₂ for domestic customers, the steam cost produced by natural gas equals 1.5 million US\$ per year. The steam production costs are reduced by 80 % when the surplus hydrogen is used instead of natural gas. Moreover, in terms of emission issues, it can reduce the level of NO_x and CO₂ rather than burning natural gas to produce the same amount of steam [16].

Furthermore in Kashima plant [6], in order to balance the amount of hydrogen generated by salt electrolysis equipment with the amount of hydrogen used by the users, a hydrogen fired boiler with a high turndown ratio was installed. By this installation, the following results were obtained:

- Steam reductions 89540 t/year (crude oil conversion of 6552 kl/year)
- The proportion of hydrogen released into the air reduced from 28.1 % to 3.3 %.

In addition, in another studied case [17], the hydrogen produced from chlor-alkali plants in Jordan, which is typically

wasted and vented to the atmosphere, has been recovered by a hydrogen boiler next to the existing fuel boiler and utilized to generate steam for on-site process heating purposes. In this case, the effectiveness of this cleaner production option was discussed in terms of technical and environmental feasibility. The results showed that the on-site utilization of hydrogen could provide 34 % of the total steam needed at full capacity. This in return yields a saving percent-age of around 33.37 % and a payback period of 0.947 year. Also, from the environmental viewpoint, the carbon dioxide emission reductions can be up to 1810 tons based on the chlor-alkali productions pattern for 24 consecutive months.

Also, the JOC (Jiangsu Overseas Group) Company has supplied more than 50 boilers in both China and India. For example, one of the implemented projects has been in Gujarat Fluorochemicals Ltd. in which 1 set hydrogen boiler with capacity of 10 t/h H₂ was installed in 2012 [18].

In the paper, technical and economic assessment of a hydrogen recovery system is thermodynamically analyzed via alkaline fuel cell and hydrogen boiler systems considering an operational chlor-alkali plant as a case study. The selection of the recovery technology is discussed based on technical and economic issues; the work also discusses energetic and environmental considerations of applying alkaline fuel cell and hydrogen boiler systems. To the best of our knowledge, no studies have yet been reported on the comparison of these proposed recovery systems in an industrial chlor-alkali plant from technical, economic, and environmental viewpoints.

The paper is organized as follows: Section 1 describes the case study process description in terms of block diagram, gas analyses (flow rate, chemical composition, LHV (Low Heating Value)) and operational data. Section 2 illustrates the design of the proposed recovery systems including alkaline fuel cell and hydrogen boiler. Section 3 reports the results of the study in terms of energy, economic analyses, and emission reduction. Finally, conclusions are reported.

2. CASE STUDY PROCESS DESCRIPTION

In the case of chlor-alkali plant studied here, the electrolysis process is carried out by the membrane process and products such as chlorine, hydrogen, javalle water (NaOCl), and caustic soda solution 32 % are produced, as well.

Fig. 1 illustrates the PFD (Process Flow Diagram) of the chlor-alkali plant studied here. The process consists of 24 electrolyzer each of which contains of 168 electrolysis cells. In each electrolysis cell, the concentrated brine is decomposed between two positive and negative poles or anode and a cathode and converted to Na⁺ and Cl⁻ ions. The Cl⁻ ion is converted to chlorine gas by electrons and Na⁺ produces a mixture of OH⁻ and NaOH through the membrane.

One of the important issues in this process is the considerable amount of the hydrogen stream with high purity, which is being flared now. With the assistance of the technical team at the facility, the most valuable operational data were obtained through detailed walk-through assessment and consultations with experts. The operational data analysis and material balance (thermodynamic analysis) in this process show that more than 6200 tons of hydrogen gas with relative humidity around 53 % is annually being vented. The thermodynamic analysis consists of material and energy balance for the hydrogen waste stream in the whole chlor-alkali process. Table 1 shows the physical properties of the surplus hydrogen stream.

3. DESIGN OF THE PROPOSED HYDROGEN RECOVERY SCENARIOS

The most important topic in the design of a hydrogen gas recovery system is the selection of the most viable technology can be applied to the chlor-alkali plant.

As has already been mentioned, the two studied technologies here are alkaline fuel cell and hydrogen boiler.

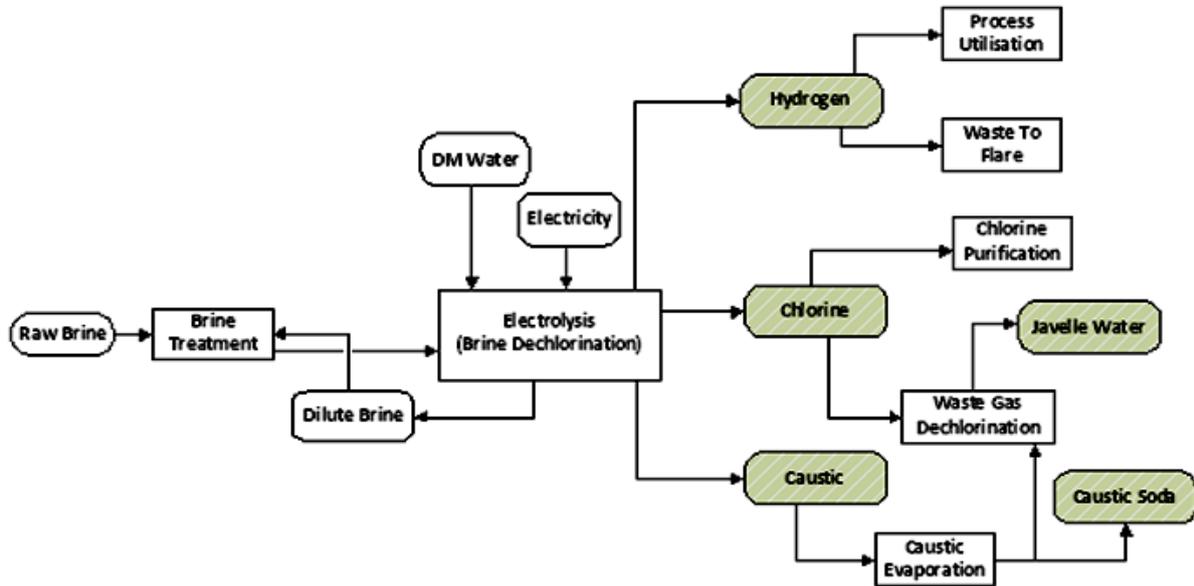


Figure 1. The schematic diagram of the chlor-alkali plant

Table 1. The physical properties of the surplus hydrogen stream

T (°C)	43
P (kPa)	142
V (m ³ /h)	7653
Relative humidity (%)	53

3.1. Hydrogen recovery by alkaline fuel cell system

Alkaline fuel cell systems consume hydrogen and pure oxygen-producing potable water, heat, and electricity. They are among the most efficient fuel cells with the performance up to 70 %. The fuel cell produces power through a redox reaction between hydrogen and oxygen. At the anode, hydrogen is oxidized according to the reaction, which results in water production and releasing electrons (Reaction 2):



Then, the electrons flow through an external circuit and return to the cathode, reducing oxygen in the reaction and producing hydroxide ions (Reaction 3).



The net reaction consumes one oxygen molecule and two hydrogen molecules in the production of two water molecules. Electricity, water, and heat are formed as the by-products of this reaction. The two electrodes are separated by a porous matrix saturated with an aqueous alkaline solution, such as potassium hydroxide (KOH).

A number of studies have examined various aspects of fuel cell performance as a function of operating conditions. The performance of a fuel cell is influenced by many factors

including operating temperature, pressure, gas flow moisture, and geometrical parameters [19-21].

Regarding AFC Energy products, each 350 kWel can be produced by every 350 Nm³ per hour surplus hydrogen. Therefore, by 6200 tons of the vented hydrogen gas, 7.65 MWel can be generated. These 350 kWel units can be readily adapted in a modular fashion to build into a 7.65 MWel FC.

FC power plant is designed with a unit or rack footprint located in a weather proof (rain/sun/wind) structure with a sheet metal or plastic rooftop and natural ventilation.

The design has to be suitable for ambient temperatures from T=-20 °C to T=+50 °C and an assumed maximum humidity of 85 %. Table 2 provides the main gas flows of hydrogen and ambient air to a 350 kWel unit and 7.65 MWel based on the whole surplus hydrogen.

Table 2. Total fluid supply w/o H₂ recirculation

		350 kWel	7.65 MWel Based on the whole surplus hydrogen
Gross hydrogen flow rate	Nm ³ /h	350	7653
Air volumetric flow rate	Nm ³ /h	4200	91836

In addition to electricity, the reaction between hydrogen and oxygen in the alkaline cells produces approximately 0.5 l/kWhel of water (Table 3).

Table 3. Formation of water from reaction

		400 kWel	7.65 MWel Based on the whole surplus hydrogen
Process water flow rate	Nm ³ /h	0.18	3.83

At the start time of the alkaline fuel cell power plant, the ambient air is discharged with the nitrogen entry from the hydrogen-containing tubes and the anode compartment for fuel cell. Nitrogen is also used at the decommissioning time to remove all the remaining hydrogen in the system. This operation is performed to prevent the formation of any explosive atmospheres in the system.

Moreover, due to the fact that the input pressure in the fuel cell should be in the range of 1.1-1.5 bara, it is fully compatible with the hydrogen outlet pressure of 1.42 bara. The schematic diagram of hydrogen recovery by alkaline fuel cell technique is presented in Fig. 2.

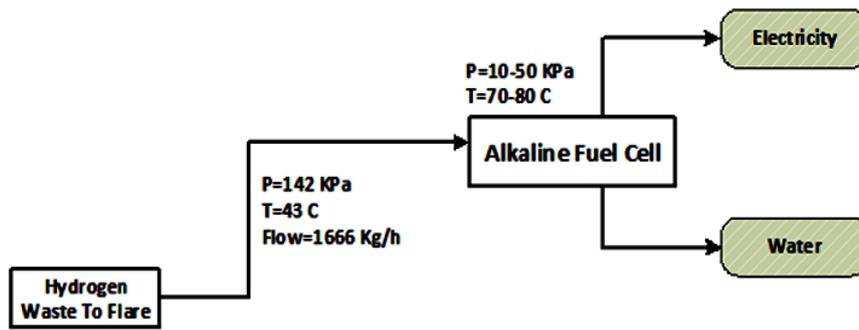


Figure 2. The schematic diagram of hydrogen recovery by alkaline fuel cell technique

3.2. Hydrogen recovery by hydrogen boiler system

Basically, boilers are divided into two categories: waterpipe (water in the pipe) and firewall (fire in the tube), depending on the operation type.

Boilers can also be designed horizontally or vertically, single-burned or combined fuel or with the ability to fuel type change. One of the boiler types is hydrogen boilers.

Hydrogen boiler is referred to as a steam generator which produces heat by burning hydrogen and oxygen at a stoichiometric ratio in a combustion chamber. The reaction heat of oxygen and hydrogen, transmitted through three methods of radiation, convection, and conduction, heats the water and produces steam or hot water [22].

Various industrial samples from these boilers have been designed and utilized in the world. These boilers can be

horizontal or vertical, in which the efficiency is usually higher than 90 %. Hydrogen flow rate for burning varies from 400 m³/hr to 30,000 m³/hr. This kind of boilers can [22] also produce vapor up to the pressure of 4000 kPa according to the present technology. Also, the temperature in the range of 190 to 400 °C can be changed. In comparison to gas-fueled boilers, the NO_x amount is lower and the combustion output is water and nitrogen [18].

In some cases, by heat recycling, the water vapor in the outlet of the combustion chamber can be recovered and used as the deionized water.

In the following, the schematic diagram of hydrogen recovery by hydrogen boiler technique in our case is presented in Fig. 3.

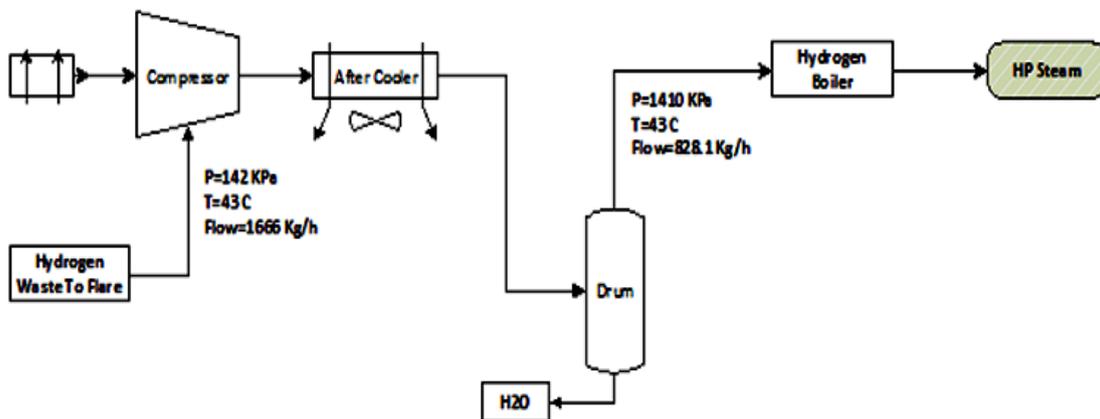


Figure 3. The schematic diagram of hydrogen recovery by hydrogen boiler technique

As can be seen, in case of hydrogen boiler installation in order to solve the high humidity issue of the inlet hydrogen (for burning in a hydrogen boiler), some treatment should be

provided. In order to reduce moisture, the best way is to increase the hydrogen pressure by a compressor system, reduce its temperature, and isolate the liquid moisture. By

increasing the pressure and cooling to very low temperatures, the hydrogen stream humidity also decreases. In other words, at first, the H₂ wasted stream with a temperature of 43 °C, pressure of 142 KPa, and humidity of 53 % enters the compressor and after increasing the pressure and cooling in the after-cooler with temperature 43 °C and pressure 1410 KPa, it enters the drum. The water vapor cooling to a liquid in the drum separates from the hydrogen stream and is sent to the hydrogen boiler as fuel at a temperature of 43 °C and pressure 1410 KPa. Table 4 shows the results of this compressor system simulation.

Table 4. Physical characteristics of the vented hydrogen stream at two compression stages

Compressor		Stage 1	Stage 2
T _{in}	°C	43	43
T _{out}	°C	216	200
P _{in}	kPa	142	470
P _{out}	kPa	471	1410
V _{in}	m ³ /h	7653	2214
V _{out}	m ³ /h	3571	1110
m ⁰ (H ₂ O)	kg/h	319.2	86.93
Power consumption	kW	577	500

Table 5. The results of hydrogen boiler calculation [18]

Steam production capacity (ton/h)	H ₂ consumption (m ³ /h)	Steam pressure (bar)	Temperature (°C)	Air consumption (kg/h)	H ₂ O production (kg/h)
4	1120	14	198	3446	897
6	1680	14	198	5169	1346
8	2240	14	198	6892	1795
10	2800	20	220	8615	2243
15	4200	20	220	12923	3365
20	5600	25	245	17230	4487
25	7000	25	245	21538	5608
35	9800	25	245	30153	7852
70	19600	25	245	60305	15703

4. RESULTS AND DISCUSSION

In the following section, the techno-economic assessment of the above scenarios will be discussed in terms of payback, NPV, and IRR. The required data for technical and economic analysis will be provided from Table 6.

Table 6. The required data for technical and economic analysis

Hydrogen L H V (kJ/kg)	119960	Power cost (€/kWh)	0.03
Natural gas L H V (kJ/kg)	48370	HP steam (€/ton)	9.97
Interest rate (I), (%)	15	Maximum payback (Yr)	5
* All the utility prices are from project owner.			

4.1. Energy analysis

As the average mass flow rate of hydrogen gas (782.83 kg/h), its average LHV value (120000 kJ/kg), and the running time of the chlor-alkali plant (8000 h/year based on process operating hours) are known, it is possible to evaluate the energy obtained by the combustion of the vented hydrogen gas. The yearly primary energy saving obtained by the recovery of the vented hydrogen gas equals about 93.9 TJ corresponding to 1992.5 kg of natural gas.

In general, for the steam production, the main equipment includes hydrogen boiler, compressor, pipe, and control devices. In order to increase hydrogen pressure as a fuel, two compressor packages, one of which is stand-by, are considered and each package includes two stages.

Table 5 provides the main flow rate of hydrogen and ambient air consumed in, generated steam pressure and temperature, and the amount of water produced based on the whole surplus hydrogen.

Given the fact that 7653 m³/h of hydrogen is normally available at present, the choice of two boilers with different capacities of 8 and 20 tons of steam per hour, which totally require 7840 m³/h of hydrogen as fuel, provides the flexibility to prevent shutdown of the boilers due to fluctuations in hydrogen flow.

Moreover, if the produced hydrogen flow rate is less than 7840 m³/h, the smaller boiler can continue to operate down to 60 % of its capacity. Also, reduction of production capacity for larger boiler can be operational. Thus, choosing two boilers with capacities of 8 and 20 tons per hour can be a good choice for process flexibility.

The investigations of hydrogen boiler scenario show that hydrogen boiler can produce 28 ton/hr steam at pressure of 25 bar and temperature of 245 °C. The thermodynamic analysis of the hydrogen boiler shows that the input energy by the hydrogen waste equals 26 MW; however, the energy output by the steam generated is about 21 MW. Therefore, the amount of 5 MW wasted energy is released to the atmosphere by the exhaust steam.

As explained in Section 3.2, in the case of hydrogen recovery by hydrogen boiler system, a compressor should be used for removal of hydrogen stream moisture. So, in order to assess a correct energetic and economic analysis of hydrogen boiler, the electricity required for compressor consumption was calculated. The compressor can be coupled with an electric motor and the final electrical energy consumed by the compressor is equal to 8610 MWh for 8000 h.

In addition, the alkaline fuel cell system (based on the calculations in Section 3.1) also can produce 7.65 MW of electricity as well as 3.83 m³/h of deionized water.

4.2. Economic analysis

In this section, the main capital costs of the installation of the recovery system including alkaline fuel cell and hydrogen boiler systems are reported and a techno-economic assessment

is performed. Of course, as it was mentioned in the case of capital costs of hydrogen boiler, the compressor cost for increasing pressure should also be considered. The main considered costs are the civil works required for the installation of the above systems and the engineering works for the system design [23]. Based on the manufacturing scale and 28 ton/hr steam generation, two-boiler package with a conventional capacity of 20 and 8 ton/hr (JOC Company) was considered.

The economic parameters of steam production using hydrogen boiler are shown in Table 7. In this table, the Internal Rate of Return (IRR), Net Present Value (NPV), and Payback time are calculated. In this scenario, the results of NPV and IRR are relatively reasonable. The following formula is used to calculate NPV:

$$NPV = \left(\sum_{t=1}^n \frac{\text{Net Cash Inflow}_t}{(1+r)^t} \right) - \text{Initial Investment} \quad (1)$$

where t represents the time in years, r is R/100 (R= the interest or discount rate), and n is the number of periods or years. Furthermore, IRR formula is the following one:

$$IRR = r_a + \frac{NPV_a}{NPV_a - NPV_b} (r_b - r_a) \quad (2)$$

where r_a and r_b represent the lower and the higher discount rates, respectively, NPV_a is the net present value at r_a , and NPV_b is the net present value at r_b .

Regarding the steam price (9.97 €/ton), the hydrogen boiler project revenue is estimated showing that the IRR is fairly good at around 29 %. Moreover, considering a 15 % discount rate, the NPV is also positive. Thus, the option of using a hydrogen boiler could be an appropriate and economical idea for steam production in our case.

Furthermore, the IRR, NPV, and Payback time are calculated for alkaline fuel cell approach in Table 8. In the case of the alkaline fuel cell scenario, the IRR and NPV are negative. Thus, in terms of calculations based on electricity prices (0.03 €/kwh), because of the high cost of investment and the cheapness of the unit price of electricity, the alkaline fuel cell scenario will not be cost-effective. The NPV of the base case configuration is negative, thus with the assumed prices and conditions, the alkaline fuel cell scenario is not an attractive choice. The value of the NPV is -8270000€

Table 7. Economic parameters for steam production using hydrogen boiler

Items	Unit	Scenario 1
2 Boiler package (8 ton/hr+20 ton/hr)	Euro	2,411,450*
2 Compressor package		1,590,350
Piping, instruments, controls and electrical		298,350
Commissioning, installation cost		197,200
Direct cost		4,497,350
Indirect cost		296,650
Fixed capital investment	Euro	4,794,000
Annual cost	Euro/y	575,450
Annual benefit		2,076,550
Discount rate	%	15
IRR	%	29
NPV	Euro	2,739,550
Payback time	year	4
One compressor package is standby mode.		
* The price reference is from JOC Company.		

Table 8. Economic parameters of electricity and water production using alkaline fuel cell

Items	Unit	Alkaline Fuel cell scenario
Alkaline fuel cell package	Euro	9476403*
Installation cost		1895280
Total direct cost (carbon steal)		11371684.29
Total indirect cost		947640
Fixed capital investment	Euro	12319324
Annual cost	Euro/y	1231932
IRR	%	-7.03
NPV	Euro	-8.27E+06
Payback time	year	15.3
* The price reference is from AFC Company.		

According to the sensitivity analysis (Fig. 4), variations in the electricity price have significant impact on NPV value. With increase in electricity value to 0.15 €/kWh which is a normal average price in the world, this scenario will become completely reasonable and profitable. In addition, Fig. 5 shows the rate of IRR fluctuations versus the surplus hydrogen volume. Fig. 5 Sensitivity analysis of the surplus

hydrogen volume variable in a fuel cell and hydrogen boiler scenarios. With an increase in hydrogen flow rate due to the energy-saving increment generated by steam or electricity, the IRR rises. However, because of the electricity cheapness (0.03 €/kWh) and high cost of initial investment, the IRR is still very small even at the large flow rate of hydrogen, thus confirming the results obtained from Fig. 4.

4.3. Emissions reduction estimation

The increase in the concentration of greenhouse gases causes the temperature rise of the earth [23]. The gases that have greenhouse effect can be reduced by the implementation of the proposed ideas (using hydrogen boiler and alkaline fuel cell instead of fossil fuel technologies). The emission of greenhouse gases and the resultant pollutants due to fossil fuel from the equipment is referred to as combustion emissions.

Most of the greenhouse gases emitted from combustion include CO₂, N₂O, and CH₄ (due to incomplete combustion). The most accurate and reliable method for estimating the amount of carbon dioxide from combustion sources is the mass balance method based on fuel consumption and carbon content of the fuel [24].

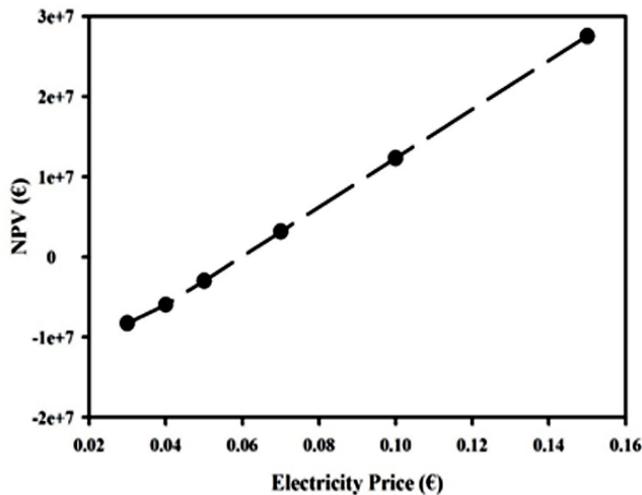


Figure 4. Sensitivity analysis of the electricity price variable in the fuel cell scenario

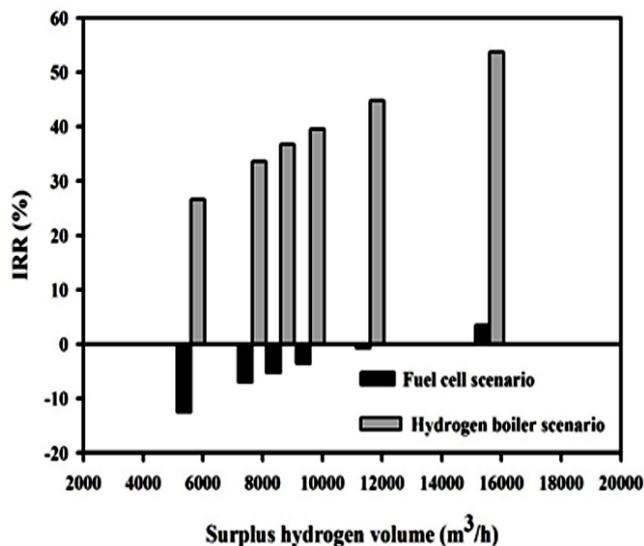
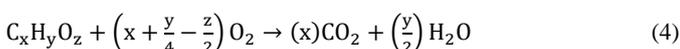


Figure 5. Sensitivity analysis of the surplus hydrogen volume variable in a fuel cell and hydrogen boiler scenarios

Generally, the hydrocarbon combustion with the assumption of complete combustion follows Reaction (4):



The carbon content of the fuel mixture is the average of carbon content of each component. To achieve this, at first, the percentage of carbon per fuel component is calculated and then, is completed by multiplication of the molecular weight of carbon in the number of carbon molecules divided by the molecular weight of the compound.

The carbon content, which is equal to the average carbon content of the constituent components of a compound, is calculated through Equation (3).

$$Wt \%C_{Mixture} = \frac{1}{100} \sum_{i=1}^{\#components} (Wt \%_i \times Wt \%C_i) \quad (3)$$

In this equation, Wt %_i is the weight percentage of i component in the fuel mixture and Wt%_{C_i} is the carbon content based on the weight.

Therefore, the amount of carbon dioxide emissions from combustion sources with natural gas is calculated using Equation (4).

$$E_{CO_2} = FC \times \frac{1}{molar\ volume\ conversion} \times MW_{Mixture} \times Wt \%C_{Mixture} \times \frac{44}{12} \quad (4)$$

where FC is the amount of fuel consumed (Sm³), MW_{mixture} is the molecular weight of the fuel mixture, and the molar volume conversion is the conversion factor of molecular volume to mass, which is equal to 23,685 m³/kgmole.

In addition to estimating CO₂ emissions based on 100 % carbon oxidation, the Compendium API estimates the emission of CH₄ and N₂O from the combustion source based on emission factors, as presented in Table 7.

After calculating the amount of greenhouse gas emissions using their heating potential, they are converted to carbon dioxide equivalents which are equal to 1, 25, and 298 for CO₂, CH₄, and N₂O, respectively [24]. To estimate the emission of pollutants from combustion, the global emission factors related to AP-42 reference presented in Table 9 are used.

Table 9. Greenhouse gas emissions factors and pollutants in the combustion process with natural gas [25]

	VOCs	PM	CO	NO _x	N ₂ O	CH ₄
Unit	kg/10 ⁶ Nm ³					
Emission factor	83.24	115.03	1271.35	4237.84	10.55	37.88

Thus, by determining the amount and percentage of the fuel, the amount of emission reductions and greenhouse gas emissions can be calculated. Obviously, all the actions that are taken to reduce fossil fuel consumption can be considered as one way to reduce greenhouse gas emissions in the energy sector.

This study shows that the implementation of each scenario can reduce the average annual consumption of natural gas with the composition given in Table 10 and their corresponding greenhouse gas emissions, significantly. Now, using Equation (6), the amount of CO₂ emitted from each of the scenarios can be calculated. Also, with the coefficients given in Table 11, the amounts of N₂O, CH₄, pollutants, and greenhouse gases can be calculated for each of the scenarios presented in Table 12.

Table 10. The composition of the natural gas consumed in our case study

Unit	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₄ H ₁₂	C ₆ H ₁₄	N ₂	CO ₂
	Methane	Ethane	Propane	Butane	Butane	Hexane	Nitrogen	Carbon dioxide
%	84.98	5.47	2.09	0.87	0.31	0.35	3.02	2.91

Table 11. The amounts of greenhouse gases emission reduction per year

Scenario	CO ₂	CH ₄		N ₂ O		Total
	kg CO ₂	kg CH ₄	kg CO ₂ e	kg N ₂ O	kg CO ₂ e	kg CO ₂ e
Alkaline fuel cell	58,776,900	1,830.3	45,600	223.7	66,700	58,889,200
Hydrogen boiler	49,287,700	917.2	22,900	255.3	76,100	49,386,700

Table 12. The amounts of pollutants emission reduction per year

Scenario	NO _x (kg)	CO (kg)	PM (kg)	VOCs (kg)	Total (kg)
Alkaline fuel cell	44,416.1	37,908.2	10,331.2	2,521.8	95,200
Hydrogen boiler	104,733.1	31,419.9	2,842.8	2,057.2	141,000

The basis of the CO₂e reduction calculation in the two scenarios is the power generation using gas turbine and boiler fuel, respectively. The results in Table 11 show that if the surplus hydrogen is used to generate electricity using fuel cell, approximately 58800 tons of CO₂e will annually be emitted and if steam hydrogen boiler is used for steam productions, the CO₂e emissions reduction will be around 49300 tons.

The reduction in greenhouse gas emissions for the electricity generation scenario is higher than that for the steam generation scenario, because the electricity generation in this study is based on a gas turbine with less than 30 % efficiency in the best conditions of a gas turbine, whereas the boilers have an efficiency rate of at least 60 %. On the other hand, due to the fact that boilers use heavy fuel like gasoline, they produce more emissions than gas turbines. Thus, the emission reductions in the steam generation scenario are higher than that in the electricity generation scenario using the fuel cell (Table 12).

5. CONCLUSIONS

In the work presented here, two important technologies for the hydrogen gas recovery in one industrial chlor-alkali plant were reported: (a) the alkaline fuel cell for electricity and water production and (b) the hydrogen boiler for steam generation.

The use of an alkaline fuel cell system can be a suitable solution for hydrogen recovery in chlor-alkali plants, where energy consumptions are high and high-purity hydrogen is available as by-product. Furthermore, using hydrogen boiler systems can be beneficial as they can produce half of the steam needed in the chlor-alkali plant.

According to the running conditions of an industrial chlor-alkali plant, the concept design and the performance of the two proposed technologies for hydrogen recovery were reported. The results showed that almost 6200 tons hydrogen gas with a pressure of 142 kPa and 99 % purity was annually being vented.

In the case of hydrogen boiler system, a two-stage compressor was adopted to increase the hydrogen pressure to a level that can be used as input pressure in the boiler system: its main characteristics and energy consumption are evaluated. The steam amounts that can be produced are 28 ton/hr steam at pressure of 25 bar and temperature of 245 °C. Whereas this

pressure increase is not required in alkaline fuel cell scenario as the input pressure should be in the range of 0.1-0.5 bar which is completely compatible with the hydrogen outlet pressure from the vent stream. This approach can generate 7.65 MW of electricity and 3.83 m³/h of deionized water.

Moreover, an economic analysis is reported considering the capital and operating cost of the system to evaluate IRR and NPV parameters: with an interest rate of 15 %, the alkaline fuel cell scenario has negative IRR and NPV, whereas the hydrogen boiler project has the fairly good IRR and positive NPV.

Moreover, in terms of emission reduction, hydrogen boiler and alkaline fuel cell techniques can significantly reduce greenhouse gas emission by 49300 and 58800 tons/year, respectively. Also, the other pollutants can be diminished by 141 and 95 tons/year in hydrogen boiler and alkaline fuel cell scenarios, respectively. Therefore, the obtained results showed that by applying the hydrogen boiler solution, all the technical, economic and environmental advantages could be achieved.

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NOMENCLATURE

IRR	Internal Return Rate
NPV	Net Present Value
FCH JU	Fuel Cells and Hydrogen Joint Undertaking
AFCEN	AFC energy
JOC	Jiangsu Overseas Group
LHV	Low Heating Value
PFD	Process Flow Diagram
T	Temperature (°C)
P	Pressure (kPa)
V	Gas volumetric flow rate (m ³ /h)
m ^o	Gas mass flow rate (kg/h)
t	Time in years
R	The interest or discount rate

n	The number of periods or years
r_a	The lower discount rate
r_b	The higher discount rate
Wt % _i	The weight percentage of i component
Wt %C _i	The carbon content based on the weight
FC	The amount of fuel consumed (Sm ³)
MW _{mixture}	The molecular weight of the fuel mixture

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