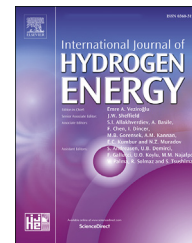




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Turkey's industrial waste heat recovery potential with power and hydrogen conversion technologies: A techno-economic analysis

Funda Ates ^a, Hasan Ozcan ^{b,*}^a Faculty of Engineering, Karabuk University, Karabuk, Turkey^b Faculty of Engineering and Natural Sciences, Ankara Yildirim Beyazit University, Ankara, Turkey

HIGHLIGHTS

- Turkey's industrial waste heat potential is 71 PJ.
- Selected hydrogen production cases are investigated for waste heat recovery.
- Gas Turbine Driven Hybrid Sulfur cycle is the most economically viable case.
- Waste to hydrogen can compensate 5% of Turkey's residential NG consumption.
- A significant reduction on CO₂ emission is possible with selected technologies.

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ABSTRACT

In this study an investigation of Turkey's overall industrial waste heat potential is conducted, and possible power and hydrogen conversion technologies are considered to produce useful energy such as power and hydrogen. The annual total industrial waste heat was has a 71 PJ in 2019 and is expected to double by 2050. The temperature range of the waste heat differs by sector at a large range of 50 °C–1000 °C. Absorption power cycle (APC), Organic Rankine Cycle (ORC), Steam Rankine cycle (SRC) and Gas Turbine (GT) systems are adapted for power production based on the waste heat temperature while electrochemical and electro-thermochemical hydrogen production systems are adapted for hydrogen generation. Proton Exchange Membrane, Alkaline, and high temperature steam electrolysis methods are selected for pure electrochemical conversion technologies and Hybrid Sulfur (HyS), Copper Chlorine (CuCl), Calcium–Bromine (CaBr), and Magnesium Chlorine (MgCl) cycles are utilized as hybrid thermochemical technologies. Many cases are formed, and best temperature matching power-hydrogen system couples are selected. It is possible to produce enough hydrogen to compensate up to 480 million m³ natural gas equivalents of hydrogen annually with selected technologies which corresponds to ~5% of residential natural gas consumption in Turkey. Economic analysis reveals that lowest hydrogen generation cost belongs to the GT-HyS system. When hydrogen is used for heating applications by a certain mixture fraction to NG pipelines, it may reduce more than 720 thousand tons of CO₂ reduction annually due to natural gas use.

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* Corresponding author.

E-mail address: hozcan@ybu.edu.tr (H. Ozcan).

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Introduction

As one of the energy dependent countries, Turkey spends billions of dollars to import energy while as a developing country, its energy use exponentially increases especially in industry and residential applications with increased well being of its people. Total annual energy consumption of Turkey is close to 2000 PJ by 2019, and slightly less than half of it is utilized by its industry while the remaining is shared by transportation and residential applications [1]. Turkey's total industrial energy consumption is 900 PJ and its waste heat potential are around 71 PJ (~2.24 GW). The rates of this waste heat are 40% at 100–200 °C, 14% at 200–300 °C, 6% at 300–400 °C, 9% at 400–500 °C, and 31% at 500–1000 °C [1]. Quantity and temperature range of the waste heat differ by the industrial sector and its mostly occupied by low and ultralow temperature waste heat [2]. Most small enterprises exhaust waste heat at lower than 150 °C while paper, cement, plastics, textile, food and tobacco industries emit gases between 150–500 °C. Additionally, metal, glass, ceramic and peak iron industry may emit waste heat at temperatures as high as 1000 °C to complete their processes [3]. Rate of waste heat to total consumed energy differs by sector, and highest waste heat rate belongs to iron-steel industry (almost 15%) due to very high temperature operations to form metals [4].

Rate of industrial waste heat ratio and quantity of waste heat from different sectors with their temperature ranges are provided in Fig. 1a and b. Food/Beverage, paper/pulp and non-ferrous metal production facilities mostly emit gasses at a range of 100–200 °C while highest temperature waste heat is emitted by Iron/Steel, non-metallic minerals, and petrochemicals production sectors. Turkey is abundant with energy intense and high temperature operation facilities as a developing country. Therefore the metal industry consumes a significant fraction of total industrial energy consumption followed by petrochemical and non-metals industries. Even though other sectors, in general emit gasses at lower temperatures, amount of energy rate from these industries equals to around 180 MW which can be utilized with energy conversion systems that are eligible to operate at lower temperatures [5].

It is expected that the energy consumption of Turkey will double by 2050 and use of waste heat recovery applications will help ease the dramatic need of increased energy consumption. An average of 9% waste heat fraction results in more than 140 PJ waste energy by 2050, in which use of waste heat for useful energy production can also help ease the high load of increased energy requirement in upcoming decades in short and long terms. Change in industrial energy consumption per year is illustrated in Fig. 2 by considering a linear regression to predict its change in upcoming years as well [1].

Recovery of waste heat can be accomplished in many ways based on the required useful energy form. Low temperature waste heat is preferred for power generation with novel power conversion technologies such as Kalina and Organic Rankine Cycle systems [6,7]. Absorption power cycles (APC) are also promising technologies to recover low temperature sources into power at acceptable efficiency ranges by also maximizing the efficiency at certain temperatures based on the used working fluid couple [8–11]. A suitable and systematic

approach is inevitable to decide on use of waste heat for various applications. In many countries, present facilities for waste heat recovery and potential technologies are reported [12]. Use of heat pump applications, absorption refrigeration systems, district heating, power generation and energy storage are considered as useful energy conversion technologies for waste heat recovery [13]. Ultra-low industrial waste heat shares one of the highest fraction and use of this waste is not possible at this range. Therefore further research is still inevitable to utilize ultra-low temperature waste heat by using thermoelectric generators for power production, heat pump applications for district heating and heat upgrading with chemical heat pumps to increase the Carnot efficiency for possible low temperature power generation applications. Kalina Cycle and ORC systems are feasible candidates for low to medium temperature applications while higher efficient steam and gas turbine systems can be used with high temperature waste heat applications [14–17].

As a clean and sustainable energy carrier hydrogen is a holistic solution for decreased environmental impact of fossil driven energy systems. For more than half a century, researchers studied on many ways to produce hydrogen with different methodologies [18]. Low temperature splitting of water requires high amounts of electricity consumption with electrochemical conversion while pure thermochemical splitting of water requires very high temperatures. Proton Exchange Membrane Electrolysis (PEME) and Alkaline Electrolysis (AE) are the most developed electrochemical conversion technologies that use electricity for hydrogen production [19]. High temperature steam electrolysis (HTSE) also carries the potential to produce hydrogen sustainable by consuming less electricity while requiring high temperature operation [20]. Hybrid systems are also proposed especially to both decrease the electricity consumption for water splitting and the maximum operating temperature [21]. Hybrid Sulfur Cycle (HyS) has been one of the most promising hybrid hydrogen production systems with low electricity consumption (0.18 V) with a maximum temperature above 850 °C. It is considered a system that can be integrated with next generation very high temperature nuclear reactors along with HTSE and the pure thermochemical Sulfur Iodine Cycle by Japan Atomic Energy Agency (JAEA) [22]. Maximum temperature of next generation nuclear reactors differs with the technology and based on the reactor technology many other hybrid thermochemical hydrogen production systems are also proposed. Canadian supercritical water reactor (SCWR-CANDU) has a maximum reactor temperature above 500 °C. Hybrid Copper–Chlorine and Magnesium–Chlorine cycles are proposed and investigated to match with the SCWR-CANDU reactor technology [23]. There have been several studies to investigate reactions of the CuCl cycle individually with international projects and reactor integration has been accomplished [24]. MgCl cycle showing similar maximum temperature values as in CuCl cycle has also been studied to develop new cycle configurations with its feasible reactor operations and low electricity consumption compared to those of pure electrochemical systems [25–28]. Further details on techno-economics of hydrogen generation from pure and hybrid hydrogen production technologies can be found elsewhere [18].

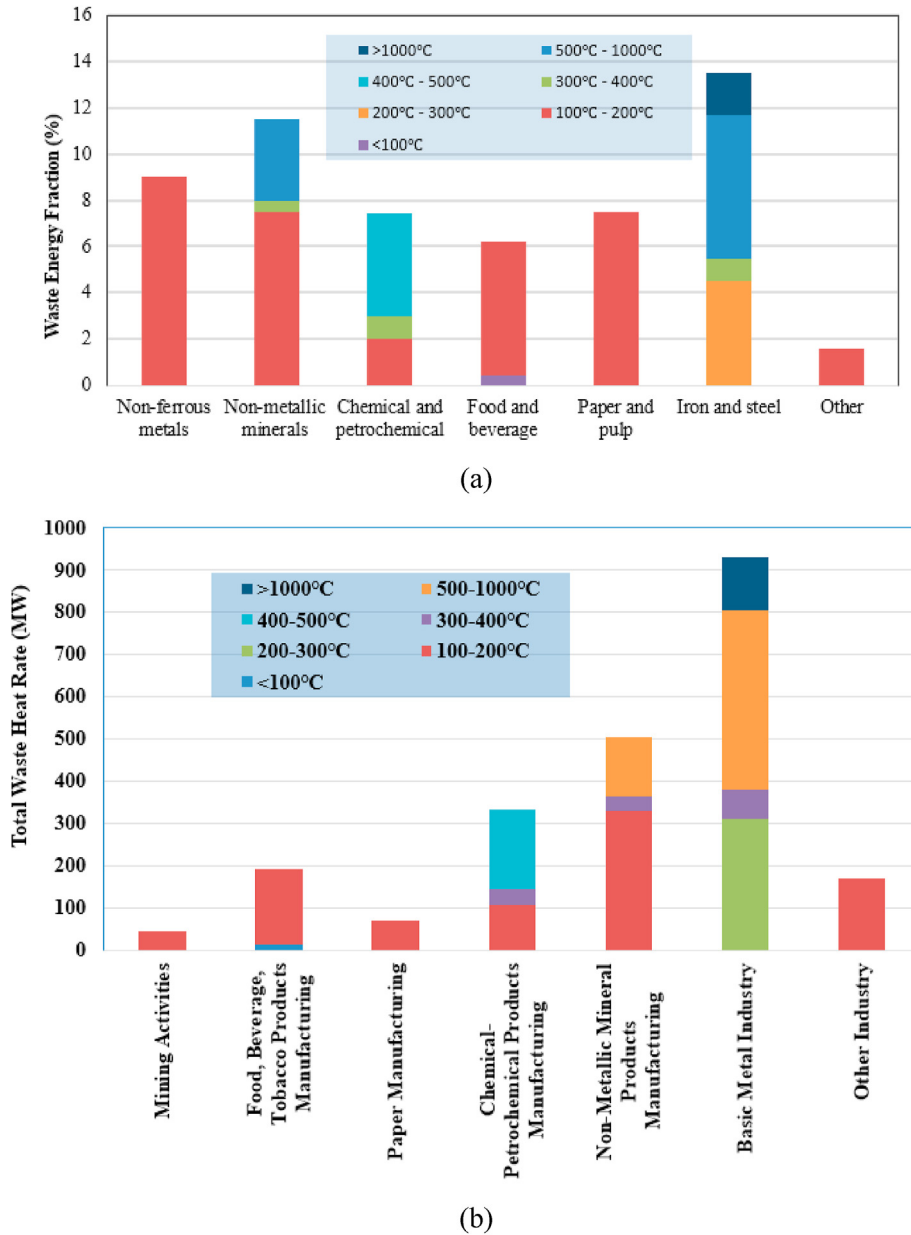


Fig. 1 – Turkey's (a) waste heat ratio based on sector and temperature ranges (b) Amount of waste heat in rate form by 2019 [1,3].

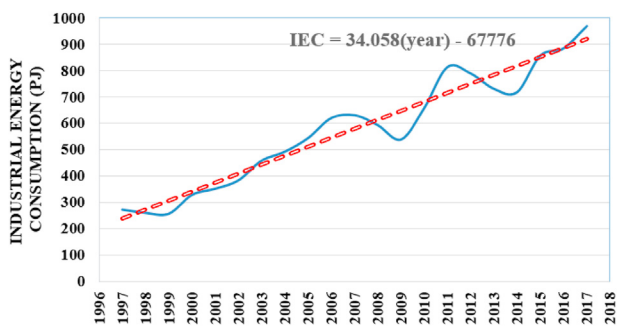


Fig. 2 – Industrial energy consumption per year in Turkey [1].

Economic analysis reveal that low electricity consumption leads to low hydrogen production costs in a hydrogen generation plant. Therefore, pure electrochemical technologies result in high costs while decreased electricity consumption with assistance of thermal energy in hybrid cycle results in lower hydrogen generation costs. Many economic studies also reveal that cost of electricity is a significant factor on hydrogen production cost. Nuclear and geothermal energy driven electricity has cost competitive to fossil driven plants and other renewable based electricity production costs due to low cost source. Waste heat can be considered as a free of charge source of thermal energy that can be used for power conversion technologies to produce low cost electricity which would directly favor cost of hydrogen [29].

Cost of hydrogen is strongly dependent on the cost of source and the used technology. The source varies from waste heat to solar energy while electricity input may be provided from grid or renewables. Cost of electricity varies between 0.04 \$/kWh to 0.24 \$/kWh based on the technology. Geothermal and nuclear sources provide the lowest electricity generation costs followed by fossil driven technologies and solar thermal based electricity is among the highest. Cost of thermal energy is also lowest for nuclear energy while it is at its highest for concentrated solar technologies. Above all, lowest cost hydrogen can be obtained from less electricity consuming hydrogen technologies such as S-I, HyS and CuCl cycles while pure electrochemical systems result in highest hydrogen costs due to use of intense electricity to complete the process [18].

In this study, Turkey's total industrial waste heat potential is investigated, and possible power and hydrogen technologies are considered to recover the waste heat. Many case studies are considered to determine best power-hydrogen system couple at different waste heat temperature and a down selection is made to further study the feasible systems economically. Turkey's overall waste heat to hydrogen recovery potential is discovered with the selected technologies. This work provides an outlook on the advantageous and economic feasibility of utilizing industrial waste heat to recover hydrogen that can be used as an energy carrier, a storage medium and a fuel for many applications.

Down selection of energy recovery technologies

Based on the waste heat temperature variation and their energy content, some selected power and hydrogen recovery technologies are considered in 20 cases to further assess the

potential for daily hydrogen production with optimistic and pessimistic approaches based on their efficiency ranges as represented in Table 1. Until 500 °C MgCl cycle is the only selected hybrid thermochemical cycle with its low maximum temperature along with PEME and AE systems. ORC, Kalina and APC systems are considered as power conversion systems. Above 500 °C, HTSE, CaBr, CuCl and HyS systems are selected to recover high temperature waste heat. In cases 1, 4, 7, and 14, power production is considered only with the compatible power conversion technology. Total power conversion is possible at a rate range of 300–565 MW when power only option is considered. Potentially recovered waste heat can cover 0.9%–1.7% of Turkey's overall electricity consumption at peak times when suitable technologies are utilized for power production.

Selection of the hydrogen production technology is considered by solely considering the amount of daily hydrogen production. Fig. 3 represents the daily hydrogen production for pessimistic and optimistic conditions for all 16 cases. For the waste heat temperature range of 100–200 °C PEME is selected with its low heat requirement and low temperature operation and APC system is considered as the power conversion system since it is eligible to maximize efficiency at a certain waste heat temperature showing superiority to others [11]. AE technology is utilized at the range of 200–400 °C waste heat temperature along with ORC, since the hydrogen production is higher than the PEME at this temperature range. Between 400 and 500 °C, rate of hydrogen production with the MgCl cycle is higher than that of the AE and thus MgCl cycle is utilized to convert waste heat to hydrogen along with the steam turbine system. Above 500 °C selection of the hydrogen conversion technology should be made carefully due to maximum temperature operation of the technologies. Even though the MgCl cycle recovers the highest amount of

Table 1 – Considered scenarios with potential power and hydrogen systems based on the temperature range and amount of industrial waste heat [11,18].

Case #	Waste Heat Amount (MW)	Temperature Range (°C)	Power System	Power System Efficiency Range	Hydrogen System	Hydrogen System Efficiency Range	Hydrogen System ΔG (kJ/mol H ₂)	Hydrogen System ΔH (kJ/mol H ₂)	Hydrogen System Heat/Work Ratio
1	900	100–200	ORC/KL/APC	8–14	-	-	-	-	-
2			ORC/KL/APC	8–14	PEME	75–85	237,4	4	0.017
3			ORC/KL/APC	8–14	AE	60–90	237,4	50	0.210
4	310	200–300	ORC	18–25	-	-	-	-	-
5			ORC	18–25	PEME	75–85	237,4	4	0.017
6			ORC	18–25	AE	60–90	237,4	50	0.210
7	140	300–400	ORC/ST	24–30	-	-	-	-	-
8			ORC/ST	24–30	PEME	75–85	237,4	4	0.017
9			ORC/ST	24–30	AE	60–90	237,4	50	0.210
10	189	400–500	ST	26–34	-	-	-	-	-
11			ST	26–34	PEME	75–85	237,4	4	0.017
12			ST	26–34	AE	60–90	237,4	50	0.210
13			ST	26–34	MGCL	42–51	191.0	152	0.793
14	568	500–1000	ST/GT	33–45	-	-	-	-	-
15			ST/GT	33–45	PEME	75–85	237.4	4	0.017
16			ST/GT	33–45	HTSE	52–75	191.0	75	0.393
17			ST/GT	33–45	MGCL	42–51	191.0	152	0.793
18			ST/GT	33–45	CUCL	37–54	133.1	308	2.313
19			ST/GT	33–45	CABR	33–46	115.8	282	2.435
20			ST/GT	33–45	HYS	35–55	77.2	249	3.220

hydrogen at this temperature range at pessimistic conditions, CuCl and HyS cycles show the highest potential at optimistic conditions. Since it is known that HyS cycle requires waste heat temperatures above 750 °C, it is not wise to select only one power-hydrogen couple at this waste heat temperature range [18]. Therefore, steam turbine driven CuCl cycle and GT driven HyS cycle are considered in two different cases by considering the waste heat above 500 °C is distributed evenly. Finally, 5 cases are considered as potential systems to recover waste energy at different waste heat temperatures.

Fig. 4 represents detailed power-hydrogen systems integrated for waste heat utilization. APC-PEME system is selected to harvest energy from 100 to 200 °C heat source as in Fig. 4a. Here waste heat is transferred to generator of the APC system to increase the temperature of the working fluid. Steam is used to generate power in the turbine and strong solution is used to reheat the weak solution and mixed with the steam in an ejector for enhanced pressure before the absorber. Generated power is used for the electrolyser and based on the provided electricity amount of hydrogen generated is determined. The mass balance leads to heat requirement to increase the temperature of water to electrolyser temperature. The ORC-AE system schematics is provided in Fig. 4b. Similar to the APC-PEM system, heat from 200 to 400 °C waste heat source is used to run the ORC system and produced electricity from the turbine is used in the AE system based on the heat provided.

The four-step MgCl cycle is selected to harvest heat from the 400–500 °C waste heat as in Fig. 4c. Electricity produced

from the steam Rankine cycle is provided to both dry and aqueous electrolyzers of the system and amount of produced hydrogen is specified based on the electricity amount. Here, decomposition reactor and the steam generation for hydrolysis reactor are the exothermic components of the system. Mass balance of the system leads to required heat from the waste heat at a certain temperature. Hydrolysis process produces MgOHCl and HCl gas, where the HCl gas is in aqueous form and utilized in the electrolyser directly. MgOHCl is split in to MgO and dry HCl in the decomposition reactor and fed to the dry electrolyser. Chlorine gases from both electrolyzers are fed to oxygen reactor to complete the cyclic process with the help of system heat exchangers.

Schematics of the four-step hybrid CuCl cycle is illustrated in Fig. 4d. Here steam Rankine cycle is used for power supply to electrolyser as in MgCl cycle. Water reacts with the dried CuCl₂ in the hydrolysis reactor and produced Cu₂OCl₂ is decomposed into oxygen and CuCl. CuCl and HCl are the electrolysis reactants to produce hydrogen. The aqueous CuCl₂ is than dried and sent back to hydrolysis to complete the cyclic process. Here dryer and the electrolyser are the electricity consuming components while decomposition and hydrolysis reactors are endothermic and require external heat at temperatures above 400 °C up to 550 °C. Fig. 4e illustrates the schematics of the GT-HyS system. Here high temperature waste heat is used through the open cycle GT and produced power is sent to the SO₂ electrolysis process. Here water heating requirement could be compensated by exothermic heat exchangers while the highest temperature requiring

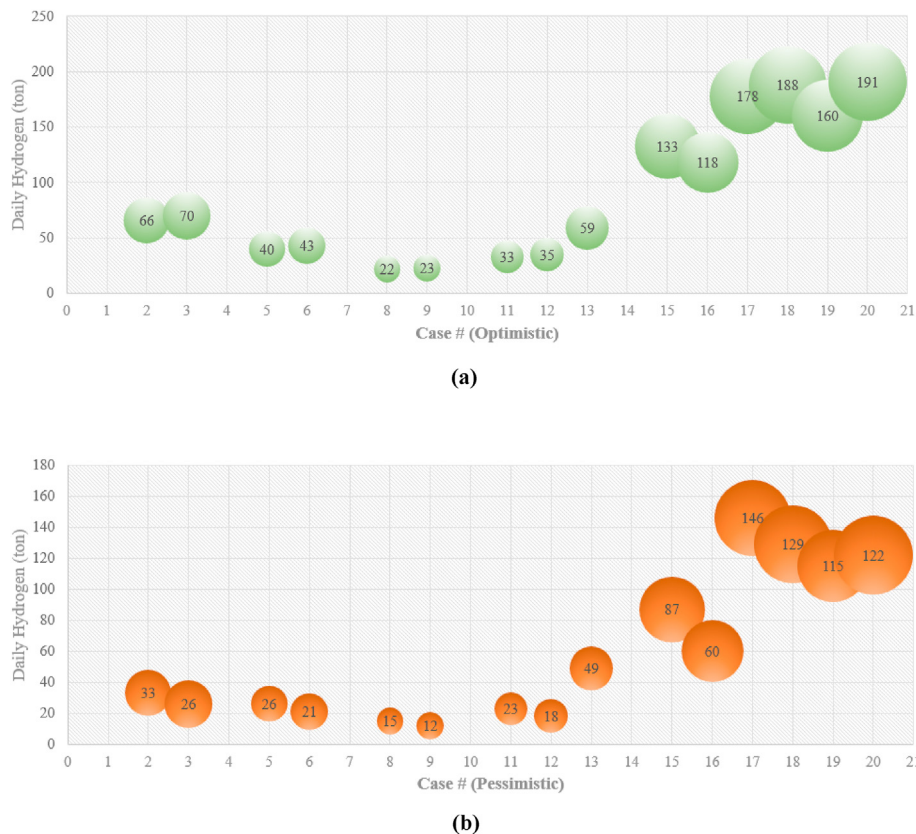


Fig. 3 – Daily hydrogen production from power-hydrogen technologies at worst- and best-case scenarios (Power only cases are not considered).

component is the H_2SO_4 decomposition reactor. H_2SO_4 from the electrolyser is decomposed into oxygen, water, and SO_2 . Energy balances of considered cases with their heat and work requirements, as well as their economic aspects are explained in detail in the next subsection.

Analysis and assessment

For all cases considered, a certain amount of waste heat is selected from different waste heat source temperatures. To

keep the comparative assessment fair, system sizes, environmental conditions and common assumptions are kept same for all cases. Since it is well known that electricity consumption of the electrolysis steps are major cost effecting parameters, current density of all electrolyzers in considered cases are kept constant at 5 kA/m^2 . In an electrolysis cell, it is crucial to calculate the overpotentials that add up to the theoretical value resulting in increased cost of the component. Therefore, calculation of overpotentials are of importance for more practical cost assessment. Change in free Gibbs energy of formation of a substance is related with its enthalpy and

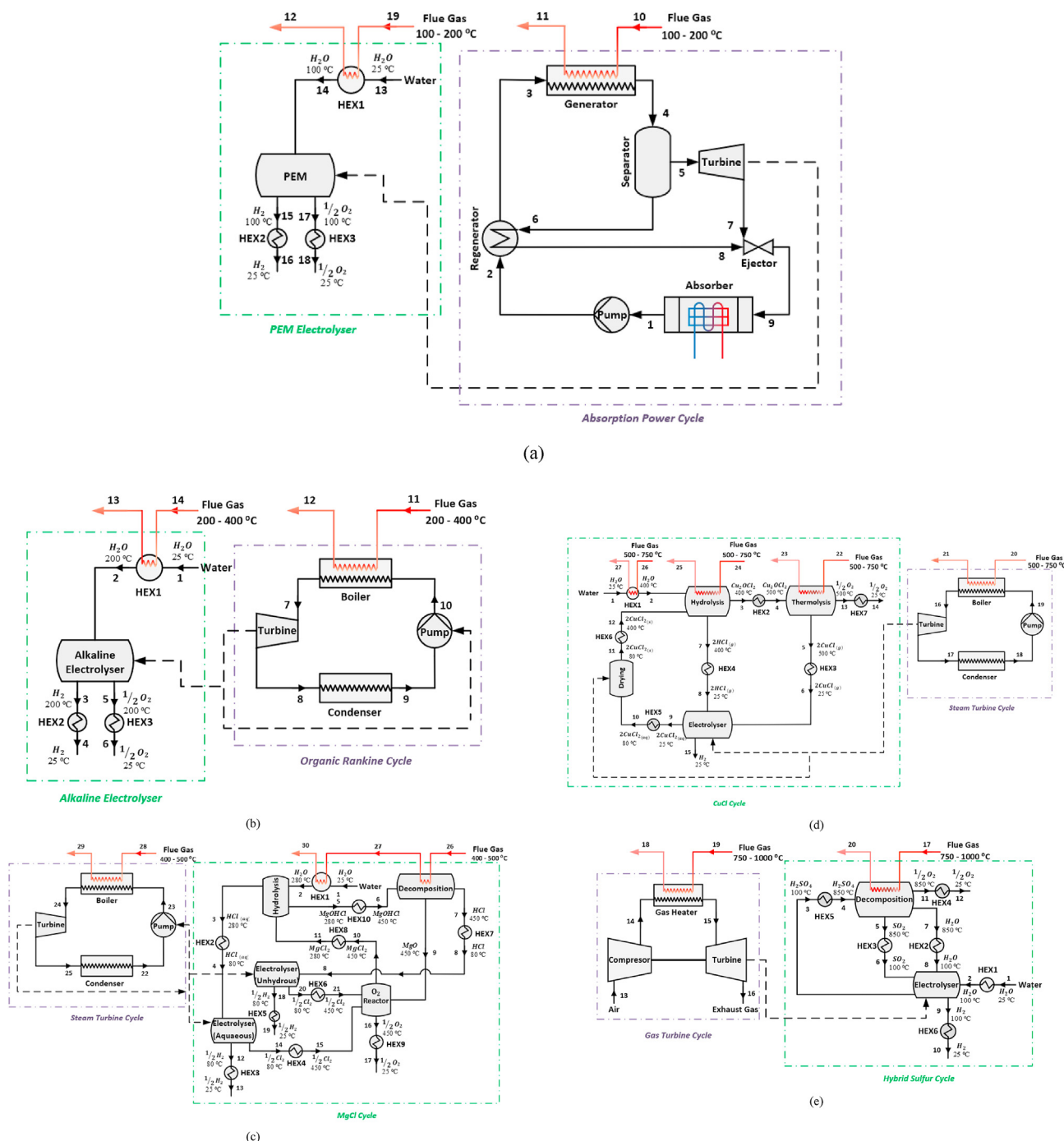


Fig. 4 – Selected power-hydrogen technologies (a) APC-PEM, (b) ORC-AE, (c) ST-MgCl, (d) ST-CuCl, and (e) GT-HyS.

entropy change while Gibbs energy change of a reaction is defined with changes in reactants and products as follows [30]:

$$\Delta G = \Delta H + T\Delta S \quad (1)$$

$$\Delta G_{rxn} = \Delta G_{prod,f} - \Delta G_{react,f} \quad (2)$$

Considering the water electrolysis formation Gibbs energy of hydrogen and oxygen are zero since they are in their molecular structure while it is -237 kJ/mol for water. Then based on the voltage definition below and knowing the number of transferred electrons (z):

$$E_0 = -\Delta G_{rxn} / zF \quad (3)$$

Theoretical voltage of splitting water electrochemically is 1.229 V. Overpotentials increase the required voltage and they are generally related to activation, concentration and ohmic losses.

$$E = E_{rev} + E_{act} + E_{ohm} + E_{conc} \quad (4)$$

Reversible cell voltage is provided with the well-known Nernst equation:

$$E_{rev} = E_0 + \frac{R \times T_{cell}}{Z \times F} \times \ln(K_{eq}) \quad (5)$$

where T_{cell} is cell temperature, and K_{eq} is equilibrium constant and can be defined as follows:

$$K_{eq} = P_{cell} \left(\frac{1 - y_{H_2O}}{1 + 0,5 \times y_a \left(\frac{1 + \lambda_a}{\lambda_a - 1} \right)} \frac{1 - y_{H_2O}}{1 + 0,5 \times y_c \left(\frac{1 + \lambda_c}{\lambda_c - 1} \right)} \right) a_w \quad (6)$$

Here y_a and y_c are molar fractions of hydrogen and oxygen in anode and cathode while λ_a is excess air coefficient $\lambda_c = 2\lambda_a$. Activation and concentration overpotentials are defined with the current density and cell characteristics:

$$E_{act} = \frac{J}{J_0} \times \frac{R \times T_{cell}}{Z \times F} \quad (7)$$

$$E_{conc} = \frac{R \times T_{cell}}{Z \times F} \times \ln \left(\frac{1 - J/J_{lim}}{1 + J/J_{lim}} \right) \quad (8)$$

$$E_{ohm} = J \int_0^L dx / \lambda \sigma(x) \quad (9)$$

where J , J_0 , and J_{lim} are current density, exchange current density and limiting current density respectively while σ is ionic conductivity through the cell and L is the cell length. Efficiency of the electrolyser can now be written as:

$$\eta_{elec} = \frac{LHV_{H_2}}{EzF} \quad (10)$$

Regarding thermochemical cycles, a general energy balance should be written by considering any component with and without chemical reactions. The general energy balance for a reaction can be written as follows:

$$\dot{Q} - \dot{W} = \sum \dot{n}_p \left(\bar{h}_f^0 + \bar{h} - \bar{h}_o \right)_p - \sum \dot{n}_r \left(\bar{h}_f^0 + \bar{h} - \bar{h}_o \right)_r \quad (11)$$

\bar{h}_{ol}^0 is the standard molar formation enthalpy, \bar{h} and \bar{h}_o are molar enthalpy values at a certain temperature and reference conditions, respectively. Here, $\bar{h} - \bar{h}_o$ and molar entropy change $\bar{s} - \bar{s}_o$ are correlated as a function of temperature with the Shomate equations as follows [31]:

$$\bar{h} - \bar{h}_o = AT + B \frac{T^2}{2} + C \frac{T^3}{3} + D \frac{T^4}{4} - E \frac{1}{T} + F - H \quad (12)$$

$$\bar{s} = A \ln(T) + BT + C \frac{T^2}{2} + D \frac{T^3}{3} - E \frac{1}{2T^2} + G \quad (13)$$

Here the constants can be found for many substances in NIST database and T is $1/1000$ of the considered temperature [31]. For all thermochemical cycles with reactions, reaction heats are calculated with above equations and electricity consumption of electrochemical components are determined using the universal electrochemical model given above. Heat loads of heat exchangers are also calculated by using the molar enthalpy change at the inlet and outlet conditions and it is assumed that exothermic heat exchangers provide 85% of their heat to endothermic heat exchangers for thermal management purposes. For a hybrid thermochemical cycle, efficiency of the plant can be written as the ratio of produced hydrogen per heat and electricity used:

$$\eta_{elec} = \frac{\dot{n}_{H_2} LHV_{H_2}}{\dot{Q} + \dot{W}} \quad (14)$$

Overall system efficiencies are based on the production of hydrogen per the utilized waste heat energy for both the hydrogen production system and the power plant. For each case study considered, overall efficiencies are defined as follows:

$$\eta_{APC - PEM} = \frac{\dot{n}_{H_2} LHV_{H_2}}{\dot{m}_{fg} C_{pfg} (T_{10} + T_{19} - T_{11} - T_{12})} \quad (15)$$

$$\eta_{ORC - AE} = \frac{\dot{n}_{H_2} LHV_{H_2}}{\dot{m}_{fg} C_{pfg} (T_{11} + T_{14} - T_{12} - T_{13})} \quad (16)$$

$$\eta_{ST - MgCl} = \frac{\dot{n}_{H_2} LHV_{H_2}}{\dot{m}_{fg} C_{pfg} (T_{26} + T_{28} - T_{29} - T_{30})} \quad (17)$$

$$\eta_{ST - CuCl} = \frac{\dot{n}_{H_2} LHV_{H_2}}{\dot{m}_{fg} C_{pfg} (T_{20} + T_{22} + T_{24} + T_{26} - T_{21} - T_{23} - T_{25} - T_{27})} \quad (18)$$

Table 2 – PEC of components used in case studies [10,32,34].

Component	PEC Correlation	Explanation
Gas Turbine	$PEC_{gt} = c_1 \frac{266, 3 \cdot \dot{m}_g}{0, 92 - \eta_{is}} \ln \beta_t \cdot [1 + \exp(0, 036 \cdot T_{max} - 54, 4 \cdot c_2)]$	β_t : Pressure ratio c_1, c_2 : Constants T_{max} : Turbine inlet temperature η_{is} : Isentropic efficiency
Compressor	$PEC_c = c_1 \frac{39, 5 \cdot \dot{m}_g}{0, 9 - \eta_{is}} \beta_c \cdot \ln \beta_c$	β_c : Pressure ratio
Steam turbine	$PEC_{st} = 6000(\dot{W}_t)^{0,7}$	\dot{W}_t : Turbine power
ST and ORC pumps	$PEC_p = 1120(\dot{W}_p)^{0,8}$	\dot{W}_p : Pump power
Heat exchangers (Buoyant type)	$\log_{10} PEC_{HEX} = 4, 3247 + 0, 3030 \log_{10} A + 0, 1634(\log_{10} A)^2$	A: Heat exchanger area
Heat exchangers (power cycles)	$PEC_{HEX} = 1200 \left(\frac{A}{100} \right)^{0,6}$	$A = \frac{\dot{Q}}{U \cdot \Delta T_{lm}} \Delta T_{lm} = \frac{\Delta T_1 - \Delta T_2}{\ln \left(\frac{\Delta T_1}{\Delta T_2} \right)}$
Reactors	$\log_{10} Z_R = 3, 4974 + 0, 4485 \log_{10} V_R + 0, 1074(\log_{10} V_R)^2$	V_R : Reactor volume based on the vapor substance present in the reactor and its residence time. Based on the residence time the reactor is expected to be as large as possible to keep the reactor conditions stable.
Electrolyzers	$Z_{elec} = 1230 \cdot A_{cell}$	A_{cell} : Cell area $A_{elec} = \dot{W}_{elec} / FEJ$

$$\eta_{GT-HyS} = \frac{\dot{n}_{H_2} LHV_{H_2}}{\dot{m}_{fg} C_{pfg} (T_{17} + T_{19} - T_{18} - T_{20})} \quad (19)$$

In all cases, flue gas is considered as an ideal gas with a Cp value ranging from 1008 to 1014 J/kgK based on the common content of the flue gases from industrial facilities which is mainly formed by high amounts of nitrogen rich air, carbon monoxide, carbon dioxide, Nitrous oxides and steam.

Economic analysis of the cases is kept simpler than those of complex economic assessment tools such as exergy based economic assessments. Plant life, interest rates, annual operation hours and maintenance costs are included in the calculation of equipment purchase costs (PEC) and total cost of the plant is simply divided by the total hydrogen production in order to make a reasonable and simplified economic comparison between considered systems [32]:

$$\dot{Z}_k = \frac{CRF \times \Phi}{\tau} PEC_k \quad (21)$$

$$CRF = \frac{i(1+i)^n}{(1+i)^n - 1} \quad (22)$$

Cost rate of each component is \dot{Z}_k , which is a time independent cost factor that also includes other economic parameters, namely, maintenance factor (Φ), annual operation hours (n), effective interest rate (i) and plant life (n). PEC of each component of the system are provided in Table 2. Resulting hydrogen generation costs are compared to those of generic software packages [33]. Some of the component costs are considered by taking into account available cost values in the open literature [34].

Capital investment cost rate of the plant, levelized cost of electricity and cost of hydrogen can be calculated as follows [34]:

$$\dot{Z}_{tot} = 3600 \sum_{i=0}^n \dot{Z}_k \quad (23)$$

$$z_{el} = \frac{\dot{Z}_{PC}}{\dot{W}_{net}} \quad (24)$$

$$z_{H_2} = \frac{\sum_{i=0}^n \dot{Z}_k}{\dot{m}_{H_2}} \quad (25)$$

\dot{Z}_{PC} is total cost rate of the considered power cycle and it is provided in \$/h, cost of electricity in \$/kWh, and cost of hydrogen is provided in \$/kg.

Results and discussion

Selected case studies are studied in a large range of input variables from ideal and practical conditions and this leads to provide a large range of thermal efficiencies and hydrogen costs for all cases. Some ideal results of all cases are summarized in Table 3. The most important idealization is carried out by taking the electrochemical cell voltage values at their theoretical values. The required heat from the waste heat is calculated withing the waste heat temperature range. The required heat is at its highest for the HyS cycle for decomposition reactor and H₂SO₄ heating and its electricity consumption is based on 0.18 V. Under ideal conditions MgCl cycle shows the highest hydrogen cost even though the electricity cost is one of the lowest. Low electricity cost in all cases are

Table 3 – Results of the considered conditions under ideal conditions.

	Input energy (kW)	Cost of electricity (\$/kWh)	Cost of hydrogen (\$/kg)	Overall system efficiency (%)	Total investment cost (\$/h)	Daily hydrogen production (kg/day)
APC-PEM	1076	0.034	1.76	12.9	7.33	99.1
ORC-AE	3709	0.035	1.81	9.9	20.01	262.2
ST-MgCl	2482	0.019	2.47	26.5	48.75	469.7
ST-CuCl	9974	0.015	1.81	27.3	148.10	1944.3
GT-HyS	13,611	0.043	0.77	44.8	140.1	4354.0

due to considering cost of waste heat as zero. This is due to high investment costs of the hydrogen system components. The same can be considered for the CuCl cycle even though it is competitive with PEM and AE systems. Highest plant efficiency belongs to HyS cycle while lowest efficiency belongs to ORC-AE system due to low efficient operation of AE. Highest investment cost belongs to CuCl cycle while it is at its lowest for the APC-PEM system. This parameter can not provide a

certain information for stakeholders since high investment cost -in general-significantly related to size of the system.

Fig. 5 represents change in hydrogen production costs based on the electricity consumption of the hydrogen production systems for all cases. APC-PEM system provides low hydrogen cost values and one of the highest hydrogen plant efficiencies at ideal conditions since not many components are required to produce hydrogen. However, since it is solely dependent on electrical energy to produce hydrogen,

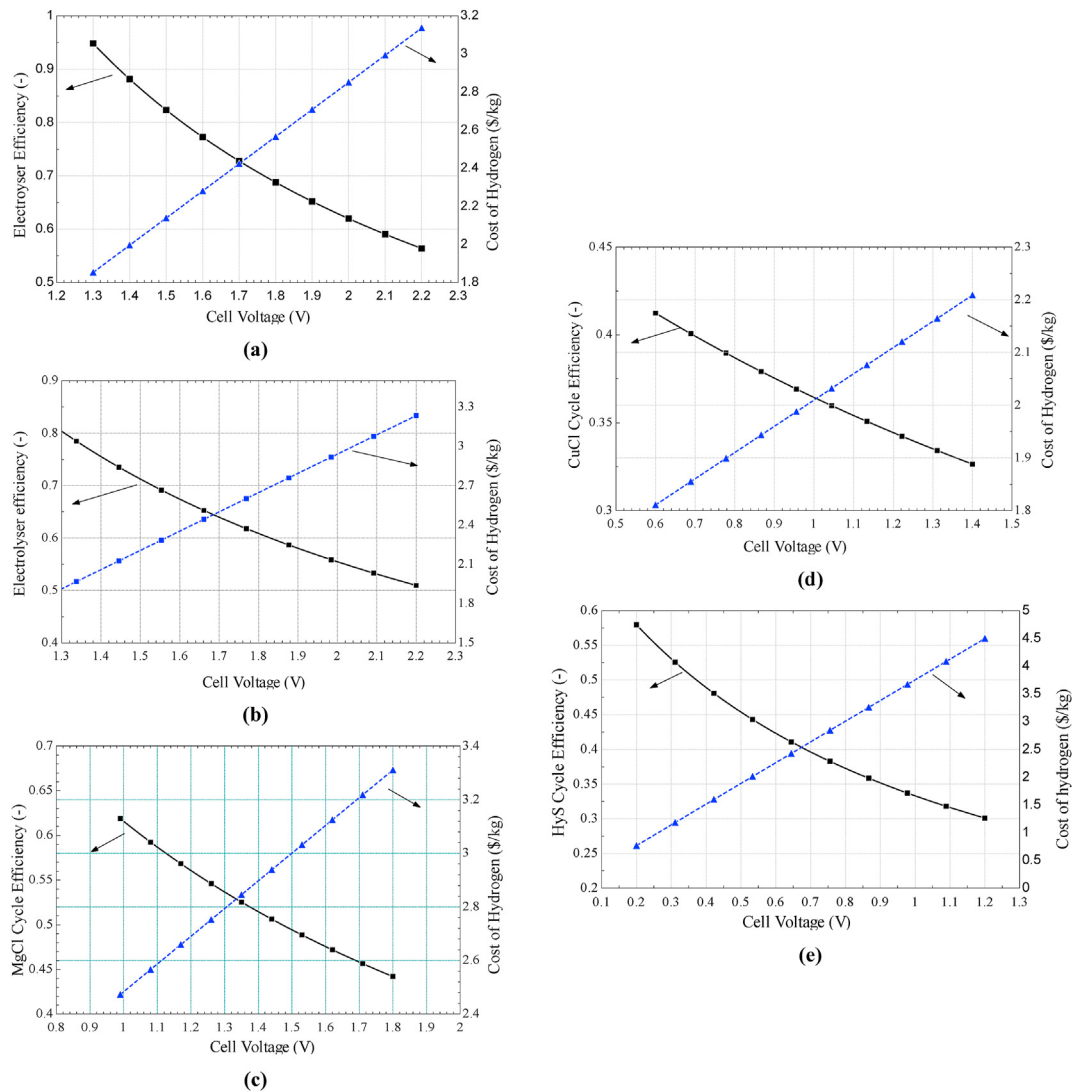


Fig. 5 – Cell voltage effect on hydrogen production system efficiencies and hydrogen costs for (a) PEME, (b) AE, (c) MgCl, (d) CuCl, (e) HyS.

product costs significantly increase when more practical conditions are utilized. At an accepted practical cell voltage with overpotentials cost of hydrogen increases up to 3.5 \$/kg even when a free source of energy is used for power generation system. Same case is valid for the ORC-AE system as well, where hydrogen cost is increasing while electrolyser efficiency decreases at higher cell voltage values. The range in the hydrogen cost change is significant in systems solely dependent on electricity while the dependency is even higher for the HyS cycle in this case due to high electricity cost of the GT system. A 1 V overpotential addition increases the cost of hydrogen up to 4.5 \$/kg while it is even competitive with fossil driven hydrogen production technologies at low cell voltage values. It should be noted that change in MgCl and CuCl cycle electrolyser voltages are also significant on hydrogen costs. Higher voltage requirement at the HCl electrolysis step leads the MgCl cycle hydrogen cost increasing up to 3.3 \$/kg. Dry HCl electrolysis is eligible to work at 1.4 V cell voltage which in this case the hydrogen cost corresponds to around 2.9 \$/kg. CuCl cycle is the least effected hydrogen generation system by the change in overpotentials. There are many other configurations of this cycle with various hydrogen generation costs based on the cost of electricity and thermal energy.

Hydrogen production cost ranges for considered cases are represented in Fig. 6. Here minimum costs refer to the ideal conditions while maximum costs designate more practical conditions such as addition of overpotentials, decrease in system size and less effective use of thermal management through the hydrogen production systems. For instance, APC system shows its maximum efficiency and lowest electricity cost at 140 °C waste heat temperature while cost of electricity may go up to 0.14 \$/kWh and resulting in a significant increase in hydrogen cost. Therefore, these conditions are also taken into account to provide a large range of hydrogen generation costs. Hydrogen cost from MgCl and CuCl cycles are more stable while HyS cycle represents the highest range. However, HyS provides the lowest cost of hydrogen at ideal conditions, it is so far the only method to be competitive with fossil driven technologies such as steam methane reforming and coal driven hydrogen production. In pure electrochemical technologies, the highest cost contributor is electricity cost, and therefore, cost of electricity from the selected cycle is of importance. ORC cycle can work at different operating temperatures with various working fluids to decrease the cost of electricity as well many system configurations are present at the cost of increasing the investment costs. CuCl in this case presents the best average hydrogen cost followed by HyS and MgCl cycles showing similar costs while highest average costs belong to the pure electrochemical systems. Even though product costs from thermochemical cycles show better performances than pure electrochemical systems, none of these cycles are industrially available and they are under development stage. On-the-shelf PEME and AE technologies are under use to split water sustainably by utilizing grid electricity or renewables at high hydrogen production costs. Further development of thermochemical cycles may provide decreased hydrogen costs by utilizing medium and high temperature sources and decrease electricity consumption

more sustainable than those of pure electrochemical technologies.

Finally, it is also possible to provide an insight on use of hydrogen produced from waste heat. Hydrogen can be used as a source of electricity, a storage medium and also for residential heating applications when mixed with natural gas at a certain fraction (up to 10 vol%). An overall assessment now can be made by considering the selected cases for hydrogen generation from waste heat with given temperature ranges. When 100–200 °C sources are used for APC-PEME system, it is possible to produce 30,259 tons of hydrogen annually which corresponds to 132.1 million m³ natural gas (assuming 100% CH₄). The ORC-AE system is eligible to produce 11,610 tons of hydrogen annually which is corresponding to 50.7 million m³ natural gas when 200–400 °C sources are used. For the thermochemical cycles, natural gas equivalents of annual hydrogen production correspond to 57.3, 88.2, and 144.7 million m³ natural gas for MgCl, CuCl and Hys cycles, respectively. Total potential to produce hydrogen from selected systems corresponds to 473 million m³ natural gas equivalents as represented in Table 4. Considering Turkey's natural gas consumption in 2019, the total productions is eligible to compensate 1% of overall NG consumption while it corresponds to 5% of residential NG consumption when used for heating applications. It is also possible to determine the reduction in CO₂ emissions when H₂ replaces a part of NG. A simple stoichiometry of methane combustion provides that for every kilogram of methane combusted, 3 kg of CO₂ is produced. For this case ~721 thousand tons of CO₂ emissions can be prevented when industrial waste heat can be used to its full. Produced hydrogen can also be used in fertilizer industry, a clean agent for iron-steel industry replacing coke, for onboard power production applications via fuel cells.

Conclusions

In this study, amount and temperature range of Turkey's industrial waste heat is investigated and potential energy recovery options are considered to produce useful energy. 20 case studies are considered by considering various power and hydrogen recovery systems. A down selection is made based on the of the most effective power-hydrogen system couple that match with the waste heat temperature range. Below conclusions are retrieved from the study:

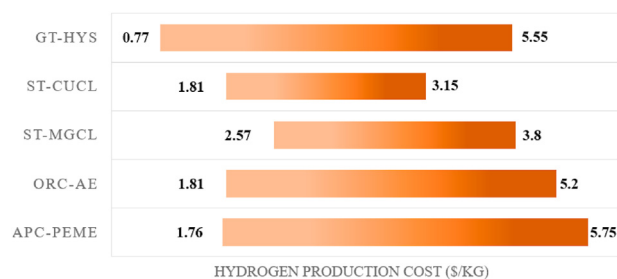


Fig. 6 – Hydrogen production cost range for selected cases at ideal and practical conditions.

Table 4 – Annual hydrogen production potential with natural gas equivalence and emission reduction.

System	Waste heat amount (MW)	Temperature Range (°C)	Annual Hydrogen Production Potential (tons)	Natural Gas Equivalent (million m ³)	CO ₂ emission reduction potential (thousand tons)
APC-PEM	900	100–200	30,259	132.1	201.3
ORC-AE	450	200–400	11,610	50.7	77.2
ST-MgCl	189	400–500	13,122	57.3	87.3
ST-CuCl	284	500–750	20,207	88.2	134.4
GT-HyS	284	750–1000	33,160	144.7	220.5
TOTAL	-	-	108,358	473.0	720.7

- Turkey's annual waste heat potential is around 71 PJ and expected to double in the next 30 years. The rates of the waste heat are 40% for 100–200 °C, 14% for 200–300 °C, 6% for 300–400 °C, 9% for 400–500 °C, 31% for 500–1000 °C
- High temperature waste heat is generally cooled in high chimneys or fans and discharged to atmosphere at certain temperatures designated by environmental regulations.
- Among the case studies, highest efficient option is the GT-HyS couple followed by ST-CuCl and ST-MgCl couples which have significant potentials to produce hydrogen at medium to high temperatures and superior than those of pure electrochemical hydrogen generation.
- Ideal conditions designate economic competitiveness of HyS cycle compared to fossil driven hydrogen methods while realistic conditions such as overpotentials and thermal energy cost increase the cost of hydrogen significantly. Cost of electricity has influence on all hybrid systems while it is more significant on pure electrolysis systems and the HyS cycle.
- Lowest average hydrogen costs are obtained from selected hybrid thermochemical cycles followed by electrochemical hydrogen generation.
- When waste heat is used for power generation only, 0.8–1.5% of Turkey's total peak electricity consumption can be compensated from waste heat with suitable technologies.
- When selected cases could be carefully accomplished, generated hydrogen corresponds to 473 million m³ of natural gas equivalents which is more than 5% of Turkey's annual residential natural gas consumption. When added to the NG pipelines at certain fractions, more than 720 thousand tons of CO₂ reduction is possible by preventing NG use.

\dot{W}	Power (kW)
\dot{Z}	Component cost rate (\$/h, \$/s)
A	Area (m ²)
C _p	Specific heat (kJ/kgK)
E	Cell Voltage (V)
F	Faraday's constant
G	Gibbs free energy
h	Specific enthalpy (kJkg ⁻¹)
i	interest rate (–)
J	Current
n	plant life (year)
P	Pressure (kPa)
P	Pressure (kPa), Primary (–)
s	Specific entropy (kJkg ⁻¹)
T	Temperature (C, K)
U	Overall heat transfer coefficient (W/m ² K)
y	Fraction

Greek Letters

β	Pressure ratio (–)
η	Efficiency (–)
λ	excess air coefficient
σ	ionic conductivity
τ	annual operation hours
ϕ	Maintenance factor (–)

Subscripts

a	anode
act	actual
c	cathode
cell	cell
conc	concentration
elec	electrolyser
eq	equilibrium
eq	equilibrium
hex	heat exchanger
is	isentropic
o	reference
ohm	ohmic
p	pump
prod	product
R	reactor
reac	reactant
rev	reversible
rxn	reaction
t	turbine

Acronyms**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Nomenclature

\dot{m}	Mass flow rate (kgs ⁻¹)
\dot{Q}	Thermal Energy Rate (kW)

AE	Alkaline Electrolysis
APC	Absorption power cycle
CaBr	Calcium Bromine
CANDU	Canada Deuterium Uranium
CRF	Capital Recovery factor
CuCl	Copper chlorine
GT	Gas Turbine
HyS	Hybrid Sulfur
IEC	Industrial Energy Consumption
JAEA	Japan Atomic Energy Agency
KL	Kalina cycle
LHV	Lower heating Value
MgCl	Magnesium Chlorine
ORC	Organic Rankine cycle
ORC	Organic Rankine Cycle
PEME	Proton exchange membrane electrolyser
SCWR	Super Critical Water Reactor
ST	Steam Turbine

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