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Hydrogen production by high temperature electrolysis with waste heat

A.Coskun Avci[1,a], E.Toklu[1], M.Yegin[2]

[1]Duzce University, Mechanical Engineering, Duzce, Turkey.
[2]Kocaeli University, Electrical Engineering, Kocaeli, Turkey.

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Abstract

Energy is one of the most important needs for fulfillment of humankind's main inputs, for social and economic development of the country [1]. Along with the constantly developing technology the most advanced technology is known that hydrogen energy system which is environmental friendly and sustainable can be met the increasing energy requirements [2]. The rapid progress of science, engineering and technology is quickly depleting natural energy reserves worldwide. Population growth has also spurred the demand for energy. The world is predicted to consume 66% more energy in 2030 [3] and twice as much in 2050 [4] than it is today [5]. The idea is to improve hydrogen production efficiency through a solid oxide electrolysis process with the help of waste heat. This research aims to create an effective and multi-disciplinary solution package within the circle drawn to produce hydrogen evaluating the waste heat.

Keywords: Energy, electrolysis, hydrogen, high temperature electrolysis, waste heat

1.Introduction

Hydrogen has advantages in the highest energy density, environmental friendliness and safety. It is considered as a universal energy carrier for the future. Large-scale hydrogen production without fossil consumption and various gas emissions such as COx, SOx and NOx is the key to achieving the "Hydrogen Economy [6-11,23]. Hydrogen can produce with water electrolysis [13-16,23], thermochemical cycles [17-19,23] and photocatalysis processes [20-23]. This methods are non-fossil fuel based process. New and more efficient energy conversion systems are required in the near future, due in part to the increase in oil prices and demand and also due to global warming. Fuel cells and hybrid systems present a promising future but in order to meet the demand, high amounts of hydrogen will be required. Until now, probably the cleanest method of producing hydrogen has been water electrolysis [23]. Theoretically, the efficiency of a solid oxide electrolysis cell improved with increased temperature as a result of reduction in the Gibbs free energy change [5]. In this field, Solid Oxide Electrolysis Cells (SOEC) have attracted a great interest in the last few years, as they offer significant power and higher efficiencies compared to conventional low temperature electrolysers [23]. In this research, the idea is to improve hydrogen production efficiency through a solid oxide electrolysis process with the help of waste heat.

2. Material and Methods

Flue gas released to the athmosphere from Düzce Cam A.Ş. plants's chimneys causes

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[a] Corresponding author;
Phone: +90-507-338-59 15, Email : arzucoskun@duzce.edu.tr

internal heat pollution. This research is investigated to recovery the portion of the used in the analysis of waste heat are all Düzce Cam A.Ş. real data. Research for the design and analysis is performed parametrically. The solution package which will be created for the purpose of the thesis consists of two main processes:

- The first process is to catch the waste heat with a heat exchanger. In this process, design limits are determined by an acceptable pressure drop of fluid and the total amount of heat that can be transferred.

heat and to convert to useful work released into the atmosphere by flue gases. All data

- The second process is to produce hydrogen using high-temperature steam electrolysis. Captured heat in the first process provides the heat of the electrolysis. In this process, the geometry of the electrode and material are focused on fundamental issues. In this process, the efficiency of the different options and economic analysis is performed.

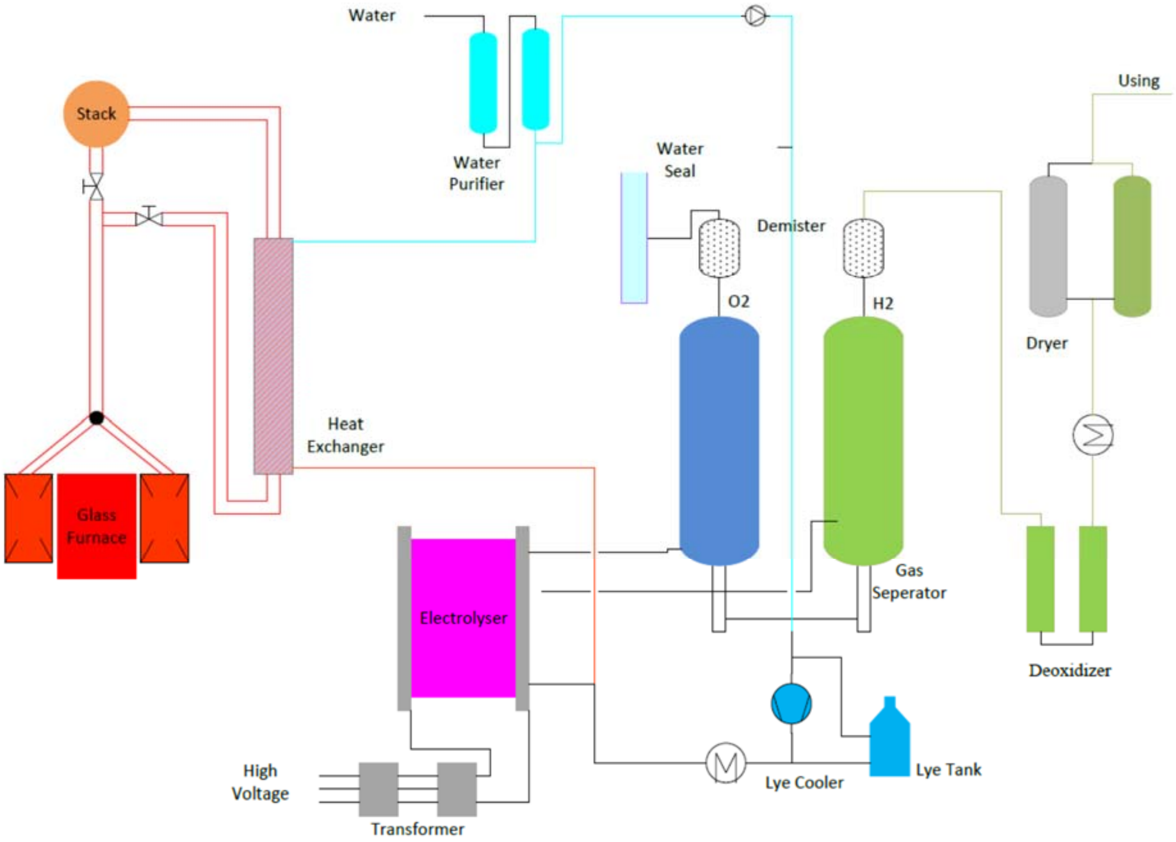

Figure 2.1. Schematic Diagram of Designed System.

The first stage of the solution is recovered the heat energy which is contained in the flue gas by using a heat exchanger. At this point, heat exchangers are investigated that are available on market and heat exchanger which provides the package has been designed on. However, heat transfer capacity and pressure loss of heat exchangers which are available on market are not within acceptable limits for solution package. Therefore, it is decided to design a heat exchanger which is suitable for solution package. Thermohydraulic analyzes were performed in MATHCAD Prime 3.0 platform. This situation makes it adaptable solution package. Parametric analitic heat transfer calculations based on geometry having optimal values were performed. Then pressure of the fluid and heat trasfer losses are limite taking in to account enviromental factors. Parameters that affect the operation of the solid oxide electrolysis cells are area specific resistance, steam utilization, electrolysis voltage, thermoneutral voltage, current density, number of electrolysis cell and number of stack. Number of electrolysis cell, the number of stacks and cell area are determined on the basis of previous studies with a literature search. Steam temperature and steam flow rate that are calculated parametrically on MATHCAD 3.0 platform are defined input values of electrolysis unit. Flue gas exit temperature which is the main factor for steam temperature and steam flow rate dependence on the factors affecting the thermal electrolysis are analyzed for the designed system.

3. Results and Discussions

3.1. Thermohydrolic Analysis of Heat Exchanger

The first module of the package is a heat exchanger. Calculations made in Mathcad Prime 3.0 reveal that each of the heat exchanger unit would be 1634 kW. Boundary conditions and assumptions are as follows: Total flue gas mass flow rate is 68.810 m^3/hr. This gas flow rate divided equally 4 parallel heat exchangers each having 17.200 m^3/ hr flow rate. Considering the cross sectional area of the heat exchanger unit, average speed of gas molecules which passes through the exchanger would be 345.6 m/s. The inlet temperature of flue gas to heat exchanger is 534ºC. Discharge temperature of the flue gas to the atmosphere takes different values within the constraints in a certain probability. Discharging of the flue gas at high temperature causes reduction of efficiency and economic sense of solution package. In addition, environmental advantages of solution package about reducing thermal pollution plant causes would disappear. In spite of these justifications, flue gas exit temperature from the heat exchanger is determined to be 100 ° C. According to these data, total amount of heat transfer of flue gas cooling from 534ºC to 100ºC calculated using Mathcad Prime 3.0 and amount of transferred heat as linear gradient is shown in Figure 3.1.

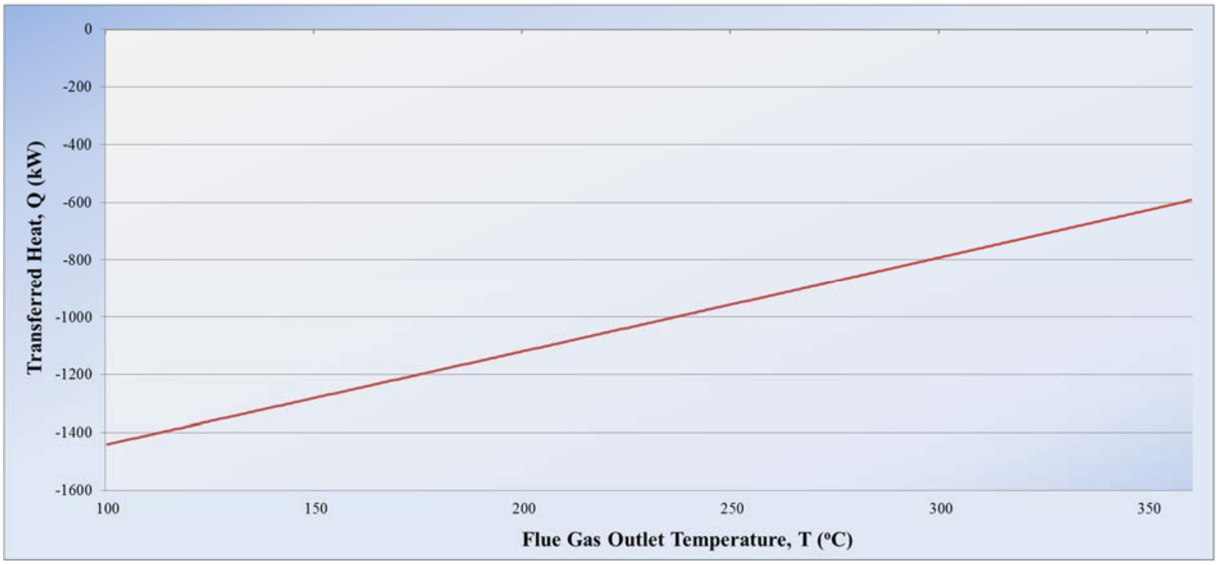

Figure 3.1. Plot of flue gas outlet temperature versus transferred heat.

The temperature dependence of specific heat is a polynominal function indicated with Equation 3.1.

$$C(T) = -2.28.10^{-11}.T^{3} + 2.66.10^{-8}.T^{2} + 5.99.10^{-5}.T+0.249233 \text{ kcal/kg.K} \quad (3.1)$$

As seen this function, the temperature of the higher order terms has very little importance coefficient. In spite of this, the graph shows a character very close to linear.

The second layer that transfer heat flux are fed with distilled water at 15 ° C. Water must leave this layer in the form of dry steam at 250 ° C and so steam mass flow rate is 0.516 kg/s. The flow rate of dry steam delivered by the heat exchanger is dependent on outlet temperature of steam and flue gas because water and flue gas inlet temperature are constant. Dry steam flow rate is shown in Figure 3.2 as a function of steam outlet temperature and gas outlet temperature. As shown graphs, the flow rate of steam is depend steam outlet temperature more strong than flue gas exit temperature.

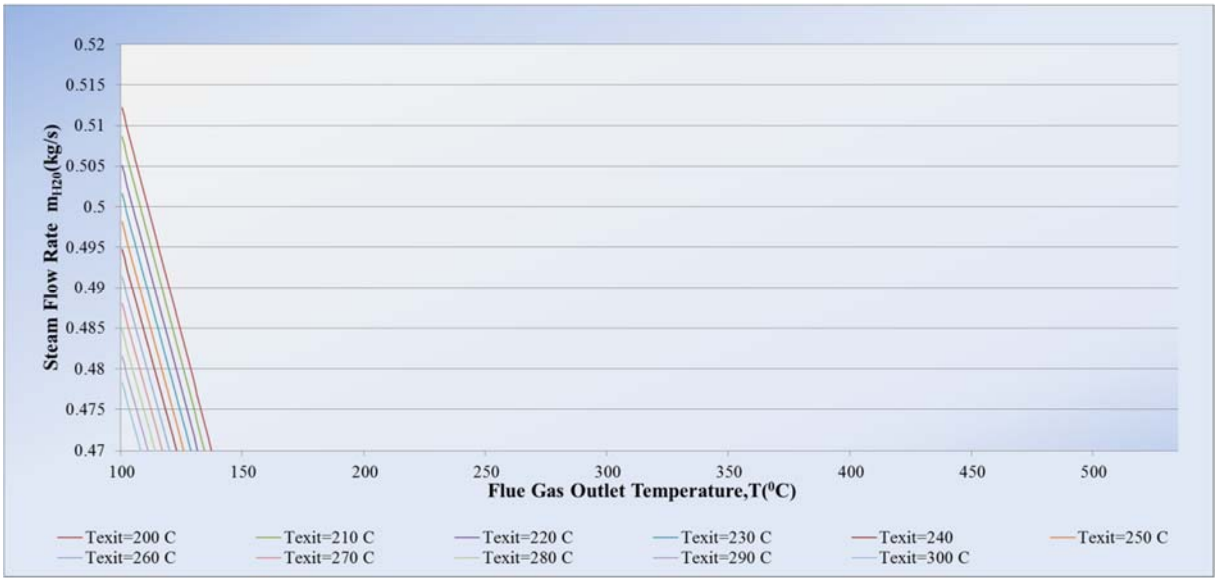

Figure 3.2. Temperature profiles of steam flow rate according to flue gas exit temperature or steam exit temperature.

3.2. Analysis of Electrolyser

Parameters that affect the operation of the solid oxide electrolysis cells are area specific resistance, steam utilization, electrolysis voltage, thermoneutral voltage, current density, number of electrolysis cell and number of stack. Open cell voltage (E_{ocv}), usually determined by the thermodynamic properties of the gas streams. The factors that determine the open cell voltage are the temperature (T), standard cell potential (E°), P is the ambient pressure, P_{std} is the standard pressure and mole fractions of the gas streams on either side of the electrodes [5]:

$$E = \frac{\Delta G}{zF} - \frac{RT}{zF}\ln\left[\left(\frac{X_{H2O}}{X_{H2}.X_{O2}^{\frac{1}{2}}}\right)\left(\frac{P}{P_{std}}\right)^{\frac{1}{2}}\right] \quad (3.2)$$

Current density is calculated by fixing the area specific resistance. It is given by [5,25]

$$i=\frac{E-E_{ocv}}{ASR} \quad (3.3)$$

The unit is given by Amp/cm^2. E is the operating voltage; ASR is the area specific resistance. The current density multiplied by the area of the electrolyte gives the net current.

The inlet molar flow rate of water can be found by fixing the steam utilization value using the following equation:

$$\dot{N}_{H20,inlet}=\frac{n.N.I}{z.F.SU} \tag{3.4}$$

where SU is the steam utilization, I is the current, Z is the valency, F is the Faradays constant, N is the number of stacks and n is the number of cells. The mass flow rate can be calculated by using the following:

$$\dot{N}_{H2,out}=\dot{N}_{H2O,inlet}\cdot\frac{X_{H2}}{XH2O}+\frac{n.N.I}{z.F} \tag{3.5}$$

3.2.1. Current Density

It is shown that in Equation 3.4, current density of the electrolysis unit is proportional to steam utilization and mass flow rate of steam entering the electrolysis unit [5]. Steam utilization is the measure of the steam utilized for the production of hydrogen. Dependence of the current density versus the flue gas outlet temperature is shown in Figure 3.3 if the SU is between 0.5-0.9. Changes are expected to be linear. Amount of steam will be maksimum with the smaller flue gas temperature. The production of hydrogen will depends on steam utilization. The higher the utilization rate of steam causes higher hydrogen production consequently, the current density will increase. Calculations shows when the SU is 0.9, inlet steam flow rate is 0,4977 kg/s and flue gas temperature is 100 ^{0}C, the current density will be 2.65 A/m^2.

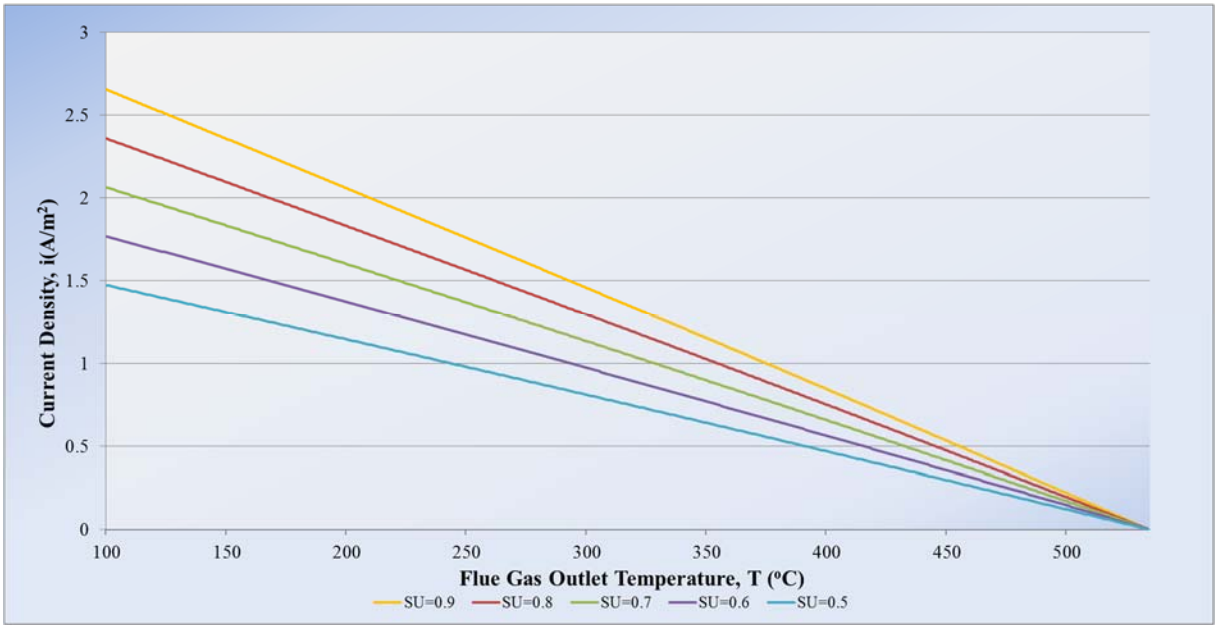

Figure 3.3. The effect of steam utilization to current density.

3.2.2. Electrolysis Voltage

When potential applies to electrodes in electrolysis cell, the electrolyis voltage equation that is reqired for hydrogen production is given in Equation 3.2. It is shown in Equation 3.3 and 3.4 that electrolysis voltage depends on hydrogen and oxygen molar consentration, inlet steam flow rate, inlet steam temperature, SU and

ASR. Dependence of the electrolysis voltage versus the flue gas outlet temperature is shown in Figure 3.5 if the SU is between 0.5-0.9. Electric charges move in the electrolyte medium as negatively charged oxygen ions in the solid oxide electrolysis cells. The resistance to the movement of oxygen ions of the electrolyte, ASR, is equal to 1 is Figure 3.4. Here is a case of change is expected to be linear. If the steam utilization is higher, higher the hydrogen production and and according hydrogen production current density and the electrolysis voltage will also increase. Due to increasing the flue gas exit temperature, less steam is produced. In this case, depending on the current density, the electrolysis voltage is decreased. Calculations shows when the SU is 0.9, inlet steam flow rate is 0,4977 kg/s and flue gas temperature is 100 ^{0}C, the electrolysis voltage will be 1.44939 V.

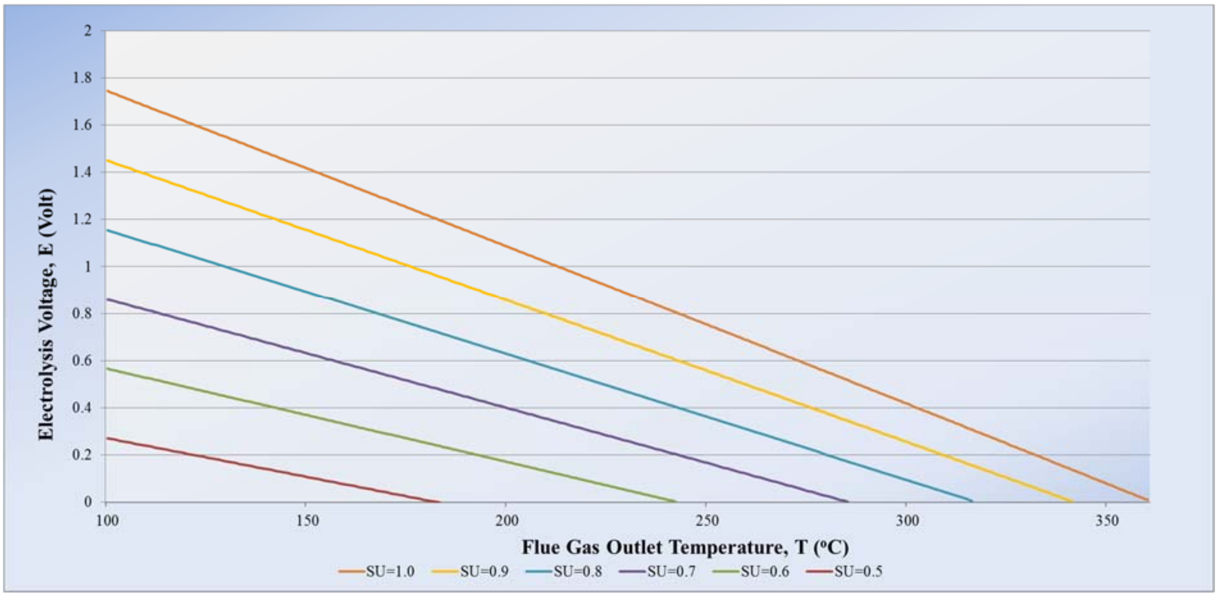

Figure 3.4. The effect of steam utilization to electrolysis voltage.

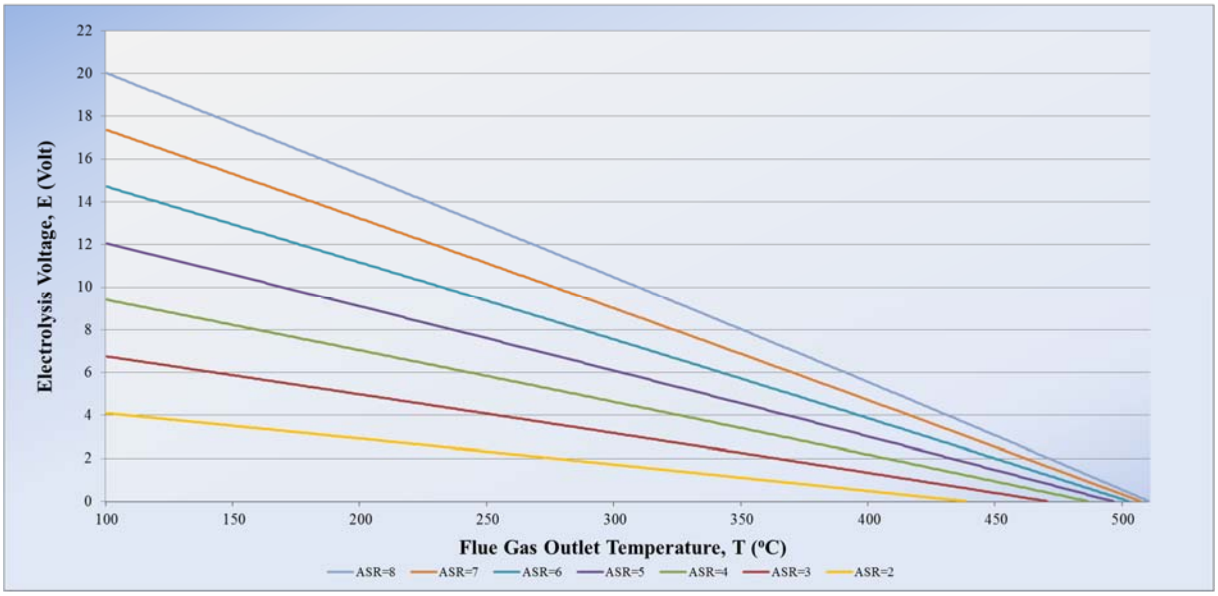

Figure 3.5. The effect of area specific rezistance to electrolysis voltage.

ASR, which is the change of electrolyte resistance to oxide ions in the analysis of electrolysis voltage is shown in Figure 3.5. SU value of 0.9 has been considered here. By increasing the amount of ASR, is much more than the increase in the electrolysis voltage. SU is 1 and ASR is 0.9 is shown in Figure 3.4. When the ASR is 8, electrolysis voltage is increase 14 times according to 1.44 V. If we assume that an electrolyte in electrolysis cell works similarly a dust filter, electrolyte rezistance is also expected to increase over time such as dust filter's increasing rezistance to air flow over time. It means ASR is expected to increase over time.

3.2.3. Producing Hydrogen

It is expressed in Equation 3.5, the mass flow rate of producing hydrogen is dependent to the hydrogen and steam molar concentration, steam inlet flow rate and current density. Minimum the flue gas temperature at the point, maxsimum hydrogen production.If SU is 0.9, ıt is possible to produce a 18 kg/sa hydrogen generator as in Figure 3.6.

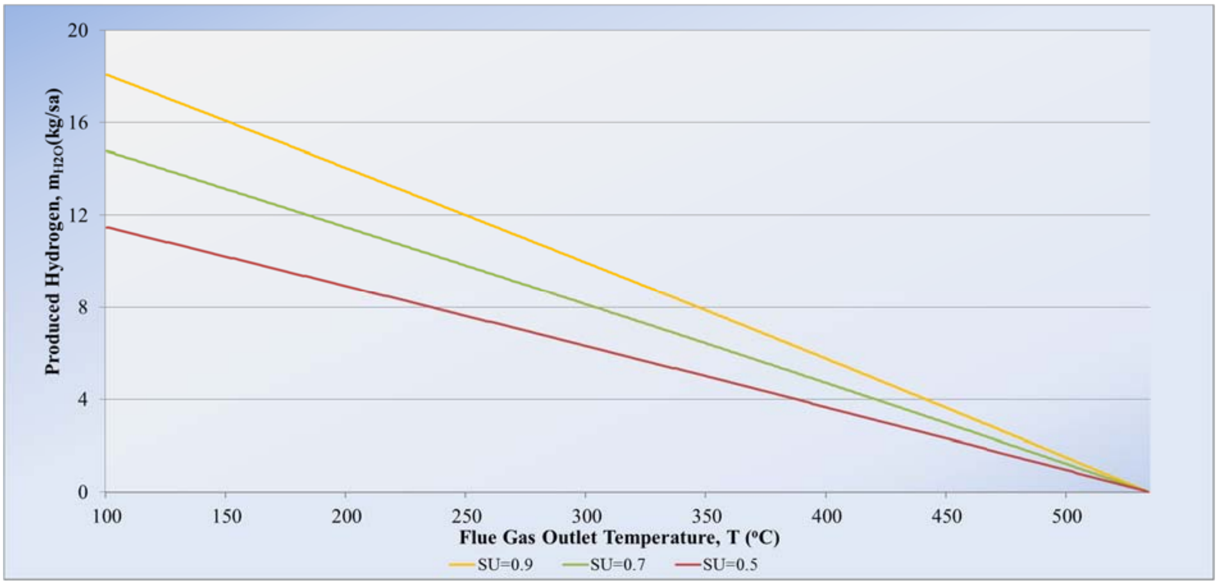

Figure 3.6. The effect of steam utilization to produced hydrogen versus flue gas outlet temperature.

The amount of hydrogen produced in dependence with ASR that is the change of electrolyte resistance to oxide ions in solid oxide electrolysis cell is shown by Figure 3.7 and Figure 3.8 for two different SU values. SU value of 0.9 has been considered here. It is quite clear to see that increasing ASR causes reducing hydrogen production in Figure 3.7 and Figure 3.8. SU effect is so over at low ASR value (ASR = 1). Amount of hydrogen produced decreases by about % 40 when SU takes the value 0.5 instead of 0.9. This decrease is at level %25 when ASR is 4. The reduction of hyfrogen production capacity is only %10 due to reduction of SU.

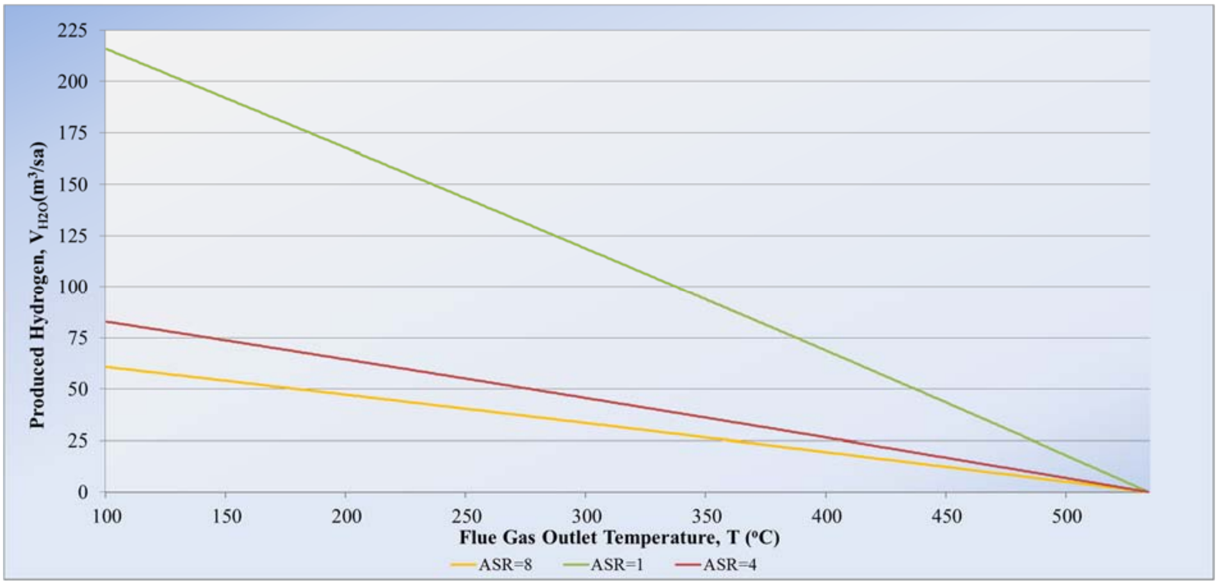

Figure 3.7. The effect of ASR to produced hydrogen, if steam utilization is 0.9.

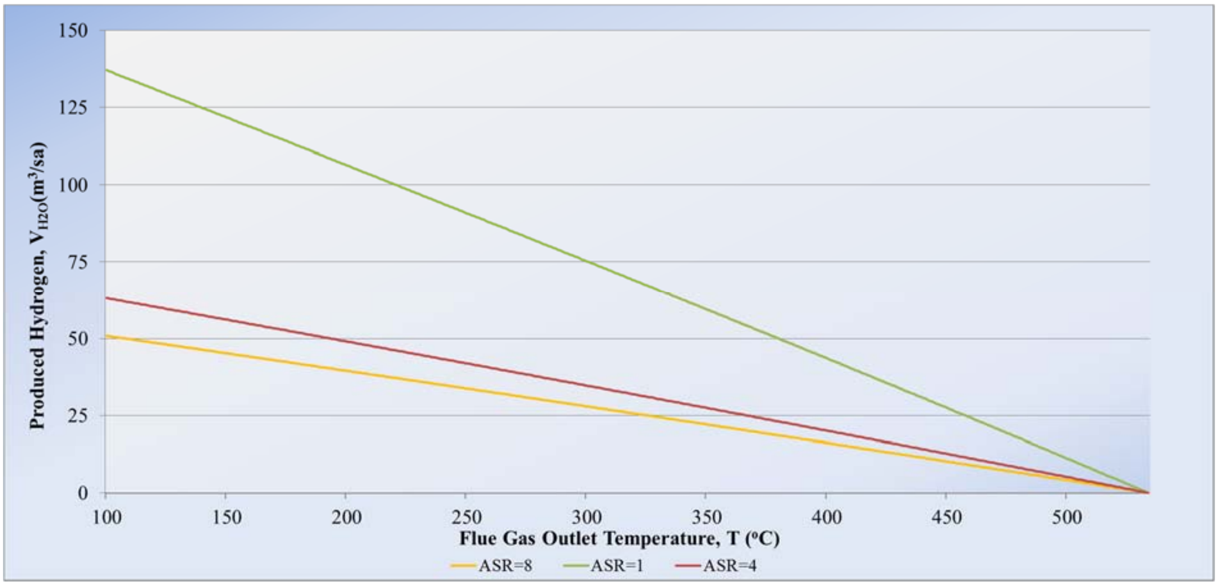

Figure 3.8. The effect of ASR to produced hydrogen, if steam utilization is 0.5.

4. Conclusion

Hot flue gas which is released to the athmosphere from Düzce Cam A.Ş. plants's chimneys causes internal heat pollution. This research is investigated to recovery the portion of the heat and to convert to useful work released into the atmosphere by flue gases. All data used in the analysis of waste heat are all Düzce Cam A.Ş. real data. Thesis for the design and analysis was performed parametrically. This situation makes it possible to have adapted well for other industrial facilities which produce waste heat. Düzce Cam A.Ş. uses pure hydrogen 80 m^3/hr for producing glass and this hydrogen is purchased from a foreign company. In this thesis, values that can vary according to the materials and manufacturability of hydrogen are analyzed. The boundary condition that is determine the solution package's yield and economic value is temperature of the flue gas that is released to the atmosphere is shown by thermal analysis. This is to be expected, because the main energy input of all processes within the package is the difference in entalphy between the gas terminals of the flue gas. In the solutions provided with the package have an electrolysis unit which is enough to supply the hydrogen needs and have the waste heat which is free of charge heat source. Thus each steam inlet temperature above ambient temperature results will constitute an economically meaningful. This is significant in today's economy and also it is a preliminary work for for tomorrow's energy efficiency-oriented industry.

References

[1] Koşar M., Benzinli motorlarda hidrojen kullanımının performans ve emisyonlara etkisi, *Yüksek Lisans Tezi*, Zonguldak Karaelmas Üniversitesi, (2007).

[2] İşcanlı Y., Nikel bakır çöktürülmüş karbon keçe elektrotta hidrojen gazı çıkışının araştırılması, *Yüksek Lisans Tezi*, Çukurova Üniversitesi, (2010).

[3] Dorian,_J. P., Franssen, H. T., & Simbeck, D. R., Global challenges in energy. Energy Policy, 34, 1984-1991, (2006).

[4] Baruch, J. J., Combating global warming while enhancing the future. Technology in Society, 30, 111-121, (2008).

[5] Gopalan S., Efficient Production of Hydrogen Through Recuperative Solid Oxide Electrolysis, *Ph.D. Thesis*, Howard University, Washington-United States, (2008).

[6] Balthasar W. Hydrogen production and technology: today, tomorrow and beyond. Int J Hydrogen Energy;9:649-68, (1984).

[7] Goltsov VA, Veziroglu TN. From hydrogen economy to hydrogen civilization. Int J Hydrogen Energy ;26:909-15, (2001).

[8] Barreto L, Makihira A, Riahi K. The hydrogen economy in the 21st century: a sustainable development scenario. Int J. Hydrogen Energy;28:267-84, (2003).

[9] Winter CJ. Into the hydrogen energy economy-milestones. Int J Hydrogen Energy; 30:681-5, (2005).

[10] Holladay JD, Hu J, King DL, Wang Y. An overview of hydrogen production technologies. Catal Today;139:244-60,(2009).

[11] Moriarty P, Honnery D. Hydrogen's role in an uncertain energy future. Int J Hydrogen Energy; 34:31-9, (2009).

[12] Kelly NA, Gibson TL, Cai M, Spearot JA, Ouwerkerk DB. Development of a renewable hydrogen economy: optimization of existing technologies. Int J Hydrogen Energy ; 35:892-9, (2010).

[13] Onda K, Kyakuno T, Hattori K, Ito K. Prediction of production power for high-pressure hydrogen by high-pressure water electrolysis. J Power Sources;132:64-70, (2004).

[14] Udagawa J, Aguiar P, Brandon NP. Hydrogen production through steam electrolysis: model-based steady state performance of a cathode-supported intermediate temperature solid oxide electrolysis cell. J Power Sources;166:127-36, (2007).

[15] Liu M, Yu B, Xu J, Chen J. Thermodynamic analysis of the efficiency of high- temperature steam electrolysis system for hydrogen production. J Power Sources;177:493-9, (2008).

[16] Wang M, Wang Z, Guo Z. Water electrolysis enhanced by super gravity field for hydrogen production. Int J Hydrogen Energy;35:3198-205, (2010).

[17] Beghi GE. Review of thermochemical hydrogen production. Int J Hydrogen Energy; 6:555-66., (1981).

[18] Steinfeld A. Solar thermochemical production of hydrogen: a review. Solar Energy ; 78:603-15, (2005).

[19] Gonzales RB, Law VJ, Prindle JC. Analysis of the hybrid copper oxide-copper sulfate cycle for the

thermochemical splitting of water for hydrogen production. Int J Hydrogen Energy;34:4179-88, (2009).

[20] Ohta T. Photochemical and photoelectrochemical hydrogen production from water. Int J Hydrogen Energy;13:333-9, (1988).

[21] Clark CD, De Bruyn WJ, Jones JG. Photochemical production of hydrogen peroxide in size-fractionated Southern California coastal waters. Chemosphere;76:141-6, (2009).

[22] Burgess G, Ferna´ndez-Velasco JG. Materials, operational energy inputs, and net energy ratio for photobiological hydrogen production. Int J Hydrogen Energy; 32:1225-34, (2007).

[23] Laguna M.A., Bercero, Recent advantages in high temperature electrolysis using solid oxide fuel cells: Journal of Power Sources, 203,4-16, (2012).

[24] Hydrogen Fuel Cell Engines and Related Technologies – Module 1:Hydrogen Properties, College of Desert, (2001).

[25] James E. O’Brien, Carl M. Stoots, J Stephen Herring, Joseph Hartvigsen, Performance of planar high-temperature electrolysis stacks for hydrogen production from nuclear energy, Nuclear technology, 158, 118-131, (2007).