

HIGH TEMPERATURE ELECTROLYSIS, BRAYTON POWER CYCLE AND METHANOL PRODUCTION

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ABSTRACT

This paper presents heat exchanger technology that is the key technology in three processes i.e. hydrogen and oxygen production using high temperature steam electrolysis; Brayton power cycle where sCO₂ is recycled to the combustor in aim to reduce high temperature achieved after natural gas is combusted in oxygen and methanol production. These processes are combined into one process that enables methanol and electricity production with 100% carbon capture.

Industrial hydrogen has been used in many different applications e.g. oil refineries, ammonia and methanol production with demand that has been increasing continuously and expect to rise in days to come. To date, Steam Methane Reforming (SMR) process where methane (natural gas) reacts with steam at high temperature in an endothermic reaction has been adopted as the conventional way to produce industrial hydrogen.

However, there are other processes developed to produce hydrogen with electrolysis of steam being one of them. Steam electrolysis includes few different cell types with Solid Oxide Electrolysis Cell (SOEC) that operates at high temperatures being considered in this paper. It needs to be noted that hydrogen produced by steam electrolysis is of highest purity. As steam electrolysis requires electricity which can be provided by either renewable or non-renewable energies, this paper is considering electricity provided by renewable energies (wind, solar or hydro) and electricity produced by Brayton power cycle, so hydrogen is produced without Green House Gas (GHG) emission.

To reduce electricity requirement for steam electrolysis diffusion bonded heat exchangers are employed to use heat from turbine exhaust gas and heat realized during hydrogenation of CO₂ in methanol production.

INTRODUCTION

A continuous improvement and process optimization has stretched current heat exchanger technologies beyond their design capabilities, and to achieve better efficiencies, safer

operations with more reliable equipment, a complete shift of our understanding is required. And to achieve new design requirements, the new heat exchange technologies have to be considered very seriously. Diffusion bonded process equipment including heat exchangers and reactors has been identified by process licensor companies, End Users, EPC as equipment of choice within wide broad industries including oil & gas (particularly off-shore gas exploration), chemical industries, power generation including Brayton cycle and ORC, Carbon Capture & Storage, Waste Heat Recovery etc. Also, Printed Circuit Heat Exchanger (PCHE) has been identified as heat exchanger of choice for intermediate heat exchanger (IHX) for the next US Generation IV nuclear programme.

NOMENCLATURE

ΔG	[kWh/m ³ H ₂]	Electrical energy demand
$T\Delta S$	[kWh/m ³ H ₂]	Thermal energy demand
I_1	[mm ⁴]	Moment of inertia for short plates
I_2	[mm ⁴]	Moment of inertia for long plates
α	[-]	Rectangular box parameter
K	[-]	Vessel parameter
E_1	[-]	Joint efficiency for short-side (long-side) plates
E_2	[-]	Joint efficiency for stay plates
$S=S_{all}$	[N/mm ²]	Allowable tensile stress for material at design temperature
S	[N/mm ²]	Allowable membrane stress
$S_{all-tot}$	[N/mm ²]	Allowable total stress
$NFPI$	[-]	Number of fins per inch

One of main reasons for diffusion bonded equipment being the preferable choice is their capability to operate at extreme pressure and temperature design conditions as presented in **Figure 1**.

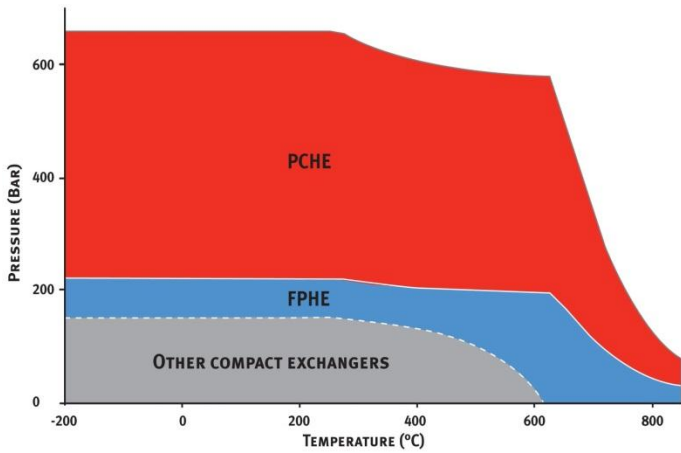


Figure 1 Temperature and pressure design envelope

From **Figure 1** it can be noted that Printed Circuit Heat Exchangers (PCHE) could operate at pressures above 600 barG for low design temperatures (just above 300°C) or at extremely high temperatures (up to 982°C) when lower operating pressures are applied. At the same time Formed Plate Heat Exchangers (FPHE) are limited to lower design parameters (app. 200 barG) depending on choice of material of construction (Alloy 617 is material candidate for high temperature applications). Except alloy 617 there are other materials that potentially could be used for high temperature applications; however a detailed material assessment that include material cost, strength, corrosive resistance, creep life etc. needs to be undertaken.

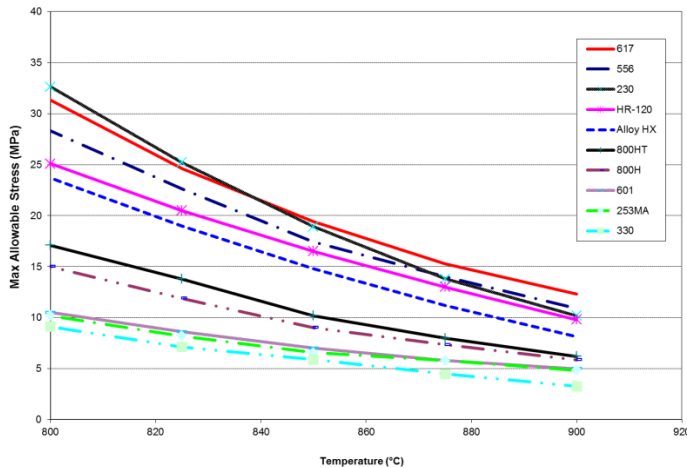


Figure 2 Temperature – maximum allowable stress relationship

From **Figure 2** it can be noted that alloy 617 appears to be the strongest material candidate for high temperature applications. Although the temperature – maximum allowable stress relationship is given up to 900°C, the maximum operation temperature for alloy 617, HR-120 and 230 is as high as 982°C.

The compact core of a PCHE is constructed by forming flow passages in flat metal plates, and then stacking and diffusion bonding the plates together into a single block. The chemical milling technique typically used to form the flow passages is analogous to that used for the manufacture of electronic printed circuit boards, and this gave rise to the “Printed Circuit” exchanger name.

At the same time solid state diffusion bonding is a process by which two nominally flat interfaces can be joined at an elevated temperature using an applied pressure for a time. As the result of this process, a monolithic joint through the formation of bonds at atomic level, which itself is a result of closure of the mating surfaces (encouraged grain growth across metal boundaries) due to the local plastic deformation at elevated temperatures, is achieved (**Figure 3**).

This process has the ability to produce high quality joints resulting in the elimination of any metallurgical discontinuity and porosity across the interface. If properly controlled this joint would have strength and ductility equivalent to those of the parent material.

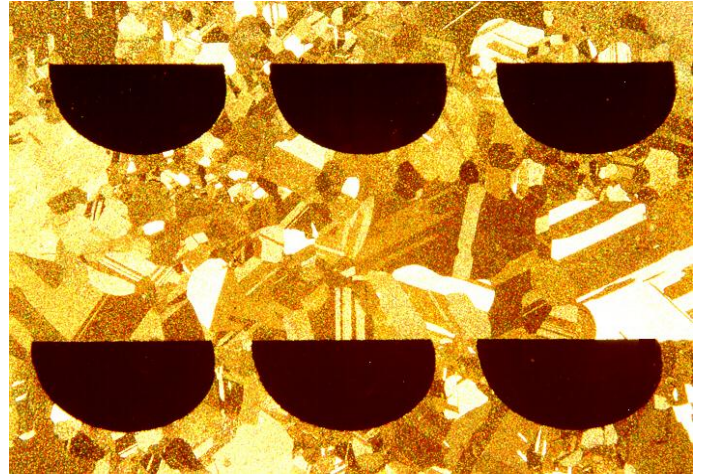


Figure 3 No boundaries between surfaces with perfect grain growth

The compact core of a FPHE is constructed by corrugated plates, and then stacking and diffusion bonding these plates together into a single block (**Figure 4**).



Figure 4 Typical FPHE core

A combination of PCHE and FPHE makes a H²X called “Hybrid Heat Exchanger” that offer benefits of both technologies i.e. capability to handle fluids at high pressures (sCO₂ side) while keeping low pressure drop on other stream (**Figure 5**).

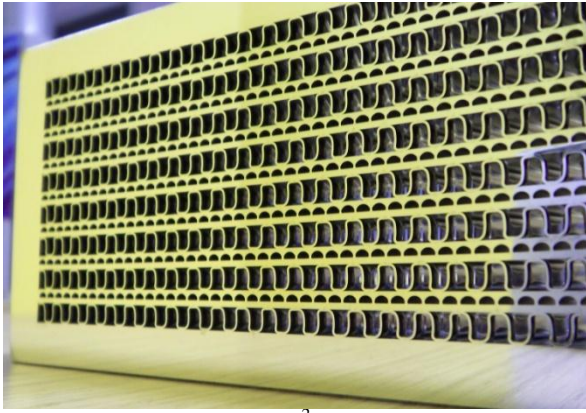


Figure 5 H²X section

Also, it needs to be added that Hybrid heat exchangers have been identified as a reliable choice for sCO₂ application as a working fluid within Brayton (Oxy-fuel) cycle for power generation.

Mechanical Design of Diffusion Bonded Heat Exchangers

As the cross section of Heatric's products is somewhat non-conventional to the ASME standard it was agreed with ASME regulatory body that all mechanical calculations should be governed by ASME VIII, Division 1, Appendix 13, Paragraph 13-9. For the mechanical design of Printed Circuit Heat Exchangers this approach is very conservative giving oversized channel structures, while for the Formed Plate Heat Exchangers it gives less conservative results.

The second potential way to design and manufacture heat exchangers (or parts) when non-conventional geometry is considered, is by Proof test and using FEA.

We at Heatric, use Proof test and FEA to assess Appendix 13 whether results obtained (designs) are mechanically robust and safe.

In the Figure 6, given below, FEA results are presented for a sample composed of Titanium grade 2 with fin geometry where fin height is 2.12 mm, fin thickness 0.3 mm, NFPI is 15, ambient design temperature and design pressure of 100barG.

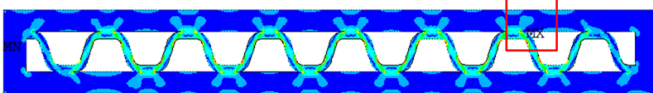
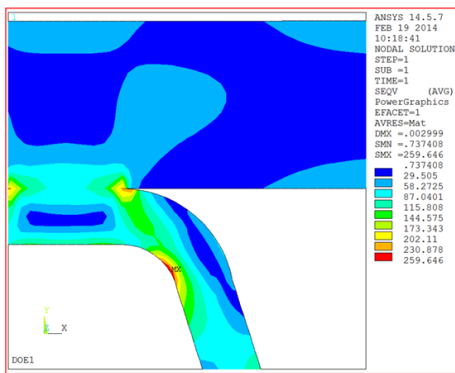


Figure 6 Results of FEA using Ansys

Apart being used for mechanical calculation of diffusion bonded heat exchanger Paragraph 13-9 is used for the mechanical designs of air cooled heat exchanger boxes (headers) as well. Actually, this paragraph governs all stayed vessels with rectangular cross section. Before we explain these calculation methods it is worth mentioning that all equations included in this paragraph i.e. the moments of inertia, are calculated on a per-unit-width basis.

Nomenclature:

$$I_1 = \frac{(t_1)^3}{12}$$

$$I_2 = \frac{(t_2)^3}{12}$$

$$\alpha = \frac{H}{h}$$

$$K = (I_2/I_1)\alpha$$

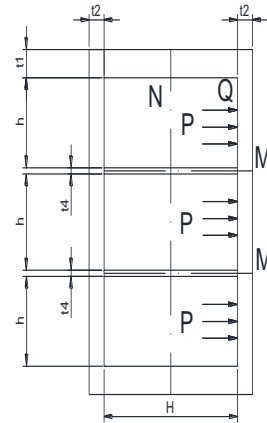


Figure 7 Stayed vessel (header) with two or more stays

(1) Membrane stress:

Short-side plates:

$$S_m = \frac{Ph}{2t_1} \left\{ 3 - \left[\frac{6+K(11-\alpha^2)}{3+5K} \right] \right\} \quad (1)$$

Long-side plates:

$$S_m = PH/2t_2 \quad (2)$$

Stay plates:

$$S_m = \frac{Ph}{2t_4} \left[\frac{6+K(11-\alpha^2)}{3+5K} \right] \quad (3)$$

(2) Bending stress:

Short-side plates:

$$(S_b)_N = \frac{Pc}{24I_1} \left[-3H^2 + 2h^2 \left(\frac{3+5\alpha^2K}{3+5K} \right) \right] \quad (4)$$

$$(S_b)_Q = \frac{Ph^2c}{12I_1} \left(\frac{3+5\alpha^2K}{3+5K} \right) \quad (5)$$

$$c = \frac{t_1}{2}$$

Long-side plates:

$$(S_b)_M = \frac{Ph^2c}{12I_2} \left[\frac{3+K(6-\alpha^2)}{3+5K} \right] \quad (6)$$

$$(S_b)_Q = \frac{Ph^2c}{12I_2} \left(\frac{3+5\alpha^2K}{3+5K} \right) \quad (7)$$

$$c = \frac{t_2}{2} \quad (8)$$

(1) Total stress:

Short-side plates:

$$(S_T)_N = Eq. 1 + Eq. 3 \quad (9)$$

$$(S_T)_Q = Eq. 1 + Eq. 4 \quad (10)$$

Long-side plates:

$$(S_T)_M = Eq. 2 + Eq. 6 \quad (11)$$

$$(S_T)_Q = Eq. 2 + Eq. 7 \quad (12)$$

Stay plates:

$$S_T = Eq. 3 \quad (13)$$

(2) Allowable stresses:

$$S_{all-tot} = 1.5(S)$$

Short-side plate membrane stress:

$$S_{all} = S \geq S_m(Eq. 1)/E_1 \quad (14)$$

Long-side plate membrane stress:

$$S_{all} = S \geq S_m(Eq. 2)/E_1 \quad (15)$$

Stay plate membrane stress:

$$S_{all} = S \geq S_m(Eq. 3)/E_2 \quad (16)$$

Short-side plate total stress:

$$S_{all-tot} \geq (S_T)_N/E_1 \quad (17)$$

$$S_{all-tot} \geq (S_T)_Q/E_1 \quad (18)$$

Long-side plate total stress:

$$S_{all-tot} \geq (S_T)_M/E_1 \quad (19)$$

$$S_{all-tot} \geq (S_T)_Q/E_1 \quad (20)$$

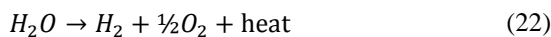
Stay plate total stress:

$$S_{all-tot} \geq S_T/E_2 \quad (21)$$

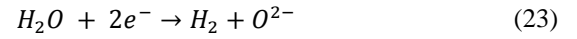
HIGH TEMPERATURE ELECTROLYSIS

High temperature electrolysis with solid oxide electrolyser cells (SEOC) offers a great potential for hydrogen production, as SOECs can split water (H₂O) into hydrogen (H₂) and oxygen (O₂) in a very efficient and economical way.

The overall chemical reaction (this is an endothermic reaction, so heat input is required) of water electrolysis is:



with reaction on Cathode side being:



and reaction on Anode side being:



In comparison to the conventional water electrolysis the high temperature electrolysis has few advantages such as:

- High efficiency that increase with temperature (see **Figure 8**), especially when Allothermal process is used. Allothermal process is a process where SOEC operate below the thermoneutral voltage (1.29V). Depending on operational temperature the total efficiency for Allothermal process could be up to 50%. It is high in comparison to 27 to 30 % for conventional electrolysis.
- Low overall energy demand (reduction of electrode overpotentials which cause power losses in the electrolysis cell).
- Heat required for electrolysis could be provided from different high temperature sources (nuclear, solar, geothermal, industrial waste etc.).

On the other hand due to the high operation temperatures that could be from 700 (800°C) to 1000°C (operation pressure being about 5 MPaG) there are few requirements that SOEC components have to meet for a cost effective hydrogen production.

The total (minimum) energy demand (ΔH) for SOEC hydrogen production is equal to the change in the Gibbs free energy (ΔG):

$$\Delta H = \Delta G + T\Delta S \quad (25)$$

As per formula (4) and **Figure 8** it can be concluded that an increase of operation temperature will decreases electrical energy demand but increases the thermal energy demand. As shown in **Figure 8** the ratio of ΔG to ΔH changes from about 93% at 100°C to about 70% at 1000°C.

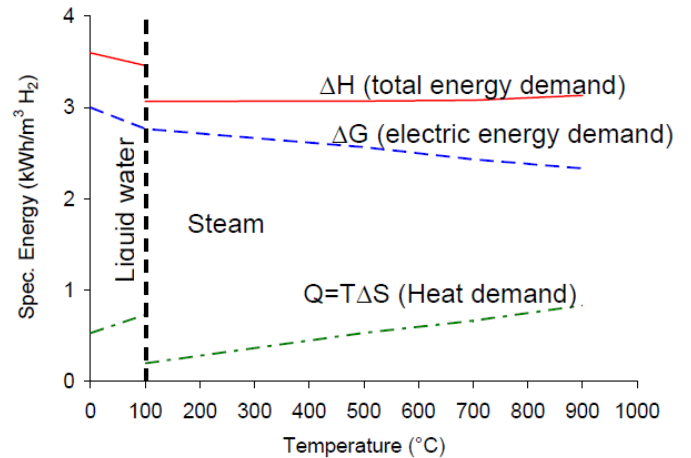


Figure 8 Total, electrical and heat energy demand

Although hydrogen is the main product, HTE produces oxygen where on every 1 kg/s of H₂ approximately 7.88 kg/s of O₂ is produced. This is very important as oxygen produced by electrolysis is used for natural gas combustion within oxy-fuel power cycles (explained in more detail further in the text).

High Temperature Electrolysis and Diffusion Bonded Technology

As per Process Flow Diagram (PFD) shown in **Figure 9** heat is required to boil water and later superheat steam generated. Also, Steam/H₂ and Sweep Gas/O₂ recuperators are included to improve plant efficiency, so for all these reasons it is obvious that achieving closer temperature approach is of essential importance to improve plant efficiency. There are several analysis reported to date, where HTE was coupled with various heat sources e.g. high-temperature gas-cooled reactor (HTGR), solar power with particular interest in formulating the hydrogen production efficiency. As it could be expected the hydrogen production efficiency is highly dependent on heat exchangers temperature approach. As one of examples we may consider that major heat exchangers have a 50°C temperature approach with results obtained later compared to the case where 25°C is the minimum temperature approach. The results of comparison showed a better hydrogen production efficiency (42.8% against 40.4%), lower CO₂ emission (about 12%), increased hydrogen and oxygen productions (about 5.5%) for closer temperature approach. A further plant optimisation with a closer temperature approach (approximately 5°C) is desirable with plant efficiency estimated to be about 44.8%. Furthermore, Heatric's heat exchanger could operate with a temperature approach as small as 1°C, so further plant efficiency improvement is achievable. However, one needs to make comparison between capital and operational investment when/if high efficiency is considered.

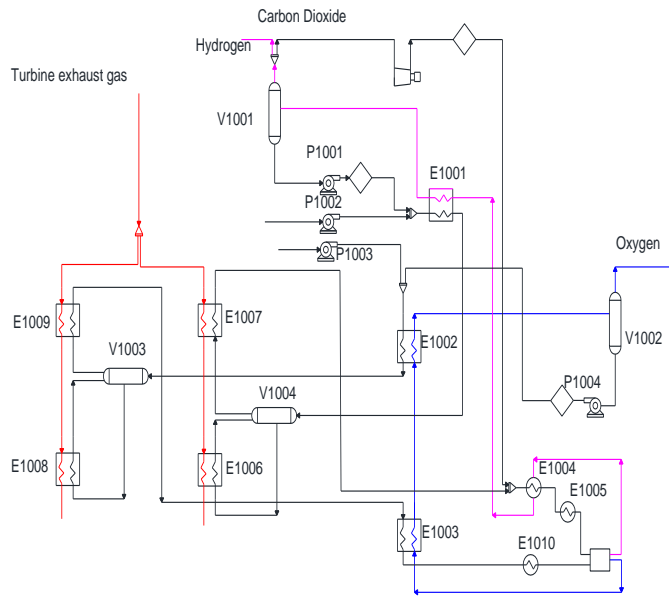


Figure 9 High Temperature Electrolysis-Schematic Flow Diagram

In two following figures, **Figure 10** and **Figure 11**, a heat exchanger (recuperator) used for a test loop to demonstrate High Temperature Electrolysis is presented.

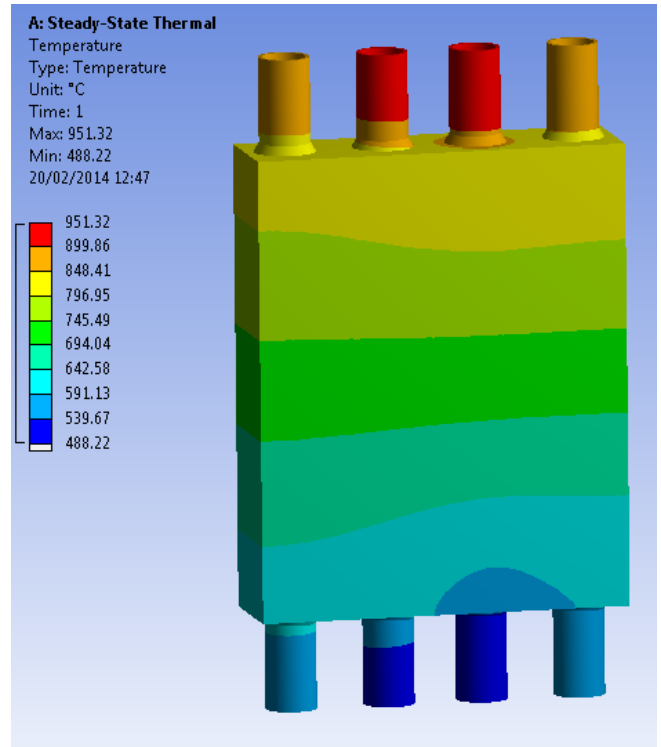


Figure 10 Temperature distribution in steady state

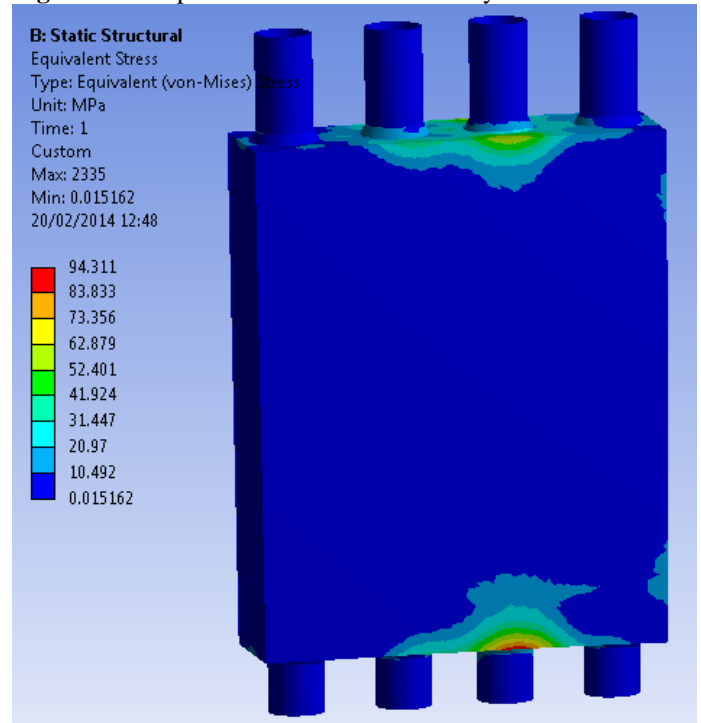


Figure 11 von Mises stresses distribution

The main function of this heat exchanger is to provide heat to electrolysis from a heat source (process industry) with design temperature as high as 951°C and design pressure of 5barG. The material of construction was alloy 617 with PCHE configuration.

OXY-FUEL AND BRAYTON CYCLE

Our growing concerns over greenhouse gas emission with high possibility this promote global warming and potentially devastating consequences to our planet, have driven extensive research into new more efficient power cycles, especially to those that enable CO₂ capture and sequestration. Regarding to those concerns, we are presenting oxy-fuel combustion that is found to be a promising new technology where natural gas is burned in an environment of oxygen and recycled combustion gases.

The recycled gases are used to control the flame temperature which result that flue gases consist predominantly of CO₂ and water. After water is condensed and separated from CO₂, CO₂ is compressed obtaining super critical properties and pumped further to pressures exceeding 300 barG.

To date, there has been extensive research to identify the relationship between pressure at which oxy-fuel combustion take place and plant performance (efficiency). The results from research completed to date have shown that pressurised oxy-fuel combustion system offer increased net efficiency and the reduction of the capital cost and the cost of electricity produced.

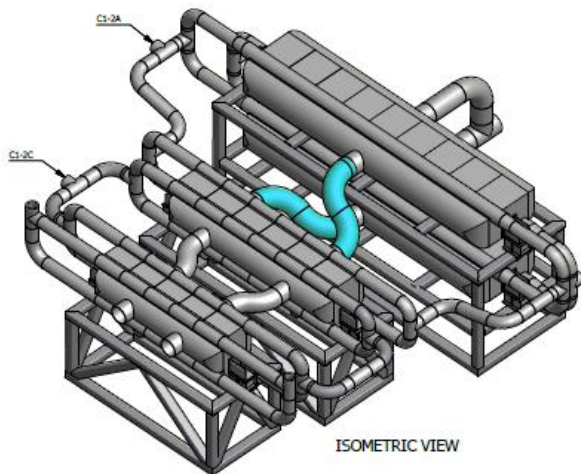


Figure 12 Main recuperator in an Oxy-fuel, sCO₂ power cycle

Figure 12 presents main recuperator with multi stream connections to optimise power cycle. sCO₂ as working fluid is used at operation conditions above 700°C and above 300barG, with aim to harvest all benefits that sCO₂ brings, smaller piping and better heat transfer in heat exchangers.

METHANOL PRODUCTION

Once when CO₂ is produced by oxy-fuel combustion, it could be disposed into natural fields (depleted gas or oil wells, injection for enhanced oil recovery, disposal into ocean etc.), or it could be used directly as an additive to beverage, as a solvent etc.

The last option which is included into this paper is CO₂ hydrogenation to methanol.

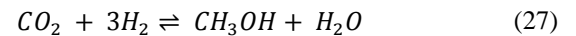
Methanol is the simplest alcohol that can be made in a very different way. Basically, it is one oxygen atom inserted into methane; however methanol is a liquid which is easily stored, transported, and used. Another advantage of methanol over hydrogen is that methanol has a twice energy density than liquefied hydrogen.

Currently, about 90 percent of the worldwide production of methanol (CH₃OH) is derived from methane (CH₄) that is the main component of natural gas. As it is known all traditional methods of making methanol have two stages: converting methane into syngas, a mixture of primarily carbon monoxide and hydrogen, and then into methanol.

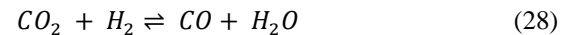
Traditionally, Methanol synthesis is expressed in terms of the hydrogenation of CO₂:



Also, it is known that methanol synthesis over Cu-based catalyst proceed exclusively via CO₂ hydrogenation:



At same time, simultaneously with methanol synthesis, the reverse water-gas shift reaction, known as RWGS, takes place (it depends on the reaction conditions):



Only two of three reactions presented are stoichiometrically independent and define the equilibrium composition of the gas mixture.

Also, we need to add that many other side reactions to the formulation of methanol can take place, e.g. formation of higher alcohols, hydrocarbon and waxes formation (Fischer-Tropsch reaction), ethers, esters and ketones.

However, combining the conventional methanol production with High Temperature Electrolysis and Oxy-fuel Power Cycle the number of units is reduced, e.g. reforming section is taken out. The second benefit of joining this process with other two processes is that CO₂ is distributed to Methanol Converter at pressure above 80barG which is operation pressure of reformed gas, reducing energy demand significantly, e.g. synthesis gas compressor being one of them. At the same time H₂ exit HTE process at pressure around 50barG. Therefore an additional energy to compress H₂ from 50 barG to over 80barG would be required, unless HTE operate at pressures above 80barG, so water is pumped to these pressures as a liquid, rather than compressed as H₂ in gas phase in later stages.

Therefore, Methanol production would include, but not limited to:

- Methanol converter (depending on flow rate and the rate that process is optimized, could be one single converter or multiple converters connected in 2 units in series, or 2 units in parallel, or finally 2 units in parallel with further 2 units in series),
- Loop interchangers (as process in methanol converter is exothermic the effluent gas is at higher temperature and need to be cooled),

- Crude methanol condensers,
- Crude methanol separators,
- Topping column,
- Refining column,
- Product cooler, and
- Storage tank.

The most critical part of CO₂ hydrogenation to methanol is the methanol converter (reactor) with main challenge being the catalyst CO₂ conversion to CH₃OH.

One of catalyst manufacturers Ceramatec with its proprietary catalysts showed significantly higher CO₂ conversion (up to 30.58%, CO₂ conversion to methanol in a single pass) over commercial CuO/ZnO/Al₂O₃ catalyst.

As equipment included into methanol plant operate at, rather to say, mild conditions for Heatric's diffusion bonded units, it was identified that FPHE technology fit perfectly. As an example, a potential design of a loop interchanger is presented in **Figure 13**.

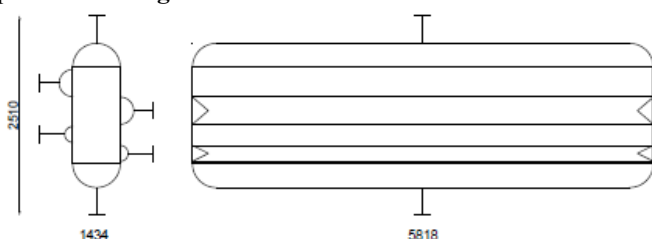


Figure 13 Loop interchanger

The loop interchanger given in **Figure 13** is the replacement for the Loop interchanger and the Crude methanol condenser which are conventional Shell & Tube solutions. Using benefits that Heatric's heat exchanger technology offers i.e. multistream connection into one core and a close temperature approach two heat exchanger units are combined into one reducing capital cost, footprint and carbon emission as more heat is recuperated.

CONCLUSION

This paper describes three processes i.e. High Temperature Electrolysis, Oxy-fuel Power Cycle and Methanol Production which are combined into one process with 100% Carbon Capture. Furthermore, electricity demand by High Temperature Electrolysis could be fulfilled from renewable energy sources such as wind, hydro, solar or nuclear.

Introducing heat integration on these processes would result in each process harvesting benefits (energy) from other processes by using waste heat or energy that would be lost otherwise.

The review of a potential material candidate for the high temperature application, i.e. High Temperature Electrolysis, Oxy-fuel-sCO₂ power cycle would suggest that alloy 617 is the most suitable alloy for these applications. However, design conditions, especially used for Oxy-fuel-sCO₂ cycle are pushing materials to the limit potentially seeking for new materials (alloy 740H is very promising) to expand design envelope and improve cycle efficiency without increasing capital investment.

Also, in this paper the critical importance of Heatric's heat exchangers is described with all advantages they bring e.g. high

efficiency, small foot print and high safety as well, so using a closer temperature approach on heat exchangers included into THE will improve plant efficiency and further applying multistream connections reduce number of units.

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