NOVEL CONCEPTS FOR CO_2 CAPTURE WITH SOFC

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Contribution to the 6th International Conference on Greenhouse Gas Control Technologies (GHGT-6),
30th September - 4th October 2002, Kyoto, Japan.

Revisions		
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B		
Made by: J.W. Dijkstra	Approved: D. Jansen	ECN-Clean Fossil Fuels
Checked by: M.Weeda	Issued: C.A.M. van der Klein	

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ABSTRACT

This paper aims to describe the possibilities for power generation with solid oxide fuel cells (SOFC's) in combination with CO_2 capture. First the underlying programs in the Netherlands and at ECN are introduced. A literature overview of systems for power generation with fuel cells in combination with CO_2 capture is presented. Then a novel concept is introduced. This concept uses a watergas shift membrane reactor to convert the CO and H_2 in the SOFC anode off-gas to gain a CO_2 rich stream, which can be used for sequestration without elaborate treatment. Several implementation schemes of the technique are discussed such as atmospheric systems and hybrid SOFC-GT systems.

INTRODUCTION

Growing concerns about the impact of CO_2 emissions have let to a number of proposed measures in the Netherlands to reduce these emissions. Next to materials and energy efficiency improvement and the use of renewable sources also CO_2 capture and storage has been recognised as necessary. A contribution of up to 50-60 Mton CO_2 reduction in 2030 is foreseen.

Commercially available CO_2 capture technologies for power conversion are in general post-fuel cell technologies, i.e. the CO_2 is captured from the flue gases after the conversion of fuel into power. Post- fuel cell CO_2 capture results in a significant drop in cycle efficiency, and increase in plant investment and operating costs. Typically, CO_2 capture with an amine absorption/desorption unit at a gas fired combined cycle results in an efficiency drop of 9%-points (16% relative), and in an investment increase of 59% and in cost of 55-70 Euro/ton CO_2 captured. For coal fuelled power generation units even much higher penalties are encountered. The energy consumption of the amine absorption/desorption unit is mainly caused by the steam demand of the desorption step. The recovery of CO_2 is largely hindered by the dilution of the CO_2 with nitrogen from the combustion air.

To improve the overall cycle efficiency of power generation with CO_2 capture alternative schemes have been proposed. These include technologies such as pre-fuel cell CO_2 capture (including sorbent enhanced reforming), O_2/CO_2 firing and chemical looping. All of these technologies are focussed on formation and capture of the CO_2 before dilution with nitrogen, or the separation of air in nitrogen and oxygen before conversion.

Another promising solution to this problem is to use a Solid Oxide Fuel Cell (SOFC). The special property of the SOFC is that in the SOFC fuel conversion takes place without the dilution of the CO_2 with nitrogen. In the SOFC a stream with a high CO_2 content is formed. Therefore, SOFC offers the prospect of reducing the CO_2 capture penalty in terms of efficiency and costs.

At the Energy Research Centre of the Netherlands ECN a new program (DECAFF) has been initiated for the development of advanced technologies for power generation with CO_2 capture. The aim is to reduce the CO_2 capture financial and efficiency penalties with 50% or more. The program will aim at two fields of technologies: process integrated CO_2 capture in (decentralised) power production and process integrated CO_2 capture in (small-scale) hydrogen production. The program is guided by the results of integral chain analysis and by assessments of possibilities for CO_2 conversion and re-use.

In this paper technologies for power generation with CO_2 capture using SOFC will be discussed. First, an overview of published systems will be given. Then, a novel technology for power generation with CO_2 capture using SOFC will be proposed. Finally the path forward on this issue in the DECAFF program will be presented.

SOFC WITH CO_2 CAPTURE IN LITERATURE

In the last decade several authors have proposed concepts for more efficient power production through the use of fuel cells. An overview of these systems will be presented. Earlier overviews of CO_2 systems with fuel cells have been made by van Schie [1] and Goettlicher [2]. Excluded are chemical looping systems sorption enhanced reforming, and co-production of electricity and chemicals. The fuel is assumed to be natural gas, though some concepts can also be incorporated in coal gasification systems. The systems are classified into three groups, as depicted in Table 1.

TABLE 1

OVERVIEW OF SOFC SYSTEMS WITH CO_2-CAPTURE IN LITERATURE

Author(s)	Treatment type	Use of H_2 stream
Systems with pre-fuel cell CO_2-capture		
Hirschenhofer [3] Goettlicher [2]	Chemical or physical adsorption	Anode feed
Wolsky [4]	H_2-selective membrane	Anode feed
Systems with post-fuel cell CO_2-capture		
Namie [5]	Cryogenic separation, physical or chemical absorption	Recycle to anode feed
Campanari [6]	Compression followed by chemical absorption	Combustion chamber (in cathode-off-gas stream)
Carson [7]	Compression, shift conversion, Pressure Swing Adsorption	Recycle to anode feed
Campanari [6]	Compression, 2-step shift conversion, physical absorption	Combustion chamber (in cathode off-gas stream)
Galloway [8]	Only H_2O knock-out	Recycle to reformer in anode feed
Judkins [9]	Shift, absorption of CO_2 in water	Second H_2 fuelled SOFC
Systems with post-fuel cell off-gas oxidation		
Lygre [10]	Oxidation with O_2 (source not specified)	
Haines [11]	OCM afterburner	

Pre-fuel cell CO_2 capture

The basic concept of this group is depicted in Figure 1. In pre-fuel cell CO_2 capture the fuel is first converted into syngas using steam reforming. The CO_2 is then separated from the main stream. The CO_2 stream is exported for CO_2 compression and storage. The remaining stream consists of H_2 and H_2O. Table 1 gives the systems published. The systems published differ mainly in technology for CO_2 separation. In both systems the H_2 rich stream is fed to the SOFC anode. The system of Wolsky [4] had been proposed earlier for a molten carbonate fuel cell by Oudhuis [12]. Also possible is the integration of the shift and H_2 separation step to a watergas shift membrane reactor, placed instead of the shift reactor and separator in Figure 1. This concept has been worked out for IGCC by Alderliesten [13] but is also feasible for an SOFC system.

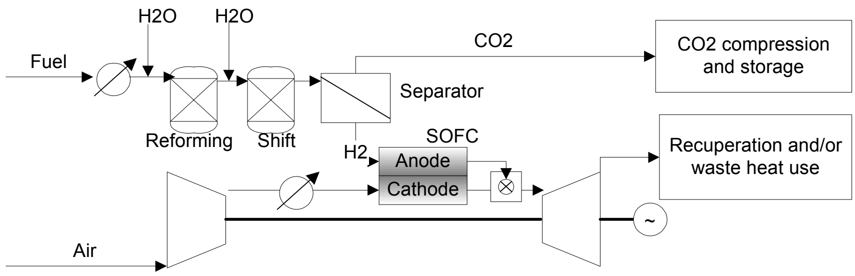

Figure 1: **SOFC-GT with pre-fuel cell CO_2 capture**

Post-fuel cell CO_2 capture

The basic concept of this group is depicted in Figure 2. Table 1 lists the specifications for the anode off-gas treatment of the various authors. The treatment section always gives a CO_2 stream. The remaining stream consists of H_2 and, depending on the type of treatment also CO, CO_2 and other components. The use of this stream is also listed in Table 1. Serious doubts exist whether the system of Galloway [8] is feasible and will not result in unlimited built-up of CO_2 in the system. The system of Judkins [9] is very complex and consists of three gas turbines, two fuel cells a reformer and a membrane separator.

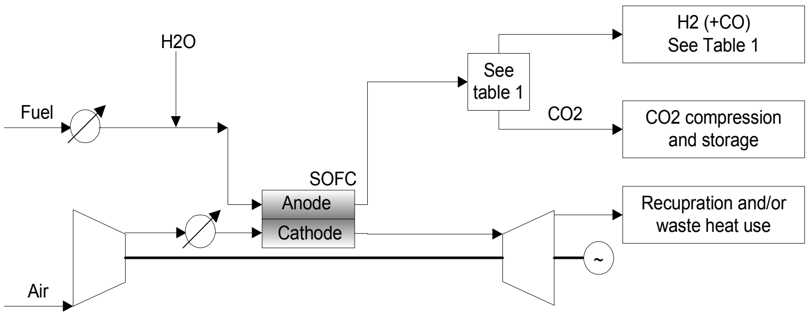

Figure 2: SOFC-GT with post-fuel cell CO_2 capture

Post-fuel cell oxidation

The basic concept of this group is depicted in Figure 3. The anode off-gas has a high CO_2-content, but also contains H_2O, CO and H_2. The water can easily be removed by conventional techniques (cooling, knock-out, additional drying). Oxidizing all the H_2 and CO from the SOFC anode with air will result in a too high dilution of the stream with nitrogen. The options for oxidizing these components are listed in Table 1. Lygre [10] chooses to oxidize with pure oxygen, but this will probably result in significant additional costs and energy consumption if oxygen is not available.

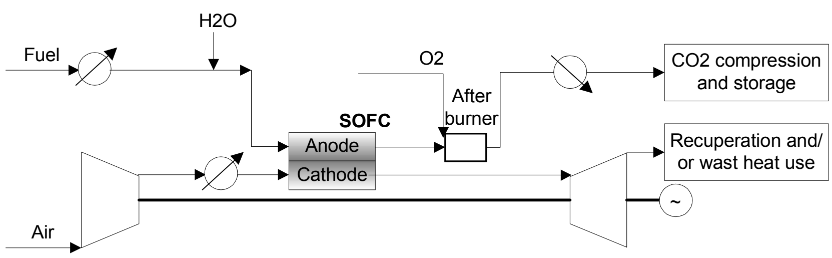

Figure 3: SOFC-GT with post-fuel cell hydrogen oxidation

Haines [11] therefore chooses to use an oxygen-conducting membrane reactor (OCM-reactor) placed after the SOFC(See Figure 4). The anode off-gas is fed to one side of the membrane, the cathode off-gas is fed to the other side of the membrane. The membrane is selective to oxygen, which permeates from the cathode off-gas stream to the anode off gas. In the membrane unit the H_2 and CO are oxidised. The retentate of the membrane unit consist of CO_2 and water. The water can be removed using conventional techniques.

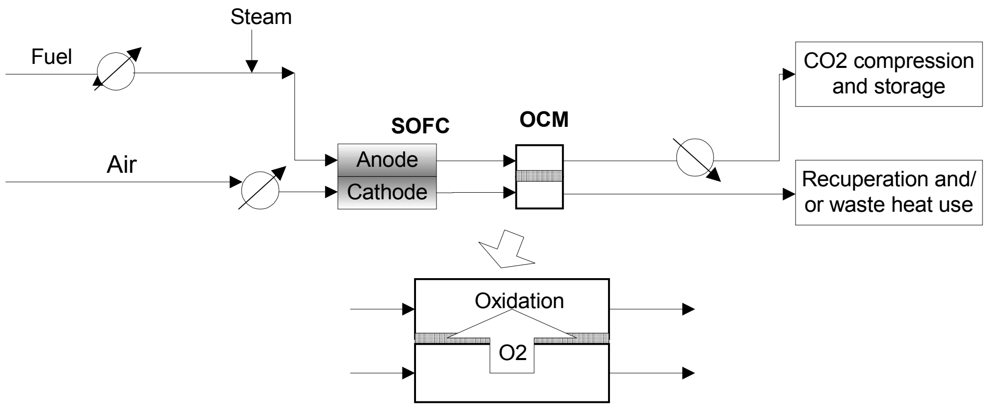

Figure 4: SOFC-GT with OCM-afterburner

This concept has the prospect of a good projected cycle efficiency, and elegant combination with existing tube-design SOFC. The system does not contain voluminous or complex absorption equipment.

A NOVEL CONCEPT FOR CO_2 CAPTURE IN SOFC SYSTEMS

A novel concept has been developed for CO_2 capture at SOFC and hybrid systems (Jansen [14]). The concept uses a watergas shift membrane reactor afterburner (WGSMR-afterburner). The working principle is depicted in Figure 5. Air is fed to the SOFC cathode, fuel is fed to the SOFC anode. The SOFC produces DC power. The cathode off-gas is fed to the permeate side of the membrane reactor, the anode off-gas is fed to the feed side of the membrane reactor. On the feed side the watergas shift reaction takes place producing H_2 and CO_2. The H_2 permeates through the hydrogen selective membrane in the WGSMR-afterburner. At the permeate side this hydrogen is burned with O_2 present in the SOFC cathode off-gas. This results in a very low hydrogen partial pressure on the permeate side, thus resulting in a high H_2 permeation rate.

The WGSMR-feed side products are CO_2 and H_2O, and small amounts of H_2 and CO, which can be removed by (catalytic) oxidation with air resulting in only a small dilution with nitrogen. The water can be removed easily e.g. with cooling. The resulting CO_2 can be used for sequestration without the need for further treatment. The WGSMR permeate side product is N_2,H_2O and O_2.

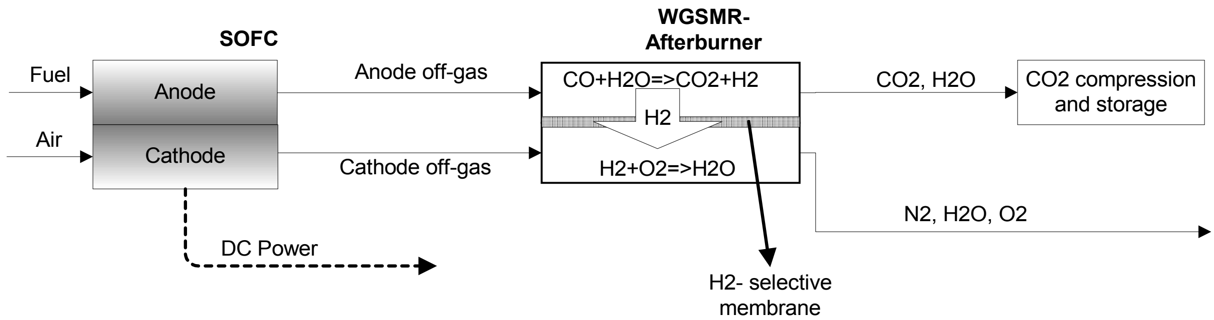

Figure 5: Working principle of theWGSMR-afterburner

Three types of hydrogen selective membranes are considered for this concept. Microporous membranes are characterized by high flux densities but are limited to low temperatures. Palladium membranes have high flux densities, are very selective and have a moderate working temperature. Proton conducting membranes have the highest working temperature but are far less developed than the other membrane types.

The concept has the same advantages as the OCM-afterburner concept of Haines [11]. A highly pure CO_2 stream is available after water-knock out, without the requirement of large, complex and steam-consuming CO_2 scrubbing equipment. Thus the system offers the prospect for power production with CO_2 capture. Moreover, the system has some additional advantages above the OCM-afterburner concept:

- The flux through the membrane is towards the gas turbine side. Thus, the mass flow through the

expander is increased (higher power production), and the dilution of CO_2 with water is decreased.
- With the projected membrane materials higher fluxes may be achieved without the necessity for imposing a current on the membrane material as might be required with OCM membranes.

IMPLEMENTATION SCHEMES

Implementation of the SOFC with post fuel cell oxidation or with a WGSMR is possible for all classes of SOFC and SOFC-GT hybrid cycles (Jansen [15]):
- Atmospheric SOFC
- Atmospheric hybrid cycle
- Pressurised hybrid cycle with pressurised WGSMR-afterburner
- Pressurised hybrid cycle with atmospheric WGSMR-afterburner

The atmospheric SOFC cycle is that of Figure 5. In the atmospheric hybrid cycle a gas turbine is placed before the SOFC. The exhaust gas of the gas turbine is used as cathode feed gas.

The pressurised hybrid cycle with WGSMR-afterburner is depicted in Figure 6. Air is fed to the gas turbine compressor, heated and fed to the SOFC cathode. Fuel is heated, mixed with steam and fed to the SOFC anode. The anode off-gas is fed to the feed side of the WGSMR. Cathode off-gas is used as a sweep gas for the permeate side of the WGSMR. The H_2 and CO from the anode off-gas are largely converted. The retentate stream from the WGSMR-afterburner is cooled and flows to the CO_2 compression and storage section. The permeate stream from the WGSMR-afterburner passes an optional combustion chamber for additional firing to increase the temperature. It is then expanded in the gas turbine. The gas turbine drives a generator, which produces additional AC current. The expander off-gasses can be used for recuperation to heat the cathode feed stream, or can be used in a waste heat boiler. Instead of the using the cathode off-gas, also the gas turbine exhaust gas can be used as a sweep stream for the WGSMR-afterburner. In that case a pressurised hybrid cycle with atmospheric WGSMR-afterburner is obtained.

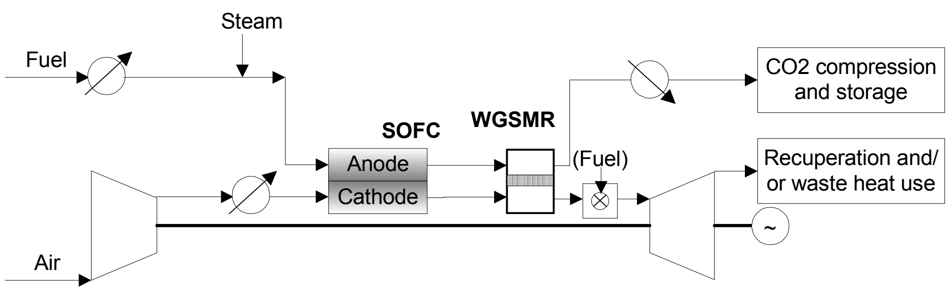

Figure 6: Hybrid cycle with WGSMR-afterburner

For all implementation schemes well-known options for gas turbines and hybrid cycles are possible such as prereforming, anode recycle, recuperation, intercooling of the air compressor, combined cycle operation, combined heat and power etc.

FUTURE WORK

Currently the novel concept presented above is evaluated in several implementation schemes for it's thermodynamic efficiency. Several membrane material types are evaluated. In 2002 a proof op principle of the use of the WGSMR for CO and H_2 is foreseen at ECN. ECN aims at a fully developed the system in 2010.

ACKNOWLEDGEMENT

The work presented has been funded by the Dutch Ministry of Economic Affairs (EZ).

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NOVEL CONCEPTS FOR CO_2-CAPTURE

The marriage of technologies in “ZEPP” concepts

J.W. DIJKSTRA

D. JANSEN

ECN

CONTENTS

- **CONTEXT**
- **TECHNOLOGIES**
  - Gas turbines, membranes, fuel cells
- **CAPTURE COSTS BREAKDOWN**
- **NOVEL CONCEPTS**
  - **Marriage of technologies**
- **CONCLUSIONS**

CONTEXT

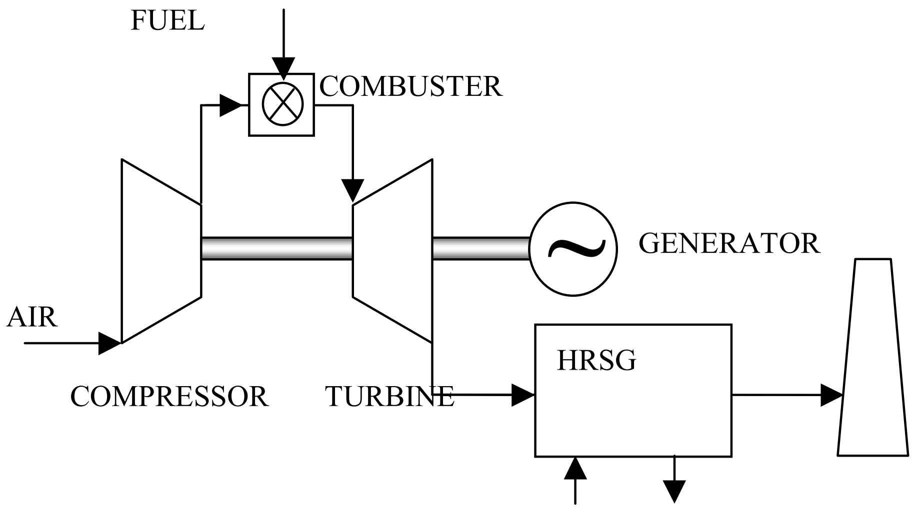
DeCaFF; **De-Ca**rbonisation of **F**ossil **F**uels

Long term R&D programme at ECN aimed at:

- Development of **integrated** CO_2 capture technologies for electricity and hydrogen production systems which:
  - reduce efficiency penalty with at least 40% and
  - reduce CO_2 capture costs with 50%
- Market introduction 2010

KEY TECHNOLOGIES

GAS TURBINE



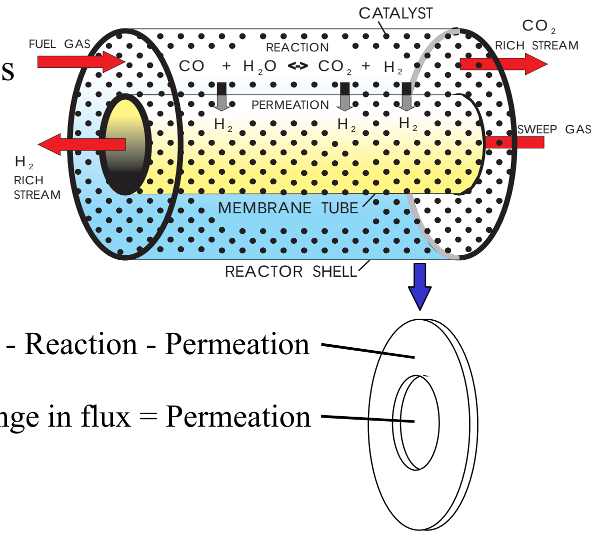
- Mature technology
- Potential for efficiency increase
- Relatively easy to adopt for H_2 rich fuels
- Higher efficiency when H_2 fuelled

KEY TECHNOLOGIES

MEMBRANES

WGSMR model

- Differential mass balances:



$\int$ Change in flux = - Reaction - Permeation

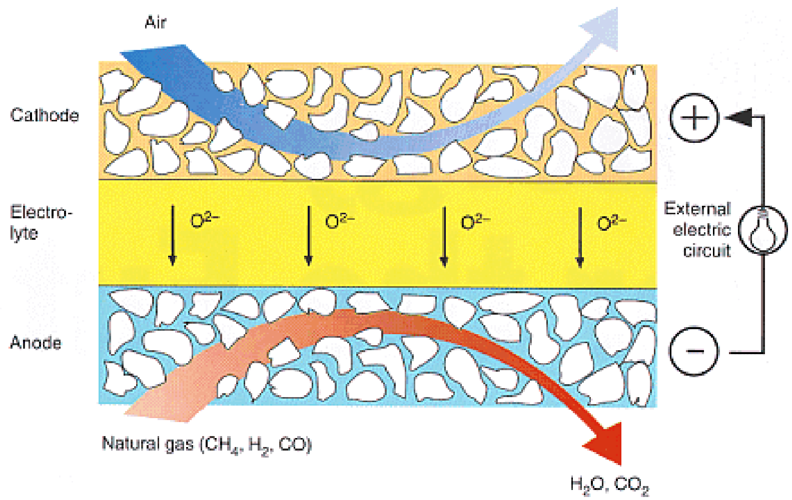
Change in flux = Permeation

- High temperature and pressure operation possible
- Low energy consumption for separation
- Sufficient selectivity for CO_2 capture
- Integration with reactors
- Sweep gas required

ECN

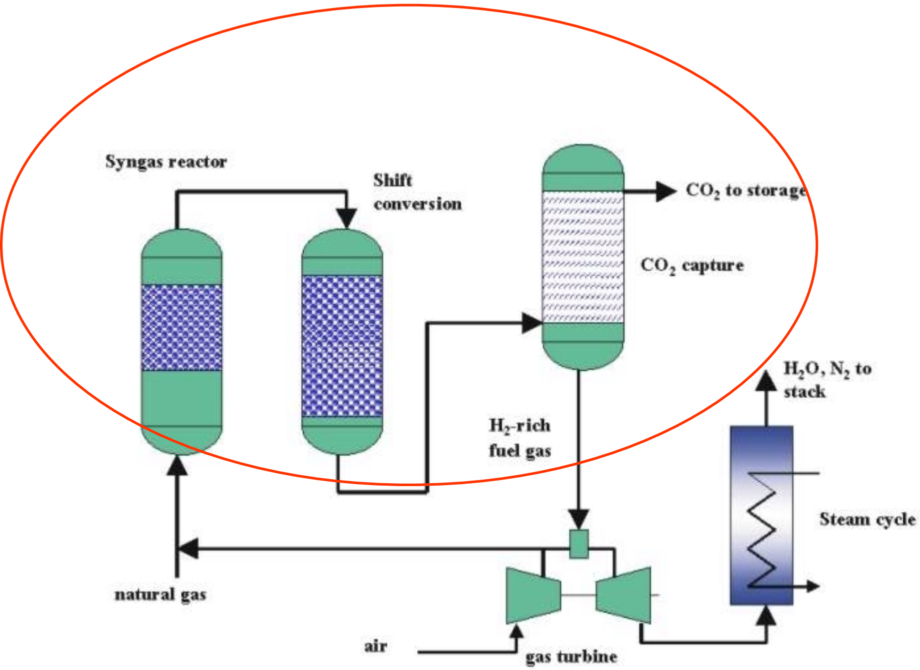
KEY TECHNOLOGIES

SOFC



- Fuel conversion up to 85-90% directly in electricity and heat
- Nitrogen-oxygen separation
- Heat can be used for NG-reforming thus no need for fuel processing
- CO_2 pressure is NG supply pressure

GAS TURBINE WITH CO_2 CAPTURE

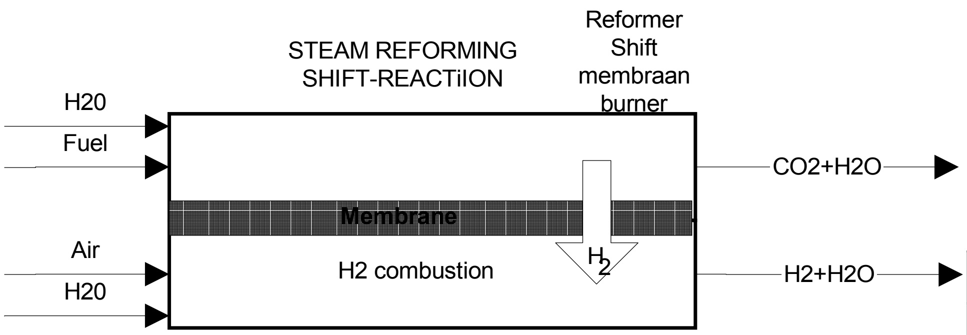


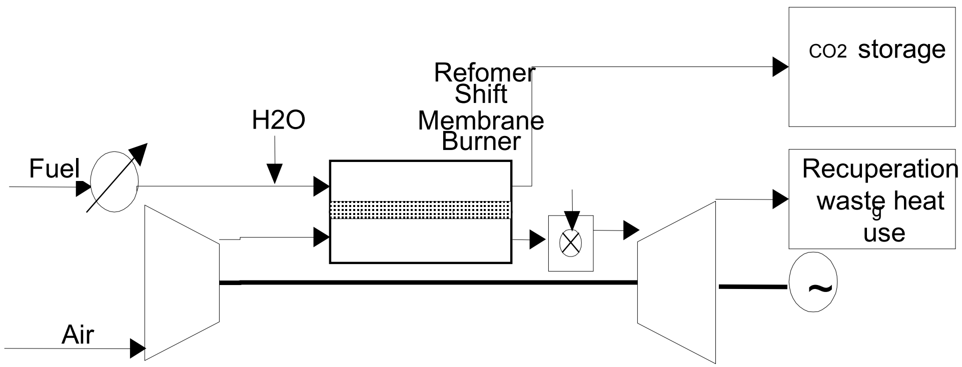
COST BREAKDOWN

	€ per ton CO_2	% points
Additional Investment	25	-
Compression energy	3,5	2
Separation	12,5	7
Totaal	41	9

Process integration to reduce investment costs!

GAS TURBINE WITH CO_2 CAPTURE



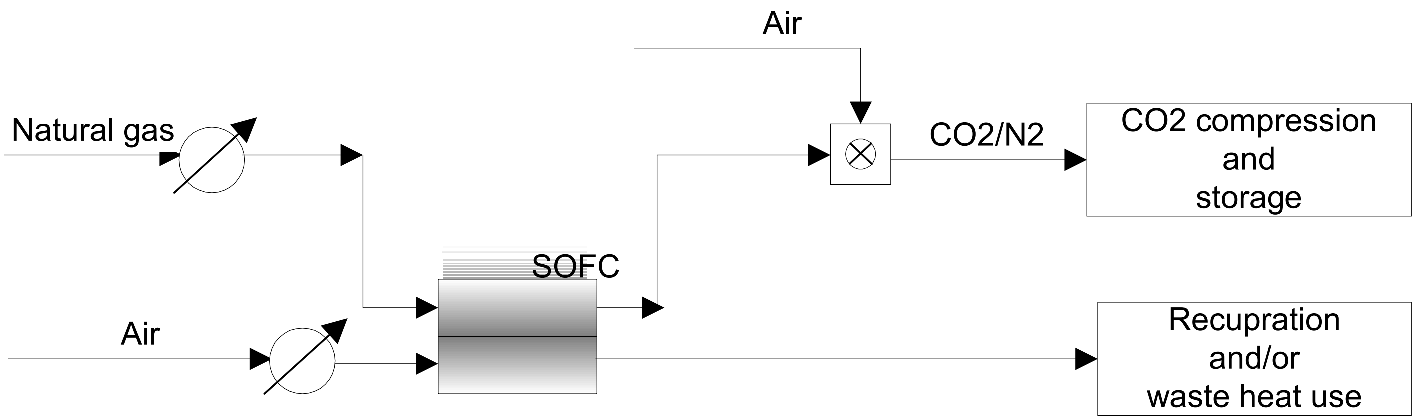


COST BREAKDOWN

	€ per ton CO_2	% points
Additional Investment	**15**	**-**
Compression energy	**1,5**	**1**
Separation	**6**	**3-4**
Totaal	**23**	**4-5**

Possibility for chemical recuperation

SOFC WITH CO_2 CAPTURE

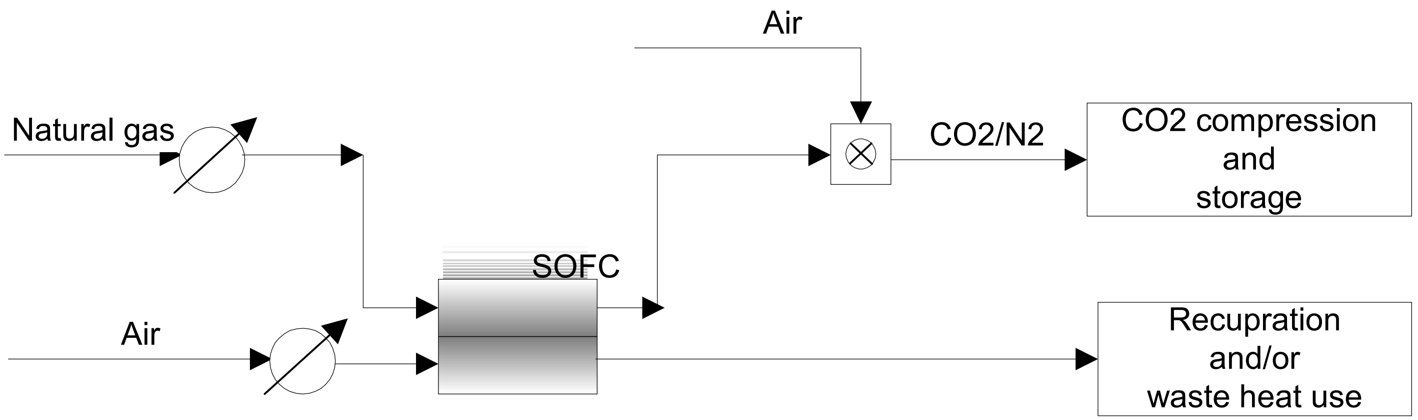


Via high fuel utilisation direct CO_2 capture

Critical issues:

- Reducing conditions in anode
- Anode material
- Stack design
- Nitrogen dilution of the CO2 stream

SOFC WITH CO_2 CAPTURE



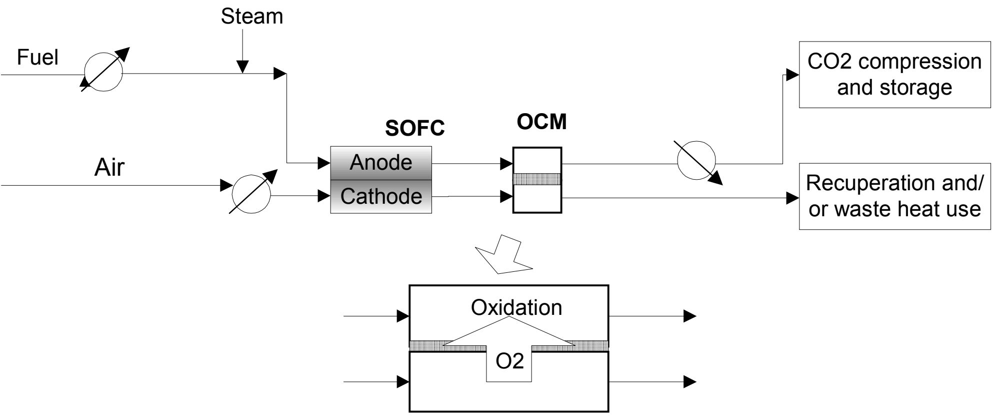
$pH_2/pH_2O > 0.05$, and $pCO/pCO_2 > 0.05$

	μ_f70%	μ_f80%	μ_f90%
pH_2/pH_2O	0.28	0.17	0.08
pCO/pCO_2	0.44	0.26	0.12

Fuel utilisation	Vol N2 (%)	Vol CO2 (%)
100	14	86
99	18,5	81,5
98	22,8	77,2
95	33,3	66,7

SOFC WITH CO_2 CAPTURE

Oxygen Conducting Membrane OCM Reactor



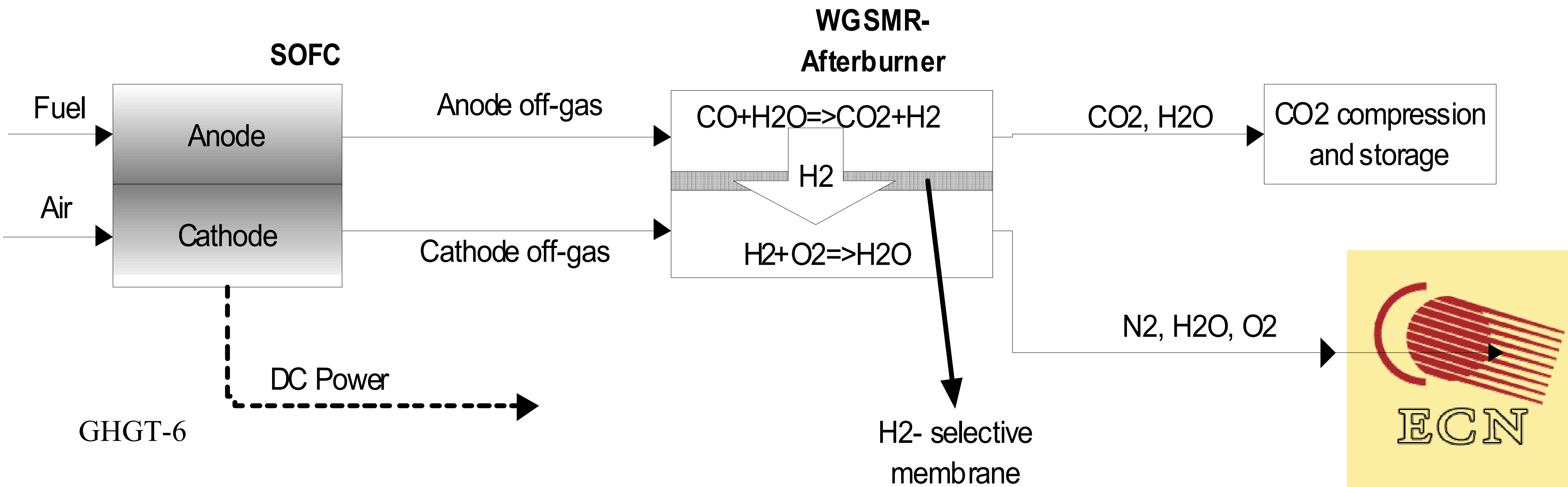
Shell/Siemens-Westinghouse

- Anode gas is sweep gas
- Afterburner very similar to SOFC tubes
- Low efficiency penalty
- Current imposed (CIEM) variant
  - prevent membrane degradation
  - higher oxygen flux

SOFC WITH CO_2 CAPTURE

Water gas shift membrane reactor (WGSMR)

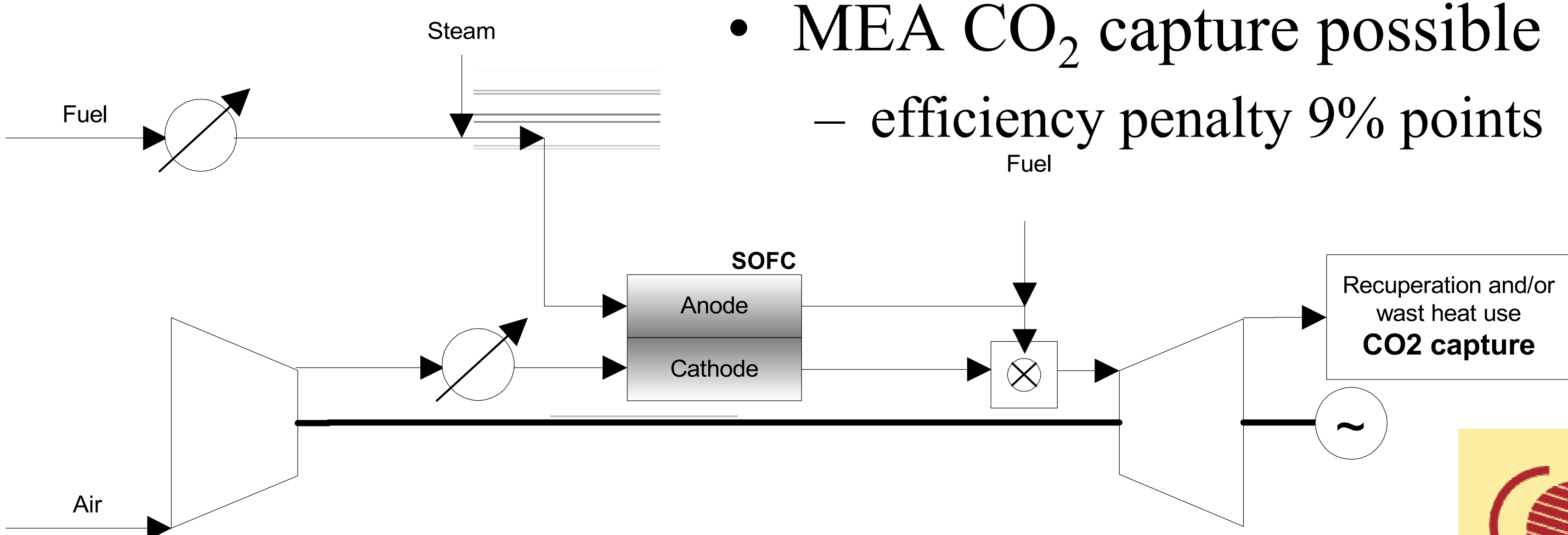
- Novel concept
- Pd membrane
- Hex membrane reactor
- Cathode (in/out) is sweep gas
- Low efficiency penalty



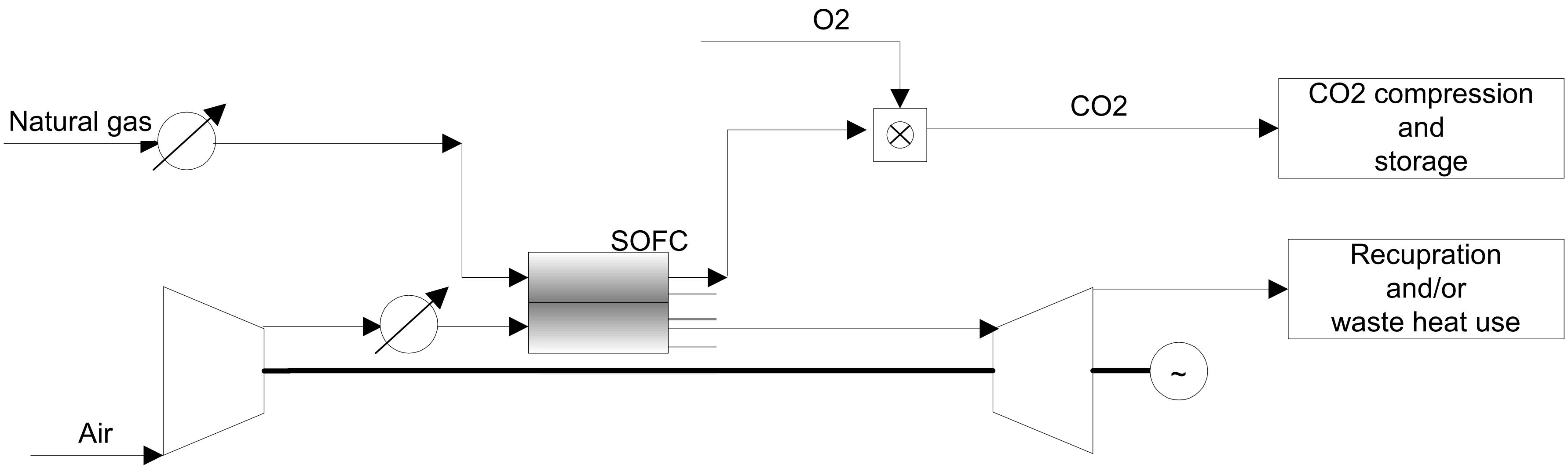
ECN

SOFC- GT COMBINATION

- Efficiencies up to 70%
- Small to medium capacities
- Investment cost 1000 USD/kW_e
- MEA CO_2 capture possible
  - efficiency penalty 9% points



SOFC-GT WITH CO_2 CAPTURE



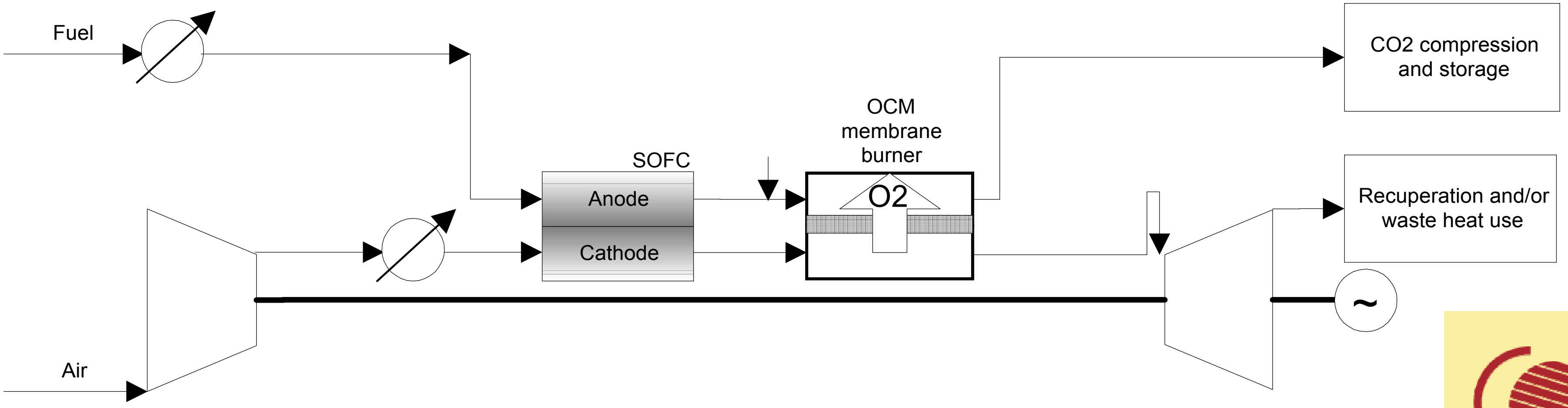
- Fuel utilisation optimised for hybride cycle
- Air is not an option
- Oxygen required

ECN

SOFC-GT WITH CO_2 CAPTURE

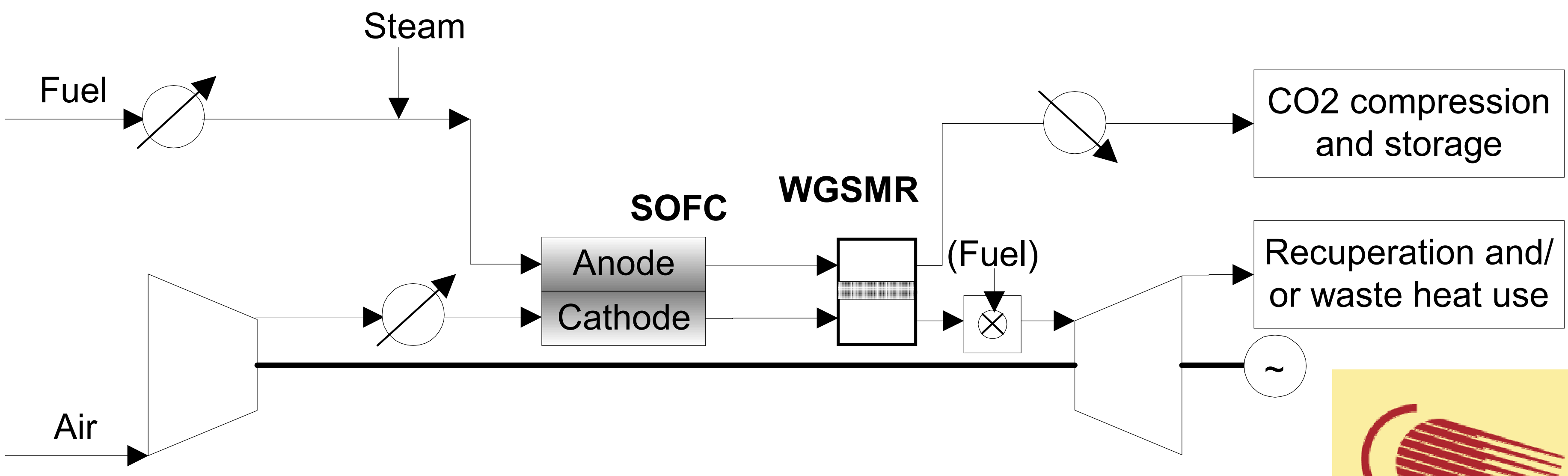
OCM-afterburner: efficiency up to 65% LHV

CIEM-afterburner: efficiency 54-59% LHV



SOFC-GT WITH CO_2 CAPTURE

WGSMR-afterburner: efficiency up to 65% LHV



CONCLUSIONS

- Gas turbines, membranes and fuel cells (SOFC) will be the key technologies in “ZEPP”
- Exiting liaisons of these key technologies are possible, but need to be assessed in more detail to determine the potential;
- Operating conditions of the key technologies must be kept with in realistic ranges