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Advanced Membrane Reactors for Fuel Decarbonisation in IGCC: H_2 or CO_2 separation?

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Abstract

This paper presents the results of preliminary system assessments that were conducted in order to pursue optimum operating conditions for advanced separation enhanced water-gas-shift membrane reactors. The project is entitled: "Advanced Membrane Reactors in Energy Systems" and appertains to the Global Climate & Energy Project (GCEP), which is coordinated by Stanford University. The implementation of hydrogen- and carbon dioxide-selective water-gas-shift membrane reactors in Integrated Gasification Combined Cycles was optimized with exergy analyses and compared with respect to efficiency penalties. The optimization resulted in optimum operating conditions, which serves the selection of a designated material for the development of advanced carbon dioxide-selective membrane reactors.

Introduction

Carbon capture and storage is widely recognized as the designated pathway towards sustainable application of fossil fuels. However, the efficiency penalty induced by carbon capture within energy conversion systems poses a threat to the economic viability of these systems. An opportunity lies in the integration of various unit operations, which reduces the efficiency penalty and consequently enhances the outlook for commercial application.

In advanced membrane reactors fuel conversion reactions such as reforming or the water-gas-shift reactions are combined with separation of one of the reaction products. Thus the fuel chemical equilibrium is shifted and conversion is increased significantly. The equilibrium shift results in reduced thermodynamic losses, when compared with conventional unit operations.

The use of coal for electric power generation by Integrated Gasification Combined Cycles (IGCC) regained interest upon the recent increase of oil and natural gas prices. The ample availability of coal which is secured for a number of centuries and its more homogeneous distribution across the globe, compared to oil and natural gas are the main factors. IGCC will play a predominant part for electricity generation in the near future. This coal conversion technology is cleaner and more efficient compared to pulverized coal boilers. Its main disadvantage remains the CO_2 emission, the main cause of anthropogenic global warming. Therefore IGCC with carbon dioxide capture and storage appears inevitable in pursuit of stabilization of the atmospheric carbon dioxide concentration.

Delft University of Technology and ECN cooperate in the "Advanced Membrane Reactor in Energy Systems" Project, which appertains to the Global Climate & Energy Project coordinated by Stanford University. This project pursues the development of innovative separation enhanced reactors, i.e. membrane reactors, for application in carbon-free hydrogen production or electricity generation. ECN identified hydrotalcites as designated material for carbon dioxide-selective water-gas-shift membrane reactors (WGS-MR). The work presented here is part of preliminary system assessments to identify optimum operating parameters for the carbon dioxide-selective WGS-MR.

Two advanced membrane reactor configurations were compared with respect to use in an IGCC with carbon capture. The configurations have a water-gas-shift reactor for synthesis gas conversion, which is integrated with a hydrogen- or carbon dioxide-selective membrane. We used exergy analysis to optimize each of the energy conversion systems. Then the efficiency penalties for CO_2 removal were compared for the reference IGCC, for an IGCC with a carbon dioxide-selective or hydrogen selective WGS-MR and for an IGCC with a high- and low-temperature WGS reactor and carbon capture by a Selexol absorber.

Reference IGCC

Coal gasification technologies can be divided in slurry- and dry-fed gasifiers. Slurry-fed gasifiers generally demonstrate lower cold-gas efficiencies than dry-fed gasifiers, due to the evaporation of the water content in the slurry. However, slurry-fed gasifiers can be operated at higher pressures when compared to dry-fed gasifiers. A significant amount of the water content within syngas obtained from a slurry-fed gasifier condenses within the acid gas removal (AGR) train. This requires a sour syngas water-gas-shift to prevent excessive downstream steam addition in order to make up for this condensation. AGR must be placed upstream of the membrane reactor, since membrane reactors are expected to demonstrate vulnerability for sulphurous impurities present in syngas, particularly when Palladium alloy membranes are applied. Consequently, the dry-fed Shell Coal Gasification Process (SCGP) [1] is initially selected for the implementation of advanced membrane reactors in an IGCC.

The reference IGCC that is applied during the system assessments is depicted in Figure 1. It displays the integration between the Air Separation Unit (ASU) and the gas turbine. The Shell gasifier is not refractory-lined but comprises a membrane wall that is cooled by steam generation. Further syngas cooling occurs in the gas cooler, again by steam generation. The integration of the steam flows from the gasifier and the gas cooler are omitted in all process schemes, however this steam is also expanded in the steam turbine to generate electricity. A small amount of the nitrogen produced by the ASU is applied to transport the pulverized coal and to feed it into the gasifier. The remaining nitrogen is fed to the combustion chamber of the gas turbine to lower the combustion temperature in the chamber. An H-class gas turbine combined cycle (General Electric S109H) is applied for electricity generation [2,3]. This combined cycle comprises a single shaft lay out and a steam cycle with reheat, however these are also omitted in the graphical representations for the sake of simplicity.

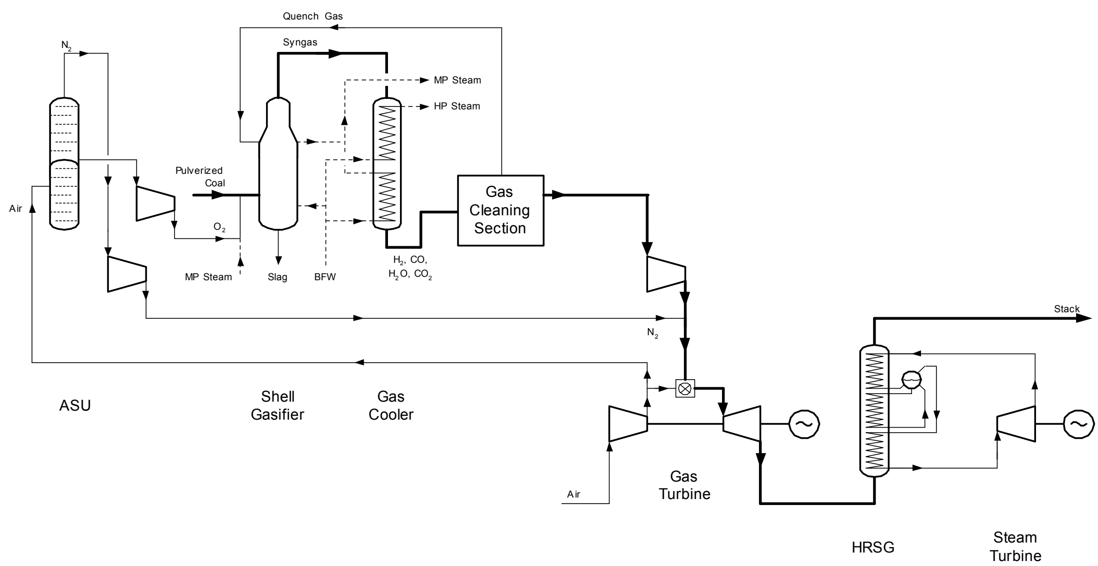

Figure 1 Reference IGCC

IGCC with H_2-selective WGS-Membrane Reactor

In the first case a H_2-selective WGS-MR is used downstream of the preliminary high-temperature shift reactor, as depicted in Figure 2. The WGS-MR is swept with nitrogen from the ASU lowering the H_2 concentration in order to enhance the H_2 permeation. Fuel conversion and H_2 separation will not reach 100% in practice; therefore CO and H_2 will still be present in the feed of the CO_2 liquefaction section. The latter requires stoichiometric combustion with oxygen from the ASU in an afterburner to ensure total fuel conversion prior to CO_2 liquefaction.

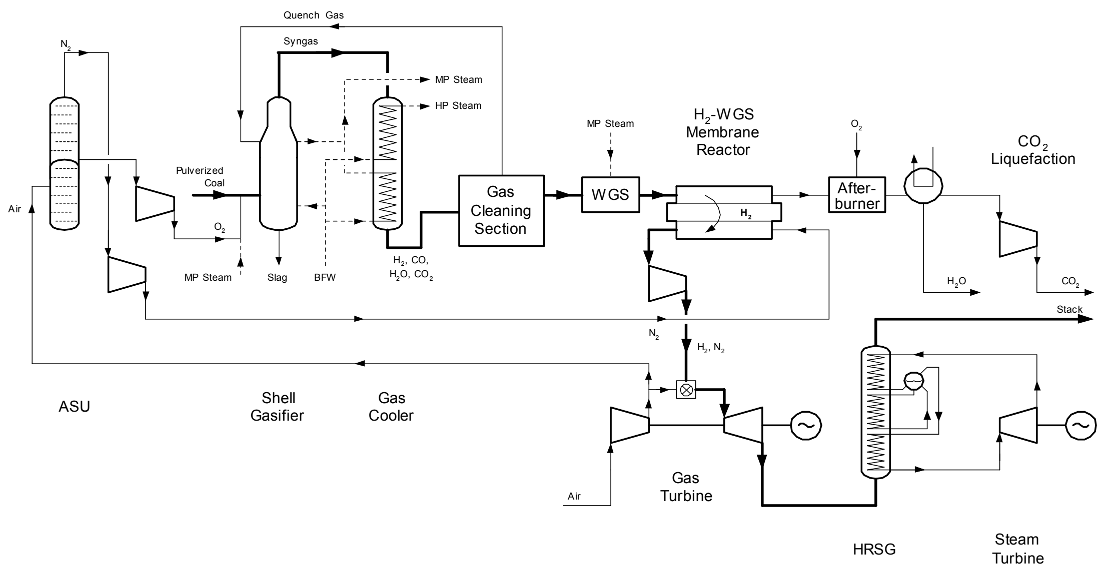

Figure 2 IGCC with H_2-selective WGS-Membrane Reactor

IGCC with CO_2-selective WGS-Membrane Reactor

In the second case a CO_2-selective membrane reactor (WGS-MR) is used downstream of the preliminary high-temperature shift reactor, as depicted in. Figure 3. The WGS-MR is swept with steam lowering the CO_2 concentration in order to enhance the CO_2 permeation. Fuel conversion and CO_2 separation will not reach 100% in practice, however this poses no problems since CO_2 is permeated through the membrane and any unconverted CO is fed to the combustion chamber of the gas turbine.

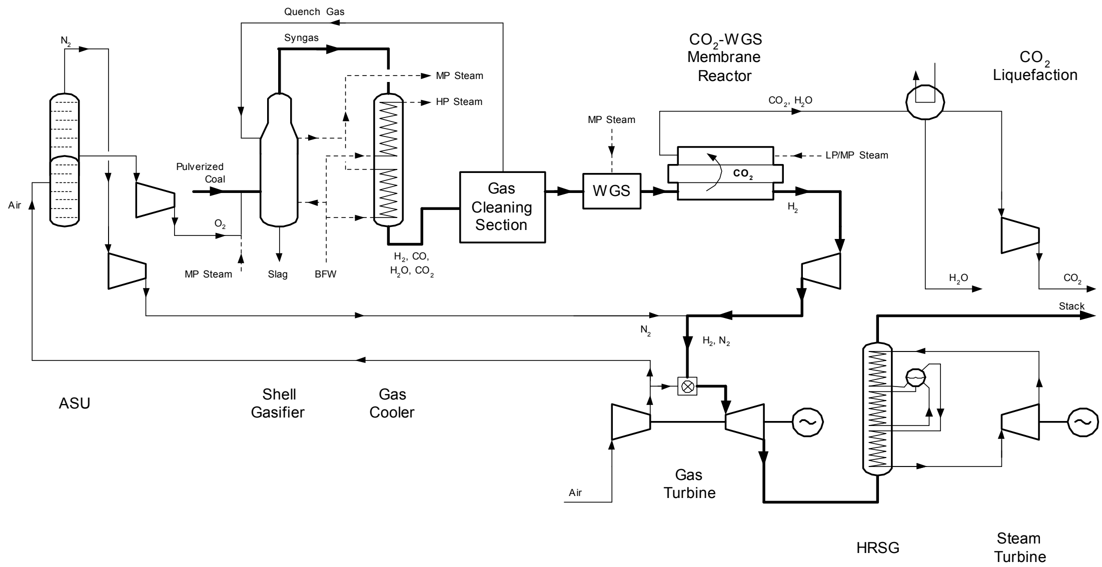

Figure 3 IGCC with CO_2-selective WGS-Membrane Reactor

IGCC with HT/LT-WGS and Selexol CO_2 Capture

An additional case where CO_2 is captured by commercially available technologies was added in order to compare the H_2- and CO_2-selective WGS-MR. In addition to the process depicted in Figure 1, a high-temperature (inlet: 350 ºC) and low-temperature (inlet: 150 ºC) WGS reactor with intermediate temperature quench are placed downstream of the AGR. CO_2 is captured by physical absorption in a Selexol absorber [4].

Analysis

The different cases were analyzed using AspenPlus, which was enhanced with a dedicated Fortran-based user model for the WGS-MR that was developed in-house at ECN [5]. This model comprises counter-current dense membrane reactor configurations (amongst others) at non-isothermal conditions. Kinetic rate expressions for high-temperature WGS catalysts and temperature dependent permeation are both integrated in the model [6]. The WGS-MR cases were optimized through exergy analysis, the exergy (chemical, physical, mixing and total exergy) per flow sheet stream is obtained from the AspenPlus subroutine ‘Exercom’ (developed by Jacobs Consultancy Nederland B.V.). Exergy defines the potential for power conversion of process streams with respect to a given environment [7]; exergy analysis of a process therefore identifies the opportunities to reduce losses. Exergy analyses of the two WGS-MR cases in AspenPlus was conducted by sensitivity analyses, during which the following parameters were varied:

Steam addition syngas for the WGS:	1.0 – 1.5 x ($n_{CO,syngas}$- $n_{H2O,syngas}$)/$n_{H2O,steam}$
Inlet pressure of the sweep flow:	8.0 – 20.0 bar
Inlet temperature of the feed & sweep stream:	250 – 500 °C
Sweep steam flow (only CO_2-selective WGS-MR):	50 – 250 t/h

The most important assumptions with respect to the system assessments are:

Coal type:	"Wambo" (Australia)
Outlet pressure gasifier:	25 bar
Outlet pressure AGR:	20 bar
Operation both WGS-MR:	counter-current
Permeation of the H_2-selective WGS-MR:	$1.0 \cdot 10^{-6}$ mol m^{-2} s^{-1} Pa^{-1}
Selectivity of the H_2-selective WGS-MR:	$H_2/CO_2 \rightarrow \infty$
Permeation of the CO_2-selective WGS-MR:	$1.0 \cdot 10^{-6}$ mol m^{-2} s^{-1} Pa^{-1}
Selectivity of the CO_2-selective WGS-MR:	$CO_2/H_2 \rightarrow \infty$
Membrane area:	30,000 m^2
CO_2 pressure after liquefaction:	110 bar

The assumptions regarding the CO_2-selective membranes are predominantly based on data taken from H_2-selective membranes (Pd/Ag), as CO_2-selective membranes are still under development.

Results and Discussion

Table 1 displays the results of the system assessments of the WGS-MR cases, as well as the results of the reference case (no CO_2 capture) and the Selexol CO_2 capture case.

Table 1 Results Optimization

Case	**Net output [MW$_e$]**	**η [%]**	**η$_{penalty}$ [% pt]**	**Carbon capture ratio [%]**	**Shift steam flow [kmol/kmol]**[1]	**Sweep flow pressure [bar]**	**Inlet temp. WGS-MR [ºC]**	**Sweep steam flow [t/h]**
Reference IGCC	500.0	48.9	-	-	-	-	-	-
IGCC with H_2-selective WGS-MR	443.9	43.4	5.5	100	1.0	19	260[2]	-
IGCC with CO_2-selective WGS-MR	403.3	39.4	9.5	90	1.0	8	250	50
IGCC with HT/LT-WGS & Selexol CO_2 Capture	413.5	40.4	8.5	90	1.1	-	-	-

1 $(n_{CO,syngas} - n_{H2O,syngas})/n_{H2O,steam}$

2 H_2-selective WGS-MR are commonly operated at temperatures of 400 ºC, changing the inlet temperature to this value results in an efficiency of 42.9%

The overall efficiency for the reference case is relatively high in comparison with reported values, which is mainly to ascribe to the application of the H-class gas turbine combined cycle, as well as to the integration between the ASU and the gas turbine. The results indicate that the H_2-selective WGS-MR case results in the lowest efficiency penalty, whereas the CO_2-selective WGS-MR case results in the highest efficiency penalty. The Selexol case results in an absolute efficiency penalty of 8.5%, which corresponds with values reported in literature [8].

The CO_2-selective WGS-MR case is less efficient than the H_2-selective WGS-MR case, however it should be noted that the obtained CO_2 stream in the latter case is only 93 mol% pure (with N_2 and Argon as predominant impurities). These impurities originate from the application of N_2 to feed and transport pulverized coal into the gasifier, and the combustion with 95 mol%

pure oxygen obtained form the ASU in the afterburner. Furthermore, a small amount of oxygen (typically 1.5 mol%) is present in N_2 obtained from the ASU, which is applied as sweep flow within the H_2-selective WGS-MR case. Combustion of this oxygen on the retentate side of the membrane was neglected during the assessments, however this could result in unacceptable high temperature gradients across the counter-current membrane configuration. Subsequently, this also results in a reduction of H_2 availability for the combustion chamber of the gas turbine.

The application of steam as sweep flow within the CO_2-selective WGS-MR case results in an absolute efficiency penalty of approximately 3.0%. Reduction of the steam sweep flow by operating the WGS-MR at lower retentate pressures appears mandatory to facilitate competition with the H_2-selective WGS-MR. Furthermore, the CO_2-selective WGS-MR allows flexibility in carbon capture ratio. This enables utility companies to speculate on CO_2 market fluctuations by adjustment of the carbon capture ratio.

Conclusions and Future Work

The results of the system assessments require further research with respect to the issues discussed in the previous paragraph. IGCC with CO_2 capture through CO_2-selective WGS-MR has one important disadvantage compared with the H_2-selective WGS-MR, being the elevated efficiency penalty. However, advantages of the CO_2-selective WGS-MR are the resulting CO_2 purity and the flexibility with respect to fuel conversion and CO_2 separation. The application of slurry-fed gasification will also be assessed in future system assessments, possibly with preliminary sour WGS upstream of the AGR.

The development and experimental evaluation of hydrotalcites as CO_2-selective membrane material are performed at present. The results of these evaluations will be applied in future system assessments, including costs associated with carbon capture for the presented cases.

Acknowledgement

The authors would like to express their gratitude for the financial support of the Global Climate & Energy Project (http://gcep.stanford.edu), which is coordinated by Stanford University and sponsored by ExxonMobil, General Electric, Schlumberger and Toyota.

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Structure Presentation

- Introduction ECN
- Outline GCEP – ECN/TU Delft activities
- Qualitative comparison H_2 & CO_2 selective membrane reactors
- Implementation Advanced Membrane Reactors in IGCC
- Exergy Analysis
- Results
- Conclusions & Future Work

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Introduction ECN

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Key research areas:

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- Biomass
- Energy Efficiency in Industry
- Built Environment
- Wind
- Solar
- Policy Studies
- Nuclear (within subsidiary)

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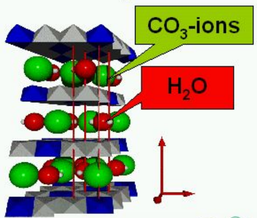
Outline GCEP – ECN/TU Delft Activities (1)

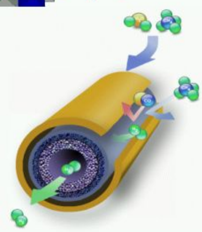
Global Climate & Energy Project coordinated by Stanford University

"Advanced Membrane Reactors in Energy Systems: Development of Novel Membranes for Membrane Reactors"

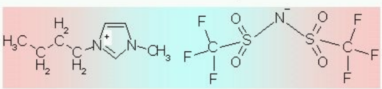
- ECN: CO_2 selective membranes (hydrotalcite):



- TU Delft: Nano-structured ceramic membrane for perm selective H_2 separation:



- TU Delft: Ionic liquids for CO_2 separation:



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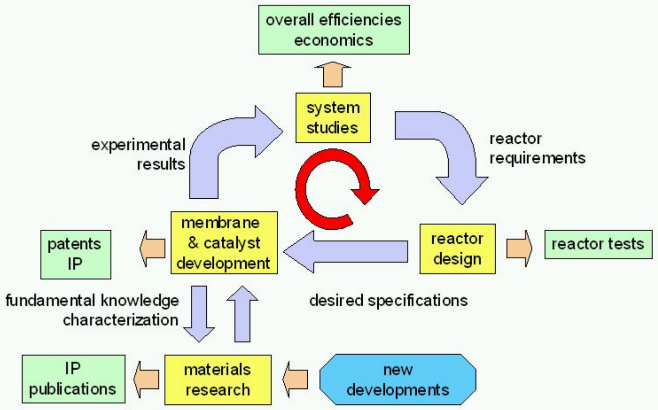
Outline GCEP – ECN/TU Delft Activities (2)



Task 1.	System analysis and thermodynamic evaluations	Executed by ECN
Task 2.	Hydrogen membrane research & development	Executed by TUD
Task 3.	CO_2 membranes research & development	Executed by ECN+TUD
Task 4.	Catalyst screening	Executed by ECN
Task 5.	Reactor modelling and design	Executed by ECN

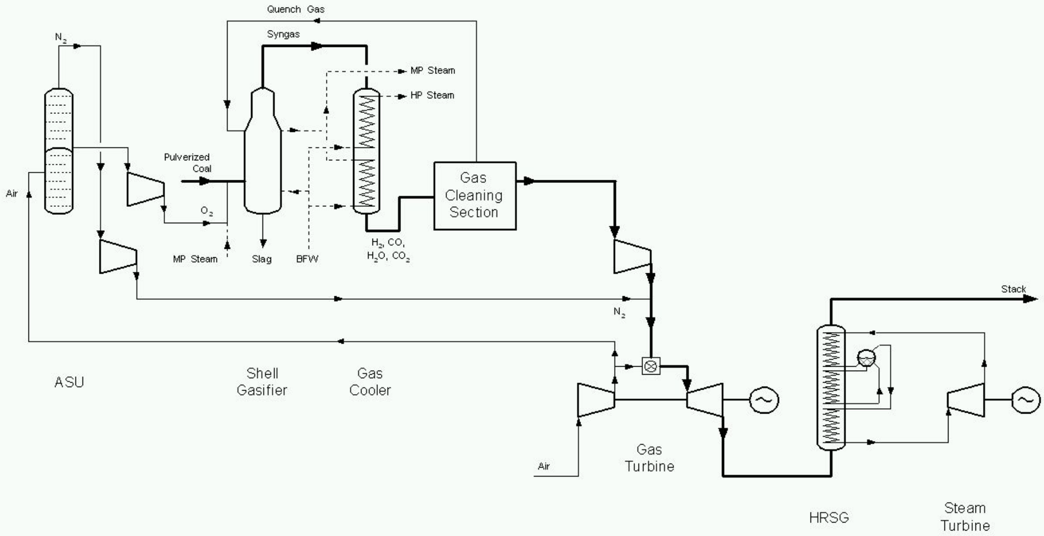
Qualitative Comparison H_2 & CO_2 Membrane Reactors

High partial pressure difference of permeating compound eases membrane permeation:

- Coal gasification: CO_2 WGS membrane reactors
  - Incomplete conversion WGS enhances efficiency but lowers carbon capture ratio
  - H_2 rich stream remains at elevated pressure
  - CO inhibition of membrane not foreseen
- Natural gas reforming: H_2 steam reforming membrane reactors
  - Conversion relatively easy enhanced by separation of H_2 → favourable kinetics
  - “Mature” membrane technology

CO_2 selective WGS membrane reactors appear to be a viable solution for application in an IGCC

Reference IGCC



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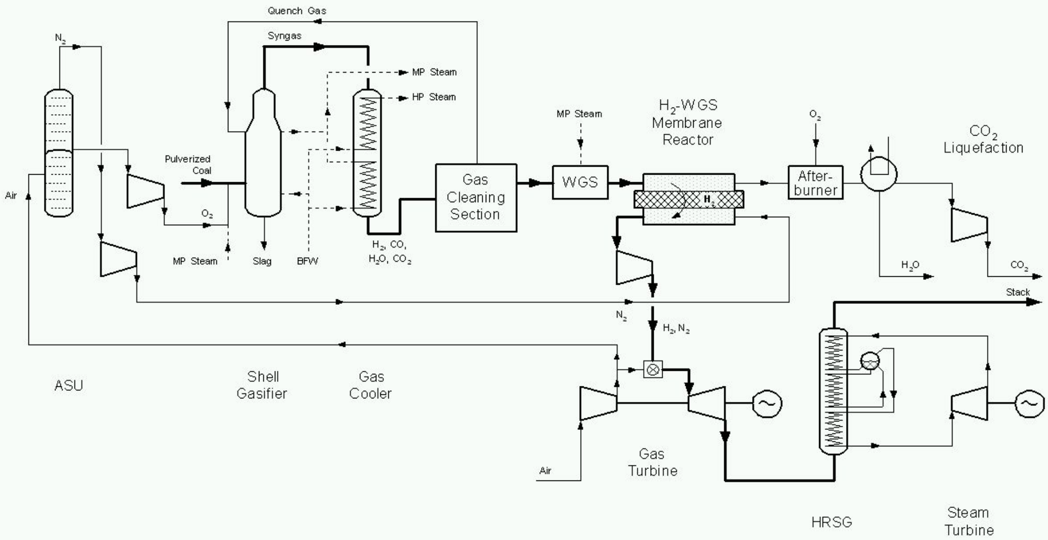
IGCC with H_2 WGS Membrane Reactor



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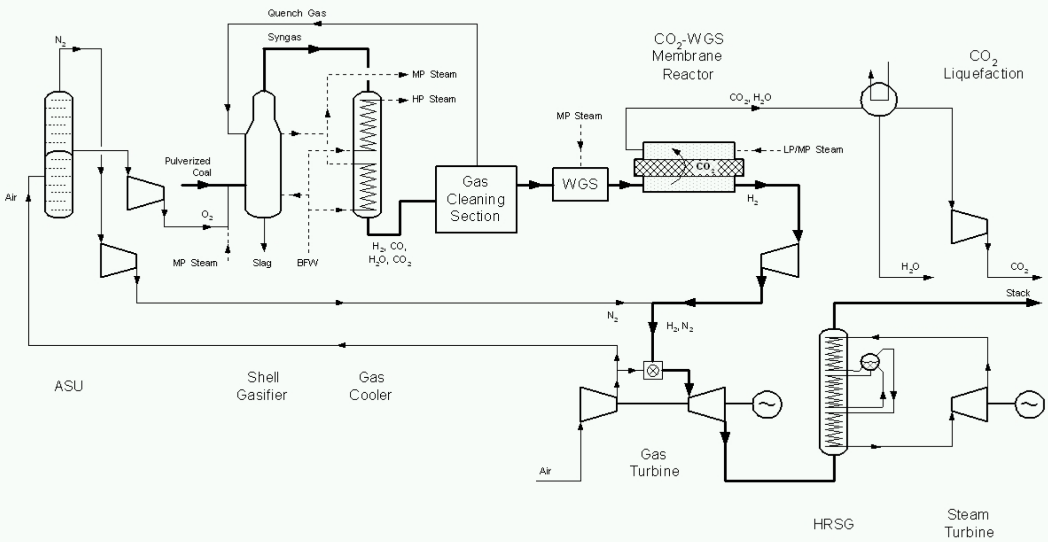
IGCC with CO_2 WGS Membrane Reactor



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Exergy Analysis (1)

Exergy analysis applied to minimize losses and select appropriate operating conditions on system level:

- IGCC configurations modelled in AspenPlus
- In-house Fortran model for water-gas-shift membrane reactor (WGS-MR) simulations
- Exercom for exergy analysis of process streams

Manipulated variables during WGS-MR exergy analysis :

- Steam addition for WGS (1.0 – 1.5 × $(n_{CO,in} - n_{H2O,in})/n_{H2O,steam}$)
- Inlet pressure sweep flow (8 – 20 bar)
- Inlet temperature feed & sweep (250 – 500 °C)
- Sweep steam (50 – 250 t/h; CO_2 membrane only)

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Exergy Analysis (2)

- Net output: 500 MWe
- Gasification technology: Shell Coal Gasification Process
- Gasifier outlet pressure: 25 bar (20 bar at WGS inlet)
- Feedstock: Australian coal ("Wambo")
- Combined Cycle: Modified GE "H" Combined Cycle (50 Hz)
- Permeation H_2 membrane reactor: $1.0 \cdot 10^{-6}$ mol H_2 m^{-2} s^{-1} Pa^{-1}
- Permeation & diffusion mechanism CO_2 membrane reactor unknown, therefore: $1.0 \cdot 10^{-6}$ mol CO_2 m^{-2} s^{-1} Pa^{-1}
- Membrane: 30,000 m^2; counter-current configuration
- CO_2 Pressure: 110 bar

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Results

Near future reference IGCC: η_{LHV} = 48.9

IGCC H_2 WGS-MR: η_{LHV} = 43.4

(capture ratio ~100%, but impure)

Shift steam:	1.0 × $(n_{COin} - n_{H2Oin})/n_{H2O,steam}$
Sweep flow pressure:	19 bar
Inlet temperature WGS-MR:	260 °C

IGCC CO_2 WGS-MR: η_{LHV} = 39.4 (capture ratio 90%)

Shift steam:	1.0 × $(n_{COin} - n_{H2Oin})/n_{H2O,steam}$
Sweep flow pressure:	8 bar
Inlet temperature WGS-MR:	250 °C
Sweep flow (steam):	50 t/h

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Conclusions & Future Work

- Minimise steam consumption for WGS and/or sweep flow
- High sweep flow pressure beneficial for H_2 WGS-MR → less compression duty, $\Delta P_{partial}$ results in sufficient driving force
- No afterburner required in CO_2 WGS-MR → high flexibility regarding CO_2 capture & high purity residual CO_2 stream

- Incorporate GE gasifier in models, possibly with pre-shift of raw syngas
- Synthesis and experimental assessment hydrotalcites for CO_2 separation

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Acknowledgements & Questions

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