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Water gas shift membrane reactor for CO_2 emission reduction and hydrogen production

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Abstract

The use of water gas shift membrane reactors for carbon dioxide sequestration in fossil fuel fired energy production plants has been studied for more than a decade. In general CO_2 emission reduction is possible at the cost of the efficiency of electricity production. Here we present a water gas shift (WGS) membrane reactor concept in which CO_2 capture at a refinery is combined with the production of hydrogen as energy source and of pure hydrogen that can be used as chemical feedstock. A base case refinery process has been chosen in which several unit operations, e.g. heaters, boilers and furnaces, produce flue gas containing CO_2. A feasibility study into the removal of CO_2 from these flue gases using the conventional amine absorption process as best available technology has been performed [1]. Based upon this study a new process using a WGS membrane reactor is proposed in which syngas is converted into a hydrogen rich and a CO_2 rich stream. This hydrogen stream is used as fuel gas for the existing refinery heaters, boilers and furnaces and the process is suggested as an improved CO_2 capture alternative [2]. In the present study this WGS membrane reactor process has been modified further by using two WGS membrane reactors in series. One reactor is for the production of chemical feedstock grade hydrogen and one for a hydrogen rich fuel gas stream. This new process still meets the energy demands of the refinery and, of course, the CO_2 capture demands set. A modelling study has been performed using ASPEN+ flowsheeting calculations. A WGS membrane reactor model has been implemented in ASPEN+ and was combined with gas separation data of inorganic membranes for hydrogen separation. It has been found that a membrane selectivity of at least 100 is needed for obtaining a hydrogen stream with a purity of 97.5 mol.% and meeting the hydrogen and carbon recovery demands. A total membrane area of 16,750 m2 is needed for the refinery, which has a total energy demand of approximately 800 MW. Economic calculations show that a feasible process can be obtained that could compete with the CO_2 capture option using the amine absorption technology. The economics, however, very much depend on energy and hydrogen prices. Flowsheeting reults have shown that by using a ceramic membrane based water gas shift process the energy demand of a refinery can be combined with a carbon recovery of >90% and the production of chemical grade hydrogen.

References

[1] M. Simmonds et.al., Amine based CO2 capture from flue gas, Gas Processors Association Europe – Sept. 2002 Annual Meeting.

[2] C. Lowe, et.al., Hydrogen membrane selection for a water gas shift reactor, 2nd Conf. on carbon sequestration, Arlington, VA, 5-7 May 2003.

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Introduction

High temperature H_2 separation with inorganic membranes is proven, but

- Reproducibility?
- Long term behaviour (stability) under process conditions?
- Comparison of different types of membranes and scale-up?
- Most separation processes not viable: high H_2 compression costs, so extra feature needed

Take 'well known' membrane reactor processes

- Chose processes based upon operating range of membranes
- Petrochemistry needs cleaner/better processes and more hydrogen
- Water Gas Shift Membrane Reactor studied and (on paper) proven for:
  - CO_2 abatement →
  - H_2 production →

  Combine

Goal: Combine membrane development, process testing and evaluation under realistic conditions and <u>calculate the technical and economic viability</u>

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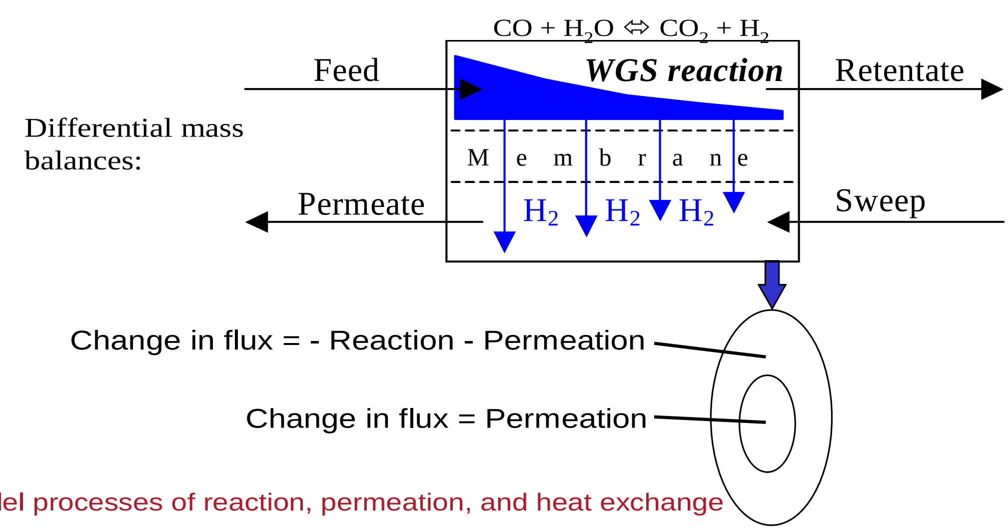
Membrane reactor model: working principle



Parallel processes of reaction, permeation, and heat exchange

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Membrane reactor model: working principle

<u>Implemented in ASPEN+:</u>

- Kinetics of water gas shift reaction
- Transport of hydrogen through:
  - Microporous membranes
  - HT proton conductors
  - LT proton conductors (simulated as palladium type), and
  - Transport of all gases through defects

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Semi-empirical H_2 transport models in ASPEN

Micropores: Phenomenological flow

$$J_i = Q_i * dP_i \qquad Q(T) = Q_0 . e^{\left(-\frac{Eact}{R.T}\right)}$$

LT solid state membranes: suggested palladium type equation

$$J_{H2} = Q_{H2} * (P^n_{f,H2} - P^n_{p,H2}) \qquad Q(T) = Q_0 . e^{\left(-\frac{Eact}{R.T}\right)}$$

Other components/defects: Poiseuille flow

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Water gas shift reaction thermodynamics+kinetics

$CO + H_2O \Leftrightarrow CO_2 + H_2$ exothermic (ΔH= - 41.1 kJ/mol).

Equilibrium constant: $K_p = \dfrac{c_{H2}c_{CO2}}{c_{CO}c_{H2O}}$ [-]

$K_p = \exp\left(\dfrac{4577.8}{T} - 4.33\right)$ [-] (Moe, 1962):

FeCr catalyst (300-450°C) and reaction rate by (Keiski, 1992)

$R_{CO} = -k_1 c_{CO}^{0.73} c_{H2O}^{0.55}(1-\beta)$ [mol/m^{3}s]

and $k_1 = 828{,}535 \exp\left(\dfrac{-9407}{T}\right)$ [mol/m^{3}s]

Implemented in ASPEN+

with β, the reversibility factor: $\beta = \dfrac{c_{CO2}c_{H2}}{K_p c_{CO}c_{H2O}}$ [-]

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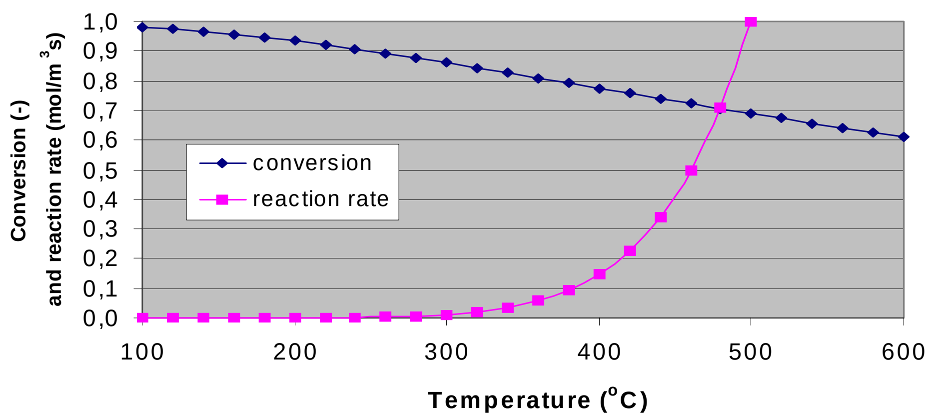
Water gas shift reaction thermodynamics+kinetics

CO conversion and reaction rate vs. temperature



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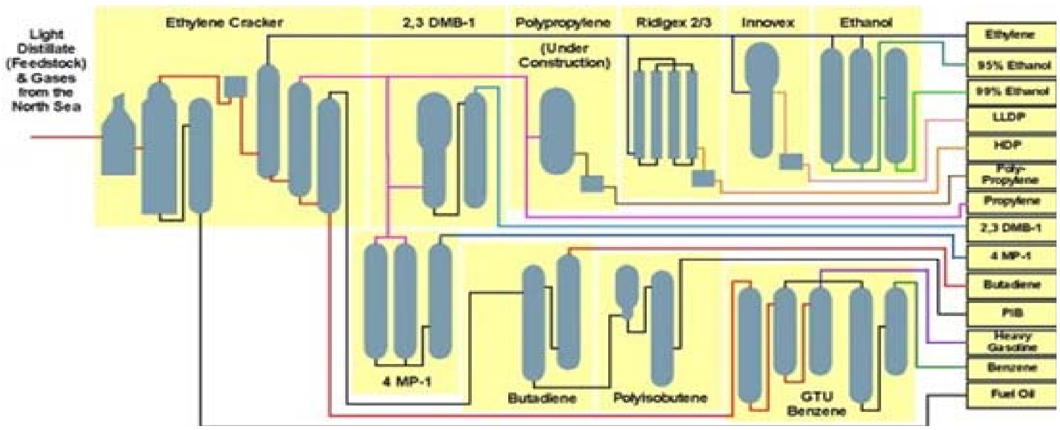
WGS process overview and choice



CCP and GRACE programme pre-combustion base case: Grangemouth refinery
Energy use in furnaces, heaters, etc. 812 MW (=72 el+640 thermal)
No CO_2 reduction

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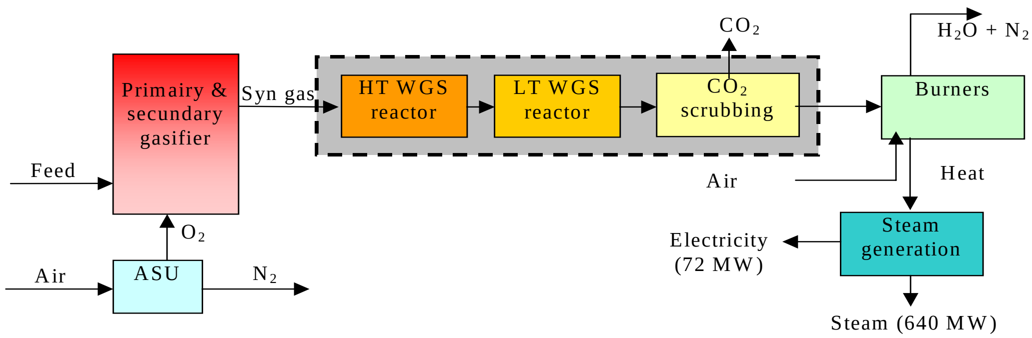
WGS process overview and choice

CCP and GRACE programme pre-combustion: CO_2 reduction with scrubbing = BASE CASE



Water gas shift reaction
$CO + H_2O \Leftrightarrow CO_2 + H_2$

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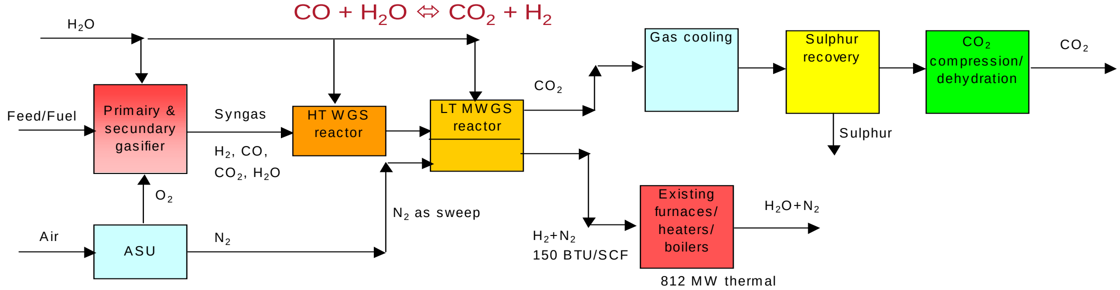
WGS process overview and choice

CCP and GRACE programme pre-combustion: CO_2 reduction with WGSMR

Water gas shift reaction
$CO + H_2O \Leftrightarrow CO_2 + H_2$



Conclusions for GRACE/CCP project (Middleton 2005 and Melien 2005)

Pre-combustion decarbonisation is technically and economically feasible: appr. 80 \$/ton CO_2 for scrubbing and 50\$/ton CO_2 for membrane WGS

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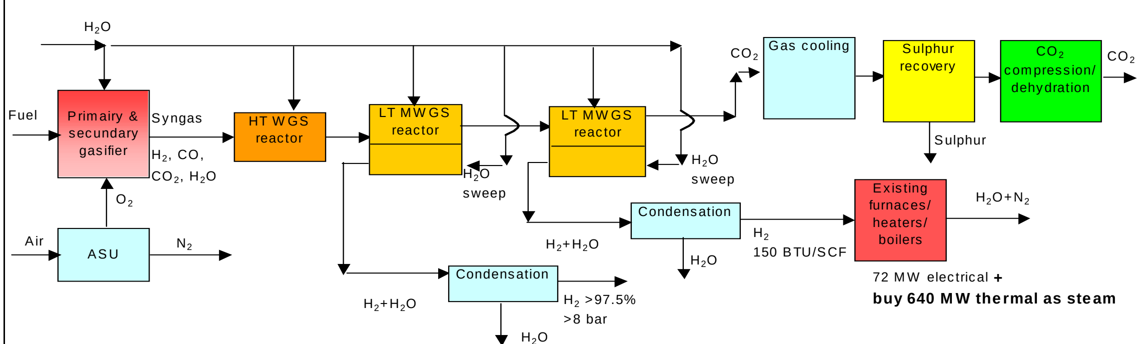
WGS process overview and choice

New process option: CO_2 reduction + hydrogen production for on-site use
Hydrogen: 97.5 mol% and 8 bar



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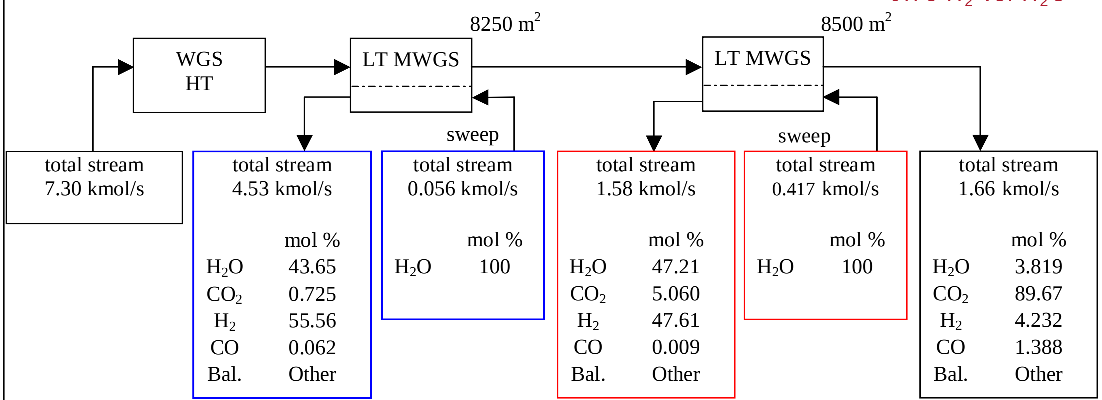
Water gas shift process calculations and TEE

Permeability: $3.38 \cdot 10^{-7}$ mol/m^{2}sPa
Selectivity: 100 (H_2 vs. others) and 0.73 H_2 vs. H_2O



Hydrogen: 97.5 mol% and 8 bar
Energy: 72 MW electricity (or 180 MW thermal energy) + 640 MW thermal (buy steam)

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Water gas shift process calculations and TEE

Demands	Results	Wish
Primary		
Pressure pure hydrogen [bar]	8.0	8.0
Hydrogen purity [mol%]	97.77	97.5
Electricity demand [MW]	73.2= 183 ther	72.0= 180 therm
Heat of combustion [BTU/SCF]	167.36	150.0
CO_2 in retentate [mol%]	93.23	90.0
Secundary		
Carbon Recovery [mol%]	92.78	90.0
Hydrogen Recovery [mol%]	97.11	90.0
Conversion of CO in total process	96.95%	90.0

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Membrane in module = 2000 Euro/m^2

Water gas shift process calculations and TEE

Income	Base case M Euro/year	MR case low H_2 price 1.35 Euro/kmol M Euro/year		
Electricity	28.80	29.29		
Steam	81.27	22.53		
Hydrogen	-	97.86		
Costs				
Fuel	58.77	58.77		
Process water	16.86	19.36		
Cooling water	0.37	0.38		
H_2S removal+CO_2 tax	1.48+1.15	1.48+1.15		
Steam as energy	-	59.29		
Result (Income-Costs)	**+ 31.46**	**+ 9.24**		
Capital charges	M Euro	M Euro		
Gasifier	77.04	77.04		
After gasifier	177.37	124.16		
Membrane system	-	83.75		
Total capital costs	**254.37**	**284.95**		
Return on Investm.	**8.1 year**	**30.8 year**		

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Membrane in module = 2000 Euro/m^2

Water gas shift process calculations and TEE

Income	Base case M Euro/year	MR case low H_2 price 1.35 Euro/kmol M Euro/year	MR case high H_2 price 3.13 Euro/kmol M Euro/year	MR case realistic H_2 price 1.65 Euro/kmol M Euro/year
Electricity	28.80	29.29	29.29	29.29
Steam	81.27	22.53	22.53	22.53
Hydrogen	-	97.86	226.89	129.12
Costs				
Fuel	58.77	58.77	58.77	58.77
Process water	16.86	19.36	19.36	19.36
Cooling water	0.37	0.38	0.38	0.38
H_2S removal+CO_2 tax	1.48+1.15	1.48+1.15	1.48+1.15	1.48+1.15
Steam as energy	-	59.29	59.29	59.29
Result (Income-Costs)	**+ 31.46**	**+ 9.24**	**+ 138.26**	**+ 30.99**
Capital charges	M Euro	M Euro	M Euro	M Euro
Gasifier	77.04	77.04	77.04	77.04
After gasifier	177.37	124.16	124.16	124.16
Membrane system	-	83.75	83.75	83.75
Total capital costs	**254.37**	**284.95**	**284.95**	**284.95**
Return on Investm.	**8.1 year**	**30.8 year**	**2.1 year**	**9.2 year**

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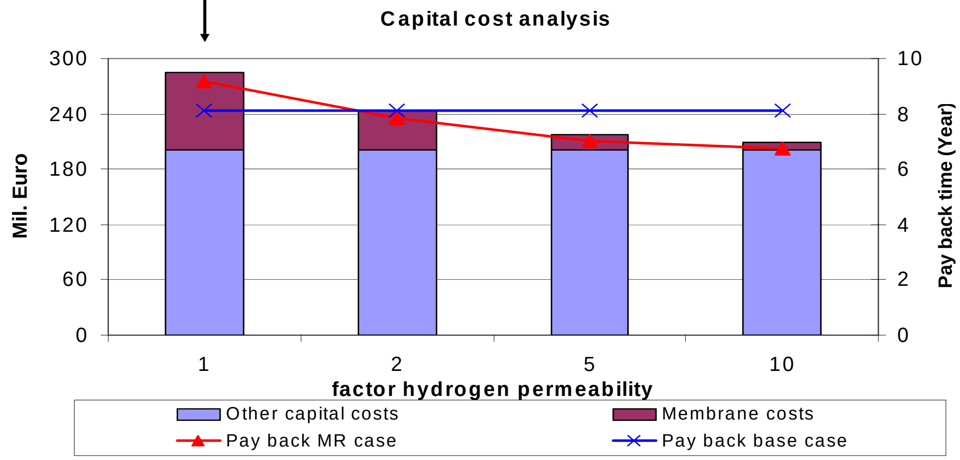
Water gas shift process calculations and TEE

H_2 permeability: 3.38*10^{-7} mol/m^{2}sPa,
H_2 price 1.65 Euro/kmol



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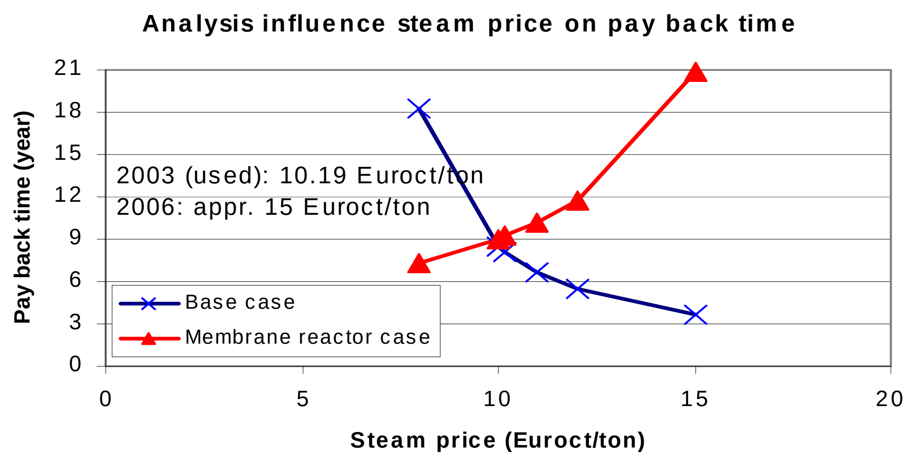
Water gas shift process calculations and TEE



Constant hydrogen price: 1.65 Euro/kmol

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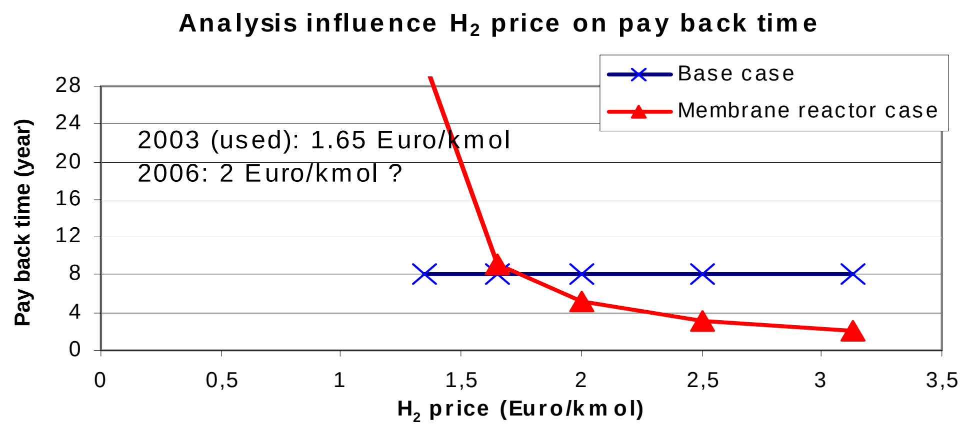
Water gas shift process calculations and TEE



Constant steam price: 10.19 Euroct/ton

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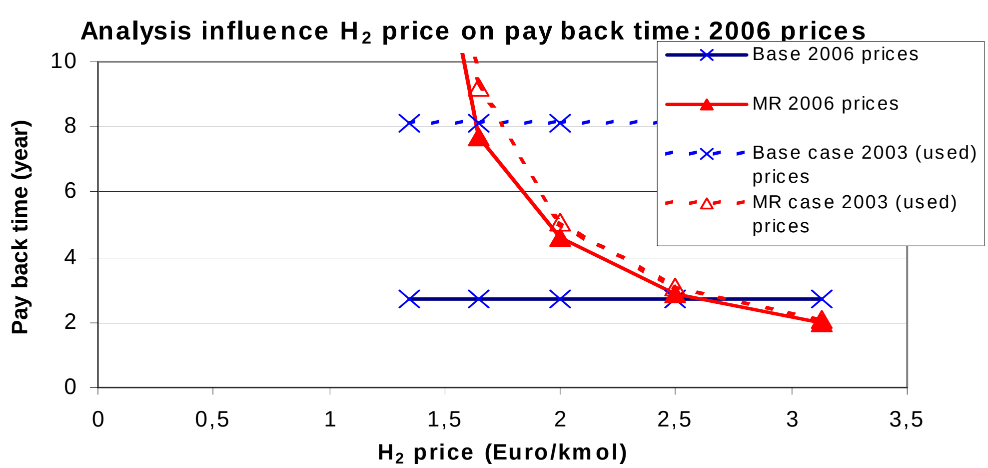
Water gas shift process calculations and TEE



Constant steam price: 15 Euroct/ton

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Concluding remarks

1. The payback time of the MR case is a bit higher than the (scrubbing) base case, but besides >90% CO_2 emission reduction (both cases) you obtain hydrogen.
2. The selectivity of H_2 vs. other gases must be ≥ 100 to reach a H_2 permeate purity > 97.5%. With this selectivity all demands set can be met.
3. The economics are strongly influenced by the energy and hydrogen prices.
4. As the price of hydrogen is comparable to steam and these prices are coupled, changes in these prices (energy price increase) lead to similar changes in the total economics for the MR case.
5. An increase in hydrogen permeability leads to better economics but an increase by more than a factor of 5 is not necessary.

A. What is the meaning of return on investment in this WGS case: the plant calculated is an energy source for a complete refinery and energy costs will be taken into account in the final product prices. However, the cheaper the energy production process, the better.

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Questions?

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