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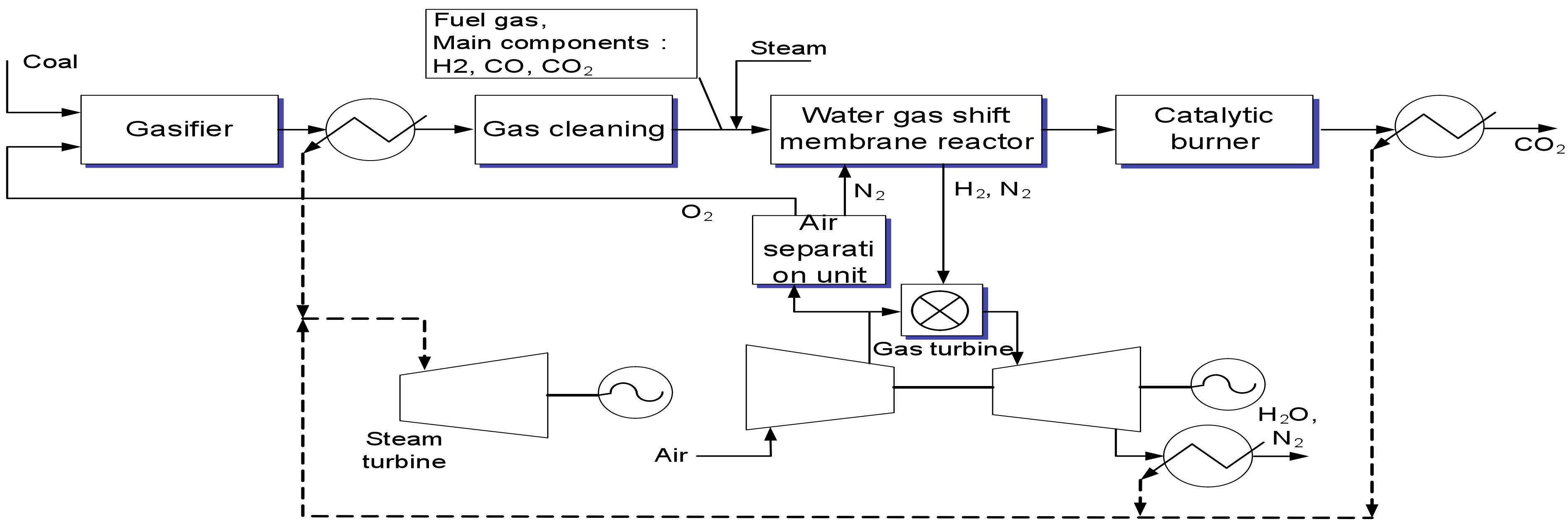
DE-FE0001322 Hydrogen Selective Exfoliated Zeolite Membranes

Proposal in response to Funding Opportunity NO. DE-PS26-08NT00699-01

Pre-combustion carbon capture technologies for coal-based gasification plants

Topic Area 1 – High-Temperature, High-Pressure Membranes

Hydrogen Selective Membranes in IGCC Plants

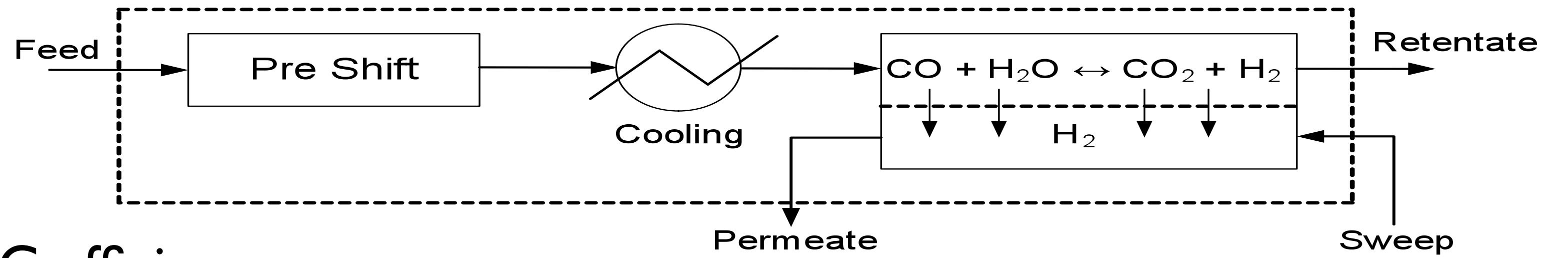


Challenges under WGS conditions of IGCC plants

- high temperature and pressure
- presence of impurities (H_2S)

Bracht et al., **Energy Convers. Mgmt** 38, S159-164 (1997)

IGCC w/ WGS-MR



IGCC efficiency

- without CO_2 capture: 46.7%
- with conventional CO_2 removal: 40.5%

With WGS-MR and CO_2 recovery: 42.8% (LHV) based on

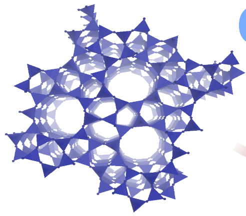
- 35 atm feed, 20 atm permeate (15 atm pressure drop)
- 330°C in the feed
- hydrogen/carbon dioxide selectivity = 15
- hydrogen permeability = 0.2 mol/(m^2.s.bar)

Membrane Area Needed: 2,200 m^2 (400MW)

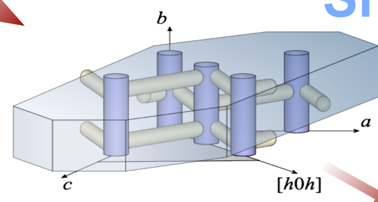
Bracht et al., **Energy Convers. Mgmt** 38, S159-164 (1997)

Motivation: Hierarchical Manufacturing of Zeolite Films

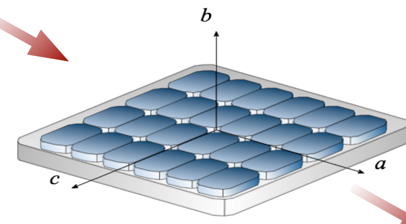
For a Review:
Mark A. Snyder, Michael Tsapatsis,
Angew. Chem. Int. Ed. **2007**, *46*, 7560–7573



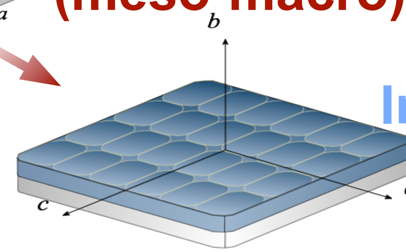
Crystal Structure (nm)



Shaped Crystal (10-100nm)



Oriented Monolayer of Crystals (meso-macro)



Intergrown Film

AIChE Journal, 42(11), 3020-3029 (1996)

Chemistry of Materials 10, 2497-2504 (1998)

Science 300:(5618), 456-460 (2003)

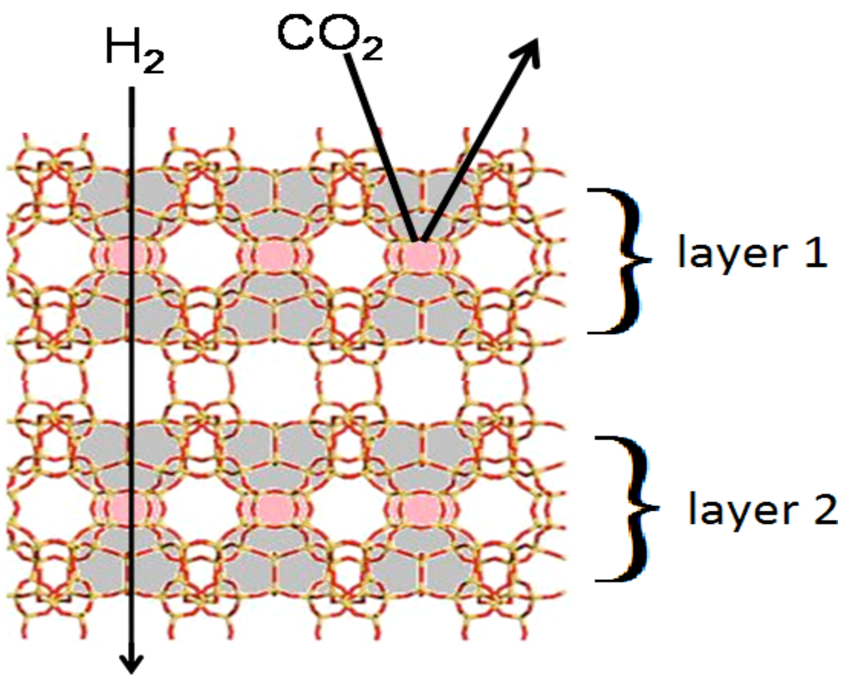
Angew. Chem. Int. Ed. 45, 1154-1158 (2006)

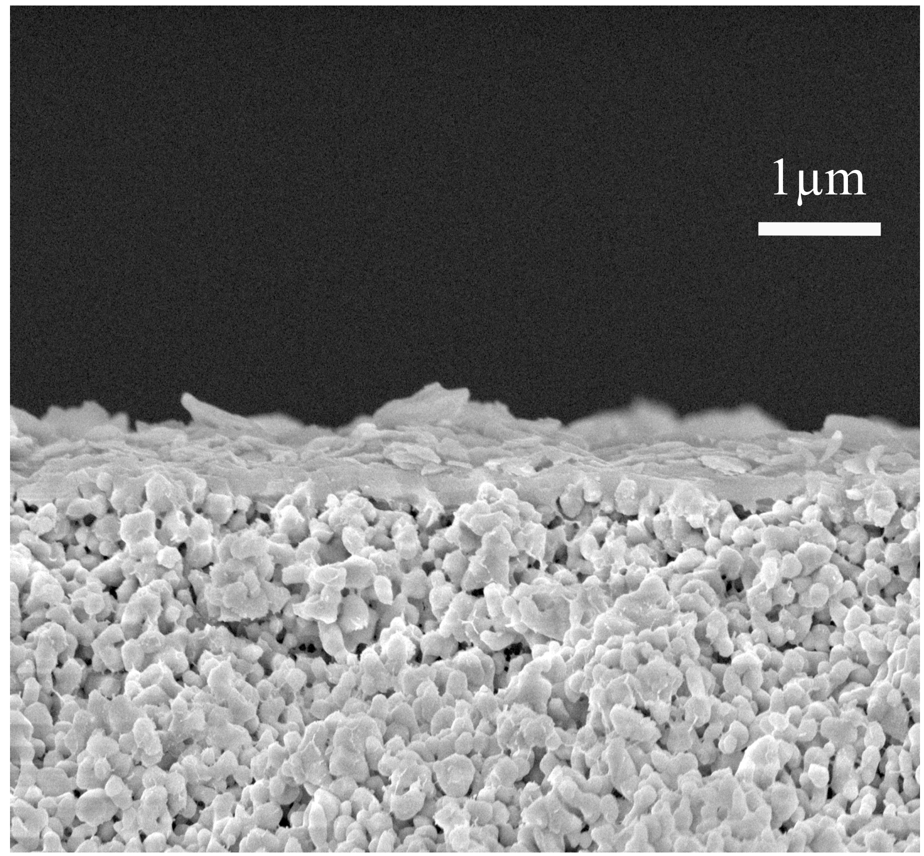
Nature Materials, 7(12), 984-991(2008)

Science 325 (5940), 590-594 (2009)

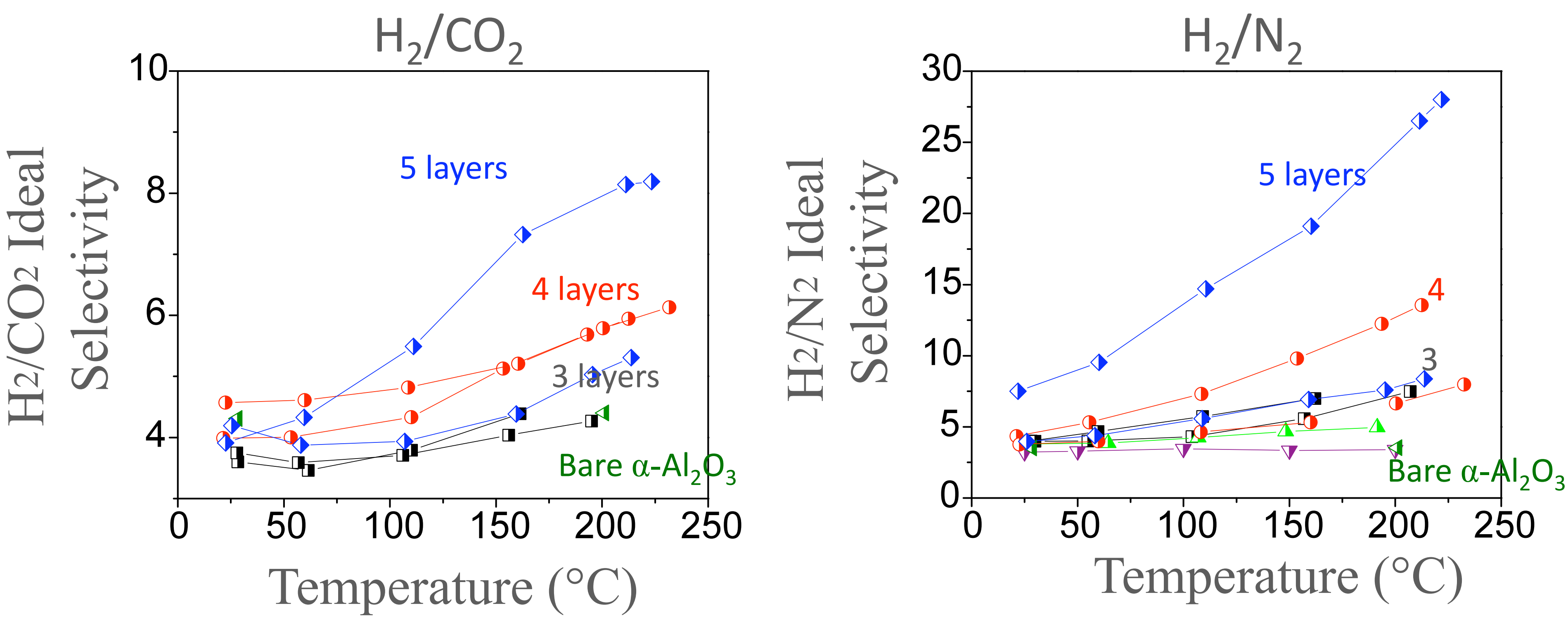
Layer by Layer Deposition (JACS 132(2), 448-449 (2010))

5 layers of MCM-22/surfactant-templated-mesoporous-silica on porous alumina





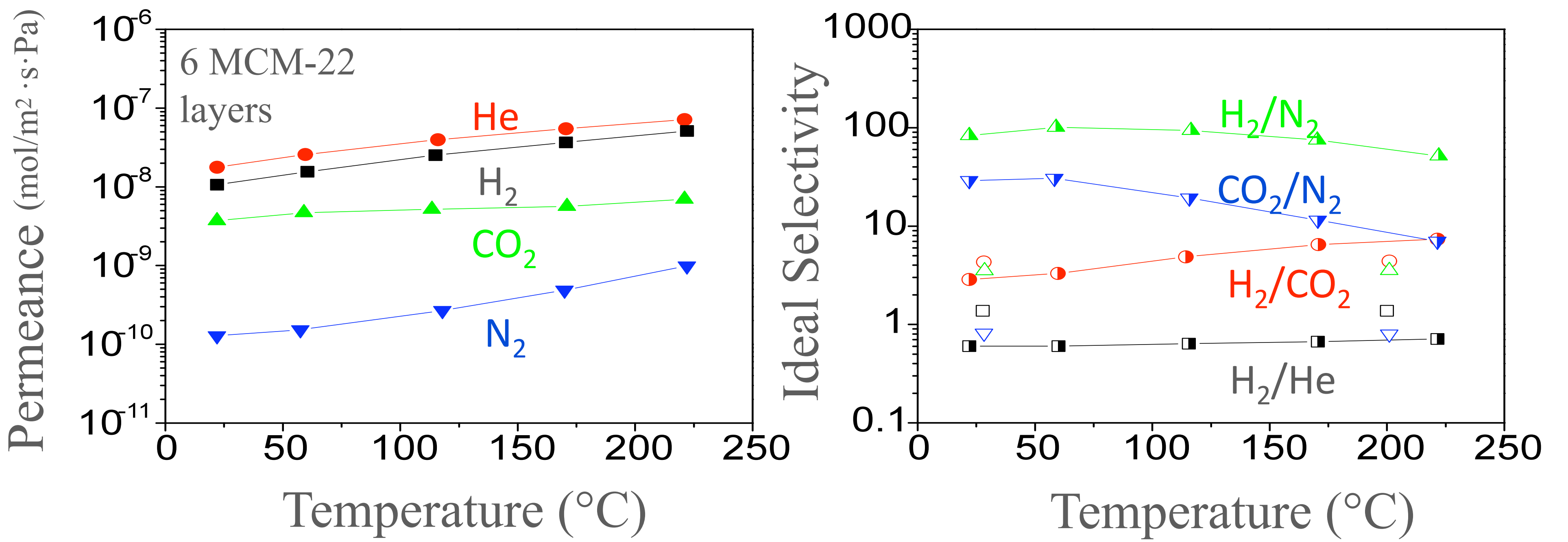
Comparison of Ideal Selectivity



The ideal selectivity (H_2/CO_2 and H_2/N_2) increased monotonically with temperature and improved with the number of deposition cycles.

MCM-22/Silica Membranes for Hydrogen Separations

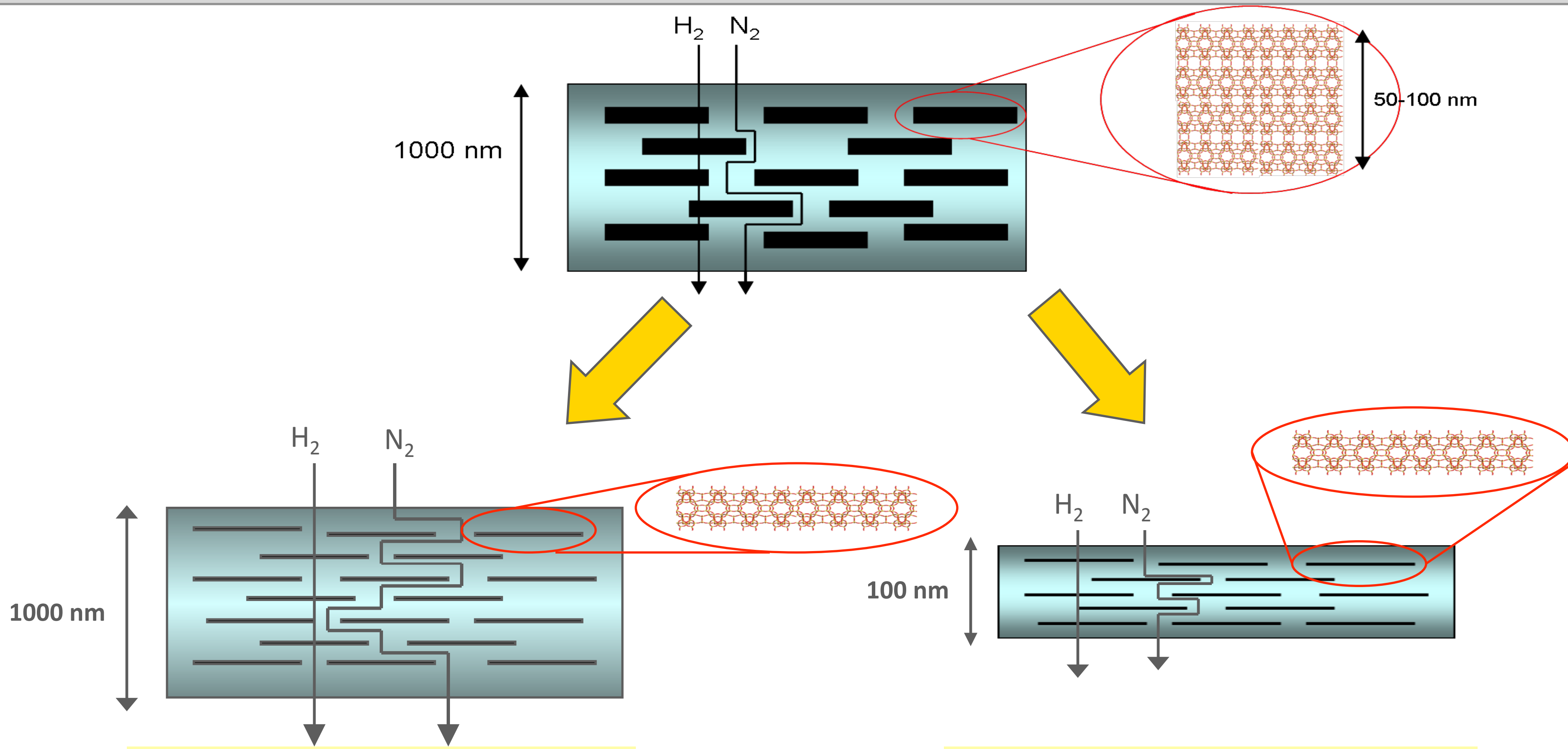
*Open symbols : selectivity through α-Al_2O_3 discs



Choi J. and Tsapatsis M. **Journal of the American Chemical Society** 132(2), 448-449 (2010)

Experimental Demonstration of Selective Flake Composite Concept

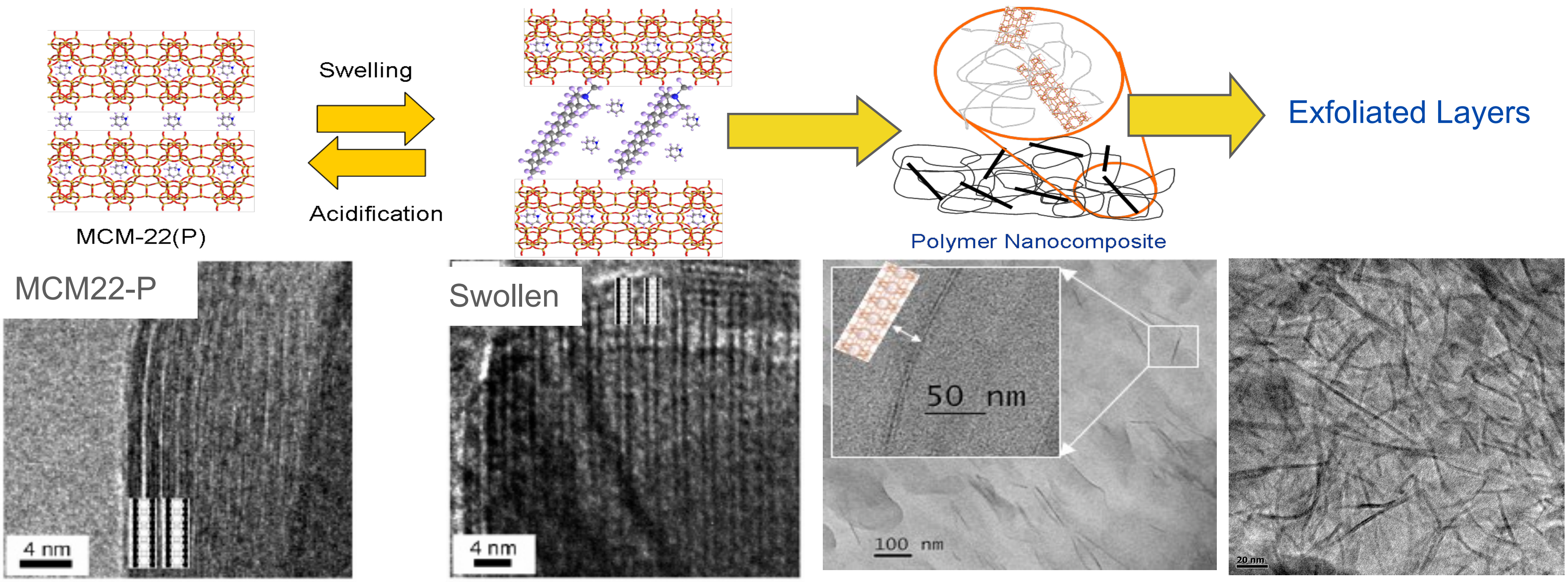
Advantages by Reduction in Flake Thickness



Increase selectivity without decreasing throughput

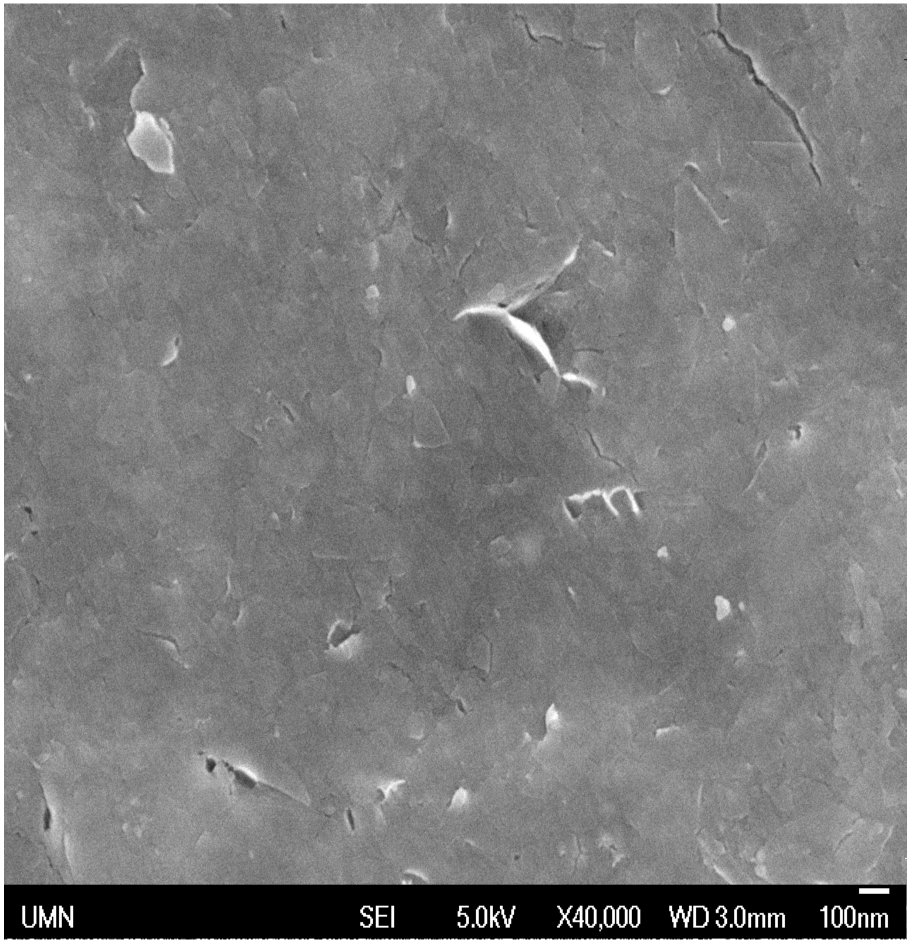
Increase throughput without decreasing selectivity

Membrane Preparation Procedure

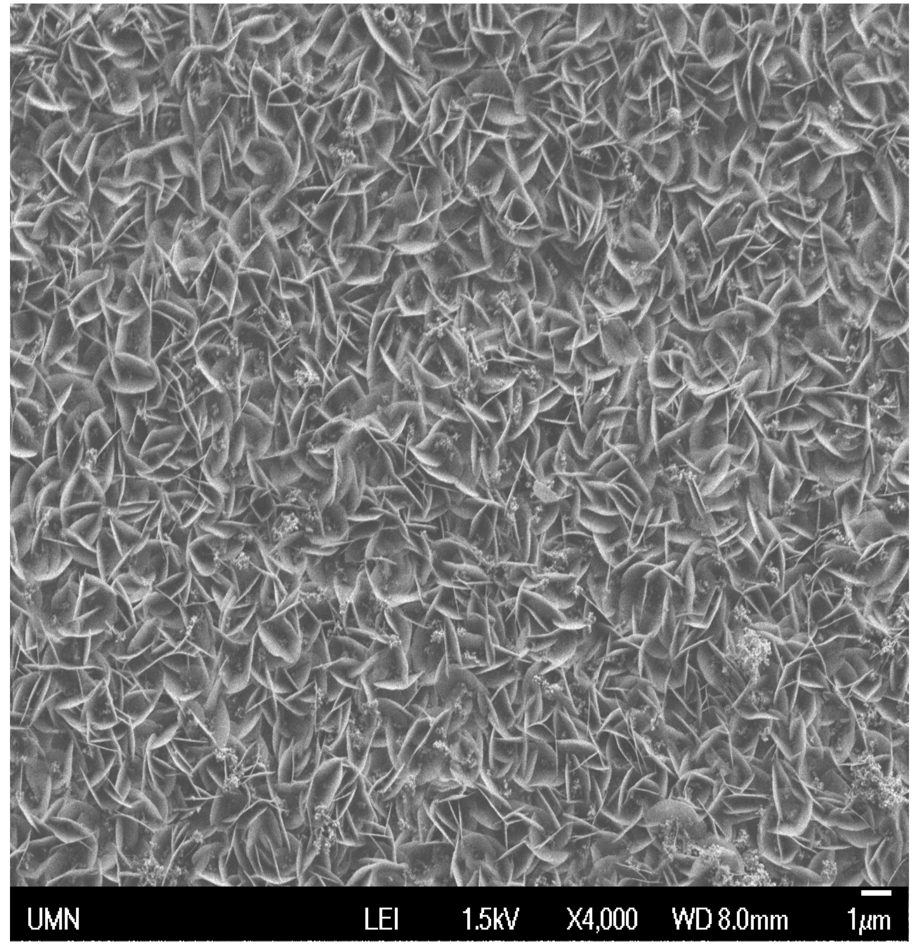


Purified nanosheets in toluene were filtered through porous alumina supports and then secondary growth was conducted.

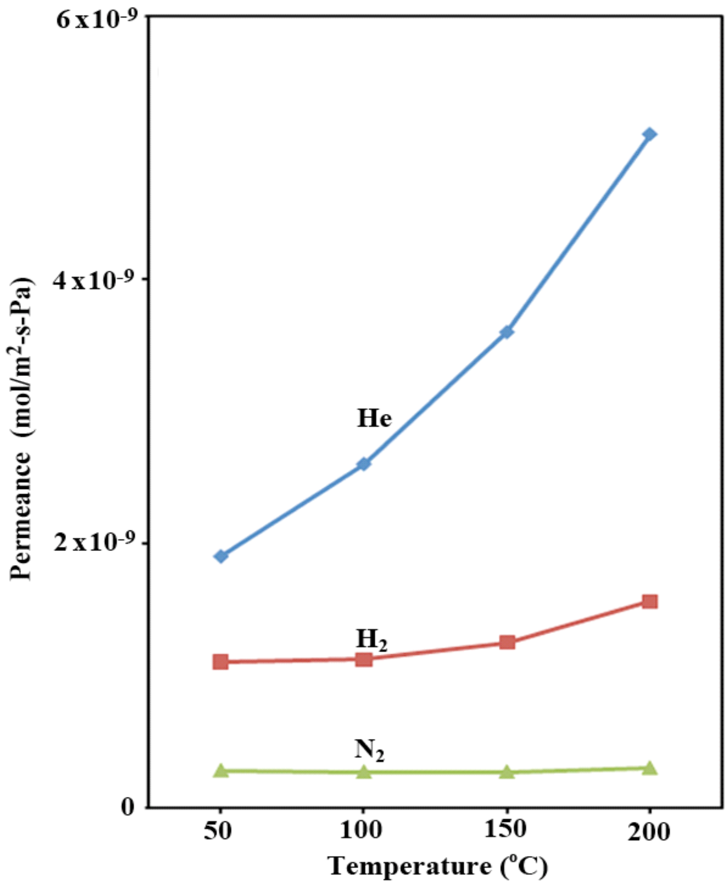
- Exfoliated ITQ-1 on Alumina Disk

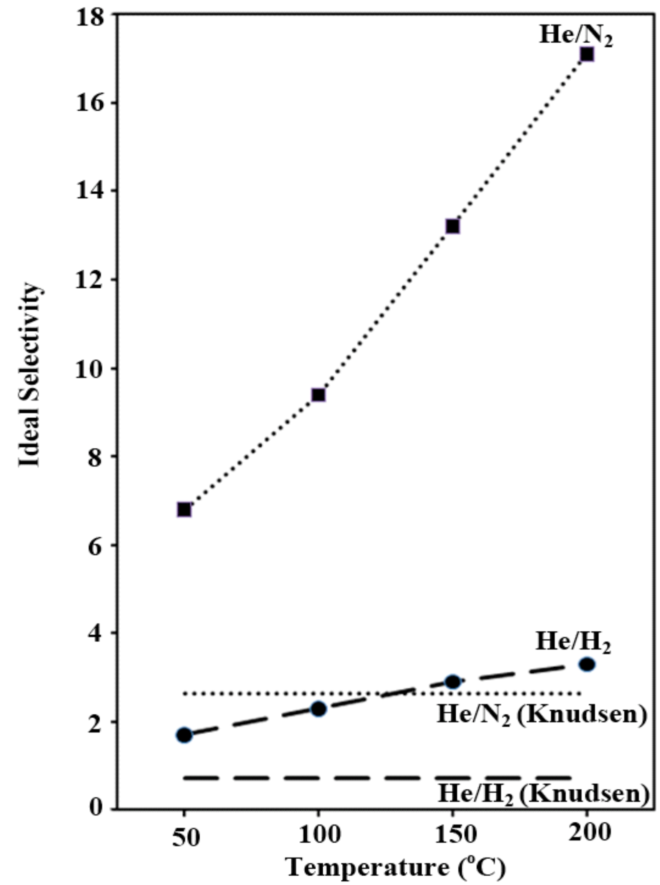


- After Secondary Growth of ITQ-1



Performance of ITQ-1 Membrane

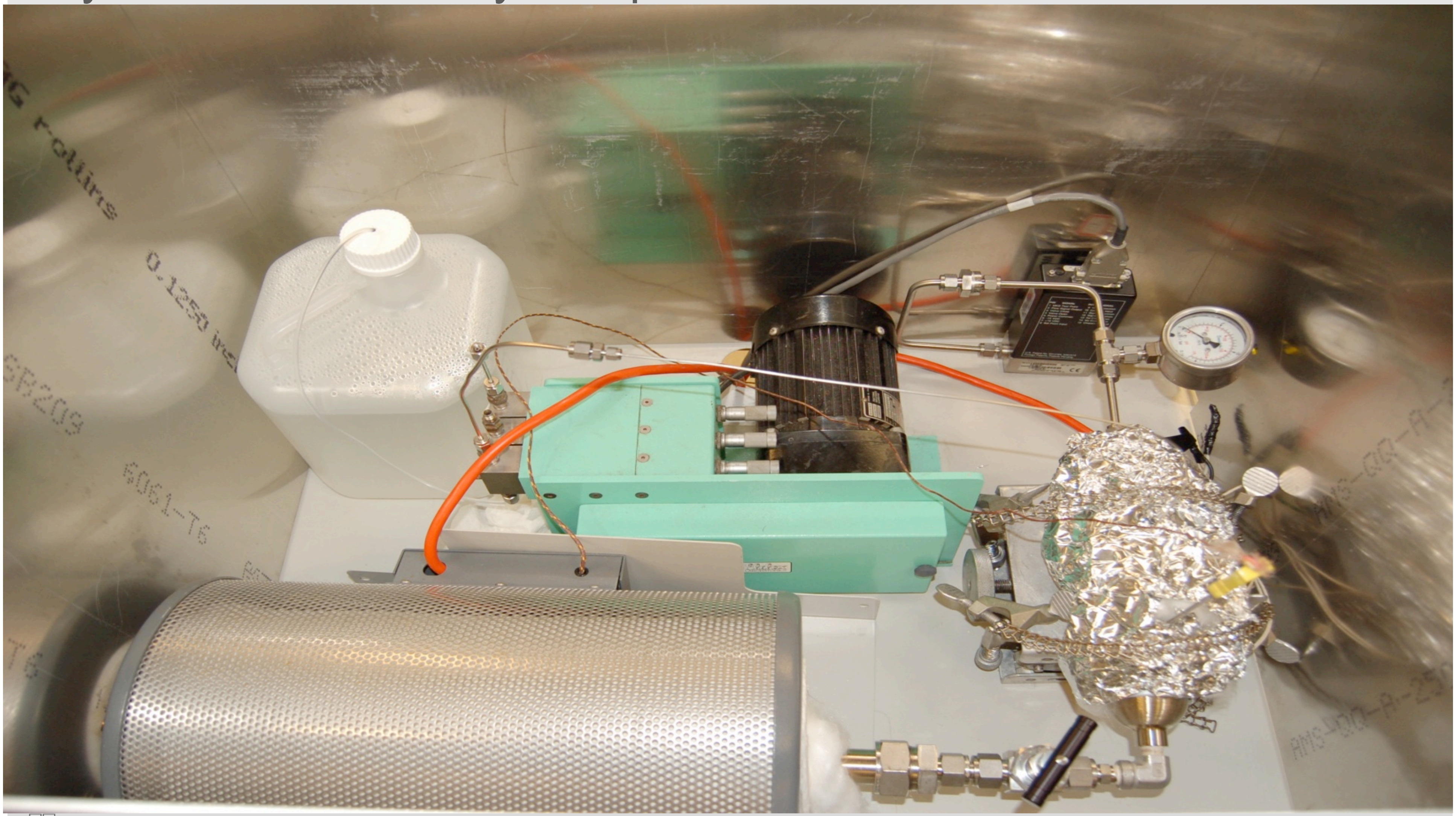




Varoon et al., **Science** 334:(6052), 72–75 (2011)

Four layered zeolites (MCM-22, ITQ-1, NU-6(2), RUB-24) with 6-MR perpendicular to the layers were investigated.

Hydrothermal Stability Setup



Hydrothermal Stability of MCM-22 and ITQ-1

- Temperatures: 350°C, 600°C
- Pressure: 10 bar (95% steam, 5% nitrogen)
- Samples were analyzed in 21-day intervals for 84 days

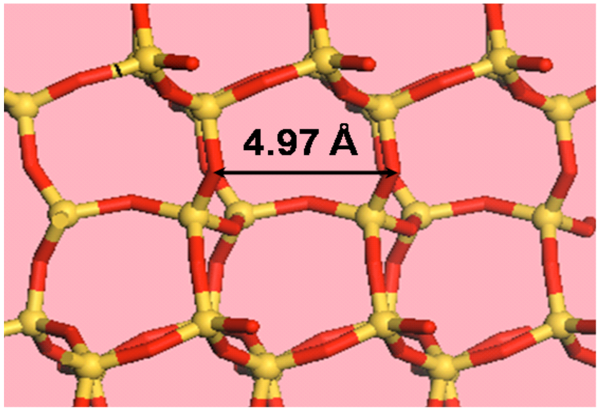
Both MCM-22 and ITQ-1 showed poor steam stability at 600°C.

MCM-22 outperformed its all silica counterpart (ITQ-1) at 350°C. This behavior was related to the lower concentrations of structural defects in MCM-22.

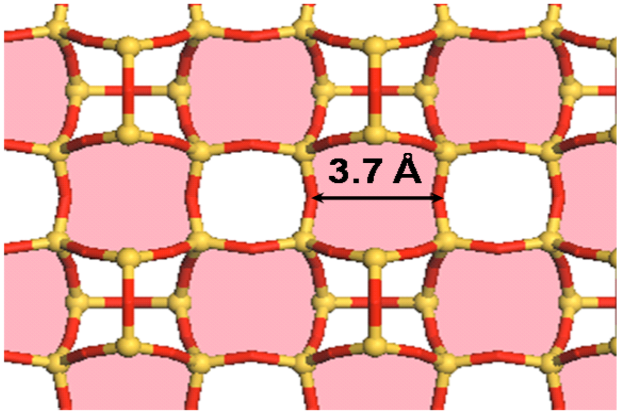
Hydrothermal Treatment Conditions for RUB-24 and NU-6(2)

- Temperature: 350°C
- Pressure: 10 bar (35% steam in nitrogen)
- Duration: 6 months

Nu-6(2) was structurally stable after 6 months of steaming.



RUB-24 lost its crystallinity after 6 months of steaming.



Summary of Stability Analysis & Future Work

- **Achievement**
  - **long-term steam stability of zeolites MCM-22, ITQ-1, NU-6(2), and RUB-24 were investigated**
  - **NU-6(2) preserved its crystallinity after 6 months of steaming (35% H_2O, 65% N_2) at 350°C**

- **Future Work**
  - **study of membrane performances at high temperatures**
  - **hydrothermal stability study of membranes**

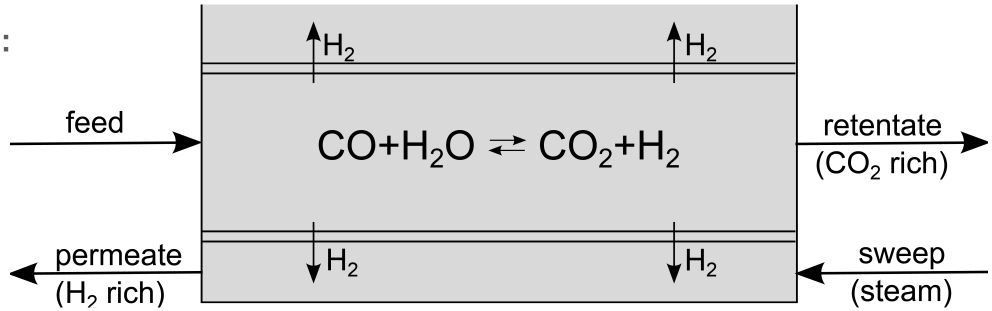
Systems Modeling: Objectives and Approach

- **Develop a WGS membrane reactor (MR) model**
- **Integrate MR model into IGCC system model**
- **Analyze effect of reactor design and membrane characteristics on integrated plant performance**
  - **achieve DOE R&D target goal of 90% CO_2 capture [1],[2]**
  - **satisfy stream constraints for CO_2 capture and gas turbine fuel (H_2 rich) [3]**
  - **quantify process efficiency and power generation**
- **Perform preliminary techno-economic analysis of integrated IGCC-MR process**
- **Received input from DOE/NETL personnel (John Marano and Jared Ciferno)**

(1) Marano, **Report to DOE/NETL** (2010)
(2) Marano and Ciferno, **Energy Procedia** 1, 361-368 (2009)
(3) Lima et al., **Ind. Eng. Chem. Res.** 51, 5480-5489 (2012)

MR Modeling Assumptions and Simulation Set Up

Composition [1]:
CO = 30.63%
H_2O = 36.76%
CO_2 = 8.41%
H_2 = 23.57%

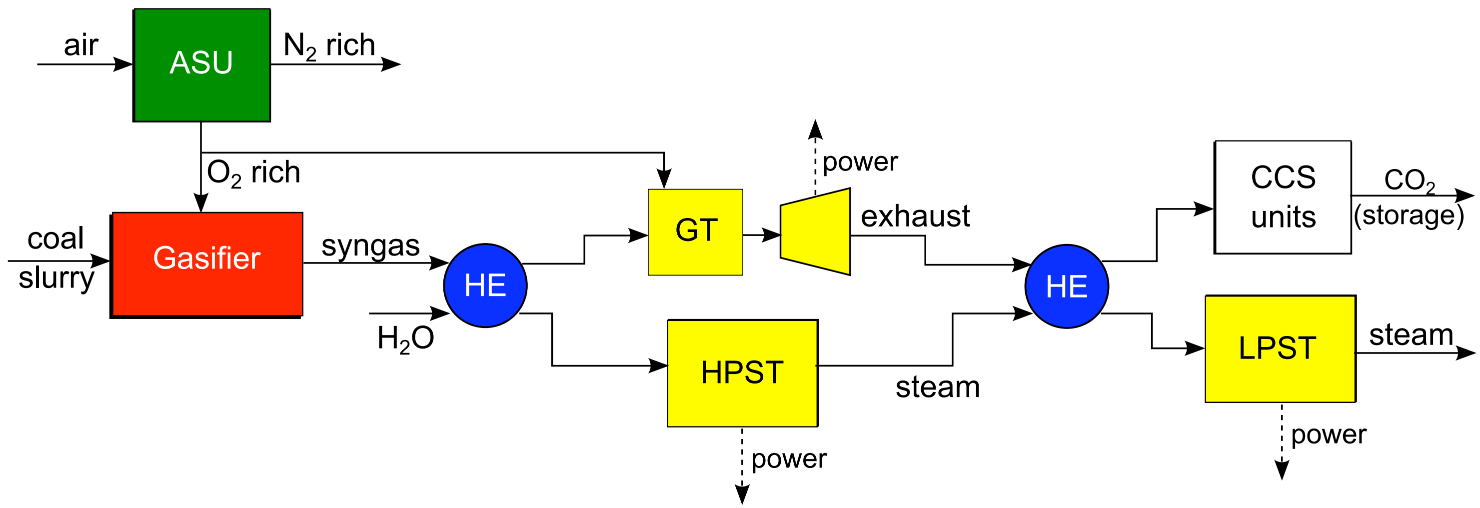


- **Assumptions**
  - **1-dimensional shell and tube reactor**
  - **catalyst packed in tube side**
  - **thin membrane layer placed on surface of tube wall**
  - **sweep gas flows in shell side**
  - **plug-flow operation**
  - **constant temperature and pressure**
  - **steady-state operation**
  - **ideal gas law**

(1) Jillson et al., **J. Proc. Cont.** 19, 1470-1485 (2009)
(2) Choi and Stenger, **J. Power Sources** 124, 432-439 (2003)
(3) Lima et al., **Ind. Eng. Chem. Res.** 51, 5480-5489 (2012)

- **Flow configurations**
  - **co-current**
  - **counter-current**
- **Simulation conditions**
  - **catalyst type and reaction rate** [2]
  - **reactor dimensions (lab)**
  - **consistent with IGCC specifications**
- **Model used to perform simulation and optimization studies** [3]

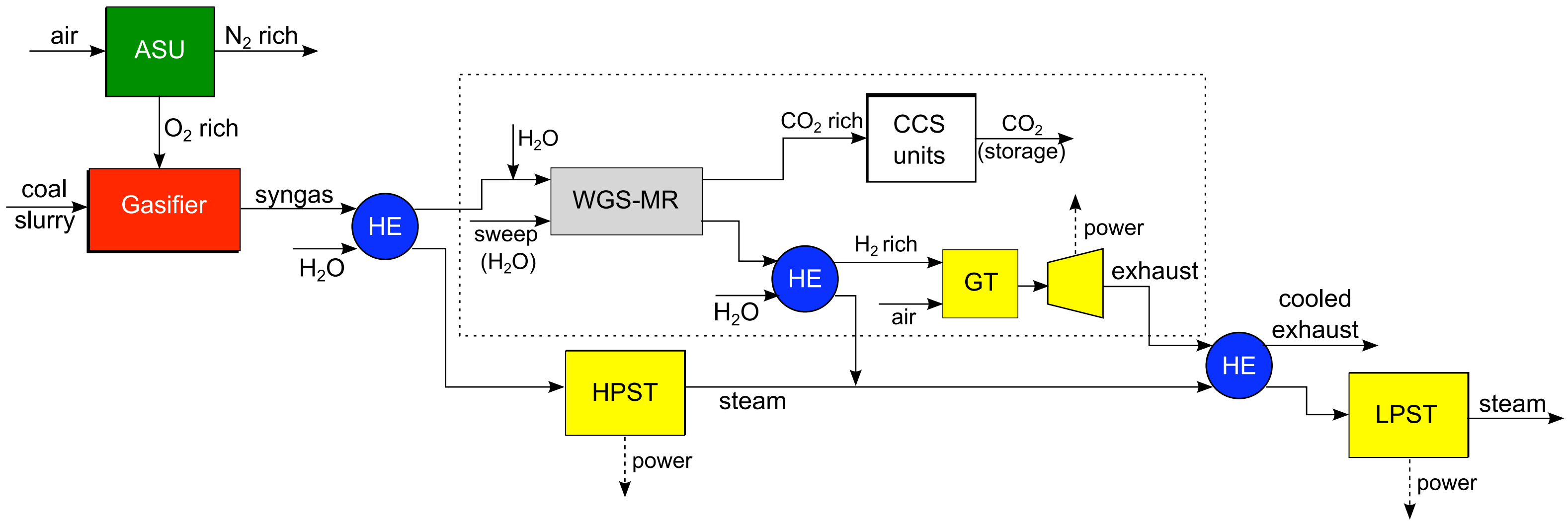
IGCC Plant Modeling Assumptions



- **Simplified systems-level model of entire process (ASU, gasifier, turbines, and heat exchangers) in MATLAB**
- **Assumptions: few basic components, lumped compartments in gasifier/ turbines, static heat exchanger models [1]**
- **Developed model validated using published simulation data [1]**

(1) Jillson et al., **J. Proc. Cont.** 19, 1470-1485 (2009)

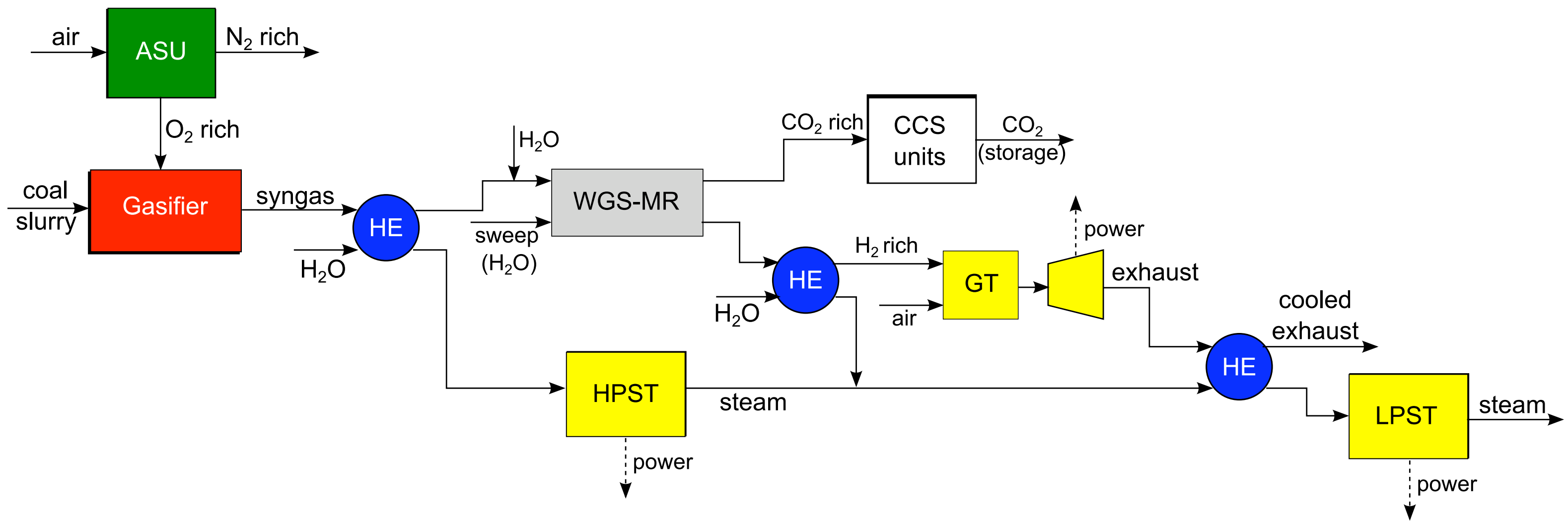
Integration of MR into IGCC Plant (MATLAB)



- **Scale up MR model at steady state**
- **Integration directly downstream of gasifier** [(1),(2)]
- **Effect on heat exchangers/turbines**
- **Perform preliminary technical assessment of IGCC-MR integrated plant**

(1) Marano and Ciferno, **Energy Procedia** 1, 361-368 (2009)
(2) Bracht et al., **Energy Convers. Mgmt** 38, S159-164 (1997)

Integration of MR into IGCC Plant (MATLAB): Simulation Results

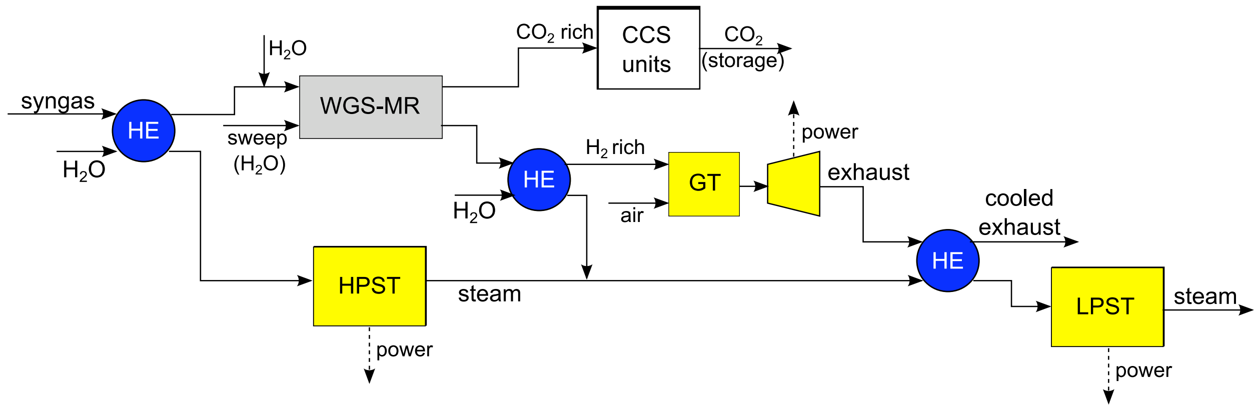


- **Process simulation conditions** [(1),(2),(3)]
  - **P_t = 53.29 atm, P_s = 25.86 atm**
  - **T_t = 380°C, T_s = 380°C**
  - **$S_{H2/all}$ = 1000, Q_{H2} = 0.2 mol/(s.m^2.atm)**
  - **A_m = 6800 m^2**

- **Performance variables** [(2)]
  - **carbon capture** $C_{CO_2} = \frac{\text{carbon captured}}{\text{carbon in feed}} = 98.94\%$
  - **process efficiency** $\eta = \frac{\text{power generated}}{\text{HHV energy in coal}} = 40.83\%$
  - **power generation** $W = 716.78$ MW

(1) Jillson et al., **J. Proc. Cont.** 19, 1470-1485 (2009)
(2) Haslbeck et al., **Baseline Report to DOE/NETL** (2010)
(3) Field and Brasington, **Ind. Eng. Chem. Res.** 50, 11306-11312 (2011)

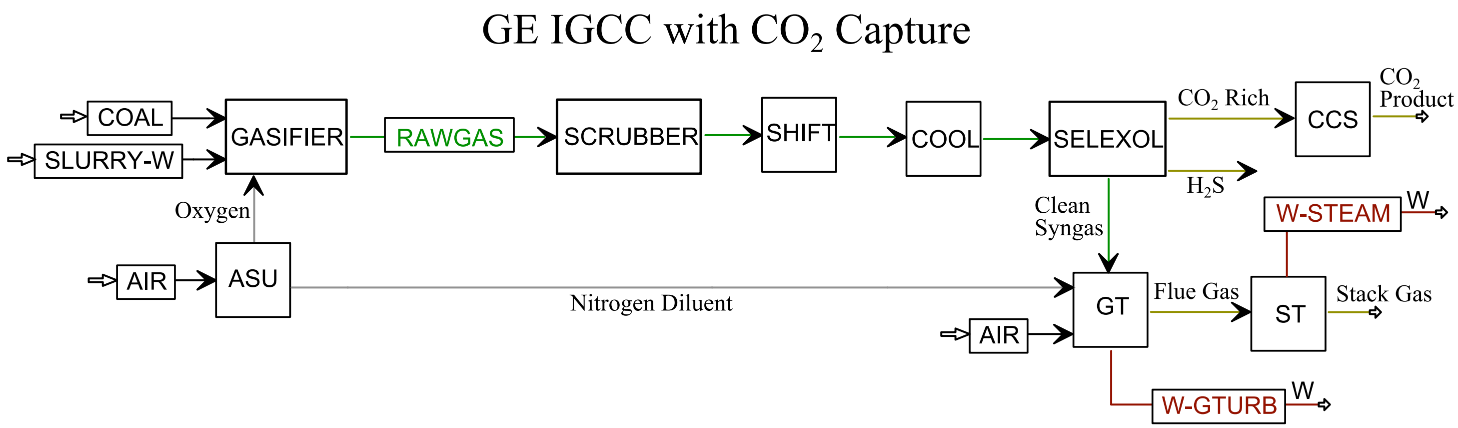
IGCC-MR Simulation Results: Changing Membrane Characteristics



IGCC Performance Variable	Value ($S_{H2/all}$ = 1000, Q_{H2} = 0.2)	Value ($S_{H2/all}$ = 1000, Q_{H2} = 0.1)	Value ($S_{H2/all}$ = 100, Q_{H2} = 0.2)
$C_{CO_2} = \frac{\text{carbon captured}}{\text{carbon in feed}} [\%]$	98.94	99.55	89.79
$\eta = \frac{\text{power generated}}{\text{HHV energy in coal}} [\%]$	40.83	34.14*	41.15
$W = \text{power generated} [\text{MW}]$	716.78	599.31	722.27

(*) $P_{H2,P} \leq 44$ %

Integration of MR into IGCC Flowsheet (Aspen)

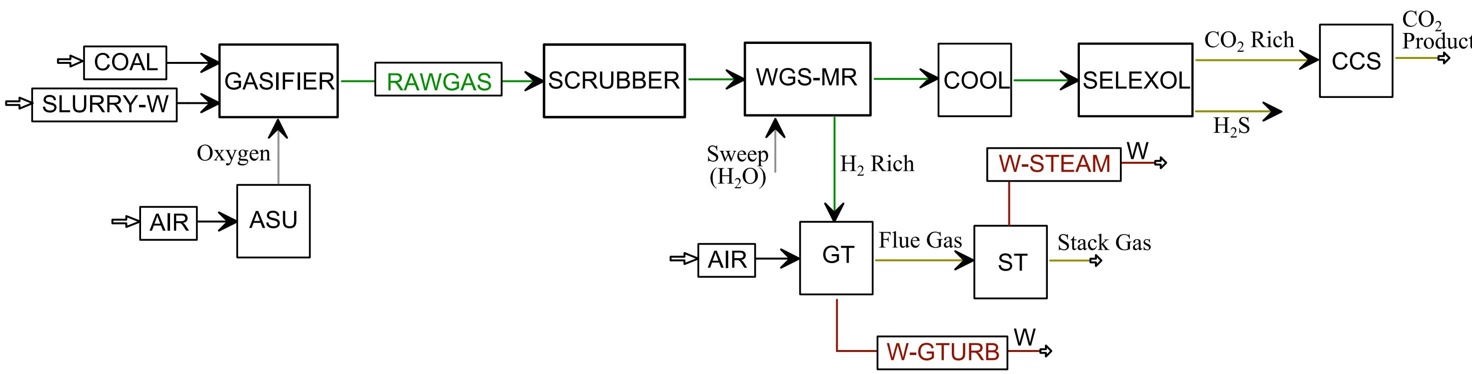


- **MR integration into Aspen flowsheet (Ongoing)**
  - **use available baseline IGCC model (MITEI)** [1]
  - **MR model implemented (co-current) in Aspen Custom Modeler**
  - **similar results to MATLAB model obtained**
- **Perform simulation & techno-economic analysis**
  - **feasibility of replacing current technology (CO shift followed by physical absorption) for CO_2 capture**
  - **achieve DOE target goals (CO_2 capture, COE)**

(1) Field and Brasington, **Ind. Eng. Chem. Res.** 50, 11306-11312 (2011)

Integration of MR into IGCC Flowsheet (Aspen)

IGCC with MR for CO_2 Capture



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(1) Field and Brasington, **Ind. Eng. Chem. Res.** 50, 11306-11312 (2011)

Modeling Conclusions & Future Work

- **Conclusions**
  - **MR model integrated into IGCC process model in MATLAB**
  - **preliminary technical assessment of IGCC-MR plant performed**
  - **MR model (co-current) implemented in Aspen**
- **Future Work**
  - **develop relationships between membrane parameters and cost**
  - **carry out IGCC-MR design optimization (MATLAB)**
  - **develop counter-current MR model (Aspen)**
  - **adjust MR model to incorporate into Aspen IGCC baseline model [1]**

(1) Field and Brasington, **Ind. Eng. Chem. Res.** 50, 11306-11312 (2011)