



DOE Hydrogen Program



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Pressurized Steam Reforming of Bio-Derived Liquids for Distributed Hydrogen Production

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Overview

Timeline

- Project start date: FY2005
- On-Hold: FY2006
- Continued: FY2007-08
- Project end date: Open

Barriers

- A. Fuel Processor Capital Costs
- E. Greenhouse Gas Emissions
- H. System Efficiency

Budget

- Funding, FY 07: \$350 K
- Funding, FY 08: \$400 K
- Funding, FY 09: TBD

Partners/Collaborators

- Other Argonne divisions
- Interactions: REB Research and Consulting

Rationale and Objective

Rationale

- Steam reforming of liquid fuels at high pressures can reduce hydrogen compression costs
 - Hydrogen is produced at a higher pressure
 - Much less energy is needed to pressurize liquids (fuel and water) than compressing gases (reformat or H₂)
- High pressure reforming is advantageous for subsequent separations and hydrogen purification

Objective

- Develop an efficient distributed hydrogen production process
 - From hydrated ethanol and other bio-derived liquids
 - Using a pressurized steam reforming reactor to reduce the H₂ compression penalty

DOE FY12 Efficiency Target	72%
DOE FY12 Cost Target	\$3.8 / gge

Approach

- Study the steam reforming of bio-derived liquids at high pressure
 - Define conditions suitable for reforming of bio-derived liquids
 - Define system concepts that can meet efficiency targets
 - Develop reactor concepts through simulations
 - *Incorporate membrane technology (O_2 , H_2 , CO_2)*
 - *Incorporate developments in catalysis*
 - Validate concepts at successive scales
 - *micro-reactor, bench-scale, tech transfer*

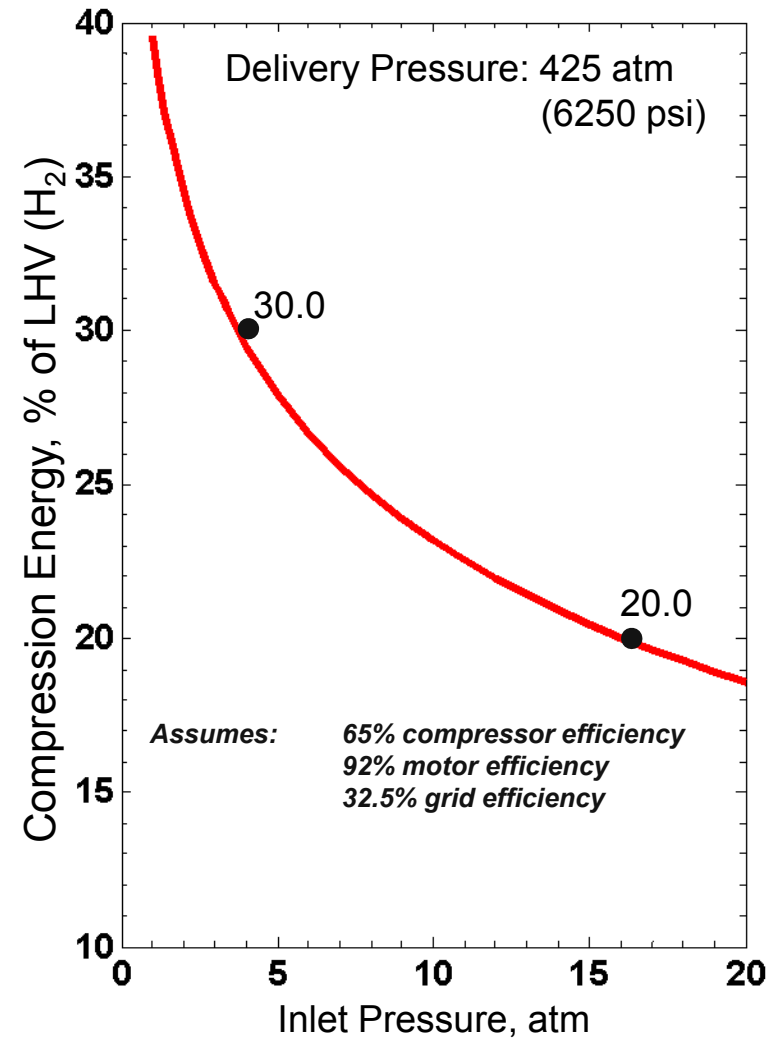
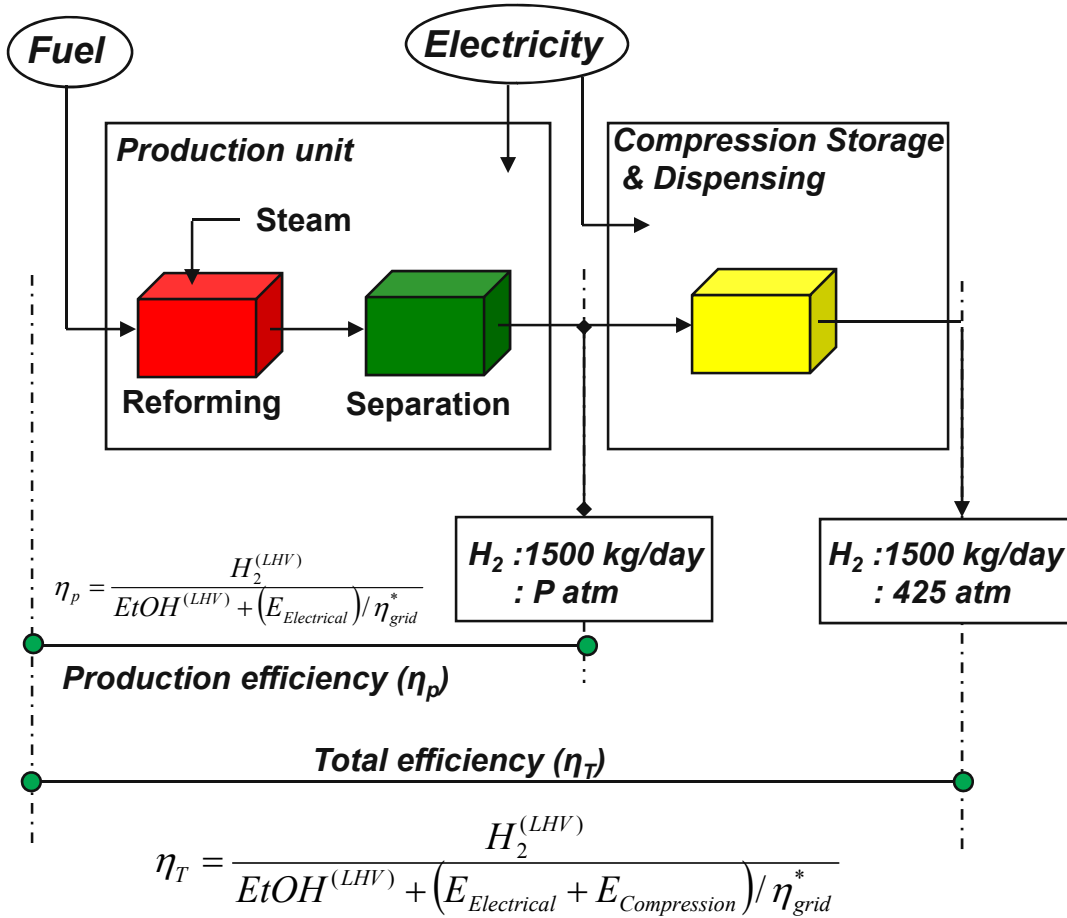
- Systems analysis to evaluate process concepts and Go/NoGo decisions

Milestone

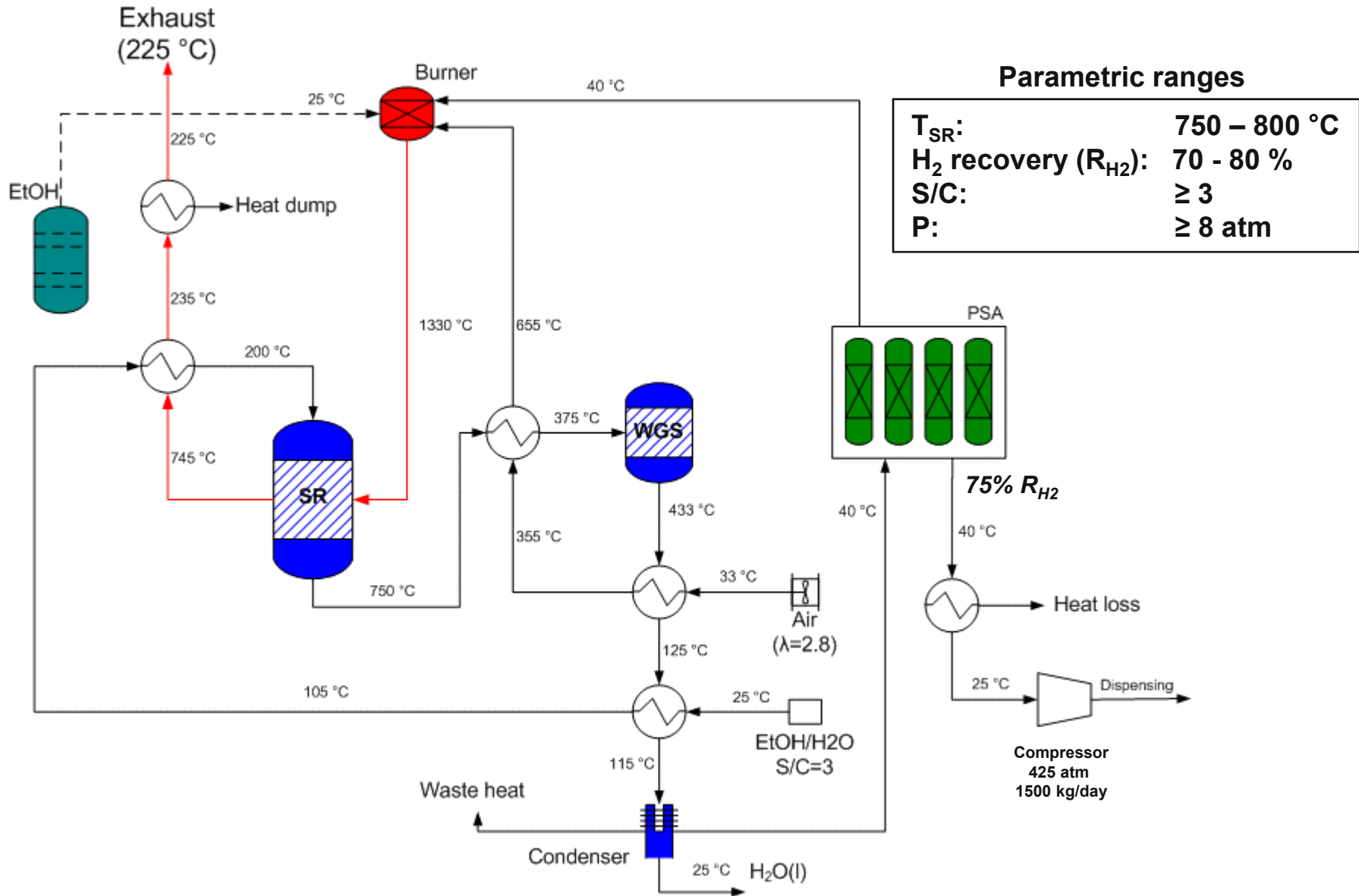
September 2008	Go / No-Go on using H_2 extraction in a membrane reactor for high pressure steam reformer based systems
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Basis: Production of 1500 kg/day of H₂ delivered at 425 atm (6,250 PSI)

*Grid electricity is assumed available at 32.5% efficiency



A Reference Case: Ethanol SR followed by PSA



The reference system efficiency is limited by the reformer temperature and H_2 -recovery in the PSA

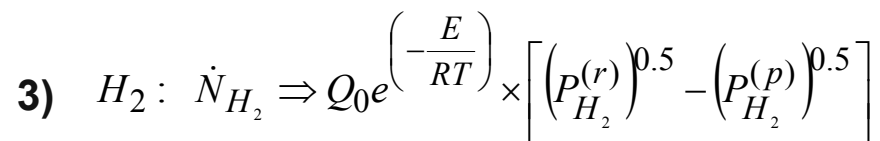
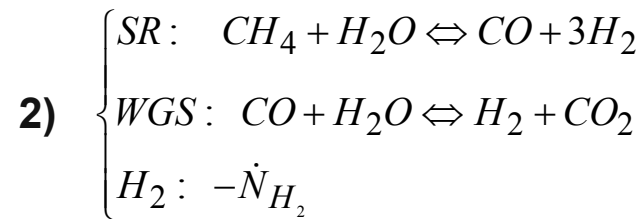
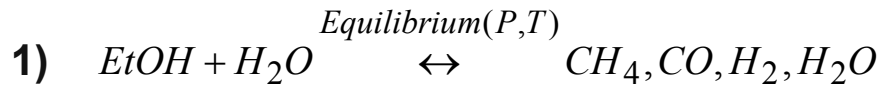
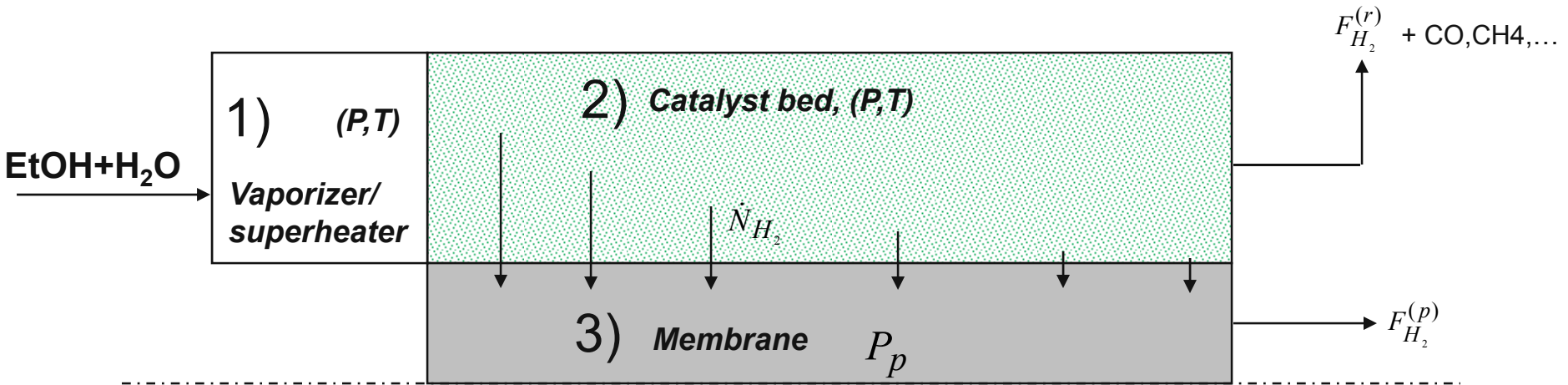
- For the reference system, *pressure, reformer temperature and steam-to-carbon* for a given H_2 recovery was varied to optimize total system efficiency
- Increasing reformer temperature increases H_2 yield and efficiency peaks at higher system pressures

		$T_{SR}=750\text{ }^\circ\text{C}$				$T_{SR}=800\text{ }^\circ\text{C}$			
Recovery (%)		η_{Prod} (%)	η_{Tot} (%)	P (atm)	S/C (-)	η_{Prod} (%)	η_{Tot} (%)	P (atm)	S/C (-)
SR-PSA (Ref 1) →	70	70.1	59.9	8	3.4	71.8	61.9	10.5	3.2
	75	72.7	61.8	8	3	73.5	63.7	13.5	3
	80	73.7	63.2	10	3	74.4	65.2	17.5	3

← SR-PSA (Ref 2)

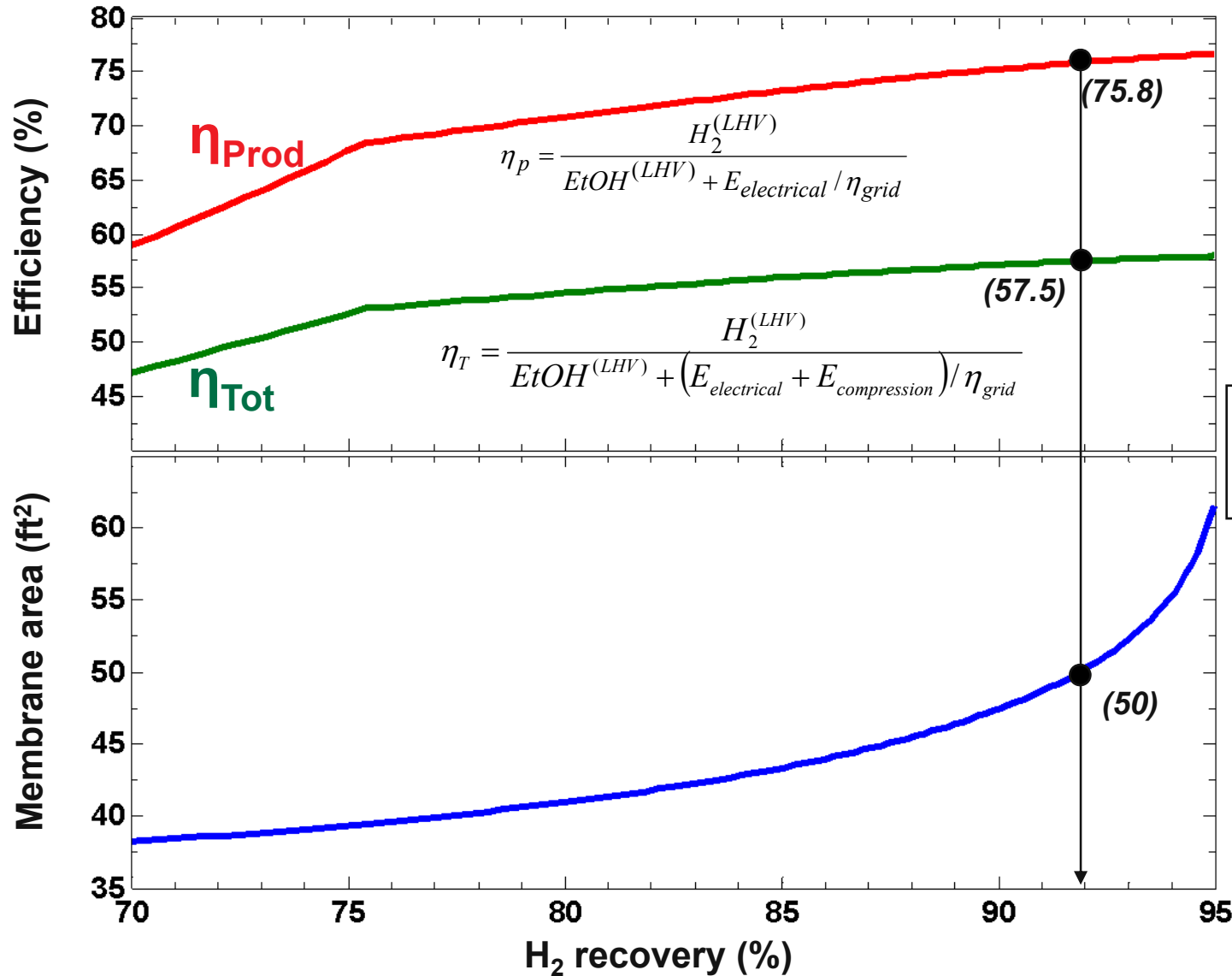
Optimal efficiency as function of reformer temperature and recovery

Reactor model assumes hydrogen permeation flux rates based on DOE 2010 targets (250 scfh/ft²)



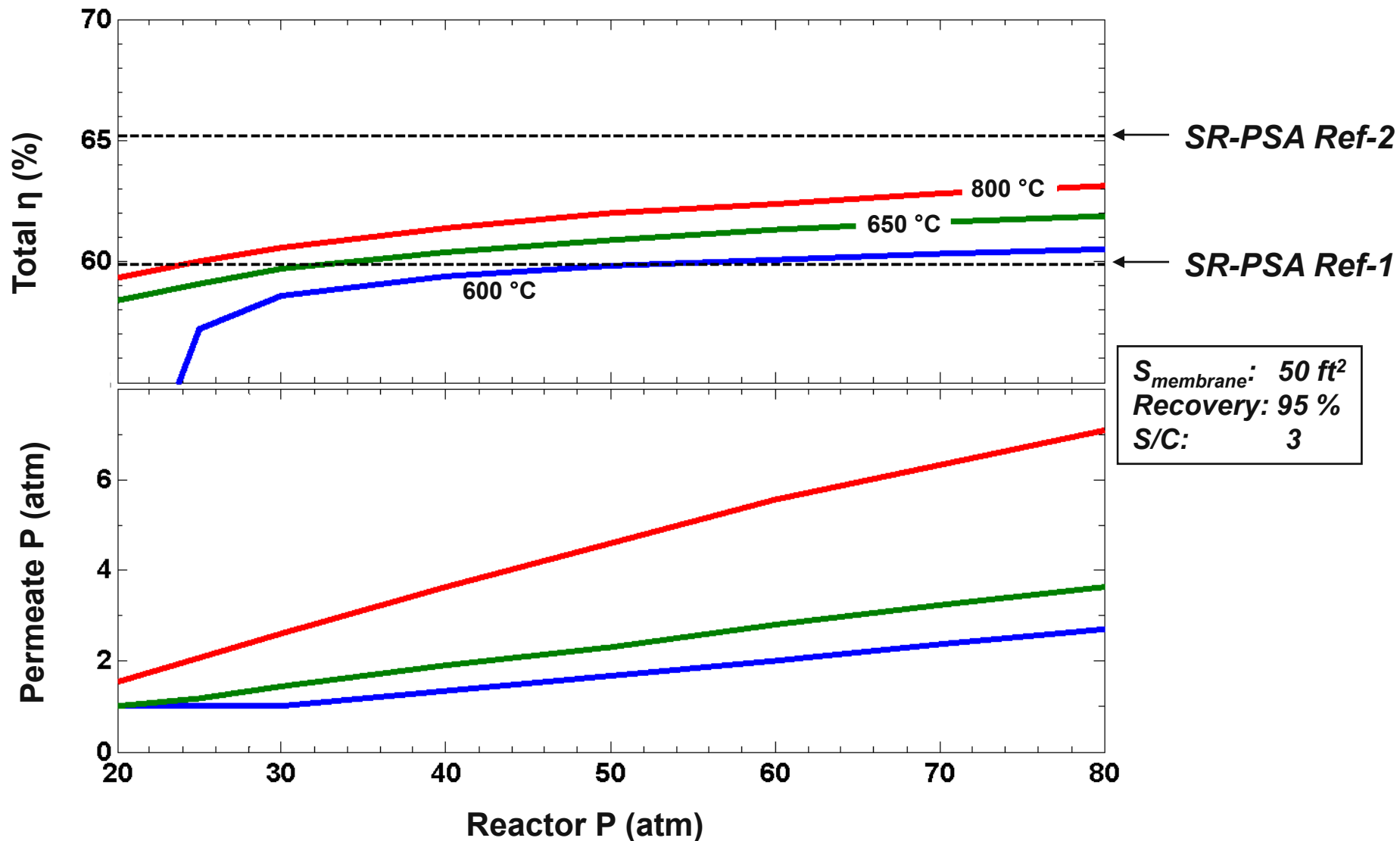
$$\text{Recovery (\%)}: \frac{F_{H_2}^{(p)}}{\left(F_{H_2}^{(p)} + F_{H_2}^{(r)}\right)} \times 100$$

The membrane system (SR-M) achieves high production efficiency but total efficiency is low due to low permeate pressure

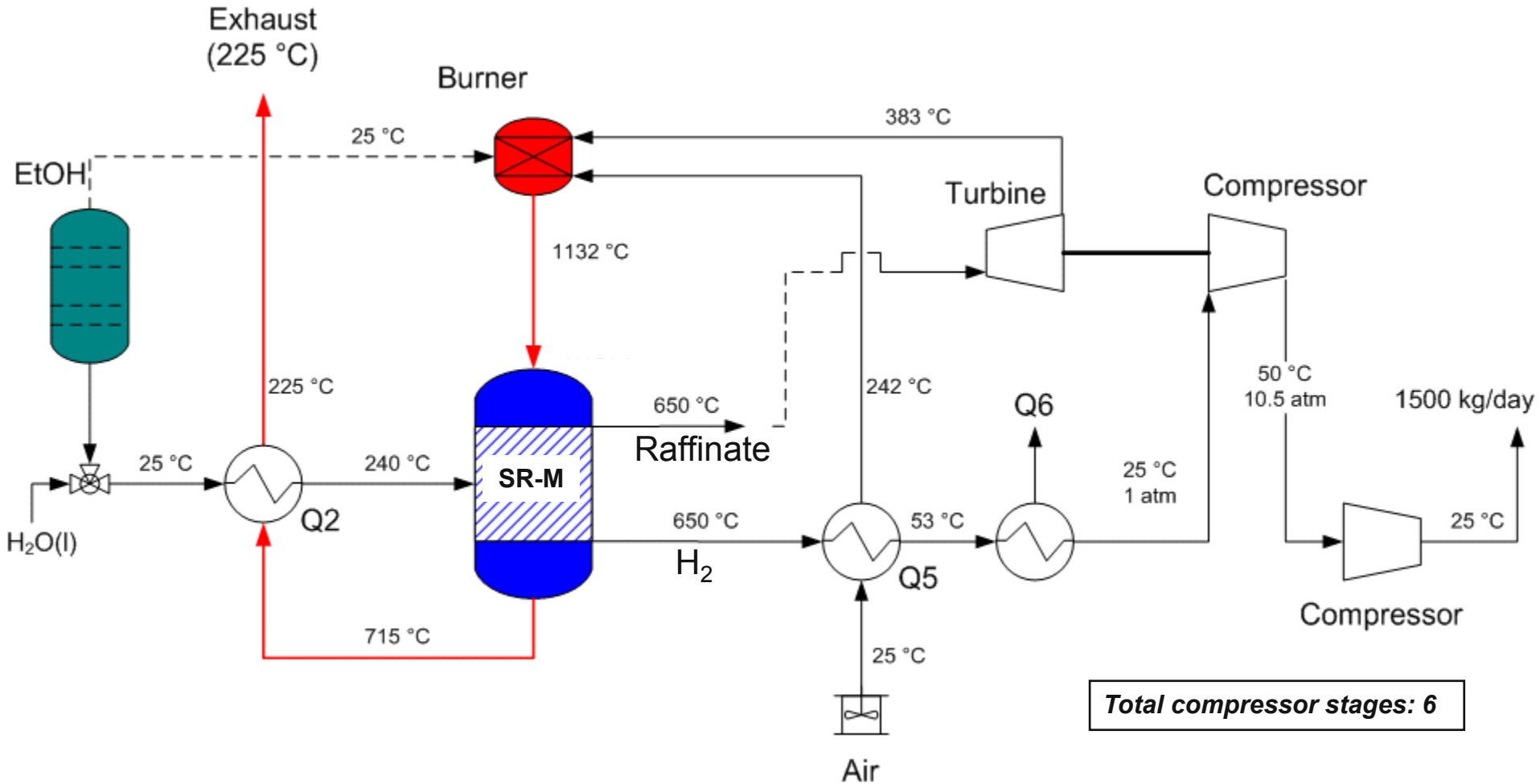


Reactor P:	20 atm
Permeate P:	1 atm
Reactor T:	650 °C

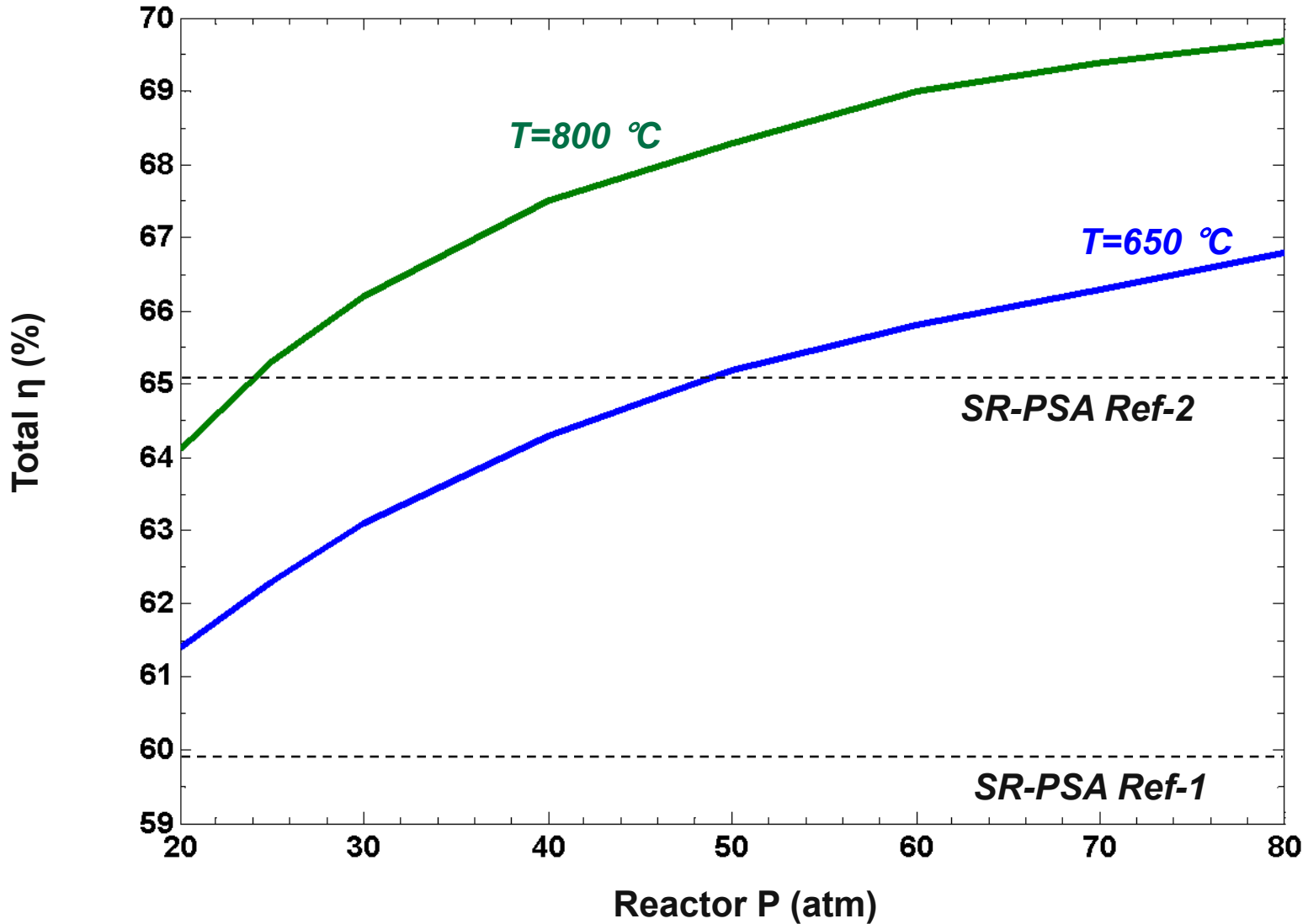
Higher total efficiencies of the membrane system are achieved at high reactor pressures and temperatures



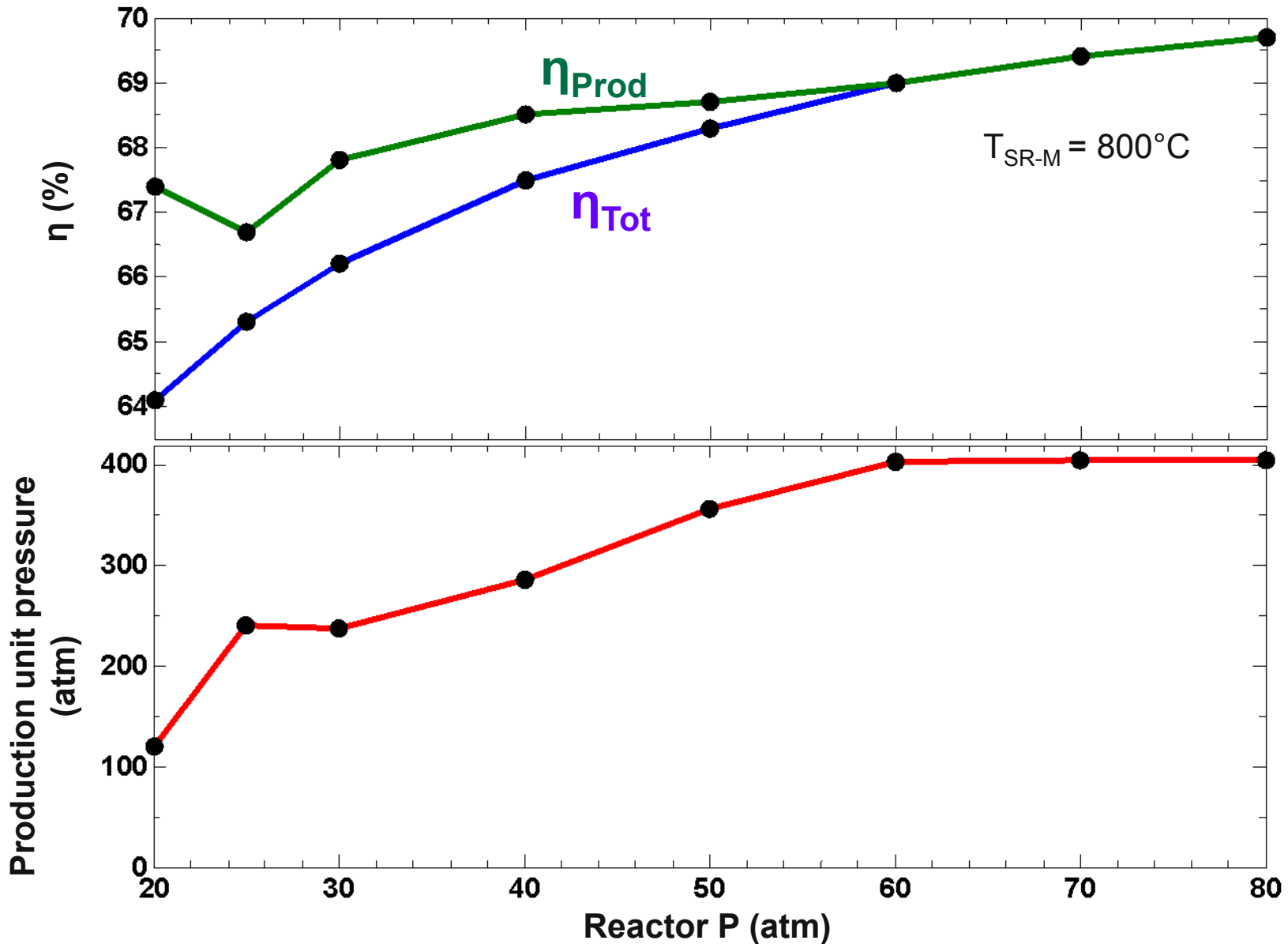
Total efficiency for the membrane system can be improved by recovering the pressure energy in the raffinate stream



The membrane/turbo-compressor system can surpass the efficiencies achieved by the SR-PSA systems, especially at high pressures



At high pressures the turbo-compressor system is very effective in recovering the compression energy in the raffinate



Summary

A membrane reactor system for the production of hydrogen from bio-derived fuels (ethanol) was analyzed and compared to a SR-PSA system:

- A SR-PSA system has the advantage of delivering purified H₂ at the system pressure.
 - *High system pressure is limited, however, due to lower hydrogen yields (and fuel efficiency) as pressure increases.*

- A membrane reactor system has higher production efficiency than the SR-PSA system as hydrogen removal improves hydrogen yield.
 - *It has higher compression cost than the SR-PSA system because of low H₂ permeate pressure, even at high system pressures*
 - *Efficiencies improve at higher pressures*

- A membrane reactor system combined with a turbo-compressor can recover the compression energy of the raffinate and exceed the total efficiency obtained with a SR-PSA system.
 - *The advantage is significant at higher delivery pressures (e.g. 10,000 psi)*

Future work

- Evaluate membrane reforming systems based on CO₂ removal
- Study the kinetics and conversion during the pressurized steam reforming of other bio-derived liquids
- Estimate cost of hydrogen from proposed process

Publication / Presentation

- Presented to DOE Fuel Production Tech Team, September 2008
- Fuel Cell Seminar, Phoenix, AZ, October 2008

Acknowledgment

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