

Hydrogen From Bio-Derived Liquids

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Innovation / Overview

- ▶ Project comprises two components
 - Ethanol steam reforming
 - Aqueous phase reforming (APR)
- ▶ Importance to small scale hydrogen production
 - ◆ Ethanol is rapidly becoming an infrastructure fuel and is a logical feedstock for distributed reforming for hydrogen production
 - ◆ APR provides vehicle for facile reforming of a variety of bio-derived feedstocks available in the biorefinery that are not conducive to conventional vapor phase reforming
- ▶ Distinctive technology approach/innovation
 - We are investigating single step ethanol reforming with emphasis on lower temperature operation for compatibility with water gas shift and thermal efficiency; have proposed novel swing bed reactor approach to handle catalyst life/regeneration issues if needed
 - Our work in APR has focused on understanding the mechanistic details of the APR conversions in order to design catalysts having improved activity and selectivity; and exploring alternate reactor designs based on microchannel concepts to improve heat transfer and minimize mass transport resistances

Key Performance Metrics

▶ Ethanol

- Note: we are operating at high space velocities to stress the catalyst and identify deactivation under relatively short term tests; actual space velocities in a plant will be significantly lower
- WHSV: 57g EtOH/g-h or 1.23 moles EtOH/g-h
- Feed concentration: 24.2 wt.% or 11.1 mol% (balance H₂O)
- O/C = 4.5
- EtOH conversion: 100% (declining to 90% over 120h)
- Hydrogen yield: 5mol/mol EtOH fed (theoretical 6 mol/mol w/ complete wgs)
- Catalyst density = 1.5 g/cc
- H₂ productivity: 9.3×10^3 mol H₂/L rctr-h or 18.9 kg H₂/L rctr-h

▶ APR

- WHSV: 7.6 g GLY/g-h or 0.085 mol GLY/g-h
- Feed concentration: 10 wt.% or 1.1 M
- O/C = 10.8
- Feed conversion: 99+%
- Hydrogen yield: 3.4 mol/mol GLY fed (theoretical 7 mol/mol w/ complete wgs)
- Catalyst density = 0.39 g/ml
- H₂ productivity: 113 mol H₂/L rctr-h or 0.23 kg H₂/l rctr-h

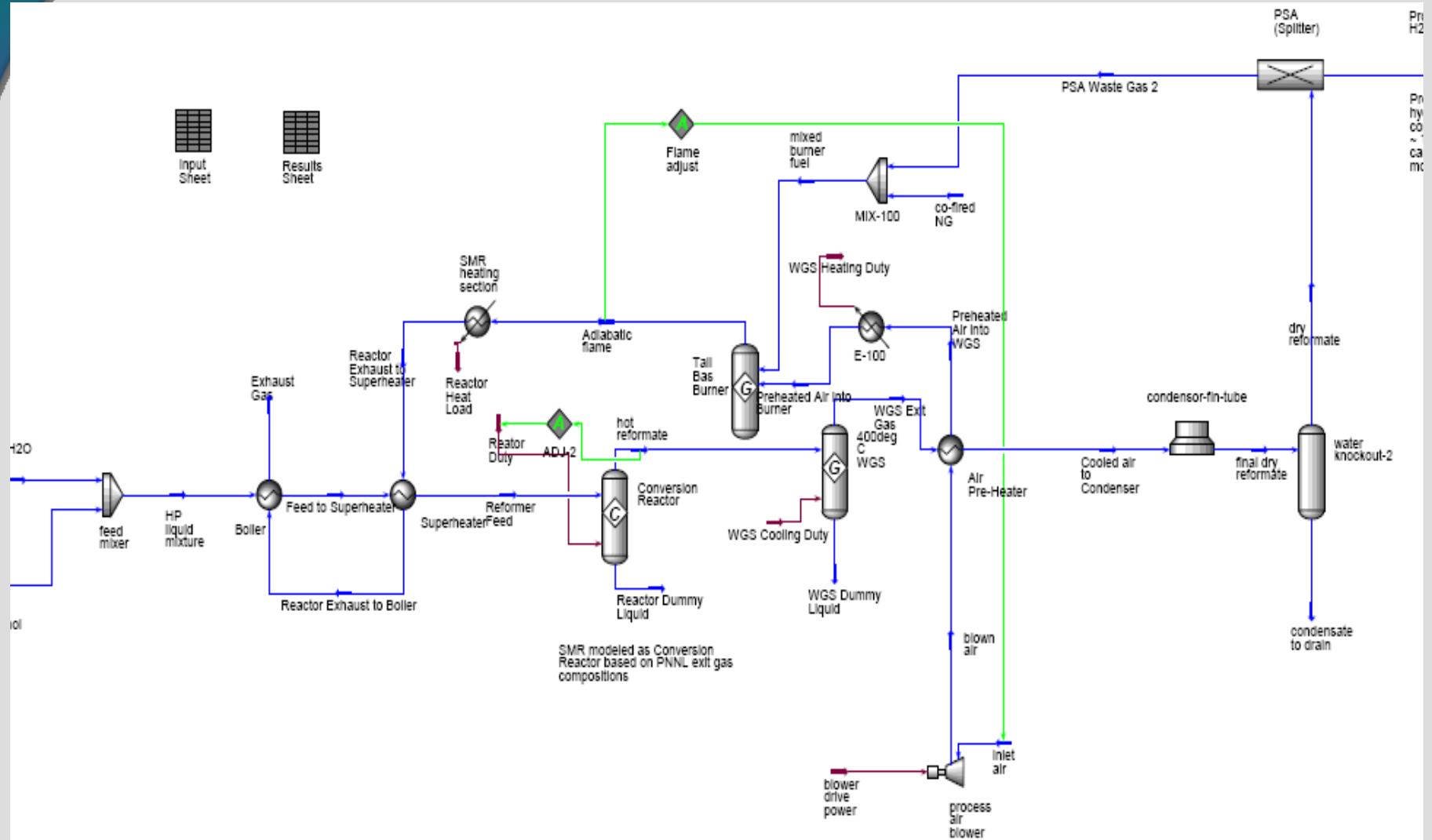
Unique H2A Inputs

- Feed concentration
- Reaction temperature
- Reactor pressure
- Reactant purity
- Heat balance requirements
- Materials of construction
- In-line water gas shift reactor

System Definition

- ▶ Define the elements of a complete plant (just initiating)
 - Define the capacity (kg/day of hydrogen produced) for EtOH reforming
 - For 1500kg H₂/day, conversion and selectivity data indicate 3.3 L reactor! (18.9 kg H₂/L-h)
 - Operation will be difficult under these conditions and reactor will be larger
 - Assume best case is 100h at 100% conversion and catalyst life indirectly proportional to space velocity (amount of feed processed);
 - For 8760 h (1 year) at 100 % conversion, lower space velocity by 87.6
 - $3.3 \times 87.6 = 290$ L reactor volume packed bed
 - Larger if monolith-loaded catalyst
 - For APR: 271 liter reactor assuming complete conversion and maintained selectivity for 1 year

Process Flow Diagram for EtOH Reforming Plus WGS and PSA H₂ Purification (Courtesy Brian James)



Energy Input and Output of the Plant

(Courtesy of Brian James)

10/25/07: PNNL Complex with 8:1 Steam/Eth molar ratio and 75% PSA Recovery and 400C WGS

H2 product	63.173448	120010.91	140353.17		
Fuel ethanol	418.8445	26817.293	29487.8	Steam Molar Flow	72.732
Co-fired NG	0	50034.781	55147.323	Ethanol Molar Flow	9.0915
Steam to Eth Ratio	8				
	Overall	Ethanol Eff	NG Ratio		
LHV Efficiency	0.6740433	0.6749748	0	0.746033371	
HHV Efficiency	0.716995	0.7178962	0	8.55E-02	
Burner feed air					
H2 in dry reformat	84.231264	kg/h			
PSA recovery	0.75				
Electric Consumpt	Power (kW)	kWh per kg H2			
H2O Pump	3.0223546	4.78E-02			
Ethanol Pump	1.2893873	2.04E-02			
TOTAL	4.311742	6.83E-02			
	Duty (kJ/h)	UA (KJ/C-h)	LMTD (degC)		
Boiler	(4,143,045)	27,253	152		
Superheater	(530,480)	3,568	149		
Air Preheater	(2,294,029)	15,469	148		
Reactor Internal HX	2,229,286				

Other Material Input and Output

- ▶ Define the other materials needed – e.g., catalyst, filters, water purifiers,...perhaps a little premature
 - Include the cost of the material
 - Include the usage of the material per year
- ▶ Define other material output
 - Waste products—EtOH reforming
 - Everything combustible after H₂ recovery will be burned for process heat
 - Waste products, if any, would be oxygenates in the water stream (potentially recyclable)
 - Waste products—APR
 - Presence and fate of water soluble oxygenates needs to be investigated (recyclable?)

Assessment of Status / Metrics

► Major areas of uncertainty

- Catalyst activity and selectivity maintenance (affects both capital and operational costs)
- Operating temperature—integration with wgs, materials of construction
- Effect of pressure on product selectivity
- Feasibility of use of a membrane separator for H₂ just downstream of wgs unit instead of PSA
- Larger scale and longer scale tests required

► All these items must be addressed in FY08

Response to Reviewer's Comments

Relevance to Overall DOE Objectives

- ▶ Excessive technical detail; how does technology have potential to meet DOE targets?
 - H2A analysis initiated
- ▶ Looks complementary or redundant to Virent in catalyst optimization
 - We have focused on mechanisms and effect of reaction conditions
 - Virent has focused more on catalyst and process conditions; commercialization
- ▶ Not clear whether any of biofuels to hydrogen pathways make sense from cost or efficiency perspective
 - Time will tell (H2A analysis)

Approach to Performing the Research and Development

- ▶ Gas phase system approach not clearly presented
 - Due to presentation time limits we focused on APR; will provide greater focus on EtOH reforming at next review
- ▶ Need better definition of goals
 - Our primary goal is to meet DOE H₂ production targets for distributed hydrogen production from bio-derived renewable liquids
 - We will summarize goals and proposed project milestones at review
- ▶ Minimal information provided on reactor rig and test plan
 - At the time of presentation, both projects were focusing on activity, selectivity, and life of the catalysts
 - With improvements in these parameters, we will revise a test plan
- ▶ Clear direction not presented
 - Direction will be clarified at next review

Approach to Performing the Research and Development

- ▶ Consider extending other bio-liquids beyond ethanol for vapor phase reforming
 - Our charter has been to focus on EtOH reforming
 - We are willing to examine gas phase reforming of C_3 's such as glycerol, propylene glycol
 - Limited set of targets beyond C_3 's due to thermal instability
- ▶ Project doesn't focus on any barriers other than identifying better catalysts
 - More active catalysts impact on (A) reformer capital costs by reducing reactor size and potentially allowing cheaper materials of construction; (C) O&M by lowering temperature operation
 - Long lived catalysts impact on (C) O&M by requiring less frequent regeneration
 - APR has potential for improving (D) feedstock issues in terms of being a fuel flexible reformer
 - (E) greenhouse gas emissions are automatically addressed in this project

Technical Accomplishments and Progress

- ▶ Hard to assess progress since specific goals not defined
 - We will work to better define specific goals; H2A analysis will help
- ▶ Reactor productivity seems low; unclear if levels of production are viable
 - We believe that productivity can be commercially viable
 - Being addressed under H2A
 - Different productivities for EtOH reforming and APR
 - Comparison with SMR is challenging due to higher throughput at high T
- ▶ Need to put in perspective what advances in APR catalysts are necessary to meet cost targets
 - Three knobs to turn: activity, selectivity, and catalyst life; all are important
 - Need H2A analysis
- ▶ No apparent progress on cost or efficiency
 - H2A analysis

Tech Transfer/Collaboration With Industry, Academia

- ▶ Project seems limited in terms of collaborative influence
 - What is nature of collaboration with OSU?; unclear if significant interactions have occurred
 - At this stage, collaborations are more in working group meetings and discussions at technical meetings rather than formal collaborations; we have shared our experiences and results
 - Catalyst development work and testing is not readily amenable to collaborative work unless unique analytical tools can be brought to bear
 - We are ready to test other's catalysts when they are available, and have so indicated
 - Collaborations appear to be best focused subsequent to defining a good operating catalyst, defining operating parameters, establishing good lifetime performance; collaborations are easier at the scale-up stage where experience of partners significantly builds on the capabilities of Natl. Lab

Tech Transfer/Collaboration With Industry, Academia

- ▶ Project seems limited in terms of collaborative influence
 - We have informally collaborated with Virent by sharing our test data on Virent catalysts, and effect of microchannel reactor on improvement in reactor productivity
 - Virent has provided leads (through literature identification) of potential avenues for catalyst investigation and improvement
 - Formal collaborations in the field of APR are complicated by push for Research Licenses by Virent
 - Formal PNNL collaborations with Virent are still in planning stage
- ▶ What about CO and other emissions?
 - We would intend to burn CO, CH₄, other combustible species for process heat following the H₂ separation step
 - At that time, close monitoring of CO emissions would be required

Approach To and Relevance Of Future Research

- ▶ FY08 work lacks targets for each planned task
 - Good comment; working to provide this at next review
- ▶ Evaluation of potential system performance would be helpful
 - Premature but working on it through H2A analysis
- ▶ Only some of the tasks appear relevant to Natl. Lab; unclear the competition with industry and who will develop any catalysts successfully developed at PNNL
 - Need clarification on what tasks are thought to be not relevant
 - No intention to compete with industry; we are willing to collaborate with industry once we demonstrate we have something of substantial value to offer (see previous slides)
 - Finding a company to develop the catalysts, once requested by industrial partners or licensees, will be no problem
- ▶ Need performance comparison against DOE targets
 - Will provide at next review
- ▶ Need to clarify go/no go decisions for each approach; doesn't appear to be off ramps for results that are not promising
 - Good point; we have continued to believe that better catalysts are the key need and can be developed (this has been supported by DOE)
 - We need to do better job of showing go/no decisions that we have made

Specific Recommendations

- ▶ Define a clear path forward
 - Will provide at next review
- ▶ Perform preliminary cost and “well to farm to wheel” efficiency assessments
 - Compare with EtOH in ICE (?)—don’t think that is in our charter
- ▶ Establish performance targets for go/no go decision points
 - Will provide at next review