STRATEGIC ANALYSIS INC

Analysis of Advanced H_2 Production Pathways

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Overview

Timeline

- Project start date: 3/15/2013
- Project end date: 9/30/2016
- Percent complete: 90%

Budget

- Total Funding Spent
  - ~$754,000 (FY13-FY15)
  - ~$266,000 (FY16 Budget)
- Total DOE Project Value
  - ~$1,020,000
- Cost Share Percentage: 0%

(not required for analysis projects)

Barriers

- **Monolithic Piston Type Reactor**
  - Hydrogen (H_2) Generation Bio-oil Reformation
    - F: Capital Cost
    - K: Manufacturing
- **Reforming-Electrolyzer-Purifier**
  - Hydrogen Generation from Reverse Fuel Cell Technology
    - F: Capital Cost
    - G: Electricity Cost
    - AZ: Systems Engineering

Partners

- National Renewable Energy Laboratory (NREL)
- Argonne National Laboratory (ANL)

Collaborators

- PNNL
- Fuel Cell Energy, Inc.

Relevance and Impact

- Investigating production pathways selected/suggested by DOE as relevant, timely, and of value to FCTO.
- Provide complete pathway definition, performance and economic analysis not elsewhere available.
- Analysis is transparent, detailed, and made publicly available to the technical community.
- Results of analysis:
  - Identify cost drivers
  - Assess technology status
  - Provides information to DOE that may be used to help guide R&D direction

Objectives

The objectives of this project include:

1) **Analyze H_2 Production & Delivery (P&D) pathways** to determine economical, environmentally-benign, and societally-feasible paths for the P&D of H_2 fuel for fuel cell vehicles (FCEVs).

2) **Identify key "bottlenecks"** to the success of these pathways, primary cost drivers, and remaining R&D challenges.

3) **Assess technical progress, benefits and limitations, levelized H_2 costs**, and potential to meet U.S. DOE P&D cost goals of <$4 per gasoline gallon equivalent (gge) (dispensed, untaxed) by 2020.

4) Provide analyses that **assist DOE in setting research priorities**.

5) **Apply the H2A Production Model** as the primary analysis tool for projection of levelized H_2 costs ($/kg$H_2$) and cost sensitivities.

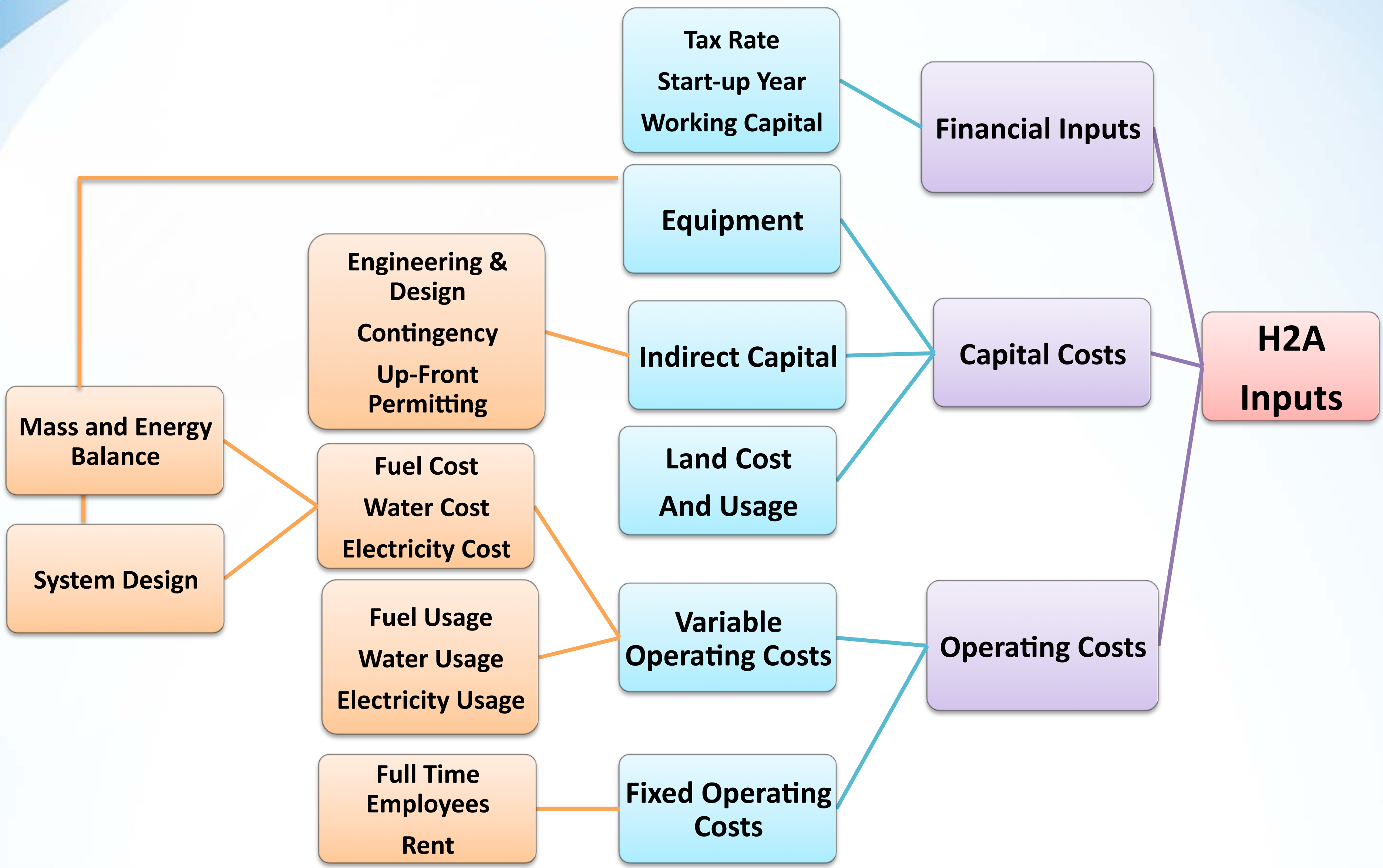
In 2015-2016, these project objectives are applied to develop two cases:

- Monolithic Piston – Type Bio-oil Reformation Reactor
- Reformer-Electrolyzer-Purifier (REP) System
- (Past years: SOEC , Dark Fermentation and PEM electrolysis)

The team gathered technical & economic data from industry/researchers and synthesized data into generalized H2A cases

- **Asked Research Organizations** to supply technical information regarding their process. When possible, economic information was also supplied.
- Requested relevant **detailed information** on:
  - Current and Future cases for Forecourt production.
- Analyzed data, and synthesized and amalgamated data **into generalized cases/input parameters**.
- Developed accurate **process and cost models**
  - Modeled system performance in Excel® and Hysys®.
  - Populated H2A Production Models v3.101.
  - Predicted levelized H_2 cost and identified key cost drivers and sensitivities.
- **Vetted the public cases** with the Research Organizations.

H2A Inputs


Tax Rate
Start-up Year
Working Capital
Financial Inputs
Equipment
Engineering & Design
Contingency
Up-Front Permitting
Indirect Capital
Capital Costs
H2A Inputs
Mass and Energy Balance
Fuel Cost
Water Cost
Electricity Cost
Land Cost And Usage
System Design
Fuel Usage
Water Usage
Electricity Usage
Variable Operating Costs
Operating Costs
Full Time Employees
Rent
Fixed Operating Costs

The team gathered data for two cases for each technology

Projected Current Case ("fabricating today at production volume")

- Case assumes high volume production that incorporates economies of scale.
- Demonstrated advances in technology are implemented.
- Potential reduction in capital cost from existing values.
- Plant lifetimes consistent with measured or reported data.

Projected Future Case ("fabricating in the future at production volume")

- Case assumes high volume production that incorporates economies of scale.
- Case assumes new materials and systems with higher H_2 production efficiency, longer plant lifetime, and improved replacement cost schedule.
- Case assumes greater reductions in capital cost.

Case parameters for a central H_2 production facility

Public Cases	Plant Start Date	Production of H_2 (kilograms (kg)/day)	Plant Life (years)
Current Central	2015	50,000	40
Future Central	2025	50,000	40

Case parameters for a forecourt H_2 production facility

Public Cases	Plant Start Date	Production of H_2 (kilograms (kg)/day)	Plant Life (years)
Current Forecourt	2015	1,500	20
Future Forecourt	2025	1,500	20

Technology Readiness Level (TRL)

- Technology Readiness Level
  - A.K.A. Technology Readiness Assessment
  - Measure of development status of a given technology
- Various TRL definitions
  - NASA
  - DOD
  - DOE
  - European Space Agency
  - Oil and Gas Industry
  - And More!
- Use in H2A
  - Future case TRL is generically assumed to be higher than the Current case
    - May estimate parameters that raise the TRL for Future case
  - If the Current case TRL is low enough, only Future case analysis might be conducted

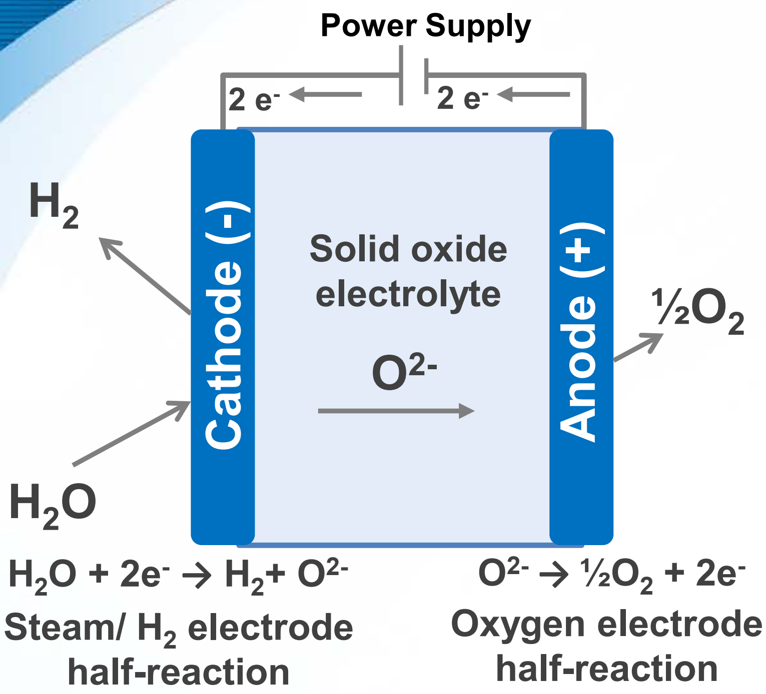
TRL Descriptions

1. Basic Concepts Conceived and Reported
2. Technology Concept and Application Formation
3. Analytical and Experimental Critical or Proof of Concept
4. Component or System Validation in Laboratory Environment
5. Bench Scale or Similar System Validation in Relevant Environment
6. Engineering Scale, system validation in a Relevant Environment
7. Full-scale, similar system demonstrated in Relevant Environment
8. Actual System Completed and Qualified
9. Actual System Operation

Overview of Recent Results

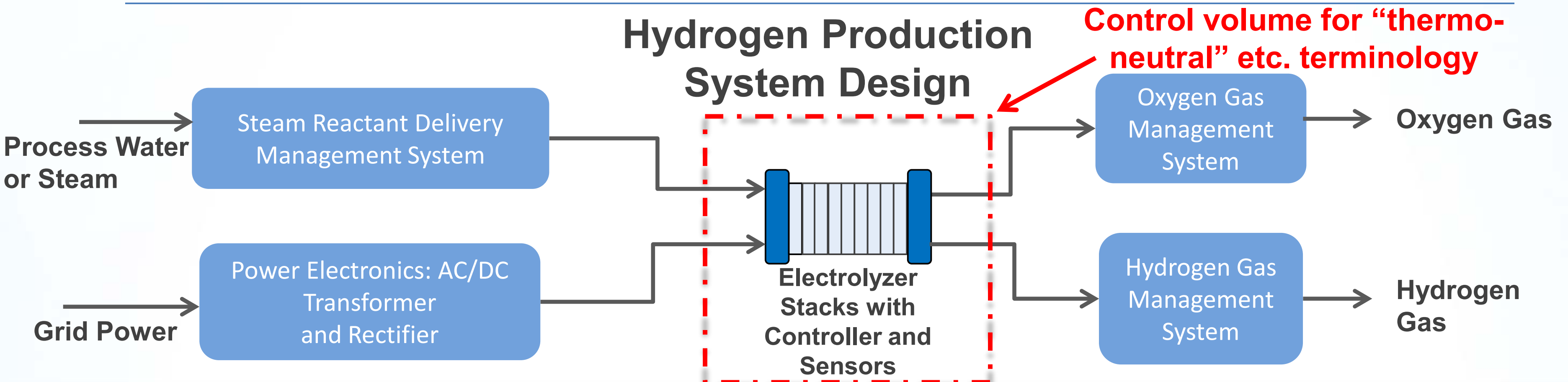
- **SOEC (Published Dec 2015)**
  - Degradation calculations (discussed today)
  - Replacement Schedule
- **Dark Fermentation (Publication is expected very soon)**
  - Finalized results
  - Updated process parameters for H2A values
- **Reforming of Bio-oil in a Monolithic Piston (Under Review)**
  - Conducted initial review and H2A case
  - Vetting process started. Looking for external review options
- **Reformer-Electrolyzer-Purifier (In development)**
  - FuelCell Energy, Inc. concept
  - Process modeling and case development in development

SOEC Technology



SOEC water electrolysis uses electricity to split water (H_2O) into oxygen (O_2) and hydrogen (H_2).

- Overall endothermic reaction: **Energy + $H_2O \rightarrow H_2 + \frac{1}{2}O_2$**
- Electrolyte: Oxygen ions (O^{2-}) traverse the electrolyte.



Degradation Values

	Units	Current Case	Future Case
Current Density (BOL)	A/cm	1.0	1.5
Cell Voltage	V/cell	1.28	1.28
Voltage Degradation	%/1000h	0.9%	0.25%
Voltage Degradation	mv/1000h	11	3.15
Ohmic Degradation Rate	mOhm-cm²/1000h	11	2.1
Stack Service Lifetime	years	4	7
% of Design Capacity at End of 1 Year Service due to degradation	%	83.2%	94.5%
H2A Plant Capacity Factor	%	90%	90%
Overall Effective Plant Capacity Factor (Linear Average per year)	%	82.4%	87.5%
BoP Service Lifetime	years	20	20
BoP Replacement Cost	%	100%	100%

We use Ohmic degradation rate to assess the annual impact on H_2 production rate. Rates calculated by methods described in Hjelm[3]

[1] BOL = Beginning of Life
[2] Absolute ASR degradation rate computed using secant method based on 0.85V open circuit voltage, BOL conditions and voltage degradation as stated.
[3] "Degradation Testing- Quantification & Interpretation", Johan Hjelm, Riso National Laboratory for Sustainable Energy, Technical University of Denmark

Stack Replacement Schedule to Achieve 100% of Plant Design Capacity at BOL

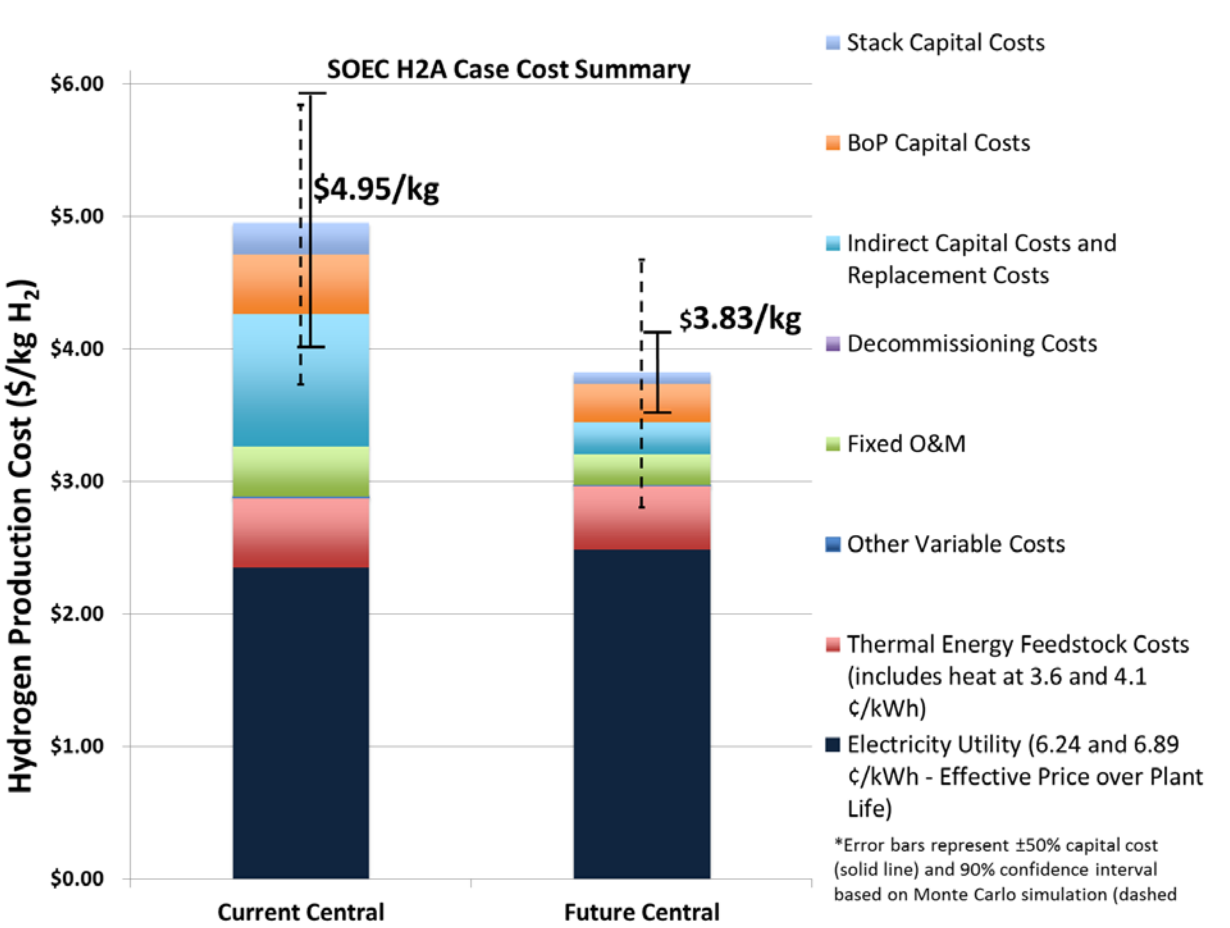
Partial replacement schedule for Current case stacks

	Year									
Stacks Purchased in year	1	2	3	4	5	6	7	8	9	10
1	1.000	0.832	0.692	0.576						
2		0.168	0.140	0.116	0.097					
3			0.168	0.140	0.116	0.097				
4				0.168	0.140	0.116	0.097			
5					0.647	0.538	0.448	0.373		
6						0.249	0.207	0.172	0.143	
7							0.249	0.207	0.172	0.143
8								0.249	0.207	0.172
9									0.478	0.398
10										0.287

- Stack Lifetime doesn't equal Operational Lifetime
- 4 year Stack replacement schedule, at which time H_2 production has dropped to:
  - Current: 58% of BOL
  - Future: 71% of BOL
- Annual stack purchases are made to bring total plant prod. up to Design Capacity
- BoP replacement schedule
  - 50% every 10 years
  - 100% every 20 years

Final SOEC Results

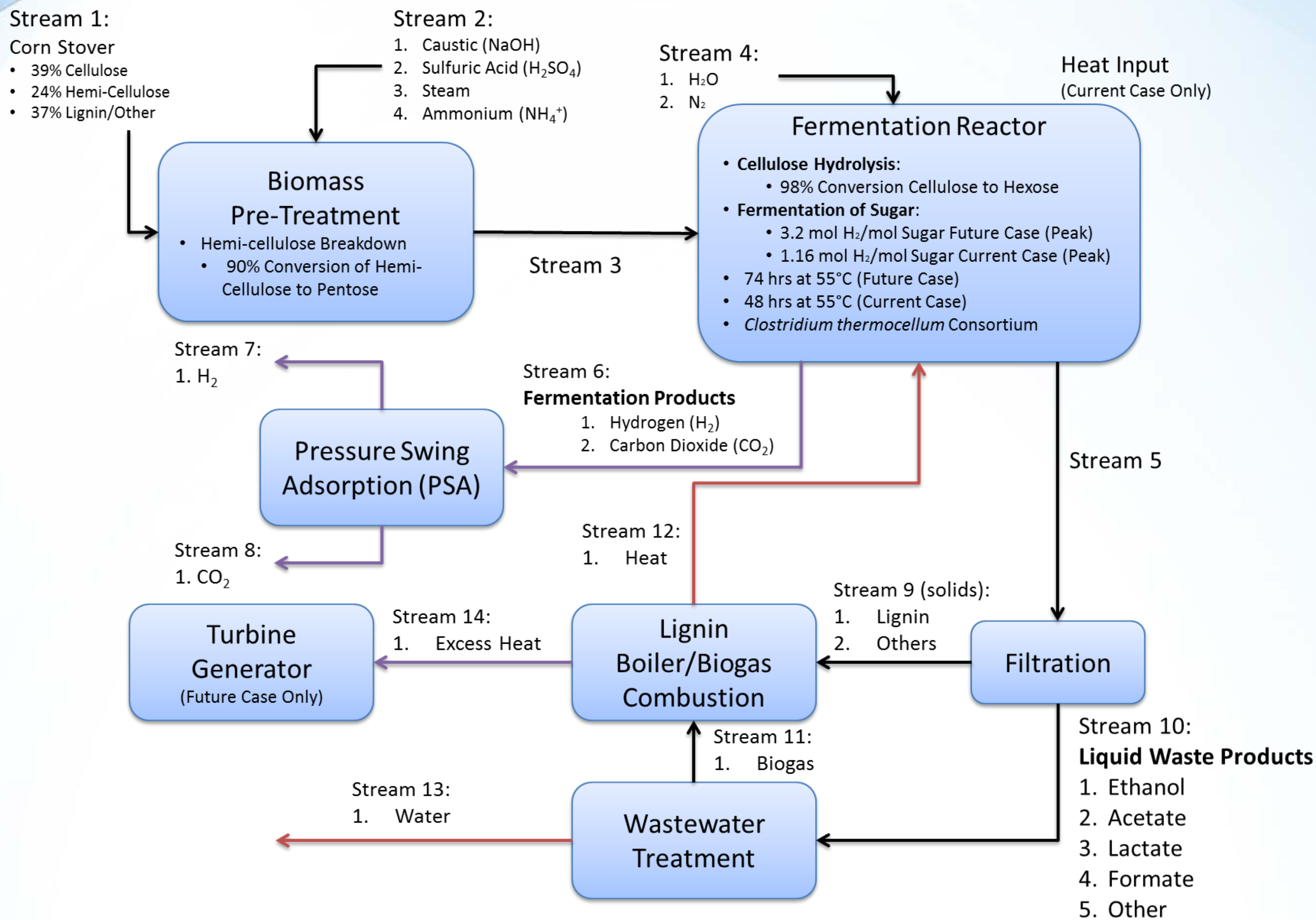
Electricity costs are the key cost driver.



** On a 2007 dollar cost basis, per standard reporting methodology for the H2A v3.1 tool (reflecting production costs only)*

- "Other Variable Costs" consist mainly of electricity costs. "Feedstock costs" are primarily heating costs.
- "Other Variable Costs" (electricity) and "Feedstock costs" (heat) are 68% to 78% of total life cycle costs.
- Between the current and the future case, the estimated H_2 production cost declines due to expected decreases in (1) SOEC system capital costs (primarily at the stack but also the BOP), (2) indirect capital costs and replacement costs, (3) fixed operations and maintenance (O&M) costs, and (4) system energy usage.

Fermentation Process Flow Diagram

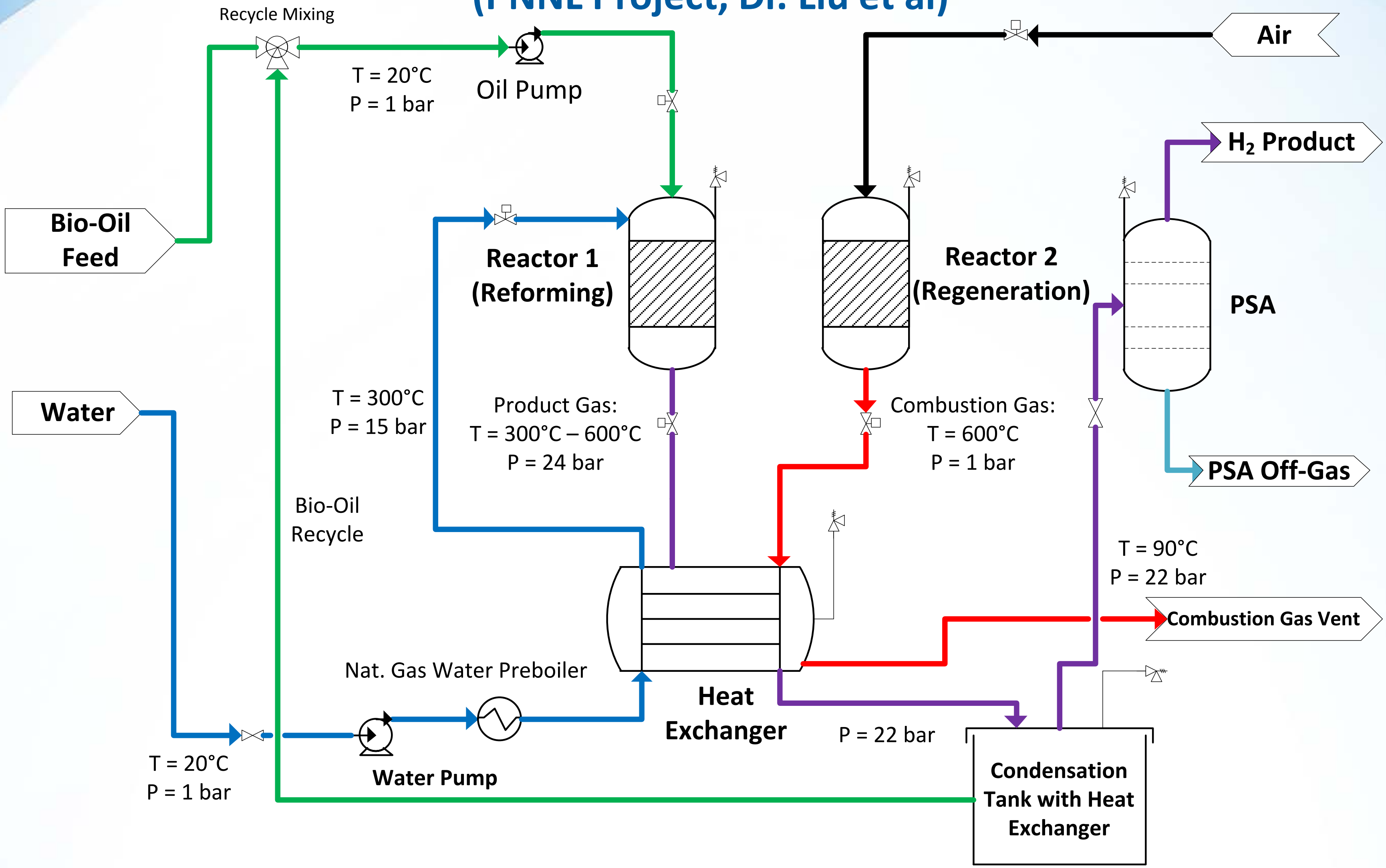


Final Fermentation Results

		Current Case (5 g/L)	Future Case (175 g/L)
Corn Stover Usage	MT/day	7,205	2,473
Fermentation Batch Time	hrs/batch	48	74
Corn Stover Concentration	g/L	5	175
Hemi-Cellulose to Pentose Conversion	%	90%	90%
Cellulose to Hexose Conversion	%	98%	98%
Mol H_2/ Mol Pentose	mol H_2/ mol Pentose	1.1 (Exp. Data at 48 hrs)	3.2 (Peak Yield at 74 hrs)
Mol H_2/ mol Hexose	mol H_2/ mol Hexose	1.1 (Exp. Data at 48 hrs)	3.2 (Peak Yield at 74 hrs)
Energy Recovery		Energy Deficient (Heat/Energy req.)	Net Electricity Sales (Lignin/Bio-Gas burned to make electr.)
H_2 Production Rate (After PSA)	kgH_2/day	50,000	50,000
Total Installed Capital Cost	$	$1.78B	$386M
\$/kg H_2 (prod. only)	**\$/kg H_2**	**$58.53**	**$5.65**

Monolithic Piston Project PFD

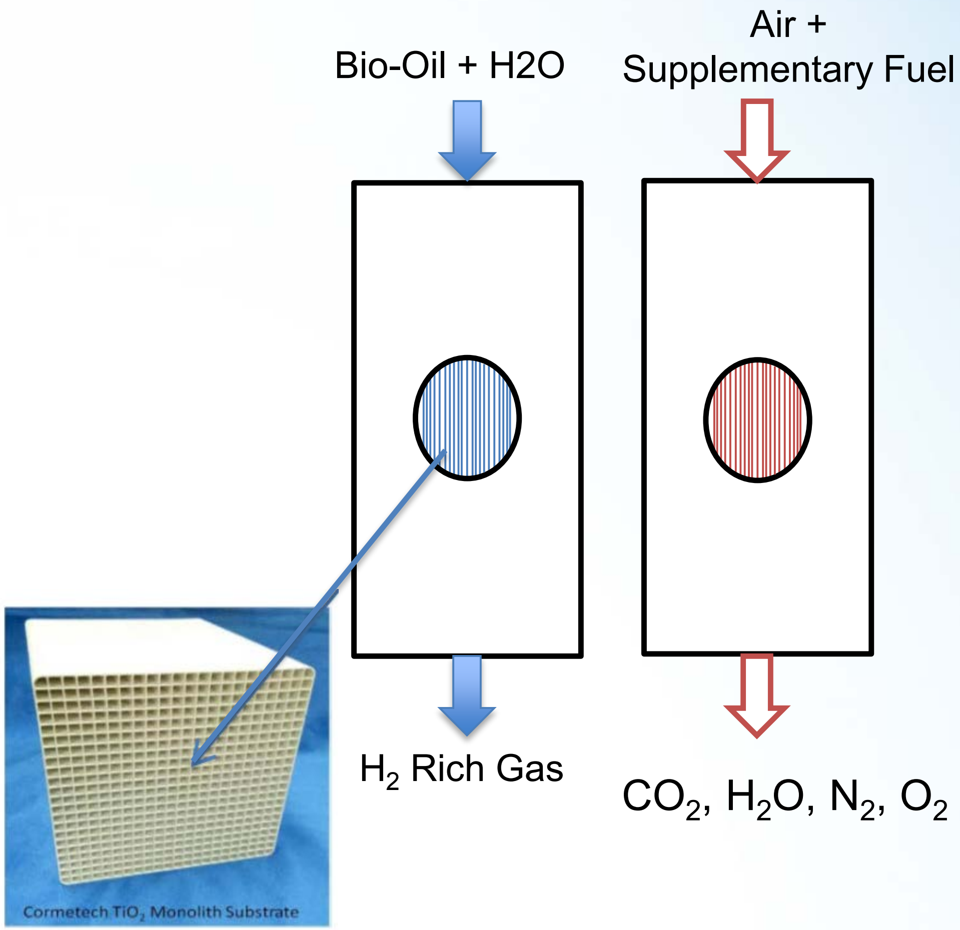
(PNNL Project, Dr. Liu et al)



PFD shows Reactor 1 in Reforming mode and Reactor 2 in Regeneration mode. For simplicity and clarity of operation, not all system connections are shown.

Monolithic Piston Operation

- **Two Reactors side-by-side**
  - **Reforming Mode**
    - Steam and oil fed to reactor at ~ 300°C across a catalyst coated TiO_2 monolith filled with dolomite
    - H_2 and CO_2 evolved. CO_2 is adsorbed to the dolomite while H_2 flows to PSA system
    - Coke deposits on the catalyst
  - **Regeneration Mode**
    - Air is blown over the catalyst monolith, burning the coke
    - Heat generated by coke burning releases CO_2 from dolomite
    - Heat warms monolith to ~700°C
    - **Cycling between modes every 10 minutes**



Reforming Reaction

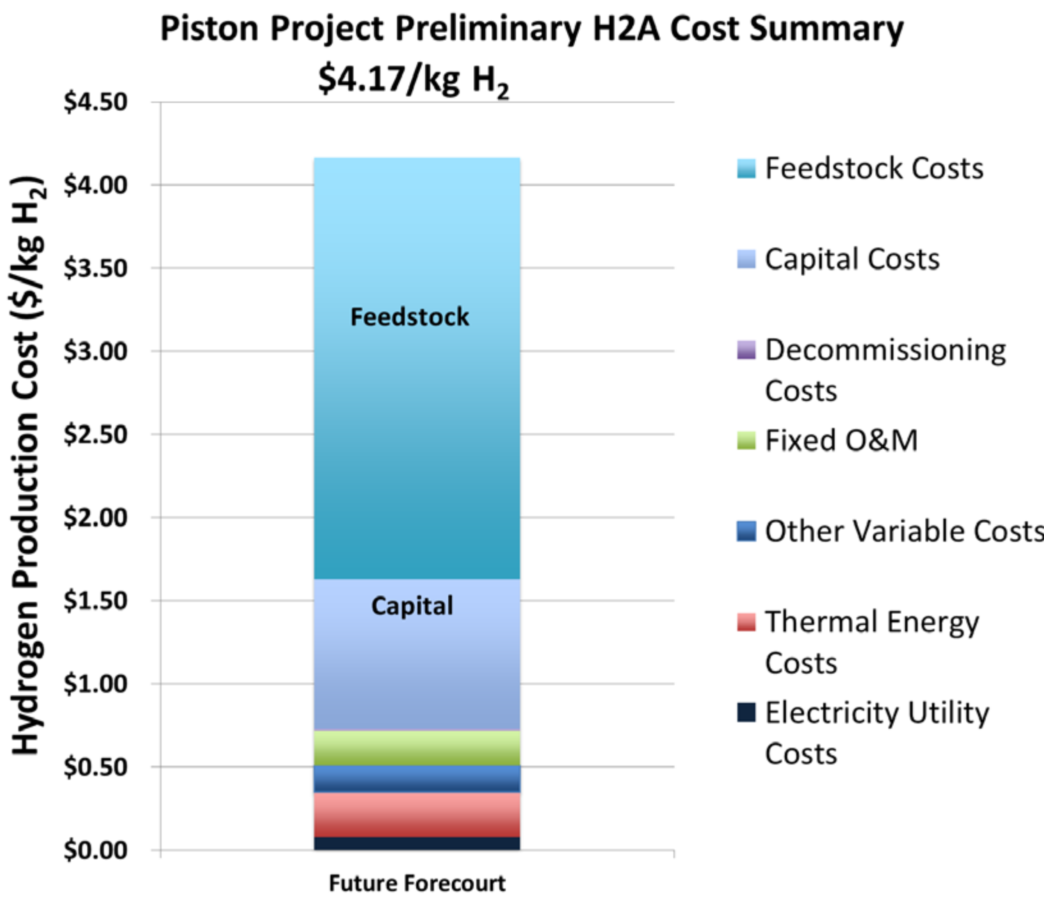
- **Bio-oil fuel is modeled as Soybean Oil**
  - PNNL used Phenol and other materials as a model for bio-oils
  - PNNL has also run preliminary studies with Pyroil
- **For performance modeling purposes:**
  - 80% of fuel is assumed to go to H_2 + CO_2 + coke production in a single pass
    - 64% to reforming, 16% to coke, 20% recycle
  - Remaining 20% is unreacted Bio-oil to be recycled
  - The fraction converted to Coke is important for performance measurements and needs to be experimental confirmed/optimized.

Fatty Acid	Wt %	Mol Wt.	Formula
Palmitic	**12**	**270.46**	$C_{15}H_{31}CO_2CH_3$
Stearic	**5**	**298.52**	$C_{17}H_{35}CO_2CH_3$
Oleic	**25**	**296.50**	$C_{17}H_{33}CO_2CH_3$
Linoleic	**52**	**294.48**	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2CH_3$
Linolenic	**6**	**292.46**	$CH_3(CH_2CH{=}CH)_3(CH_2)_7CO_2CH_3$

$$C_xH_yO_z + (2x-z)H_2O \xrightarrow{\Delta H} \begin{cases} \left.\begin{matrix} (0.5y+2x-z)H_2 + xCO_2 (80\%\ yield) \\ C_xH_{x-2z} + kH_2O + \Delta H \quad (20\%\ yield) \end{matrix}\right\} (\mathbf{80\%\ Conversion}) \\ C_xH_yO_z[Unreacted] \qquad (\mathbf{20\%\ Conversion}) \end{cases}$$

Preliminary H_2A Inputs & Results

- **Future Case Only**
  - Technology level is not high enough to warrant Current Case
  - Analyzed for Forecourt (1500kgH_2/day)
- **Bio-oil**
  - 3.652 kg/kg H_2
  - $0.66/kg (Start-up Year)
- **Natural Gas**
  - 0.03mmBTU/kg H_2
- **Electricity**
  - 0.85 kWh/kg H_2
  - $0.0659/kWh (Start-up Year)
- **Unplanned replacement at 1%/year**



Preliminary Results

- **Production cost =$4.17/kg H_2**
  - Refueling Costs = $2.21/kg H_2
  - Total Cost (Delivered) = $6.38/kg H_2

Future Work

- FuelCell Energy's Reformer-Electrolyzer-Purifier (REP)
  - Based on existing Molten Carbonate Fuel Cell Technology
  - Two system designs modeled
    - Integrated fuel cell/REP, generates DC Power and high purity H_2
    - Stand-alone REP, electricity & Natural Gas to generate high purity H_2
  - Currently working with FCE to obtain project details
    - FCE has created preliminary H2A results

Presentation Summary

- **Overview**
  - Exploration of selected H_2 production and delivery pathways to find most feasible
  - Transparent, objective, and internally consistent comparison of alternatives
  - In year 2 of 3 year project, added SOEC & Biofermentation Cases to our Analysis
- **Relevance**
  - Identify key “bottlenecks” to the success of these pathways, primary cost drivers, and remaining R&D challenges
  - Assess technical progress, levelized H_2 costs, benefits and limitations
  - Analyses assist DOE in setting research direction & priorities
- **Approach**
  - Input based on interviews of technical experts
  - Create engineering performance models of system operation
  - Projected cost results from use of H2A Production Model Version 3.1
- **Accomplishments**
  - Analysis of PEM electrolysis H_2 Production systems (2 years ago)
  - Final analysis of SOEC and Fermentation Complete
  - Vetting Monolithic Piston Project
  - Initial review of Reformer Electrolyzer Purifier system underway
- **Collaborations**
  - DOE, INL, ANL and NREL provide cooperative analysis/vetting of assumptions/results

Response to Reviewer Comments

FY15 Reviewer Comments	FY16 Response to Comment
In terms of future pathways to be analyzed, biomass gasification and pyrolysis could also be considered.	Biomass gasification has been analyzed previously. Pyrolysis was considered previously but was not selected for analysis. DOE will make selections on new pathways to be analyzed and may include pyrolysis in the future.
Collection of information could have been done through literature review as well as through questionnaires.	The suggestion is well taken and SA conducts literature reviews continuously to supplement information gathered by questionnaires and researcher telecons.
The project … is inadequate to model for the n^{th} plant as opposed to using actual numbers for current technologies. […] SOEC and bio-fermentation technologies have not been deployed at large scale (50,000 kg/day). It is not clear why the team used today's cost at scale instead of modeling today's cost at low production rates and then modeling a ramp up.	Information was collected for Existing (manufactured today), Current (today's technologies at high production scale) and Future (high production scale with advancements in technology). Existing case data was not presented in order to prevent releasing proprietary data, as in the case of SOEC, or due to the information being specifically related towards laboratory scale processes, as in the case of fermentation.

Collaborators

Institution	Relationship	Activities and Contributions
National Renewable Energy Laboratory (NREL) • Genevieve Saur • Todd Ramsden • Pin-Ching Maness	Subcontractor	• Participated in weekly project calls. • Assisted with H2A Production Model runs & sensitivity analyses • Provided laboratory data results for biofermentation • Drafted reporting materials • Reviewed reporting materials
Argonne National Lab (ANL) • Rajesh Ahluwalia • Dennis Papadias	Subcontractor	• Participated in select project calls. • Vetted process work • Sized PSA systems
Department of Energy (DOE) • Sarah Studer • Eric Miller • Katie Randolph • David Peterson	Sponsor	• Participated in periodic weekly project calls. • Assisted with H2A Model and sensitivity parameters • Reviewed reporting materials

Thank you

- This work funded by the Fuel Cell Technologies Office at DOE/EERE under DOE contract number: DE-EE0006231.

- Special Thanks to:

  Dr. Eric Miller (DOE)

  Dr. Katie Randolph (DOE)

  Dr. Sarah Studer (ORISE Fellow)

  Dr. David Peterson (DOE)

Backup Slides

Preliminary Process Parameters

	Unit	Value
Bio-Oil Mass Flow	kg/hr	284.5 (83.9 gal/hr)
DI Water Mass Flow	kg/hr	687.7 (179 gal/hr)
Steam to Carbon Ratio	mol/mol	2.1
Water Preheater	kJ/hr	1.98e6 (553 kW)
Heat Exchanger Duty (Condense oil and water)	kJ/hr	2.47e5 (68.6kW)
U_A	kJ/C-h	119
System Pressure	Bar	24
Reaction Temperature	°C	Modeled as 600°C nominal gas exit temperature (Operational Temperature Range ~700-550°C)
CO_2 Produced	kg/h	490
CO_2 adsorbed (90% of generated)	Kg/h	441
H_2 Produced	kg/h	62.5

Piston Reformer: Reactor Specs (of a single reactor)

Spec	Unit	Value
Production Capacity	kg/day	1500
Diameter (I.D.)	cm	66.76
Length	cm	333.8
Volume	m^3	1.223
Monolith Volume (Skeletal, not including channel volume)	m^3	0.083
Dolomite Volume (50% of the total channel volume)	m^3	0.57
Open Channel Volume (50% of the total channel volume)	m^3	0.57

Piston Reformer: Yield Losses for Coking

- Modeled generic de-coking reaction as
  - $C_{18}H_{14} + 21.5O_2 \rightarrow 7H_2O + 18CO_2$
  - $C_{18}H_{14}$ (terphenyl) chosen as a generic model for coke
    - Heat of formation for terphenyl was used ~ 158.8 kJ/mol
  - Can be expanded to include other coke formulas at a later date

- Solving $\Delta H_{rxn}{}^{reforming} = \Delta H_{rxn}{}^{regeneration}$
  - "Ideal" coke production is 16.2% of Bio-Oil
    - This is approximately the amount generated through 80% single pass conversion followed by a 20% yield to coke
    - PNNL current expects/targets this "ideal" level of coke production
    - Model currently assumed 16% of Bio-oil goes to coke.
    - System thermal losses would require additional energy and thus would decrease efficiency.
    - Simplified Energy Balance comparing only two overall reactions

Preliminary Efficiency Results

	Unit	Value
Net Bio-Oil Feed (net)	kmole/hr	0.8136
Bio-Oil LHV (net)	kJ/kmole	$1.02*10^7$
H_2 Produced (net)	kmole/hr	30.92
H_2 LHV	kJ/kmole	$2.419*10^5$
Water Pre-boiler Power	kJ/hr (kW)	1.98e6 (553)
Net System Efficiency	%	73.4*

$$\eta_{Net} = \frac{\dot{n}_{H_2} * LHV_{H_2}}{\dot{n}_{Bio-Oil} * LHV_{Bio-Oil} + P_{Preboiler}}$$

* This efficiency based on 100% recycle/recovery of bio-oil and reflects 90% H_2 recovery in the PSA..

Piston Reformer: Factors Affecting System Efficiency

- Bio-oil conversion to H_2
  - Currently at 64% based on PNNL input
- Coke production
  - If bio-oil conversion to coke is >16% then efficiency will drop.
  - If <16%, the bio-oil would need to be burned for heat
- H2 losses during Regeneration
  - H2 lost during purge/depressurization
  - Currently only 1.2% H2 loss based on 10 min cycle time and 50,000/h GHSV. Changes could increase losses.
- H2 Losses during PSA
  - Reactor exit gas is mostly H2 but still needs purification.
  - H2 Recovery estimated at 90% (ANL calculated value)
- % of Unreacted Bio-oil
  - Not all Bio-oil is reacted in a single pass through the reactor
  - Currently 80% single pass conversion assumed
  - There is no direct system efficiency impact if
    - Unreacted bio-oil is 100% captured for reuese
    - The ratio of reforming to coke is maintained (64%/16%)
    - However increases in the % of unreacted bio-oil would make the reactor larger and more expensive.

TRL for H2A cases

- **PEM Electrolysis**
  - TRL 9
- **STCH**
  - TRL 2 (preliminary)
- **PEC**
  - TRL 3/4 (preliminary)
- **SOEC**
  - TRL 6 (Stack)
  - TRL 5/6 (System)
    - Ground Demonstration Unit by Private Company, INL demonstrated integrated system
- **Fermentation**
  - TRL 4
    - Low level conversion of sugars to H_2.
    - Only demonstrated in laboratory setting with representative biological agents
- **Monolithic Piston-Type Project**
  - TRL 3 (preliminary)
    - Testing of each cycle done independent of other cycles
    - Representative components used for studies in some cases
- **Reformer-Electrolyzer-Purifier**
  - TRL 5 (preliminary)
    - Alternate operating mode of existing fuel cell technology
    - Sub-scale testing, not completely integrated