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Summary of On-Board Storage Models and Analyses

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Hydrogen Delivery Analysis Meeting

FreedomCAR and Fuels Partnership

Delivery, Storage and Hydrogen Pathways Tech Teams

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Columbia, MD

U.S. Department of Energy

UChicago ▶ Argonne LLC

A U.S. Department of Energy laboratory managed by UChicago Argonne, LLC

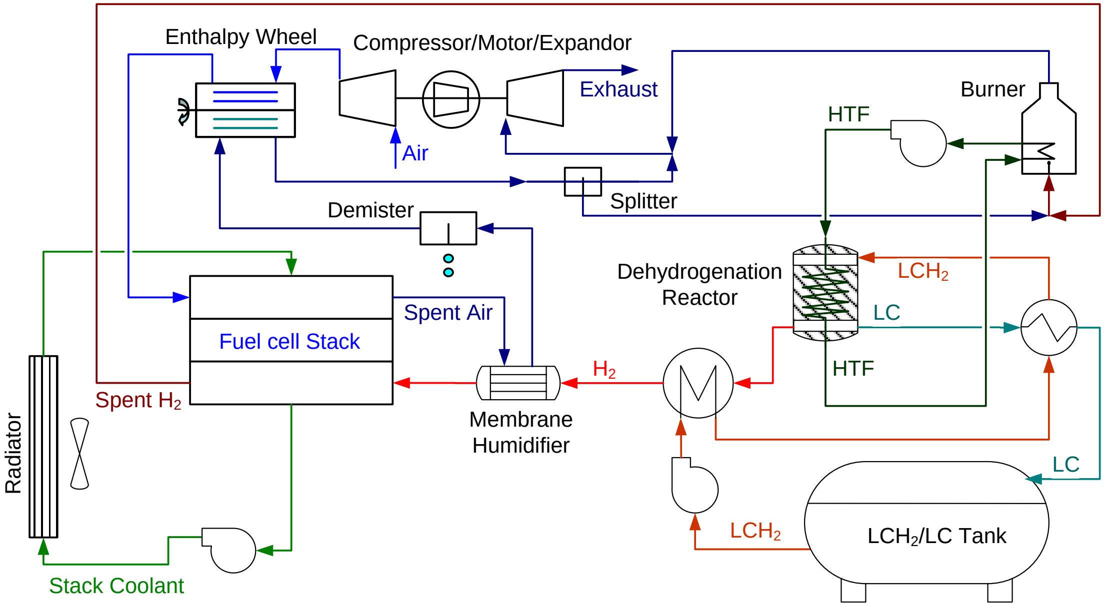
On-Board Hydrogen Storage System with a Liquid Carrier

Objective: To determine the performance of the on-board system relative to the storage targets (capacity, efficiency, etc)

1. On-Board System Configuration
2. Dehydrogenation Reactor
   - Dehydrogenation kinetics
   - Trickle bed hydrodynamics
   - Dehydrogenation reactor model
   - Reactor performance with pelletized and supported catalysts
3. System Performance
   - Storage efficiency
   - Storage capacity

Fuel Cell System with H_2 Stored in a Liquid Carrier

- Once-through anode gas system with controlled H_2 utilization
- Burner uses depleted air split-off from spent cathode stream
- Burner exhaust expanded in gas turbine to recover additional power



Argonne HTCHS

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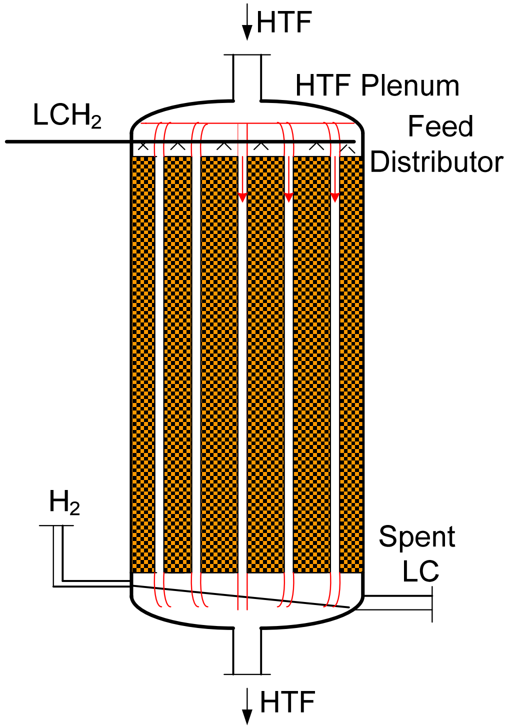
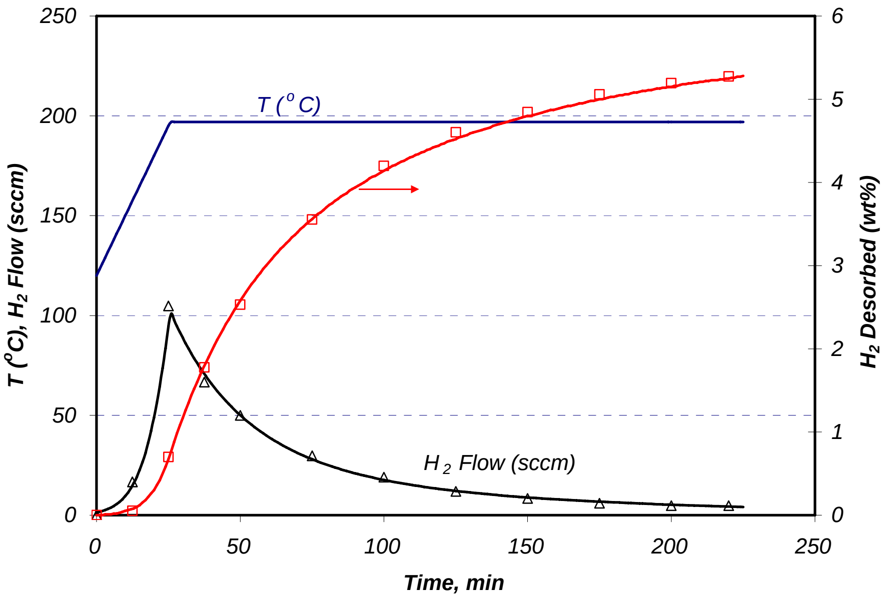
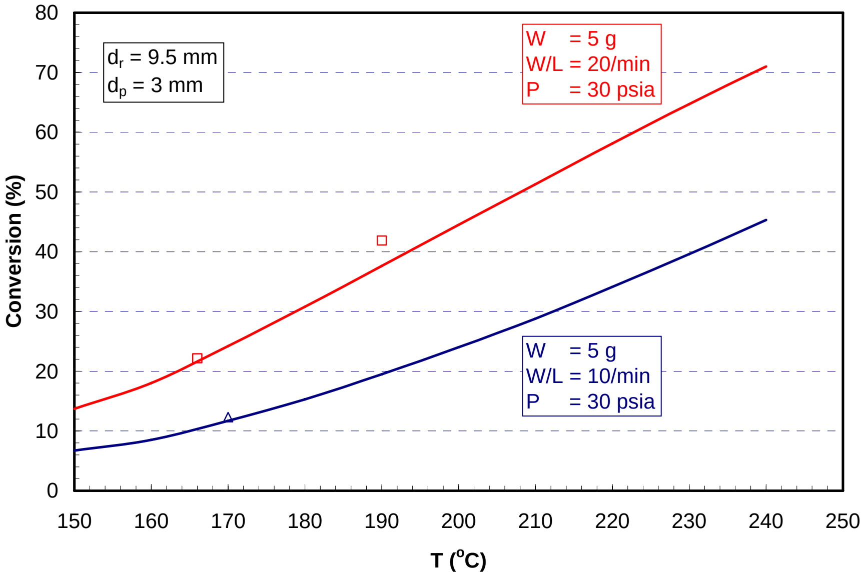


Dehydrogenation Reactor

Developing & Validating Model for DeH2 Reactor

- Dehydrogenation kinetics
  - $R_1 = R_2 + 2H_2$
    $R_2 = R_3 + 2H_2$
    $R_3 = R_4 + 2H_2$
  - Kinetic constants from batch reactor data, APCI Patent
  - 8 g N-ethylcarbazole, 20-cc reactor, 0.2-g 4% Pd on Li aluminate powder catalyst
- Trickle-bed reactor model
  - First-order kinetics with internal & external mass transfer
  - Trickle bed hydrodynamics
  - ODEs for T and species flow
  - TBR data for 5% Pd on alumina catalyst





Trickle Bed Reactor Hydrodynamics Neural Network Model

Parameter	Re_l	Re_g	Fr_l	Fr_g	We_l	X_l	X_g	St_l	St_g	Sc_l	Sc_g	Ga_l	Ca_l	Ca_g	Bi	Pe_l	Pe_g	$\rho_{g,l}$	α	$d_{p,r}$	Φ	ε
Slip factors: f_s, f_v	√	√	√		√	√		√														
Ergun constants: E_1, E_2																				√	√	√
Liquid-catalyst mass transfer coefficient	√	√						√		√		√							√			
Volumetric liquid-side mass transfer coefficient		√			√			√	√	√			√	√					√	√		
Volumetric gas-side mass transfer coefficient	√	√		√				√			√								√			
Liquid-wall heat transfer coefficient	√			√	√			√								√	√			√		
Bed radial thermal conductivity	√			√	√										√	√	√					
Wetting efficiency	√	√	√		√	√	√	√				√						√	√	√	√	√
Pressure drop	√	√			√	√						√							√			
Liquid holdup	√	√			√		√												√			

Re	Reynolds number	**Ga**	Galileo number	d_p	Catalyst diameter
Fr	Froud number	**Ca**	Capillary number	d_r	Reactor diameter
We	Weber number	**Pe**	Peclet number	Φ	Sphericity factor
X	Lockhart-Martinelli number	**Bi**	Biot number	ε	Void fraction
St	Stokes number	ρ	Density	**Subscripts:**	
Sc	Schmidt number	α	Bed correction factor	**l** Liquid	**g** Gas

References: Ind. Eng. Chem. Res., 37 (1998), 4542-4550
Ind. Eng. Chem. Res. 42 (2003) 222-242
Chem. Eng. Sci., 54 (1999) 5229-5337

Conversion with Pelletized Catalysts

- Reactor Parameters
  - Pellet diameter = 3 mm
  - Bulk density = 800 kg/m^3
  - HX tube diameter = 3/8”
  - AL 2219-T81 construction
- Analysis Method

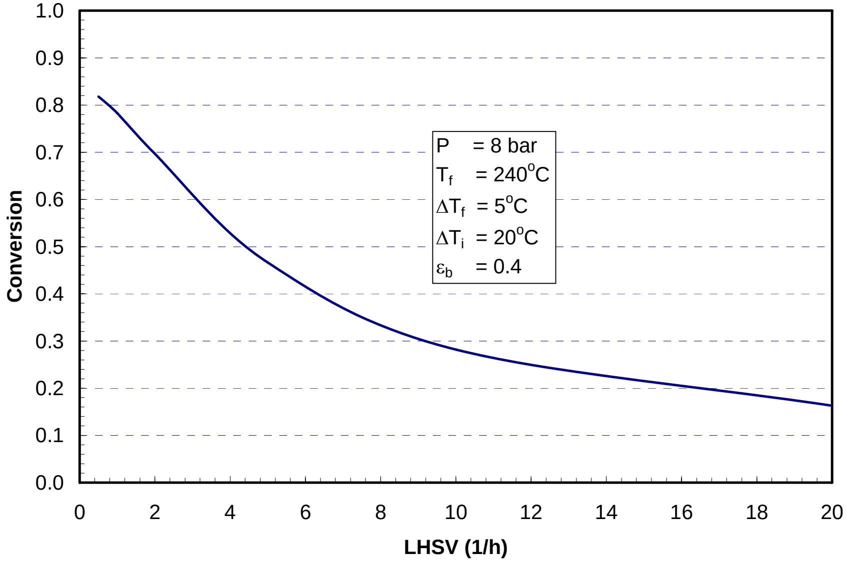
Variable	Constraint
LCH_2 flow rate	2 g/s[a] H_2 to FCS[b]
HTF flow rate	ΔT_f = 5°C
No. of tubes	Q = 83 kW[c]

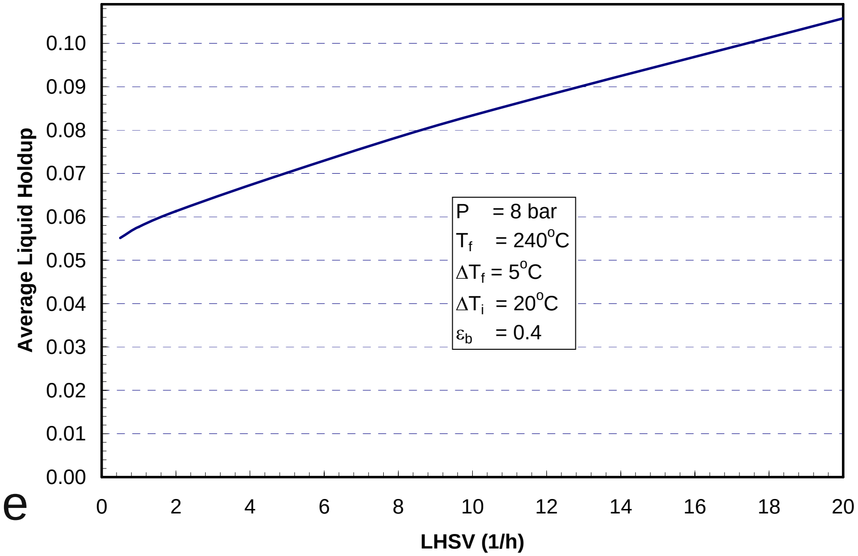
[a] 3 g/s total H_2 for N-ethylcarbazole

[b] 100-kWe FCS

[c] ΔH = 51 kJ/mol for N-ethylcarbazol

LHSV=volumetric flow rate/reactor volume

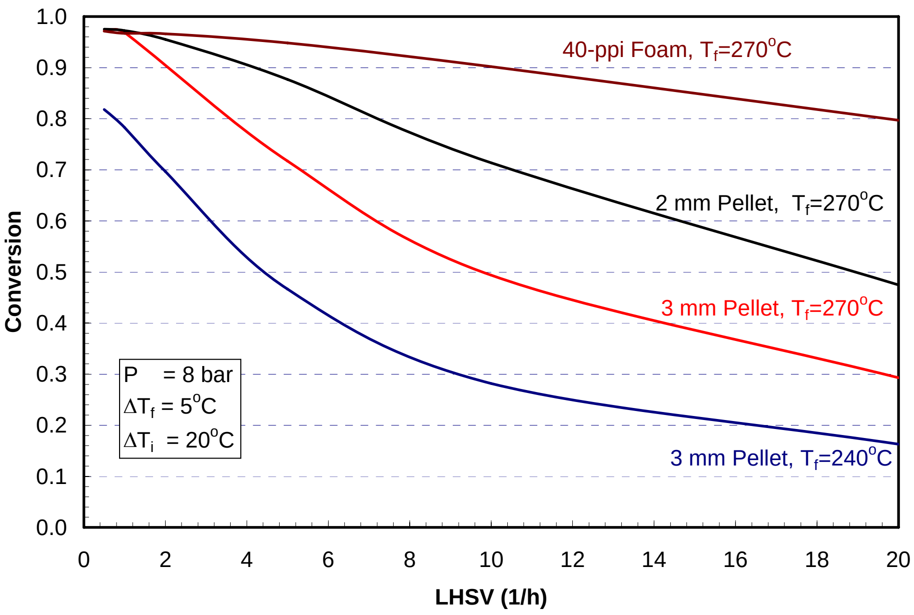


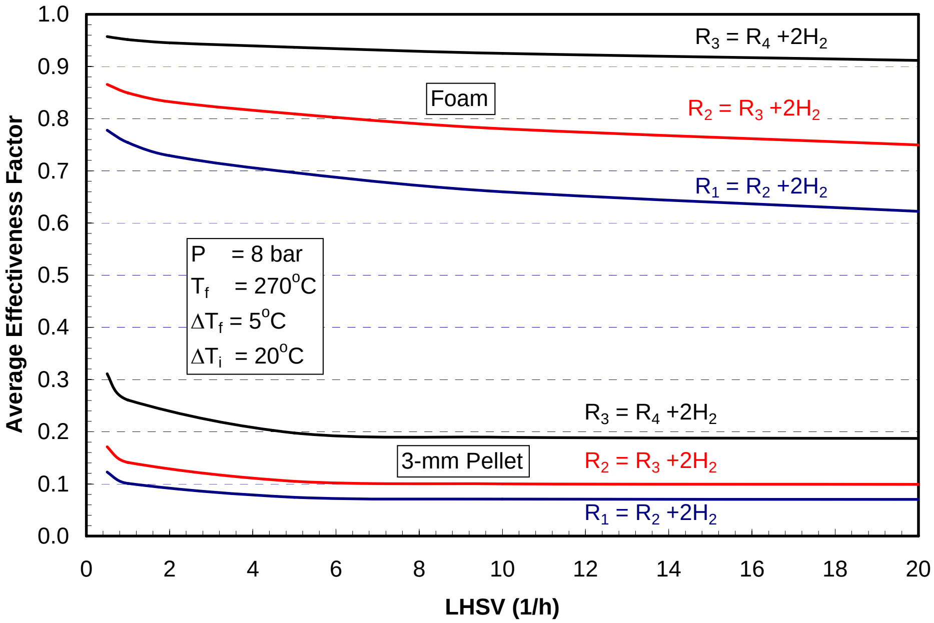


Conversion with Dispersed Catalyst

ANL-IN-07-019

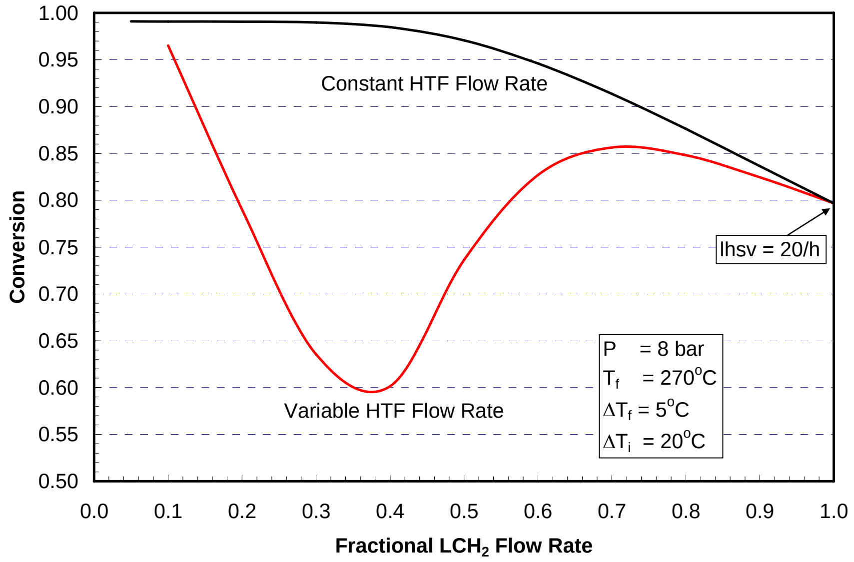
- 40-ppi Al-6101 foam, 92% porosity
  - 50-μm catalyst washcoat, 224 kg/m³ bulk density
- Marked improvement in catalyst effectiveness if supported on foam although the wetting efficiency decreases
  - Trickle flow on foam has not been demonstrated

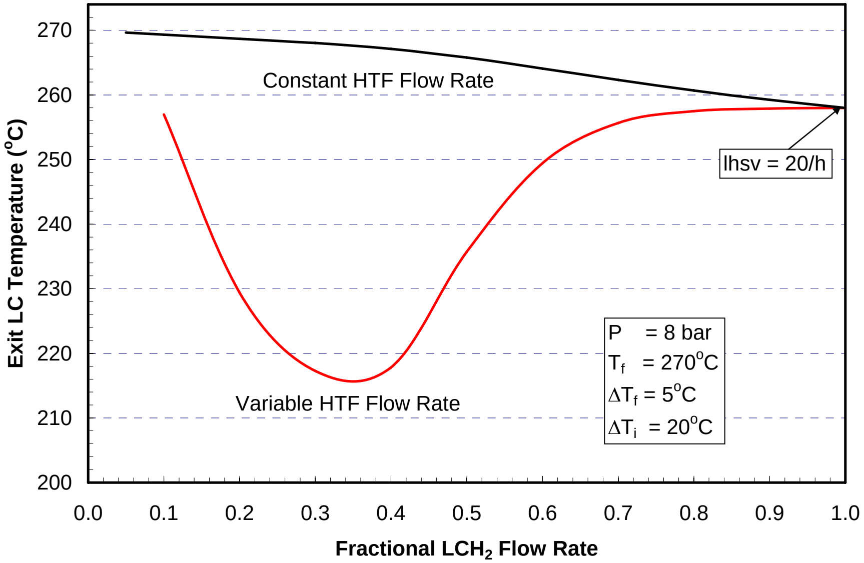




Part-Load Performance

- Higher conversion with constant HTF flow rate especially at low loads
- Transient performance
  - Actual conversion on a drive cycle may be higher or lower than the steady-state value
  - Response time
  - Pressure control?
  - Buffer storage?



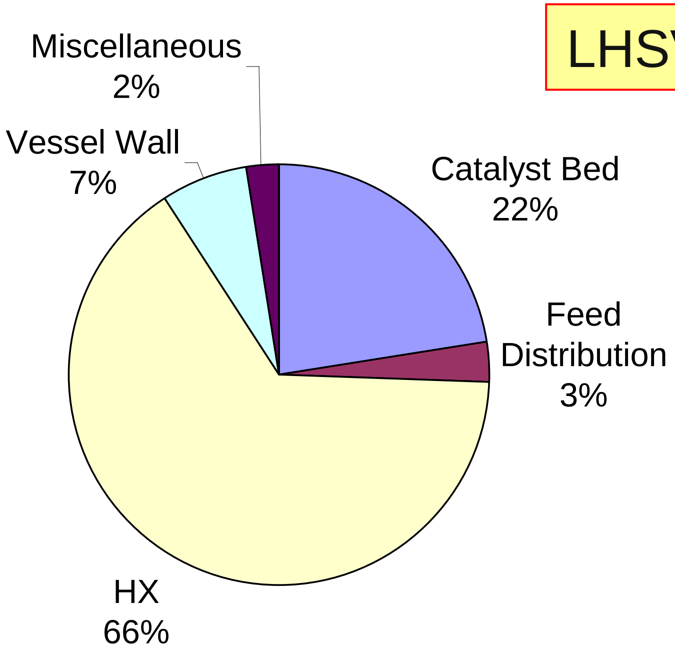


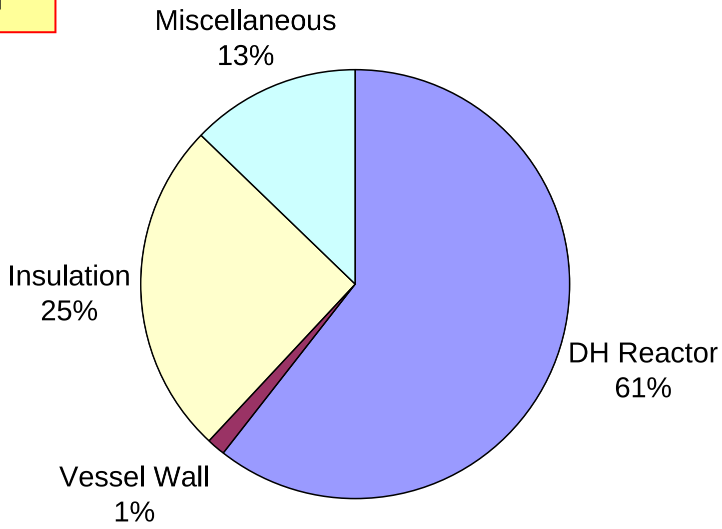
Reactor Weight and Volume Distribution

- Total weight of reactor = 23 kg
- HX tubes ~ 2/3rd of total weight
  - Larger ΔT ($T_{HTF} - T_R$) for lighter HX at expense of η_{ss}
  - Heat transfer augmentation important with more active catalyst

- Total volume of reactor = 53 L
- Possible to trade-off insulation volume with heat loss
  - 110 W heat loss with 2-cm insulation

LHSV = 20 h^{-1}





Argonne HTCHS: System Analysis

Dehydrogenation Reactor

- T_R function of $P(H_2)$, conversion, ΔH, ΔS, and ΔT_{eq}
- Trickle flow, 20 h^{-1} LHSV
- Catalyst supported on 40-PPI foam
- HX tubes with 90° inserts
- AL-2219-T81 alloy, 2.25 SF
- 2 cm insulation thickness

Heat Transfer Fluid

- XCELTHERM ®
- 5^oC ΔT in DeH2-HX, $T_{HTF} - T_R = 50^oC$

HEX Burner

- Non-catalytic, spent H_2 and 5% excess spent air
- Counterflow microchannel, inconel
- 100^oC approach temperature

H_2 Cooler

- LCH2 coolant, $T_{outlet} = T_{FC}$
- Counterflow, microchannel, SS

Recuperator

- LC/LCH2 HX, $T_{LCH2} = T_R - 10^oC$
- Counterflow, microchannel, SS

LC Radiator

- $T_{LC} = 70^oC$
- Integrated with FCS radiator
- W and V not included in HTCHS

LCH_2/LC Storage Tank

- Single tank design, HPDE construction
- 10% excess volume

Pumps

- HTF pressure head: 1 bar
- LCH2 pressure head: 8 bar

H_2 Separation

- Coagulating filter

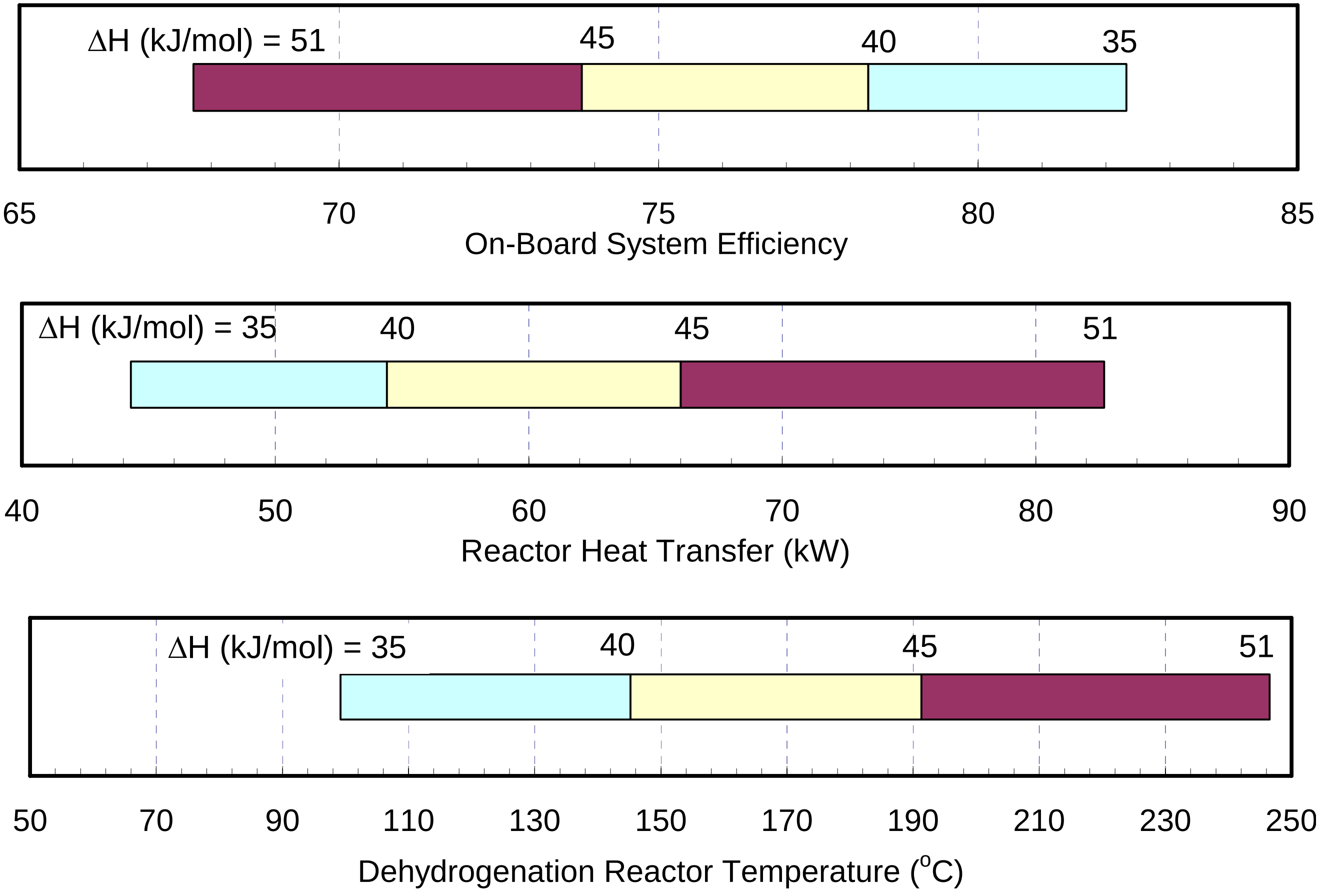
H_2 Buffer Storage

- 20 g H_2 at 80^oC, $P(H_2)$
- AL-2219-T81 alloy tank, 2.25 SF

Miscellaneous

On-Board Storage System Efficiency

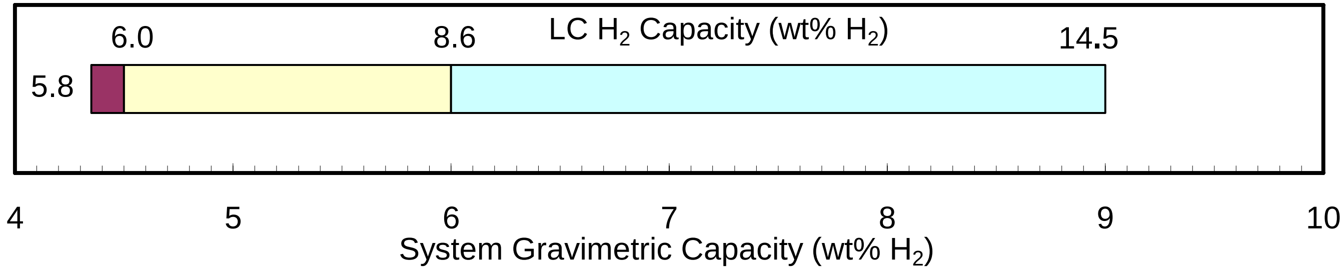
- Storage system efficiency defined as fraction of H_2 librated in dehydrogenation reactor that is available for use in fuel cell stack
- Efficiency could be ~100% if $\Delta H < 40$ kJ/mol <u>and</u> $T_R < T_{FC}$

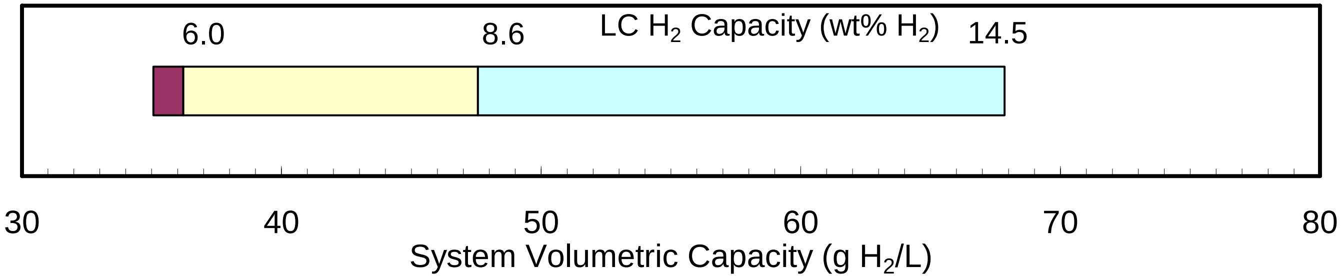


- LC: 0.95-1.2 g/cc, 5.8 wt% H_2
- 95% conversion
- DeH_2 LHSV: 20 h^{-1}
- ΔT_{eq}: 50°C
- Burner HX: 100°C approach T
- 2 g/s net H_2 output
- $P(H_2)$: 8 bar
- 0.8-1.4 kWe HTF pump
- Start-up energy not included

Reverse Engineering: H_2 Storage Capacity

- System capacity presented in terms of stored H_2
  - Recoverable H_2: 95% intrinsic material capacity (conversion)
  - Usable H_2 = Storage system efficiency x Recoverable H_2
- System capacity with N-ethylcarbazole: 4.4% wt% H_2, 35 g/L H_2 (H_2 stored basis); 2.8% wt% H_2, 23 g/L H_2 including losses
  - 95% conversion, 67.7% storage system efficiency





- LC: 0.95-1.2 g/cc
- LC tank: 10% excess volume
- ΔH_2 LHSV: 20 h^{-1}
- ΔT_{eq}: 50°C
- Burner HX: 100°C approach
- 2 g/s net H_2
- 20-g H_2 buffer
- $P(H_2)$: 8 bar

Preliminary Conclusions

1. Dehydrogenation reactor will need a supported catalyst
   - Desirable to have LHSV > 20 h^{-1} for >95% conversion
   - May need $\Delta T > 50^{o}C$ for compact HX ($\Delta T = T_{HTF} – T_R$)
2. Need $\Delta H < 40$ kJ/mol for >90% on-board storage efficiency
3. Material capacities to meet system storage targets

	System Capacity[a]	
Material Capacity	Gravimetric	Volumetric
wt% H_2	wt% H_2	g-H_2/L
5.8	4.4	35
6.0	4.5	36
8.6	6.0	48
14.5	9.0	68[b]

[a] Stored H_2 basis

[b] H_2 buffer has to decrease for 81 g/L volumetric capacity

Future Work

Continue to work with DOE contractors and COE to model and analyze various developmental hydrogen storage systems.

Metal Hydrides

- Analyze system with the most promising candidate
- Reverse engineering to determine material capacities

Carbon Storage

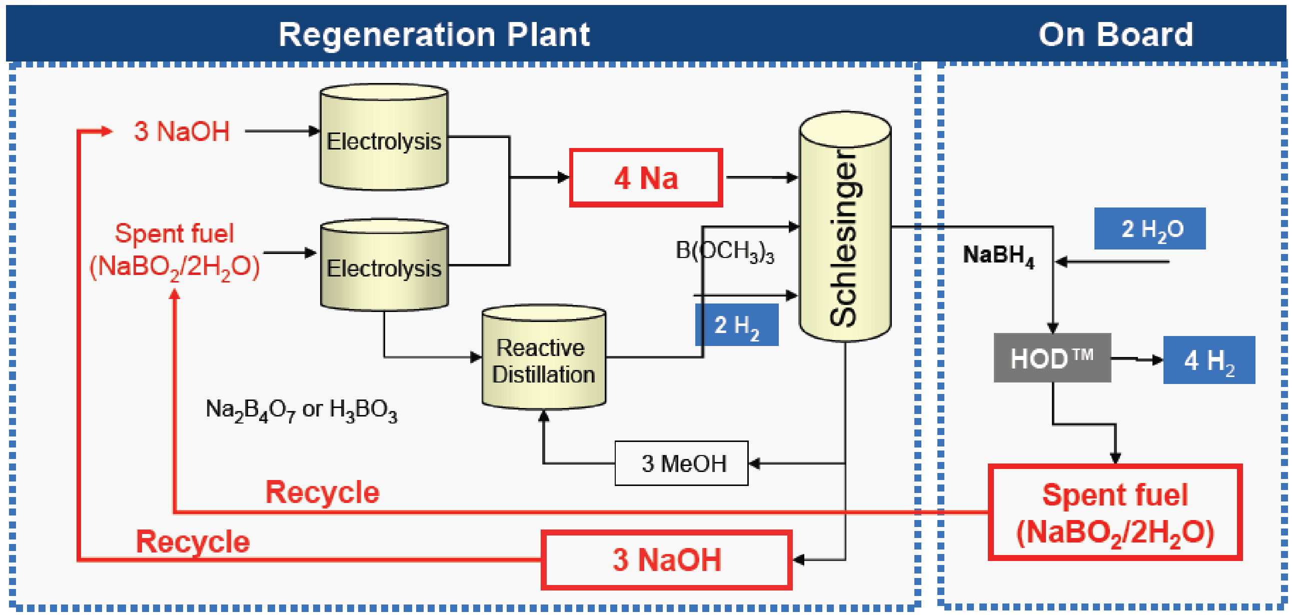
- Extend work to carbon and other sorbents

Chemical Hydrogen

- Evaluate regeneration energy consumption and fuel cycle efficiency of candidate materials and processes
- Liquid carrier option
  - Validate model with experimental data for more active catalysts
  - Sensitivity study (P, buffer H_2 storage)
  - Extension to the “best” APCI carrier with the “best” APCI catalyst
  - Fuel cycle analysis
  - Collaboration with TIAX on cost analysis

SBH Regeneration Analysis – Energy Requirements and Efficiencies

- Brown-Schlesinger process requires 4 moles Na per mole of $NaBH_4$
- Na recovery is the most energy intensive step in SBH regeneration
- MCEL has demonstrated a laboratory method for recycling Na in a closed loop
  - NaOH and $NaBO_2$ electrolysis – with or without H_2 assist
  - No make-up Na needed (assuming 100% recovery efficiency)



Source: Millennium Cell

Na Recovery

- H_2-assisted electrolysis
  - Anhydrous or aqueous NaOH

    $3\ NaOH + 3/2\ H_2 \rightarrow 3\ Na + 3\ H_2O$
  - Aqueous $NaBO_2$

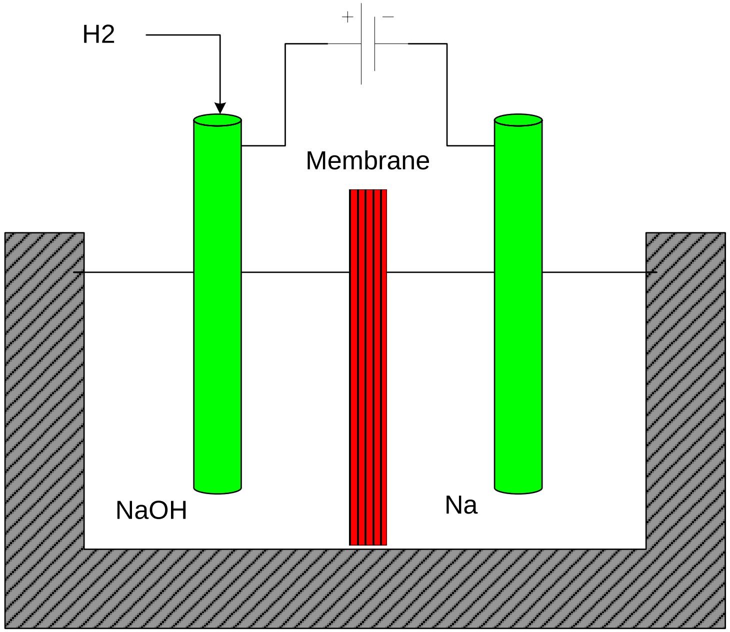
    $NaBO_2 + 1/2\ H_2 + H_2O \rightarrow Na + H_3BO_3$

- Electrolysis without H_2 assist
  - Anhydrous or aqueous NaOH

    $3\ NaOH \rightarrow 3\ Na + 3/4\ O_2 + 3/2\ H_2O$
  - Aqueous $NaBO_2$

    $NaBO_2 + 3/2\ H_2O \rightarrow Na + 1/4\ O_2 + H_3BO_3$

- Current efficiency ~100% (MCEL)
- Theoretical current efficiency without membrane is 50% (commercial ~40%).



Electrolyzer

NaOH and $NaBO_2$ Electrolysis (MCEL)

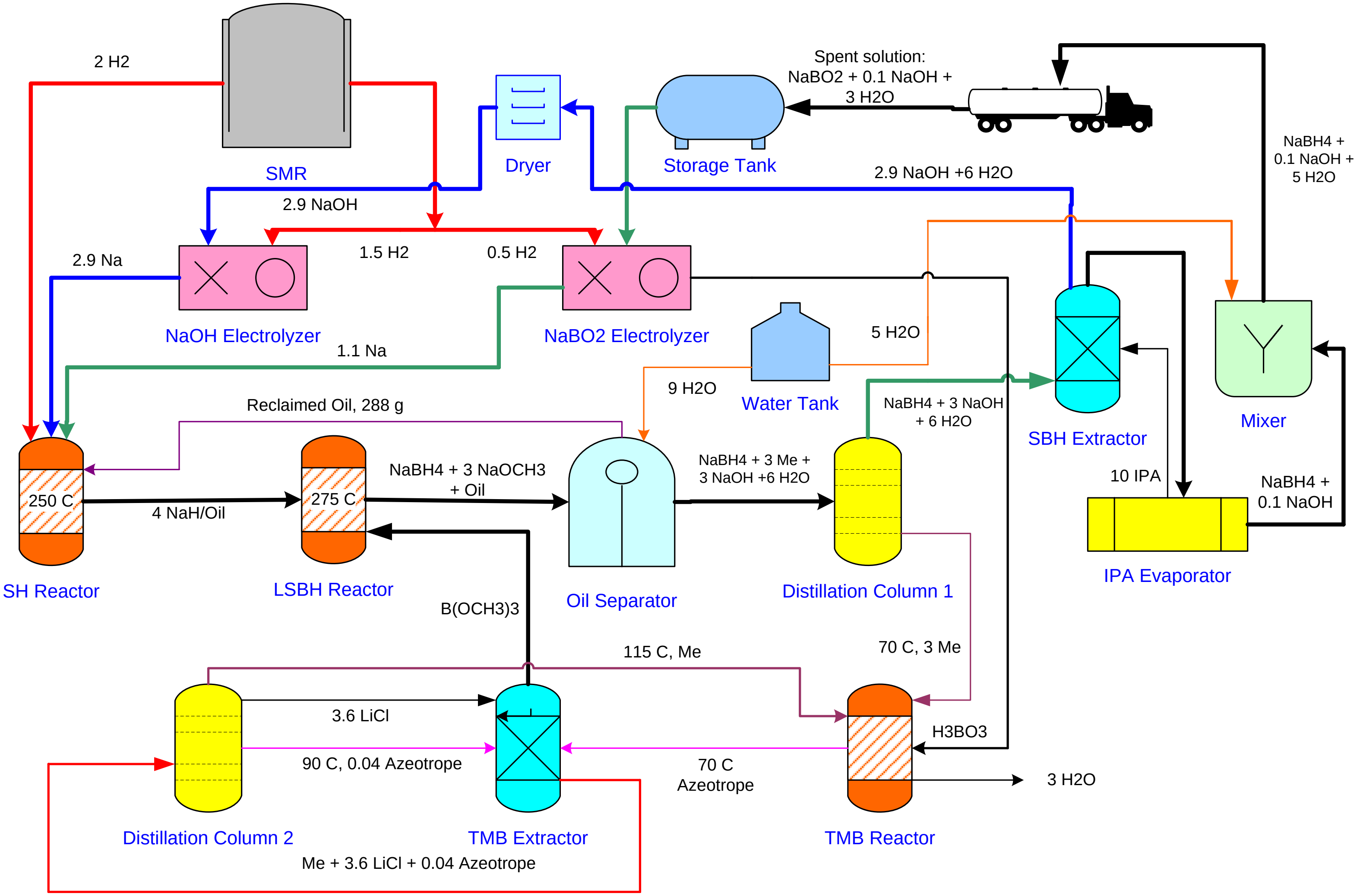
Parameters	**Anhydrous NaOH**		**Aqueous NaOH**		**Aqueous $NaBO_2$**	
	H_2 assist	**w/o assist**	**H_2 assist**	**w/o assist**	**H_2 assist**	**w/o assist**
Current efficiency, %	100	100	100	100	100	100
Voltage efficiency, %	90	80	72	70	70	77
Overall efficiency, %	90	80	72	70	70	77
Temperature, ^{o}C	350	350	110	110	130	130
Cell operating voltage, V	1.3	2.7	2.5	4.0	2.8	4.0
Electricity, kwh/kg Na	**1.5**	**3.1**	**2.9**	**4.7**	**3.3**	**4.7**

Data provided by Millennium Cell

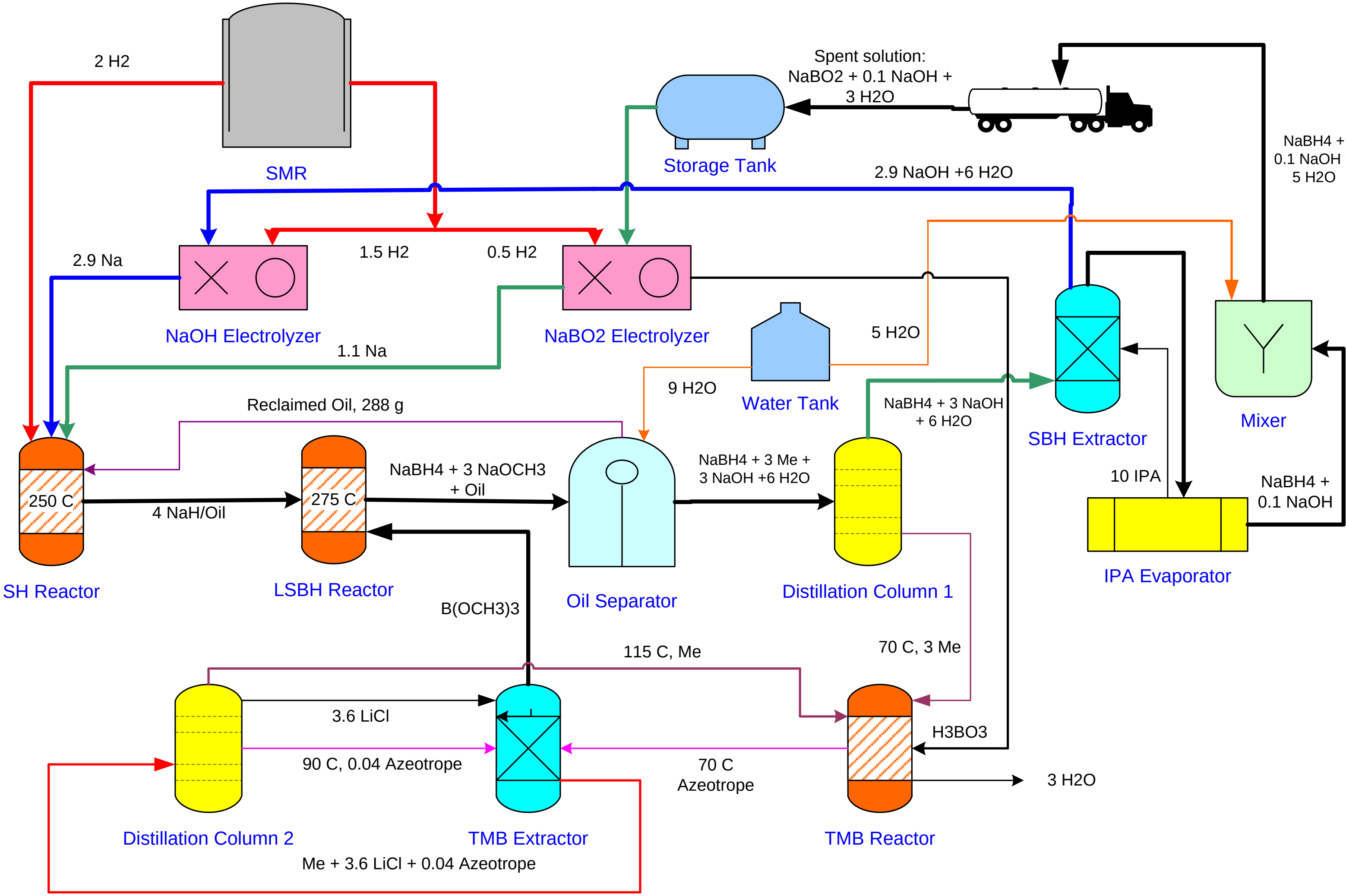
Brown-Schlesinger Processes

- *SH production*
  - React Na with H_2 in mineral oil to form SH
- *TMB production*
  - Dissolve boric acid in methanol to form TMB solution. TMB is separated by extraction and distillation
- *LSBH production*
  - React SH with TMB to form SBH and sodium methoxide
  - The product is hydrolyzed to form a solution of SBH, methanol, sodium hydroxide, and water
  - Methanol is distilled off and used in TMB production
- *Final product*
  - IPA is used to extract SBH from LSBH solution. Water is mixed with dry SBH to the desired SBH concentration

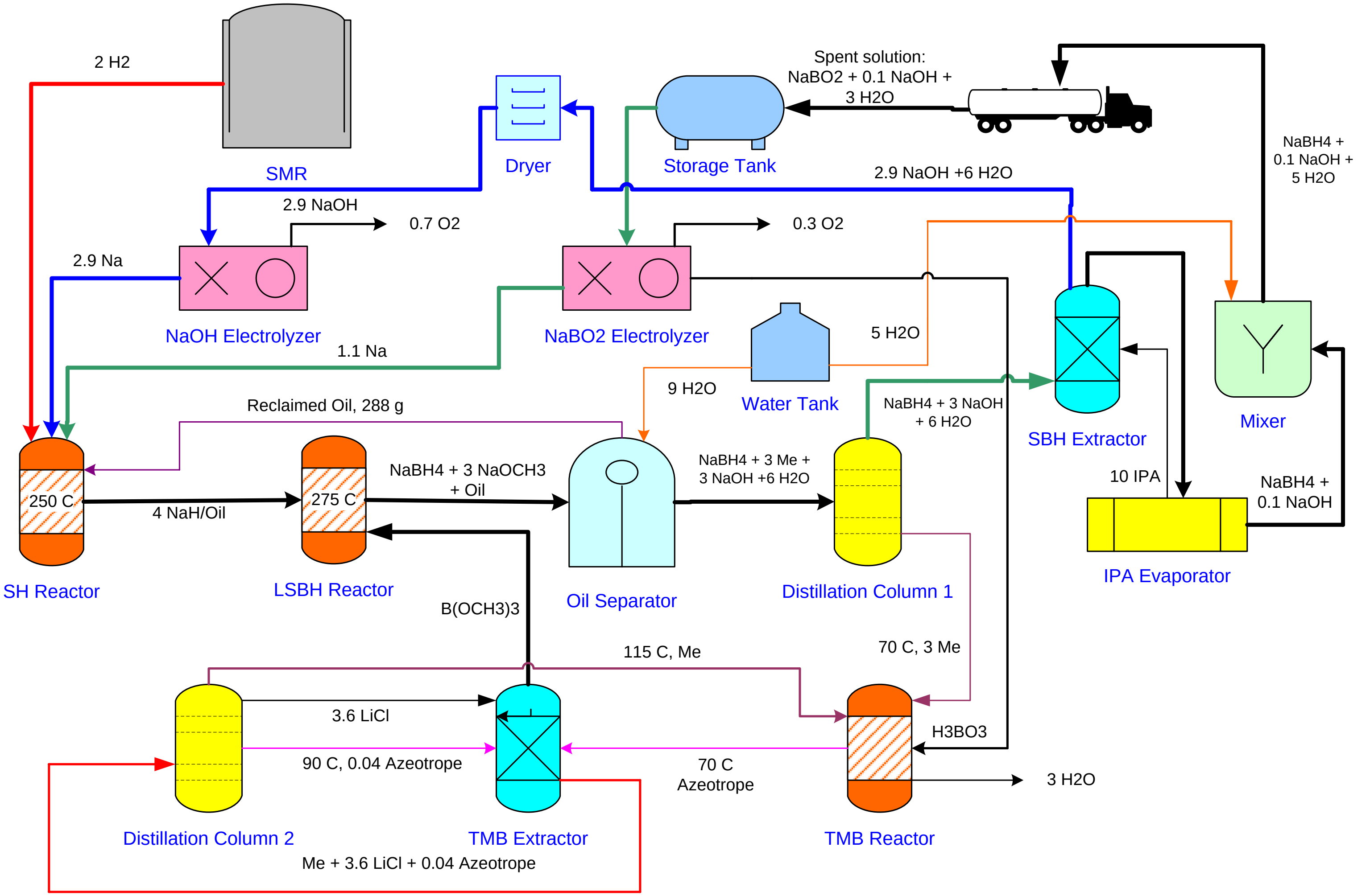
AnH-AqH: H_2-Assisted, Anhydrous NaOH/Aqueous $NaBO_2$



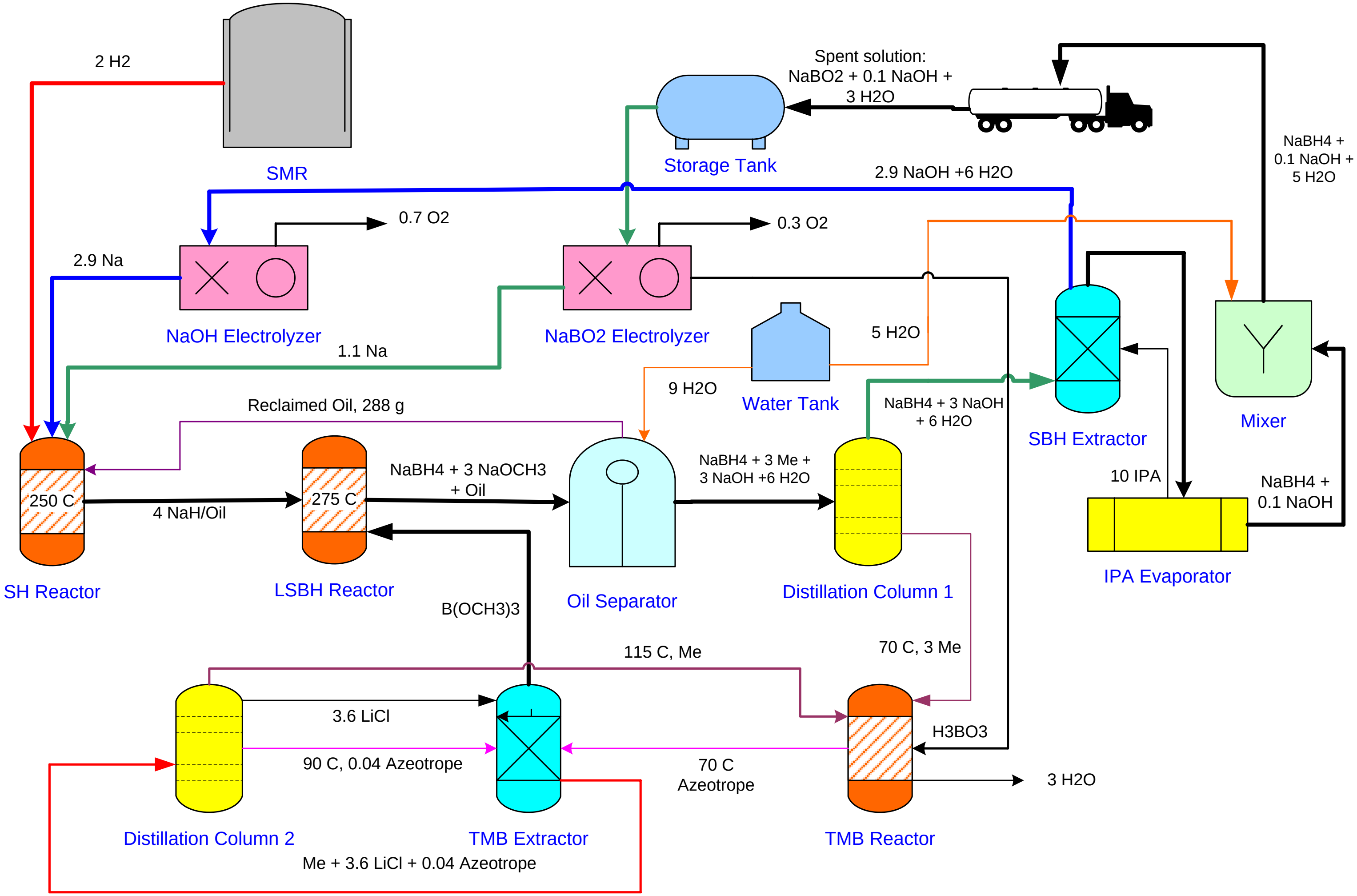
AqH-AqH: H_2-Assisted, Aqueous NaOH/Aqueous $NaBO_2$



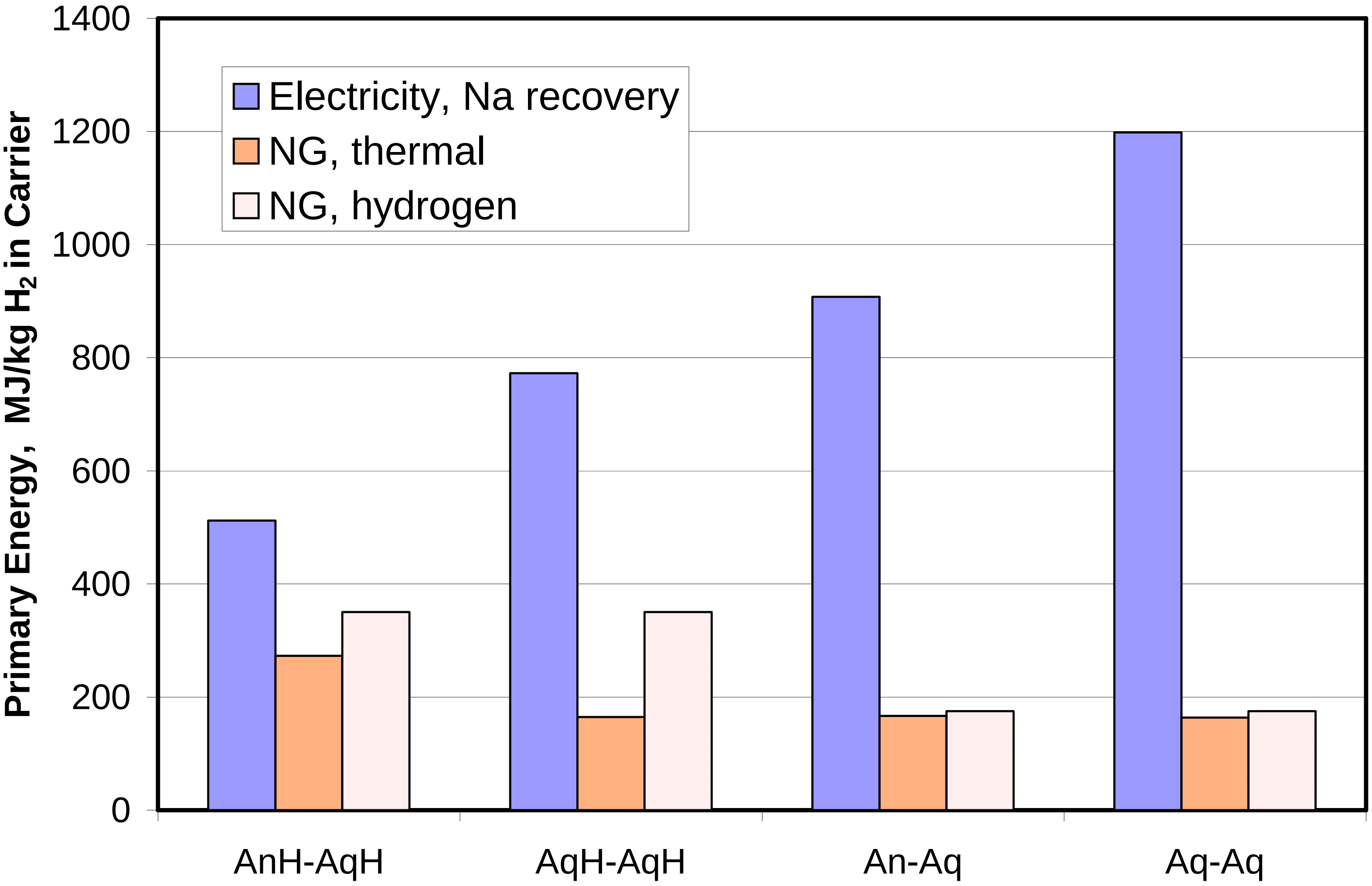
An-Aq: w/o H_2 Assist, Anhydrous NaOH/Aqueous $NaBO_2$



Aq-Aq: w/o H_2 Assist, Aqueous NaOH/Aqueous $NaBO_2$



Energy Consumption (50% Heat Integration, U.S. Grid 2015)



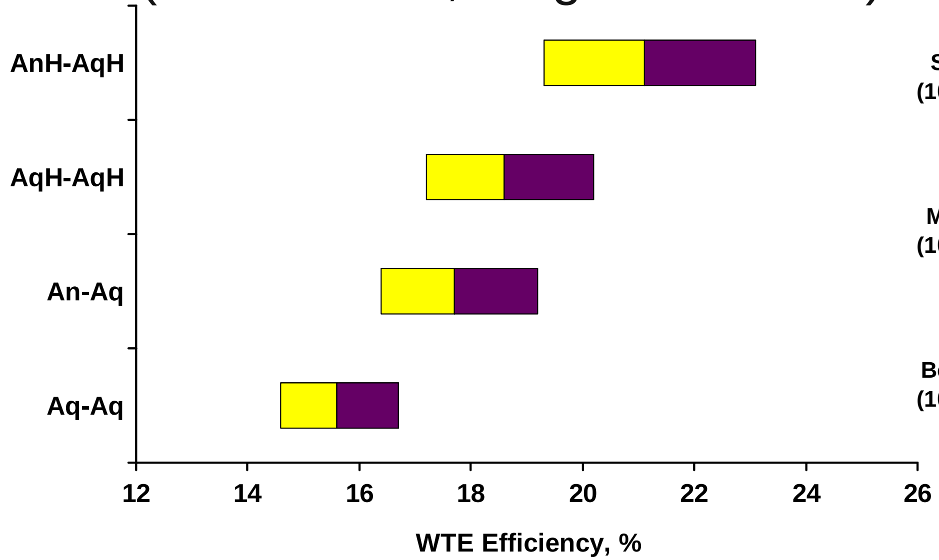
Material Losses in Regeneration Plant

- Sources of Na losses
  - Formation of Na compounds in parallel to SBH in Brown-Schlesinger process
- Sources of CH_3OH losses
  - Fugitive emissions
  - Vent gases from methanol scrubbers
- Sources of H_3BO_3 losses
  - Less than 100% yield of azeotrope in TMB production (ex., formation of methyl metaborate)
- Energy consumption to replenish lost materials
  - Na from NaCl electrolysis: 9.1 kWh/kg
  - CH_3OH from natural gas: 63% efficiency (GREET data)
  - H_3BO_3 from rxn of inorganic borates with H_2SO_4: 6.3 MJ/kg

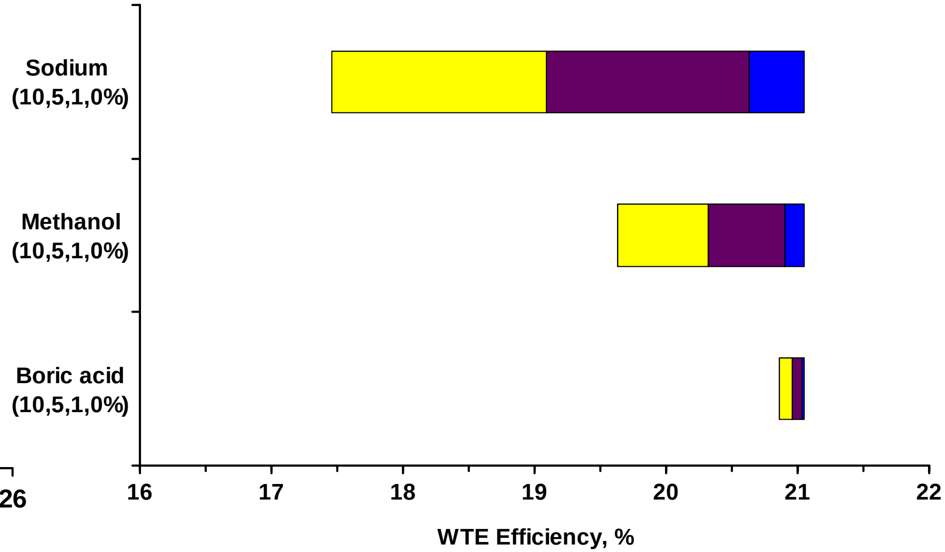
SBH Regeneration Efficiency with Closed Brown-Schlesinger Process

- WTE efficiency is 17-23% for H_2-assisted electrolysis options and 14-19% without H_2 assist.
  - Results based on 2015 U.S. grid 2015 & 80% regen plant thermal efficiency
- Na recovery accounts for 45-80% of total energy consumed in SBH regeneration.
- Loss of material, especially Na, may further reduce the efficiency.

Effect of heat integration
(Base = 50%, range 0 to 100%)



Effect of material losses



Summary and Conclusions

- Four Na recycling options (NaOH and $NaBO_2$ electrolysis) for SBH regeneration were analyzed with FCHtool.
- Current efficiency approaches 100% (MCEL data) compared to less than 50% without membrane (industrial process).
- Heat integration within the regeneration plant was varied parametrically.
- Na recovery accounts for 45-80% of the total energy consumed in SBH regeneration.
- The WTE efficiency is 17-23% for H_2-assisted electrolysis options and 14-19% without H_2 assist.
- Loss of material, especially Na, may further reduce the efficiency by up to a few percentage points.