Energy & Environmental Research Center (EERC)

HYDROGEN PRODUCTION FROM HIGH-VOLUME ORGANIC CONSTRUCTION AND DEMOLITION WASTES (FE 0032183)

NETL Review Meeting
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Project Objectives

1. Develop integrated gasification & gas cleanup process to produce 99% hydrogen from highly contaminated construction and demolition (C&D) waste feedstock.
2. Determine disposition of key contaminants: As, Cr, Cu, B, Pb, Ni, Zn, & Cl
3. Verify efficacy of proprietary techniques to sequester As, B, Cr in ash, and protect downstream hydrogen shift reaction catalysts
4. Investigate tar-cracking options for biomass including C&D contaminants.
5. Replicate commercially-available oxygen-blown fluidized-bed gasification technology on real-world C&D waste over 3 physical test campaigns.
6. Conduct technoeconomic and greenhouse gas lifecycle analysis on a commercial-scale plant to be located in Kapolei, Hawaii
7. Model integrated gasification/syngas cleanup system for modular-scale 5 to 50 MW_e scale plant utilizing high-negative-value C&D waste feedstock.
8. Model computational particle fluid dynamics (CPFD) fluid-bed gasifier bed reactions and non-organic material removal

Scope of Work

- Utilize “real world” C&D Waste feedstock and produce industrial hydrogen
- 3 trials of gasifier/syngas cleanup train testing in separate weeklong campaigns
  - Trial 1: Improve shift catalyst performance through key contaminant sorbent screening
  - Trial 2: Compare 3 tar cracking options
    - Thermal cracking through higher gasifier operating temperature
    - Commercial tar cracking catalyst, or
    - Partial oxidation of syngas to elevate temperature
  - Trial 3: Demonstrate long term steady-state operation to generate hydrogen
- Technoeconomic (TEA) and Greenhouse Gas Life Cycle Analyses (LCA)
- Computational Particle Fluid Dynamics (CPFD) modeling (in Barracuda™) to facilitate commercial gasifier design for C&D inorganic waste removal
- Develop better understanding of “ABC” heavy metals of C&D waste:

  Arsenic, Boron, and Chromium
  - Arsenic disposition in gasification effluents had been modeled but not physically tested
  - Boron behavior under thermochemical conversion conditions has not been studied
- Validate commercial applications through technoeconomic modeling and simulation

C&D Waste Background Information

- Largest solid waste stream in North America (> 600 million tons / year, per EPA SMM 2018)
- Commercial waste which is commonly source-segregated and aggregated in large quantities (>500 tons/day) near large metropolitan areas.
- >50 million tons a year is wood alone.

Of that:

  - > 8 million tons a year is treated lumber with CCA (chromated copper arsenate)-preservative treated wood and
  - ~20 million tons a year unallowable for biomass power combustion due to Borate and other treatments/paints/resins.

- Majority of C&D debris is not recycled and is disposed in landfills due to treated wood
- Typically low moisture (<20%) indicating economically viable gasification

High-Volume Mixed C&D Waste Recyclers
(C&D Recycler Magazine, May 2010)

Commercial Lumber Treatment Methods and Applications

Industry Wood Treatment Levels			**Recommended Applications**
0.25	pcf	Alkaline copper quaternary (ACQ)	Standard small-dimension wood: 2” x 4” x 8', etc.
0.4	pcf	ACQ	Joists and beams, ground contact
0.6	pcf	Chromated copper arsenate (CCA)	Freshwater, ground, extreme weather, and larger-dimensional lumber for commercial applications
0.8	pcf	CCA	Brackish water and government construction
1	pcf	CCA	Not stated
2.5	pcf	CCA Micronized copper azole (MCA)	Saltwater applications Not stated
1.25	%	Disodium octaborate tetrahydrate (SBX/Hi-Bor)	Interior only
7.5	%	SBX/Hi-Bor	General construction for termite resistance
2	%	Copper naphthenate	Field treatment for end cuts and borings

Source: American Wood Protection Association (AWPA)

C&D Waste to Fuel Processing

Figure 1 One truckload of C&D waste unloaded at Island Recycling Inc.

Figure 3 C&D waste shear-shredded to 2" minus and screened for metals, preparing for hammermilling

Figure 2 C&D waste shear-shredded to 4" minus and screened for ferrous and non-ferrous metals in a car shredder

Figure 5 Hammermilled C&D waste "fluff," preparing to be pelletized

Figure 6 Pelletized fuel feed used for C&D waste-to-hydrogen gasification trials

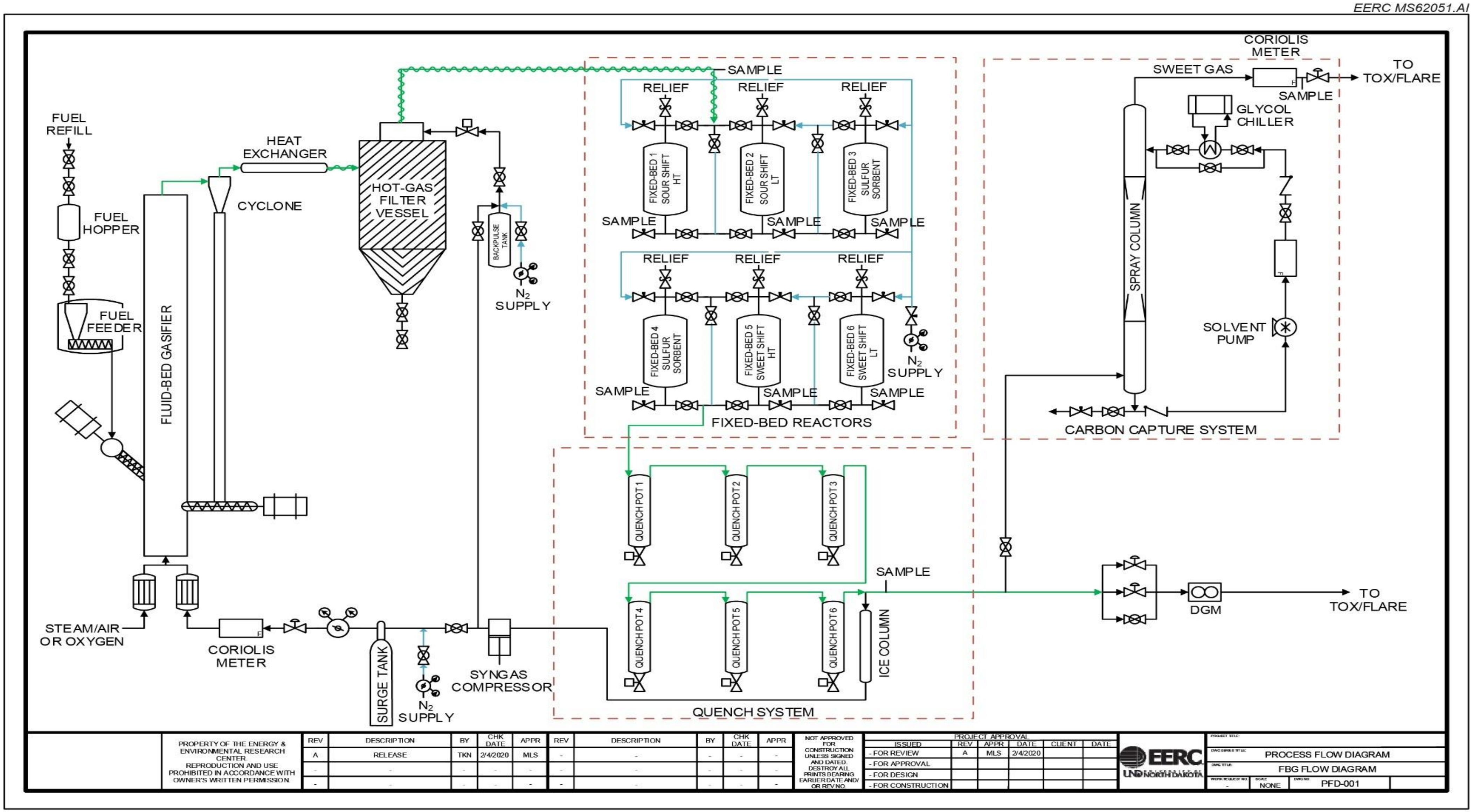
Ranges of Proximate, Ultimate, Heating Value, and X-Ray Fluorescence Analysis of C&D Waste Feedstocks

Moisture, wt% AR*	2.2–7.7
Volatile Matter, wt%	71.4–79.1
Fixed Carbon, wt%	16.4–18.8
Ash, wt%	4.4–8.7
Carbon, wt%	46.9–52.0
Hydrogen, wt%	6.7–5.8
Nitrogen, wt%	0.43–0.87
Sulfur, wt%	0.09–1.00
Oxygen, wt%	34.2–38.1
Higher Heating Value	7868–8126
Chlorine	0.10–0.59
Ash Analyses, wt%	
SiO_2 Ash Basis	19.9–23.9
Al_2O_3	6.1–7.2
TiO_2	0.91–4.90
Fe_2O_3	1.4–9.0
CaO	25.5–26.6
MgO	2.40–12.40
Na_2O	2.2–5.2
K_2O	0.79–1.20
P_2O_5	0.10–0.40
SO_3	6.02–20.60
Cl	0.68–1.60

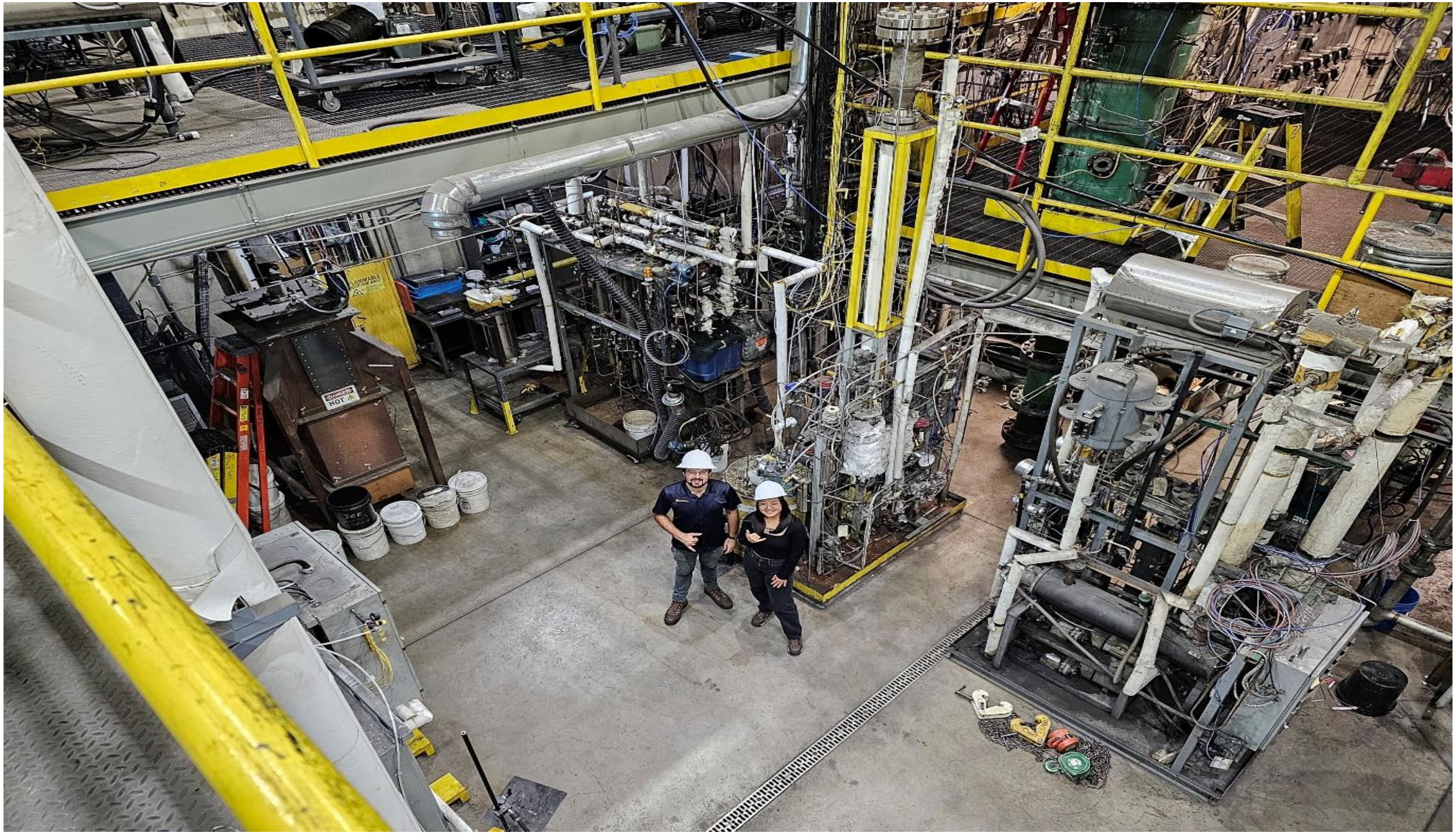
Range of Trace Metal Analyses of C&D Waste Feedstocks

As, ppmw	95–352
B	215–673
Ba	6.1–36.4
Cr	8.7–185
Cu	125–1639
Pb	42.9–480
Ni	16.0–54.9
Zn	431–915
Hg	0.037–0.150

Trial #1: C&D Feedstock Process Flow Diagram (PFD)



High-Pressure Fluidized Bed Gasification Laboratory



Primary Results: C&D Waste Gasification Test 1

Accomplishments towards objectives:

- ✓ 70 hours of continuous gasification operation were achieved
- ✓ > 99.5% Arsenic capture in bed/filter ash, upstream of catalysts
  - ✓ Successful sequestration with 3 select bed additives
  - ✓ Verified disposition in bed ash, fly ash, catalyst, sorbent, condensate, and gas Method 29 sampling
- ✓ 100% of ash samples passed Toxic Characteristics Leachate Protocol TCLP for heavy metals, VOCs, SVOCs
- ✓ Acceptable sweet shift catalyst deactivation rates were observed
- ✓ All measured arsine (AsH_3) levels were at or below permissible exposure limits
- ✓ Continuous physical operation at pilot scale on real-world C&D waste was achieved – no feeder issues

Lessons learned for future investigation:

- Some bed agglomeration at higher gasifier operating temperature was observed, requiring techniques for control of sodium/alkali silicate “clinker” formation
- Chlorine levels were high, need to be better controlled for both better catalyst/sorbent performance and lower-cost metallurgy at commercial scale
- Organic tar deposition around quench relatively high, confirming additional tar cracking would be required.

Preliminary Results:
Greenhouse Gas Lifecycle Analysis for Hydrogen

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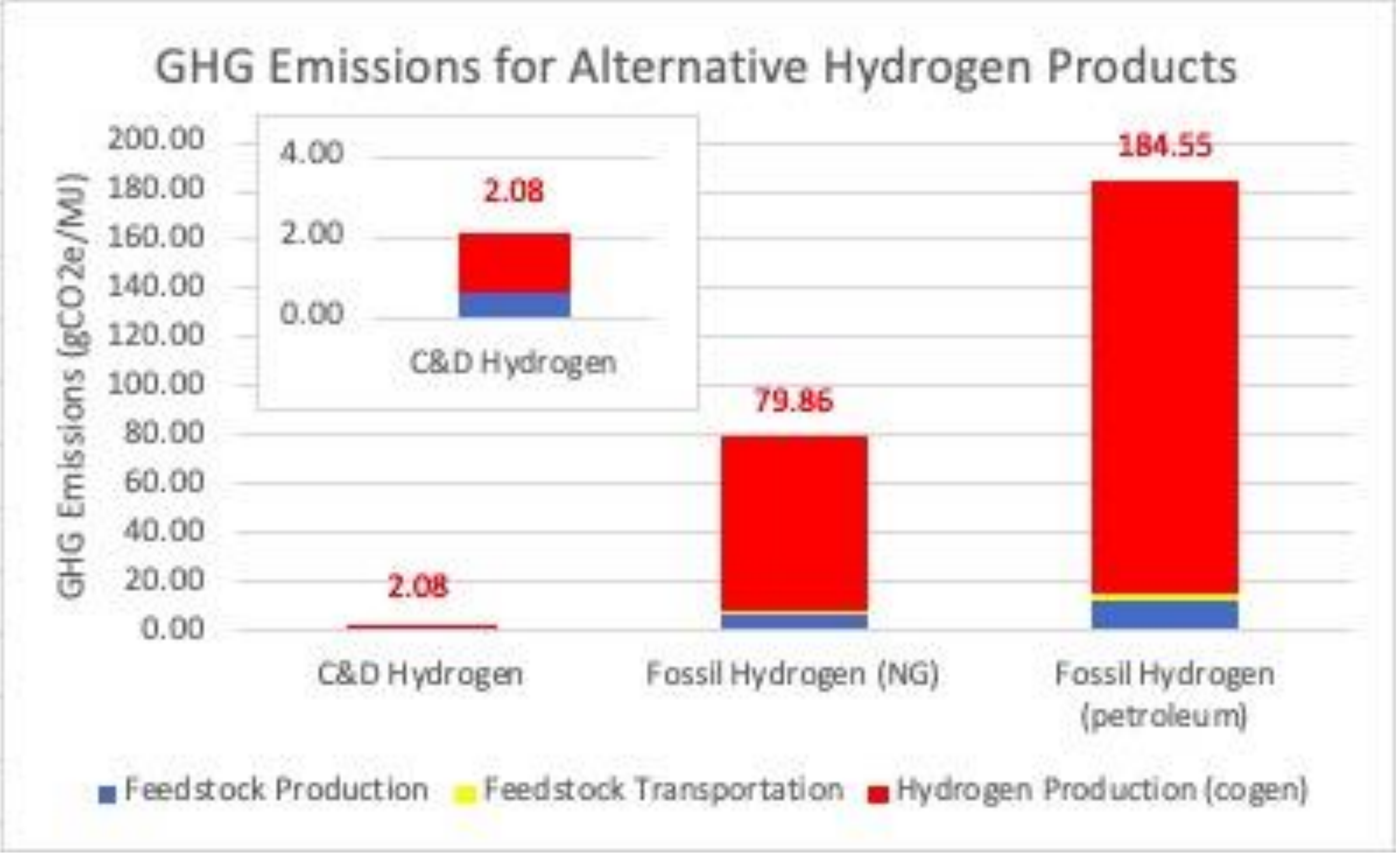
Conclusions:

- Investment-grade carbon credit eligible
- Near-zero carbon intensity at 2.08 gCO_2e/MJ
- 97% reduction when compared to North American natural gas-derived H_2
- 99% reduction compared to petroleum gas-derived H_2



Trial #2: Investigation of Tar Cracking Options

Options Considered:

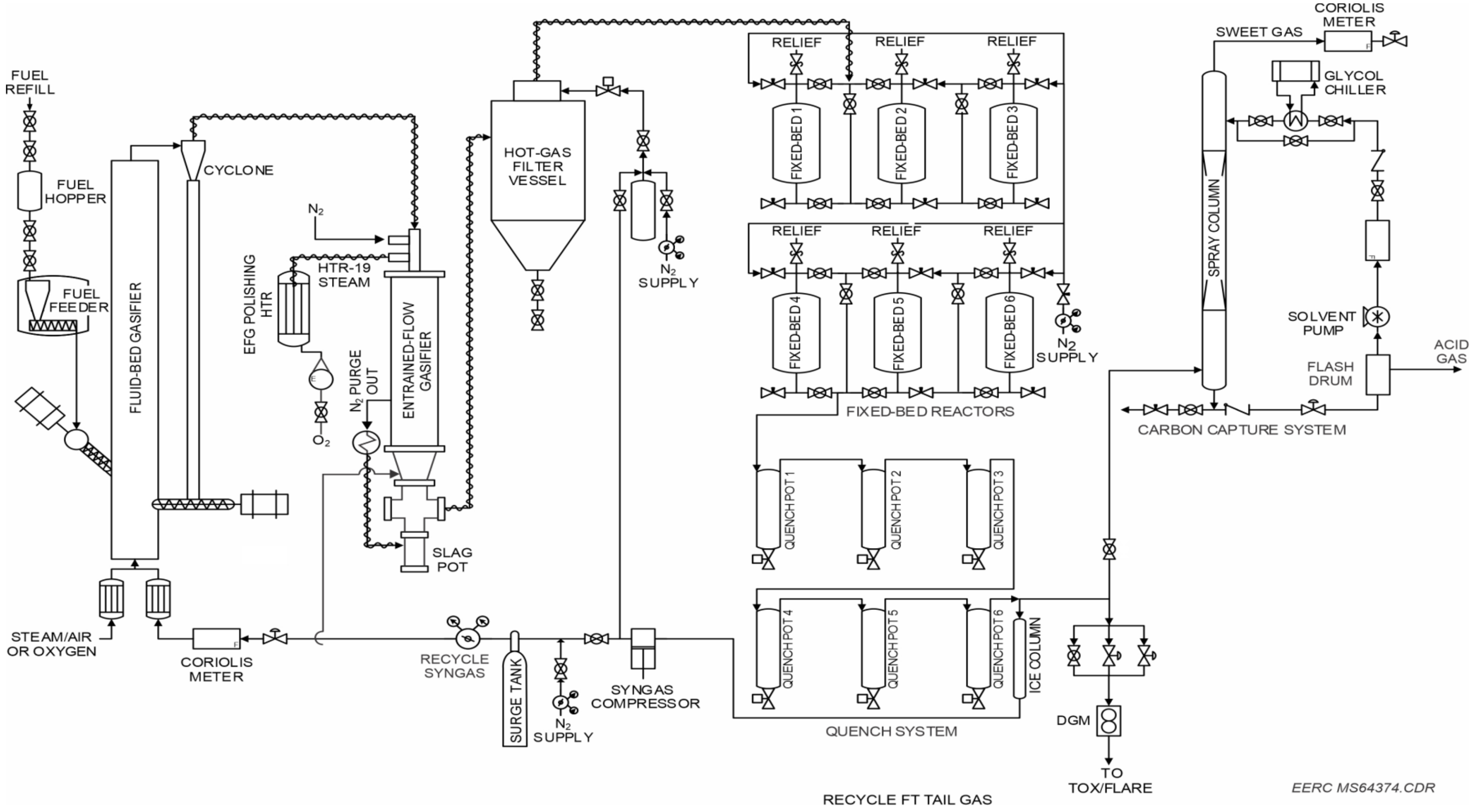
1) Catalyst: High temperature tar cracking catalyst on honeycomb matrix
2) Second-stage tar cracking on outlet of filter with no ash present
   - Requires more oxygen
   - Lose thermal efficiencies to achieve higher temperatures on syngas after lower temperature filtration
3) Linde Hot Oxygen Burner technology™ (HOB) or similar technology*
   - Test at outlet of gasifier with fine ash
   - Possible re-volatilization of arsenic at high temperatures
   - Reported greater than 99.9% tar conversion
   - Note this is the current commercial option pursued by Sungas Renewables™

Option Selected: Option 3 due to

- Lower risk compared to catalyst poisoning with contaminated feedstock, plus
- Ability to use existing entrained flow gasifier at EERC as second stage tar cracker

Trial #2: Tar Cracking of C&D Waste-Derived Syngas Process Flow Diagram

(Simulation of Sungas Renewables & Linde HOB integrated system)



EFG Test Conditions

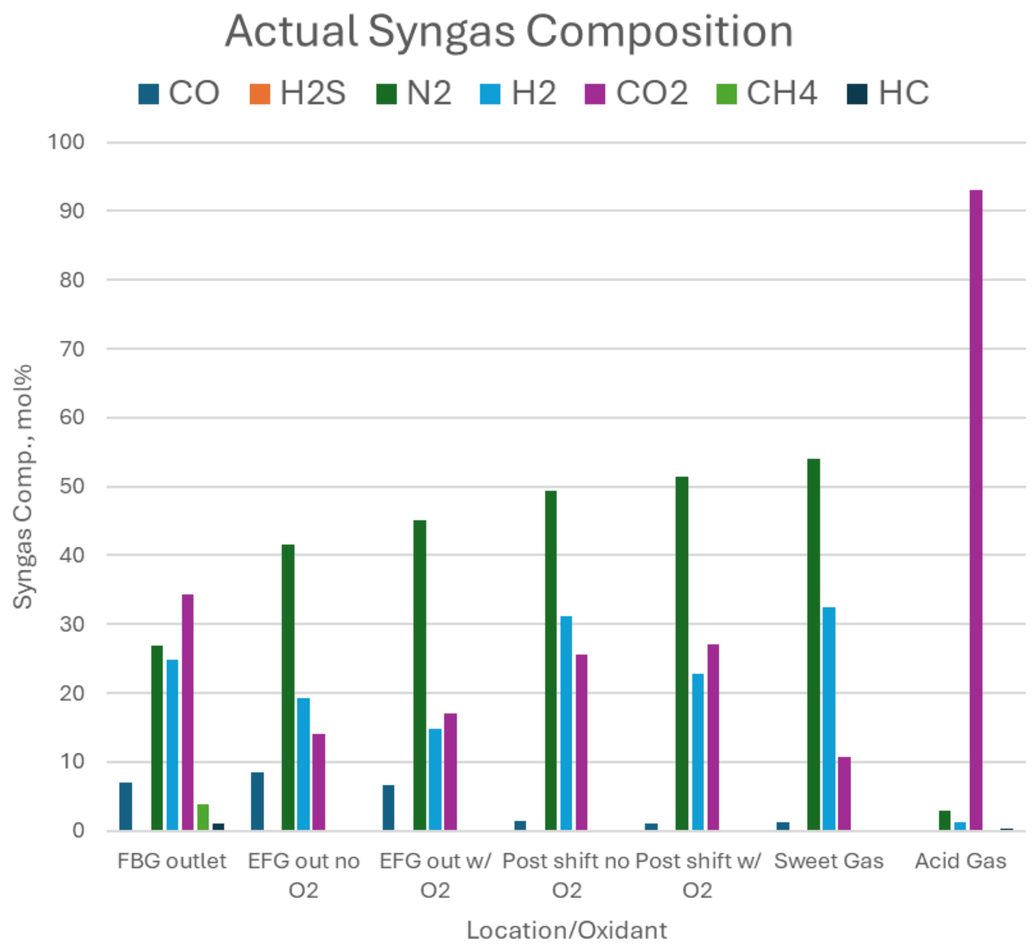
- 3 Different Bed Additives
- 2700°F & 2750°F
- 2 sec residence Time
- EFG Ø ratio adder:
  - 0% and 10%

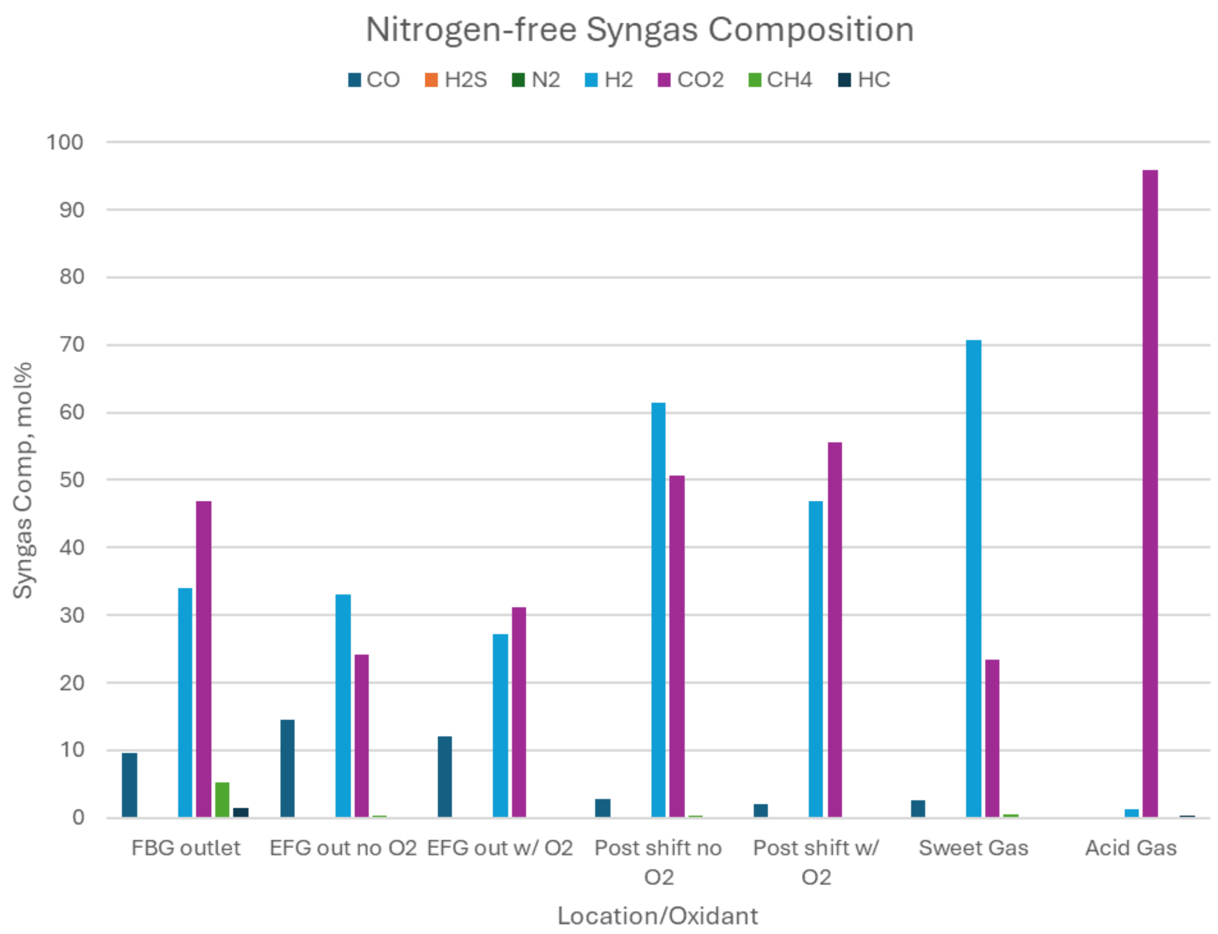
Preliminary Results: Two-Stage Tar Cracking of Syngas from C&D Waste Gasification (Nov 2023)

- Approximately 70 hours of C&D fuel feed to gasifier.
- Aromatic hydrocarbons concentrations were reduced by over 80% but were still higher than the typical outlet of oxygen-blown entrained flow gasifier test
- Aliphatic hydrocarbon concentrations were over 95% reduced and were similar to typical oxygen-blown entrained flow gasifier test
- Recovered ash was mostly fly ash instead of slag; EFG reactor exit piping not designed for that ratio and suffered ash overloading
- Significant conversion of carbon in the cyclone fines observed with much less (> 50%) carbon in the ash than without second stage due to additional carbon gasification at the high temperatures
- Oxygen addition did result in some oxidation of syngas constituents thereby reduced overall gas energy value

Syngas compositions by location in process

(EERC HPFBG Pilot Plant, C&D Waste feedstock, Nov 2023)





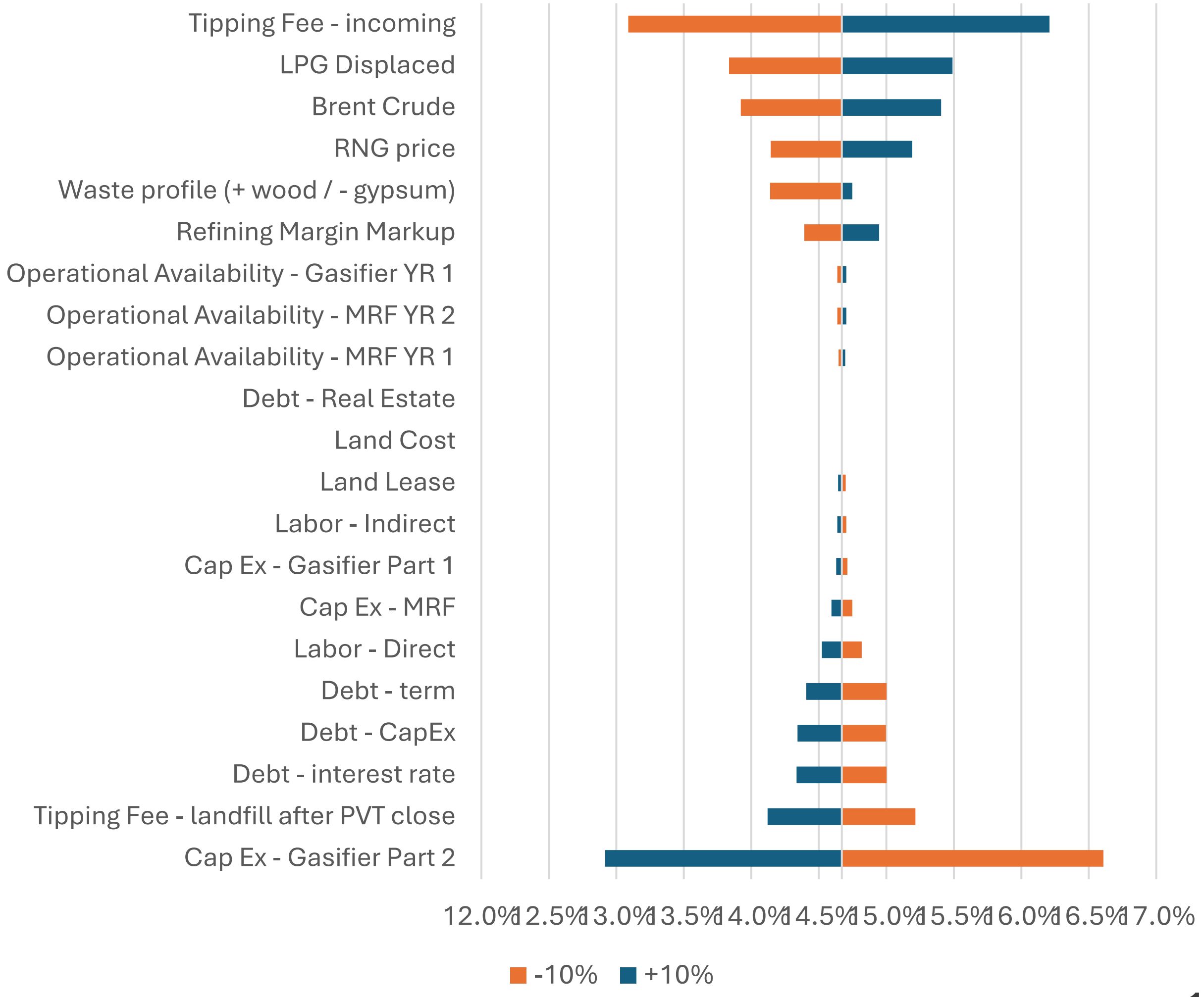
Preliminary Results: Contaminant capture in tar cracking tests

- Arsenic capture still was greater than 98.5% after second stage tar cracker and filter cake but only about 90% captured when sampled between FBG outlet and EFG inlet
- Boron approximately 86% captured after second stage and filter cake
- Chlorine < 50% captured after second stage and filter
- All other trace metals > 99.9% after second stage tar cracker and filter cake.
- No arsenic detected in arsine guard bed or further downstream in catalyst beds
- Chlorine and small amounts of boron was detected in down stream catalyst beds

Preliminary Results: Technoeconomic Modeling Sensitivity Analysis of 5 & 50 Mwe Scale Plants

Conclusions:

- Profitable at 5MWe scale in certain markets
- Investment-grade internal rate of return (IRR) at 50MWe scale
- Financial return most sensitive to
    1. Capital cost of the plant
    2. Waste tipping fee revenue
    3. Marketable volume of product
    4. Fossil fuel price competition
    5. Inorganic waste disposal cost
    6. Debt interest rate cost



Conclusions

✓Hydrogen production from gasification of C&D waste appears commercially viable for modular systems at 5 to 50 Mwe scale

✓Carbon management through Greenhouse Gas reduction appears highly favorable

✓Successful control of arsenic and other trace metals has been demonstrated

✓High level of tar cracking was achieved with oxygen-injected high temperature second stage, indicating technical feasibility for C&D Waste feedstock.

- Further testing to scale up from HPFBG ¼ ton per day to commercial scale 50 & 500 tons per day is prudent
- Further development of Boron and Chlorine capture technology recommended
- Further process engineering to support financing of a first-of-a-kind commercial plant is needed

Future plans

- 3rd and final physical C&D waste gasification trial with optimized conditions.
  - Optimize tar cracking utilizing high temperature second stage utilizing O_2 injection.
  - Focus on further syngas cleanup of chlorine and boron in last test campaign
- Process engineering model and simulation at commercial scale in Aspen™
- Iterate technoeconomic analysis (TEA) of H_2 production at 5 & 50 Mw_e
- Update greenhouse gas lifecycle analysis using optimum process conditions
- Complete CPFD model to inform modifications to a commercial fluidized bed gasifier design for C&D waste feedstock
- Output results to Simonpietri Enterprises LLC and its cost share partners:

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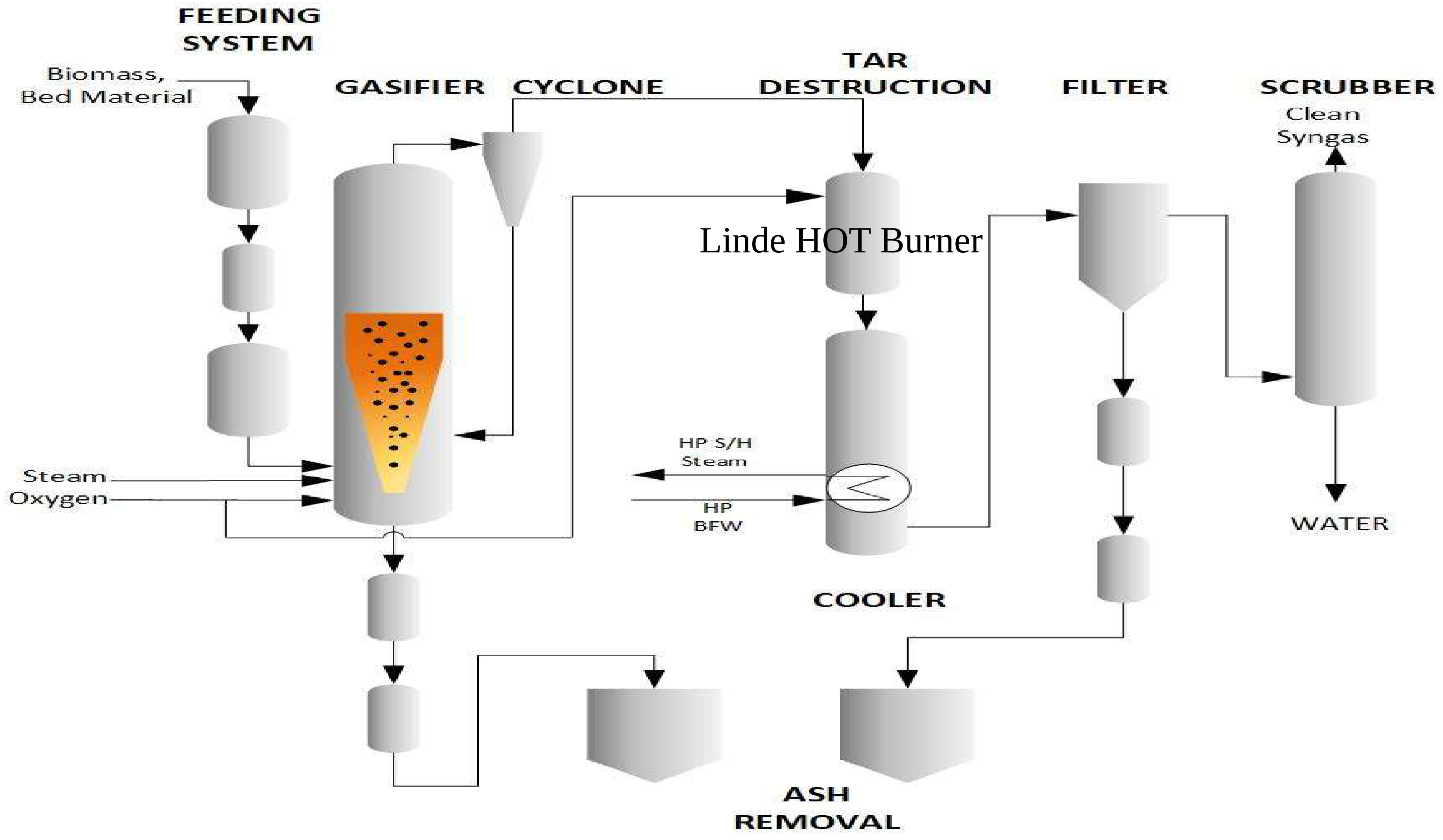
THANK YOU

Critical Challenges. Practical Solutions.

Percentage of Hazardous Ingredients in CCA-Treated Lumber

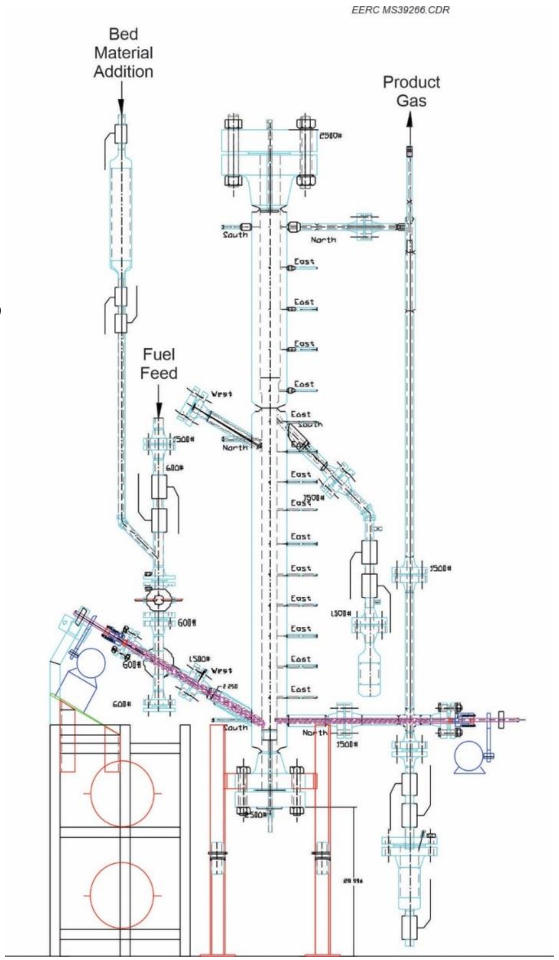
Treatment Level, pcf	0.25	0.4	0.6	1	2.5
Arsenic Pentoxide	0.3%	0.4%	0.6%	1.0%	2.6%
Copper Oxide	0.15%	0.2%	0.3%	0.6%	1.3%
Chromium Trioxide	0.4%	0.6%	0.9%	1.4%	3.3%
Wood Dust	84.3%	84.0%	83.5%	82.5%	78.9%

Sungas Renewable Gasification Island

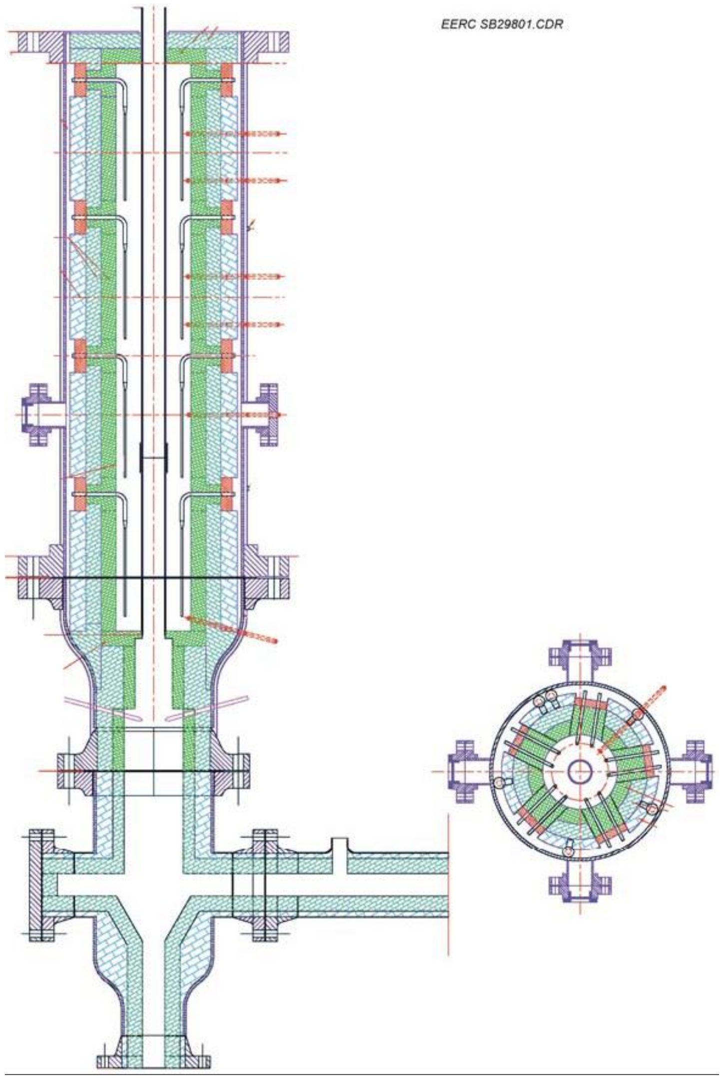


EERC High-Pressure Fluid-Bed Gasifier (HPFBG)

- High-pressure fluid-bed gasifier
- 1800°F (980°C)
- 1000 psi (68 atm)
- Process optimization, fuel behavior, ash and slag behavior, warm-gas cleanup, gas separation, chemicals and liquid fuel production.
- Biomass to petcoke.
- Highly reconfigurable systems.



Bench-Scale Entrained-Flow Gasifier



- Oxygen-blown
- Up to 4.5 kg/hr dry feed
- Temperatures to 1500°C
- Pressures 18 to 21 bar
- Fuel gas 17 to 34 Nm^3/hr
- Electrically heated to minimize heat loss
- Quench design but can operate at elevated outlet temperatures to investigate syngas cooler fouling

Gasification Reactions

$C(s) + H_2O \leftrightarrow CO + H_2$ [carbon-steam]

$C(s) + CO_2 \leftrightarrow 2\ CO$ [Boudouard]

$C_mH_n \leftrightarrow n/4\ CH_4 + (m-n)/4\ C(s)$ [tar cracking]

$CH_4 + H_2O \rightarrow CO + 3\ H_2$ [reforming]

$C(s) + (1/F)\ O_2 \rightarrow 2\ (1- 1/F)\ CO + (2/F-1)\ CO_2$ [oxidation]

$CO + H_2O \leftrightarrow CO_2 + H_2$ [water-gas shift]

$½\ C(s) + H_2 \leftrightarrow ½\ CH_4$ [carbon hydrogenation]