GTI ENERGY

solutions that transform

Spring 2024 Review: FLUIDIZED BED GASIFICATION FOR CONVERSION OF BIOMASS AND WASTE MATERIALS TO RENEWABLE HYDROGEN

Project DE-FE0032176

Martin Linck, *Principal Investigator GTI Energy Project 23302*

2024 FECM/NETL SPRING R&D PROJECT REVIEW MEETING April 23-25, 2024 – Pittsburgh, PA

GTI Energy Overview

GTI ENERGY

*We occupy a unique space between **tradition** and **innovation***

- Moving energy systems solutions from **concept to market**
- Where partners go to **de-risk experimentation**
- Expertise in integrated systems and **low-carbon gases, liquids, infrastructure and efficiency**

Valued Partners

175+

80+ years of experience and leadership in energy production, storage, delivery and use

Research & Development

$1B+

In the past decade

Leading and convening collaborative R&D

Innovation & Commercialization

1,300+

Patents

500 Products

750+ Licensing Agreements

10+ Industry Collaboratives

OTD Operations Technology Development

UTD Utilization Technology Development

ETP Emerging Technology Program

LCRI Low-Carbon Resources Initiative

Project ASTRA

Hydrogen Technology Center

CH4 Collaboratory

H2@Scale

HyPER

VERITAS

OPEN HYDROGEN INITIATIVE

We develop, scale and deploy solutions in the transition to low-carbon, low-cost energy systems

GTI ENERGY

GTI Energy is a leading energy research and training organization

SOURCE | MAKE | MOVE | STORE | USE

World-class piloting facility in Chicago area

500+ Enterprise Employees

TOP WORK PLACES 2019 Chicago Tribune
TOP WORK PLACES 2020 Chicago Tribune
TOP WORK PLACES 2021 Chicago Tribune
TOP WORK PLACES 2022 Chicago Tribune
TOP WORK PLACES 2023 Chicago Tribune

We work collaboratively to address critical energy challenges impacting gases, liquids, efficiency and infrastructure

OTD Operations Technology Development

UTD Utilization Technology Development

ETP Emerging Technology Program

LCRI LOW-CARBON RESOURCES INITIATIVE

GTI Energy Gasification Heritage

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Feedstocks
- Coal
- Biomass

Syngas to Products
- Fuels
- Chemicals
- Synthetic Natural Gas

Syngas to Power
- Integrated-Gasification Combined Cycle
- Gasification to Direct Super-Critical CO2
- Partial Oxidation Turbine

Renewable Energy Transition

Early PDU

HYGAS Pilot Plant

Lab Facility - 1947

IGT

1941 1950 1960 1970 1980 1990 2000 2010 2020

U-GAS Pilot Plant

RENUGAS Pilot Plant

Shanghai Plant - 1995

Flex Fuel Test Facility

R-GAS™ Pilot Plant

Advanced Gasification Test Facility

Shanxi - 2020

R-GAS™ 800 tpd Demo

gri

gti

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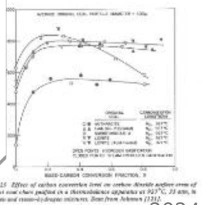
Dr. James L. Johnson



Skive - 2007

Zaozhuang - 2007

Yima - 2012

SunGas RENEWABLES

HALDOR TOPSØE CATALYSING YOUR BUSINESS

AEROJET ROCKETDYNE

ANDRITZ

e.on

UPM

GreatPoint ENERGY

SES SYNTHESIS ENERGY SYSTEMS

Process Concept - Biomass and Waste Materials to Renewable Hydrogen

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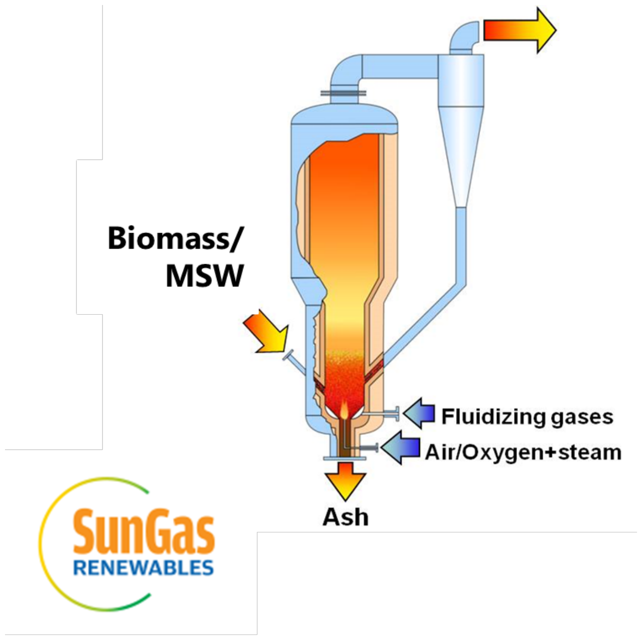
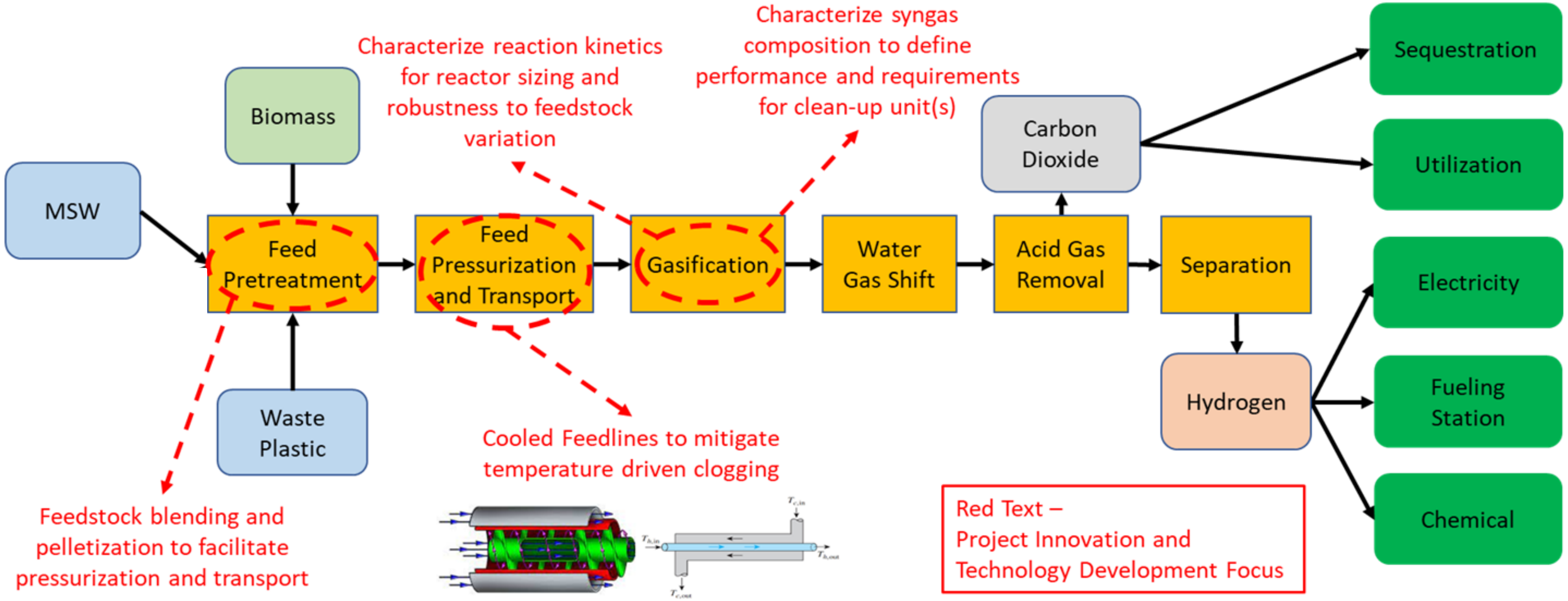
U-GAS

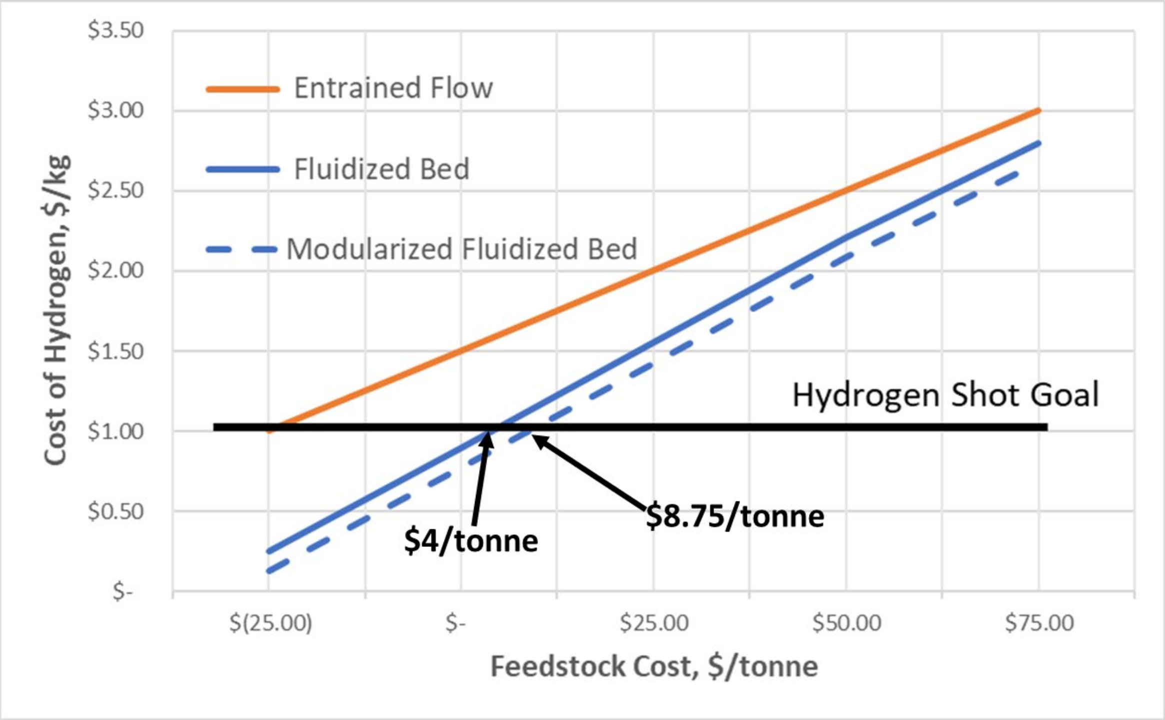


Commercially offered by SunGas Renewables for biomass applications



- Gasification pathway advancements to enable zero emission conversion of waste feedstocks - progression to TRL5

Project Concept – Leverage both Biomass and MSW



- $1/kg of hydrogen is achievable with combined feedstock costs below $8.75/tonne
- Challenges:
  - **Biomass** can reduce process carbon intensity, but is far too expensive ($75-150/ton)
  - **MSW** could generate a considerable tipping fee (~$58/ton) but is heterogeneous, hard to handle, and contains plastics
  - Characterization, ash properties, handling, blending and feeding issues?
- **Project objectives:** Feedstock characterization and pre-treatment, pressurization/injection into bed, gasification

Feedstock Procurement and Preparation

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- Biomass: Loblolly Pine, Southern Georgia, USA
- MSW: Recycle Ann Arbor, MI.
  - Only paper and plastic fractions
- Plastics:
  - 90 wt%: “waste plastic” from EFS Plastic in Ontario, Canada
  - 10 wt%: film plastic - meat packaging - Sealed Air Corporation, SC

A) B) C)

As received

After grinding

A) Biomass (Loblolly pine), B) MSW; C) Plastic.

Example Pellets:

Biomass (50%): MSW (50%)

Biomass (50%): Plastic (50%)

Biomass (50%): MSW (25%): Plastic (25%)

Feedstock Analysis

- Plastics content of MSW and "Plastics" samples not compatible with equipment and protocols
- Significant differences between biomass ash and ash from the two other feedstock types

Sample ID		Biomass		MSW		Plastic waste	
Proximate Analysis result (wt.%)							
	Method	adb[1]	db[2]	adb	db	adb	db
Inherent moisture content	ISO 11722: 2013 [5]	5.4	–	1.5	–	0.9	–
Ash yield	ISO 1171: 2010 [6]	1.0	1.0	12.7	12.9	7.8	7.9
Volatile matter content	ISO 562: 2010 [7]	81.1	85.8	81.1	82.3	87.2	88.0
Fixed carbon content	By difference	12.5	13.2	4.7	4.8	4.1	4.1
Ultimate analysis (wt.%)							
Carbon content	ISO 17247: 2020 [8]	48.2					
Hydrogen content	ISO 17247: 2020 [8]	5.9					
Nitrogen content	ISO 17247: 2020 [8]	0.17					
Sulphur content	ISO 19579: 2006 [9]	N.D[3]					
Oxygen content	By difference	39.4					
Cl and F elemental analysis (mg/kg)							
Chlorine		96					
Fluoride		< 50					
Bulk density (kg/m³)							
Bulk density		228.3		183.3		145.8	

[1]-adb- Air dry basis; [2]-db- Dry basis, [3]- Not determined

Sample ID / Properties	Biomass ash	MSW ash	Plastic waste ash
Ash fusion temperatures (oxidising atmosphere) (°C)			
Initial deformation temperature	1190	1130	1160
Sphere temperature	1210	1150	1170
Hemispherical temperature	1250	1190	1180
Flow temperature	1310	1210	1210
Ash fusion temperatures (reducing atmosphere) (°C)			
Initial deformation temperature	–	1120	1140
Sphere temperature	–	1140	1150
Hemispherical temperature	–	1180	1160
Flow temperature	–	1210	1190
XRF results (wt.%)			
Al_2O_3	31.69	10.09	10.38
CaO	5.19	17.64	20.64
Cr_2O_3	0.03	1.83	0.89
Fe_2O_3	3.63	8.61	5.56
K_2O	0.63	0.42	0.65
MgO	2.03	1.90	4.36
MnO	0.03	0.18	0.13
Na_2O	0.15	7.16	5.68
P_2O_5	0.92	0.36	0.38
SiO_2	48.65	48.20	45.88
TiO_2	1.51	2.34	3.51
V_2O_5	0.05	0.01	< 0.005
ZrO_2	0.09	0.01	0.02
BaO	0.25	0.07	0.20
SrO	0.24	0.02	0.04
ZnO	0.02	0.09	0.16
SO_3	4.73	0.54	0.51
Loss on ignition	0.16	0.53	1.00

Feedstock Tar Characterization

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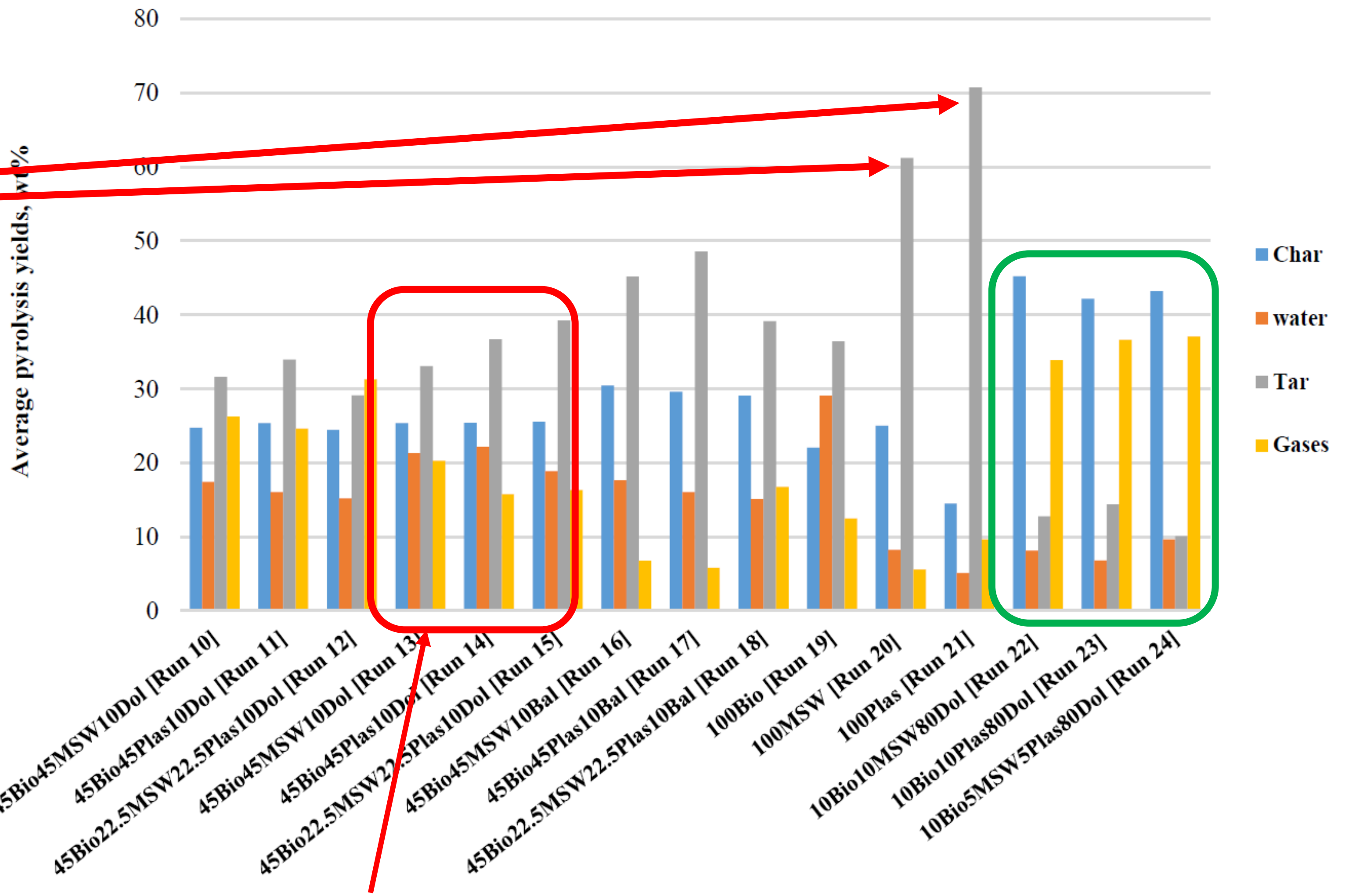
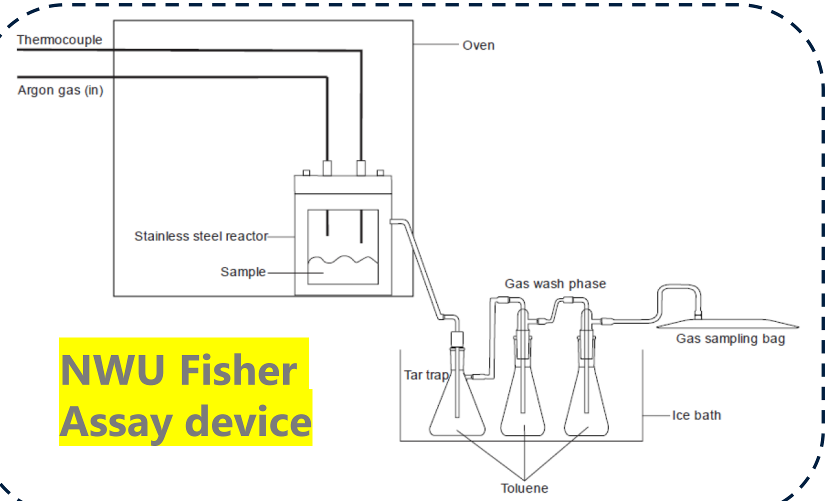
- Work conducted at Northwest University (NWU) in South Africa
- High production of tars from 100% MSW and 100% Plastics feedstocks.
- **Loaded 80% by mass catalyst in Runs 22-24; tar yield dropped! Char yield increased – promising indication**



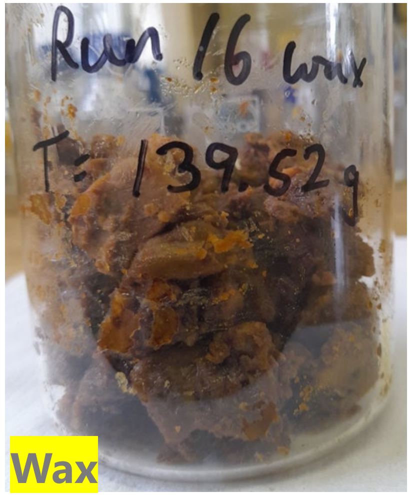


NWU Fisher Assay device

Note: Runs 13, 14, and 15 were carried out at temperatures up to 850 C to match usual U-Gas bed temperatures. All other runs in this series were at 950 C following usual NWU protocol

Feedstock Pyrolysis

- Work conducted at Innoventon lab in South Africa
- Innoventon subjected the pellet samples to a devolatilization protocol (to 650 °C), using various amounts of feedstock pellets and bed material (brown alumina or dolomite)
- The goal of the pyrolysis was to produce char and ash materials from the various feedstocks to be then tested for reactivities using a thermo-gravimetric analyzer (TGA).



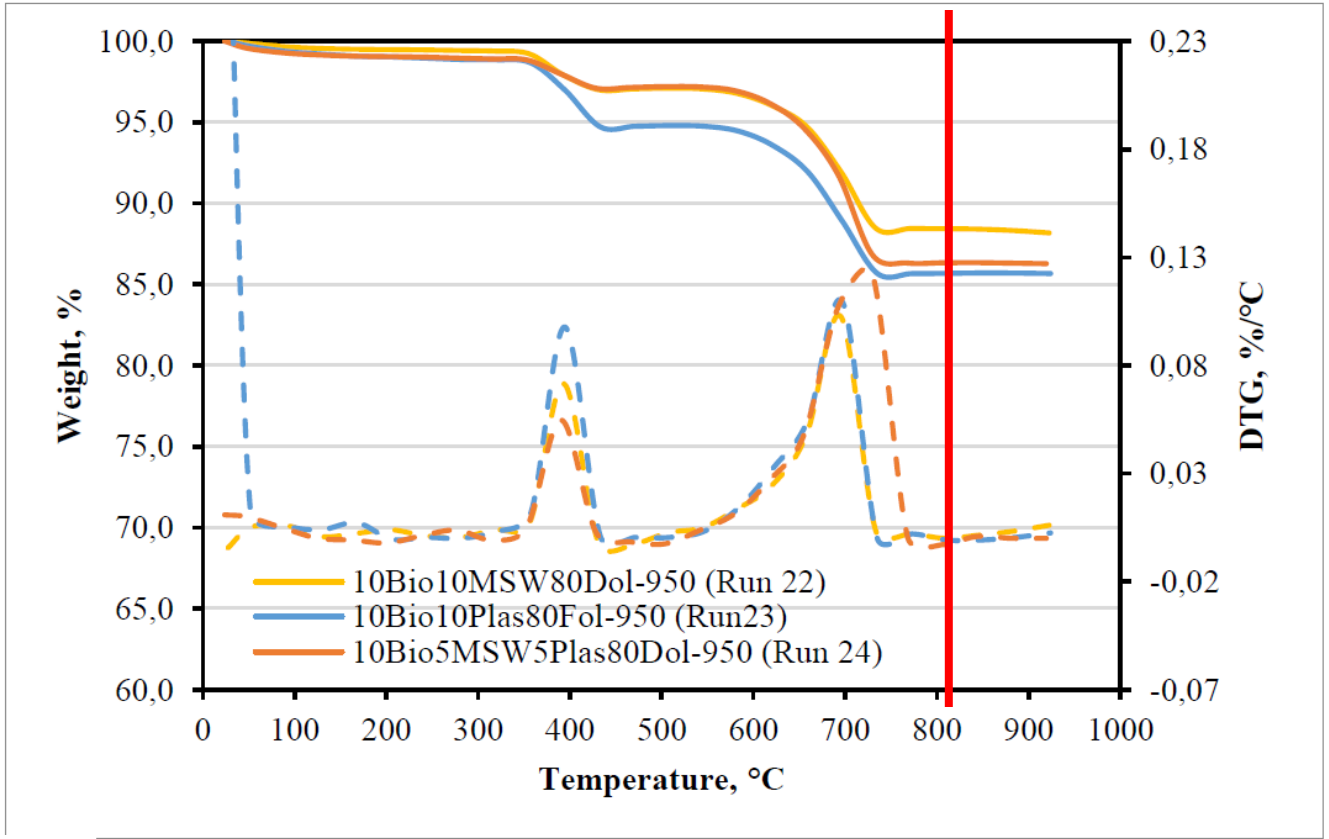
Innoventon Gasifier

Feedstock TGA

- Work performed at NWU
- NWU CO2 Reactivity TGA – carried out in connection with all chars produced from the pyrolysis work at Innoventon.
- The CO2 Reactivity TGA curves associated with chars from all three runs displayed a unique two-step mass loss trend – sequential reaction of different types of compounds comprising the char/coke on the bed material

NWU TGA

Viable Bed Temperature ~ 815 C

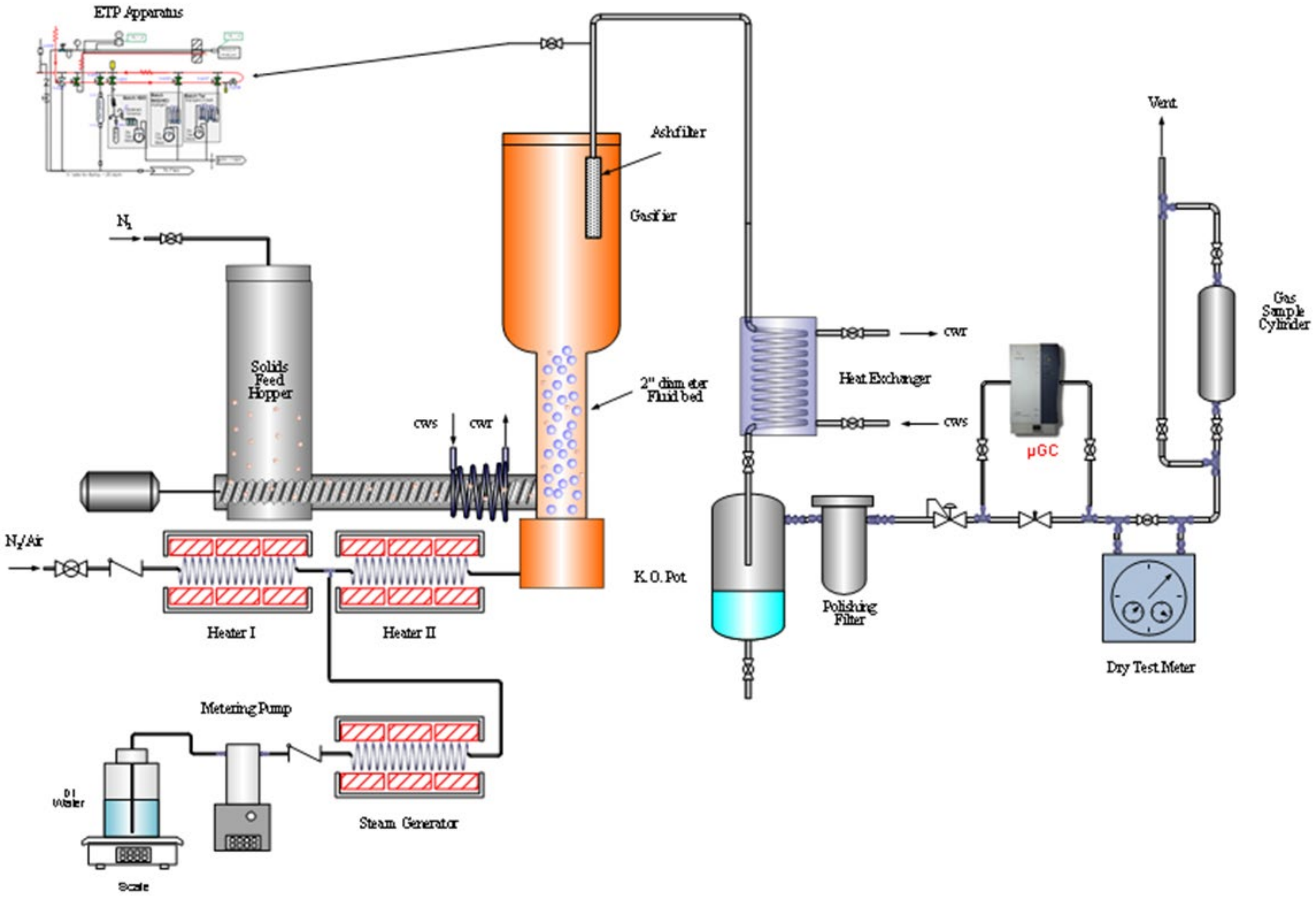


TGA pyrolysis mass loss curves of blends of runs 22 – 24.

Feedstock Bench-scale Gasification

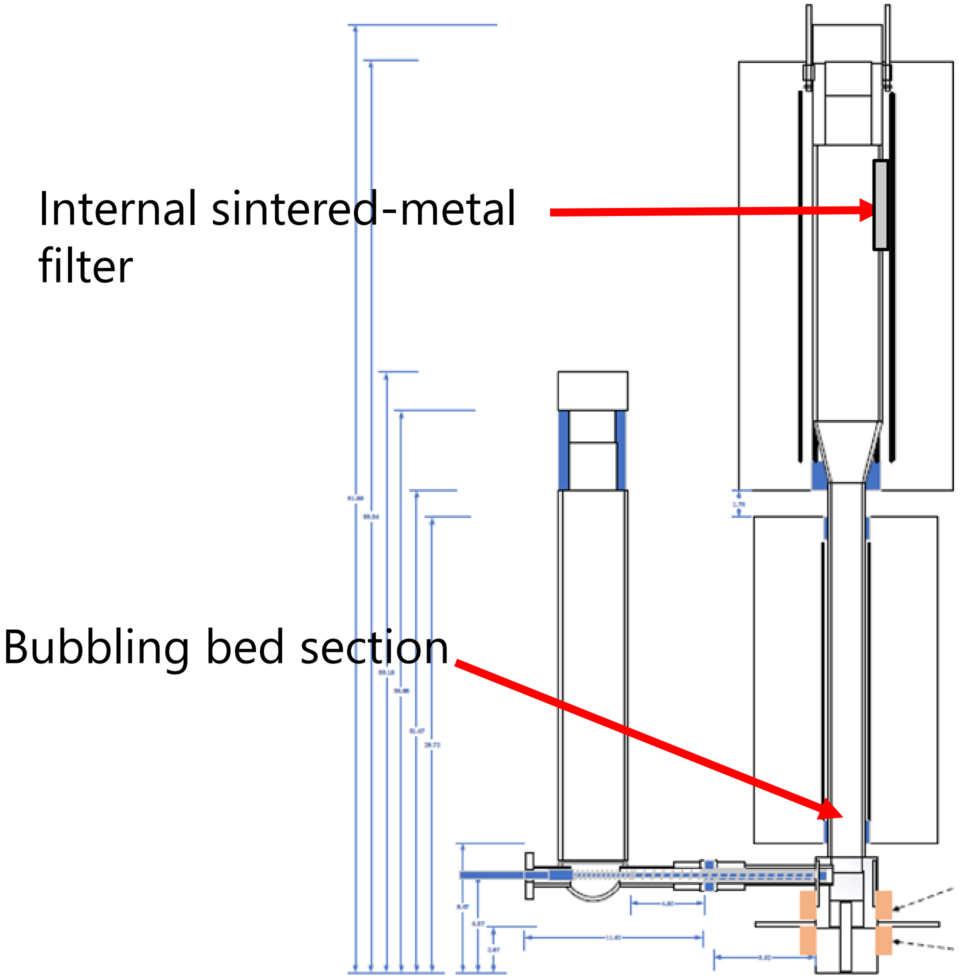
- Work performed in the Mini-bench Unit Gasifier (MBU-G) fluidized-bed gasifier at the GTI Energy campus in Des Plaines, IL.
- Data from South African laboratories indicated that:
  - There was little functional difference between our MSW and Plastics feedstocks – high plastics content in both, similar ash content
  - Both the MSW and Plastics feedstocks were likely to produce very high yields of tars when devolatilized – possible operational problems
  - Very low fixed carbon in all three primary feedstocks – not a problem for U-GAS, though
  - Contacting with large amounts of bed material during devolatilization might react away tar and help produce clean syngas
  - An 800-850 C was likely hot enough to fully react feedstock without melting ash (slag) – desired for U-GAS

Feedstock Bench-scale Gasification



MBU-G Operation Summary

- Dolomite (industrially-relevant), Bed depth ~24″ once fluidized (-80+120 Mesh)
- Dolomite was baked out at 1000 F before loading
- 2″ Sched 40 pipe high-temp alloy lower section
- 4″ Sched 40 pipe disengagement section
- Feed rate 7-10 grams/minute of feedstock
- 50 psig operating pressure; fluidized via N2 and steam
- Sintered-metal filter located inside vessel to remove fines
- Bed target temperature 815 C (1500 F)



MBU-G Test Plan




- Received three INL pellet sample formulations, bought a fourth type of pellet (commercial hardwood for shakedown) – crushed/sieved
- Highly successful series of four experiments
  - 8/16/2023: Shakedown – commercial hardwood pellets
  - 9/12/2023: 50/50/0 (INL Pine Biomass-MSW Pellet fragments)
  - 09/29/2023: 100/0/0 (INL Pine Biomass pellet fragments)
  - 10/05/2023: 50/25/25 (INL Pine Biomass-MSW-Plastics pellet fragments)

MBU-G Feedstocks Analysis

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	100% Biomass - Shakedown	50% Biomass – 50% MSW	100% Biomass	50% Biomass – 25% MSW – 25% Plastics
Feedstock Proximate Analysis (as-received basis)				
Moisture (107°C) wt%:	6.1	6.45	7.25	4.08
Volatile matter as rec'd wt%:	80.1	77.91	79.62	81.6
750°C ash as rec'd wt%:	0.5	6.63	0.72	6.59
Fixed carbon (by diff.) wt%:	13.4	9.01	12.41	7.73
Feedstock Ultimate analysis (dry basis), no SO3 correction on ash				
750°C ash dry basis wt%	**0.5**	**7.09**	**0.78**	**6.9**
Carbon dry basis wt%	**49.6**	**55.71**	**50.07**	**55.16**
Hydrogen dry basis wt%	**6.0**	**7.3**	**6.16**	**7.21**
Nitrogen dry basis wt%	**0.2**	**0.12**	**0.25**	**0.28**
Sulfur dry basis wt%	**0.0**	**< 0.01**	**0.03**	**0.09**
Oxygen dry basis wt%	**43.7**	**29.78**	**42.71**	**30.36**
Bromide dry basis ug/g	**-**	**<69**	**<65**	**<67**
Chloride dry basis ug/g	**-**	**2943.0**	**733**	**3184**
Fluoride dry basis ug/g	**-**	**<69**	**97**	**<67**

MBU-G Yield Profiles

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Date:	100% Biomass - Shakedown	50% Biomass – 50% MSW	100% Biomass	50% Biomass – 25% MSW – 25% Plastics
Approximate Mass Balance Closure: (Products/Reactants), %:	95.8	99.9	101.9	100.3
Gas Bomb H2:CO Molar Concentration Ratio:	2.1	1.7	1.7	2.0
Yield profile as mass % of feedstock mass:				
Char, %	0	6.2	0.0	6.9
Hydrogen, %	5.1	4.4	5.6	4.0
Carbon Dioxide - BY DIFFERENCE, %	50.1	28.0	42.2	33.5
Carbon Monoxide, %	34.0	35.6	45.3	28.5
Methane, %	7.3	9.3	5.6	9.7
Ethane, %	0.6	2.0	0.2	1.6
Ethene, %	1.8	7.0	1.1	6.2
Hexanes Plus, %:	1.0	7.5	0.0	9.5

50/50/0 (INL Biomass-MSW Pellet fragments) – optimal pellet composition (carbon intensity and economics), promising MBU-G results – **chose this 50/50 pellet formulation for pilot-scale feed testing**

MBU-G - 50% Biomass – 50% MSW Trends

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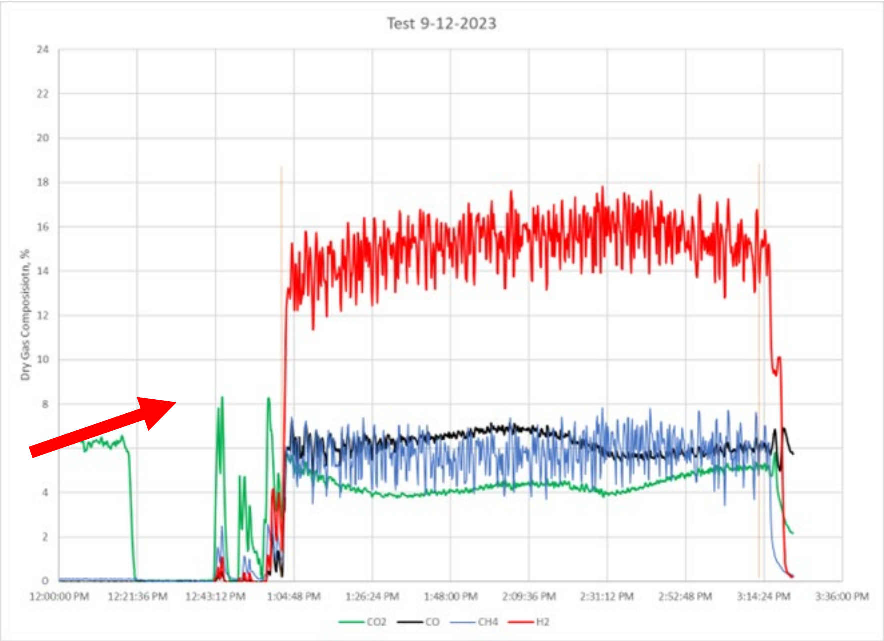
- 50% Biomass – 50% MSW Pellet fragments -4+14 Mesh
  - This pellet formulation allows for “carbon-negative” operation at the lowest feedstock cost
  - N2 (fl. gas). Steam. **Air O2-to-C = 0.14:1**
  - **Steam-to-carbon ratio: 0.4:1**
  - Targeted 0% O2 in effluent gas while maintaining bed temperature
  - Online and offline (GC) gas analysis and ETP
  - **NO PROBLEMS WITH TARS – deep bed of dolomite removed tars and prevented deposits in filters, lines, etc.**

H2:	12 %
CH4:	3.1 %
CO:	6.9 %
CO2:	4.6 %



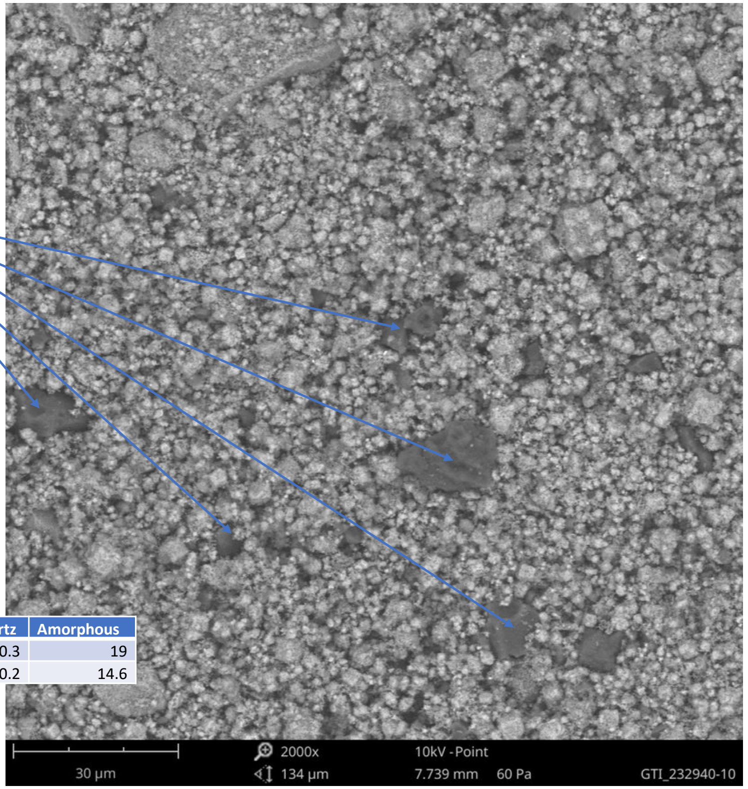
Investigated high H2/CO ratio – found no issues with instrumentation or experimental conditions

MBU-G Ash Analysis

- XRD and SEM Analyses concluded:
  - Both crystalline and amorphous phases were detected, with a ratio of 95:5 mass %. This was as expected with localized slag formation from the low melting material such as biomass
  - The bed material (dolomite) was partially transformed and decomposed to CaO and CO2 and partially un-transformed. The operating temperature of the MBU was as such and on the border of the transformation range, i.e. around 850 °C

Bulk of structure mineral / crystalline

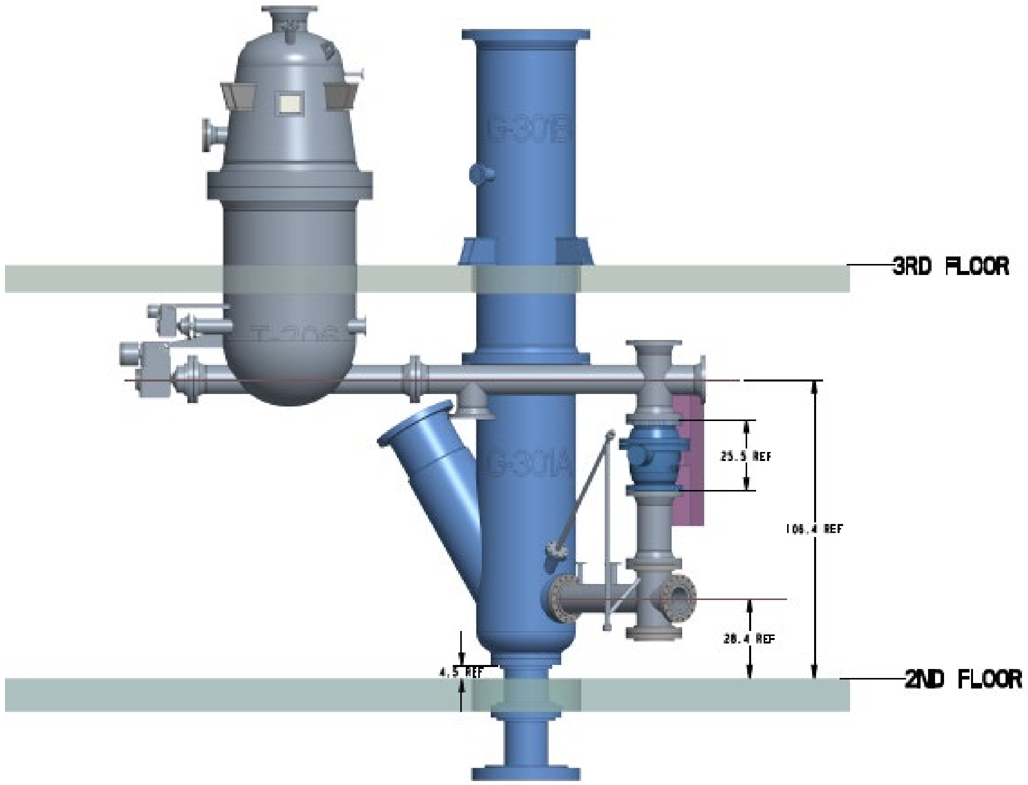
Localized slag and amorphous droplets



	Lime	Periclase	Portlandite	Calcite	Dolomite	Quartz	Amorphous
GTI_232940-007	17.3	32.5	3.8	26.2	0.8	0.3	19
GTI_232940-10	35	36.5	1.6	9.4	2.6	0.2	14.6

Pilot Scale U-GAS Feed System Testing

- Both the pilot U-GAS pneumatic feed and mechanical screw feed configurations have been tested.



Pilot Scale U-GAS Pneumatic Feed System Testing

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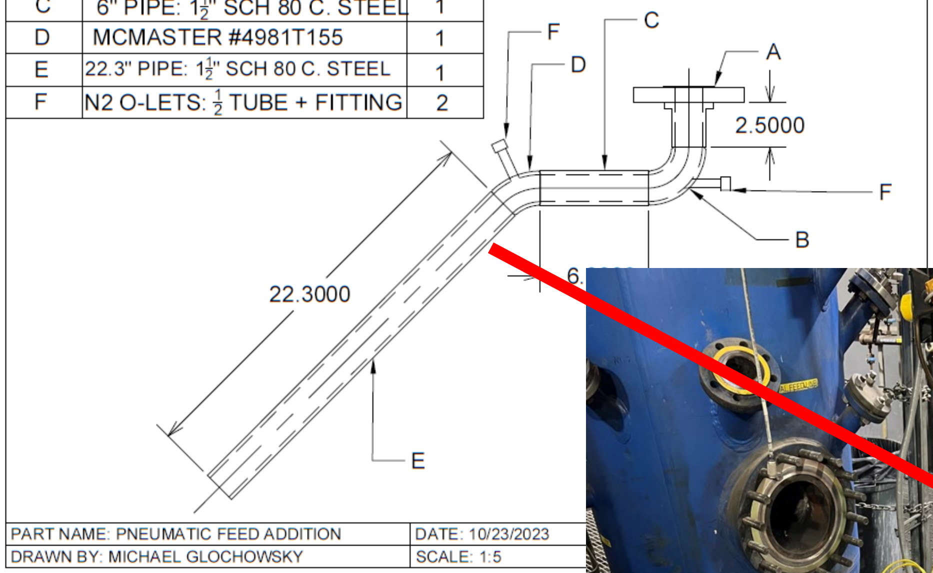
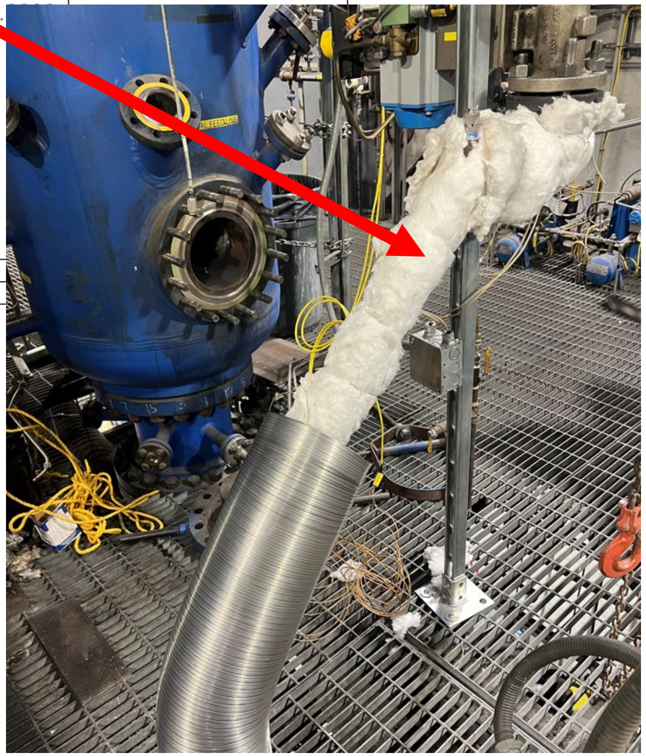
- Tested U-GAS Pneumatic feedstock injector
- GTI modified the pneumatic transfer pipe to accommodate pellets instead of powders – added electrical heating to simulate U-GAS operational conditions/pellet softening
- Supplied maximum transport gas velocity allowed by established U-GAS protocols
- Higher gas velocities not compatible with fluidization regime of the bed => excessive local cooling
- Pellets are simply too large – not mobile at relevant gas velocities – definitive result
- Did not heat the pneumatic feeder outlet during these tests – ambient temperature only

ID	DESCRIPTION	QTY.
A	$1\frac{1}{2}$" 300# SA/A182 C. STEEL B16.5 BA38 FLANGE	1
B	MCMASTER #4981T15	1
C	6" PIPE: $1\frac{1}{2}$" SCH 80 C. STEEL	1
D	MCMASTER #4981T155	1
E	22.3" PIPE: $1\frac{1}{2}$" SCH 80 C. STEEL	1
F	N2 O-LETS: $\frac{1}{2}$ TUBE + FITTING	2



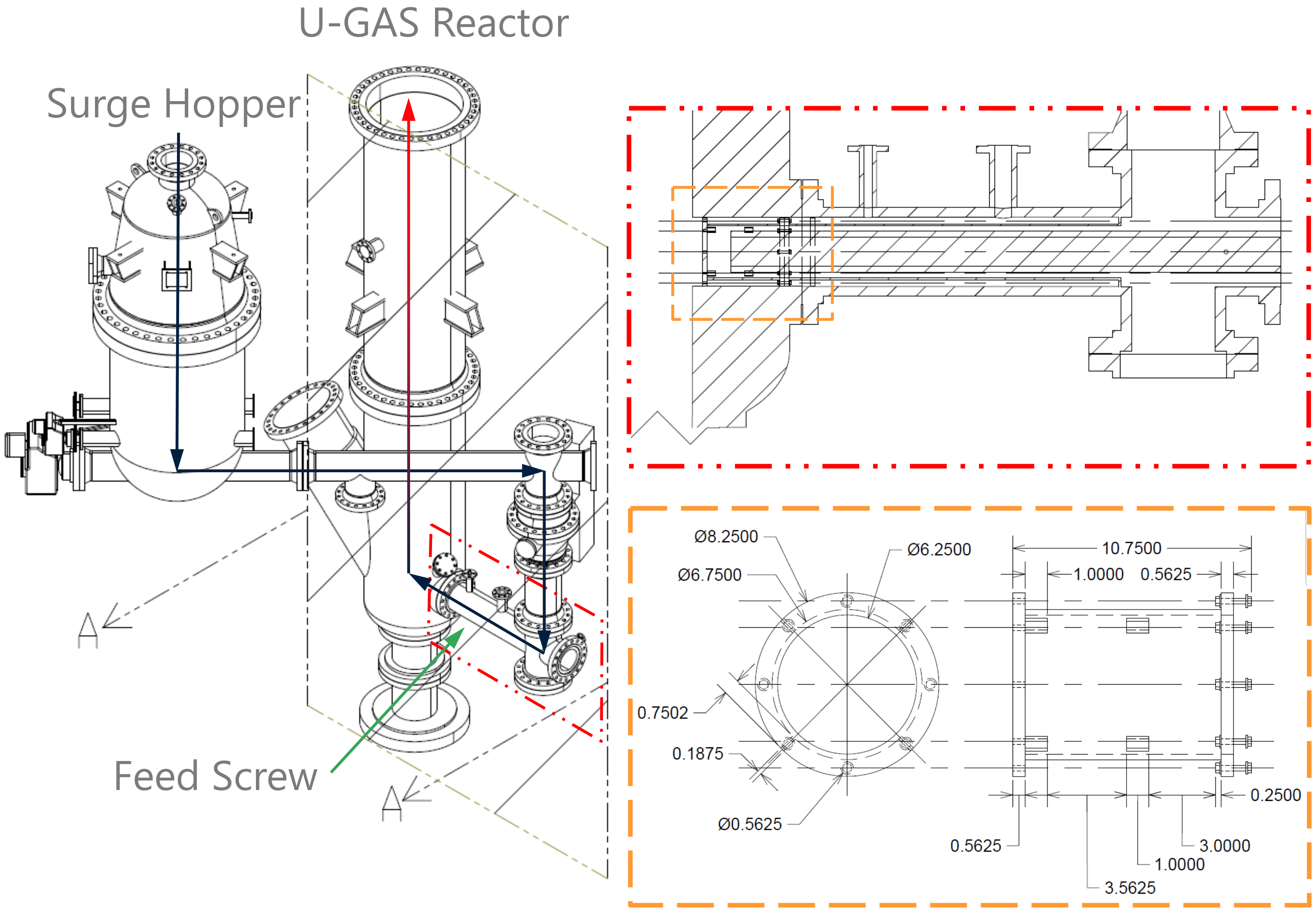


Pilot Scale U-GAS Screw Feed System Testing

- 40 rpm, pellets design rate 1200 lbs/hr
- Screw assembly features a 310 SS shroud at the front end – feedstock passes through the shroud and into the bed of the gasifier
- The screw was re-oriented to move feedstock pellets without sending them into the U-Gas vessel
- Electrical heating system and insulation installed around the shroud – up to 500 F operating temperature available – 1254 W of heating
- Objective: identify temperature at which pellets soften, disintegrated and/or agglomerate in the shroud
- Excellent results: Even at ~500 F, no effect of heating on feedstock was noted – tested 1200 lb/hr down to 300 lb/hr; no change in pellet morphology at any of the temperatures tested

Cooled Shroud Design

- Purpose
  - Design a shroud modification to ensure shroud tip does not exceed 350°C - Avoid feedstock softening and plugging injector screw



Next Development Steps for U-GAS

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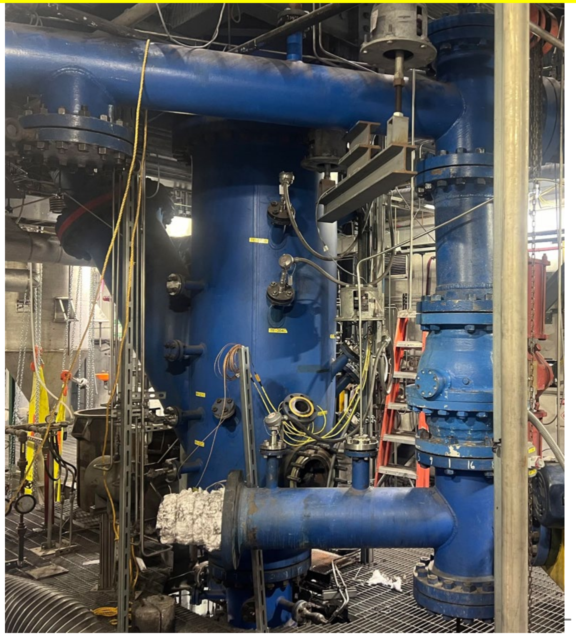
- Biomass and MSW pellets (50% / 50%) benchtop gasification work has been successfully demonstrated at the GTI Energy fluidized bed mini-bench unit gasifier (MBU-G) under project DE-FE0032176.
- Pilot-scale feeding of mixed biomass and MSW pellets (50% / 50%) has been successfully demonstrated at the U-GAS pilot-scale facility under project DE-FE0032176.
- Technology is ready to move on to pilot-scale gasification testing!! → Establish pathway to produce net zero H_2 at \$1/kg.

Define Supply Chain for 50% Biomass / 50% MSW pellets

→

500 hours of Pilot gasification testing



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Commercial System Optimization Study

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solutions that transform

GTI Energy develops innovative solutions that transform lives, economies, and the environment