HYDROGEN PRODUCTION FROM MODULAR CO₂ Assisted OXY-BLOWN GASIFICATION OF WASTE BLENDS

AOI 2A: CLEAN HYDROGEN FROM HIGH-VOLUME WASTE MATERIALS AND BIOMASS

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Sushil Adhikari, Oladiran Fasina, Sagar Kafle, Surendar Moogi, Ashish Bhattarai and Edith Ngoupeyou Auburn University Pradeep Sharma, David Dayton and Sameer Parvathikar

RTI International

Collaborators

Peter Chanin, Burcell Technologies Inc Ray Robbins, Talladega, Alabama











Sources of Greenhouse Gas Emissions (2020)



2020: 5.98 Billion tons of CO₂

"The United States has set a goal to reach **100 percent carbon pollution-free electricity by 2035**,...." The White House Briefing Room, April 22, 2021.

Source: https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions

Hydrogen Potential in Decarbonization



Source: DOE National Clean Hydrogen Strategy and Roadmap (draft). Sept., 2022.

Hydrogen Production Cost



- Reduce electricity cost, improve efficiency and utilization
- Reduce capital cost >80%; operating & maintenance cost >90%





 Reforming, pyrolysis, air separation, catalysts, CCS, upstream emissions



etc.

"Hydrogen Energy Shot (1 1 1)": \$1 for 1 kg of clean hydrogen in 1 decade. Secretary Jennifer Granholm. June 7, 2021

Source: DOE Update on Hydrogen Shot, RFI Results... in the Bipartisan Infrastructure Law. December 8, 2021.

Biomass Potential

1.3 billion dry tons/yr

Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply

April 2005



1.70:1

GROWTH REMOVAL RATE



Agricultural residues and forest residues contribute about 998 and 368 million dry tons per year, respectively. The U.S. has a potential to produce about 60 billion gallons of ethanol. Source: USDA/DOE Billion Ton Study, 2005

Legacy Waste Coal

Property	Method	Sample 1	Sample 2	Sample 3
Ash, %	D3174	10.86	37.05	23.71
VM, %	D3175	32.11	19.90	25.27
FC, %	D3172	57.03	43.05	51.02
Sulfur, %	D4239	1.30	0.49	0.60
HHV, Btu/lb	D5865	13201	9229	11577



Fig. A pile of coal waste in Alabama



Source: Ray Robbins. Talladega Foundry & Machine Co Inc

Source: Energy Justice Network. Waste Coal.

https://www.energyjustice.net/coal/wastecoal#:~:text=Waste%20coal%20 is%20 called%20%22 culm%22%20 in%20 the%20 eastern, or%20 small%20 mountains%20 that%20 are%20 dark%20 and%20 barren.



- * Generation: ~ 292 million tons annually (4.5–5 pounds per person per day)
- Land filled: ~146 million tons
- Plastic recycling: ~ 10%

Source https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/national-overview-facts-and-figures-materials#Generation

Research Objectives

- The main objective of this research is to produce hydrogen from blended feedstocks that include legacy waste coal, forest residues, and an organic-rich fraction of municipal solid waste (OFMSW) via carbon dioxide (CO2) assisted oxy-blown gasification.
- The <u>specific objectives</u> are to:
 - (i) understand the flow properties and energy requirements for preprocessing for blended feedstocks;
 - (ii) gasification behavior of the mixtures on syngas composition and contaminants;
 - (iii) Evaluate syngas conditioning and clean-up catalysts/sorbents;
 - (iv) process model(s) for hydrogen production cost; and
 - (v) develop TMP to advance the technology beyond TRL-4

Project Schedule

	3 month	6 month	9 month	12 month	15 month	18 month	21 month	24 month
Tasks/Milestones		Year 1		Year 2				
Obj. 1: Feedstock Preparation and Charcaterization								
Subtask 2.1: Prepare 3 waste samples and theis blends for the study	SA, GRA1							
Subtask 2.2: Complete flow properties such as flow index, cohesive strength, Hausn		OF,	GRA2					
Subtask 2.2: Complete fluidization segregation and sifting segregation measurement							OF, GRA2	M 8 🔴
Obj. 2: Gasification Characterization								
Subtask 3.1: Complete proximate, ultimate, heating value and ash analyses of 12 ble			SA, GRA1					
Subtask 3.2: Complete CO2 reactivity experiments for 12 blend samples and calcula				SA, GRA1				
Subtask 3.3: Complete gasification of 12 blend samples			SA, (GRA2	M 4			
Obj. 3: Gas Cleanup and Upgrading Chracterization								
Subtask 4.1: Performance characterization of H2S and metal removal			DD, RTI	M 2 🔵				
Subtask 4.2: Performance characterization of syngas conditioning (WGS activity)			DD,	RTI	M 5 (
Obj. 4: Integrated System Design and Performanace Testing								
Subtask 5.1: Design of syngas cleanup and upgrading					RTI			
Subtask 5.2: System Modification						AU		М 6 🗲
Subtask 5.3: Operation of 1 kh/hr integrated system							A	U
Obi C. Desses Madelin and TEA for body and see the distant								
Obj. 5: Process Modeling and TEA for hydrogen production from waste			00 0 00 DTI					
Subtask 6.1: A Preliminary ASPEN process model.			SP & PS, RTI		M 3	00.0		M 7
Subtask 6.2: Updated ASPEN process model						SP &	PS, RTI	
Task 1: Project Management and Reporting								
Project SOPO, PMP Update, Preliminary TMP		M 1						
Project Kickoff Meeting								
Quarterly Progress Report								
Annual and Final Report, Updated TMP								M 9 🧲

Note: M = Milestone SA: Sushil Adhikari OF: Oladiran Fasina DD: Dave Dayton, RTI SP: Sameer Parvathikar, RTI PS: Pradeep Sharma, RTI GRA: Graduate Research Assistance

Proposed Development Efforts

Developmental Effort	Description
Feedstock characterization and gasification studies	 Feedstock blends will be characterized for flowability and segregation High moisture content and blend feedstocks will be tested to determine desirable gasification metrics.
Syngas cleanup and conditioning design, integration, and testing	 Tailor FB-WDP, TCRP, and AFWGS for syngas compositions derived from CO₂-assisted oxy-blown gasification of selected feedstocks Design, build, and operate a 1 kg/h gasifier integrated with syngas cleanup and conditioning for a cumulative 100 hours on-stream.
TEA and TMP	 Create detailed TEA comparing clean H₂ production from conventional processes with proposed processes using waste blends. Formulate plan to advance TRL for integration Assess market to identify next scales for demonstration as well as supply chain for supply of feedstocks, sorbents, and catalysts for larger scale demonstrations

Task 2: Feedstock Characterization

Legacy Waste Coal





Ash Analysis of Coal Samples



For a 2000 tpd plant, we will generate about 800 tons of ash (~40 truck loads) each day. This could potentially cost $\frac{40,000}{(@\$50/ton disposal fee)}$ each day for the plant.

Processes MSW after Burcell Unit



Right. Overs from 1" from Trommel after

Left. 1" unders from Trommel after Burcell

Task 2: Feedstock Characterization

Proximate and Ultimate Analyses

			wt.% (a.r.)		
Sample	Moisture	Ash	Volatile Matter	Fixed Carbon	HHV, MJ/kg
Coal	1.59	36.80	22.70	38.91	19.65
OFMSW	5.86	20.67	72.28	1.19	15.22
Pine Residue	10.20	1.15	83.62	5.03	18.54
			wt.%		
Sample	C (%)	H (%)	N (%)	S (%)	O (%)
Coal	49.33	3.14	0.85	0.4	9.48
OFMSW	42.13	5.87	0.77	0.17	30.39
Pine Residue	48.69	6.82	0.11	0.04	43.19

Task 2: Feedstock Characterization



	Sample T		
	Coal	OFMSW	Pine
Bulk density (kg/m³)	768.55 ± 3.9	136.63 ±0.5	250.85 ± 0.8
Particle density (kg/m ³)	1655.48 ± 18.4	1664.26 ±1.7	1444.71 ± 3.9
Tap density (kg/m ³)	1049.68 ± 11.9	$194.43\pm\!\!2.3$	313.81±3.7
Hausner Ratio	1.36	1.42	1.25
Flow Index	7.7	3.2	3.0

Flow Index (FI)	Flowability
FI < 2	Very Cohesive
2 < Fl < 4	Cohesive
4 < Fl < 10	Easy Flowing
FI > 10	Free Flowing

Jenike, 1964

Task 3: Gasification Experiments

• Laboratory-scale fluidized bed CO2-assisted gasification to determine the syngas composition and contaminants under steam and oxygen gasification conditions.

Table: Composition of mixtures analyzed within the design space (mass percentage).

Sample No.	Waste Coal	Biomass	OFMSW
1	100%	0%	0%
2	50%	50%	0%
3	50%	0%	50%
4	0%	100%	0%
5	0%	50%	50%
6	0%	0%	100%
7	33%	33%	34%
8	66.6%	16.7%	16.7%
9	16.7%	66.6%	16.7%
10	16.7%	16.7%	66.6%

Lab-Scale Gasification Unit



Figure. Experimental setup **1**. Hopper, **2**. injection screw, **3**. heat exchanger, **4**. heaters, **5**. fluidized bed gasifier, **6**. filter heaters, **7**. high temperature filter, **8**. impingers for tar sampling, **9**. condensers, **10**. ESP, **11**. primary gas analyzer, **12**. FTIR gas analyzer and **13**. FPD GC

Syngas Composition Data



Syngas Composition: CO and H₂



Syngas Contaminants and Efficiency



Feedstock

Major Tar Compounds















Task 4.0: Syngas Cleanup and Upgrading Characterization

<u>Subtask 4.1 – Performance characterization of syngas</u> <u>cleanup</u>

Objective: Understand and optimize the performance of syngas cleanup technologies and derive design parameters for integration with waste blend gasification.

- Synthesis, characterization, optimization, and scale-up of regenerable fixed Bed Warm Desulfurization Process (FB-WDP) sorbent extrudates.
- □ Optimize FB-WDP process parameters for process design.

FBWDP Development Parameters





An example three column arrangement where column 1 serves as the lead and column 3 serves as the guard with column 2 in regeneration mode The mass transfer zone, indicated by the black diagonal line on each column, moves along the length of a fixed bed of adsorbent

FBWDP Cycle Optimization

Adsorbent Development

- Desired chemistry for the process
- Balance crush strength and porosity

Adsorbent Particle Size

 Smaller particle size lower mass transfer limitation but increase pressure drop, Common particle size range: 2-4 mm

Superficial Gas Velocity

 Length of MTZ increases with increasing gas velocity with a corresponding decrease in bed utilization, Typical velocity range: 0.15-0.45 m/s

Bed Length

- Longer bed allows for longer time-on-stream and higher bed utilization
- However, it is more expensive and leads to higher pressure drop

Process Conditions

- Process temperature and pressure will help determine the energy requirement of the process and optimize PTSA cycle
- Understanding the regeneration exotherm will help design the heat management system

FBWDP Sorbent Development and Process Design



Sorbent synthesis is optimized, and sorbent performance is reproduced (at high H₂S concentrations)

Task 4.0: Gas Cleanup and Upgrading Characterization

Subtask 4.2 – Performance characterization of syngas conditioning

- Procure and benchmark the activity of commercially available water gas shift (WGS) catalysts in novel AFWGS process.
- Optimize the process conditions for the AFWGS for cost-effective syngas conditioning and collect design data for integration with gasifiers for waste blends.



AFWGS Process Performance and Design

Study performance (activity and long-term stability) of high-temperature shift (HTS), medium-temperature shift (MTS) and low-temperature shift (LTS) catalysts.

□HTS Performance Testing

Parameter	Value
Catalyst	Shiftmax 120
Operating Temperature (°C)	300-425
Operating Pressure (psig)	100
Syngas Composition	mol %
H ₂	37.2
СО	23.0
CO ₂	31.6
CH ₄	3.8
N ₂	4.3



Task 5.0: Integrated System Design and Performance Testing

Subtask 5.1 – Design of syngas cleanup and upgrading

- Leverage the results from subtasks 4.1 and 4.2 and develop process design
- Develop a basic engineering design package consisting of a process flow diagram (PFD), heat and mass balance (HMB) and a process and instrumentation diagram (P & ID)
- Complete a safety hazard and operability (HAZOP) analysis an integrated operations

Subtask 5.2 – System modification

Subtask 5.3 – Operation of 1 kg/h integrated system

Task 6.0: Process Modeling and TEA

- Develop process models for the proposed process incorporating experimental performance data from individual process units resulting from Tasks 2, 3, 4 and 5.
- □ Complete TEA to produce clean H₂ from oxy-blown waste blend gasification in a conventional process that uses commercially available technology.

Process Modeling for Hydrogen Production



H₂ Production Scheme

Process Models



Technoeconomic Analysis Results



Feedstock Cost: Biomass- \$40/ton, Plastics- \$100/ton, Coal- \$36/ton

Emerging technologies can achieve about 16% reduction in hydrogen production cost (2.94\$/kg to 2.47\$/kg)

- ~22% reduction in Capex
- ~23% reduction in operating costs (fixed and variable)
- Feedstock cost can significantly impact the hydrogen production cost
- Sensitivity analysis will be completed to capture the impact of various cost components on the cost of hydrogen production (COP)



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Thank You!











