Dechlorination of Mixed-Plastics Feedstock for Downstream Gasification and Hydrogen Production

(FOA No. DE-FOA-0002903 Topic C56-26d)
Award No. DE-SC0023858

FECM/NETL Spring R&D Project Review Meeting

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April 25, 2024

Acknowledgement – DOE
Katelyn Ballard – DOE Project Manager

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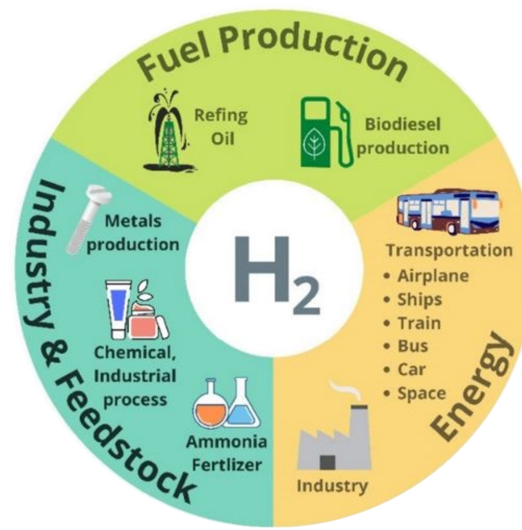
U.S. DEPARTMENT OF ENERGY

Agenda

- Microbeam's Background
- Project Team
- Project Goal
- Objectives
- Accomplishments
  - Sample Procurement
  - Pyrolysis Reactor Setup
  - Test Runs
  - Results
- Conclusion
- Phase II Proposal



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Background of Microbeam Technologies, Inc.

- **Mission:** To provide advanced analysis and interpretations of the impacts of fuel properties on plant fireside performance.
- **Growth:** Expanded laboratory in 2004 to include high-temperature small scale test equipment – slag/ash behavior in combustion/gasification systems; on-line condition-based monitoring tools in 2017
- **Clients:** Equipment developers, electric utilities, gasification (syngas methane, fertilizers), state and fede government, mining companies, consultants, universities, law firms, research organizations, and others
- **Work:** Conducted >1650 projects worldwide, >12,000 samples analyz

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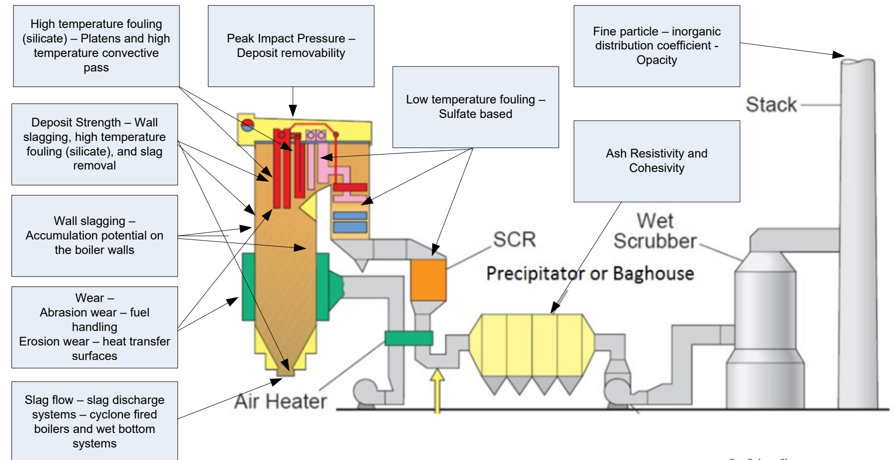
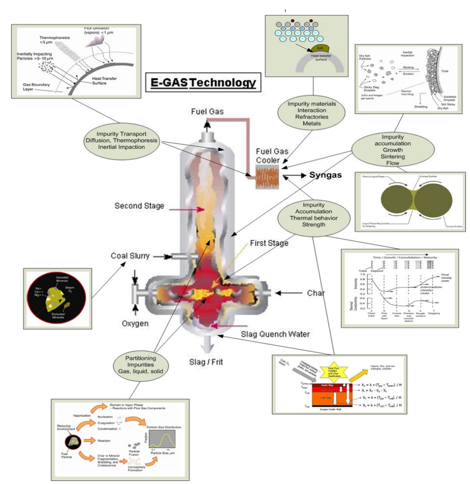
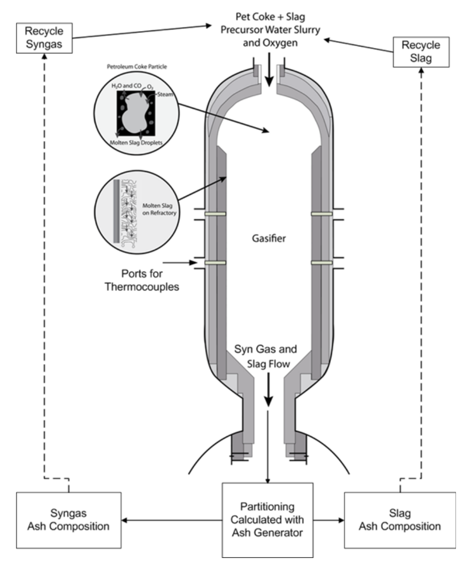
Experience Base

- Plant Thermal and Operational Performance
  - Combustion – PC, cyclone, fluid bed
  - Air pollution control systems – NOx (staging, SNCR, SCR), SO_2/SO_3 (SDA, WFGD, DSI), particulate (ESP, FF), Mercury (oxidation, sorbents)
  - Gasification – entrained flow, fixed bed, fluid bed, transport reactors
    - Fuel feedstock selection
    - Slag flow modeling and measurement
    - Refractory slag interactions
    - Syngas fouling analysis







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Project Information

- Goal : To develop a novel technology for removal of chlorine from mixed-plastics and Municipal Solid Waste (MSW) feedstock using low-temperature slow catalytic pyrolysis.
- Start Date – 07/10/2023
- End Date – 07/09/2024 (12 months)

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Project Team

Technical Team:

- Microbeam Technologies Inc. (Lead)
- Consultant – Dr. Edward Kolodka

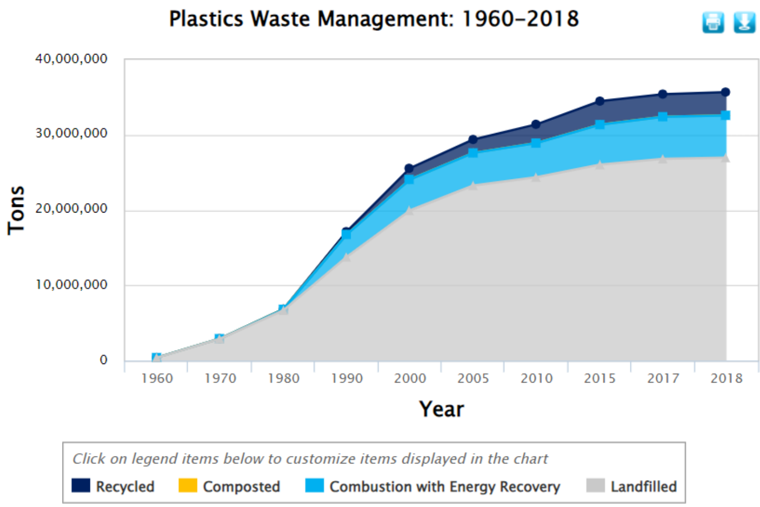
Project Supporters :

- WestRock
- SunGas Renewables
- Countrywide Sanitation

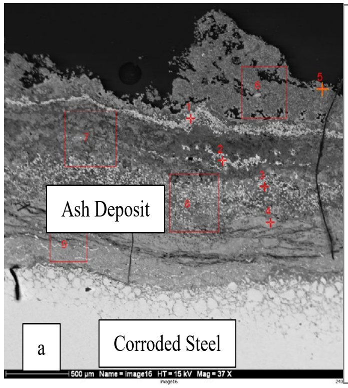
Project Background

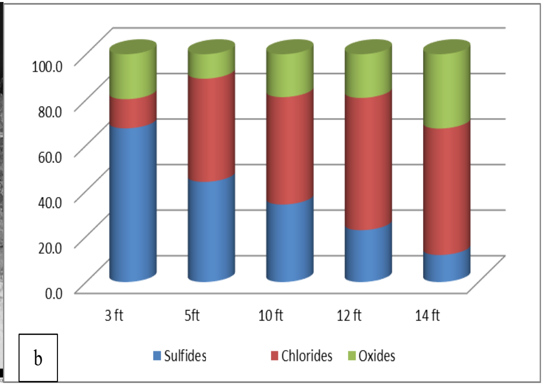
- Global plastic production has soared in the past half of century since it became commercially produced and is now ubiquitous in daily life.
- This growth has seen plastic waste become one of the biggest environmental issues worldwide, polluting land, oceans, air, and even food and human blood.
- In 2019, U.S. plastic waste generation was estimated at 73 million metric tons, corresponding to more than 220 kilograms per inhabitant.
- The majority of U.S. plastic waste is landfilled, with between 32 and 43 million tons sent to landfill sites in 2021.*
- Gasification of this huge, unutilized, plastic-rich resource offers the opportunity to produce renewable hydrogen in a sustainable way.
- Currently utilization is limited due to impacts of chlorine derived from plastics on performance, reliability, and emissions.

*Source - https://www.statista.com/topics/5127/plastic-waste-in-the-united-states



Source - https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/plastics-material-specific-data





a) SEM image of a cross-section of an ash deposit on a syngas cooler tube in a MSW gasification system, b) changes in phase distribution as a function of location in the syngas cooler (temperature change).

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Scope of Work

- Task 1. Project Management and Reporting
- Task 2. Feedstock Analysis and Test Setup
  - Subtask 2a. Source Mixed Plastics, MSW, Biomass, and Catalyst Materials
  - Subtask 2b. Analysis of Plastics, MSW, Biomass and Catalyst Samples
  - Subtask 2c. Test Apparatus Setup and Baseline Testing
  - Subtask 2d. Catalyst Properties Optimization
- Task 3. Dechlorination Tests
  - Subtask 3a. Mixed Plastics and MSW Testing with Slow Low-temp Pyrolysis
  - Subtask 3b. Sample Testing with Catalyst
  - Subtask 3c. Mixed Plastics and Biomass Blend Testing
- Task 4. Preliminary Technology Feasibility Assessment and Commercialization Plan Development

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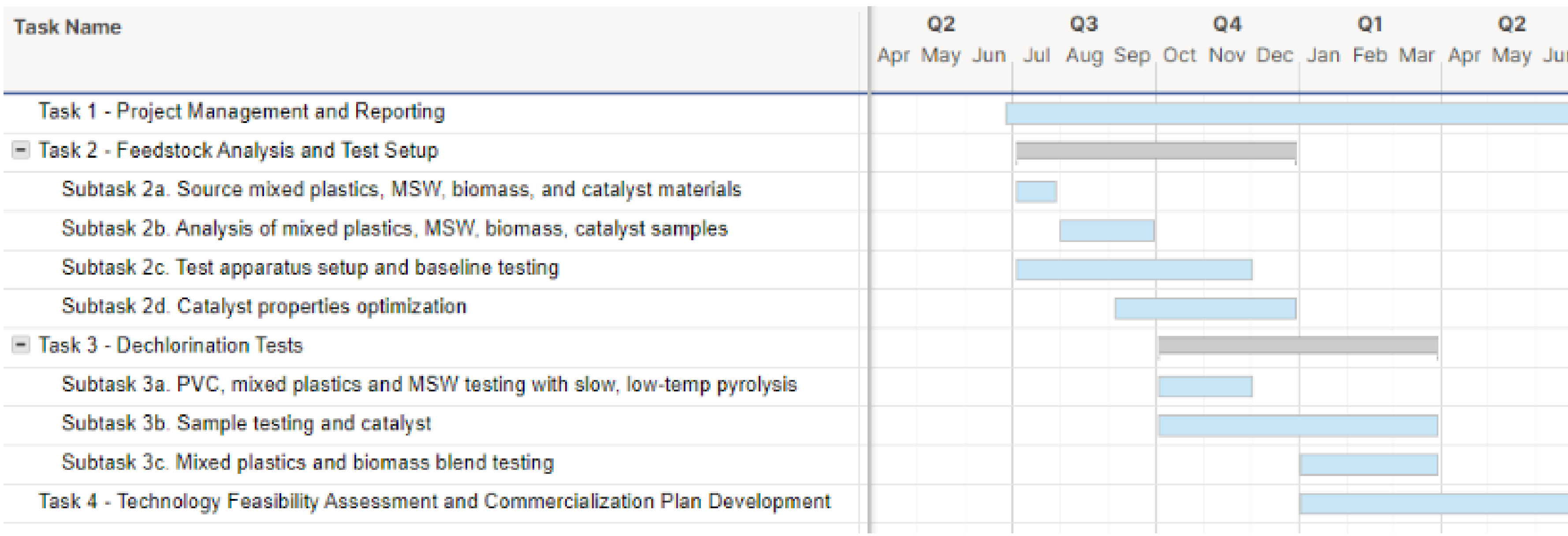
Project Schedule



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Feedstock Sourcing

- **Countrywide Sanitation Company, Grand Forks, ND**
  - The recyclable stream is collected from single-stream recycling bins in the rural region around Grand Forks County and East Grand Forks, MN.
  - The recyclable material is stockpiled in a bay at Countrywide Sanitation. Recyclable material is shipped to a recycling facility in Minneapolis, MN for materials recovery.
- **Recycling Site, Minneapolis, MN**
  - The recyclable stream is collected from single-stream recycling bins in the city of Minneapolis, parts of St. Paul, Roseville and other surrounding suburbs.
  - They also offer an onsite center where residents can come and drop off recycling dumpsters that is sent to the same facility.

Countrywide Sanitation Company, Grand Forks, ND

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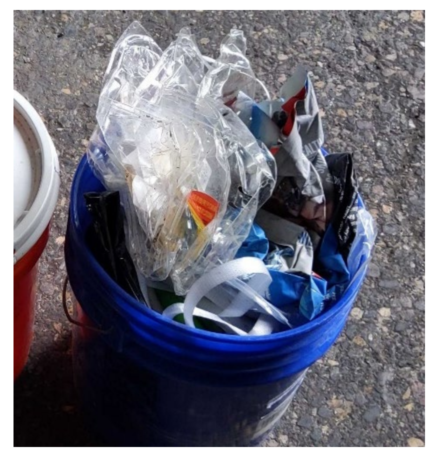
Subtask 2a. Source Mixed Plastics, MSW, Biomass, and Catalyst Materials

ND Bucket 1 – Mixed Plastics

ND Bucket 2 – Thin Plastics

ND Bucket 3 – Hard Bottles

ND Bucket 4 – Milk Jugs



ND Bucket 5 – Random Plastics

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Subtask 2a. Source Mixed Plastics, MSW, Biomass, and Catalyst Materials

MTI ID	Label	Description	Plastic Type
MTI 23-490	ND Bucket 1 **Mixed Plastics**	Intended to be semi-representative of the whole plastics fraction of the MSW	
MTI 23-491	ND Bucket 2 **Thin Plastics**	Plastic grocery bags, plastic wrapping material, and other thin plastic materials	Low-density polyethylene **(LDPE)**
MTI 23-492	ND Bucket 3 **Hard Bottles**	Mostly 20-oz soda bottles and food containers	Polyethylene terephthalate **(PET)**
MTI 23-493	ND Bucket 4 **Milk Jugs**	Standard milk containers	High-density polyethylene **(HDPE)**
MTI 23-494	ND Bucket 5 **Random Plastics**	Intended to be representative of all the unclassified plastics that were not represented by Buckets 2, 3, and 4. Included some wrapping materials that were harder, some mixed plastic/cardboard containers and other unclassified plastics	Partially High-density polyethylene **(HDPE)**
MTI 23-495	MN Bucket 1 **Mixed Plastics**	Intended to be semi-representative of the whole plastics fraction of the MSW	
MTI 23-496	MN Bucket 2 **Thin Plastics**	Plastic grocery bags, plastic wrapping material, and other thin plastic materials	Low-density polyethylene **(LDPE)**
MTI 23-497	MN Bucket 3 **Hard Plastics**	Mostly 20-oz soda bottles and food containers	Polyethylene terephthalate **(PET)**
MTI 23-498	MN Bucket 4 **Milk Jugs**	Standard milk containers	High-density polyethylene **(HDPE)**
MTI 23-499	MN Bucket 5 **Random Plastics**	Intended to be representative of all the unclassified plastics that were not represented by Buckets 2, 3, and 4. Included some wrapping materials that were harder, some mixed plastic/cardboard containers and other unclassified plastics	Partially High-density polyethylene **(HDPE)**

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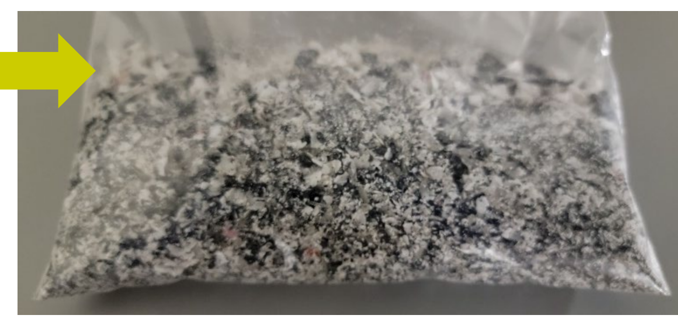
Subtask 2b. Analysis of Plastics, MSW, Biomass and Catalyst Samples

- Sample prep of plastics



*images of MTI 23-490 ND Bucket 1
Mixed Plastics
are used here for reference

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Subtask 2b. Analysis of Plastics, MSW, Biomass and Catalyst Samples

- Sample Analysis
  - Plastics – ash content (LOI), stick-tape morphology, & TGA
  - Biomass – ash content, ASTM proximate/ultimate and ash composition, Cl analysis, CCSEM, and TGA
  - Catalyst Analysis

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Subtask 2b. Analysis of Plastics, MSW, Biomass and Catalyst Samples

- Loss-on-ignition (LOI) ash content results (plastics)

Description	ND Mixed Plastic	ND Thin Plastics	ND Milk Jugs	ND Random Plastics	MN Random Plastics
Bucket No.	Bucket 1	Bucket 2	Bucket 4	Bucket 5	Bucket 5
MTI ID	MTI 23-490	MTI 23-491	MTI 23-493	MTI 23-494	MTI 23-499
Date of Collection	8/24/23	8/24/23	8/24/23	8/24/23	9/25/23
Moisture Content (%)	3.25%	2.90%	0.00%	0.00%	0.00%
LOI (%)	92.11%	98.67%	99.47%	97.50%	98.95%
Ash (%)	**7.89%**	**1.33%**	**0.53%**	**2.50%**	**1.05%**

*moisture content, loss-on-ignition, and ash content results are an average of two runs

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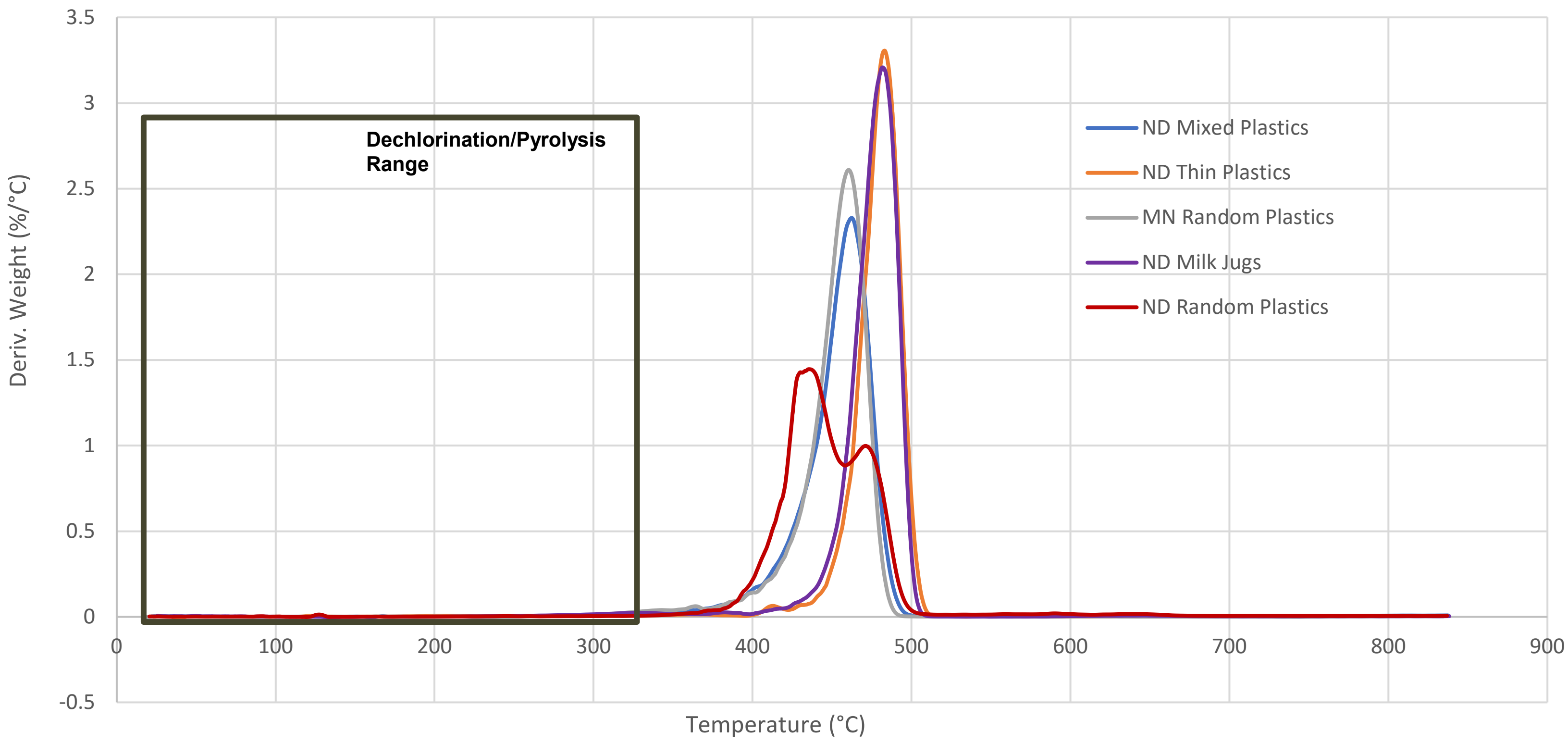
TGA Results Comparison



- TGA derivative weight loss of all 5 samples.

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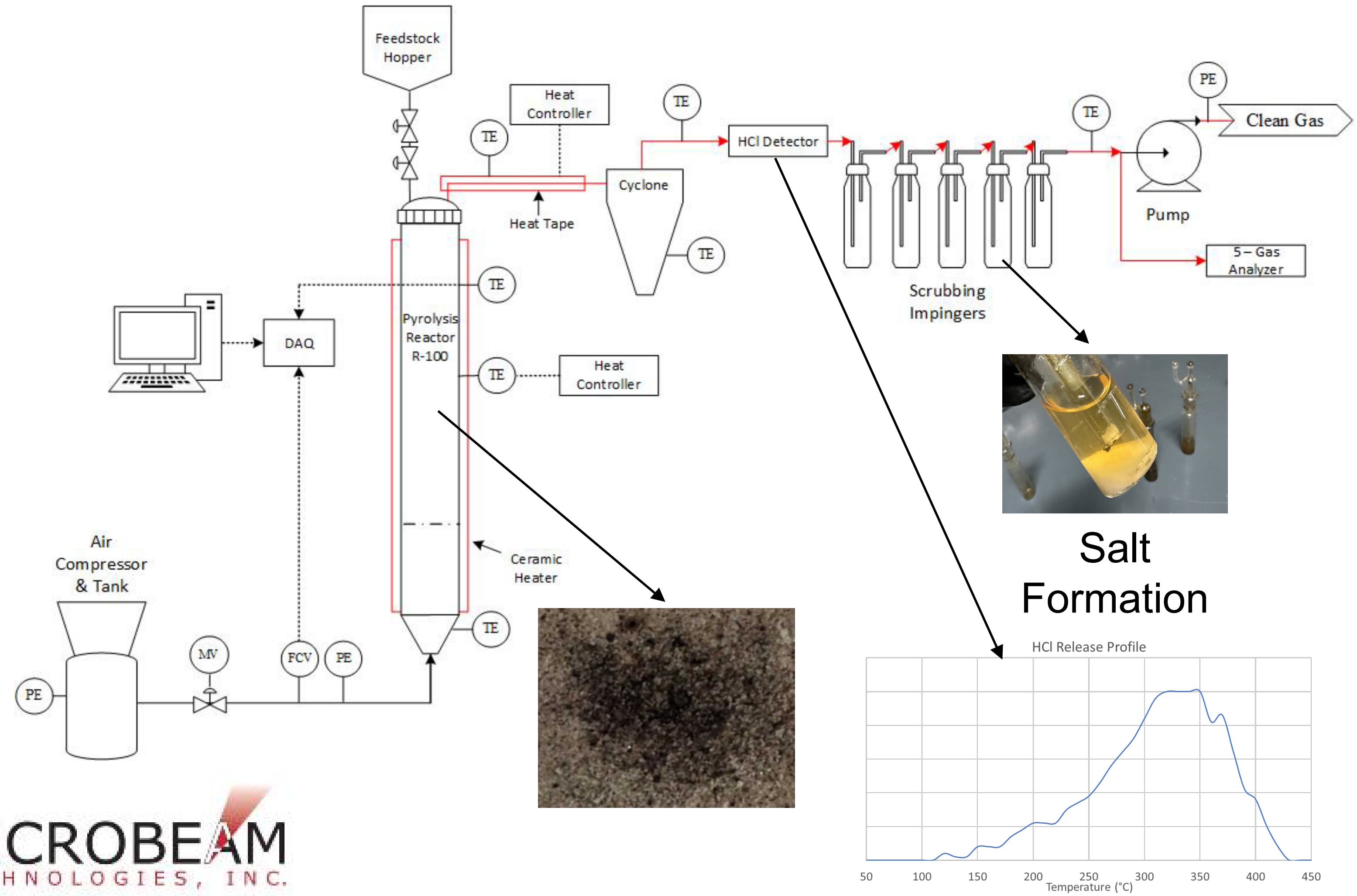
Fluidized Bed Reactor Setup



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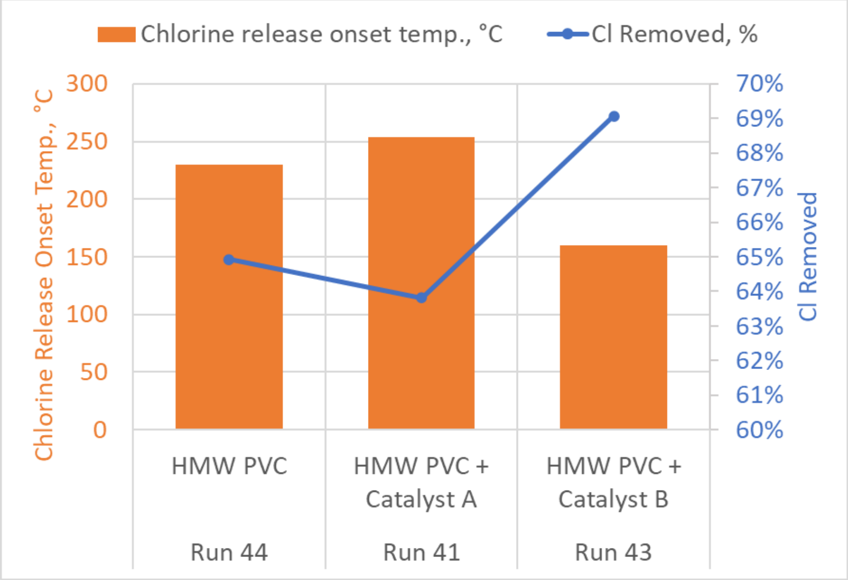
Baseline Testing Results

- Performed baseline testing with PVC only feedstock and an inert bed material.
  - Baseline/parametric testing was performed, and the products were analyzed.
  - Dechlorination testing was performed at 200 °C and 325 °C.
  - The testing results indicated that 325 °C was the most effective PVC dechlorination temperature without catalyst.

Effect of Catalyst on Dechlorination

- Baseline (Run 44): T-onset 230 °C, 65% Chlorine Removal
- Catalyst A (Run 41) similar to baseline.
- Catalyst B (Run 43): lower T-onset of 160 °C, 69% Chlorine Removal
- Catalyst B initiates Cl removal at lower temperatures.



		% Chlorine Removed	Onset temp., °C
Run 44	HMW PVC (Baseline)	65%	230
Run 41	HMW PVC + Catalyst A	64%	254
Run 43	HMW PVC + Catalyst B	69%	160

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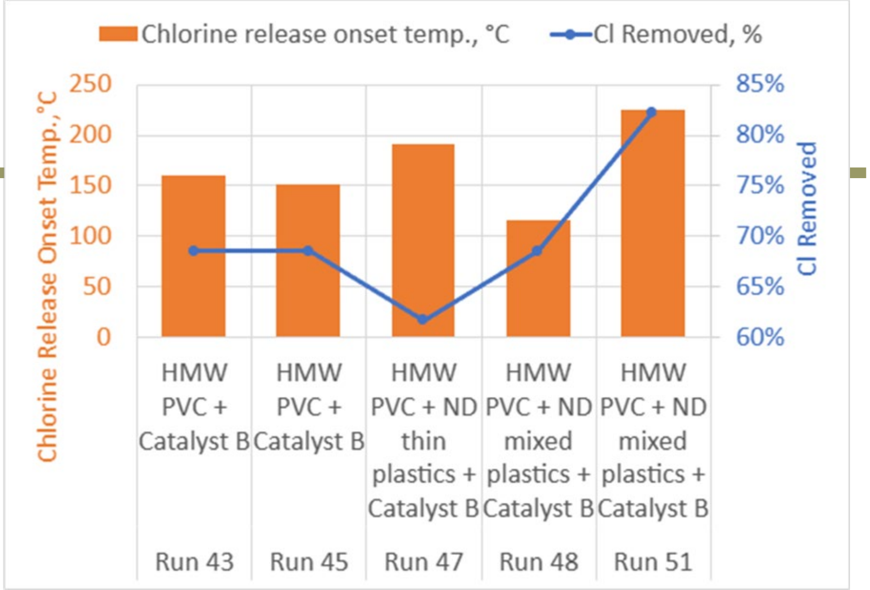
Impact of Mixed Plastics

- Catalyst B without plastics (Run 43,45): T-onset 150-160 °C, 69% Chlorine Removal.
- Thin plastics (Run 47): higher T-onset (190°C), 62% Chlorine Removal
- Polyethylene-based materials may *inhibit* dechlorination.
- Mixed plastics (Run 48,51): varied T-onset (116-224°C), 71-83% chlorine removal.
- Mixed plastics may *improve* dechlorination.



Run ID	Description	% Chlorine Removal	Onset temp., °C
Run 43	HMW PVC + Catalyst B	69%	160
Run 45	HMW PVC + Catalyst B	65%	150
Run 47	HMW PVC + ND thin plastics + Catalyst B	62%	190
Run 48	HMW PVC + ND mixed plastics + Catalyst B	71%	116
Run 51	HMW PVC + ND mixed plastics + Catalyst B	83%	224

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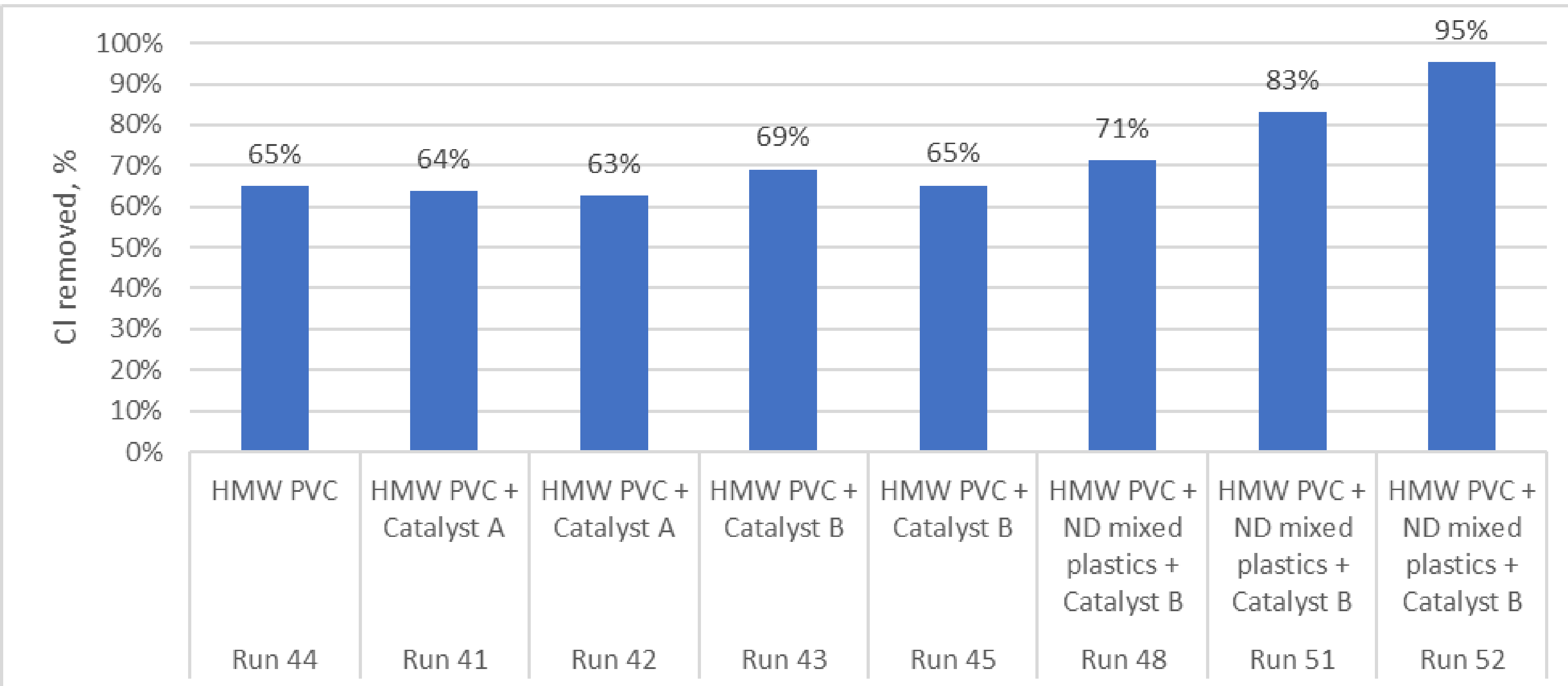
Chlorine Removal



Char Production Run

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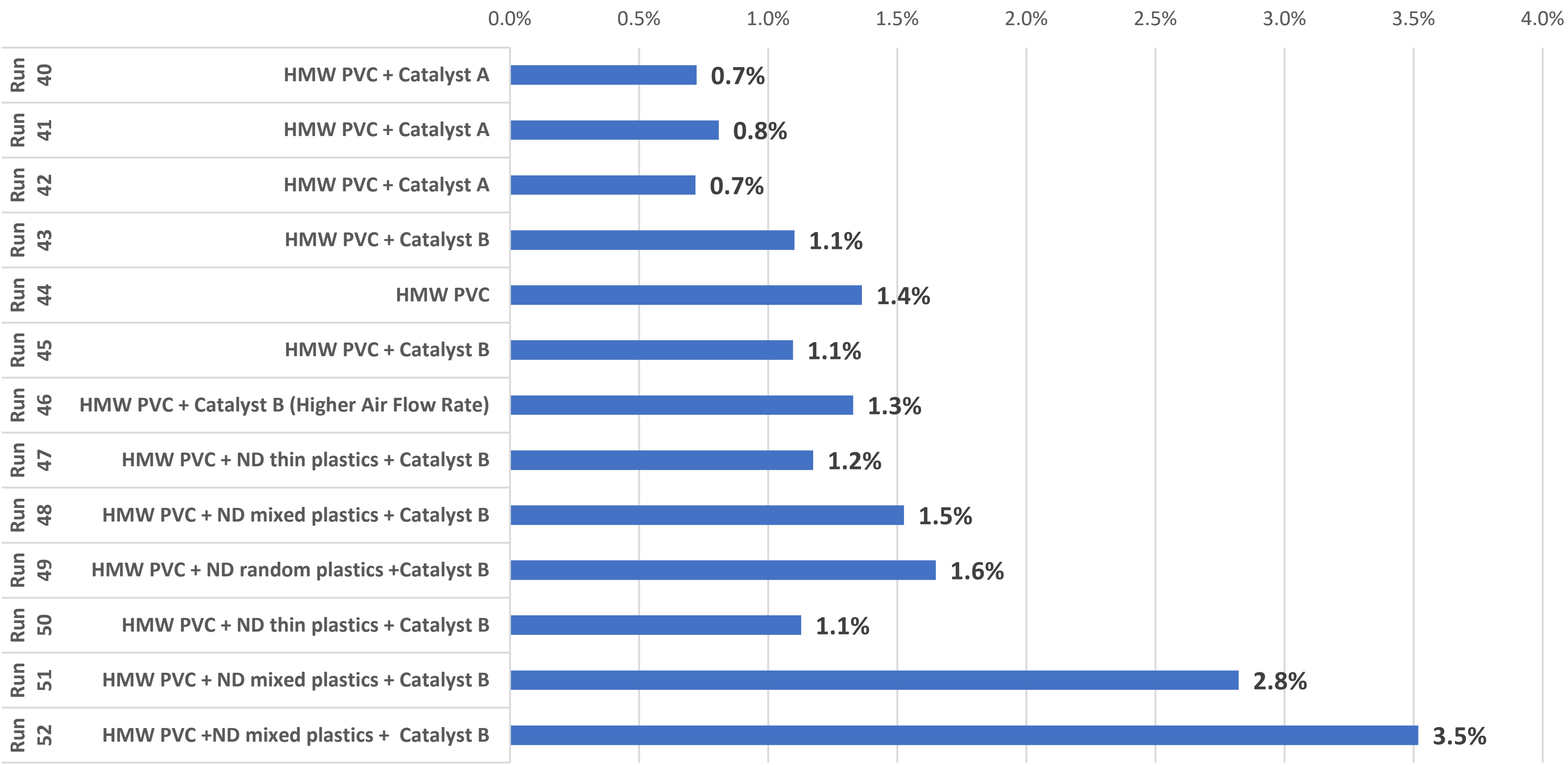
Rate of Dechlorination



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Catalyst Testing

- Performed pyrolysis runs with five potential catalysts
  - **Catalyst B proved to be the most effective of the five in dechlorinating plastics.**
  - The project team plans to optimize Catalyst B's properties and blend ratios further in Phase II.
  - Efforts focused on developing a preliminary understanding of how the varied melting points of plastics influence the conditions needed to release the chlorine.

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Effect of Testing Environment

- Performed tests comparing environments: N_2 gas versus air environment
  - The impact of interacting catalyst and plastic on dechlorination under air environment testing was observed by running PVC and Catalyst B test under these conditions.
  - Tests conducted under air environment performed similarly to test with N_2 gas.

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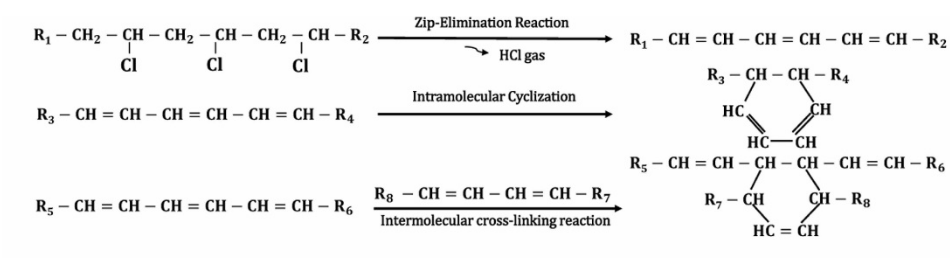
Dechlorination Mechanisms

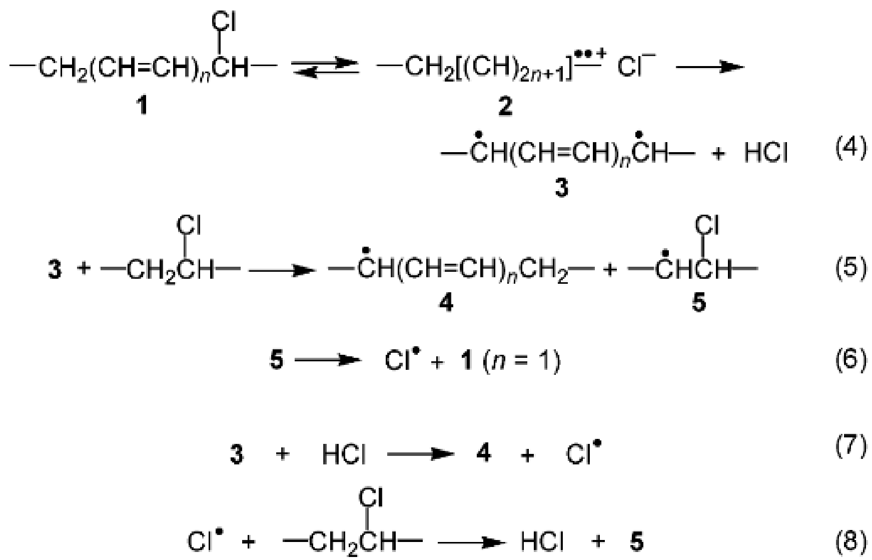
- Zip-elimination reaction (Dong et al 2023)



A. Formation pathways of de-HCl PVC from thermal dechlorination of PVC

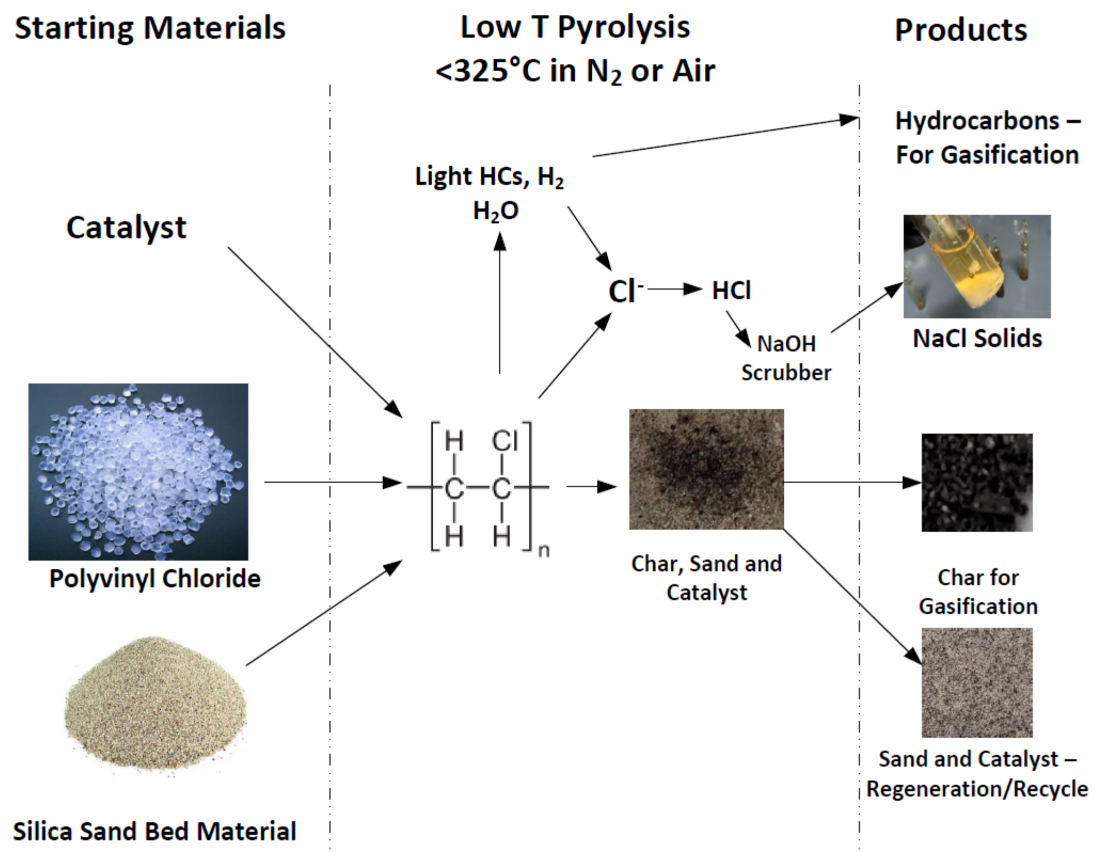
Dong, N., Hui, H., Li, S., & Du, L. (2023). Study on preparation of aromatic-rich oil by thermal dechlorination and fast pyrolysis of PVC. *Journal of Analytical and Applied Pyrolysis*, *169*, 105817. https://doi.org/10.1016/j.jaap.2022.105817

- Autocatalysis via polyene-HCl interaction (Starnes and Ge, 2004)



Starnes, W. H., & Ge, X. (2004). Mechanism of Autocatalysis in the Thermal Dehydrochlorination of Poly(vinyl chloride). *Macromolecules*, *37*(2), 352–359. https://doi.org/10.1021/ma0352835

Mechanism



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Phase I Accomplishments

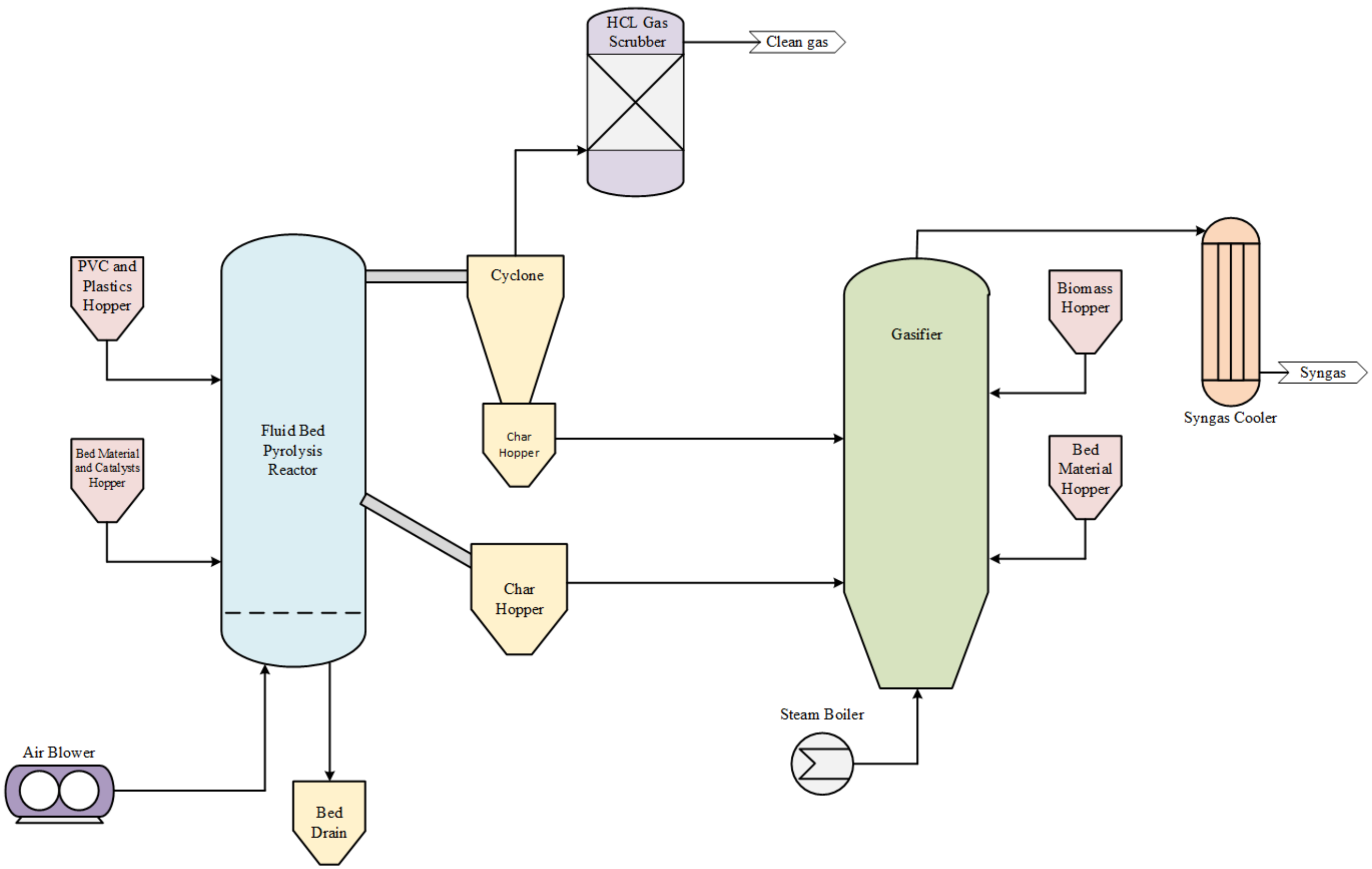
The results of the Phase I effort identified a proprietary low-cost catalyst as most effective in catalyzing dechlorinization of polyvinyl chloride during pyrolysis in a fluidized bed reactor by achieving between 70 and 95% chlorine removal at low temperatures.

Phase II Project Goal

- The goal of the Phase II project is to build on the success of Phase I to develop a novel technology for removal of chlorine from mixed-plastics and sorted Municipal Solid Waste (MSW) feedstock using low-temperature slow catalytic pyrolysis.

- In Phase II, a bench scale system will be designed and constructed to produce sufficient quantities of materials for bench scale gasification testing equipment.

Phase II Setup



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Project Objectives

- Perform catalyst properties and blend ratio optimization. Evaluate catalyst regeneration options.
- Design and construct a bench scale system capable of producing quantities of materials that can be used in bench scale gasification testing equipment.
- Conduct testing of mixed plastics combined with catalyst and biomass and measure the composition of the products.
- Perform testing at a scaled-up gasification system to determine potential impacts on gasification.
- Conduct a conceptual design for a pilot demonstration facility to process up to 0.5 tonne/day of feedstock.
- Perform a technical and economic assessment and work with project partners to scale-up the process and commercialize the process.

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- Acknowledgment : This material is based upon work supported by the U.S. Department of Energy, National Energy Technology Laboratory, Office of Science, Office of Fossil Energy and Carbon Management under Award Number DE-SC0023858.

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Questions

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