DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Integrated Chemolytic Delamination and Plasma Carbonization for the Upcycling of Single-Use Multi-layer Plastic Films

April 5th, 2023
Plastics Deconstruction and Redesign

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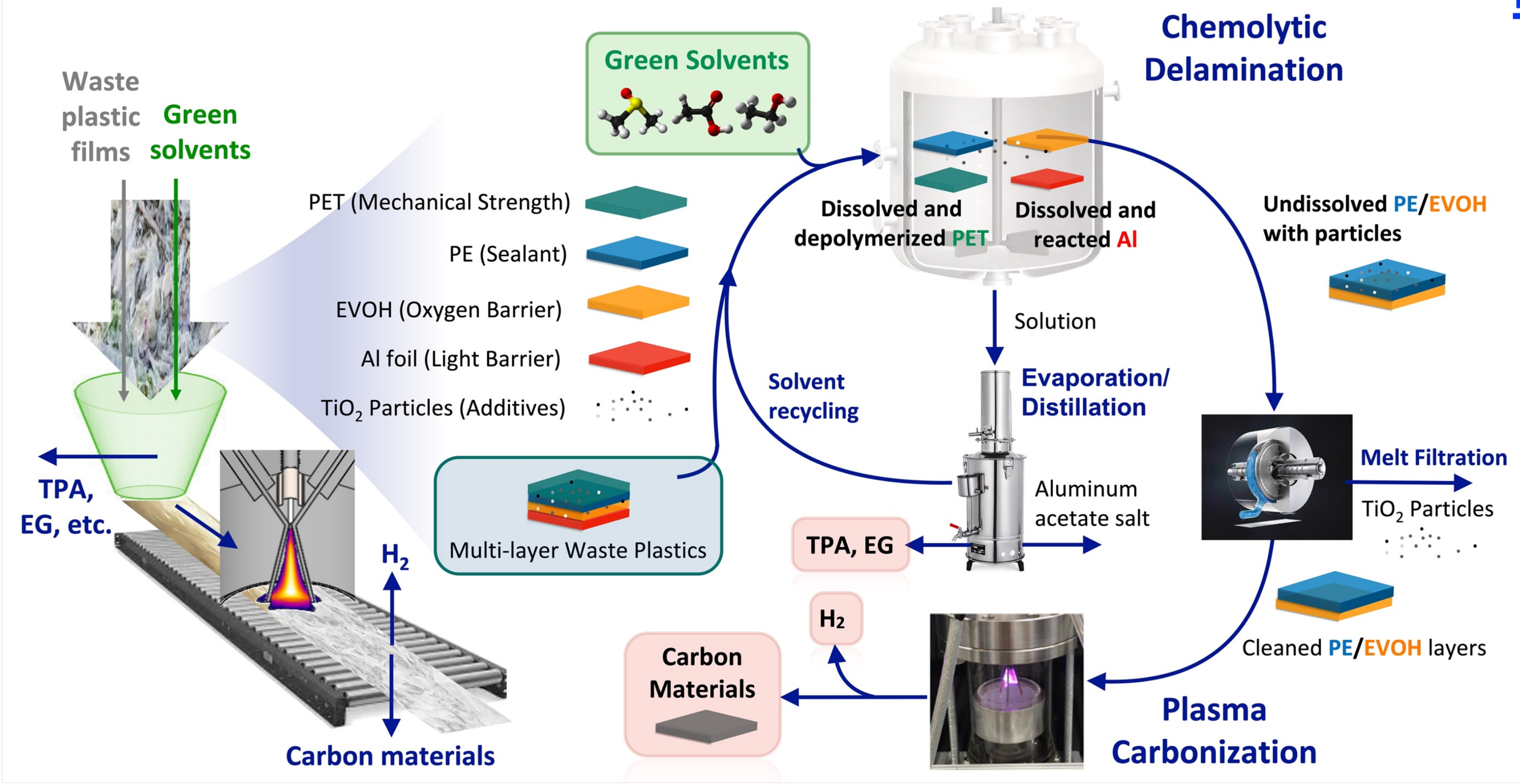
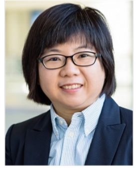
Project Overview

Technology Summary: An integrated chemolytic delamination–plasma carbonization process to upcycle multi-layer waste plastic films with heterogeneous compositions into high-value chemicals (TPA, EG), carbon materials (e.g., carbon black), and hydrogen



Project Team:

PI: Hsi-Wu Wong
(UML Chemical Engineering)
Process scalability, kinetics



Co-PI: Wan-Ting (Grace) Chen
(UML Plastics Engineering)
Film delamination

Co-PI: Juan Pablo Trelles
(UML Mechanical Engineering)
Plasma carbonization

Co-PI: Gregg Beckham
(NREL)
LCA/TEA

Cost share:

Dow, HP Indigo

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Project Overview

BETO's Single-Use Plastic Recycling (SUPR) FOA Goals (Topic Area 1):

1) Development of recycling and upcycling pathways for plastic films that are *economically favorable*, *lower green house gas (GHG) emissions*, and *reduce the embodied energy of plastics*
2) Proposed work should demonstrate an advancement in at least one aspect of the recycling/upcycling supply chain that leads to *improved economics*, *reduced greenhouse gas (GHG) emissions*, *energy savings*, and *retained carbon*

BETO Requirements:

1) Techno-economic analysis (TEA) and life cycle assessment (LCA)
2) A relevant state of the art must be identified
3) A salable product with expected market size and include an estimate of economic viability
4) Scalability of the process
5) Process on a real recycling stream

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Project Overview

Project Objectives:

1) Safe solvents and optimized reaction conditions for selective delamination and depolymerization of single-use plastic films with high product (TPA, EG) yields
2) Optimal plasma carbonization conditions for carbon utilization and hydrogen production
3) Integration, kinetics, and scalability of the process
4) Economic and life cycle outcomes of the process that meet the performance targets

End-of-Project Goals:

1) > 80% PET conversion to TPA
2) > 95% TiO_2 particle removal by melt filtration
3) > 90% carbon recovery from PE/EVOH by plasma carbonization
4) Carbon materials of > 97% carbon mass fraction
5) Meet overall economic and environmental metrics
6) Demonstrate a bench-top process at a rate of > 100 cm^2 film/hr

1 – Approach

Overall Technical Objective: Upcycle single-use multi-layer waste plastic films with heterogeneous compositions by integrating chemolytic delamination (*more substrate specific*) and plasma carbonization (*less substrate specific*) to into high-value chemicals (TPA, EG), carbon materials (e.g., carbon black), and hydrogen

Key Technology Features: (1) Capable of treating a wide range of different compositions, (2) producing high-value products, (3) using environmentally benign solvents, and (4) scaling modularly for small-scale, distributed manufacturing

Project Technical Tasks:

V 1) Initial verification (All)
2) Selective chemolytic delamination (Chen)
3) Plasma carbonization (Trelles)
4) Chemical kinetics and process scalability (Wong)
5) Technoeconomic analysis and life cycle assessment (Beckham)
6) Bench-top reactor system and process demonstration (All)

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1 – Approach

Diversity, Equity, and Inclusion Tasks

1) **Diversity:**
   - Micro-aggression bystander training (50% of project personnel by Q2 and 90% by Q6)
   - Summer camps for high school students from underrepresented groups (Q5 and Q9)

2) **Equity:**
   - Outreach activities for greater Lowell underserved communities (Q2, Q6, Q10)
   - RHSA events for first-generation college students (Q3, Q7, Q11)
   - Special lectures for learning-disabled students (Q4, Q8, Q12)

3) **Inclusion:** (50% of project PIs from underrepresented groups by Q2, 25% and 40% of project personnel from underrepresented groups by Q6 and Q10, respectively)

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1 – Approach

Potential Challenges and Mitigation Strategies

1) Insufficient solvent and catalyst reactivity, causing low TPA yields from PET decomposition
   - Plan 1: *A less safe solvent and/or more expensive catalyst for higher reactivity*
   - Plan 2: *Separating the delamination and chemolytic steps into two operations*
   - Plan 3: *Carbonizing delaminated layers with partial chemolysis or without chemolysis*
2) Lower than satisfactory quality of the carbon materials made by plasma carbonization
   - Plan 1: *Microwave or transferred arcs plasma sources for higher energy outputs (but generally lower energy efficiency due to excessive heating)*
   - Plan 2: *Stepwise plasma processing for different surfaces and materials*
3) Challenges in modular scaling due to volume scalability of certain operations
   - Plan 1: *Process integration by combining both modular (scaled by area) and conventional (scaled by volume) operations*
   - Plan 2: *Splitting the reactors into several smaller reactors, with a smaller overall volume*

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1 – Approach

Budget Period 1 (BP1) Go/No-Go (GNG) Milestones through Q7 (M21)

1) Experimental data of chemolytic delamination treating model multi-layer films showing > 80% TPA and EG mass yields and > 90% aluminum acetate mass yield
2) Experimental data of plasma carbonization treating model films showing > 90% carbon mass fraction in treated solid samples
3) Apparent reaction kinetics for both chemolytic delamination and plasma carbonization that can model experimental data with R^2 higher than 0.95
4) TEA and LCA estimations of the baseline scenario showing that the technology can achieve 30% of target performance
5) Design and engineering drawings of the bench-top reactor system
6) The evidence of completion of all DEI milestones

2 – Progress and Outcomes

Task 1: Initial Verification

Task Objectives:

1) Verify the team's data, performance metrics, baseline and targets as described in the original application
2) Establish a framework to evaluate and track progress over
3) Provide data in the Technical Datasheets
4) Identify potential major showstoppers and discuss risk mitigation strategies
5) Align project goals with DOE's expectations

Major Accomplishment:

Project baseline against which future performance and cost improvements was discussed, iterated, and finally set

Milestone:

Experimental procedures demonstrated and data and assumptions confirmed (**met**)

2 – Progress and Outcomes

Task 2: Chemolytic Delamination

Task Objectives:

1) Select safer solvents for model film delamination
2) Select proper catalysts for model film chemolysis
3) Process commercial-grade multi-layer plastic films

Major Accomplishment:

Two solvents (formic acid and acetic acid) that can fully delaminate a multilayer model films (metalized PET/PU/PE) at mild conditions (70–80°C and 1–2 h) were identified

Milestones:

1) > 3 safer solvents or blends with delamination of PET and Al of > 95% by area (***in progress***)
2) > 1 catalyst converting delaminated PET into TPA and EG with > 80% yield (future)
3) Process commercial-grade films achieving the same metrics (future)

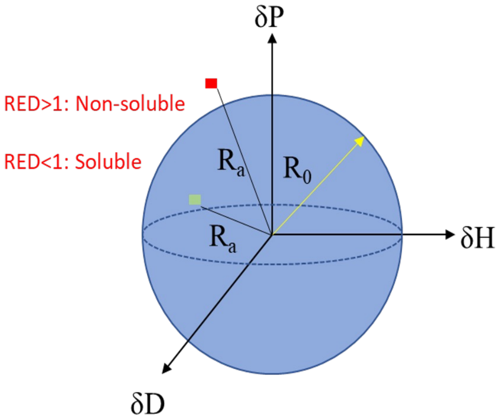
2 – Progress and Outcomes

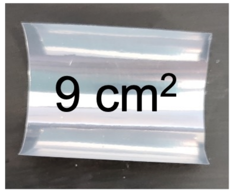
Task 2: Chemolytic Delamination

Delamination of the Uline film (metalized PET/PU/PE)

Process:

- Film: Solvent (acetic acid): 1-10 mg/ml
- **Temperature:** 80°C
- Solvents: Formic acid (~10 min) and Acetic Acid (~1 h)





Layer 1	PET
Layer 2	PUR
Layer 3	Al
Layer 4	PE

delamination

PET

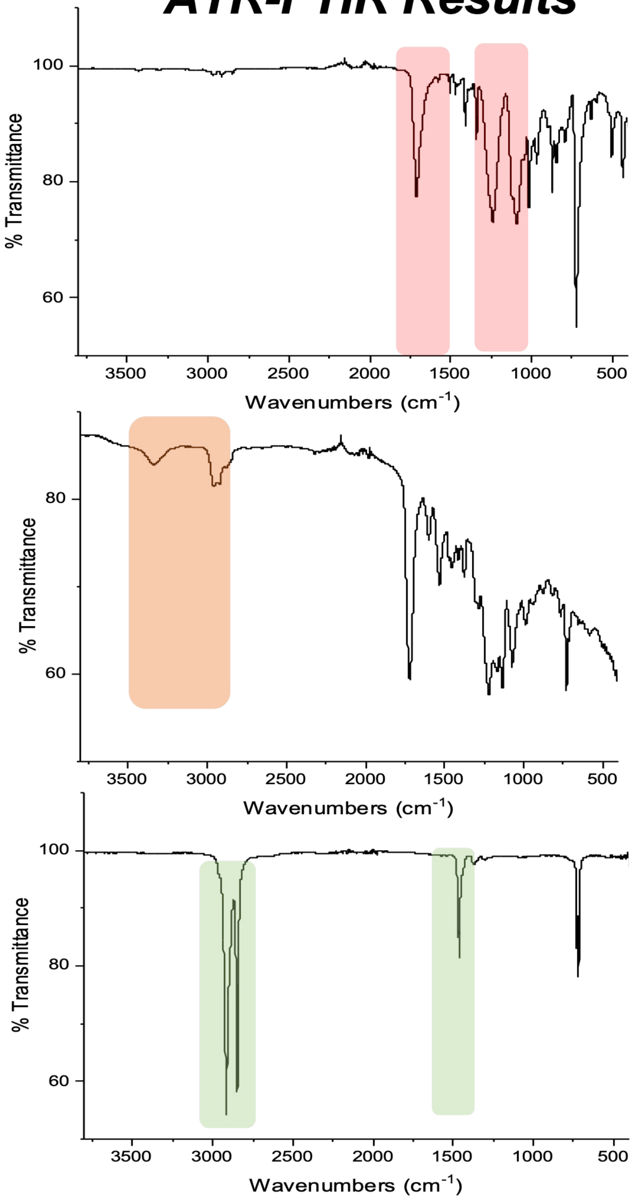
Front side polyurethane

Composition of adhesive identified

Back side PE

Shining part: Al (particles)

ATR-FTIR Results



2 – Progress and Outcomes

Task 3: Plasma Carbonization

Task Objectives:

1) Construct plasma reactors and parameter characterization
2) Carbonize model polyethylene (PE) and ethylene vinyl alcohol (EVOH) films
3) Carbonize commercial-grade films

Major Accomplishments:

1) Completed design of plasma carbonization reactor (construction 80% complete)
2) Implemented spectroscopic diagnostics estimate parameters for chemical kinetics model
3) Treatment of bulk LDPE using latest set-up led to peak yield of 20 mmol/h of H_2

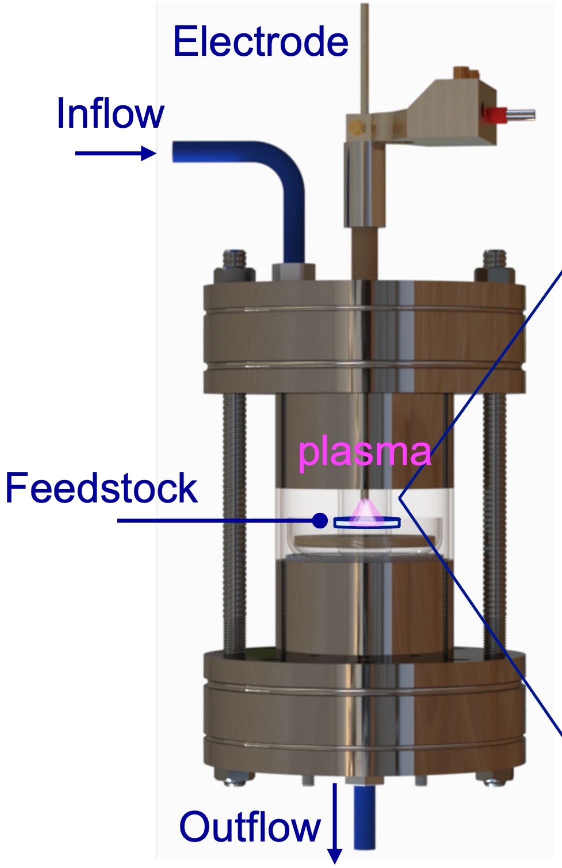
Milestones:

1) > 2 hours of continuous and a total of > 50 hours of operation of the reactors (***in progress***)
2) > 90% carbon mass in treated solid samples (future)
3) > 90% carbon recovery by mass and > 97% of carbon mass in treated solid samples (future)

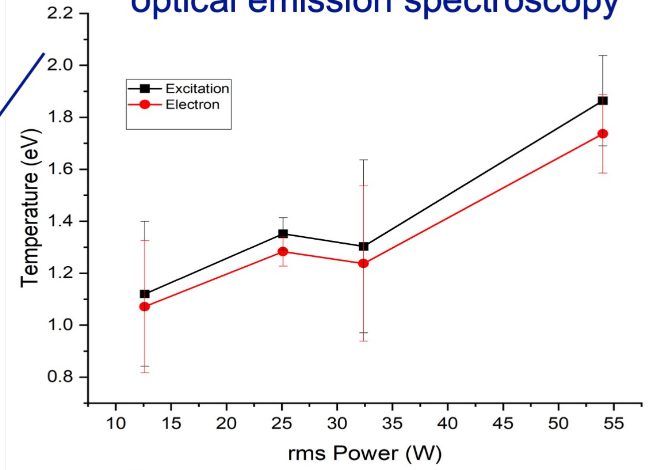
2 – Progress and Outcomes

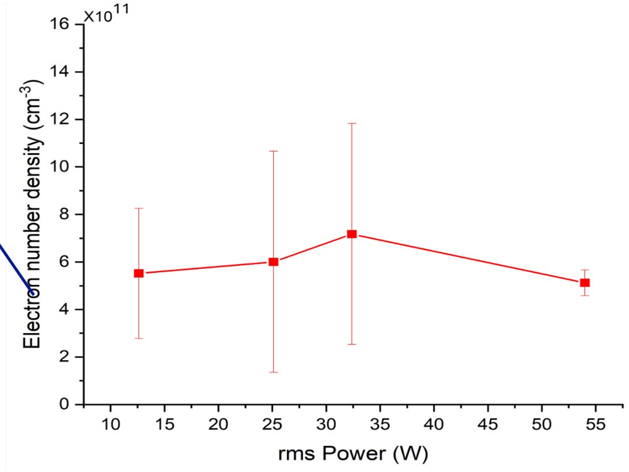
Task 3: Plasma Carbonization

Reactor design and characterization

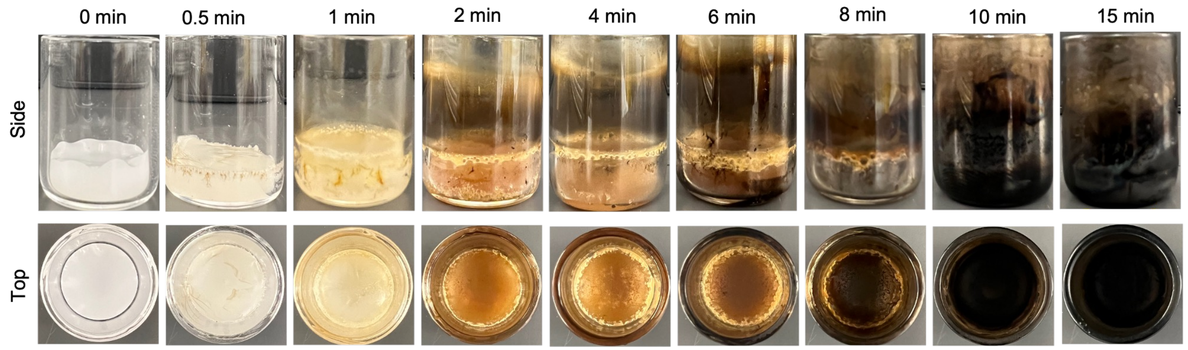


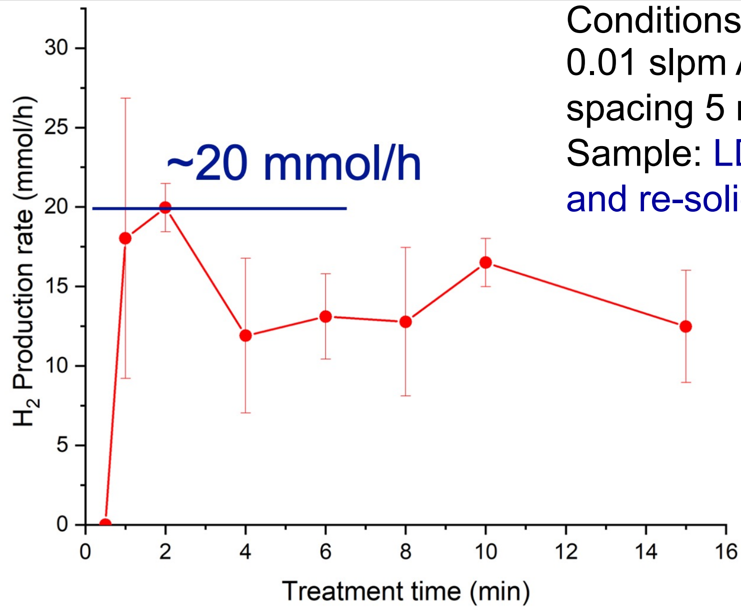
Plasma characteristics from optical emission spectroscopy





Treatment of bulk LDPE





Conditions: voltage level 60%, flow rate 0.01 slpm Ar, electrode-feedstock spacing 5 mm

Sample: LDPE 1000 mg – bulk, molten and re-solidified

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2 – Progress and Outcomes

Task 4: Process Scalability

Task Objectives:

1) Determine kinetics of non-catalytic/chemolytic delamination and plasma carbonization
2) Determine the scaling law of non-catalytic/chemolytic delamination and plasma carbonization
3) Determine overall process scalability

Major Accomplishment:

A first apparent kinetic model for non-catalytic delamination describing relevant physical phenomena that can fit published experimental data

Milestones:

1) Apparent kinetic models for non-catalytic/chemolytic delamination and plasma carbonization (***in progress***)
2) Scaling laws describing non-catalytic/chemolytic delamination and plasma carbonization (future)
3) Quantitative scaling law of the overall process (future)

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2 – Progress and Outcomes

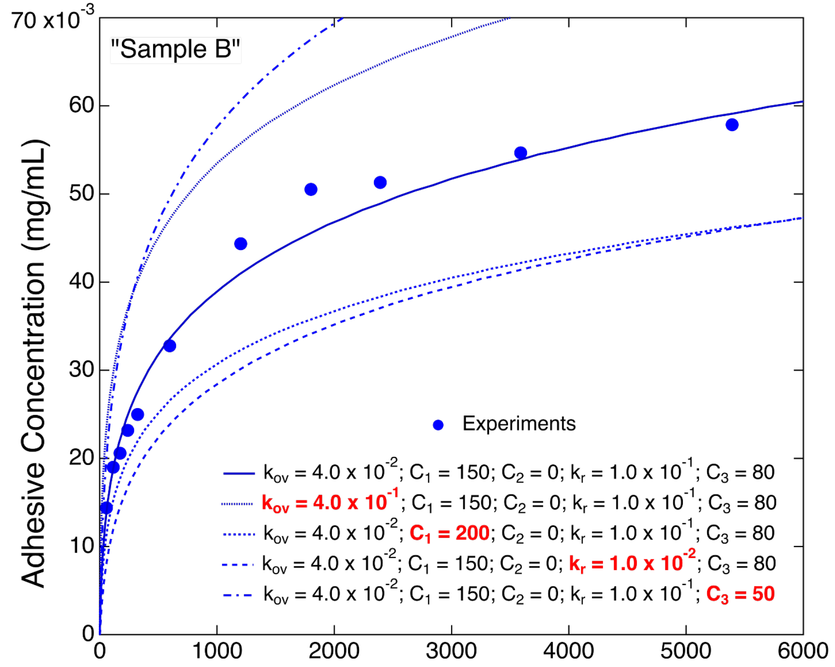
Task 4: Process Scalability

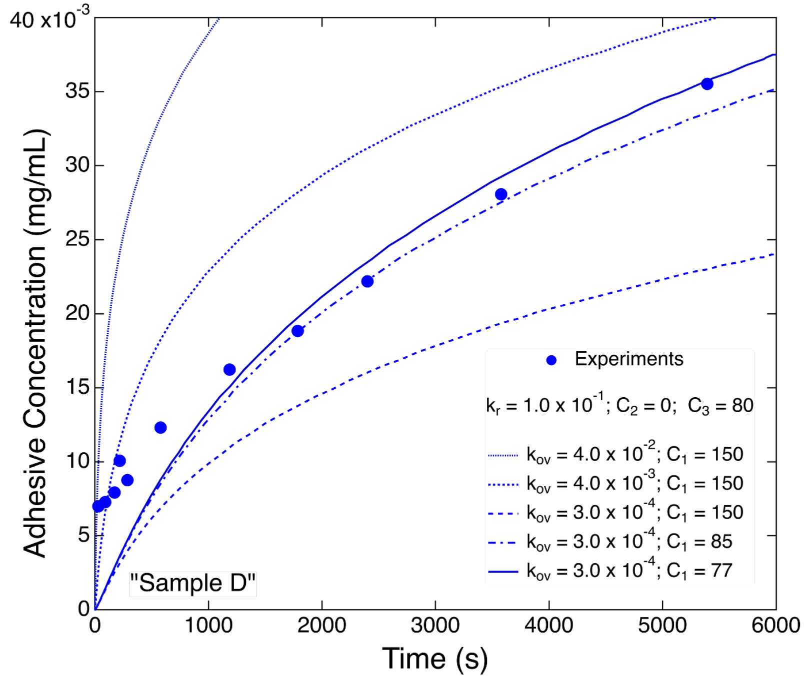
$$\frac{\mathrm{d}Q_s(t)}{dt} = nA\left(\frac{k_{ov}\,M_w\,C_{s,0}}{\rho_s}\right)\left(1-\frac{Q_s(t)}{Q_0}\right)^{C_1}\left(\frac{t}{t_0}\right)^{C_2} = r_{\text{diff}}$$

where $Q_s(t)$ is the amount of adhesive "sees" the solvent

$$\frac{dC_A(t)}{dt} = nA\,k_r\left(1-\frac{C_A(t)}{C_{A,eq}}\right)^{C_3} - \frac{r_{\text{diff}}}{Q_s(t)}C_A(t)$$

where the second term is affected by $Q_s(t)$





- Samples B and D share the same adhesive material (SB-PU) the only layer attached (transparent PE)
- 4 parameters (k_{ov}, C_1 , k_r, C_3) were optimized for Sample B, then only the diffusion parameters (k_{ov}, C_1) were varied for Sample D

Experimental data: Ügdüler et al., *Resources Conserv. Recycl.*, **2022**, 181, 106256

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2 – Progress and Outcomes

Task 5: Life Cycle Assessment (LCA)/Techno-economic Analysis (TEA)

Task Objectives:

1) Establish and analyze baseline process scenarios
2) Conduct sensitivity analysis of process parameters

Major Accomplishment:

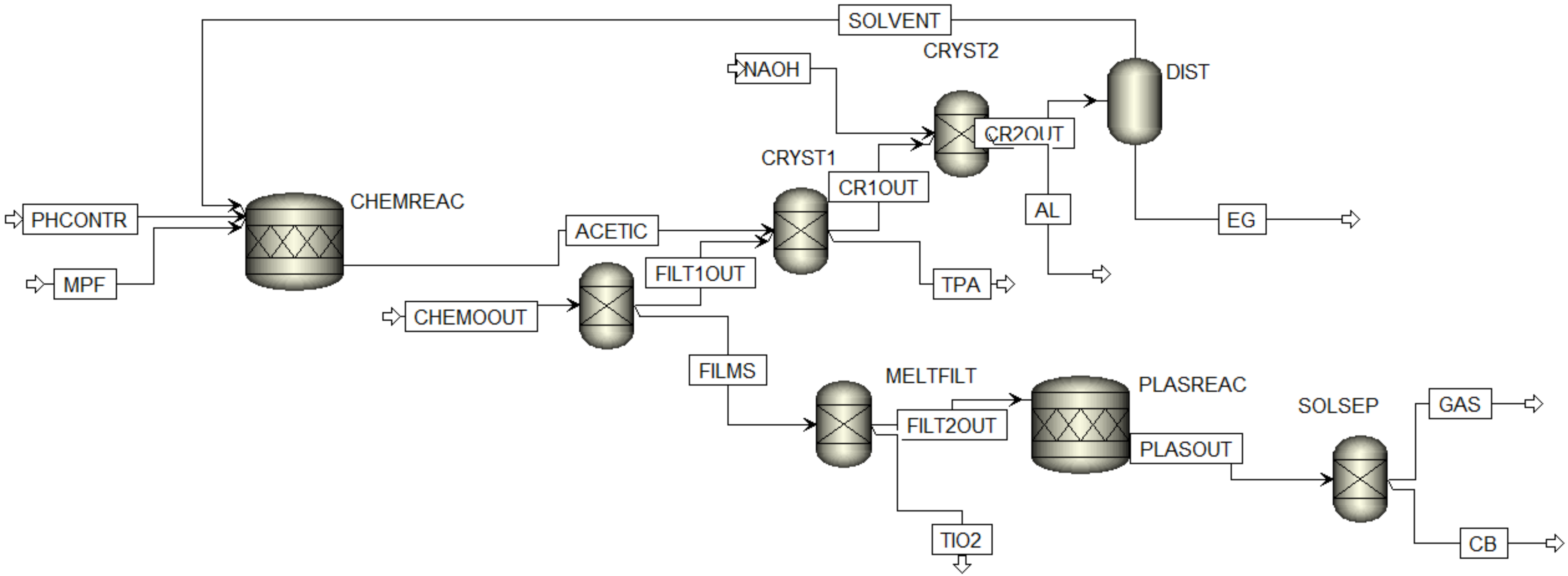
A first draft process diagram via Aspen Plus

Milestones:

1) First TEA and LCA frameworks predicting economic and environmental impacts (*in progress*)
2) Quantitative descriptions of factors affecting process economic and environmental performances (future)

2 – Progress and Outcomes

Task 5: Life Cycle Assessment (LCA)/Techno-economic Analysis (TEA)



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2 – Progress and Outcomes

Task 6: Bench-top Reactor System

Task Objectives:

1) Reactor system design and fabrication
2) Reactor system testing

Major Accomplishment:

None

Milestones:

1) Reactor design in CAD drawings (future)
2) Fabrication of the bench-top reactor system components and assembly (future)
3) Demonstration of the bench-top reactor system to achieve the target project metrics (future)

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2 – Progress and Outcomes

Diversity, Equity, Inclusion Milestones

Current Task, Timeline, and Upcoming Milestone:

Milestone D.1: 50% of project personnel trained by micro-aggression bystander training (**met**)

Milestone E.1: Outreach activities for greater Lowell underserved communities (**met**)

Introduction of plastic recycling (by Co-PI Chen) to the Lowell High School students

Milestone I.1: 50% of project PIs from underrepresented groups (**met**)

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3 – Project Impacts

Technology Impacts:

- A new paradigm to produce high-value chemicals and advanced materials
- Distributed waste upcycling for local economic growth and resiliency
- New jobs and revenue streams for the waste and materials recycling
- Decreased landfill and environmental release of single-use plastic films
- Reduced environmental exposure of hazardous materials
- Lower greenhouse gas emissions and pollutants

DEI Impacts:

- Support and engage **underrepresented students in STEM** and outreach to **underserved communities** in Massachusetts

Result Dissemination:

- Peer-reviewed publications, national and international conferences, and outreach activities

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Summary

1) An **integrated chemolytic delamination–plasma carbonization process** is being developed to upcycle multi-layer waste plastic films, with key technical objectives to:
   - Treat a wide range of different compositions
   - Produce high-value products (e.g., plastic monomers, carbon materials)
   - Use environmentally benign solvents
   - Scale modularly for small-scale, distributed manufacturing

2) The diversity, equity, and inclusion (DEI) plan aims to support and engage **underrepresented students in STEM** and **underserved communities in Massachusetts**

3) Major project accomplishments to date:
   - Two safer solvents for film delamination were identified and examined
   - A plasma carbonization reactor was designed and assembled
   - An apparent kinetic model for non-catalytic delamination was developed and tested
   - DEI milestones were met

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Quad Chart Overview

Timeline

7/01/2023 – 6/30/2025

	FY22 Costed	Total Award
DOE Funding	*(7/01/2022 – 9/30/2022)* *$5,546*	*(negotiated total federal share)* *$1,600,276*
Project Cost Share	$36,439	$675,095

Project Goal

The overall technical goal of the project is to develop and demonstrate an integrated chemolytic delamination–plasma carbonization process for the robust upcycling of single-use multi-layer waste plastic packaging films with heterogeneous compositions

End of Project Milestones

(1) A bench-top process that is capable of upcycling real-world multilayer films consisted of at least 3 out of 5 target constituents (PE, PET, EVOH, Al, and TiO_2) at a feed rate of > 100 cm^2 film/hr, with > 80% PET conversion, > 95% TiO_2 particle removal, > 90% carbon recovery from PE and EVOH by mass and produced carbon materials of > 97% carbon mass fraction.

(2) TEA and LCA results showing that the proposed technology satisfies the metrics

(3) Quantitative expression of overall scalability of the process

Funding Mechanism

Single-Use Plastics Recycling (SUPR) FOA, DE-FOA-0002473, 2021

Project Partners

National Renewable Energy Laboratory, Dow

HP Indigo Labels and Packaging (materials supplier)

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Additional Slides