Catalytic Deconstruction of Plasma-treated Single-Use Plastics to Value-added Chemicals and Novel Materials

Principal Investigator: North Carolina Agricultural & Technical State University (NCAT)

Key Partners: North Carolina State University (NCSU), University of Michigan (UM), Caltech, Dow Chemical

Consultants: U of South Carolina (USC), Manhattan College (MC)

PI: Debasish Kuila, PhD

Proposed Total Project Cost: $3,124,993.00
Proposed Project Duration: 3 years

Overview-Project's Key Ideas/Takeaway

- Application of non-thermal plasma (NTP) to functionalize polymer backbone by oxidation/hydroxylation and thereby activate subsequent low temperature selective chemical deconstruction of waste polyolefins to monomers, high value chemicals and polymers.

Approach

Data & Information

Material

Gas NTP treatment (Shannon)

- Optimize gas phase plasma treatment to maximize radical insertion in PE and PP backbone
- Characterize gas phase species
- Key parameters: power density, gas medium, treatment time ,temperature
- Key products: GPF, gas phase

experimental conditions

GPF

Plastic Film characterization (Kuila, He)

- Characterize UBF, LPF and GPF using Ultimate analysis, FTIR, XPS, Raman, EM, AFM

property data

LPF

Liquid NTP treatment (Foster)

- Optimize liquid phase plasma treatment to maximize radical insertion in PE and PP backbone
- Characterize liquid phase species
- Key parameters: power density, liquid medium, treatment time ,temperature
- Key products: LPF, oxidized species in liquid phase

experimental conditions

Caltech (Goddard) ReaXFF QM modeling

- Build model and validate with plasma treatment exptl. data
- Predict plasma treatment conditions to maximize oxygen insertion in LPF and GPF material

GPF, LPF

ChemPren & liquid by-product conversion (Kuila,Gaffney,Prokofjevs)

- Conduct baseline runs on UBF materials (PE and PP)

- Optimize ChemPren process for UBF material (PE and PP)

- Finetune GPF and LPF (PE and PP) ChemPren process conditions to achieve
  - ***Conversion to C2-C4 Olefins, BTX > 70 %**
  - ***C2-C4 Olefin yield > 40 %**

- Convert liquid phase oxidized by-products to HVC
  - * **Demonstrate > 50% conversion of hydroxyl groups to polyols**

Preliminary TEA and LCA (Maffia, Sawant))

- Conceptualize an integrated process combining NTP + ChemPren + steam cracker backend (separation) train

- Define and size unit operations to estimate capital and operating costs

- Use GABI to estimate and compare the "Cradle-to-Gate" GWP of
  - * Benchmark virgin C2-C4 olefin and BTX production
  - * Benchmark plastic pyrolysis to C2-C4 olefin and BTX production
  - * Optimized Integrated NTP + ChemPren + steam cracker backend process

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Approach contd..

ChemPren & liquid by-product conversion

- Demonstrate optimized NTP + ChemPren process from BP1 with "real-world" waste polyolefinic films

- Demonstrate synergies and intensification of integrated NTP + ChemPren process
    * Evaluate plasma insertion for by-product recovery, increased catalyst activity and recovery
    * valorize ChemPren by-products in plasma treatment steps

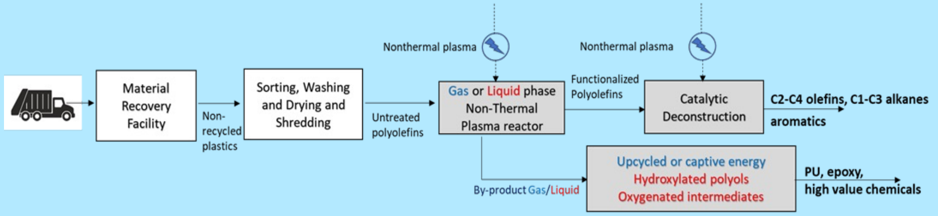
TEA and LCA of Final Integrated process

- Finalize process scales for centralized and distributed production scenarios

- Finetune and finalize TEA and LCA of integrated "waste plastics-to-olefins" process

- Develop Market Transformation Plan that includes
    * Market entry points for key products
    * Commercial viability
    * Plan for pilot scale facility

Proposed NTP + ChemPen process FOA Targets



	Benchmark[1] (Fossil)	Benchmark[2] (Pyrolysis)	NTP + ChemPren Target
Process energy consumption, MJ/kg	19 - 20		< 9 to 10 *(50% reduction over benchmark)*
GHG emissions[1,3] kgCO2eq/kg products	1.2 - 3		< 0.6 to 1.5 *(50% reduction over benchmark)*
Weight% Carbon recovered and utilized		23 – 40%*	> 50%

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Challenges

- Degree of oxygenation of plastics using plasma both in the gas and liquid phases through experiments and modeling.
- Catalytic Deconstruction (ChemPren) of modified plastics to yield higher % of C2-C4 olefins.
- TEA- Techno economic analysis to make this process more competitive over other processes

Communication and Collaboration

- Weekly, monthly, and annual meetings with the full team including Advisory Board will be scheduled to review priorities, cross-discipline issues, and short- versus long-term needs.

- Periodic reports of technical and financial progress are sent to DOE Technology Manager and Technical Project Officer.

- Internal verifications and discussions will be continued.

- The entire team will meet in person at least once per year or in a virtual conference to allow graduate students and postdocs to participate in the discussions and present their work.

Diversity, equity, and inclusion

- Improve transparency and clarify procedures to grow diversity by promoting unconscious biases in staffing and research
- Research team members will attend/acquire equity and inclusion training to develop strategies and approaches to alleviate communication barriers and unconscious biases.
- Grow pipeline of students, postdocs, and faculty from underrepresented minorities (URMs) and women
- Support and mentor at least 3 undergraduate students, 5 graduate students, and 1 postdoc fellow in year 2 and year 3 (URMs)

2 – Progress and Outcomes – key milestones

- Status of the project -1st year; 2nd quarter

- Initial verification by NREL completed in February, 2023

- Demonstrate >10% polymer structure modification using liquid phase plasma treatment (M6) to increase selectivity and yield to target products using ChemPren.

- Use ReaxFF reactive force field to predict non-thermal plasma induced bond breaking reactions for PE and PP and following reaction intermediates to target products. (examine the role of O_3 and OH radicals)

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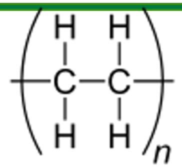
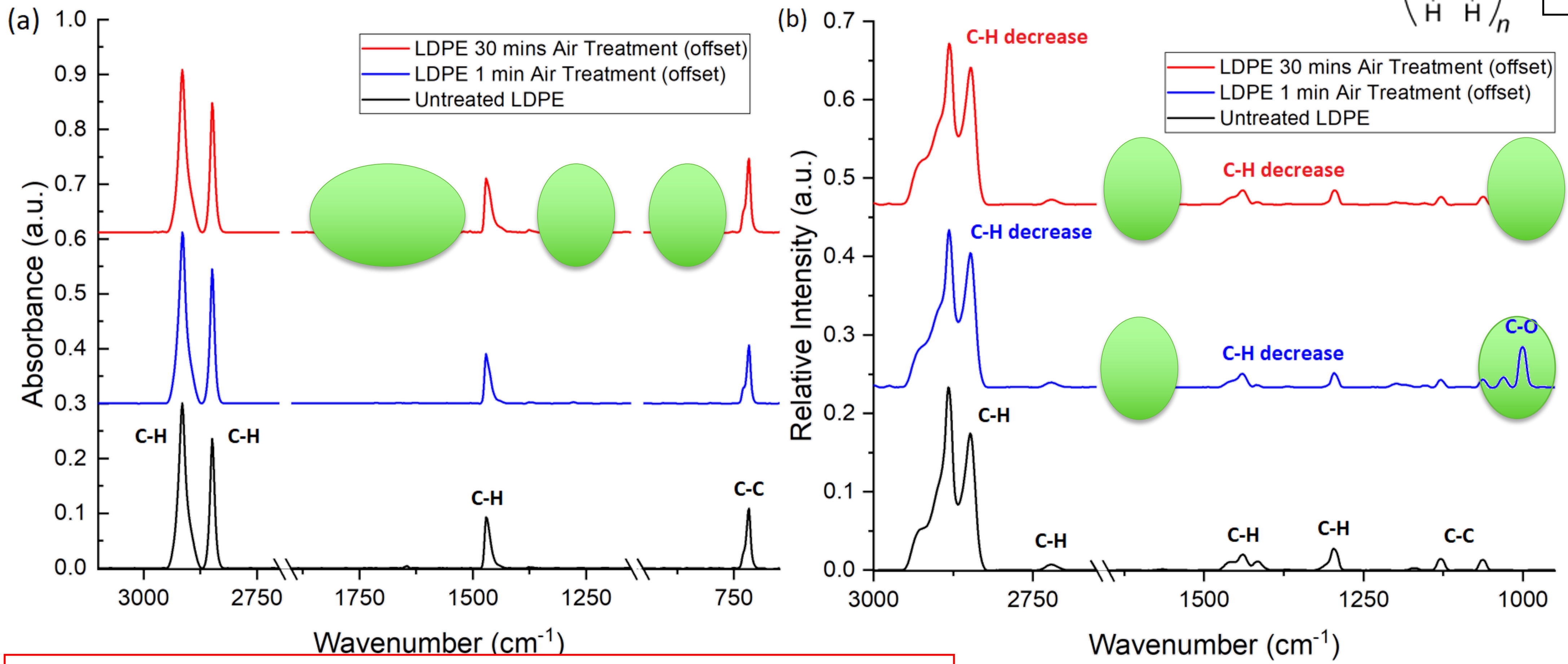
Low-density Polyethylene (LDPE) Treated with DBD Plasma (Shannon, NCSU)

$(C_2H_4)_n$



100% Air Treatment With the DBD



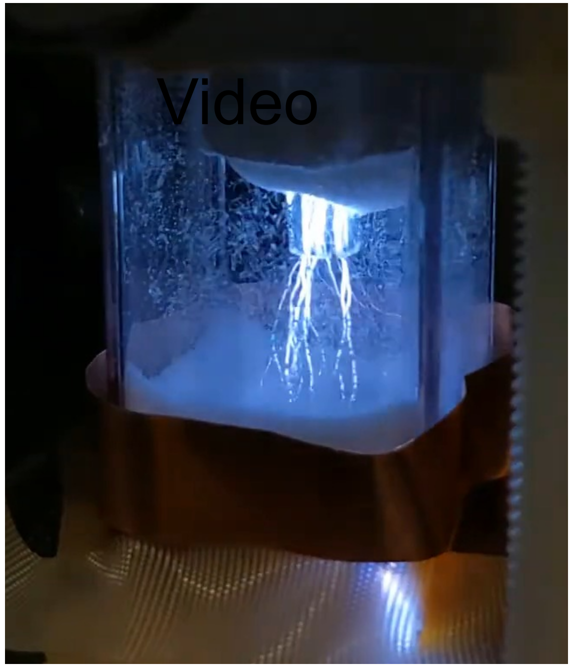
Green highlights indicate oxygen incorporation in carbon backbone (possible pathway for accelerated decomposition)
LDPE Bags were sticky and gummy after plasma treatments.

Larkin, Peter, Infrared and Raman Spectroscopy, Elsevier Inc., 2011.
Polymer Testing 2002, 21, 557.
Journal of Applied Polymer Science 2002, 86, 443.
European Polymer Journal 2006, 42, 1558.
Surf. Interface Anal. 2008, 40, 608.

Liquid Phase Plasma-PP, ~300 um (UMich)-Fluidized Bed Reactor

PP sticks to walls more than the other polymers (shown before experiment)

PP 100 ns, 1 kHz, 18 kV, 5 scfh fluidizer, 10 scfh jet



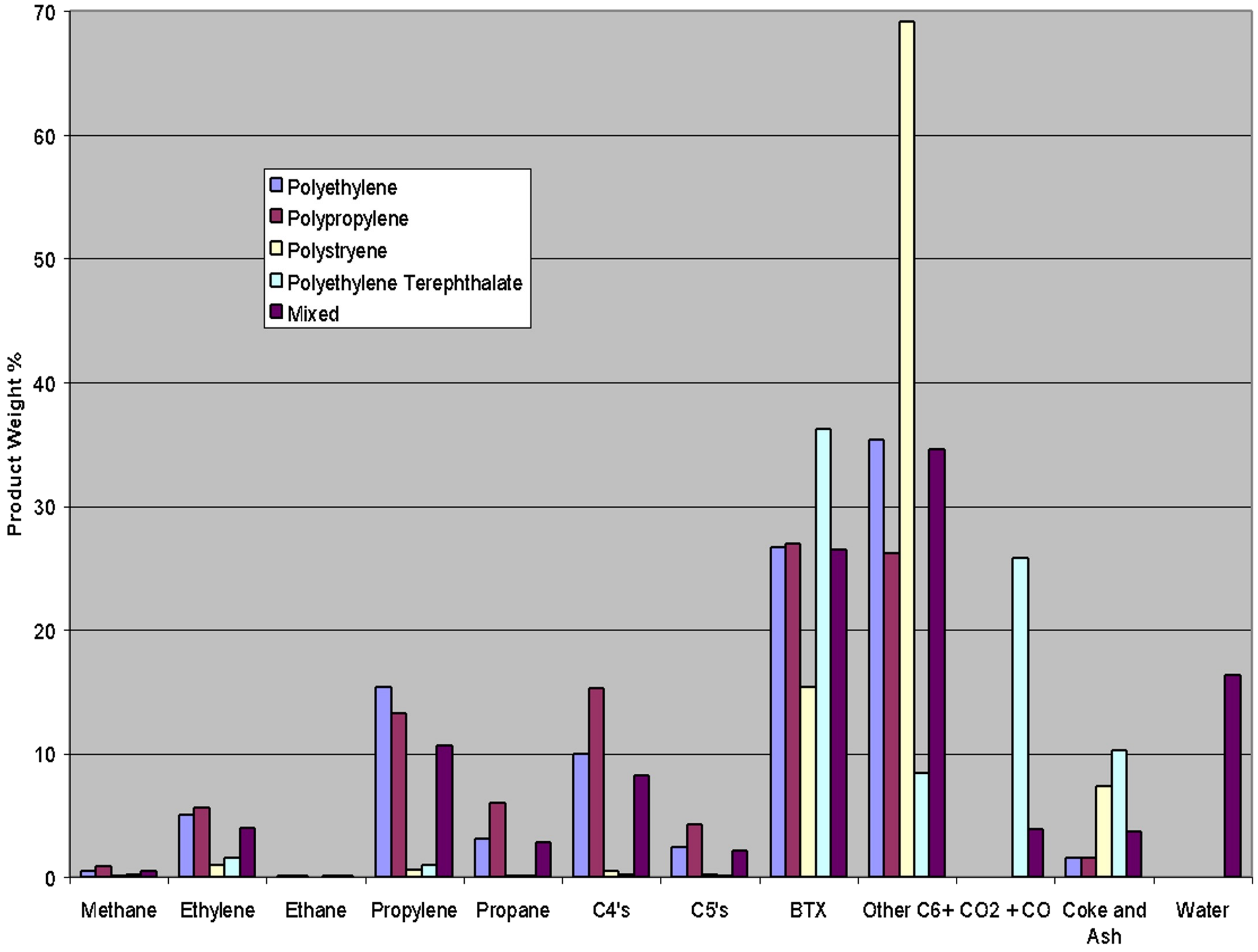
PP 100 ns, 1 kHz, 14 kV,
5 scfh fluidizer, 10 scfh jet
Note discharge under fluidizer

Current Status at NC A&T

- A ChemPren Reactor for plastic deconstruction- To be assembled(4/23)
- To ensure no delay from plasma treatment of plastics to catalytic deconstruction setup, a Non-thermal DBD plasma reactor is to be setup at NCA&T (using parameters developed at NCSU) – 3/23
- Contact angle measurement setup (to determine change of surface properties) is being procured.
- 2 PhD students working on this project (NC A&T)
- Catalysts-ZSM-5 with Si/Al ratio of 250 and 25,impregnated with 10% Co and 10% Cr have been prepared.

Fluid Bed Results- PP, PE, PS, PET- mixed Plastics

- 1 mm pieces of plastic either mixed with catalyst before heating or dropped into fluidized catalyst at reaction temperature
- 15 % ZSM-5 fluid catalyst
- 1" diameter reactor
- Turbulent flow
- Residence time 1 s
- Cracking step takes 1 minute



The mixed plastic feed was comprised of 50 wt% polyethylene, 20 wt% polypropylene, 15 wt% polystyrene, and 15 wt% polyethylene terephthalate, representative of typical post-consumer plastic waste.

Improvements to the ChemPren TEA via the processing improvements

Specific key performance parameters to be tracked through the lifetime of the project that will show progress toward your targets

Yield slate, especially relative to ethene, propene and butenes; for example yields from the TCD of polypropylene currently at 36%

		yields	WT%	NORMALIZE
16	CH4	C1	1	0.96339114
28	C2H4	C2=	6	5.78034682
30	C2H6	C2	0.2	0.19267823
42	C3H6	C3=	13.5	13.0057803
44	C3H8	C3	6.5	6.26204239
56	C4H8	C4	16	15.4142582
70	C5H10	C5	4	3.85356455
78	C6H6	B	6.825	6.57514451
92	C7H8	T	13.65	13.150289
106	C8H10	X	6.825	6.57514451
98	C7H14	C7	27.3	26.300578
12	C	C	2	1.92678227
		SUM	103.8	100

Noteworthy:

1. Carbon at 2%; used in the heat balance
2. Less acetylenes and diolefins
3. Significant BTX (27%)
4. Significant C6-C8 non-aromatics
5. C2-C4 mono-olefins, including ethene and propene at 20%
6. This stream can be interfaced with the reactor effluent from liquids cracking plant.

COP: Summary Cost of Production

Summary of Economics

			Chem Pren
			$/lb Propylene
VC	variable costs		-$1.2972
FC	fixed costs		$0.4608
CR	capital recovery		$1.0000
SUM of Required Realizations			$0.1636
	SG&A	1.50%	$0.0025
RNB	Required Netback		$0.1661

3-Impact (advantages-Why Important?)

- Pyrolysis and gasification are the current state-of-the-art feedstock technologies to convert waste plastics to olefin feed stocks.
- This project aims to specifically address the current problems with low carbon efficiency and low energy efficiency.
- Direct application of electrons to functionalize polymer backbone with tolerance to hybrid mixtures of plastics; minimizes separation
- Breakdown of organic contaminants and additives by plasma
- Use of renewable power as compared to thermal cracking with co-generation of high value products

Near Future Plans

- Build the ChemPren and Plasma set-ups at NC A&T
- Complete initial characterization of oxygenated PP and PE from Gas (NCSU) and Liquid Phase (UMich) Plasma treatment with input on modeling using ReaxFF MD.
- Do QM on model systems to resolve discrepancies (Caltech).
- Compare ReaxFF to QM for PE, PP, etc. and adjust if necessary (Caltech).
- Start Catalytic Deconstruction experiments with NTP-treated plastics and initiate TEA.

Final Verification: GNG (Go/No-Go decision)

NTP= Non-thermal Plasma

- Energy consumption of the NTP + upcycling process is more than 50% less compared to fossil olefins.
- Carbon utilization is > 70%; much higher than traditional plastic decomposition routes (58% for pyrolysis).
- The yield to C2-C4 olefins is > 40% (higher than 27% reported for pyrolysis).

Quad Chart Overview

*Only fill out if applicable.

8-01-2022
to 7-31-2025

	FY22 Costed	Total Award
DOE Funding	*(08/01/2022 – 07/31/2025)*	*(negotiated total federal share) $3,124, 993*
Project Cost Share *	$624,999	

TRL at Project Start:2
TRL at Project End: : 3

Project Goal

Cost-effective production of olefins and value added materials from single-use plastics

End of Project Milestone

Develop a Technology-to-Market Plan

Funding Mechanism

DOE-FOA -2473.

Project Partners*

- Partner 1 UMich
- Partner 2 – NCSU
- Partner 3 : Caltech
- Partner 4: Dow Chemical

Acknowledgements

- DOE-EERE- for support

- Thank you
- Any questions??