

Synergistic Upcycling of Waste Plastics and CO₂ into Oleochemicals via Non-Thermal Plasma

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tcbiomass 2024 September 10–12, 2024

Co-authors

Alif Duereh, Sultan Ul Iffat Uday, A Lusi, Haiyang Hu, Hui Hu

Plastic Wastes and Current Recycling

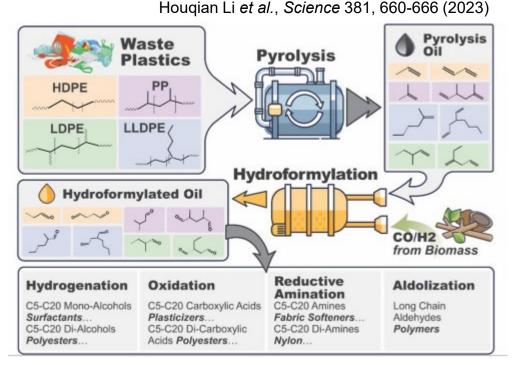
- Plastic waste globally: 2Mt in 1950, 260 Mt in 2018 and 350 Mt in 2023. ^[1, 2, 3]
- 48 Mt in the US (majority polyolefins), contributing to 12.2% of all MSW.^[2]
- Only 8.7% of plastic waste recycled in the US, mostly by mechanical routes. ^[4]

McKinsey & Company, [2] US EPA, Environmental Protection Agency
OurWorldinData, [4] US EPA, Environmental Protection Agency



Production of Oleochemicals from Polyolefin Waste

"Polyolefin pyrolysis yields low value hydrocarbons, but rich in olefins"



New Trends for Value-addition

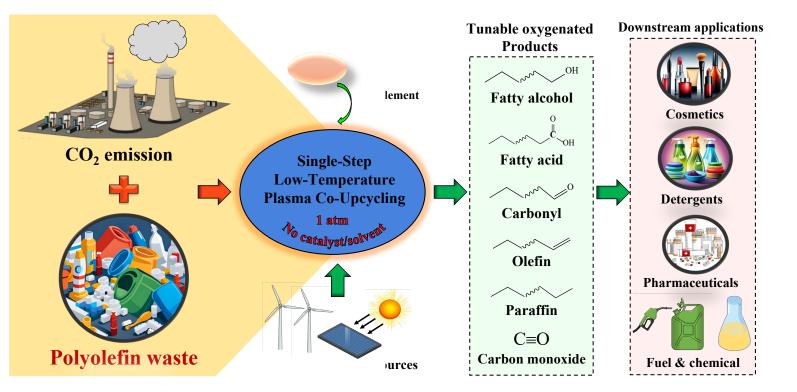
Synthetic Oleochemicals

- Ziegler process
 - Oligomerize ethylene to olefins
 - Oxidative hydrolysis to alcohols
- Oxo process
 - Olefins hydroformylation
 - Hydrogenation to alcohols
- *Catalytic oxidation* (Co/Mn) of paraffins to fatty acids, alcohols, and ketones
- Multi-step, high pressure, \$\$\$ catalysts

Plasma Upcycling of Waste Plastics and GHG CO₂

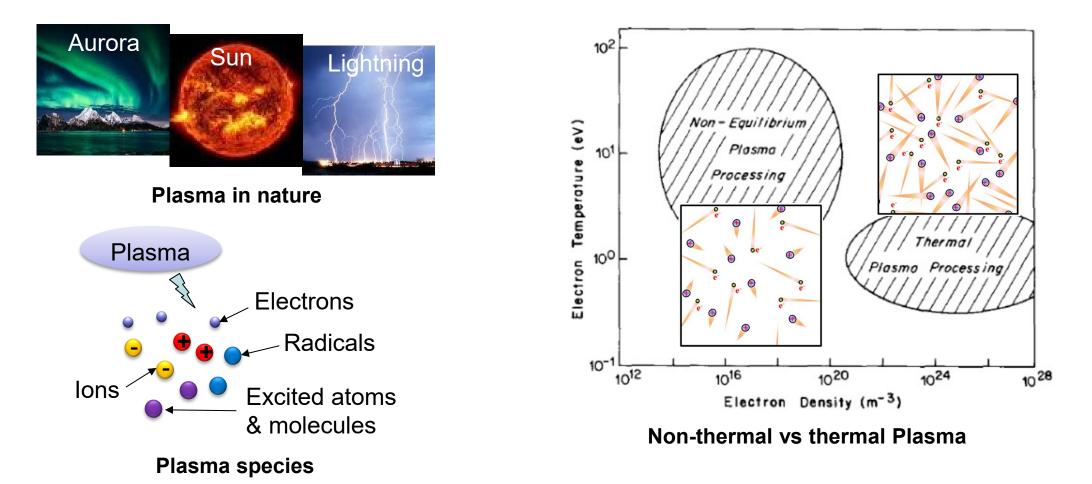
"DOE to disperse \$12 billion for carbon capture and utilization projects in coming years"

- Single-step electrified process to produce oleochemicals.
- Simultaneously upcycles waste plastics and utilizes CO₂ as a feedstock.
- CO₂ as oxidant/carbon source.
- Carbon-negative chemicals via CO₂ utilization.



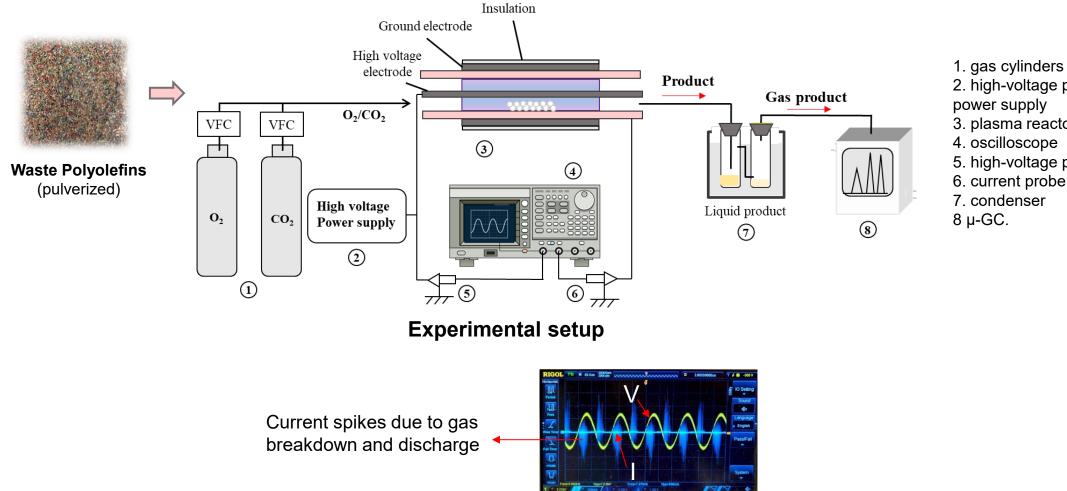
Proposed plasma-based routes to produce oleochemicals and syngas CO from polyolefin waste and CO_2

Plasma and its Classification



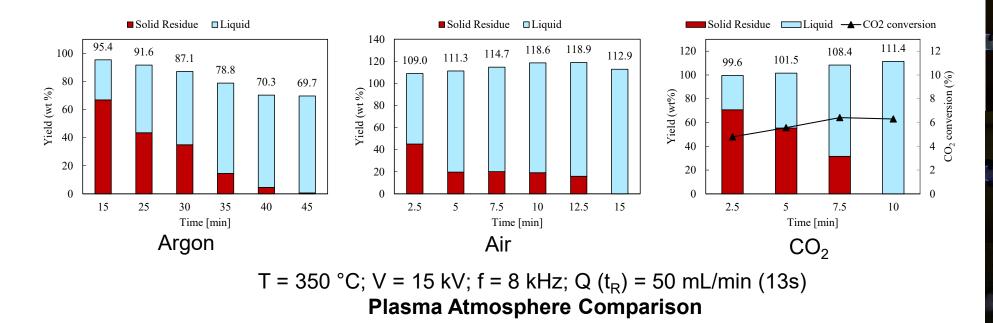
Plasma discharge creates an ionized and chemically rich environment.

Non-thermal Plasma-based Polyolefins Conversion Setup



2. high-voltage plasma power supply 3. plasma reactor 4. oscilloscope 5. high-voltage probe 6. current probe 7. condenser 8 µ-GC.

Plastic Conversion under Different Plasma Gases



- PE decomposed under different plasma atmospheres.
- CO₂ plasma (10 min) converted PE faster than argon (45 min) and air (15 min) plasma under the same plasma condition.



PE Conversion under CO₂ Plasma: Effect of Gas Residence

120

100

80

60

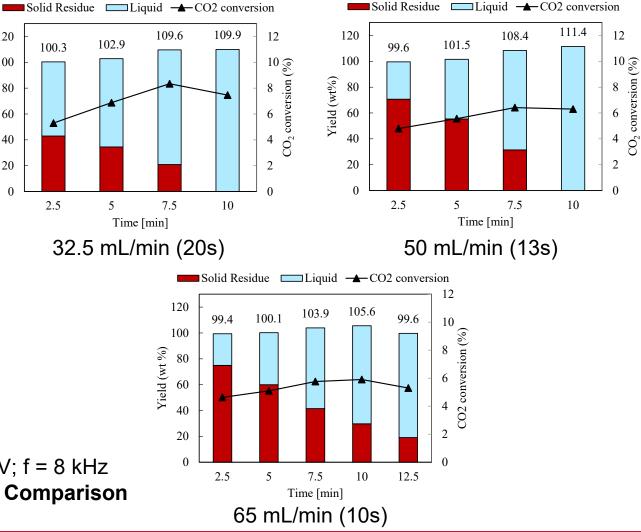
40 20

0

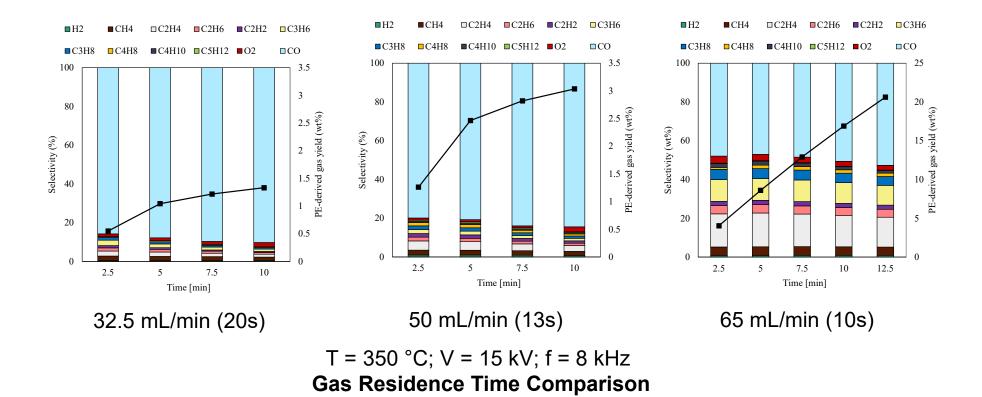
Yield (wt%)

- Both CO₂ and PE conversion increased when flow rates decreased.
- Highest CO₂ conversion of 7.5 wt% at 20s gas residence where the liquid yield was 109.9 wt%.
- Highest liquid at 13s gas residence while CO₂ conversion reduced with decreasing gas residence.

T = 350 °C; V = 15 kV; f = 8 kHz **Gas Residence Time Comparison**

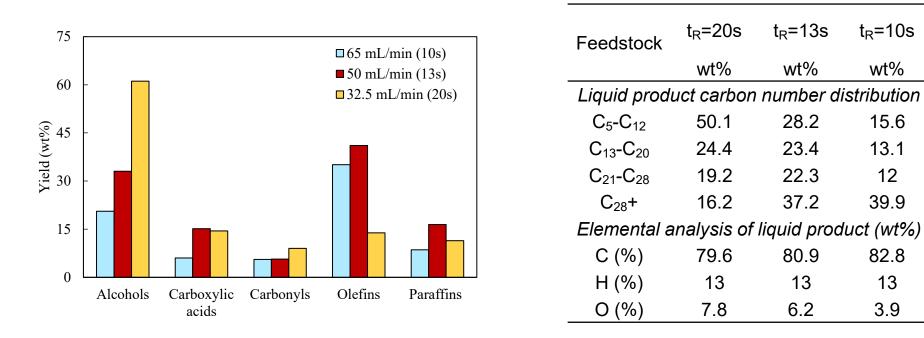


PE Conversion under CO₂ Plasma: Gas Products



- Hydrocarbon gas yield reduced with higher gas residences, from 21% to 1.3%.
- Syngas CO selectivity also increased to 85%.

PE Conversion under CO₂ Plasma: Liquid Products

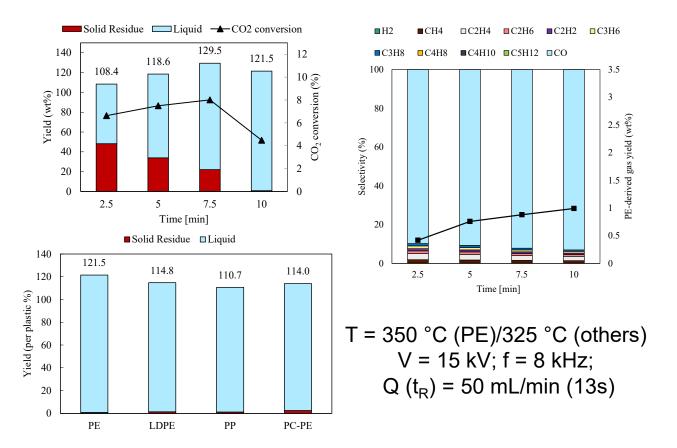


T = 350 °C; V = 15 kV; f = 8 kHz Gas Residence Time Comparison

- Liquid products: fatty alcohols (major), fatty acids, carbonyls, olefins, and paraffins.
- Lower molecular weight products are produced with increasing gas residence.

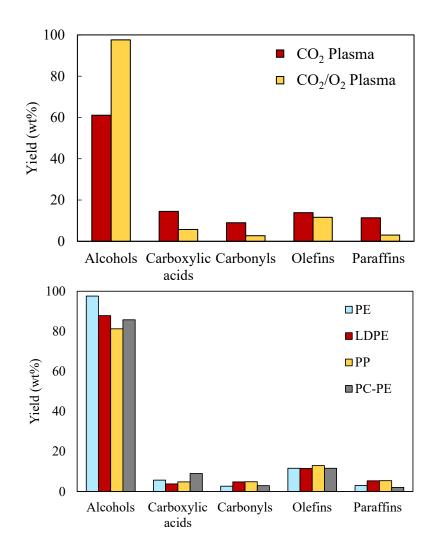
PE Conversion under CO₂/O₂ Plasma

- Adding 8 vol% O₂ to CO₂ plasma increased liquid yield to 121.5 wt%.
- CO₂/O₂ plasma produces lower PEderived hydrocarbon gas yield than CO₂.
- Gas streams are CO-rich with more than 90% selectivity from CO₂/O₂ plasma. Syngas?
- LDPE, PP, and mixed waste PE converted with 110-115 wt% liquid yields.



Time-resolved product yields and gas product selectivity

PE Conversion under CO₂/O₂ Plasma



Feedstock	HDPE	LDPE	PP	PC-PE
reeusiock	wt%	wt%	wt%	wt%
Liquid	product c	arbon num	ber distrik	oution
$C_{5}-C_{12}$	64.4	66.8	60.1	76.6
C_{13} - C_{20}	37.1	30.5	32.7	22.4
C_{21} - C_{28}	13.2	7.6	15.6	6.4
C ₂₈ +	6.1	4.7	2.6	7.8
Elei	mental an	alysis of liq	uid produ	ıct
C (%)	76.7	76.5	77	76.1
H (%)	12.1	12.2	12.1	12.1

T = 350 °C (for HDPE) and 325 °C (for others) V = 15 kV; f = 8 kHz; Q (t_R) = 50 mL/min (13s)

10.5

O (%)

11.2

- Maximum fatty alcohol yield increased from 61.1 to 97.6 wt% after O₂ induction.
- Oxygen content in the liquid increased from 7.8 to 11.2%.
- LDPE and PP produced lighter oxygenates.

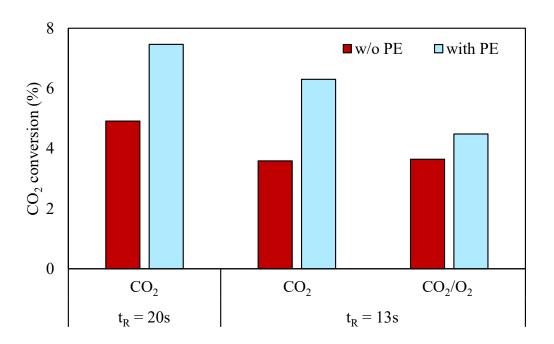
GC mass yield of different functional groups in the liquid product

11

10.9

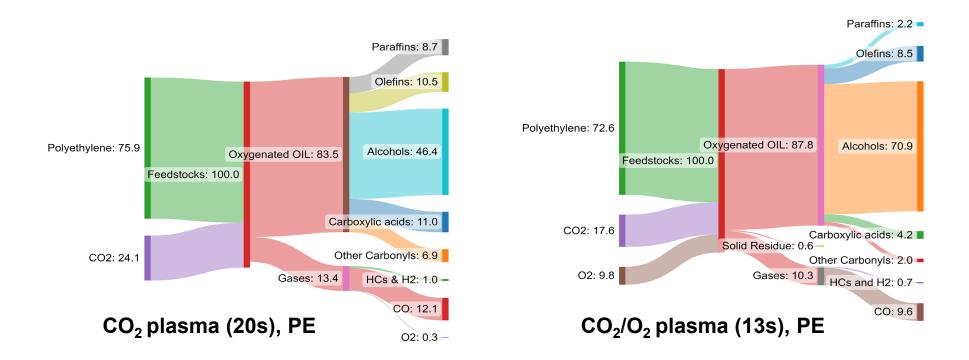
Effect of Plastic on CO₂ Conversion

- CO₂ conversion was measured under the same plasma condition without and with plastic in the reactor.
- Co-conversion with plastic showed a synergistic increase in CO₂ conversion.
- Adding O₂ resulted in lower CO₂ conversion



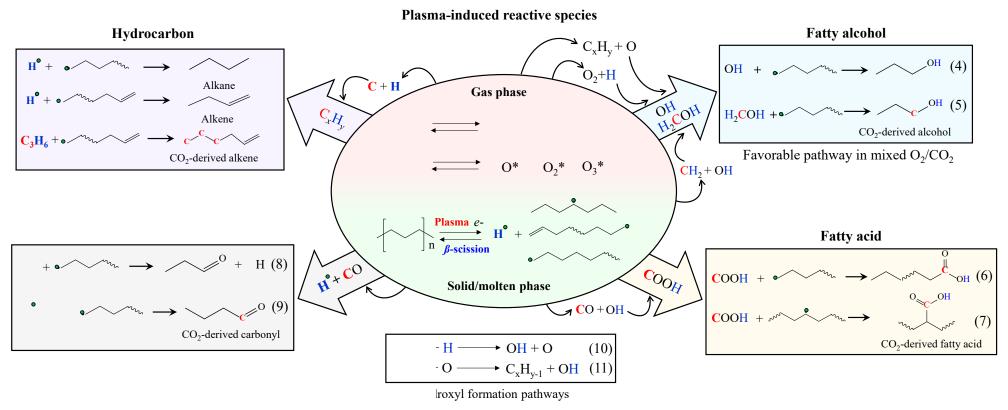
CO_{2} conversion without and with plastic

Mass balance of the plasma process



- Mass closure normalized to converted plastic and converted CO₂ or CO₂/O₂.
- Fatty alcohols constitute majority of the liquids from both CO₂ or CO₂/O₂.
- Syngas CO is the major product among gases.

Reaction Mechanism for Co-upcycling of Polyolefin and CO₂



*Plasma-induced reactive species including atoms, ions, radicals and molecules in their different states

Isotopic-study based reaction pathways for co-upcycling of polyolefins with CO₂ or CO₂/O₂ plasma

Conclusion

- Co-upcycling caused a synergistic increase in both CO₂ and plastics conversion.
- CO_2 and CO_2/O_2 had a higher conversion rate than argon or air plasma.
- Plastic acted as a scavenger and carbon sink to increase CO₂ conversion.
- CO₂ plasma-based deconstruction of HDPE can increase the liquid yield per plastic mass beyond 100% due to oxygen and carbon induction.
- Adding 8 vol% O₂ to CO₂ increased fatty alcohol yield to 97.6 wt% from 61.1 wt% without catalyst.
- Potentially carbon-negative route to produce industrial chemicals by utilizing waste CO₂ and polyolefin plastics.
- A patent-pending technology is developed to produce oleochemicals from waste plastics using CO₂ and electricity.

Acknowledgements



Advisor | Prof. Xianglan Bai

Co-authors

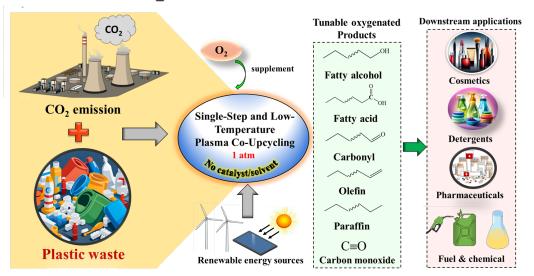
Samirah Gnangbe, Alif Duereh, Sultan Ul Iffat Uday, A Lusi, Haiyang Hu, Hui Hu, Mark Mba-Wright IOWA STATE UNIVERSITY

Issue 16, 2024





Non-equilibrium plasma co-upcycling of waste plastics and CO₂ for carbon-negative oleochemicals

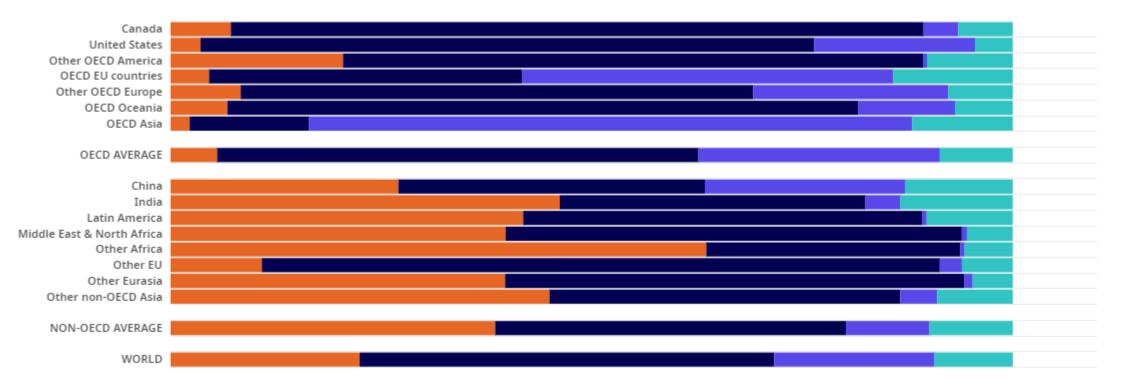


Questions?

Supplementary Information

Background





Source: OECD Global Plastics Outlook Database

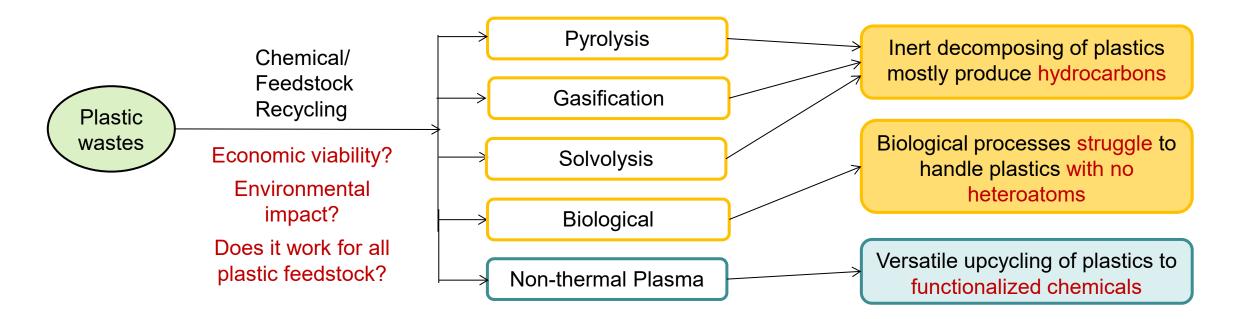


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Plastic Wastes and Current Recycling

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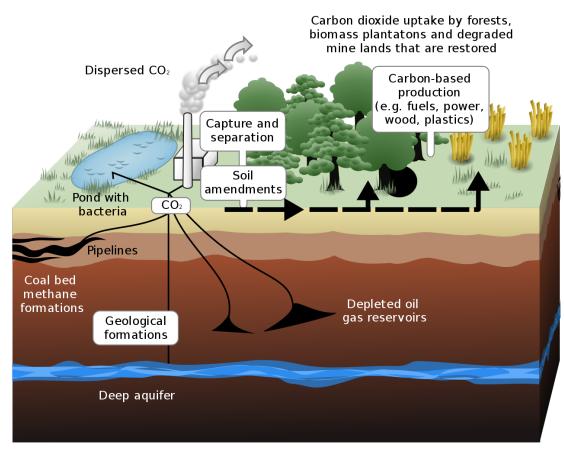


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CO₂ Utilization for Carbon Sequestration

- CO₂ releases mostly from fossil fuel combustion
- CO₂ accounts for approximately 55% of the yearly anthropogenic greenhouse gas emissions responsible for global warming
- GHG emissions have a detrimental effect on the ecosystem and weather patterns
- CO₂ utilization can reduce its concentration in the atmosphere, and using CO₂ as a carbon source can help reach global carbon neutrality goals

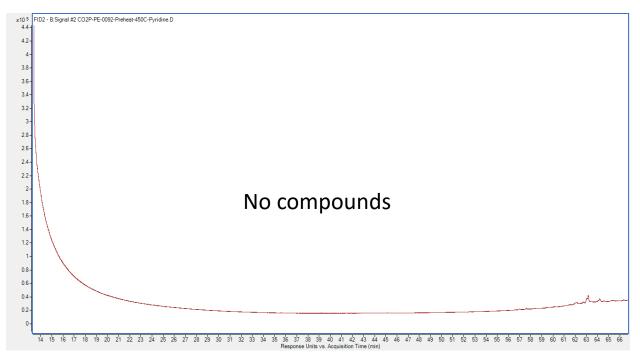


Current carbon sequestration ideas^[1]

[1] LeJean Hardin and Jamie Payne. Oak Ridge National Laboratory. http://www.ornl.gov/info/ornlreview/v33_2_00/research.htm

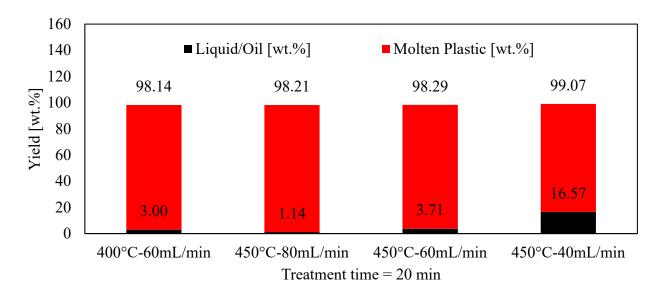
Preheating of the Reactor prior to the Plasma Actuation

- Pre-heating of the reactor to melt the plastic.
- A higher atmospheric temperature can lower the electricity conditions for the plasma actuation.
- Increasing the temperature of the gas will fasten the process of plasma breakdown.
- Prior to applying the plasma, the plastic did not devolatilize, which is proven by the GC/MS analysis of the molten plastic.



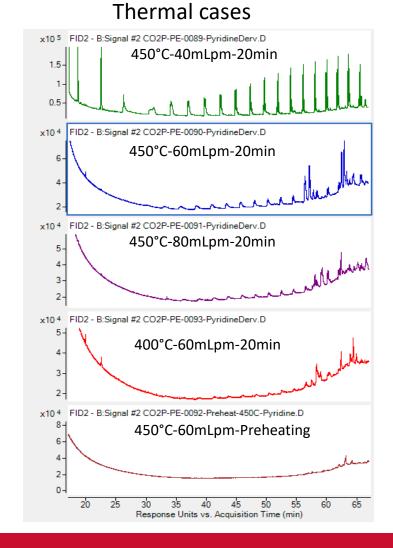
GCMS spectra of the sample with only pre-heating

Thermal Conversion with CO₂ for Comparison



- Thermal cases do not yield oxygenated products. Only hydrocarbons were produced.
- The liquid yields were also lower compared to the CO₂ plasma-based conversion of HDPE.

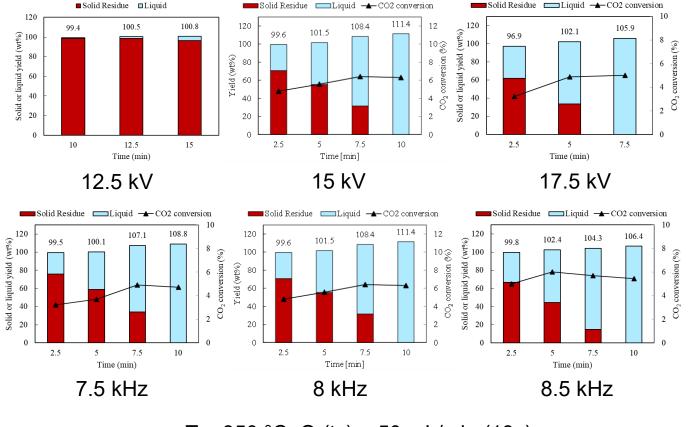
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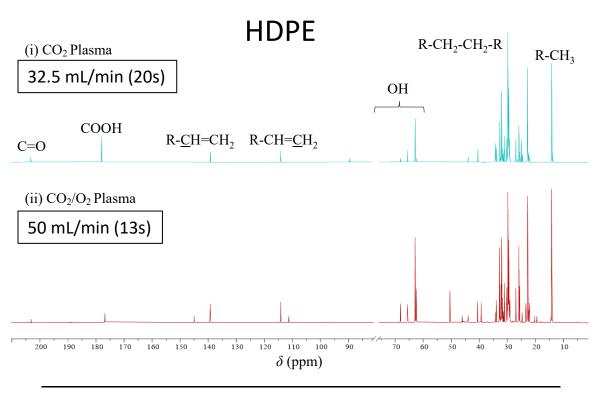
PE Conversion under CO₂ Plasma

- CO₂ plasma can decompose Polyethylene (PE) within 10 minutes.
- Highest liquid yield of 111.4 wt% per PE mass was achieved.
- The conversion rate of both PE and CO₂ increased with increased plasma voltage or frequency.

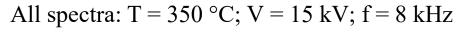


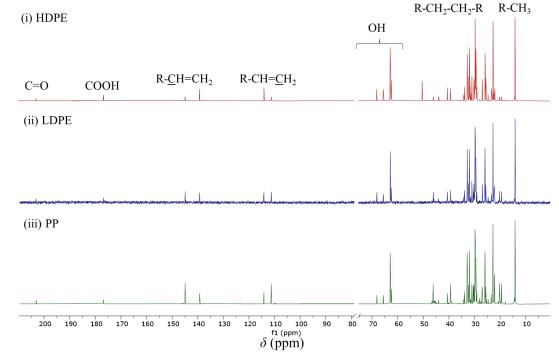
T = 350 °C; Q (t_R) = 50 mL/min (13s) Fixed *f* = 8 kHz for **voltage comparison** Fixed V = 15 kV for **frequency comparison**

NMR analysis of liquid products



Functional Group	Plasm	Plasma type		
i unotional Group	CO_2	CO_2/O_2		
Alcohols	54.3	74.9		
Carboxylic acids	16.2	5.1		
Other oxygenated compounds	3.3	1.6		
Hydrocarbons	26.2	18.5		

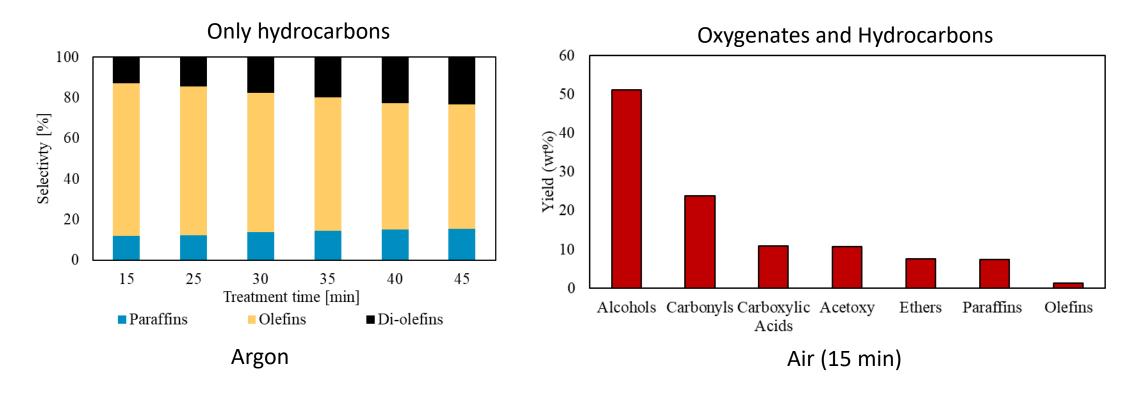




Functional Group	Feedstock			
	LDPE	РР		
Alcohols	72.6	69.8		
Carboxylic acids	2.6	3.3		
Other oxygenated compounds	0.4	3.6		
Hydrocarbons	24.4	23.3		

Different Polyolefin Comparison: CO_2/O_2 , Q (t_R) = 50 mL/min (13s)

Liquid Product Analysis of Air and Argon Plasma



T = 350 °C; V = 15 kV; f = 8 kHz; Q (t_R) = 50 mL/min (13s) Plasma Atmosphere Comparison

Characterization of liquids obtained from different feedstock and reaction conditions

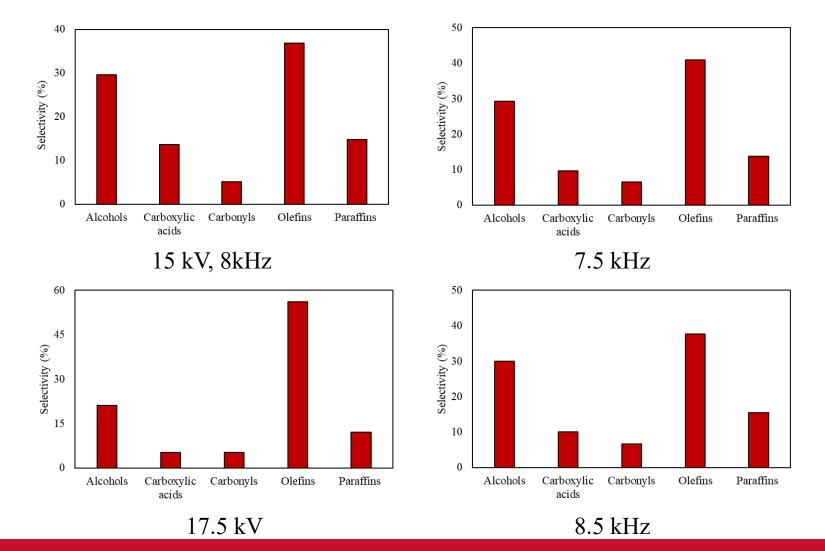
	Liquid					Eleme	ental ar	nalysis
Condition Liquid yield		Product ca	arbon numb	er distribut	ion (wt%)	(wt%)		
*	(wt%)	C ₅ -C ₁₂	C ₁₃ -C ₂₀	C ₂₁ -C ₂₈	C ₂₈ +	C (%)	H (%)	O (%)
В	111.4	28.2	23.4	22.6	37.2	80.9	12.9	6.2
С	105.9	39.6	33.3	20.1	12.9	82.2	13.1	4.7
D	108.8	22.4	21.9	21.2	43.3	81.2	13	5.8
E	106.4	39.1	25.2	27.1	15.0	80.6	13.1	6.3
F	80.6	15.6	13.1	12.0	39.9	82.8	13.3	3.9
G	109.9	50.1	24.4	19.2	16.2	79.6	12.6	7.8
Н	101.2	29.8	24.2	10.5	36.7	81.5	13.1	5.4
Ι	86.1	18.5	16.8	43.3	7.5	84.9	13.5	1.7
J	120.7	64.4	37.1	13.2	6.0	76.7	12.1	11.2
K	115.3	61.0	41.2	12.9	0.0	78.1	12.1	9.8
L	110.8	56.7	29.2	16.5	8.4	76.8	12.2	11.0
М	105.8	31.5	53.8	15.2	5.2	78.8	12.5	7.5
Ν	98.1	36.5	40.8	17.0	3.8	78.7	12.5	7.6
Ο	113.5	76.7	22.5	6.5	7.8	76.8	12.2	11
Р	109.5	66.8	30.5	7.6	4.7	77.2	12.3	10.5
Q	104.4	61.1	23.3	11.1	8.9	80.5	12.4	7.1
R	111.1	60.1	32.7	15.6	2.6	77	12.1	10.9

*Reaction conditions

A: PE, 350 °C, CO2 gas, 50 mL/min or 13s, 12.5 kV, 8 kHz, 15 min (not included)

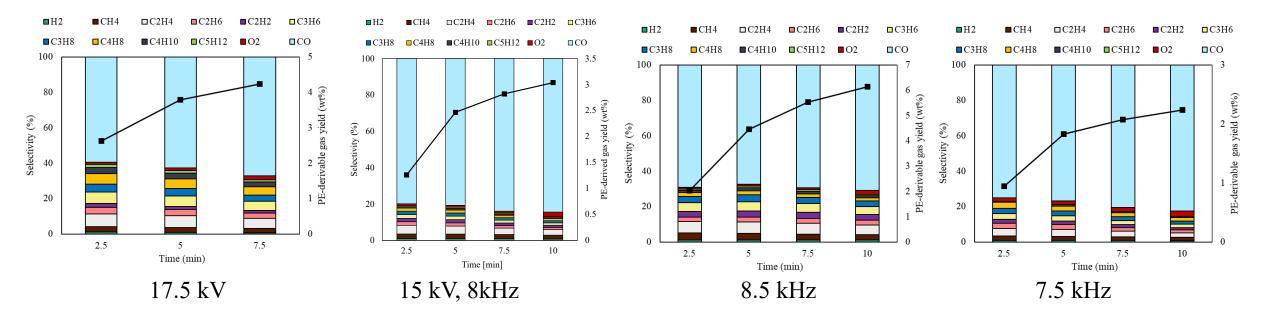
B: PE, 350 °C, CO2 gas, 50 mL/min or 13s, 15 kV, 8 kHz, 10 min C: PE, 350 °C, CO2 gas, 50 mL/min or 13s, 17.5 kV, 8 kHz, 7.5 min D: PE, 350 °C, CO2 gas, 50 mL/min or 13s, 15 kV, 7.5 kHz, 10 min E: PE, 350 °C, CO2 gas, 50 mL/min or 13s, 15 kV, 8.5 kHz, 10 min F: PE, 350 °C, CO2 gas, 65 mL/min or 10s, 15 kV, 8 kHz, 12.5 G: PE, 350 °C, CO2 gas, 32.5 mL/min or 20s, 15 kV, 8 kHz, 10 min H: PE, 300 °C, CO2 gas, 50 mL/min or 13s, 15 kV, 8 kHz, 20 min I: PE, 400 °C, CO2 gas, 50 mL/min or 13s, 15 kV, 8 kHz, 10 min J: PE, 350 °C, CO2/O2 gas, 50 mL/min or 13s, 15 kV, 8 kHz, 10 min K: PE, 350 °C, CO2/14%O2 gas, 50 mL/min or 13s, 15 kV, 8 kHz, 7.5 min L: PE, 350 °C, CO2/O2 gas, 32.5 mL/min or 20s, 15 kV, 8 kHz, 7.5 min M: LDPE, 325 °C, CO2 gas, 32.5 mL/min or 20s, 15 kV, 8 kHz, 10 min N: PP, 325 °C, CO2 gas, 32.5 mL/min or 20s, 15 kV, 8 kHz, 10 min O: LDPE, 350 °C, CO2/O2 gas, 50 mL/min or 13s, 15 kV, 8 kHz, 10 min P: PP, 350 °C, CO2/O2 gas, 50 mL/min or 13s, 15 kV, 8 kHz, 10 min Q: PC-PE, 325 °C, CO2 gas, 32.5 mL/min or 20s, 15 kV, 8 kHz, 10 min R: PC-PE, 350 °C, CO2/O2 gas, 50 mL/min or 13s, 15 kV, 8 kHz, 10 min

Effect of Plasma Intensity on Liquid Products



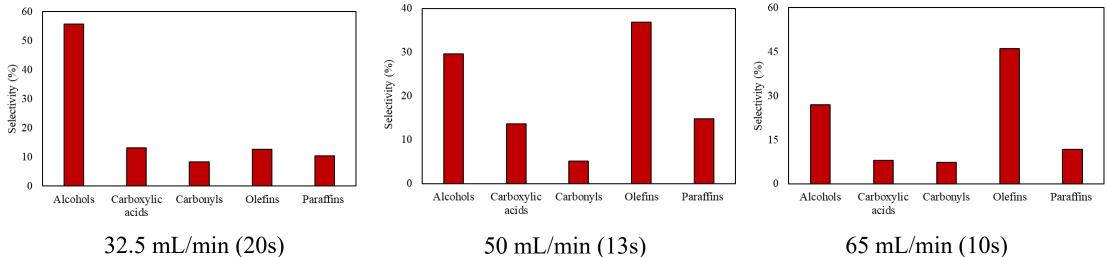
T = 350 °C; Q (t_R) = 50 mL/min (13s) Fixed f = 8 kHz for voltage comparison Fixed V = 15 kV for frequency comparison

Effect of Plasma Intensity on Gas Products



T = 350 °C; Q (t_R) = 50 mL/min (13s) Fixed f = 8 kHz for voltage comparison Fixed V = 15 kV for frequency comparison

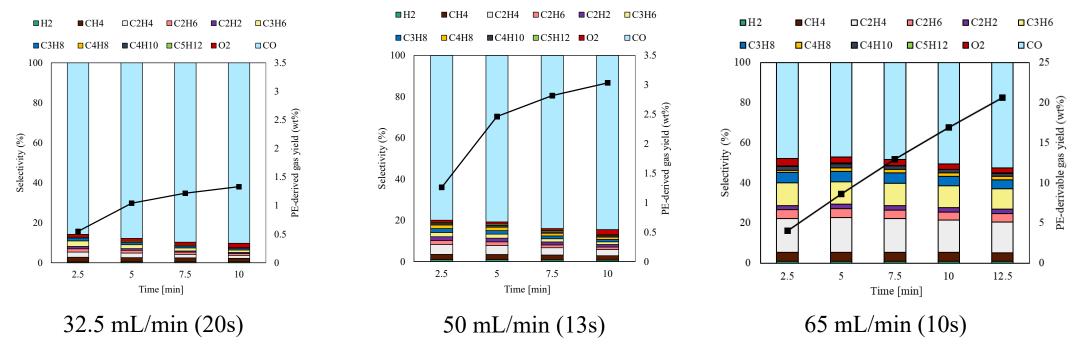
Effect of Flow Rate (Gas Residence) on Liquid Products



50 mL/min (13s)

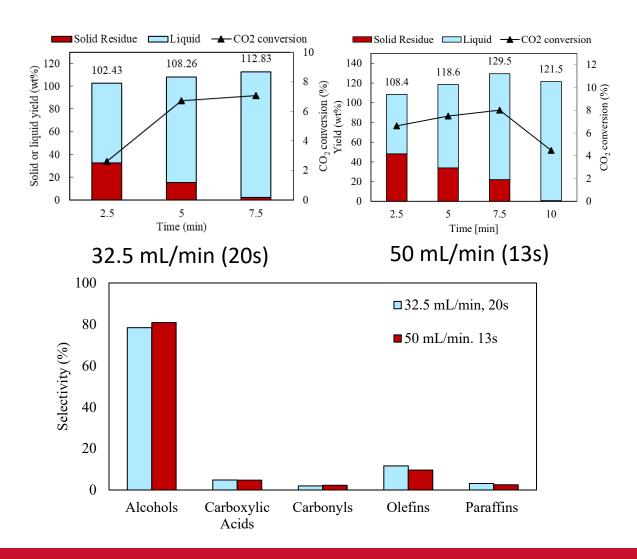
T = 350 °C; V = 15 kV; f = 8 kHz**Gas Residence Time Comparison** 65 mL/min (10s)

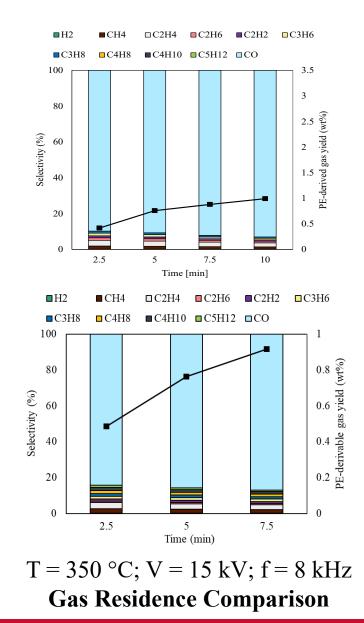
Effect of Flow Rate (Gas Residence) on Gas Products

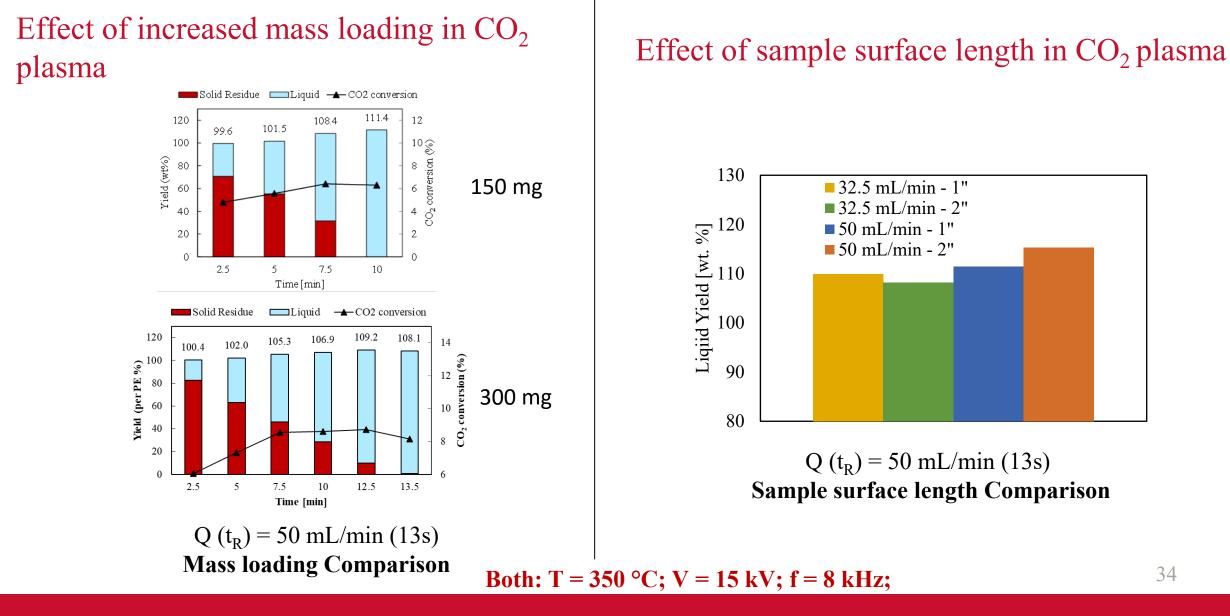


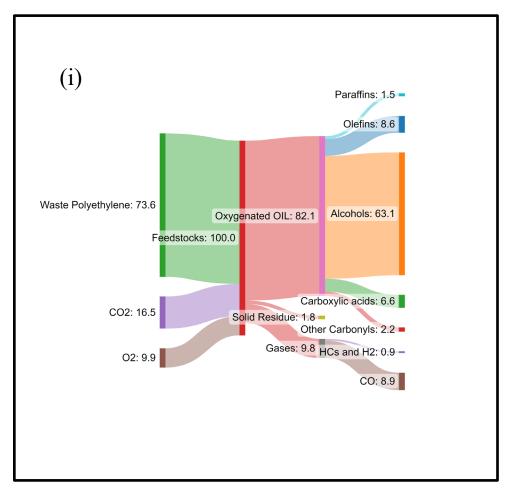
T = 350 °C; V = 15 kV; f = 8 kHzGas Residence Time Comparison

Effect of flow rate in CO_2/O_2 plasma



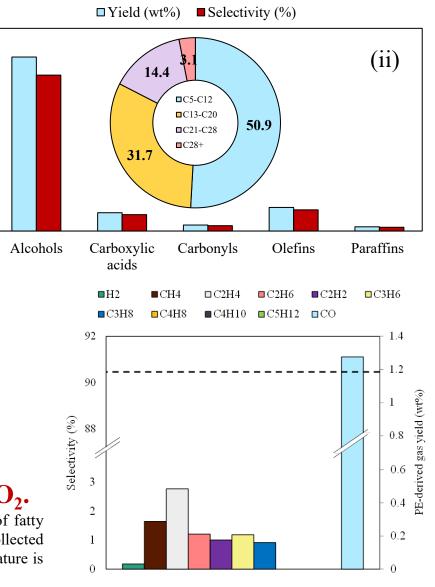




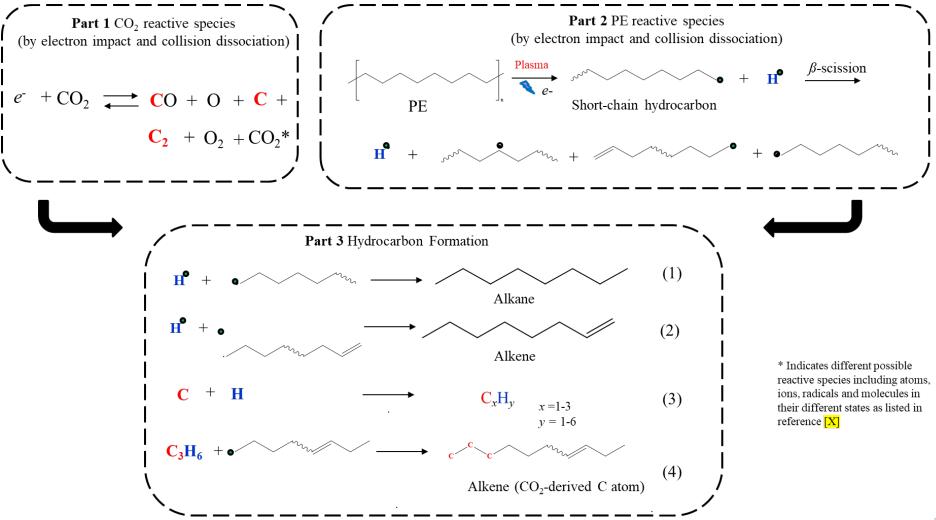


Applications of plasma-based co-upcycling for PC-PE and CO₂.

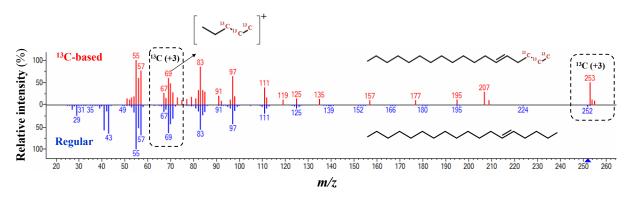
(A) (i) mass yield and selectivity of liquid products from PC-PE using CO_2/O_2 plasma, (ii) selectivity of fatty alcohols with four different carbon number range for PC-PE, and gas product selectivity from PC-PE. Collected using the residence time of 13 s (flow 50 mL/min) and reaction time of 10 min. The initial reactor temperature is 325 °C for converting PC-PE.



Detailed Reaction Mechanism

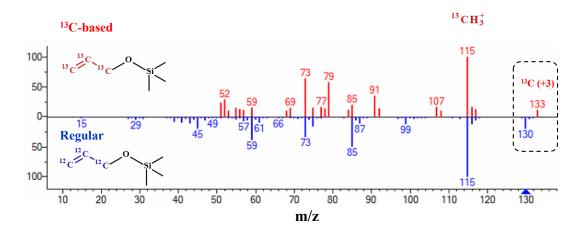


Isotopic study for reaction mechanism



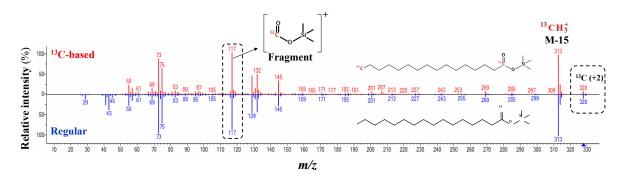
- Isotopic study was performed in a closed batch reactor
- ¹³CO₂ and PE were used as the feedstock
- MS was used to analyze resultant products

Mass spectra of 5-octadecene ($C_{18}H_{36}$, Mw = 252) compared between ¹³CO₂ plasma-based (upper) and regular (lower) molecules.

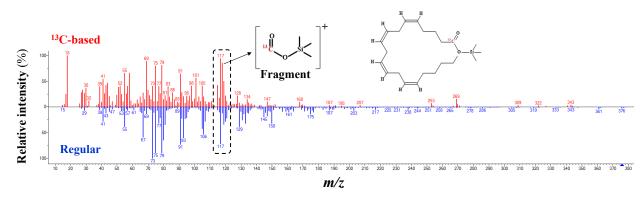


Mass spectra of allyl alcohol, TMS derivative ($C_6H_{10}OSi$, Mw = 130) compared between ${}^{13}CO_2$ plasma-based (upper) and regular (lower) molecules.

Isotopic study for reaction mechanism

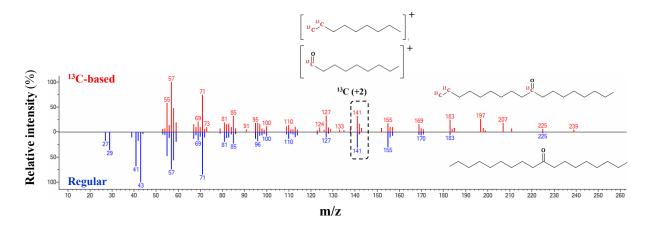


Mass spectra of palmitic acid, TMS derivative ($C_{19}H_{40}O_2Si$, Mw = 328) compared between ¹³CO₂ plasma-based (upper) and regular (lower) molecules.



Mass spectra of Arachidonic acid, TMS derivative ($C_{23}H_{40}O_2Si$, Mw = 376) compared between ¹¹³CO₂ plasma-based (upper) and regular (lower) molecules.

Isotopic study for reaction mechanism



Mass spectra of 9-octadecanone ($C_{18}H_{36}O_1$, Mw = 268) compared between ${}^{13}CO_2$ plasma-based (upper) and regular (lower) molecules.

Reproducibility of the plasma process

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Reproducibility of the experiment using PE conversion by CO_2 plasma and $t_R = 13$ s as an example. The reaction conditions: voltage 15 kV, frequency 8 kHz, CO_2 inlet flow rate of 50 mL/min, initial reactor temperature 350 °C, reaction time 10 min.

	PE mass	Reactor	mass (g)	Co	<u>Condenser mass (g)</u> Liq		Liquid	Liquid yield	CO ₂ conversion
Test No.	(g)	Before	After	Be	efore	After	mass (g)	(%)	(%)
1	0.1532	26.2991	26.3065	180	.4964	180.6585	0.1695	110.6	6.25
2	0.1481	26.5579	26.5993	169	.8593	169.9832	0.1653	111.6	6.30
3	0.1528	26.7436	26.7846	181	.8198	181.95	0.1712	112.0	6.27
Average (%)							111.4	6.27
Standard er	ror (%)							$\pm 0.7\%$	±0.03%

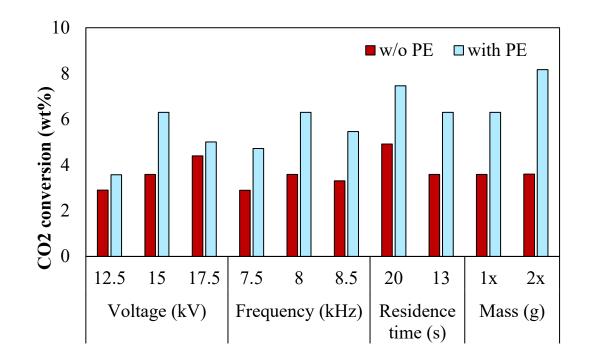
Mass closures of plasma-based co-conversion of plastics and CO_2 including all reactants and measured products. The gas, liquid and solid residue yields are calculated based on the total reactant masses, which are converted PE and CO_2 for the CO_2 plasma case, and converted PE, CO_2 and O_2 for the CO_2/O_2 plasma cases.

Plastic	t_R	Plasma	Gas (%)	Liquid (%)	Solid Residue (%)	Total (%)
PE	20 s	CO ₂	13.4	83.5	0.0	96.9
PE	13 s	CO_2/O_2	10.3	87.7	0.6	98.6
PC-PE	13 s	CO_2/O_2	9.8	82.1	1.8	93.7

Moisture content of liquid products obtained from PE or PC-PE conversion using CO_2 plasma or CO_2/O_2 plasma. Reaction conditions: 15 kV, 8kHz, 10 min, t_R is given.

		PC-PE		
Maintenne (06)	<u>t</u> R=20s	<i>t</i> ₿	<u>t</u> R=13s	
Moisture (%)	CO ₂ plasma	CO ₂ plasma	CO ₂ /O ₂ Plasma	CO ₂ /O ₂ Plasma
	0.6	0.2	0.5	0.7

Effect of plastic on CO₂ conversion during plasma-based co-upcycling



Energy consumption of PE conversion by CO_2/O_2 plasma

- Energy consumed by the plasma process was measured for CO_2/O_2 plasma with HDPE as a reference.
- Energy spent in MJ was calculated per kg of feedstock converted, considering plasma energy and sensible heat.
- The milligram scale reactor consumed 237.23 MJ/kg of energy.
- When the process was scaled to a gramscale reactor, the energy consumed dropped to 44 MJ/kg, showing the potential for energy savings with scale-up.

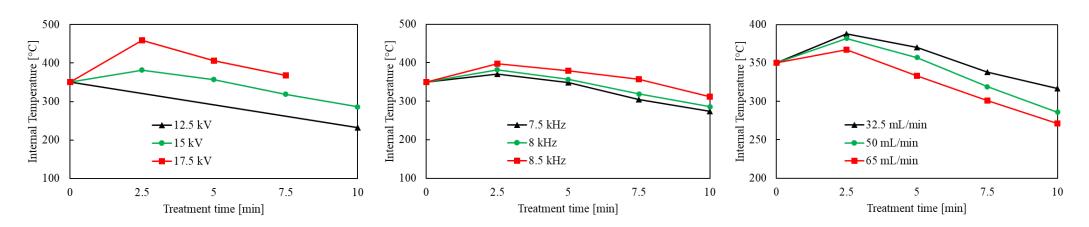
Energy consumption of PE conversion by CO_2/O_2 plasma in two reactor scales.

	Run A	Run B
PE (kg)	1.55×10^{-4}	1.015×10^{-3}
Converted CO ₂ (kg)	3.8×10^{-5}	1.08×10^{-4}
Converted O ₂ (kg)	2.1×10^{-5}	3.0×10^{-5}
Thermal energy (for pre-plasma heating) (MJ)	3.02×10^{-4}	1.479×10^{-3}
CO ₂ : sensible heating*	1.57×10^{-4}	5.24×10^{-4}
O ₂ : sensile heating*	8×10^{-6}	4.3×10^{-5}
PE: sensile heating	1.1×10^{-4}	7.31×10^{-4}
PE: latent heating for melting	2.7×10^{-5}	1.82×10^{-4}
Plasma energy (MJ)	5.0303×10^{-2}	4.9234×10^{-2}
Total energy consumption (MJ)	5.0604×10^{-2}	5.0713×10^{-2}
Energy consumption per feeds (MJ/kg)	237.23	43.97

Reaction conditions:

Run A (0.15 gram) - 50 mL/min CO₂ with 8% v/v O₂, 15 kV, 8 kHz, 10 min; Run B (1 gram) - 100 mL/min CO₂ with 12% v/v O₂, 15 kV, 7 kHz, 7.5 min. * Calculated for the total flow-in CO₂ or O₂ gas mass at the inlet during the pre-plasma heating stage.

Measured Plasma Reactor Temperature



Initial reactor temperature: 350°C; Fixed Flow Rate = 50 mL/min; Fixed Voltage = 15 kV; Fixed Frequency = 8 kHz

- Without external heating, the measured reactor temperature first increased and then decreased.
- Higher voltage and frequency resulted in higher reactor temperatures.
- Higher plasma density under lower flow led to higher reactor temperatures.