PLASTICS (POLYMERS) AND SUSTAINABILITY: SOLVING THE PROBLEM

INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH, KOLKATA
SUSTAINABILITY AND CHEMISTRY: A SYSTEMS APPROACH
CH 5106 - LECTURE 8&9
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PLASTICS AND SUSTAINABILITY

1. DEFINING THE PROBLEM

2. SOLVING THE PROBLEM

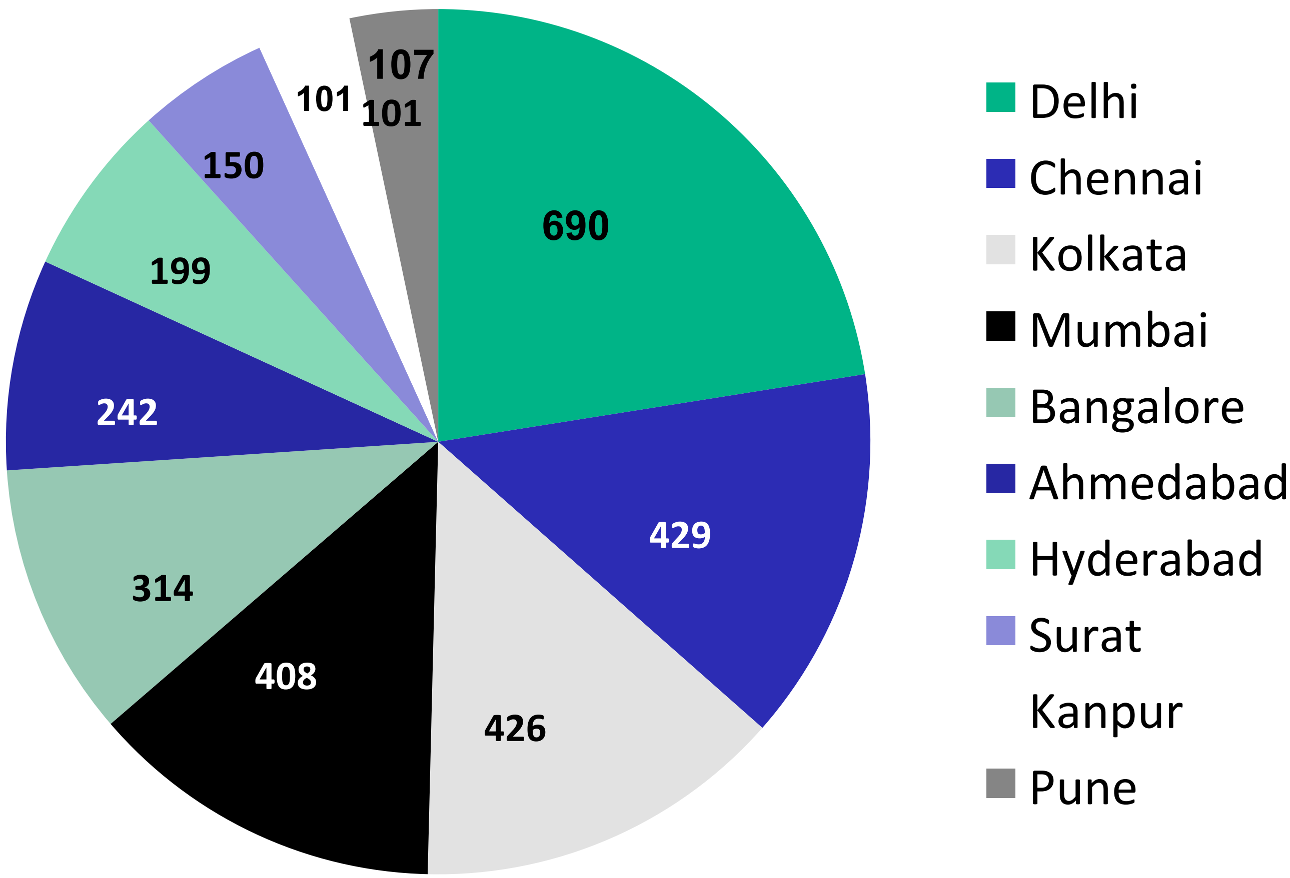
RECAP : LECTURE 7

Defining the Problem

- Understanding material flows of polymer: From cradle to grave, Global and Local
- Relationship between economic development of a nation and its ability to manage wastes; The lower the economic development (per-capita GDP) of a country, the greater the scourge of poorly managed plastic waste.
- Why is end-of-life plastic management a concern to society?
- The dimensions of the plastics waste problem in India: Facts and figures
- Five potential solutions

The plastic waste management is a classic example of a “Complex” problem in sustainability. Finding acceptable solutions requires “systems thinking” which begins with the ability to identify the components of the system, processes within the system and the relationship between them

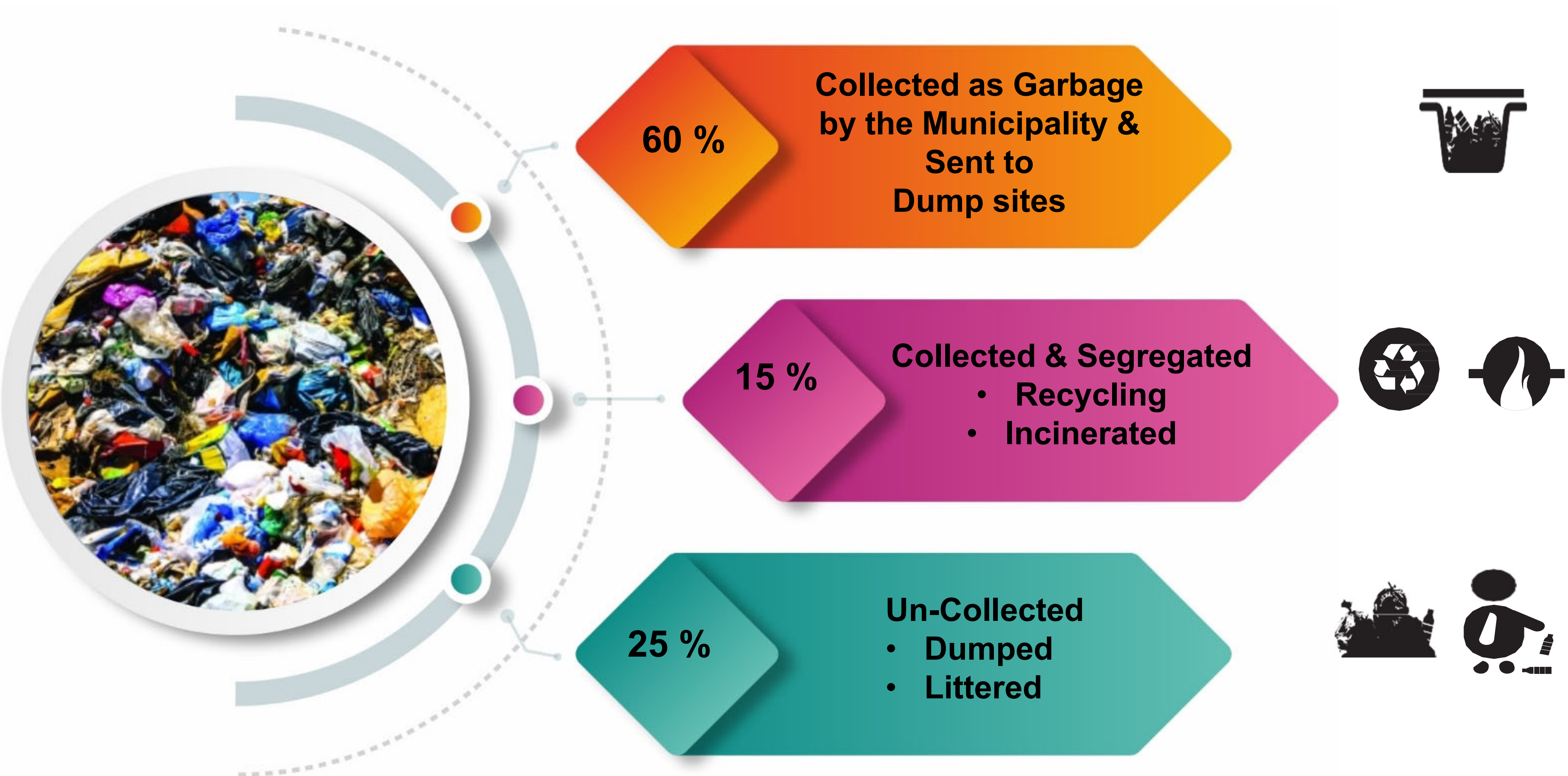
PLASTIC WASTE IN TONS PER DAY IN MUNICIPAL SOLID WASTE (2010-11)



An average of 8,5 % of the MSW is single use plastics, which when extrapolated to whole country translates into 25,000 tons per day or 10 million tons per annum

Source; Central Pollution Control Board

PLASTIC WASTE DISPOSAL: INDIAN SCENARIO



Total plastic waste generation (2020): ~ 11 million tons

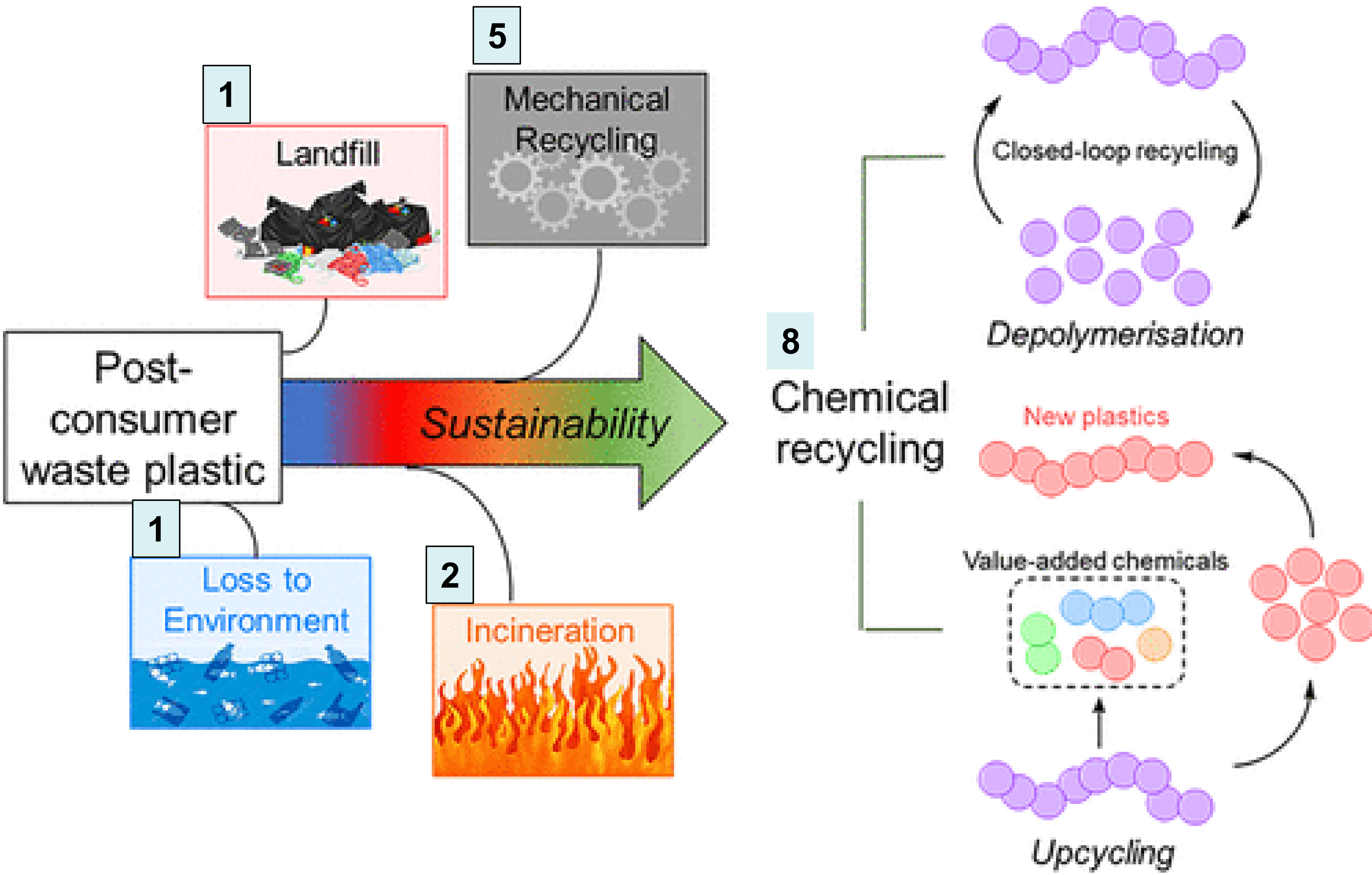
A COMBINATION OF THESE TWO MATERIALS POSES CONSIDERABLE CHALLENGES IN WASTE MANAGEMENT

Waste segregation practices essential for effective waste management

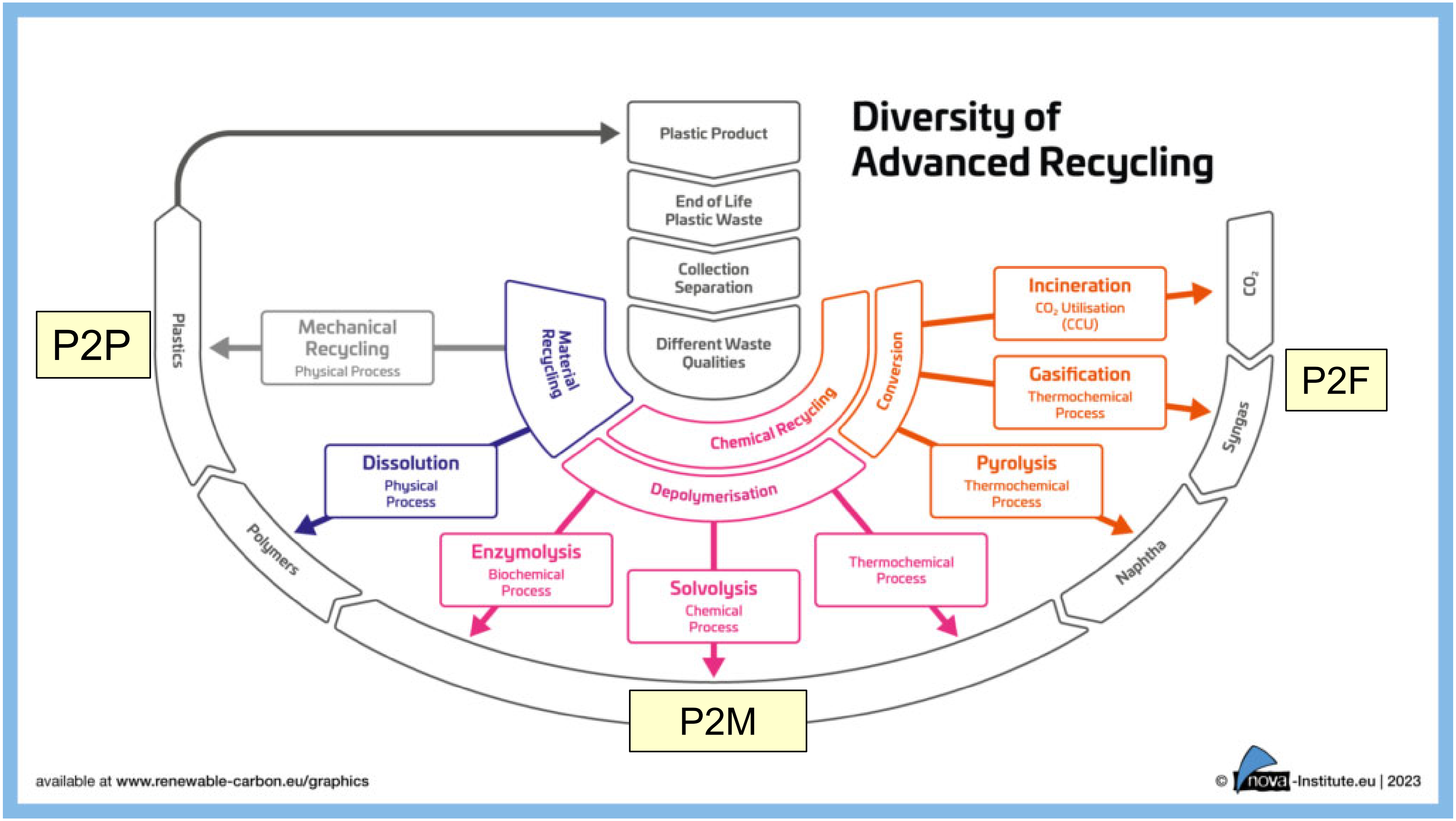
WHAT ARE THE SOLUTIONS ?

- Mechanical Recycling: Polymer to Polymer (P2P)
- Chemical Recycling : Polymer to Monomer (P2M)
- Waste plastics to fuels or energy (P2F)
- Biodegradable or compostable Plastics
- Incineration

SOLUTIONS ON A SUSTAINABILITY SCALE (1-10)



WHAT ARE THE SOLUTIONS ?

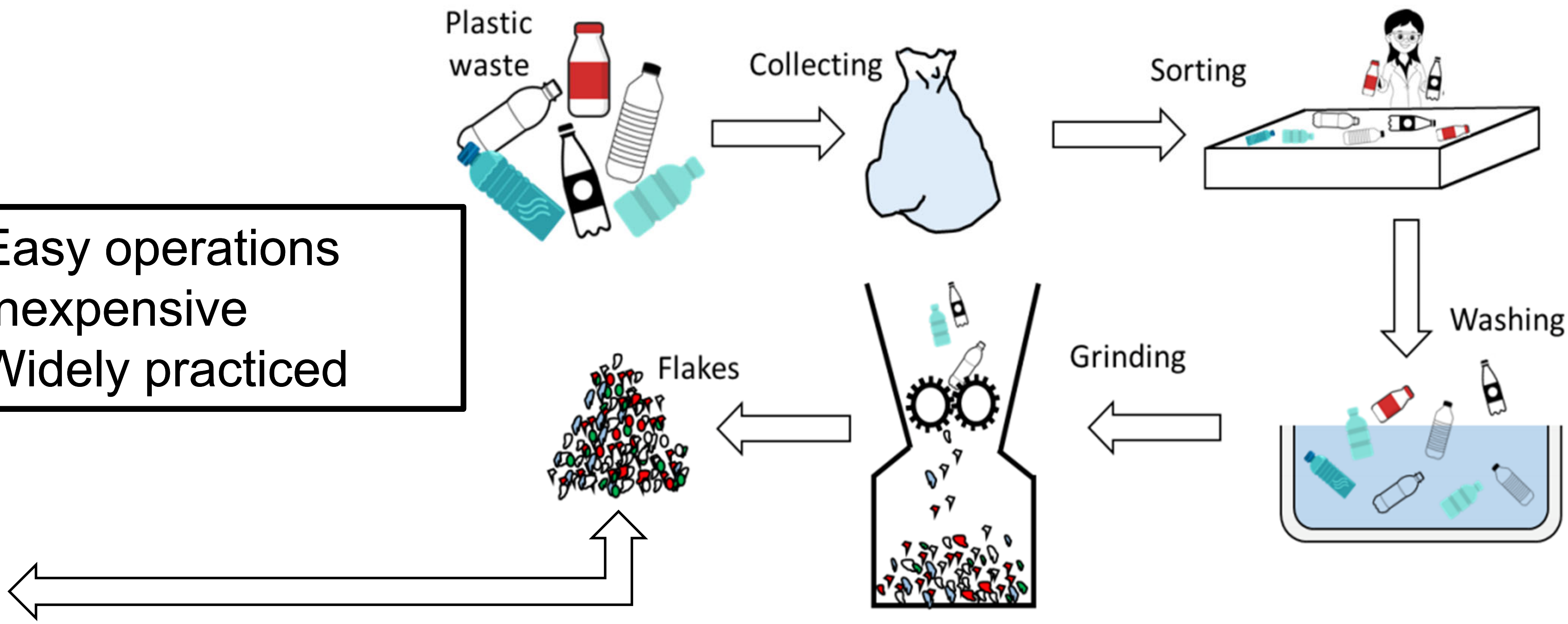


Advanced recycling: Beyond Pyrolysis, Plastics Technology, 24 November 2023

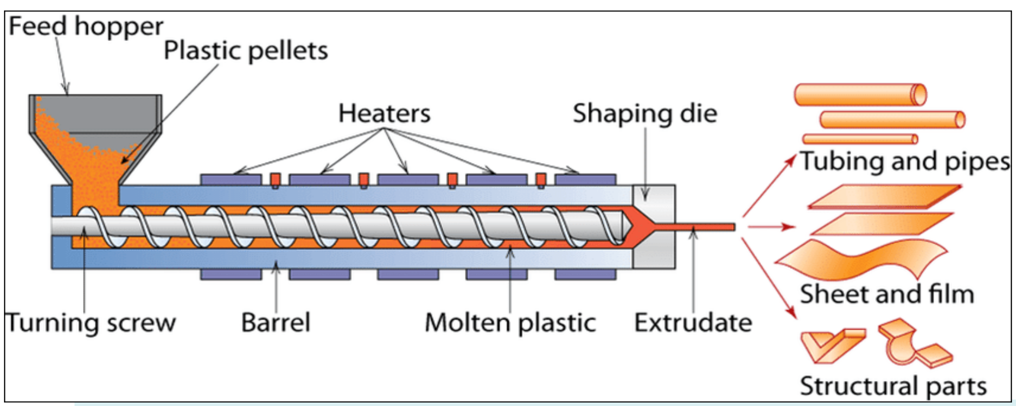
DIVERSITY OF CHEMICAL COMPOSITIONS OF PLASTICS ADD TO THE COMPLEXITY OF FINDING SOLUTIONS

- No ” one-shoe fits all” solutions
- Diversity of structure and properties
- Solutions must be tailored to suit the chemical structure as well as the end application of a given plastic

MECHANICAL RECYCLING (P2P)



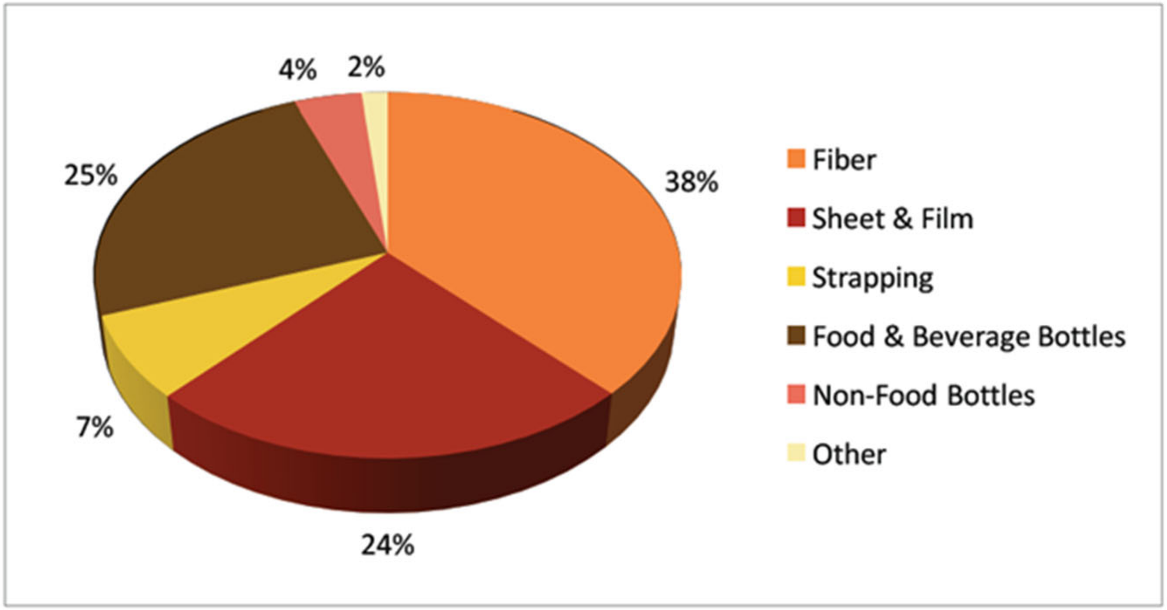
- Easy operations
- Inexpensive
- Widely practiced



Products for consumption

Repeated thermal recycling leads to progressive loss of useful material properties and finally, the product ends up in waste. Infinite mechanical recycling is not possible

REUSE OF MECHANICALLY RECYCLED PET



MECHANICAL RECYCLING OF PET IN INDIA

Manufacturers using r-PET

40 Manufacturers

46 Locations

800,000 tpa Total Capacity

60-70% of PET consumed in India is recycled through the organized sector

Rs 3000-4000 Crore

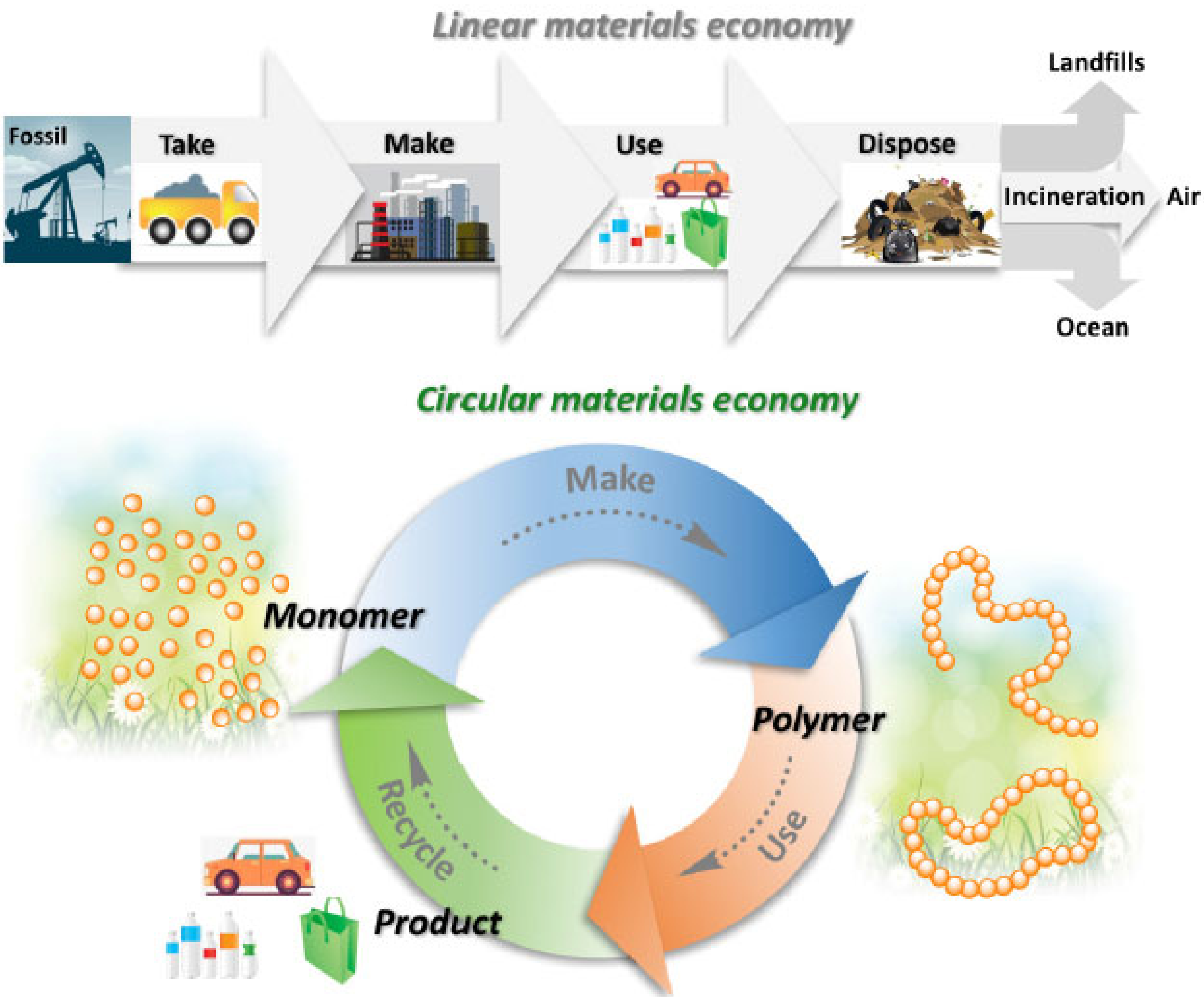
- the annual turnover generated by PET recycling operations in India (in the organized sector)

- Washed Flakes
  - Fiber Fill (FF)
  - Spinning Fiber (PSF)
  - POY
  - Sheet
  - Non woven
  - Monofilament
  - Master batch
  - Straps
  - Bottle

The jerseys worn by the Indian cricket team during the 2015 World Cup

Pillows and soft toys are filled using polyester fiber-fill made from r-PET

Blankets introduced by Emirates made from 100% r-PET



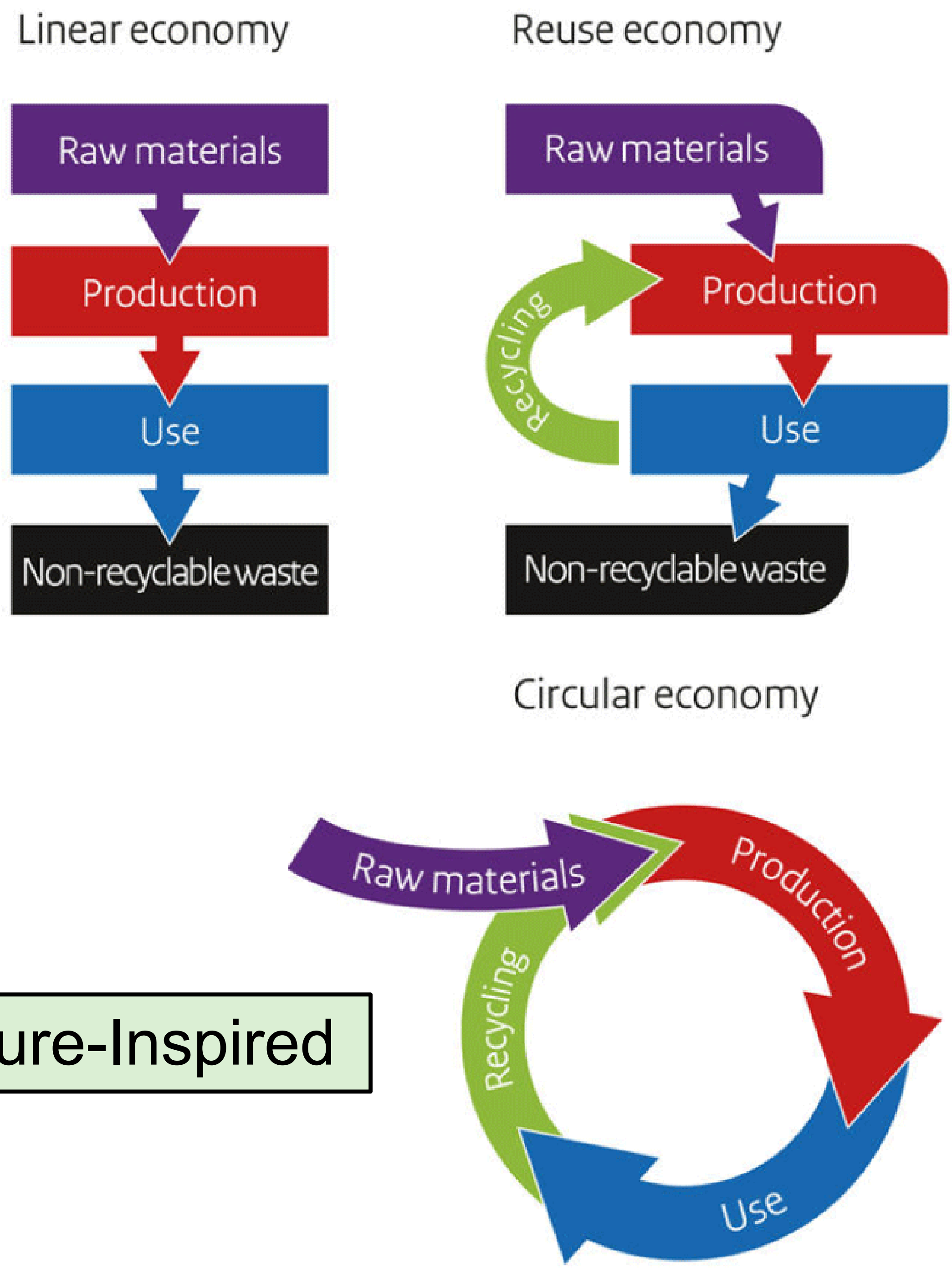
Towards catalytic chemical recycling of waste plastics. J.C. Worch and A.P. Dove, ACS Macro Letters, 2020, 9, 1494

CLOSING THE LOOP

- Circularity is a very desirable goal for plastic waste management
- Circularity keeps the material in circulation, reduces consumption of feedstocks and results in less GHG emissions compared to using virgin materials

Circularity

"A restorative and regenerative system where the societal value of raw materials, products and resources is maximized over time"



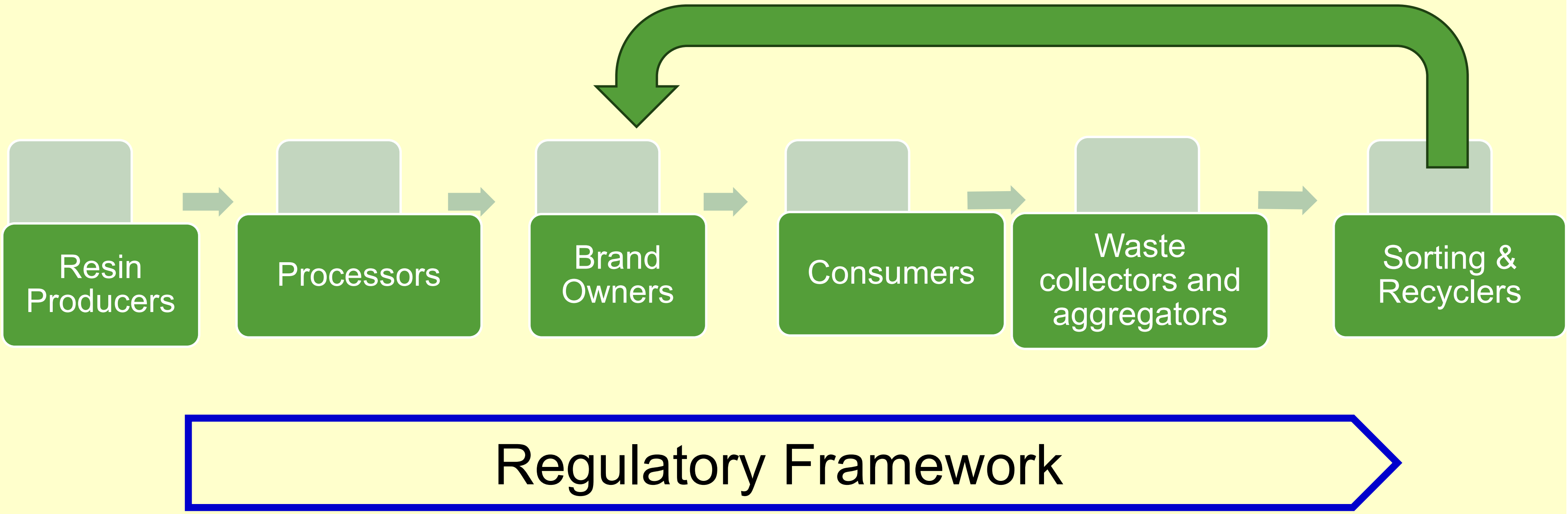
Nature-Inspired

CONCEPT OF CIRCULARITY: ELEGANT YET DIFFICULT

- Discarded plastics get contaminated and comingled. This means the material must be collected, aggregated, transported, segregated, sorted, and cleaned before it can be reused or recycled
- Many of these processes are inefficiently practised
- Energy is required at every step, from collection, transportation, sorting, cleaning, and conversion. This is not trivial
- It is much cheaper to make virgin materials than to recover and reuse discarded plastic waste
- Complexity becomes larger when you consider the widely different lifecycle of materials streams
- Since much of the environmental costs of pollution are externalized there is no economic incentive to perform these complex operations

Who will or should pay for the management of waste plastics- The plastic manufacturer, the processor, the brand-owner, the city government or the consumer?

THE CIRCULARITY VALUE CHAIN



Complex, fragmented, many actors, multiple interfaces, and different industry segments, formal and informal

CHEMICAL RECYCLING (P2M)

- Truly circular solutions require chemical processes to degrade the polymer back to its constituent monomers

- Monomers, thus derived, can be repolymerized to make the same polymer, which is indistinguishable from the original (virgin) polymer

- Whether a given polymer can be chemically recycled depends on the chemical composition of the polymer

THERMOPLASTICS : THE NATURE OF BONDING

- **Polymers containing a heteroatom in the backbone**

Polyesters, Polyamides, Polycarbonates, Polyurethanes, Polysulfones, etc.

- **Polymers containing unsaturation in the backbone**

cis-Polybutadiene. Styrene-butadiene rubbers, Natural rubber (*cis*-Polyisoprene), etc.

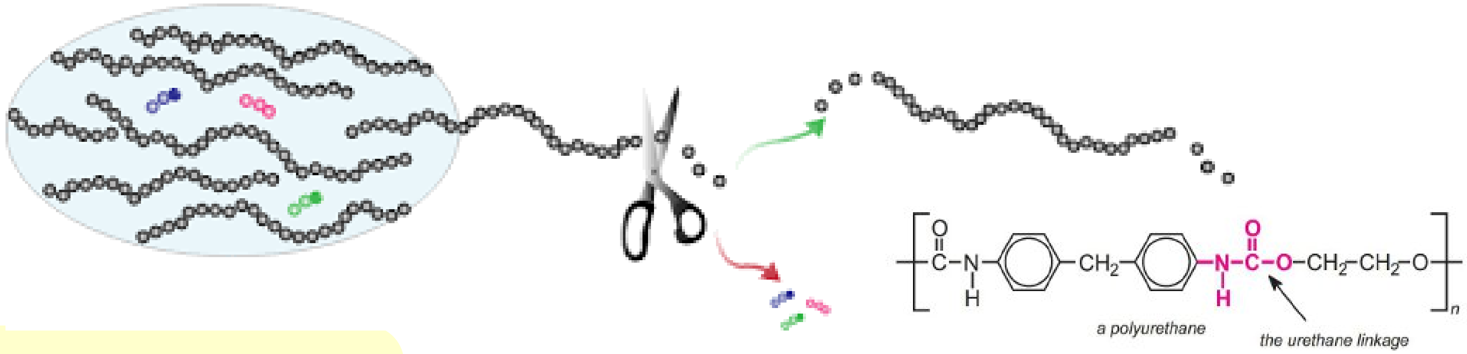
- **Polymers containing a pendant functional group**

Polystyrene, Poly(vinyl chloride), Poly(vinyl acetate), etc.

- **Polymers containing only carbon-carbon bonds**

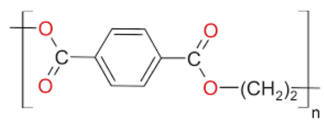
Polyethylene, Polypropylene, etc.

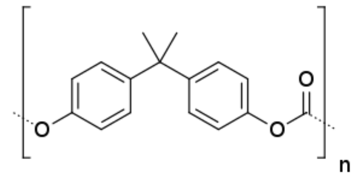
CHEMICAL RECYCLING : POLYMER TO MONOMER



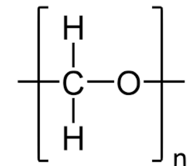
Chemically degradable involving easily cleavable bonds

Polyethylene terephthalate (PET)





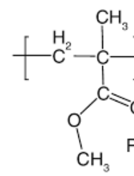
Polycarbonate



Polyacetal

Clean depolymerization where polymerization and depolymerization rates are close to equilibrium

(low ceiling temperature)

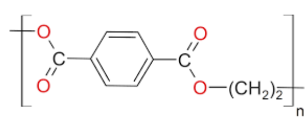


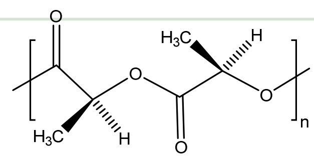
PMMA

Poly(lactones)

Microbial and enzymatic degradation of polymers

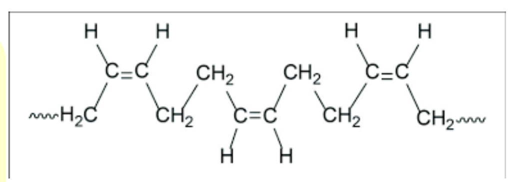
Polyethylene terephthalate (PET)



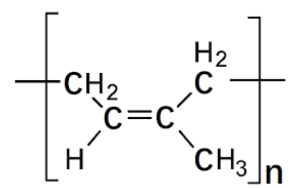


Poly(L+ lactic acid)

Polymers with unsaturation which can undergo degradation by cross metathesis reaction

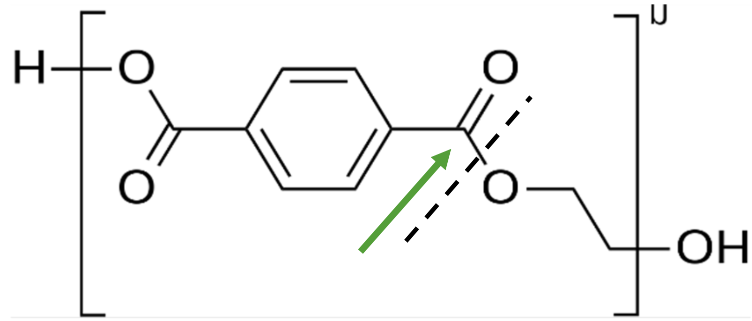


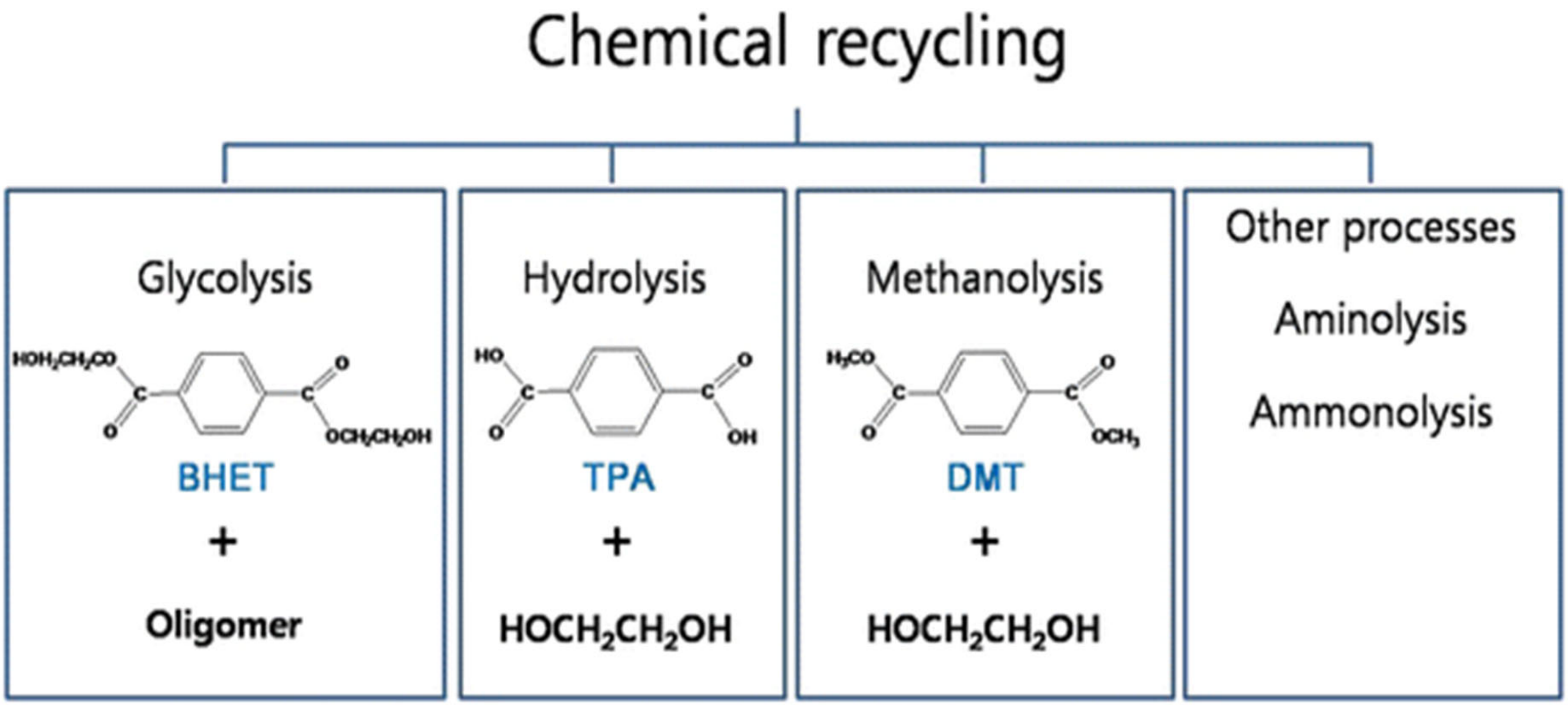
Poly-1,4-cis-butadiene



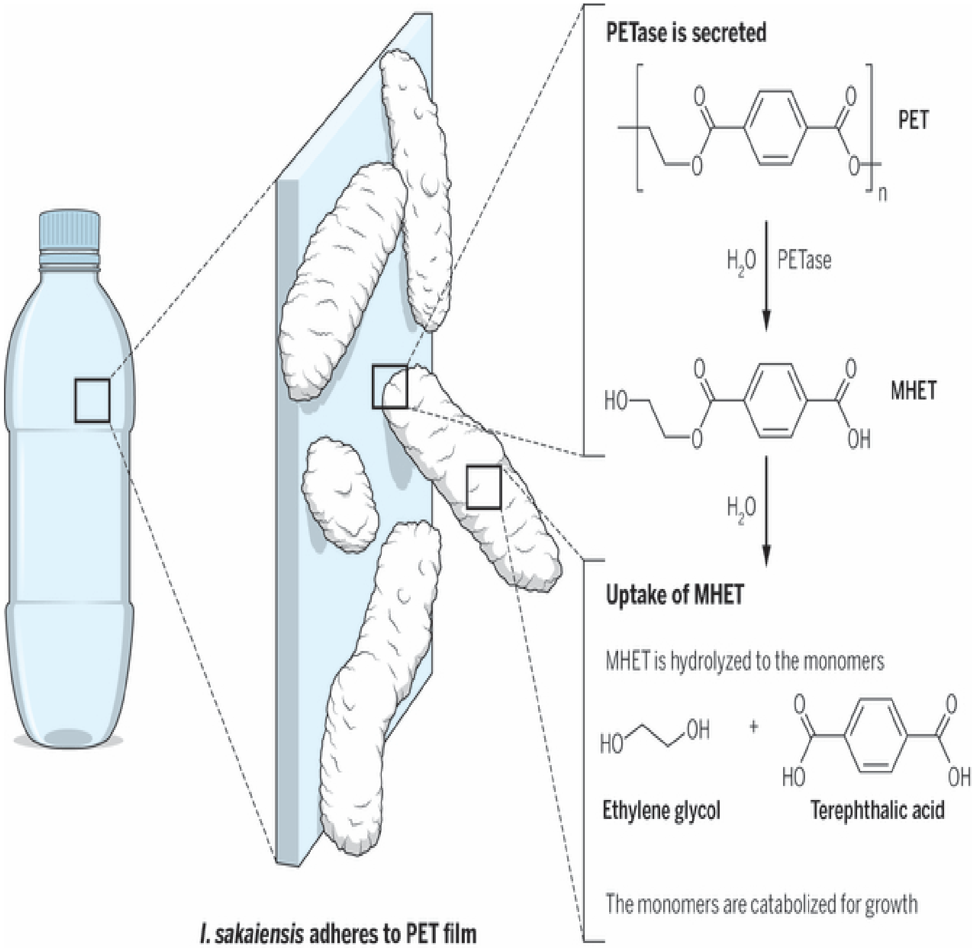
Poly-1,4-cis-isoprene

PET CAN BE DEPOLYMERIZED TO MONOMERS





DIRECTED EVOLUTION: ENZYMES THAT CAN DEGRADE PLASTICS



2016 : A bacterium that degrades and assimilates PET; Science , 351, issue 6278, 1196-99, 2016 *Sp : Ideonlla Sakaiensis*

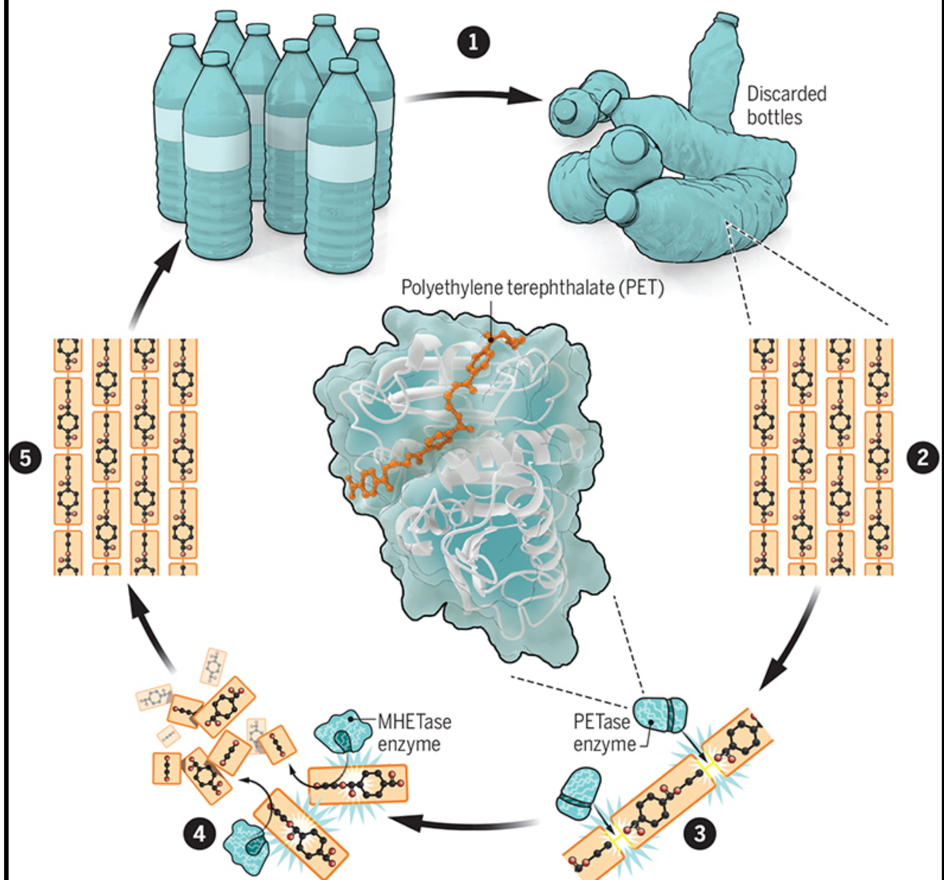
2018 : Structure of the enzyme active for degradation and design of a mutant enzyme which works even better ; PNAS, DOI: org / 10.1073 /pnas.1718804115

2020: An engineered PET depolymerase to break *down and recycle plastic bottles, V.* Tournier, et.al., Nature, 2020, 580, 216-19.

Using site-selective mutagenesis and protein engineering, the French group generated hundreds of mutant enzymes and screened them for the hydrolysis of PET. Based on this they identified enzyme mutants that are 10,000 times more active than LLC, the native enzyme found in nature. These enzymes were active at 75°C. At an enzyme concentration of 2 mg per g of PET, post-consumer PET waste was hydrolyzed to TPA with 90 % efficiency in 10 hours with an average productivity of 17 g terephthalic acid per liter per hour. It is estimated that the cost of enzyme needed to hydrolyze 1 ton of PET will be about 4% of the per-ton price of the virgin PET.

Coming full circle

Scientists are engineering enzymes to recycle plastic. These modified versions of natural proteins work at relatively low temperatures, target specific plastics in a mixture, and produce pure monomers that can then form new plastic.



1 A popular target for recycling is PET, a polymer in drink bottles and polyester clothing.

2 PET consists of long strands made from monomers of ethylene glycol and terephthalic acid.

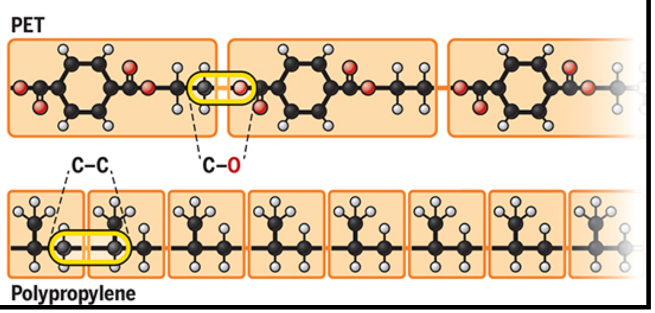
3 Enzymes that digest PET include the bacterial enzyme PETase, which breaks the polymer's oxygen-carbon bonds.

4 The resulting monomers get broken into their constituents by a second enzyme, MHETase.

5 Those products, ethylene glycol and terephthalic acid, can be made into PET again with heat, pressure, and catalysts.

Breaking bonds

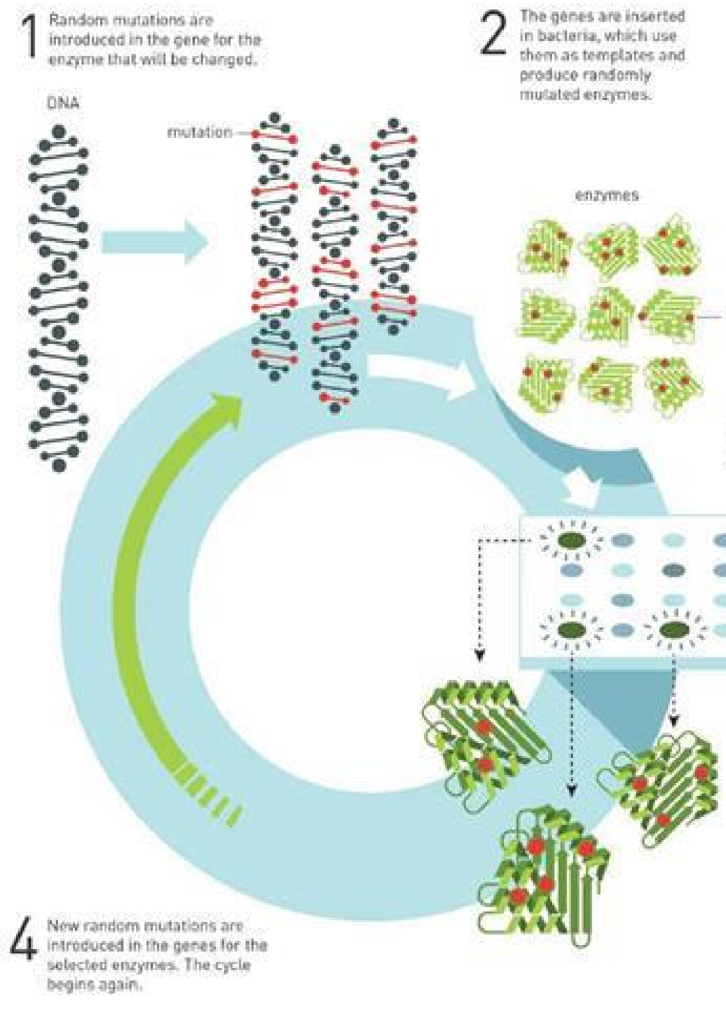
PET is held together by bonds between carbon and oxygen, which require less energy to break in a chemical reaction than those formed by links between two carbon atoms. Those bonds, found in many common plastics such as polyethylene and polypropylene, are harder to break.



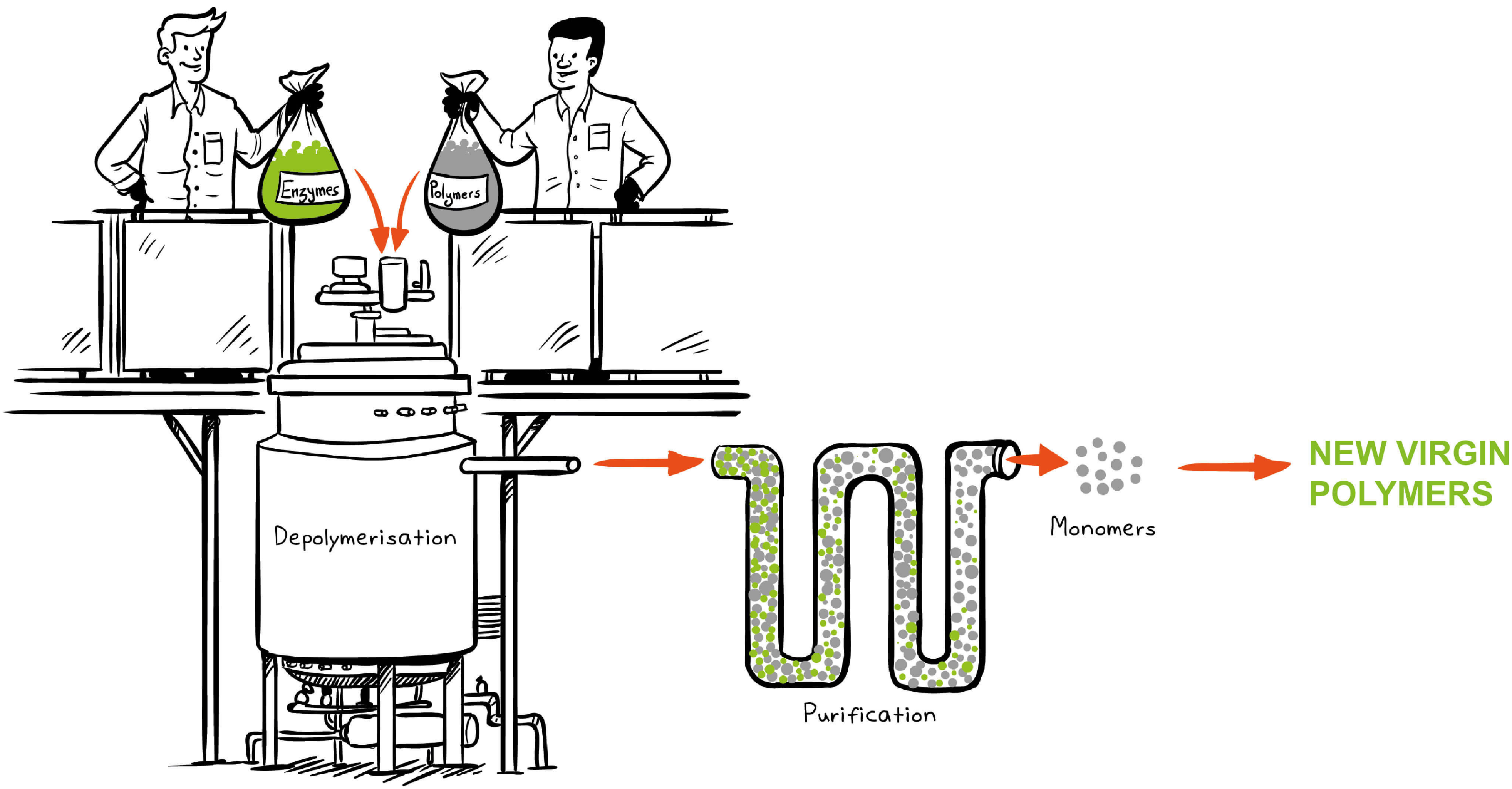
USE OF ENZYMES TO HYDROLYSE PET TO THE CONSTITUENT MONOMERS

Designing engineered enzymes capable of functioning at temperatures above 75ºC

Frances Arnold, 2018



DEGRADATION OF PET USING ENGINEERED ENZYMES NEARING INDUSTRIAL PRACTICE



Concept of a bio-recycling facility for PET

https://www.carbios.fr/en/technology/biorecycling/

POLYMERS CONTAINING A PENDANT FUNCTIONAL GROUP: WEAKENING THE C-C BOND

- Introduction of pendant heteroatom: Introduce small amounts of oxygen or sulfur, or halogen functionality

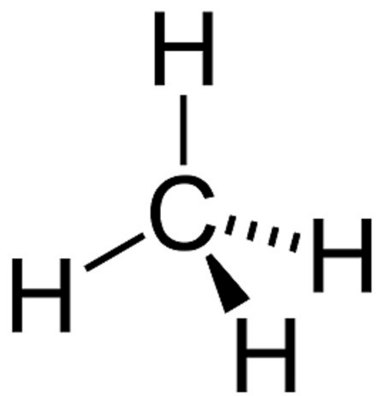
  Example: Ethane and Ethanol

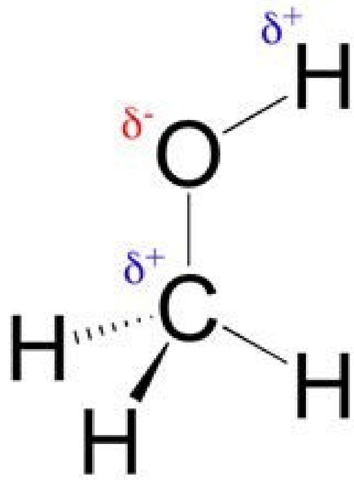
  Ethane and Ethyl Chloride
- Introduction of a keto group in the main chain, which can degrade in light by Norrish I and II processes
- Create a small amount of unsaturation in the chain by dehydrogenation; use metathesis chemistry to degrade the chain

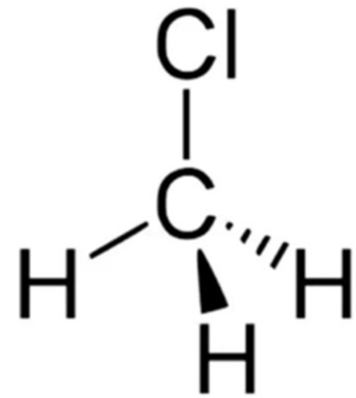
  Example: Propane and Propylene
- Chemical Oxidation

  Example: Ethane to acetic acid

C-H BOND DISSOCIATION ENERGY

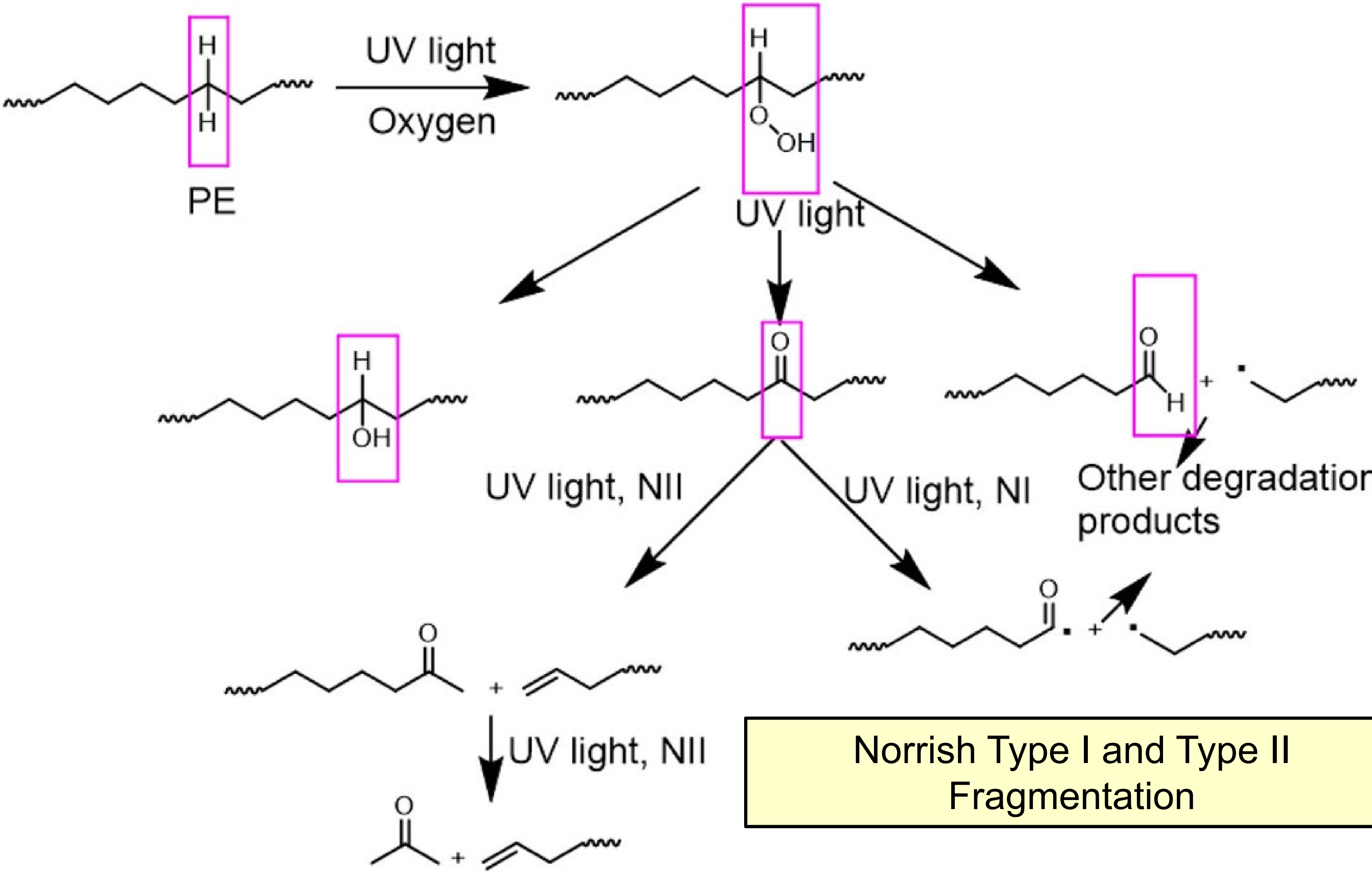






C-H Bond Dissociation Energy, kJ/mol	**415**	**381**	**351**

LIGHT INDUCED DECONSTRUCTION OF MACROMOLECULES



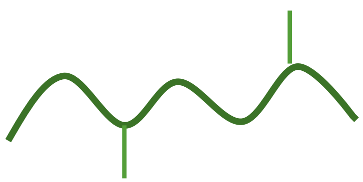
Norrish Type I and Type II Fragmentation

POLYETHYLENE AND POLYPROPYLENE

2 HDPE

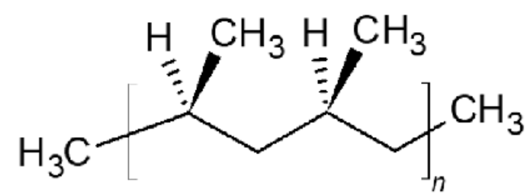
4 LDPE

5 PP



High Density PE

Low Density PE



Isotactic-Polypropylene

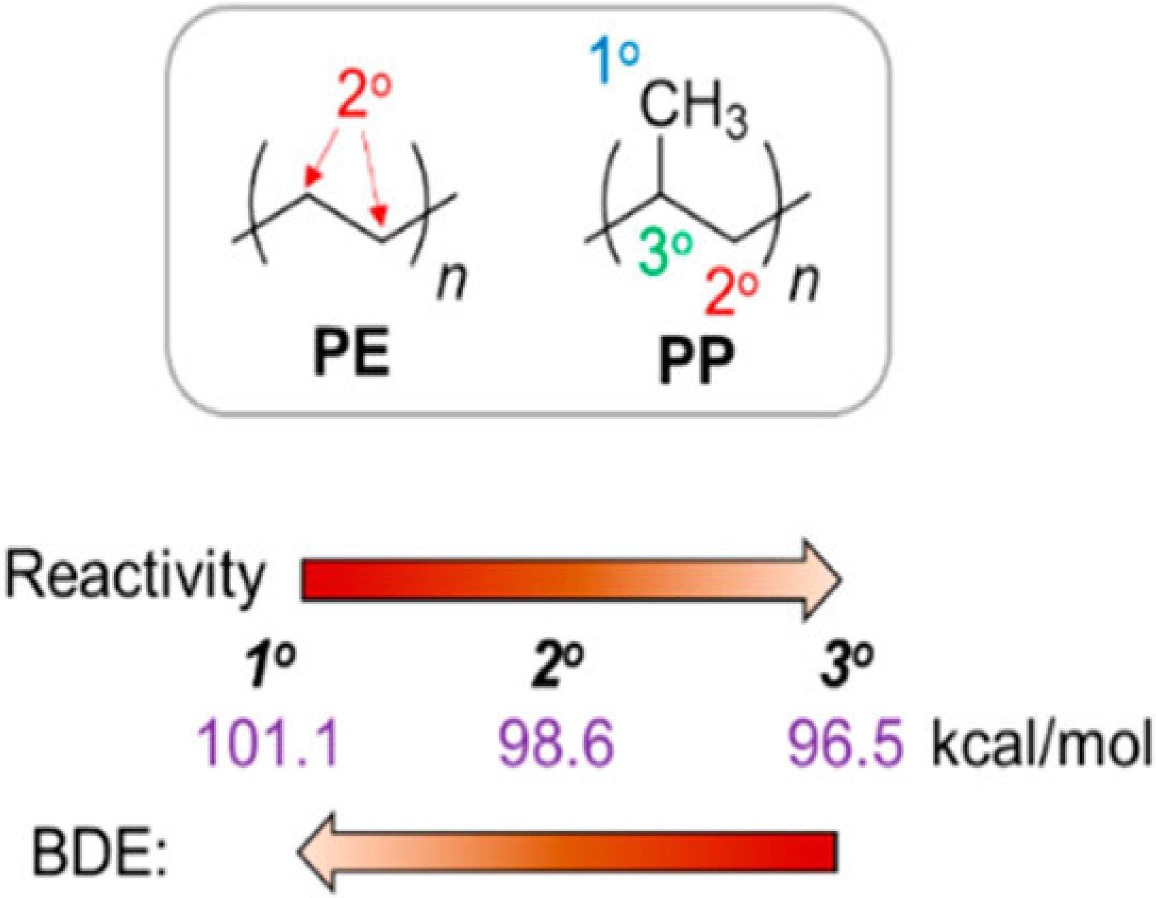
Strong C-C single bonds
Crystalline structure
Non-polar & hydrophobic

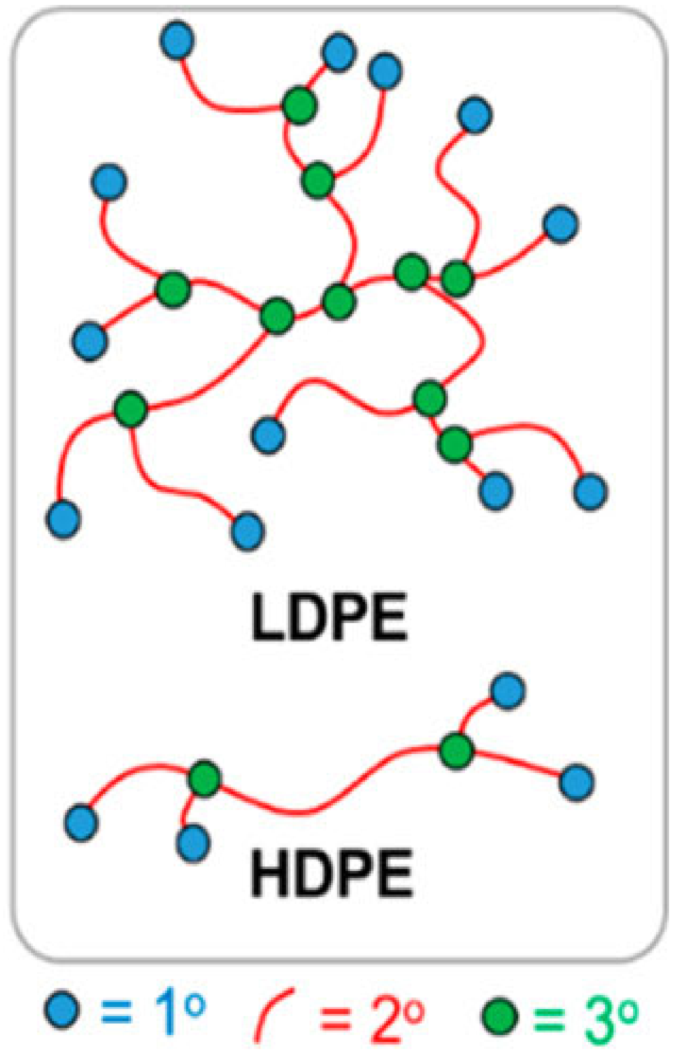
Poor environmental
and biodegradability

BREAKING C-C BONDS IS NOT EASY!

- We released enormous energy in stitching the molecules together, while converting monomers to polymers.
- Polymerizations are highly "exothermic" reactions ($\Delta Hp =$ - 25 kcal/mol of ethylene; -17 kcal/mole for propylene)
- If we have to break the polymer chains, then we have to spend, at the least, the energy that we released while stitching them together. This is demanded by the immutable Second Law of Thermodynamics
- In a net zero carbon world we now aspire for , all this energy must come carbon-neutral or carbon-negative energy resources
- This is a formidable challenge !

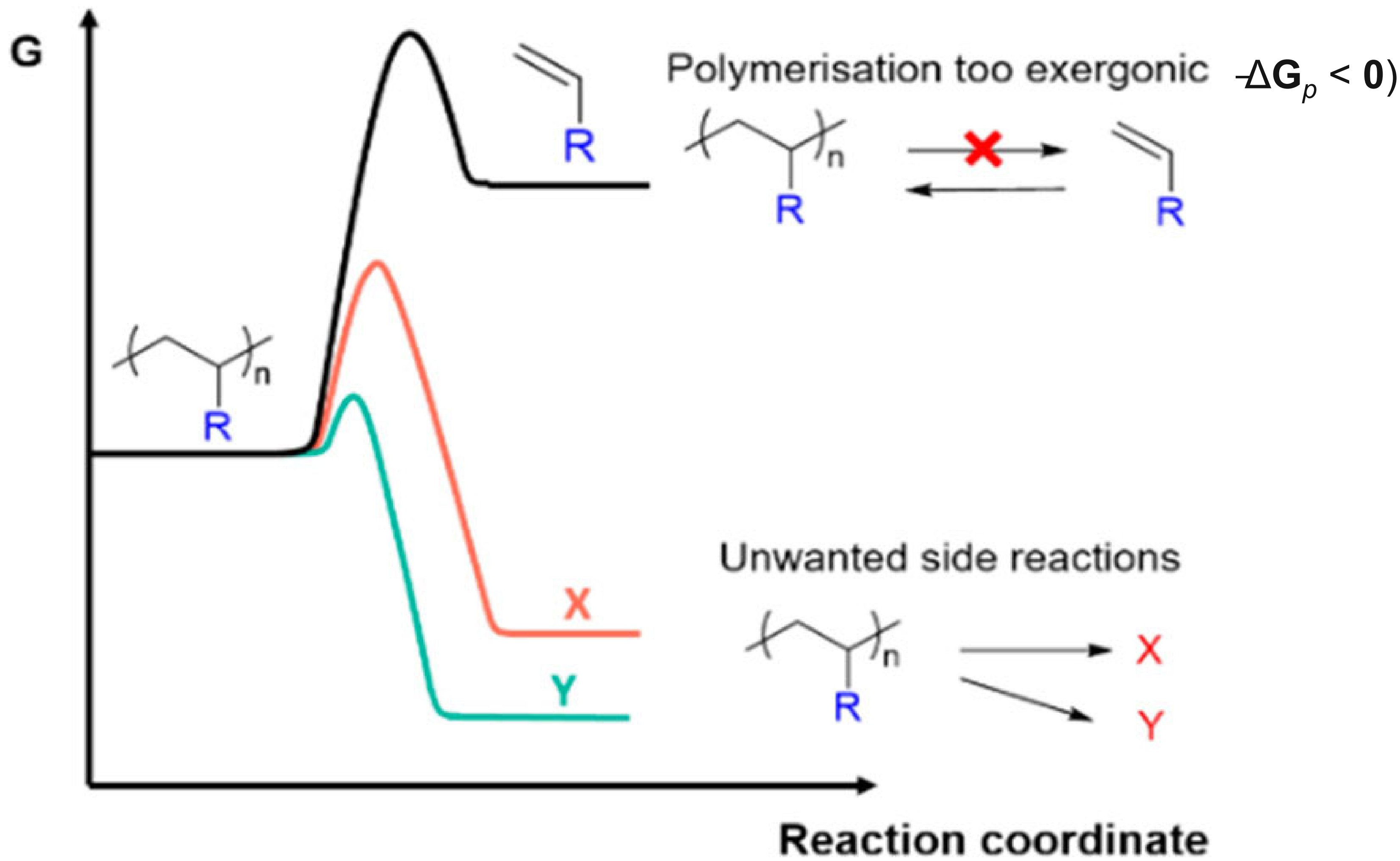
WHY IS IT HARD TO DECONSTRUCT A POLYOLEFIN?





DOI: (10.1021/acsmaterialslett.1c00490)

VERY HIGH NEGATIVE FREE ENERGY !



DOI: (10.1021/acsmaterialslett.1c00490)

POLYOLEFINS ARE TOO COMPLEX TO BE DESIGNATED BY SIMPLE NUMBERS

- Many forms and shapes
- Colors and, inorganic fillers and additives
- Blends of different plastics
- Combined with metals and paper
- Structure and topology variation
- Physical property variation
- Morphology variation

Polyethylene

- Molecular weight / MFI
- Polydispersity (Monomodal, Bimodal)
- Long and short chain branching (Nature of comonomers)
- Crystallinity and spherulitic structures
- Functional Additives
- Catalyst residues (Ti, Cr, Zr, etc.)

Polypropylene

- Molecular weight / MFI
- Polydispersity
- Comonomers (random and block)
- Functional Additives
- Catalyst residues (Ti, Zr etc.)

CHALLENGES TO MECHANICAL RECYCLING

Heterogeneity in post-consumer plastic wastes

- Chemical, molecular, structural and rheological
- Additives, organic and inorganic chemicals
- Metals, glass and other foreign materials

ACS APPLIED POLYMER MATERIALS

pubs.acs.org/acsapm Review

Why is Recycling of Postconsumer Plastics so Challenging?

Bryan D. Vogt,* Kristoffer K. Stokes, and Sanat K. Kumar

Cite This: *ACS Appl. Polym. Mater.* 2021, 3, 4325−4346 Read Online

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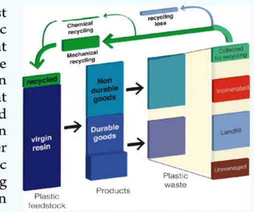
ABSTRACT: The ubiquitous use of plastics has been driven by their combination of low cost and properties, but these attributes directly challenge waste management schemes for plastic recycling. Some postconsumer recycling programs are now nearly 50 years old, but a significant fraction of plastics still finds landfills or other dumping strategies at their end of life. With the growing concern regarding plastic waste, especially ocean plastics, there is a need for innovation and alternative strategies for the economic translation of plastic waste to valued product(s) that will promote their efficient circular utilization. This review first describes the technical and economic hurdles associated with the recycling of postconsumer plastics, but then it focuses on providing an overview of emergent strategies to recover plastic waste through new polymer design, new recycling processes, and chemical transformations to value-added products. Specific challenges discussed include plastic waste sorting and separations, product variability including additives, and the high efficiency/low cost in which the existing petrochemical industry can produce virgin polymers, in particular polyolefins. Although a wide variety of technical strategies have been demonstrated for recycling of plastics through both mechanical and chemical means, the commercial success of these different strategies is generally limited by either performance, including large variance in key metrics, or economics where the products can match the performance of virgin materials but the recycling process is expensive. Successful capture of postconsumer plastic waste through recycling likely will depend on economic incentives and government regulations.



KEYWORDS: *sustainability, circular polymers, plastic waste, recycling, reprocessing*

1. INTRODUCTION

The question of recycling and reuse of refuse is an old one with evidence of materials recycling back to the Paleolithic era.[1] In more modern times, the rates for recycling wax and wane with the political and economic climate.[2] In the first half of the 20th century, recycling rates correlated well with shortages and the associated push of wartime efficacies from 1914 to 1945, but without these factors, recycling rates fell even in the face of economic challenges.[2] The continued growth of plastic production[3,4] presents a significant challenge in waste (resource) management in the 21st century. The historical data for the recycling of plastics is bleak when considering all plastics produced from 1950 to 2015.[4] Of the 5.8 billion metric tons of plastic produced that is no longer in primary use, 5.7 billion metric tons of plastic have been discarded or incinerated. From more contemporary EPA data on municipal solid waste (MSW) generation in the US from 2018, 292.4 million tons of MSW was generated, of which plastics comprised 12.2%, but they only comprised 4.4% of the 69.0 million tons of MSW that was recycled.[5] This recycled plastic is predominately from two types of polymers: natural high density polyethylene (HDPE, white translucent) and polyethylene terephthalate (PET) with recycling rates of 29.3% and 26.8%, respectively. Packaging is the dominant industrial sector for annual plastic production (146 million tons in 2015) and waste generation (141 million tons in 2015) and has a short product lifetime (mean = 0.5 yr).[4] Only a small fraction of this large potential material stream from packaging materials is recycled, despite governmental efforts to promote recycling.[6] Alternative routes to address the growing plastic packaging waste have included mandates banning some single use plastics[7−9] and larger multinational directives such as the "European Strategy for Plastics in a Circular Economy" through the European Commission.[10] However, the efficacy of limited bans on impacting environmental concerns about plastic waste has been questioned.[7,11,12] Improvements across the waste management chain from disposal practices, recycling technology, government regulations, and public incentives are likely necessary to address global challenges associated with plastic wastes.

The issues associated with plastic waste and the inefficiencies of its recycling have been recognized for some time. For example in 1990, three large German chemical companies (BASF, Bayer, and Hoechst) formed a joint venture to generate ideas on how to best address plastic waste

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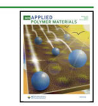
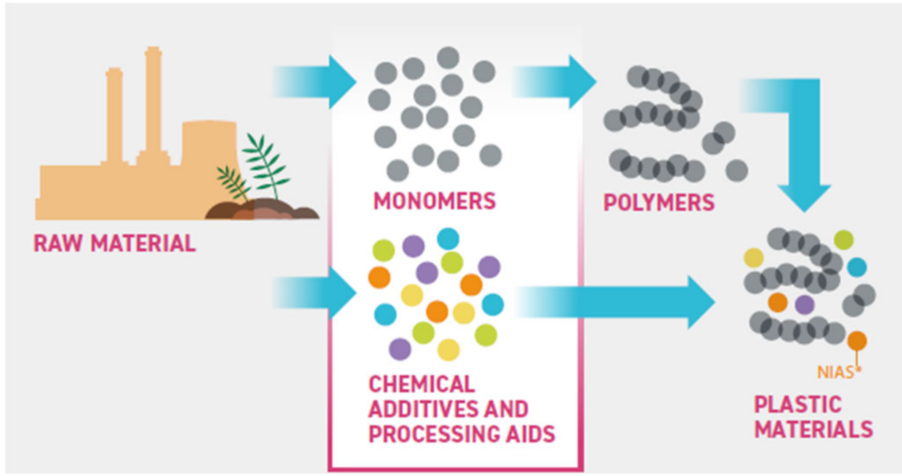


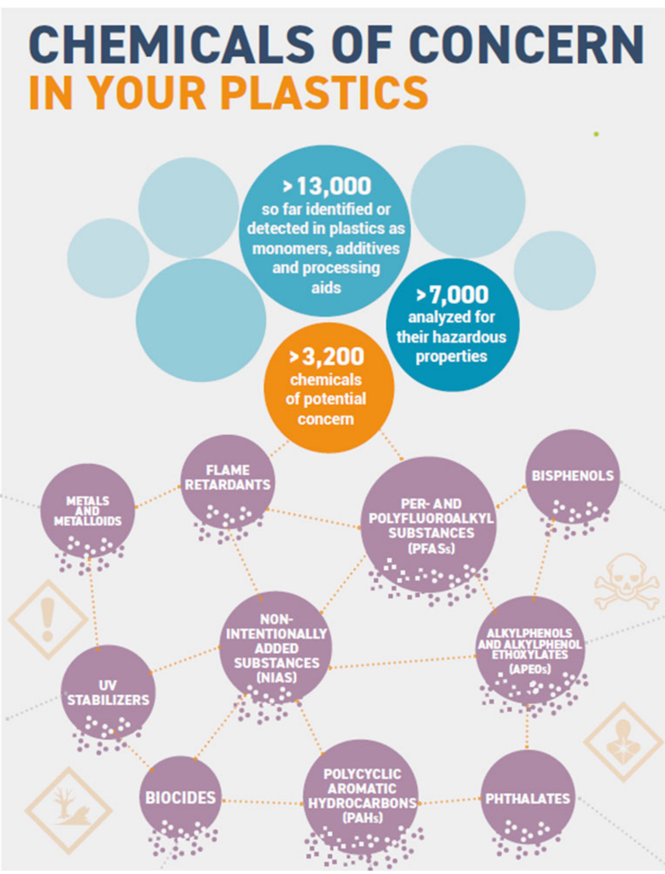
https://doi.org/10.1021/acsapm.1c00648
ACS Appl. Polym. Mater. 2021, 3, 4325−4346

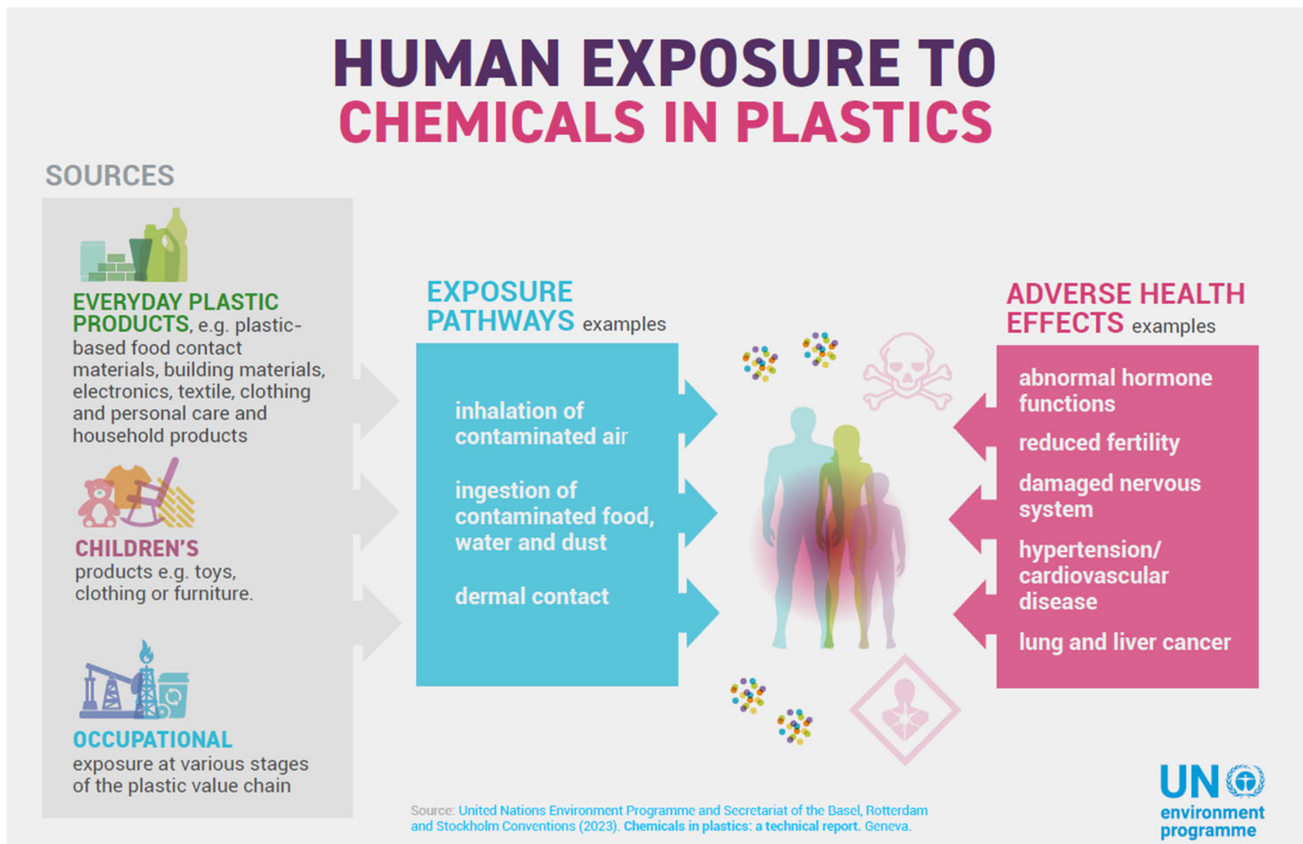
Why is recycling post-consumer plastics so challenging, B.D. Vogt, K.K. Stokes and Sanat K. Kumar, 2021, ACS Appl. Polymer Mater. https://doi.org/10.1021/acsapm.1c00648

Polyolefins as we see them are not single material. Apart from the macromolecule, there is a panoply of small organic molecules that form part of the finished products that we use. We do not know how they behave during use and after-life

CHEMICALS IN PLASTICS







REASON WHY MECHANICAL RECYCLING OF POLYPROPYLENE IS SO CHALLENGING

PP with additives after one thermal history

PP after removal of additives and after one thermal history

Therefore recycling of PP results in products of inferior quality suitable for low grade applications. Achieving closed loop recycling and circularity in PP is an unsolved problem

Polymer Communique, August –September 2022, p. 84
http://eb.mypc.co.in/PC%20Magazine/8.6/13%20-%20Dr%20Sivaram%20-%20R.pdf

MISUSE OF MECHANICALLY RECYCLED POLYPROPYLENE

Home food delivery quick commerce packaging containers

Issues

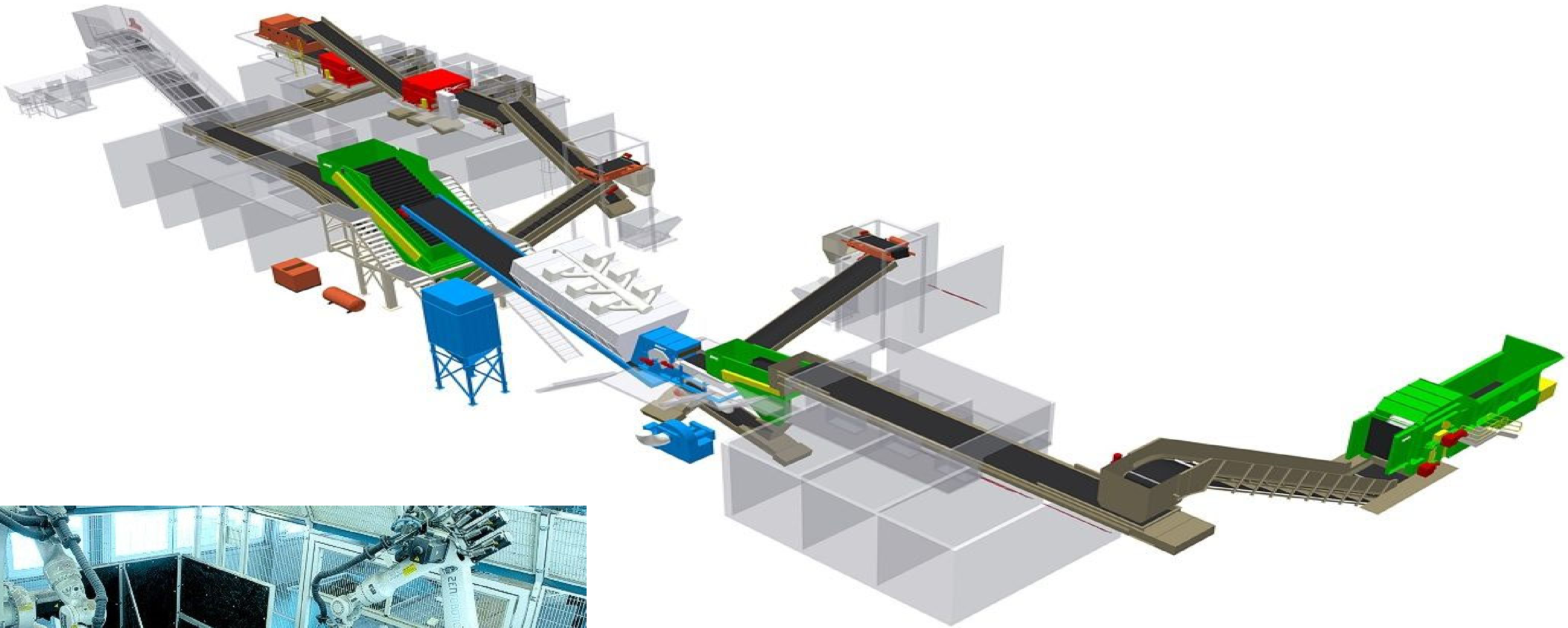
Food safety ?
Microwavable ?

CO-MINGLED PLASTICS WASTE

- In the waste streams, different types of plastics are mixed
- A mixed, co-mingled plastics waste stream cannot be mechanically recycled
- Certain types of plastics are not mutually compatible. e.g : PVC + Polyolefins; PET+ Polyolefins
- Reasons: Different processing temperature, different levels of crystallinity and differences in polarity (Cohesive Energy Density)
- These result in inhomogeneity of the melt phase (thermodynamic immiscibility), resulting in poor solid state morphology (phase separation)

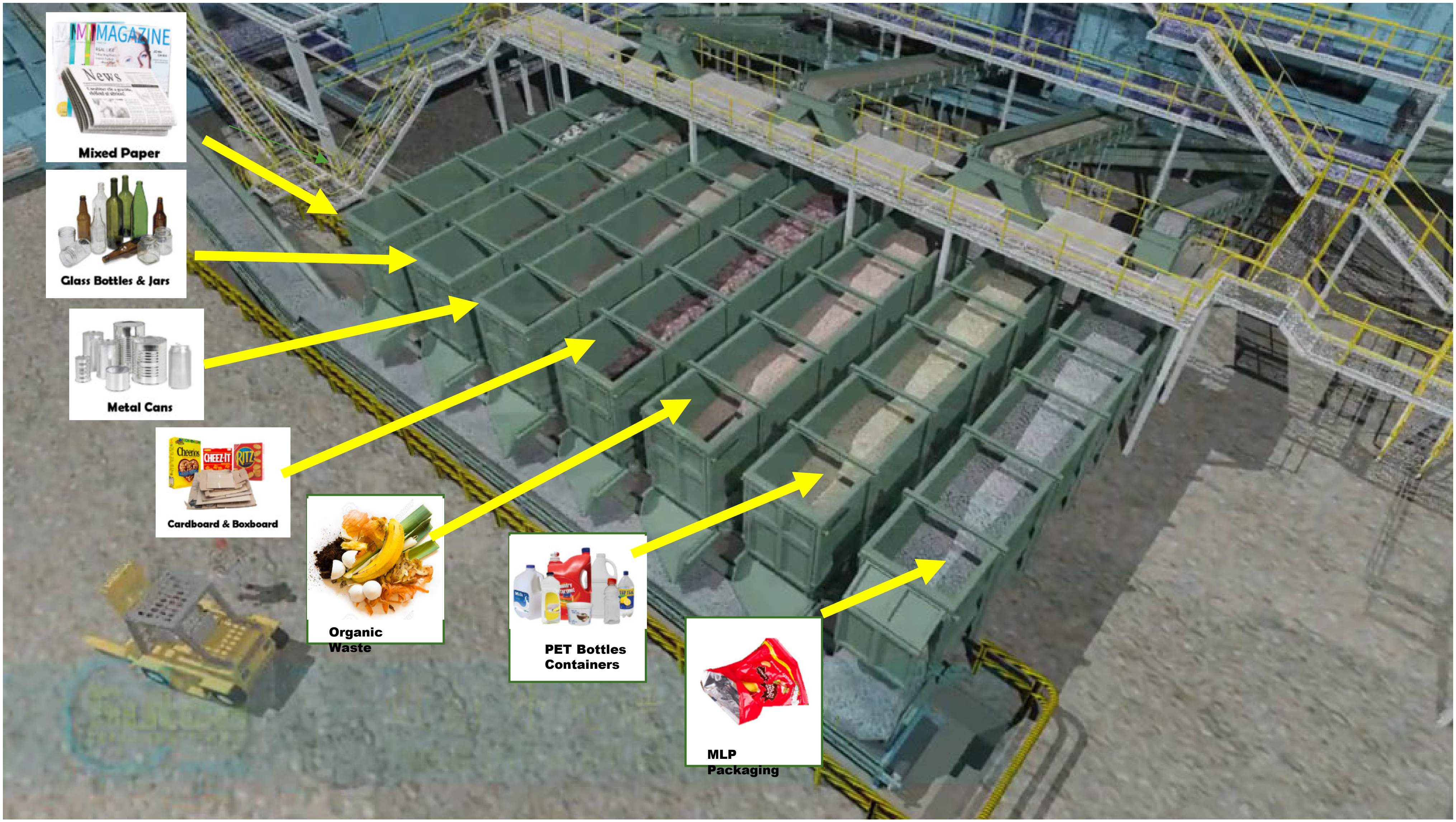
Segregation, sorting and identification of co-mingled wastes is necessary before mechanical recycling. The more efficient is the sorting process, better is the quality of the recycled material

AUTOMATED SEGREGATION

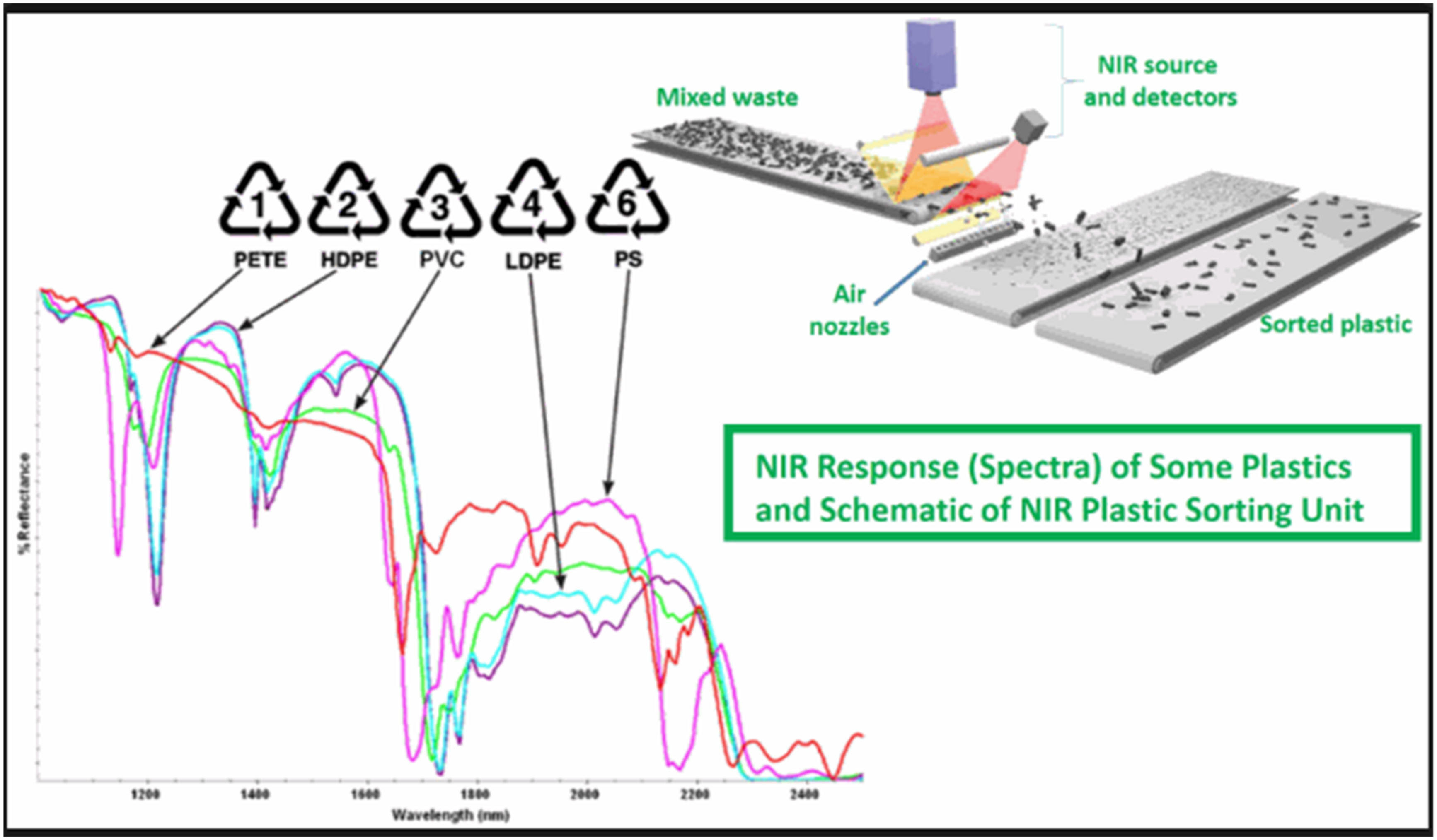


Use of robotic arms and artificial intelligence in Plastic Sorting

AUTOMATED SORTING BY SHAPE AND FORM



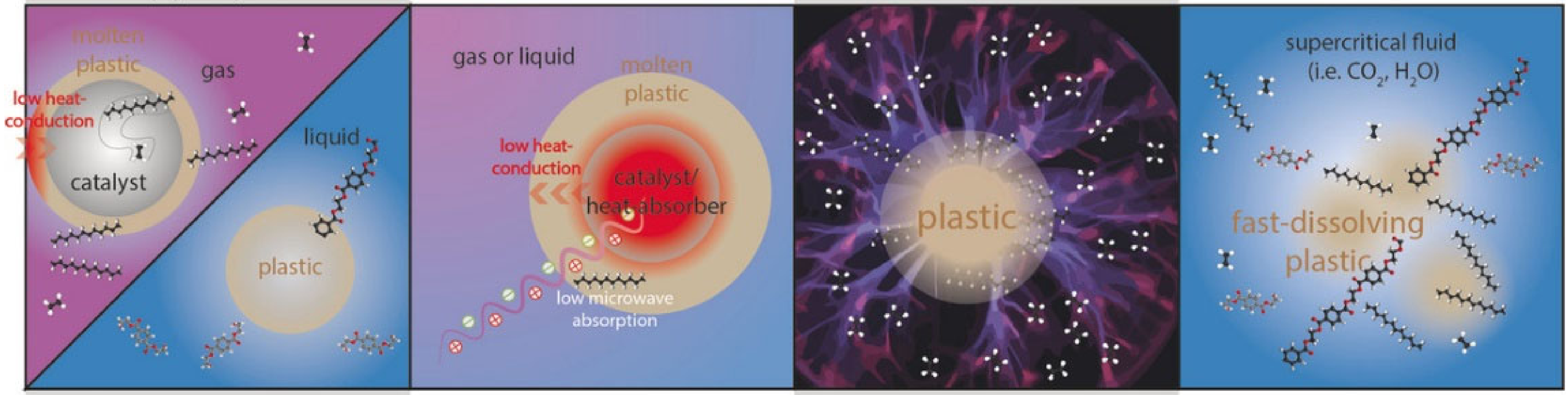
USE OF NIR TO SORT PLASTICS BY CHEMICAL COMPOSITION



Most coded plastics have distinct spectral features in the NIR. Spectrometers can be integrated into recycling processes to help sort plastic types. At NIR wavelengths (>800 nm), polymers have strong, distinct spectral features, which closely correlate to the recycling codes imprinted on plastics (Figure 1). Also, with NIR spectroscopy, there's very little sample preparation to be done. Setups are flexible and customizable to many different situations.

CHEMICAL RECYCLING OF END-OF-LIFE PLASTICS

a) conventional solvolysis and (catalytic) pyrolysis	b) microwave heating	c) plasma reactor	d) supercritical fluid



a)	b)	c)	d)
- small plastic/catalyst and plastic/liquid contact area - low efficiency of catalyst - polymers too bulky to enter pores - low heat conductivity of plastic	+ more even heat distribution in liquids - low microwave absorption and conductivity of plastics cause hotspots on heat absorber material in gas-atmosphere	+ high monomer recovery due to very efficient heating and ionisation of polymer chains - low TRL	+ efficient heating + fast dissolution of plastic + enhanced depolymerization due to catalytic effect of supercritical fluids

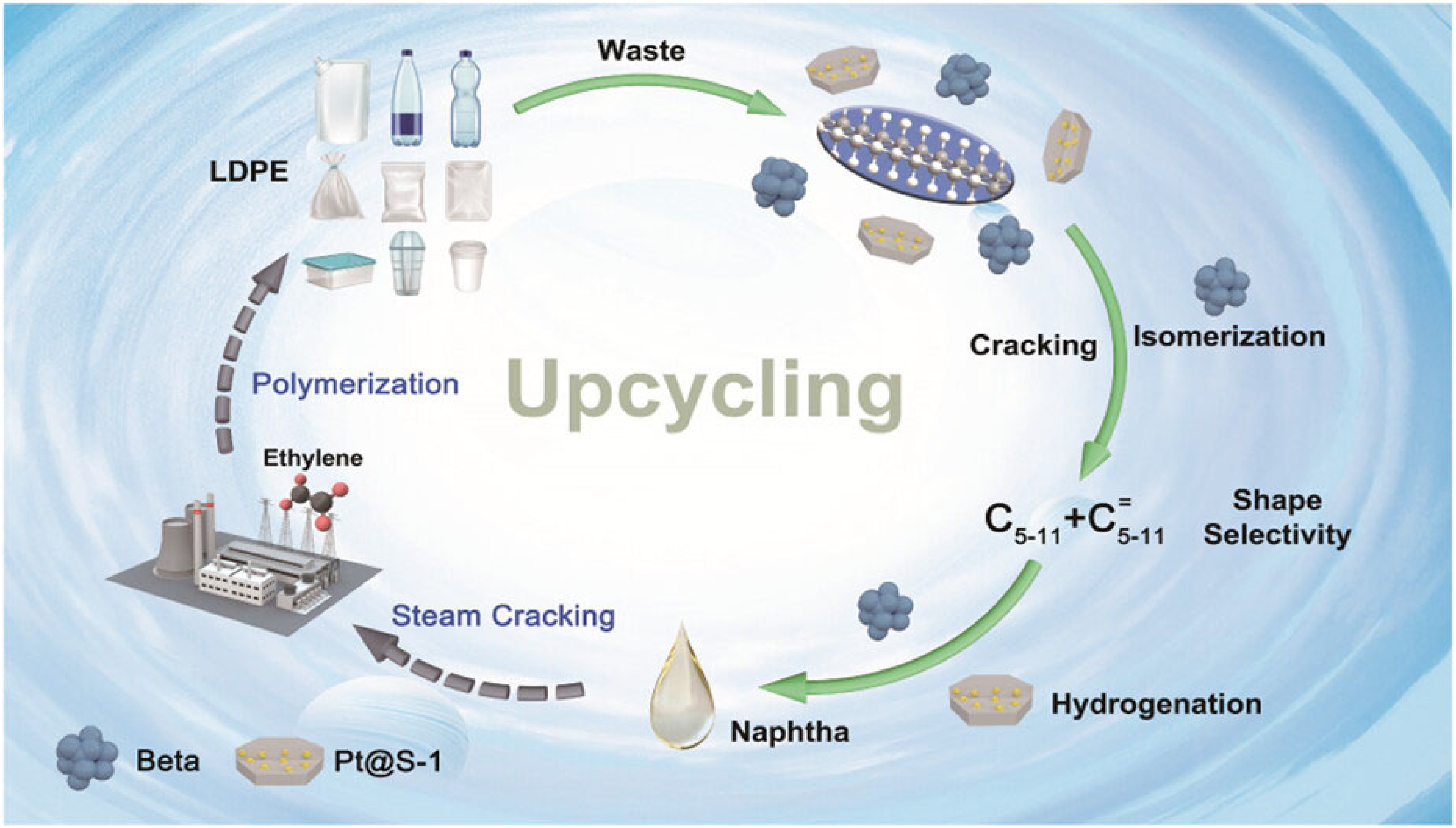
Polymers are poor conductors of heat. Heat transfer in a conventional chemical reactor is a major constraint

Angew. Chem. Int. Ed., 11 March 2020, 59(36),15402-15423, DOI: (10.1002/anie.201915651)

DEPOLYMERIZATION OF POLYOLEFINS TO HYDROCARBONS IN THE PYROLYSIS GASOLINE RANGE

- Pyrolysis gasoline are liquid hydrocarbons with carbon number range C_6 to $C_{10,}$ fully saturated
- Process involves, pyrolysis in the absence of oxygen, hydrogenation, removal of aromatics by solvent extraction and removal of trace halogens, oxygenates and other impurities. Downstream processing of the liquid product is complex and controlled by economies of scale
- Such PG streams can be co fed into a naphtha cracker to produce additional ethylene and propylene (Circular monomers)

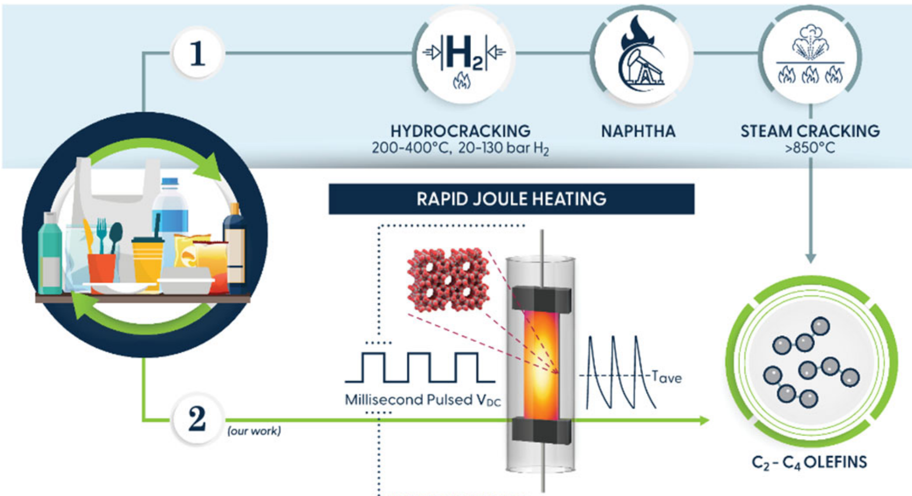
CONVERTING PLASTIC WASTES TO NAPHTHA FOR CLOSING THE LOOP

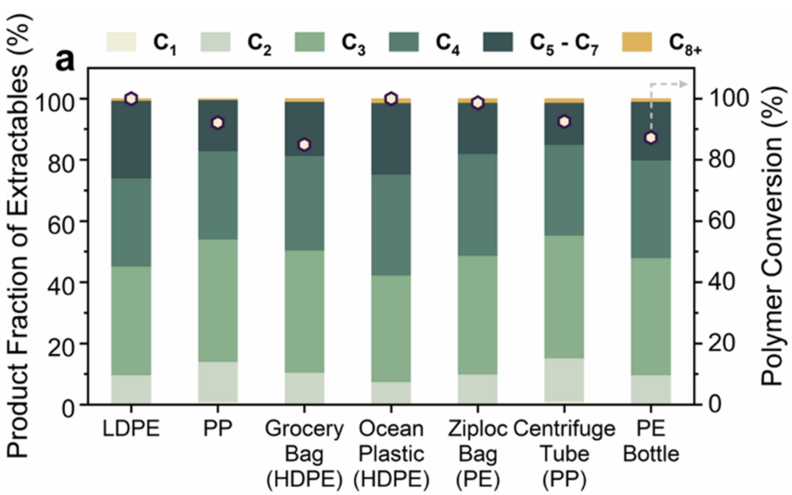


Using β zeolite and silicalite-1-encapsulated Pt nanoparticles (Pt@S-1), a naphtha yield of 89.5% is obtained with 96.8% selectivity of C_5–C_9 hydrocarbons at 250 °C in melt phase. The acid sites crack long-chain LDPE into olefin intermediates, which diffuse within the channels of Pt@S-1 to encounter Pt nanoparticles. The hydrogenation over confined metal matches cracking steps by selectively shipping the olefins with right size, and the rapid diffusion boosts the formation of narrow-distributed alkanes

Li et al. *Journal of the American Chemical Society 2023,* Vol 145/Issue 3, 1847

JOULE HEATING : APPLICATION TO END-OF-LIFE PLASTICS





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Article | Open access | Published: 05 July 2024

Recycling polyolefin plastic waste at short contact times via rapid joule heating

Esun Selvam, Kewei Yu, Jacqueline Ngu, Sean Najmi & Dionisios G. Vlachos

Nature Communications **15**, Article number: 5662 (2024) | Cite this article

Recycling polyolefin plastic waste at short contact times via rapid joule heating

Abstract

The chemical deconstruction of polyolefins to fuels, lubricants, and waxes offers a promising strategy for mitigating their accumulation in landfills and the environment. Yet, achieving true recyclability of polyolefins into C_2-C_4 monomers with high yields, low energy demand, and low carbon dioxide emissions under realistic polymer-to-catalyst ratios remains elusive. Here, we demonstrate a single-step electrified approach utilizing Rapid Joule Heating over an H-ZSM-5 catalyst to efficiently deconstruct polyolefin plastic waste into light olefins (C_2-C_4) in milliseconds, with high productivity at much higher polymer-to-catalyst ratio than prior work. The catalyst is essential in producing a narrow distribution of light olefins. Pulsed operation and steam co-feeding enable highly selective deconstruction (product fraction of >90% towards C_2-C_4 hydrocarbons) with minimal catalyst deactivation compared to Continuous Joule Heating. This laboratory-scale approach demonstrates effective deconstruction of real-life waste materials, resilience to additives and impurities, and versatility for circular polyolefin plastic waste management.

ELECTRIFIED SPATIO-TEMPORAL HEATING

nature

Article | Published: 19 April 2023

Depolymerization of plastics by means of electrified spatiotemporal heating

Qi Dong, Aditya Dilip Lele, Xinpeng Zhao, Shuke Li, Sichao Cheng, Yueqing Wang, Mingjin Cui, Miao Guo, Alexandra H. Brozena, Ying Lin, Tangyuan Li, Lin Xu, Aileen Qi, Ioannis G. Kevrekidis, Jianguo Mei, Xuejun Pan, Dongxia Liu, Yiguang Ju & Liangbing Hu

Nature **616**, 488–494 (2023) | Cite this article

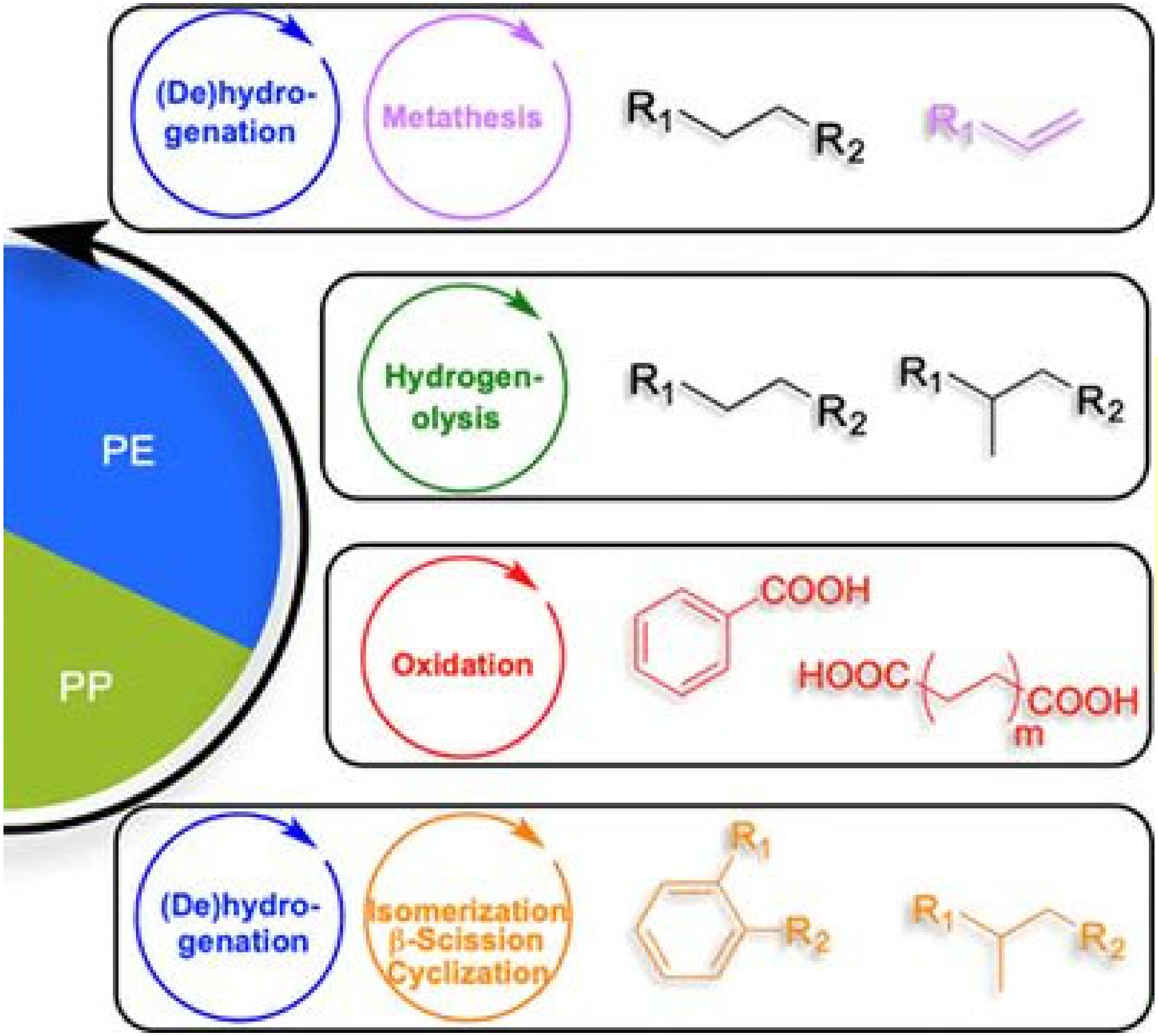
Abstract

Depolymerization is a promising strategy for recycling waste plastic into constituent monomers for subsequent repolymerization[1]. However, many commodity plastics cannot be selectively depolymerized using conventional thermochemical approaches, as it is difficult to control the reaction progress and pathway. Although catalysts can improve the selectivity, they are susceptible to performance degradation[2]. Here we present a catalyst-free, far-from-equilibrium thermochemical depolymerization method that can generate monomers from commodity plastics (polypropylene (PP) and poly(ethylene terephthalate) (PET)) by means

- Electrified spatio-temporal heating gradient conducting heat down
- Pulsing the electrical current generates a temporal heating profile

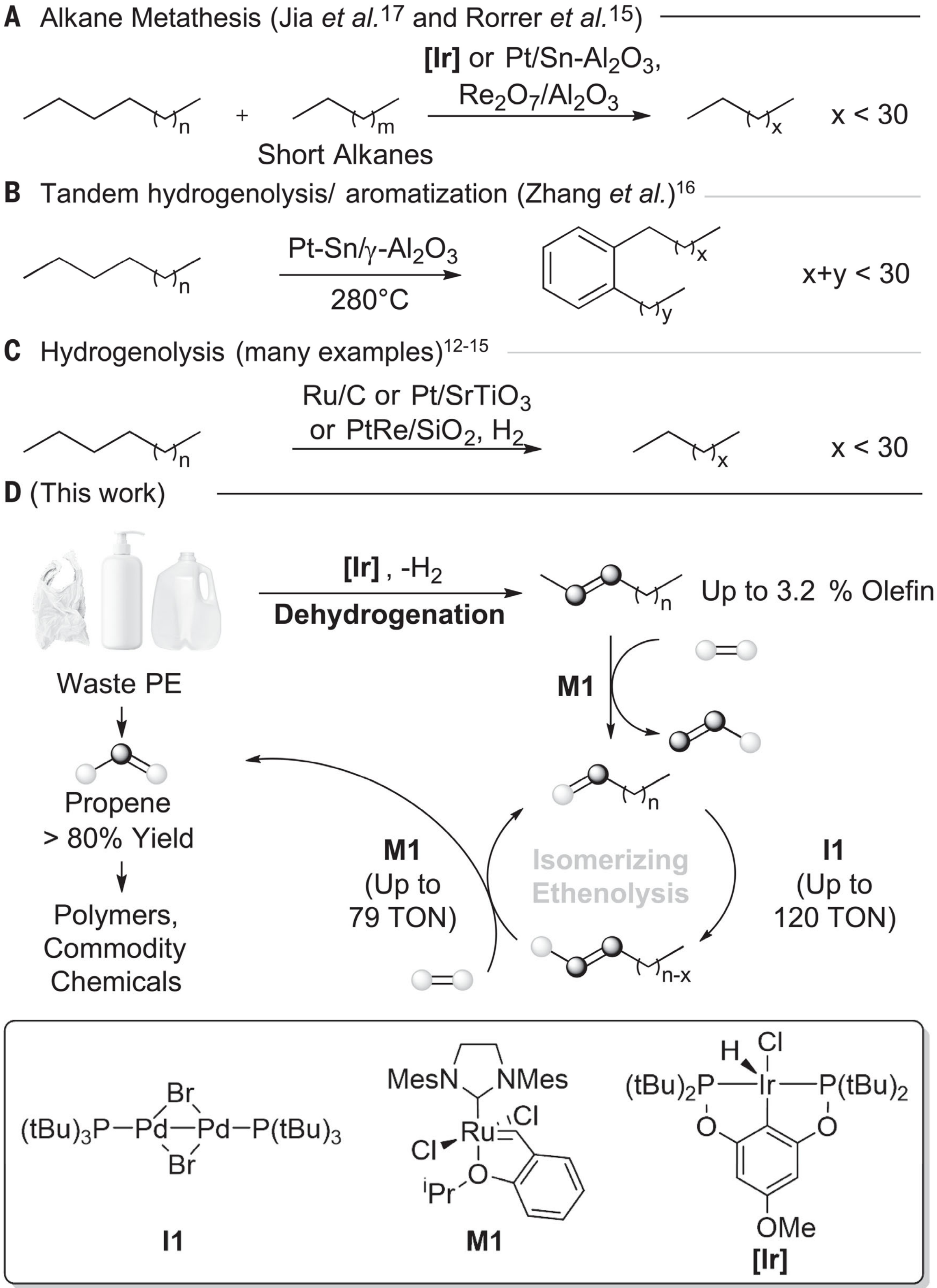
PP to Propylene in 36 % yield (600º C, 0.11 sec)
PET to TPA in 43 % yield (1000º C, 0.11 sec)

CATALYTIC DEPOLYMERIZATION REACTIONS



How do we break a carbon-carbon bond in a macromolecule?

S.L. Scott, et. Al., Catalytic Upcycling of Olefins, Chem. Rev., 2024, 124, 9457

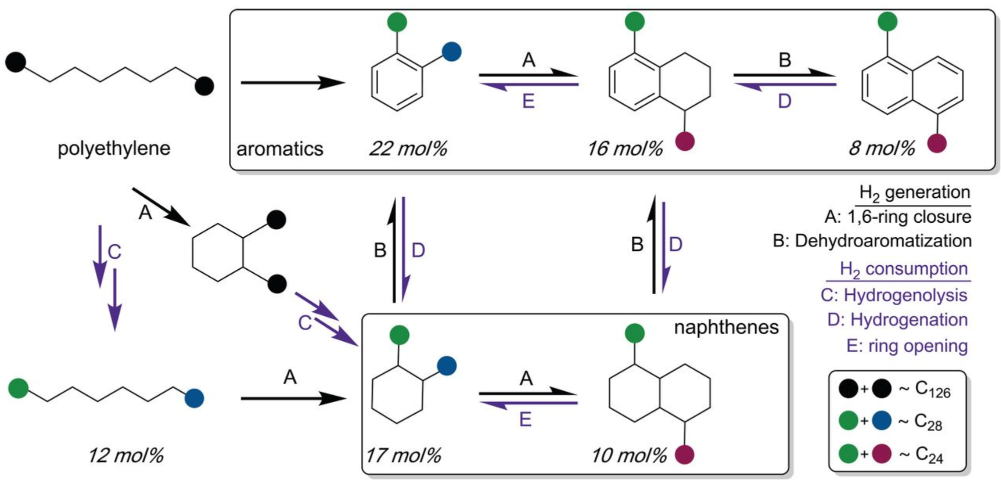


CATALYTIC DECONSTRUCTION OF WASTE POLYETHYLENE WITH ETHYLENE TO FORM PROPYLENE

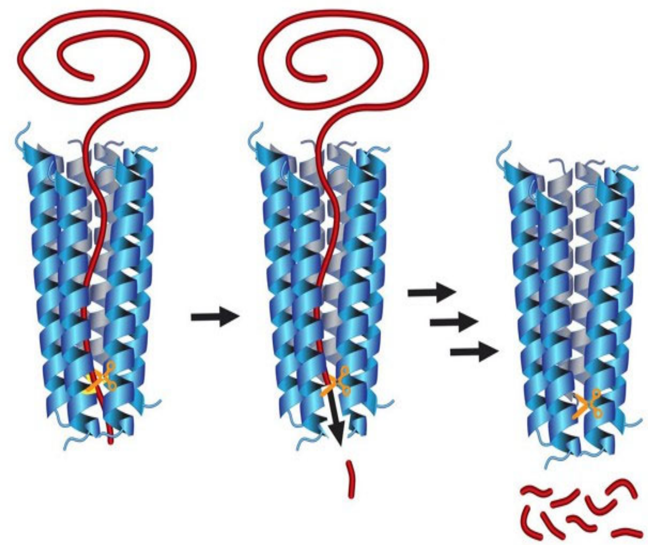
Use of an iridium-pincer complex or platinum/zinc supported on silica as catalysts to dehydrogenate PE followed by the combination of a second-generation Hoveyda-Grubbs metathesis catalyst and [PdP(tBu)3(m-Br)]2 as an isomerization catalyst to form propylene

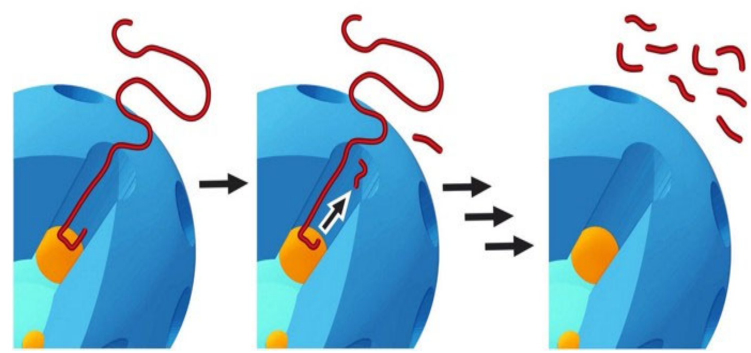
Hartwig et al, Science 2022, 377, 1561

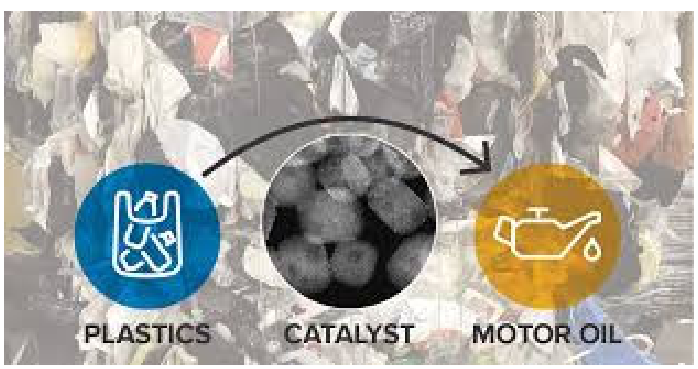
CATALYTIC DECONSTRUCTION OF POLYETHYLENE



Zhang, et. al., Science, 2020, 370, 437





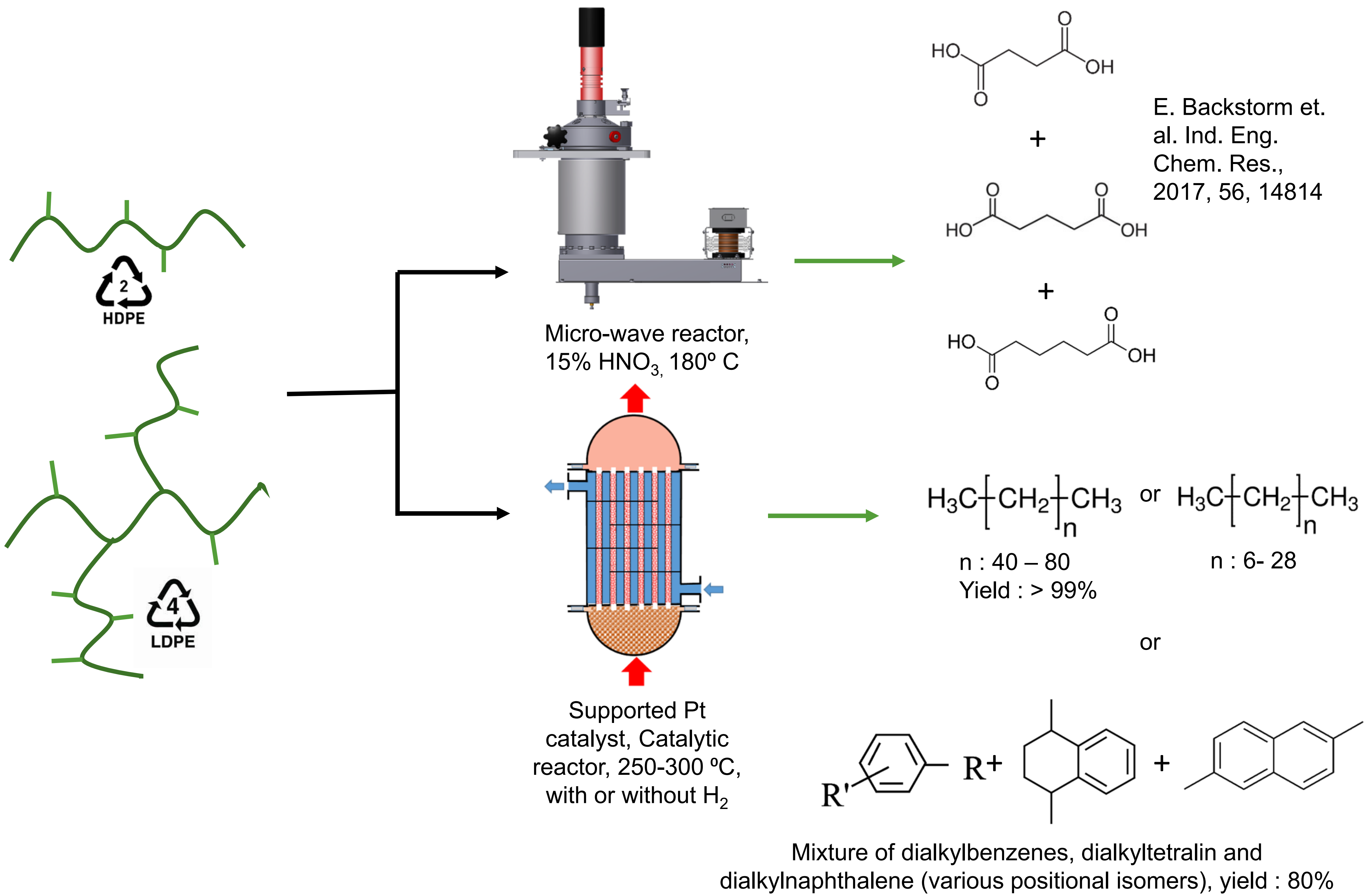


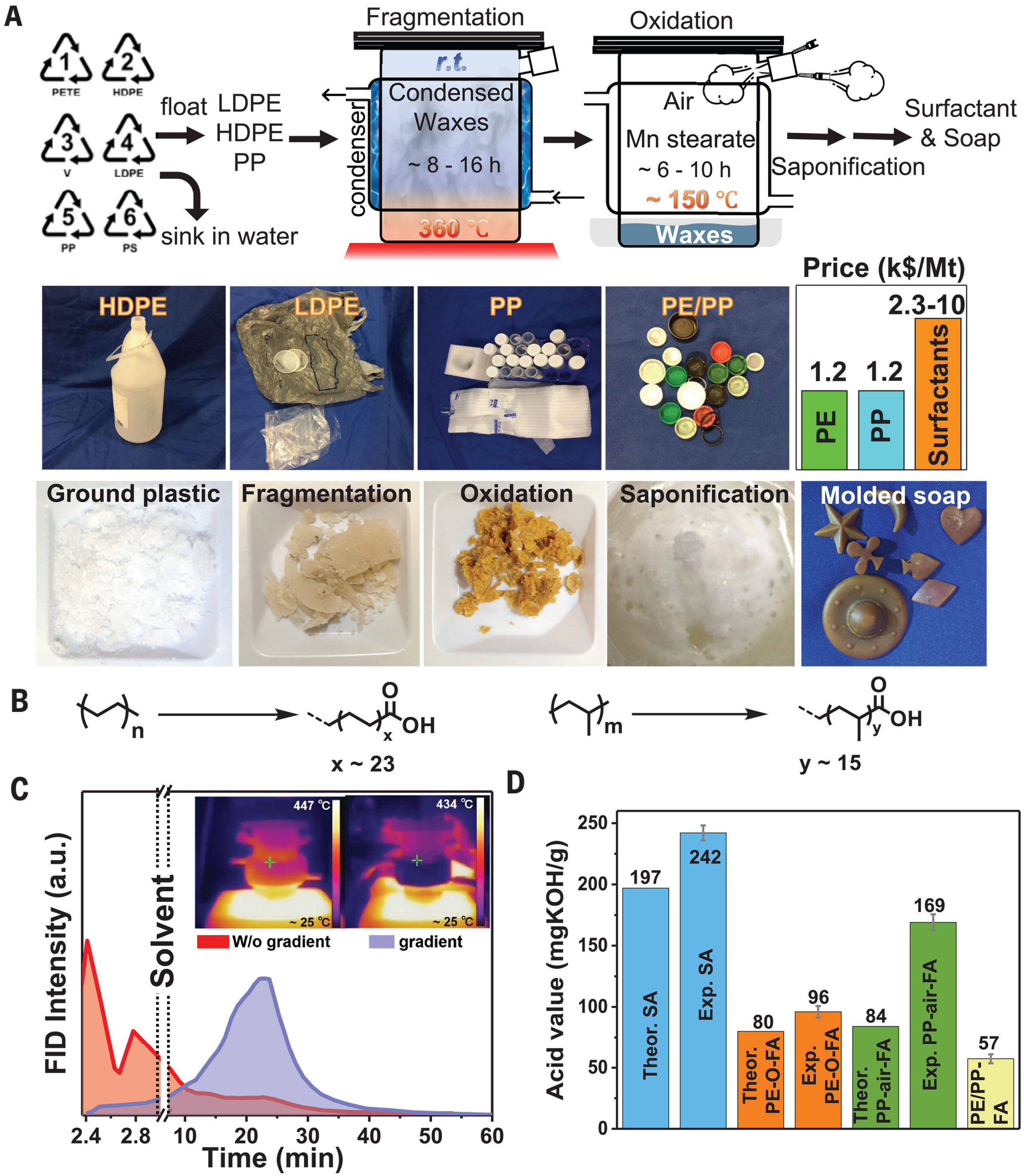
Mn = ~1000
Dispersity :
1.1 to 1.3

3 nm platinum on amine functional porous silica converts a shopping bag PE to alkanes in the C_{14} to C_{18} range
A Tennakoon, et.al., Nature Catalysis, 2020

G. Selik, et.al., ACS Cent. Sci.,2019, 5, 1795

THERMAL AND CATALYTIC DECONSTRUCTION OF POLYETHYLENE

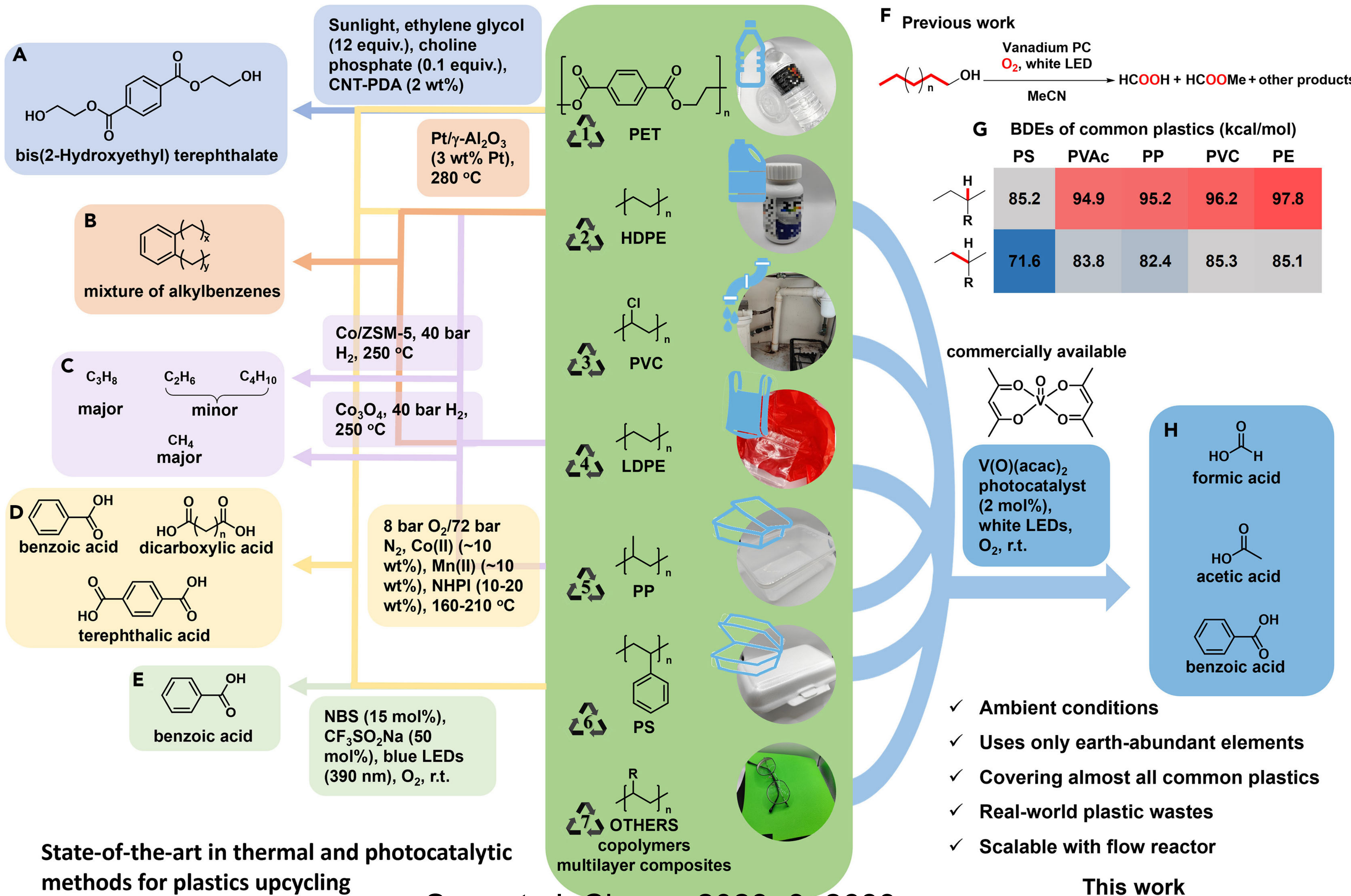




CHEMICAL RECYCLING OF POLYETHYLENE, POLYPROPYLENE, AND MIXTURES TO HIGH-VALUE SURFACTANTS

Xu et al., Science 381, 666–671 (2023)

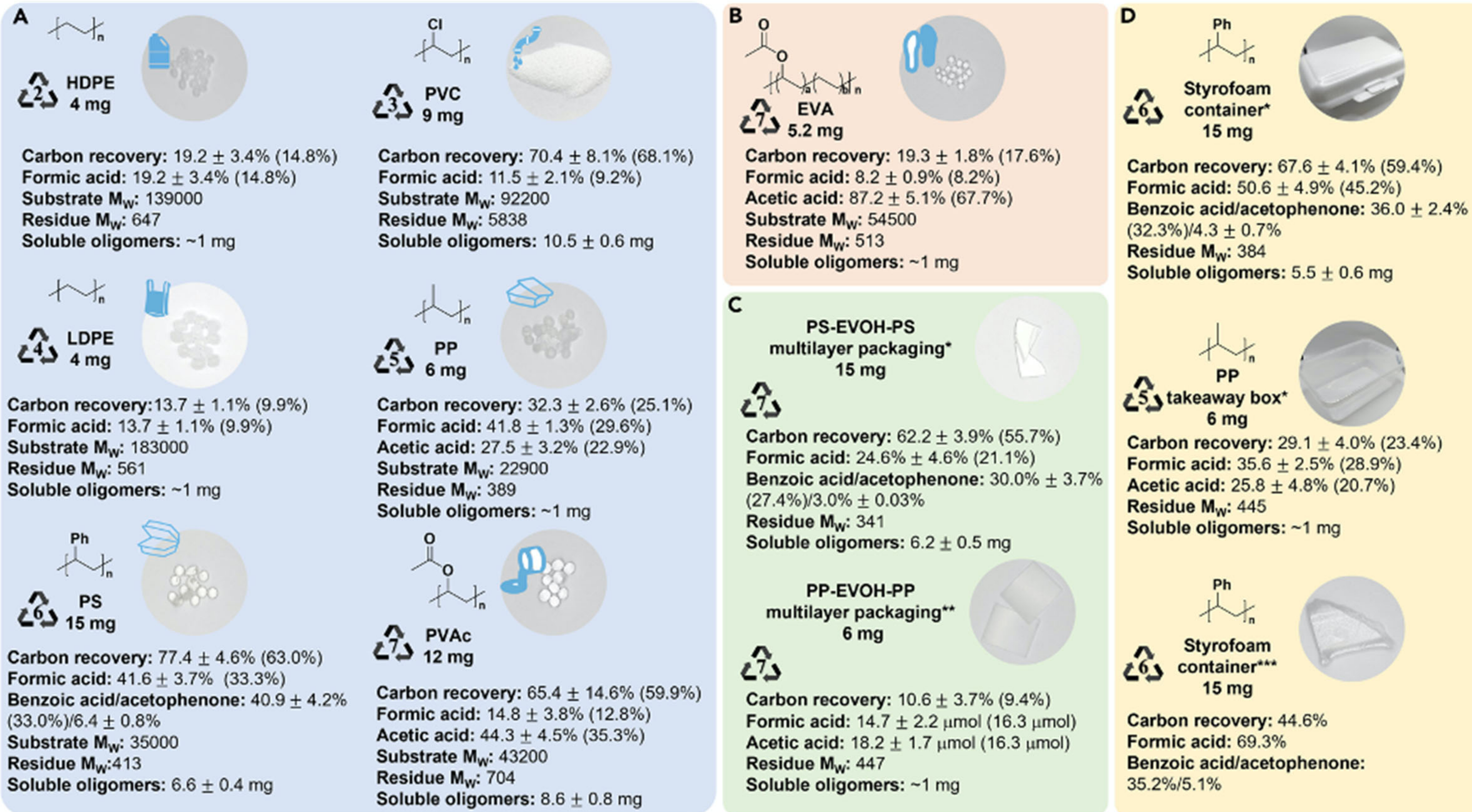
UPCYCLING OF PLASTICS BY BASE METAL PHOTOCATALYSIS



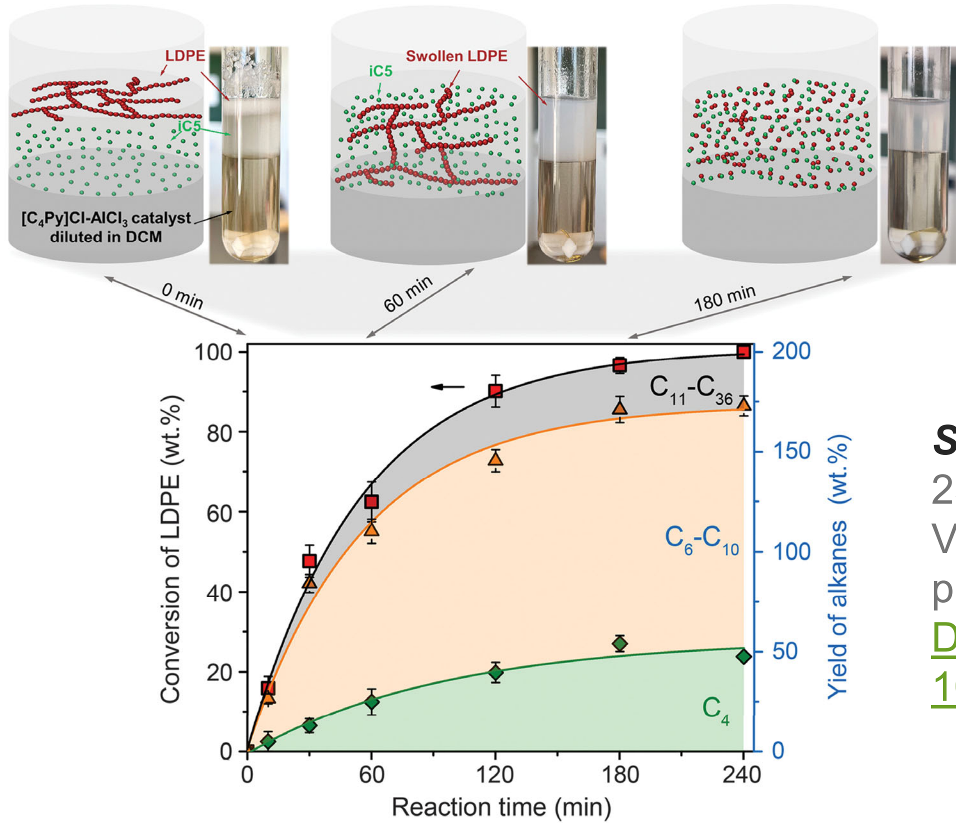
State-of-the-art in thermal and photocatalytic methods for plastics upcycling

Soo, et al, Chem., 2023, 9, 2683

UPCYCLING OF NON-BIODEGRADABLE PLASTICS BY BASE METAL PHOTOCATALYSIS



LOW-TEMPERATURE UPCYCLING OF POLYOLEFINS INTO LIQUID ALKANES VIA TANDEM CRACKING-ALKYLATION



SCIENCE
23 Feb 2023
Vol 379, Issue 6634
pp. 807-811
DOI: 10.1126/science.ade7485

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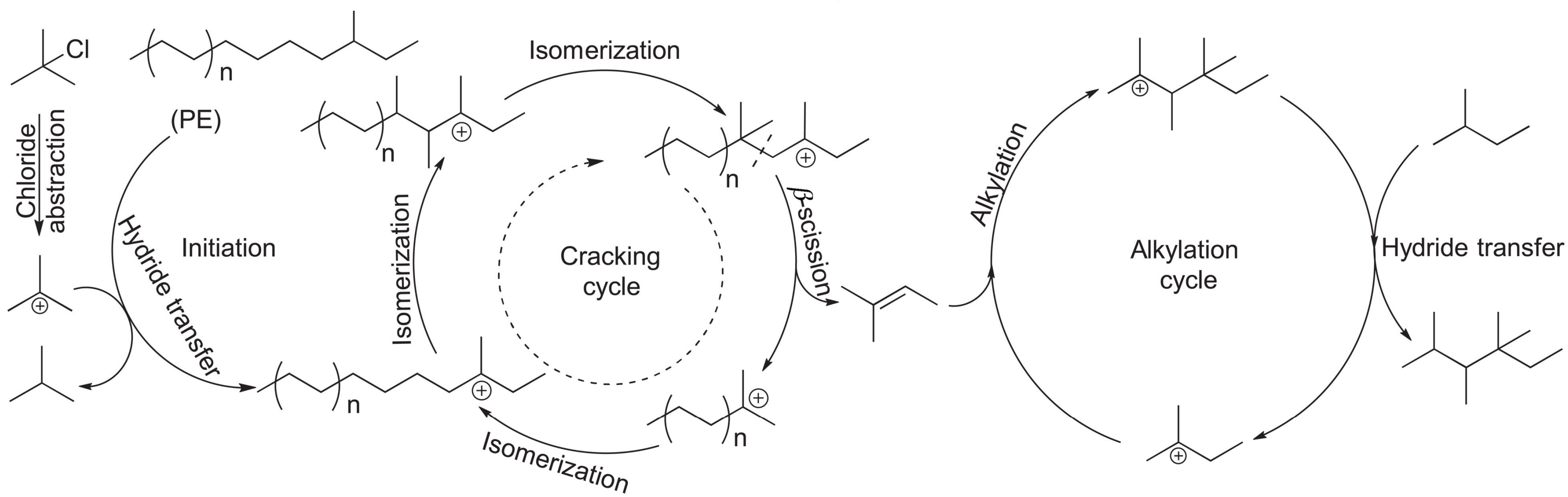
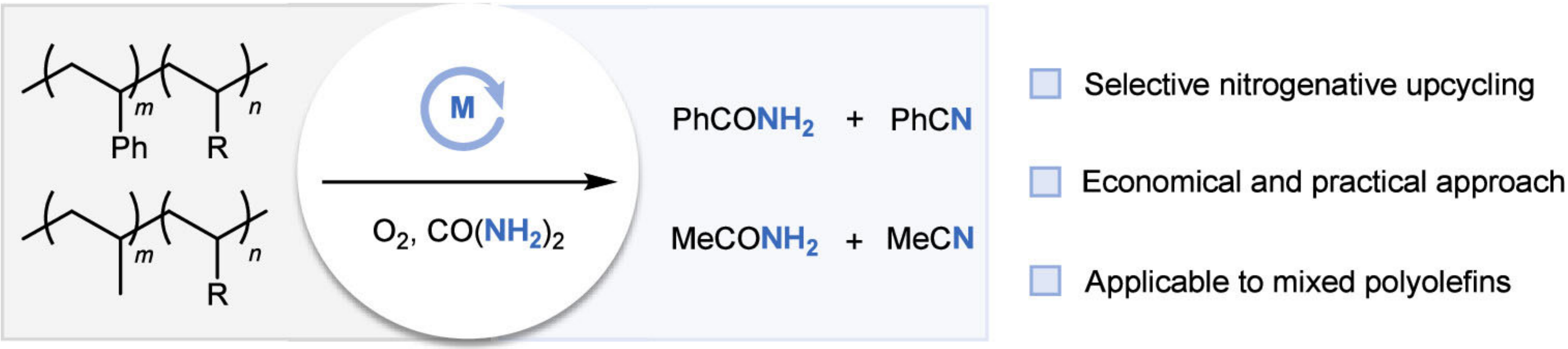
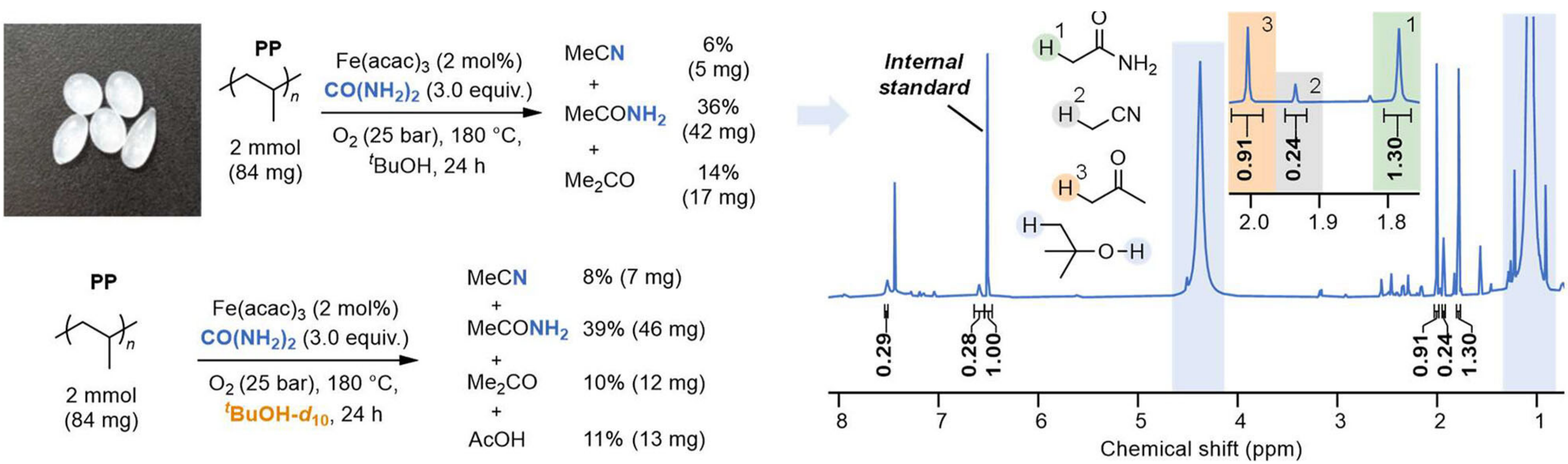
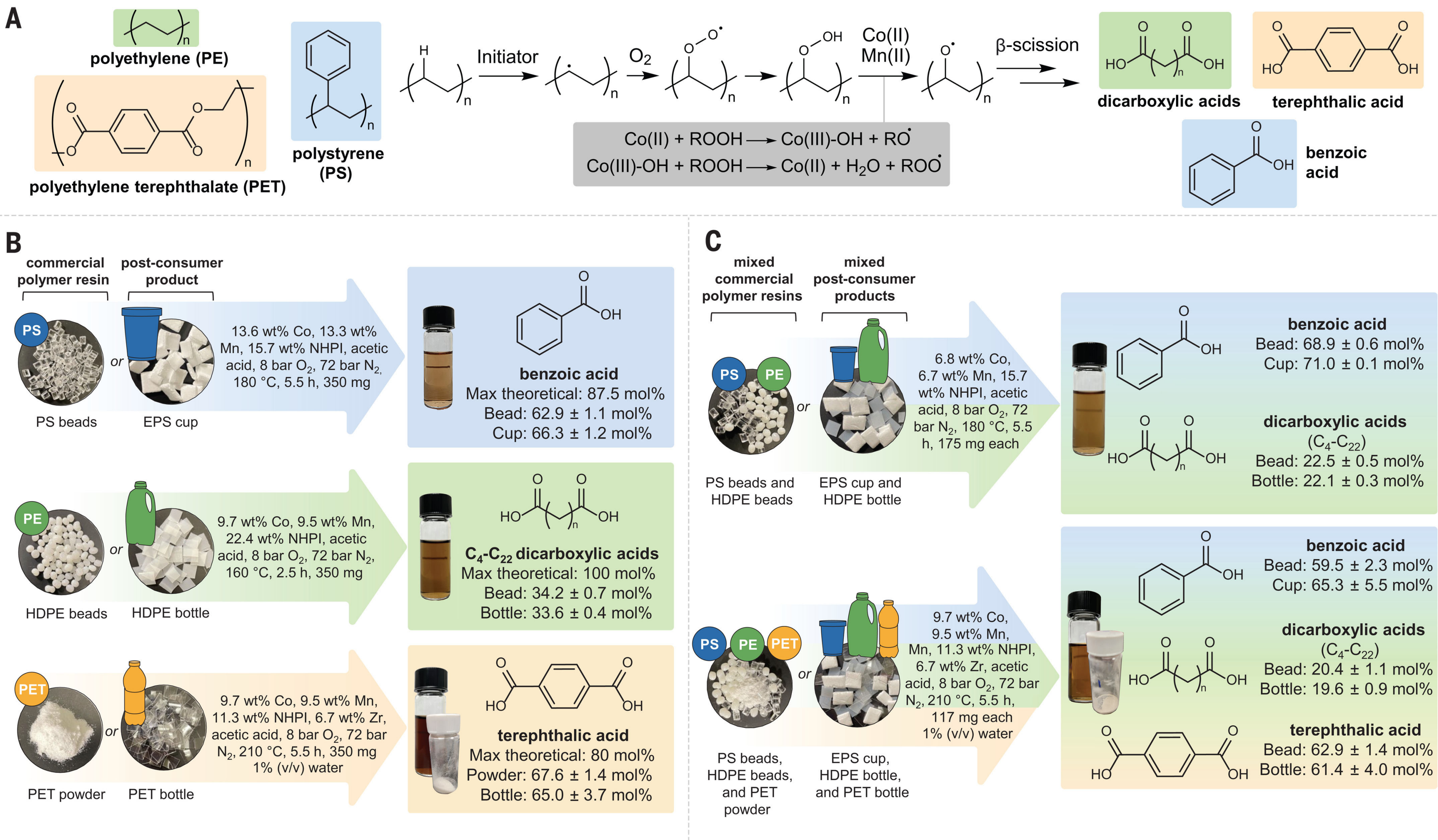


SELECTIVE UPCYCLING OF POLYOLEFINS INTO HIGH-VALUE NITROGENATED CHEMICALS



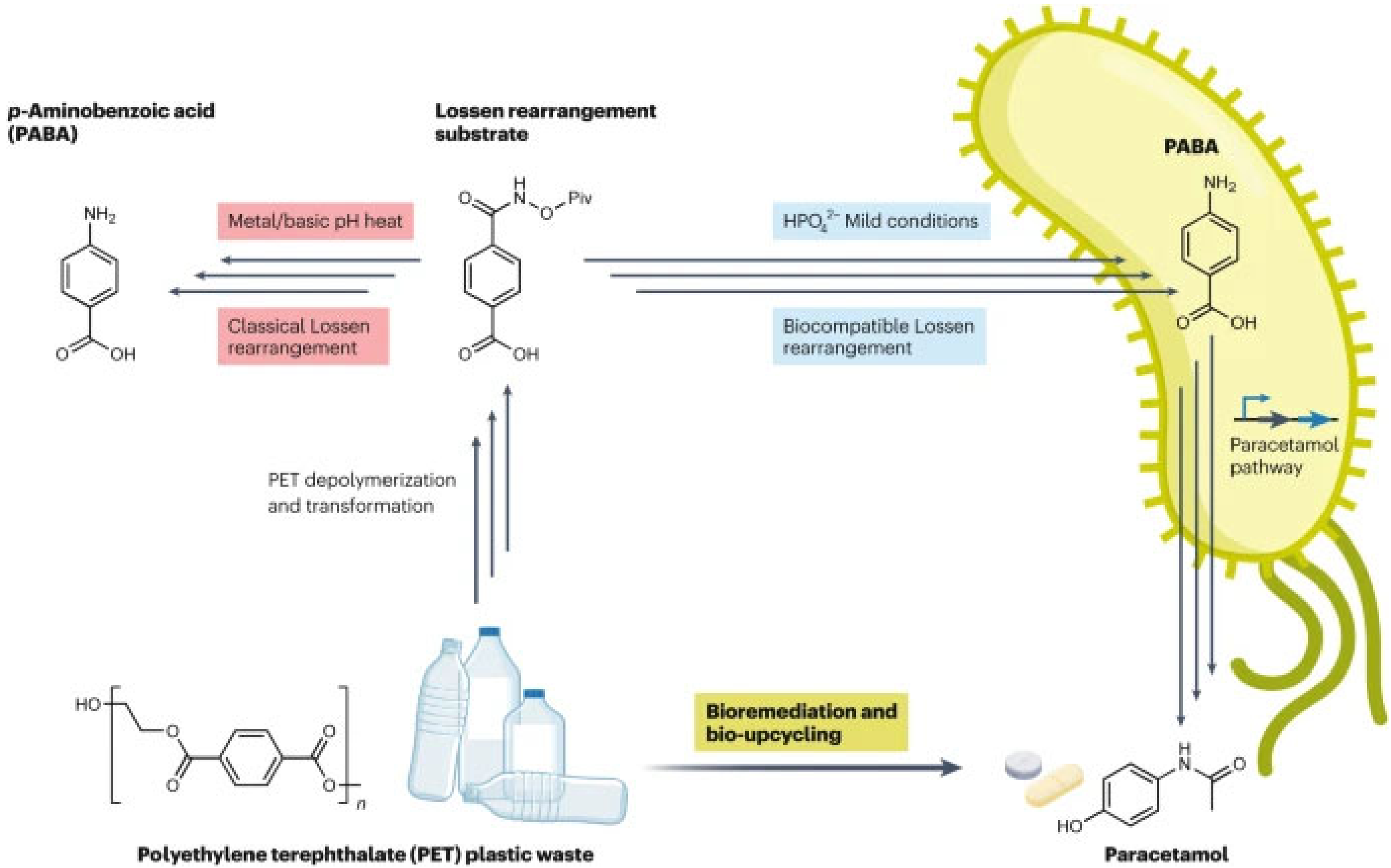


N.Jiao, et.al., J. Amer.Chem.Soc.,2024, Vol 146/Issue 42, 28605



SCIENCE 13 Oct 2022 Vol 378, Issue 6616 pp. 207-211
DOI: 10.1126/science.abo4626

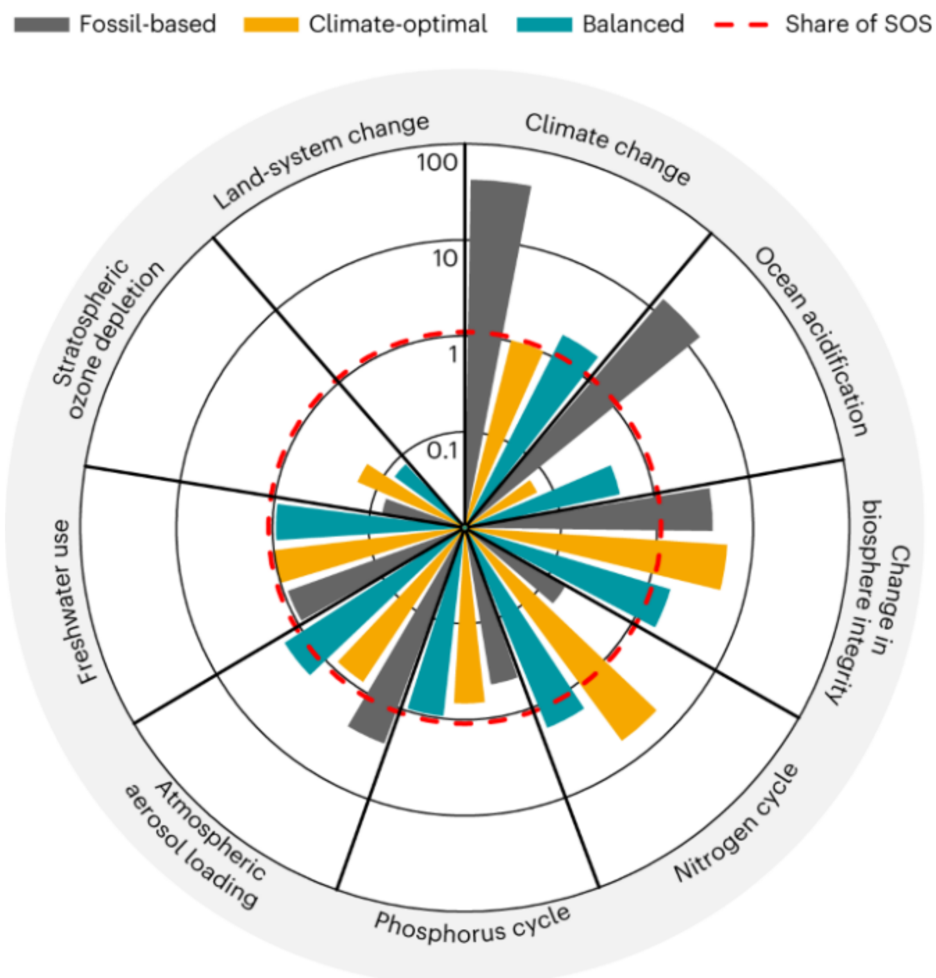
CHEMICAL RECYCLING OF PET TO PARACETAMOL



Global demand for p-acetamol : 275,000 tpa (0.275 million tons per annum)
PET Bottles : water, soft drinks : 25 million tons per annum, roughly 73 % of all rigid packaging PET based products

https://doi.org/10.1038/s41557-025-01845-5

IMPACT OF CIRCULAR STRATEGIES OF PLASTICS ON PLANETARY BOUNDARIES (2030)



The planetary footprints are shown as percentage of global SOS. The share of SOS assigned to the plastics industry is highlighted in red

Three Scenarios

- Fossil reference (Fossil-based)
- Optimal circular technologies (Climate-optimal)
- Optimal circular technologies to minimize transgression of “Safe Operating Space” (Balanced)

Nature Sustainability, 2023, 6, 599-610

FOR MANY MATERIALS, ECONOMICALLY VIABLE RECYCLING OPTIONS DO NOT EXIST!

- Multi-phase polymers: ABS, Impact PP, HIPS, blends
- Multilayer coextruded films, barrier films, PE/PET, aluminum/polymer, paper/ PE. Tetrapack®, laminated tubes, single-use sachets, etc
- All cross-linked rubbers (including natural rubber!)
- All thermosets
- Low bulk-density materials, such as foams, bubble wraps, blister packs, tea bags and the like
- Polymers that have come in contact with food, beverages, body fluids or household chemicals

Challenge : To identify substitute materials with higher sustainability quotient for these applications, meeting the cost-performance demands of the customer

OTHERS: MANY COMPOSITIONS AND COMPLEX MATERIAL STRUCTURES

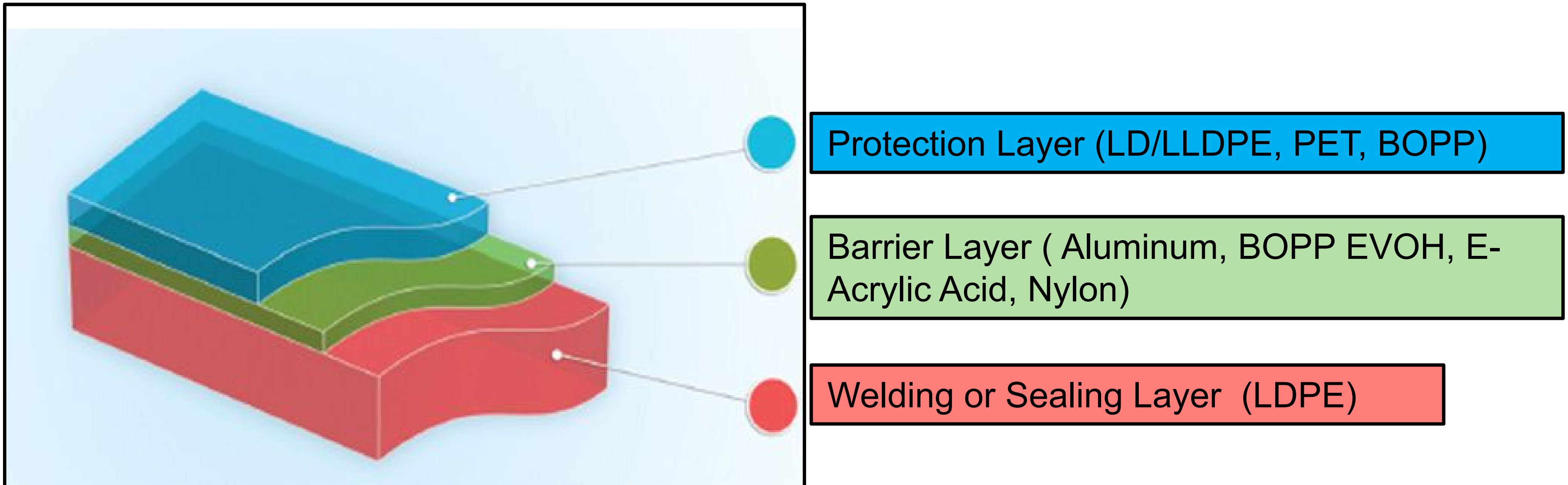
7

OTHER

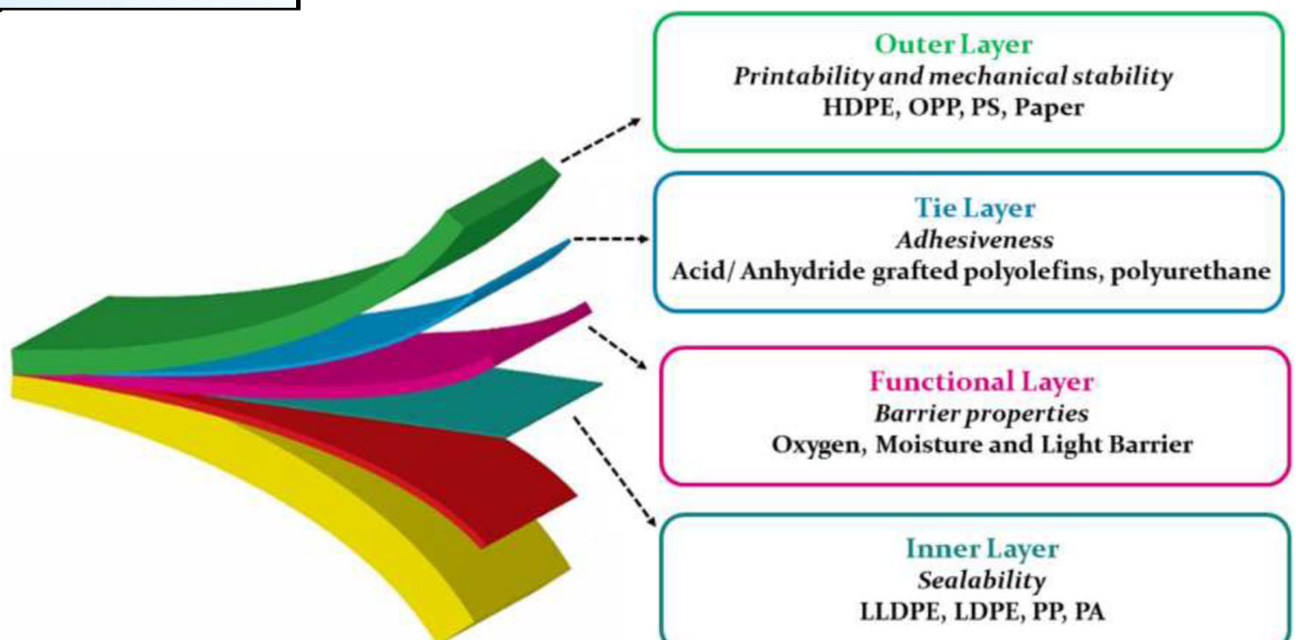
Three, five and seven layer layer sandwiched coextruded packaging films
Barrier Layer: Aluminum, EVOH, Nylon etc.

To improve functionality, we have made products more complex by introducing many materials. How can we move to mono-materials for packaging ?

STRUCTURE OF MULTI-LAYER COEXTRUDED PACKAGING FILMS



BOPP: Biaxially Oriented Polypropylene film; EVOH: Ethylene-Vinyl Alcohol Copolymers



CHALLENGES TO CIRCULARITY : ANATOMY OF A SPORTS SHOE

- A marvel of engineering
- Multiple materials
- Confluence of functionality and aesthetics

- Leather
- Nylon
- PVC
- EVA
- Hard and soft rubber
- Textile fibers
- Dyes and colorants
- Water repellent coatings
- TPUs
- PU Foam (closed and cellular)
- PU microfiber

END-OF-LIFE CHALLENGES FOR A SHOE

- Global per capita consumption of footwear: from 1 pair of shoes per year per person in 1950 to almost 2.6 pairs of shoes now.
- in 2005. In the EU, the estimated amount of post-consumer shoe waste was 1.2 million tonnes per year
- Major challenge: The vision of 'Zero Waste to Landfill'; currently, less than 5% of the 20 billion pairs of shoes produced worldwide every year are recycled or reused
- Material recycling is seen as the most suitable option. However, long-term sustainability of footwear recovery activities and an economically viable material recycling system are yet to be established. Footwear products typically contain a large mixture of materials that have relatively low recycling value

A shoe was designed for a linear economy; it is unfit for a circular economy. Are we ready to design a shoe ground-up tailored for circular economy ? This will involve, a radical re-design using fewer types of materials and design for dis-assembly

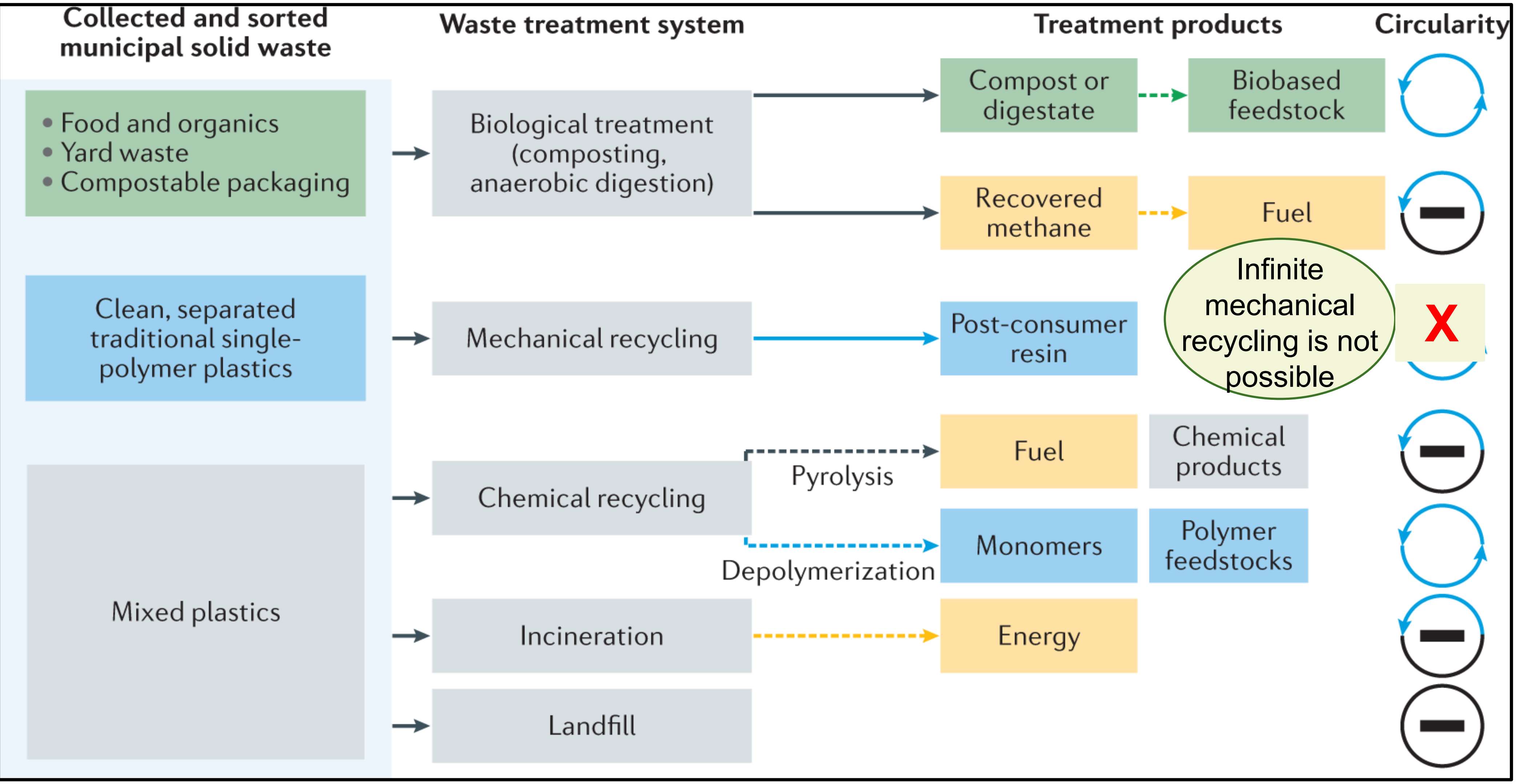
DESIGN FOR SUSTAINABILITY

- What is the sustainability problem with these products ?
- Identify and classify the materials used in these products?
- Think how you will redesign these products for circularity or reusability?
- Think in groups and note down as many ideas you can get?

SIMPLE DESIGN CHANGES FOR RECYCLABILITY

- Plastic bottles without labels
- Plastic PET bottles with natural colors; Natural colors for closure
- Plastic bottle caps : HDPE : white, PP: Natural
- PP woven sacks : Natural colors
- Tethered caps: Bottles, tooth paste tube, blow molded bottles etc.
- Simplify design: Multilayers to monolayers
- Reduce use of plastics per serving in packaging
- Avoid using aluminum and PET with polyolefins
- Eliminate printing labels on packages to machine readable labels: Avoid inks and adhesives or shift to more sustainable adhesives derived from natural resources

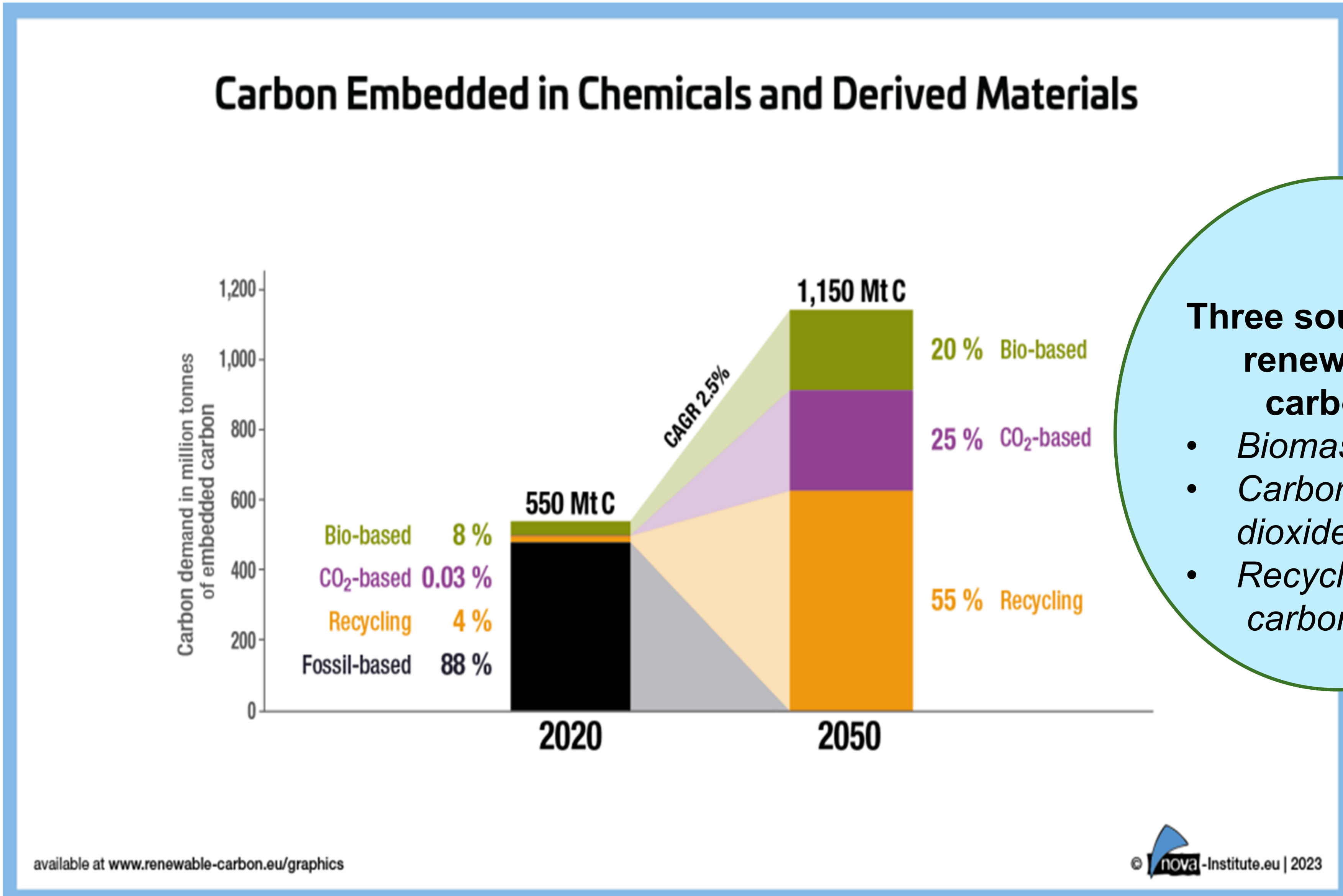
ONLY FEW SOLUTIONS FULFILL THE REQUIREMENT OF CIRCULARITY



CONSERVATION AND SEQUESTRATION OF "UNDER-THE-SURFACE" CARBON

- The carbon embedded in the polymer has to be conserved and must be in use as long as possible
- We cannot increase the available "carbon-budget" in the atmosphere. This rules out incineration or conversion of the plastics to combustion fuels
- Chemical recycling to monomers, in principle, appears to be the most acceptable solution
- If the embedded carbon cannot be conserved, then we must sequester this carbon irreversibly in the geosphere. One possible method is to crack plastics anerobically to carbon and hydrogen and immobilize the unutilized carbon under the earth and use hydrogen for energy needs

Synthesis of clean hydrogen gas from waste plastics at zero net cost, J.M. Tour, et.al., Adv. Mater, 2023, 2306763



Three sources of renewable carbon:

- *Biomass*
- *Carbon dioxide*
- *Recycled carbon*

- Global demand for embedded carbon will increase to 1.15 Gt per year by 2050
- Today's carbon budget is met by fossil feedstocks to the extent of about 88%
- If we have to completely de-fossilize by 2050, we have to meet the entire budget from renewable carbon

PLASTICS WASTE MANAGEMENT IS A GLOBAL PROBLEM REQUIRING LOCAL SOLUTIONS

Editorials
nature

Landmark treaty on plastic pollution must put science front and centre

A United Nations resolution on greening plastics is a positive step. The upcoming negotiations must be evidence-based.

On 2 March, world leaders and environment ministers agreed to start negotiations on the world's first legally binding international treaty to eliminate one of humanity's most devastating sources of pollution: plastics. This hugely positive step has the power to attack the problem as never before. But to achieve this goal, science needs to be front and centre in the negotiations.

Plastic pollution is a massive problem. Some 400 million tonnes of the material is produced each year, a figure that could double by 2040. Of all the plastic that has ever been produced, only about 9% has been recycled and 12% incinerated. Almost all other waste plastic has ended up in the ocean or in huge landfill sites. More than 90% of plastics are made from fossil fuels. If left unchecked, plastics production and disposal will be responsible for 15% of permitted carbon emissions by 2050 if the world is to limit global warming to 1.5 °C above pre-industrial temperatures.

Talks on the treaty are expected to take between two and three years and will be organized by the United Nations Environment Programme, based in Nairobi. A significant feature of the treaty is that it will be legally binding, like the 2015 Paris climate agreement and the Montreal Protocol, a 1987 treaty that led to the production and use of ozone-depleting substances being phased out.

A team of negotiators from different regions is being established. By the end of May, they will start work on the treaty's text. According to last week's UN decision, these negotiators will consider "the possibility of a mechanism to provide policy relevant scientific and socio-economic information and assessment related to plastic pollution". But they need to do more than just consider a mechanism. The UN must urgently set up a scientists' group that can give the negotiators expert advice and respond to their questions. These science advisers would need to reflect the necessary expertise in the natural and social sciences, as well as in engineering, and represent different regions of the world.

Nations want the plastics treaty to be more ambitious than most existing environmental agreements. Unlike the Montreal Protocol, which replaced around 100 ozone-depleting substances with ozone-friendly alternatives, countries have agreed that a plastics treaty must lock sustainability into the 'full life-cycle' of polluting materials. This means plastics manufacturing must become a zero-carbon process, as must plastics recycling and waste disposal. These are not straightforward ambitions, which is why research – and access to research – is so important as negotiations get under way.

> "Plastics use is increasing at a rapid rate, and this is no longer tenable."

Most plastics are designed in a 'linear' one-way process: small, carbon-based molecules are knitted together with chemical bonds to make long and cross-linked polymer molecules. These bonds are hard to break, which makes plastics extremely long-lasting. They do not degrade easily and are difficult to recycle.

Marine litter often grabs the headlines, but plastic pollution is everywhere. Landfill sites containing mountains of plastic blight our planet, and minuscule particles of plastic are found in even the most pristine environments. Such is the scale and persistence of plastics that they are now entering the fossil record. And a new human-made ecosystem – the plastisphere – has emerged that hosts microorganisms and algae[1].

As negotiators get to work, they will need scientists to help them address several key questions. Which types of plastic can be recycled[2,3]? Which plastics can be designed to biodegrade, and under what conditions? And which plastics offer the best chances for reuse[4]? Moreover, social-sciences research will be essential to understanding the implications of – and inter-relationships between – the solutions that countries and industries will have to choose from. For example, new technologies and processes will have impacts on jobs. These impacts need to be studied so that risks to people's livelihoods can be mitigated.

Mapping out the implications of various approaches to greening the plastics industry will also require cooperation between governments, industry and campaign organizations – building on the cooperation that has brought the world to the start of negotiations.

Plastics have made the modern world. They are a staple of daily life, from construction to clothing, technology to transport. But plastics use is also increasing at a rapid rate, and this is no longer tenable – around half of all plastics ever produced have been made since 2004.

It is clear from the UN's ongoing efforts to tackle climate change that it is not enough for a treaty to be legally binding. Signatories must also be held accountable, with regular reporting and checks on progress. Equally important is the need for science advice to be embedded in the talks from the earliest possible stage.

Last week's decision is the best start the planet could have had to tackling our plastics addiction. But as the hard work begins, decision-makers must be able to quickly and easily access the very best available evidence that research can provide.

1. Amaral-Zettler, L. A., Zettler, E. R. & Mincer, T. J. *Nature Rev. Microbiol.* **18**, 139–151 (2020).
2. Hopewell, J., Dvorak, R. & Edward, K. *Phil. Trans. R. Soc. B* **364**, 2115–2126 (2009).
3. Coates, G. W. & Getzler, Y. D. Y. L. *Nature Rev. Mater.* **5**, 501–516 (2020).
4. Grigore, M. E. *Recycling* **2**, 24 (2017).

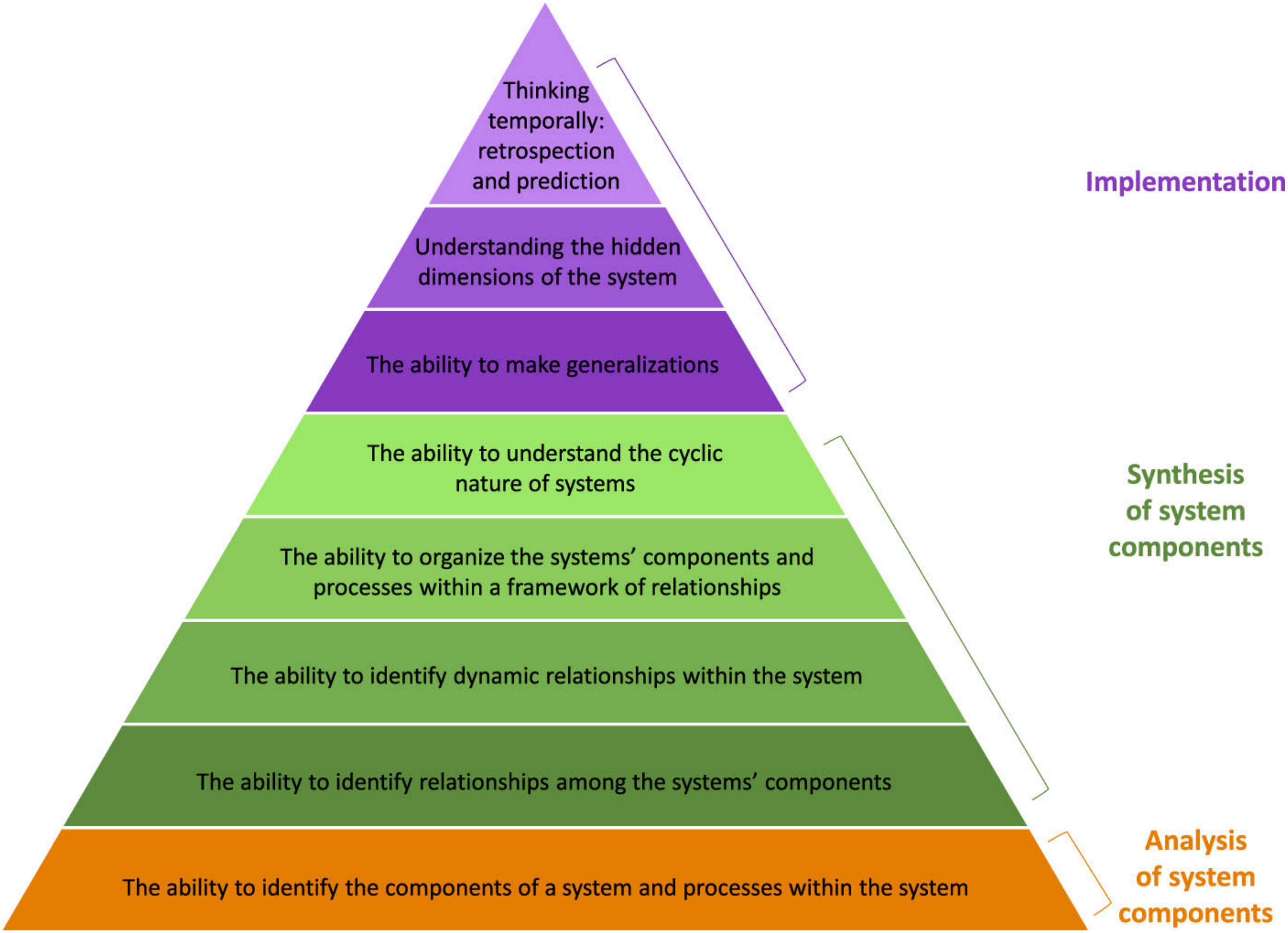
Nature, 10 March 2022; Chemistry World, April 2022, p.10-13

- Analogy : Climate Change
- United Nations " Inter-Government Panel on Plastic Pollution" began negotiations in 2022 on a legally binding international treaty to reduce plastic pollution
- The Panel has agreed that " **a plastics treaty must lock sustainability into the 'full life-cycle" of polluting materials"**
- This means that plastics manufacturing must become a **"Net-Zero-Carbon"** and plastics waste management ***"Net-Zero Waste"***
- Goal: " To evolve a mechanism to provide policy-relevant scientific and socio-economic information and assessment related to plastic pollution"

THE COLLAPSE OF THE CONVERSATION

- The conversation collapsed without any agreement on 15 August 2025 in Geneva after six rounds of negotiations
- The discussions covered what plastic products must be covered, defining harmful chemicals across the plastic life-cycle, how to design more sustainable products, improve recycling and make the global plastics system more circular
- A key area of disagreement was whether we can solve the problem without reducing plastic production and consumption, and which of the products and the harmful chemicals in plastics posed a greater problem
- Two camps appeared, one that argued that there is no need to reduce production and end–of–life solutions, if implemented, can mitigate the problems and the other, which stated that without reducing the production of virgin plastics, we cannot stem the tide of plastic pollution

SYSTEMS THINKING HIERARCHICAL MODEL PYRAMID.



MaryKay Orgill et. al, Introduction to Systems Thinking for the Chemistry Education Community, DOI: 10.1021/acs.jchemed.9b00169

COMPONENTS OF PLASTICS WASTE MANAGEMENT SYSTEM

A: Policy

- Taxation
- Ban
- Legislation & regulation
- Buy back
- Restrict supply
- Increase cost to consumer
- Incentivize circularity
- Mandatory recycle content in every product
- Improve efficiency and economics of collection
- Fund policy creation efforts
- International agreements

B : Science, Technology & Innovation

- Induce/ build degradability
- Waste to chemicals
- Waste to energy
- Modular manufacturing
- Circularity
- Product design for circularity /sustainability
- Use of natural resources
- Recycling
- Repurposing
- Substitution with alternative more sustainable materials
- Edible packaging
- Technology for sorting plastics by chemical types

C: Infrastructure & Ecosystem

- Labelling
- Identification
- Segregation
- Collection, compaction and aggregation
- Transportation
- Safe disposal and managed landfills
- Improved municipal waste management
- Create and incentivise reverse supply chain

D: Changing Consumer habits

- Social education & awareness
- Avoiding plastics in areas where large number of people gather
- Civic sense
- Nudge personal choices
- Volunteer activities
- Reduce and reuse
- Exploit the full life-cycle of a product through donation to those at the lower level of the economic pyramid

Reliable data is necessary and critical to evidence based decision making across all components

WHAT IS IT THAT YOU AND I CAN DO

- **Refuse** use of plastics where unnecessary
- **Reduce** use of plastics where unnecessary
- **Shift** to practices that are well known to be sustainable, yet not compromising on health or hygiene
- **Reuse** plastics as much as possible before throwing it away
- **Understand** what plastics you are using daily in your life; think how you can start using them less
- **Avoid** using plastics that are difficult to recycle, unless absolutely essential
- **Segregate**, as much as possible, all plastics by their type

The world is changed by your example, not by your opinion:
Paul Coelho

Refuse what you do not need
Reduce what you do need
Reuse what you consume
Recycle what you cannot refuse, reduce or reuse
Rot (compost) the rest

Béa Johnson is a US based environment activist, author of the book Zero Waste Home: The Ultimate Guide to Simplifying Your Life by Reducing Your Waste.

THANK YOU

If you do not change direction, you may end up where we are heading: Lao Tzu