Closing the carbon loop
In the circular plastics economy

Rolf Mülhaupt
University of Freiburg, Germany

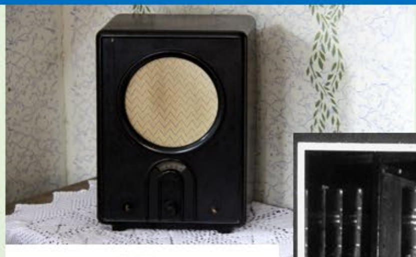
- ❑ **Do we need to reinvent plastics ?**
- ❑ **Is the future of plastics green?**
- ❑ **How to close the carbon loop?**

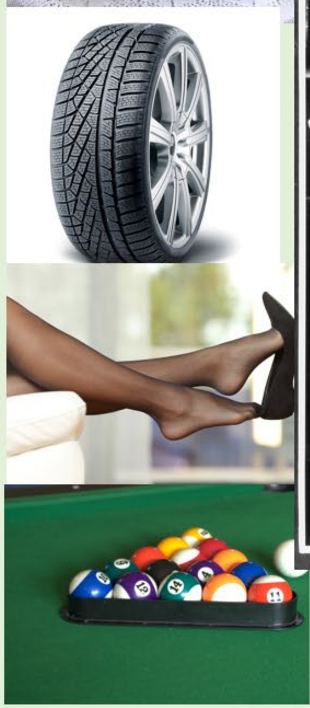
SUSTAINABILITY CENTER FREIBURG

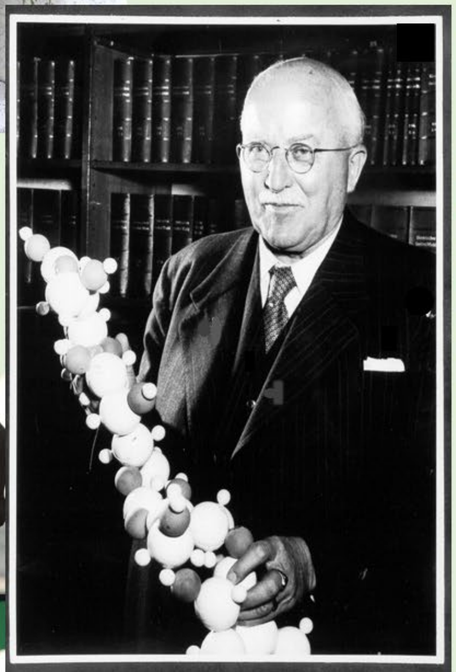
Freiburg Materials Research Center, FMF

Institute for Macromolecular Chemistry, Makro

Small molecules (drugs, food ingredients) = long life
Macromolecules = better life







Hermann Staudinger
Nobel Prize 1953

Health

Mobility

Communication

Energy

Food & Water

Shelter

Clothing

Protection

Leisure &

Sports

...

1900 — 1907 Bakelite™ — 1920 Macromolecules — **1950** — **2000**

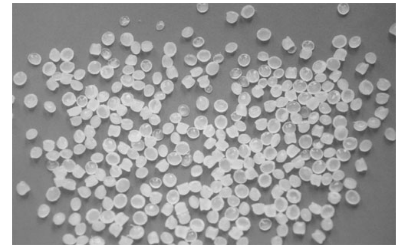
Substitutes of silk, natural rubber & ivory

Advanced materials & systems

Converting polymers into plastics

Feedstock → **Polymerisation**

Monomer



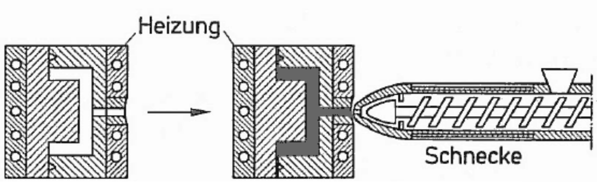
Polymer

Additives
Stabiliser,
Processing aids,
Fillers,….

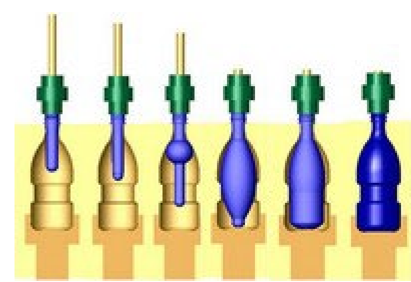
Processing
Injection Molding, Extrusion,
Spinning, Casting,Blow molding

Plastics

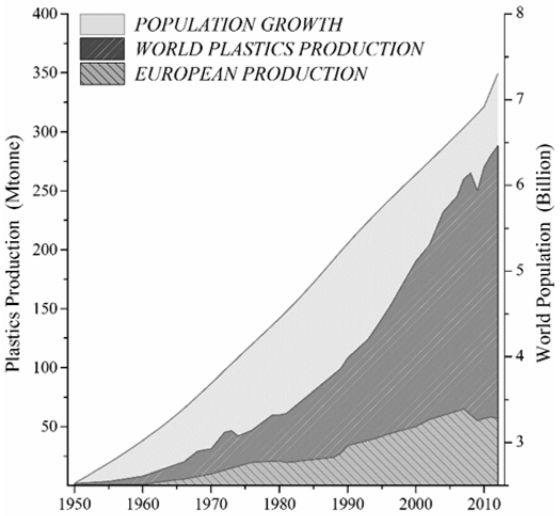
Recycling

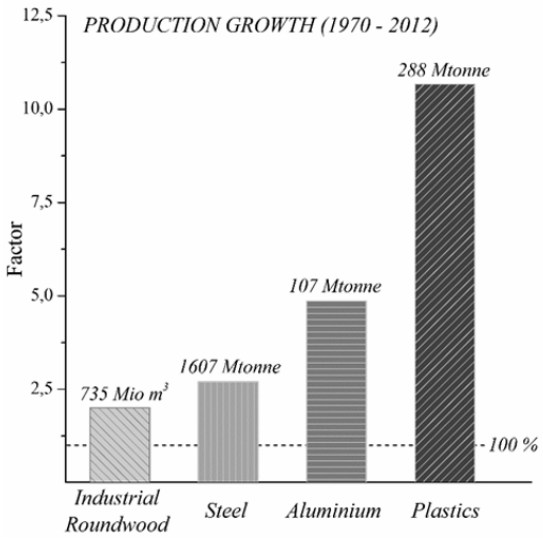


Injection Molding
1 CD in 2s!



The growing world population needs plastics!





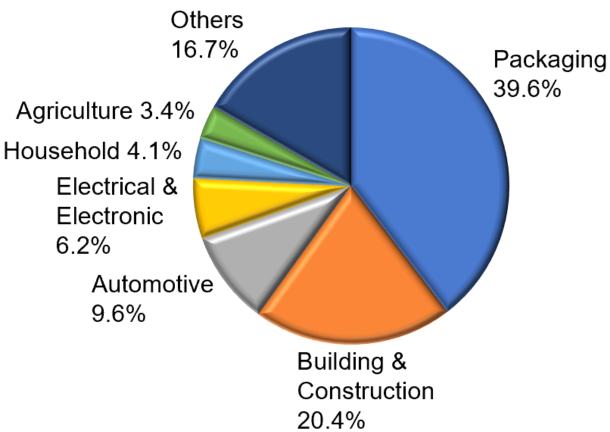
- **High benefits for mankind**
- **Extraordinary versatility**
  - ➢ Tailoring property profiles
  - ➢ Applications
  - ➢ Processing
- **Low weight > Lightweight construction!**
- **Corrosion resistance**
- **Efficiency**
  - ➢ Resources
  - ➢ Energy
  - ➢ Ecology / Recycling
  - ➢ Low cost
- **Low carbon footprint**
- **Sustainability**

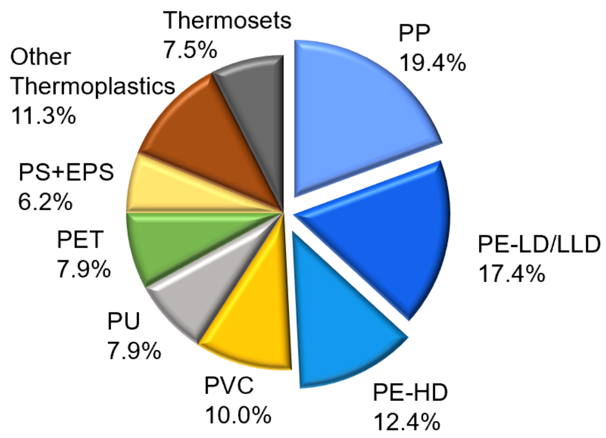
R. Mülhaupt, Ullman‘s Encyclopedia „Polymers – A General Survey“, 2015

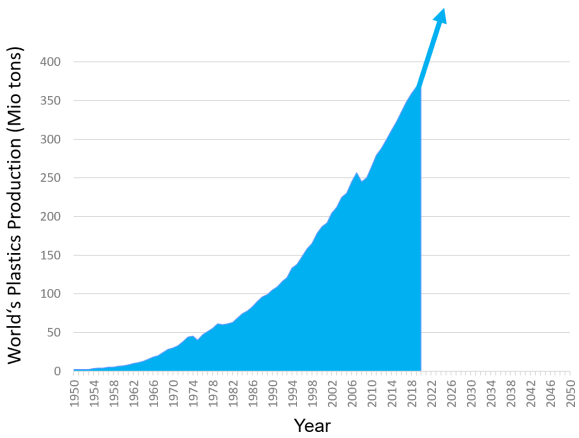
The world needs polyolefins!

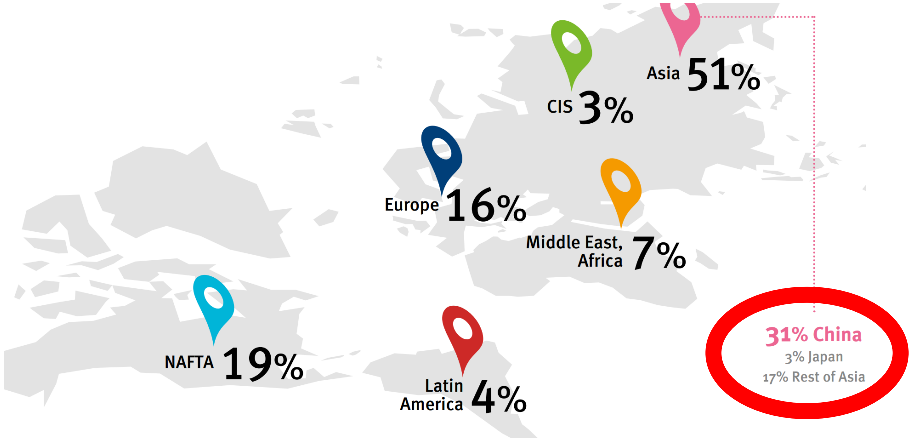
(Plastics the Facts 2020 from PlasticsEurope)

367 Mio tons in 2020







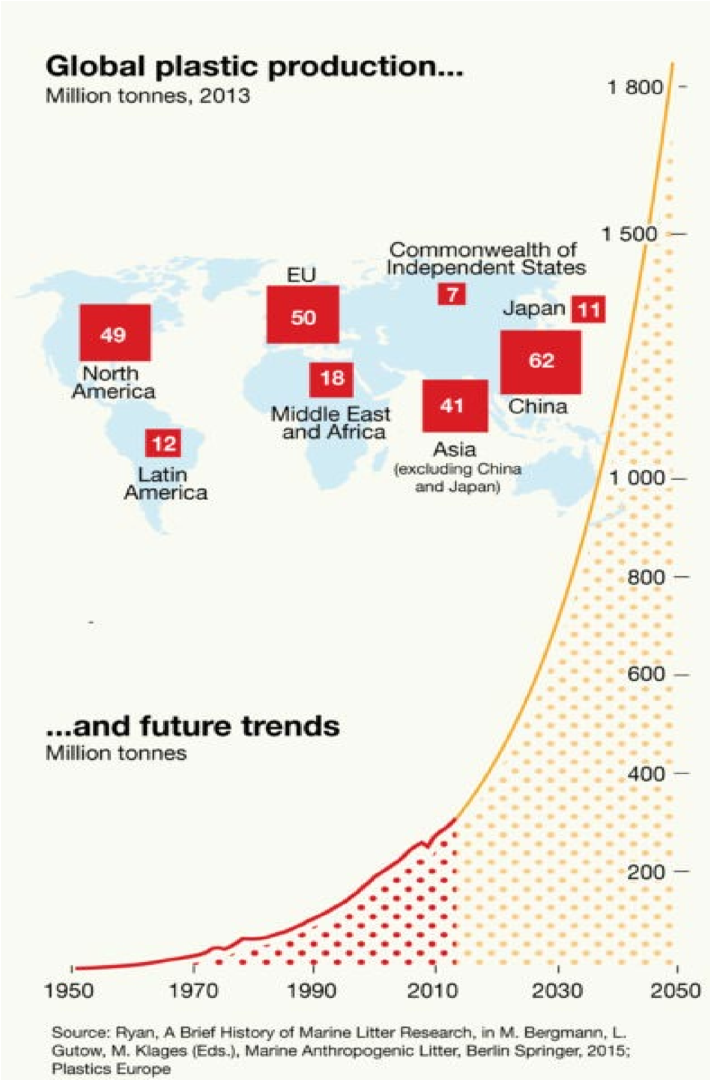


https://plasticseurope.org/knowledge-hub/plastics-the-facts-2020/

Curse and blessing of plastics

Bright side	Dark side
Low cost / easy processing	
= affordable products	= throwaway products
Versatility	
= broad application range	= recycling challenges
Low weight	
= saving energy	= floating in water
Durability	
= reliability, long life	= long life in short-life applications
Oil-like energy content	
= energy storage	= flammability
Formulated systems	
= composites, coatings,…	= mechanical recycling is difficult
Biodegradation	
= composting, biogas	= breeding ground for spores, methane
Degradation	
= molecular recycling	= microplastic formation

Curse and Blessing of Plastics Growth



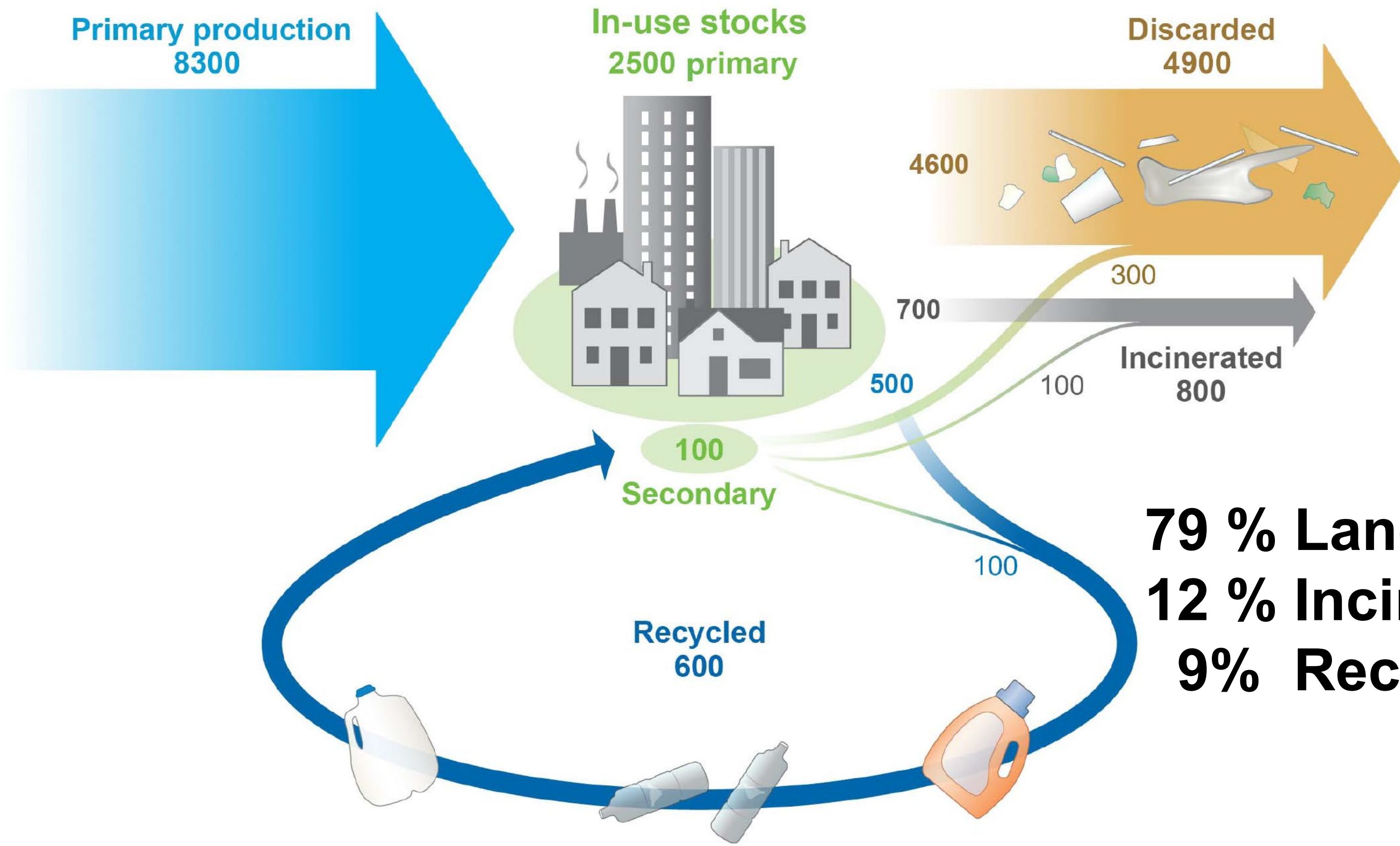
Source: UN-GRID-Arendal

Maldivies © Shutterstock

http://www.imo.org/en/MediaCentre/HotTopics/marinelitter/Pages/default.aspx

https://www.wwf.de/themen-projekte/meere-kuesten/plastik/unsere-ozeane-versinken-im-plastikmuell/

Fate of all plastics ever made till 2015 (Mio t)



2050
12000
Mio t

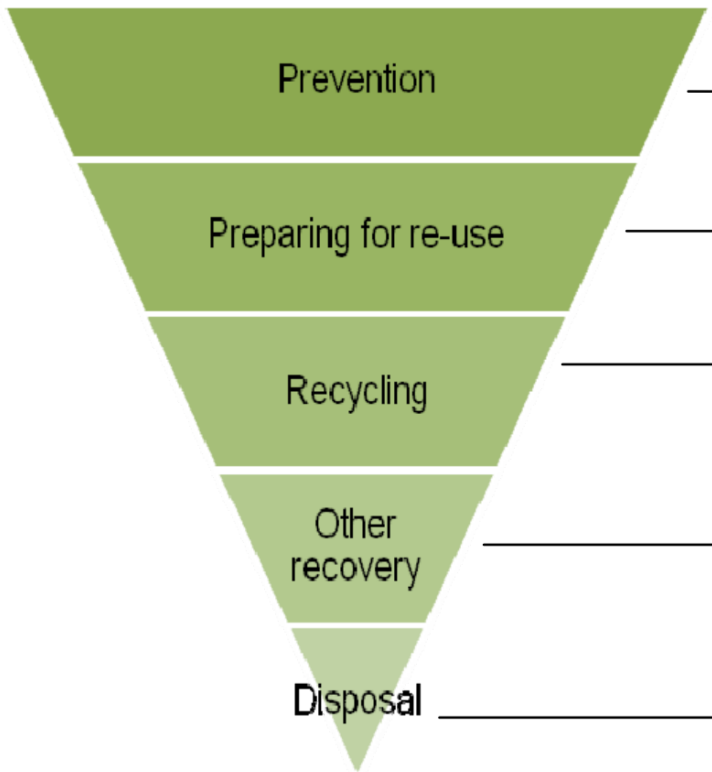
79 % Landfill
12 % Incineration
9% Recycling

R. Geyer, J.R. Jambeck, K.L. Law, Sci. Adv. 2017, Sci. Adv. 2017;3: e1700782

Plastic Waste Challenge

5 R Strategy: Reduce, Reuse, Recycle, Rethink, Restrain

Stages



Include

Using less material in design and manufacture. Keeping products for longer; re use. Using less hazardous materials

Checking, cleaning, repairing, refurbishing, whole items or spare parts

Turning waste into a new substance or product. Includes composting if it meets quality protocols

Includes anaerobic digestion, incineration with energy recovery, gasification and pyrolysis which produce energy (fuels, heat and power) and materials from waste; some backfilling

Landfill and incineration without energy recovery

Recycling quota in Europe:
Paper (50-60%)
Metal (70-90%)
Plastics (10-30%)

defra
Department for Environment Food and Rural Affairs

D.G. Bucknall, Philosophical Transactions A 2020, 378, 2176, Plastics as a materials system in a circular economy, DEFRA. 2011 Guidance on applying the waste hierarchy. PB250. www.gov.uk/government/publications/guidance-on-applying-the-waste-hierarchy.

https://bmbf-plastik.de/sites/default/files/2020-08/20-08-04_Hintergrundpapier_Plastikpolitik-final.pdf

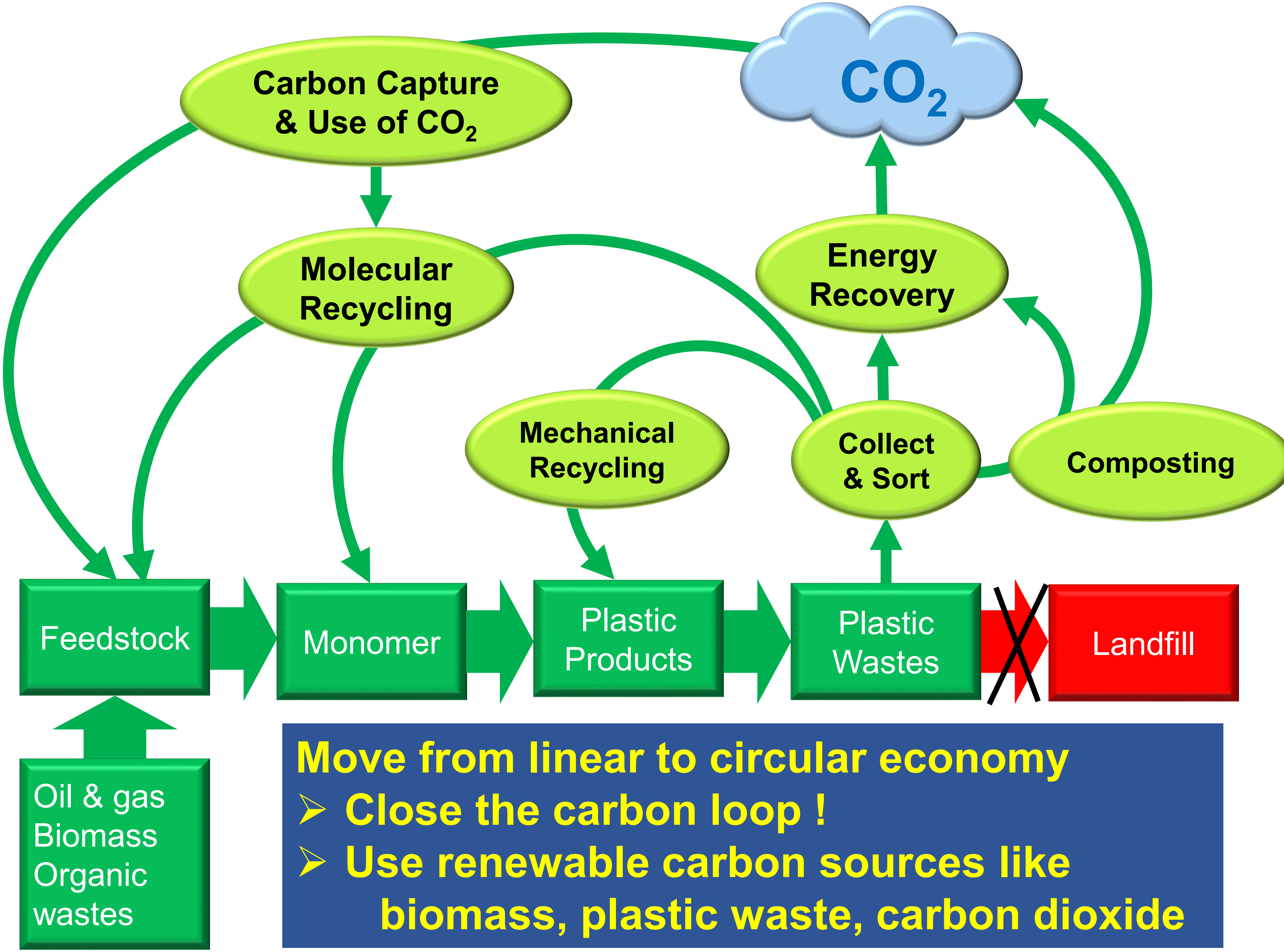
LINEAR ECONOMY
Depleting fossil resources / release of carbon!

Feedstock → Monomer → Plastic Products → Plastic Wastes → Landfill

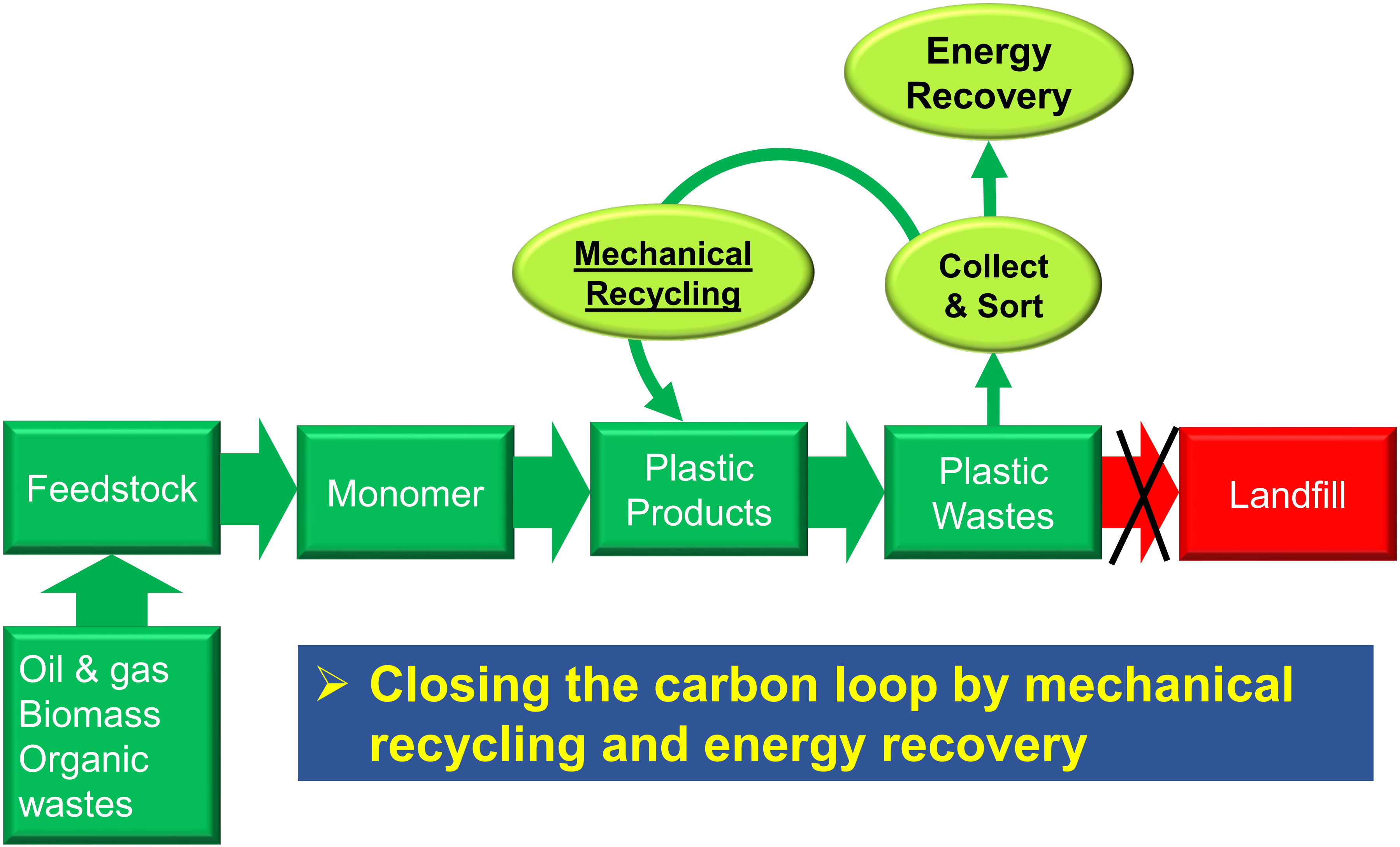
Oil & gas
> 90%
fossil
resources

↓

Micro & Nano Plastics

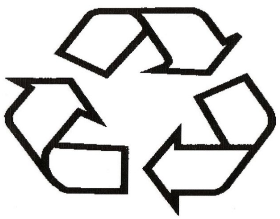


CO_2
Carbon Capture & Use of CO_2
Energy Recovery
Molecular Recycling
Mechanical Recycling
Collect & Sort
Composting
Feedstock
Monomer
Plastic Products
Plastic Wastes
Landfill
Oil & gas
Biomass
Organic wastes
Move from linear to circular economy
➢ Close the carbon loop !
➢ Use renewable carbon sources like biomass, plastic waste, carbon dioxide

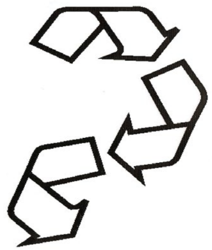


- **Closing the carbon loop by mechanical recycling and energy recovery**

Mechanical Recyling & Energy Recovery



Recycling



Downcycling

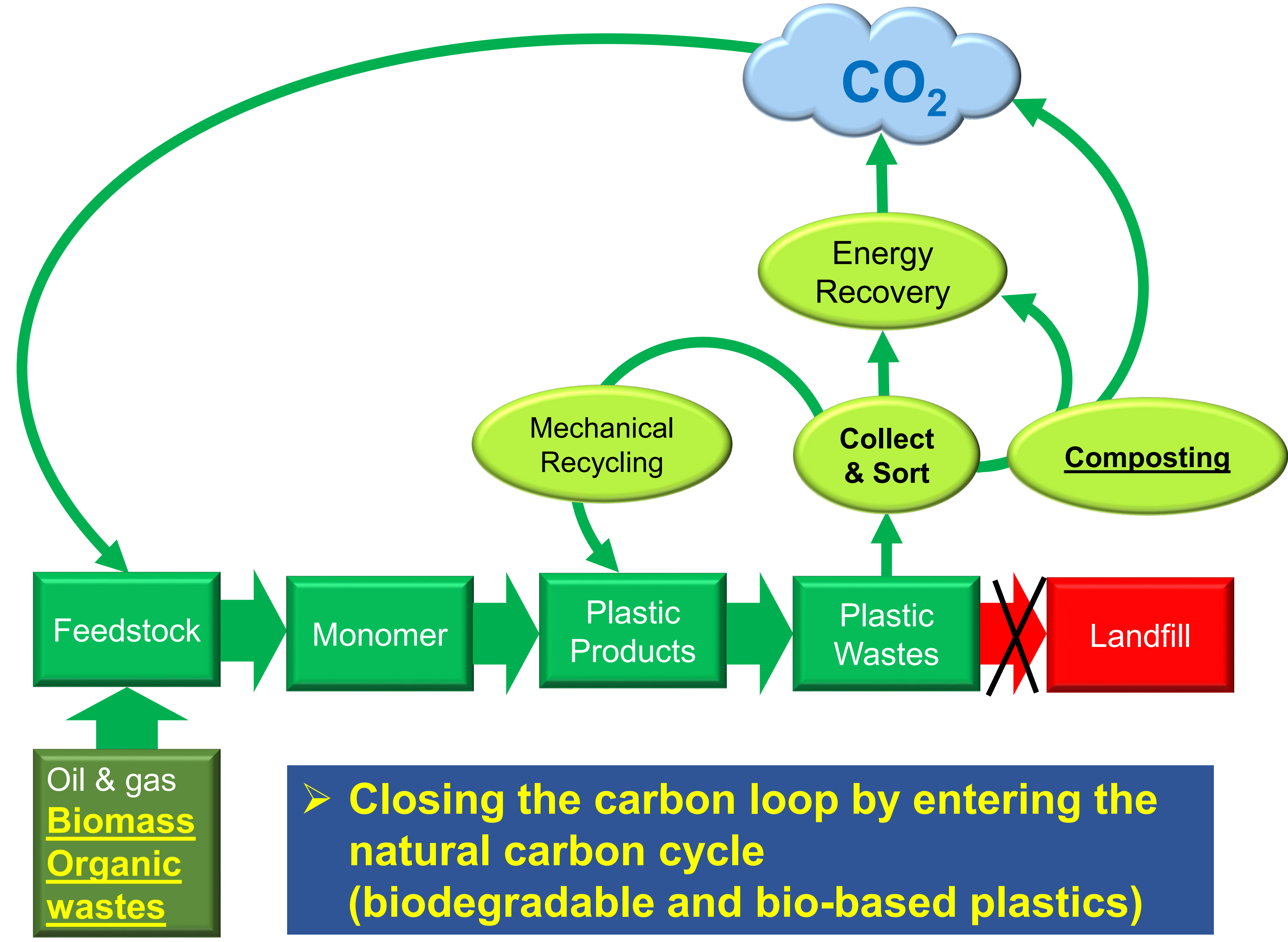
Challenges:

- Collect/sort
- Robotic sorting + AI
- Compatibilizers
- Design for recycling
- Markets for recylates

Fuel	Calorific Value (MJ/kg)
Methane	53
Gasoline	46
Fuel oil	43
Coal	30
Polyethylene	43
Mixed plastics	30-40
Municipal solid waste	10

DSM and Starboard transform discarded fishing nets into high-end surfboard component (**Akulon® RePurposed**)

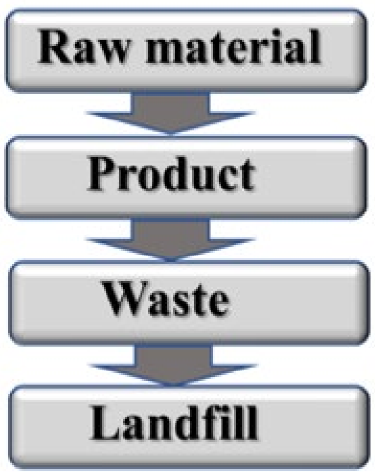
https://packagingeurope.com/coca-cola-sweden-announces-move-to-100-recycled-material-in-/
https://www.dsm.com/engineering-materials/en_US/connect/press-releases/2018-09-26-dsm-and-starboard-collaboration-transforms-discarded-fishing-nets-from-waste-into-high-end-surfboard-components.html



CO_2
Energy Recovery
Mechanical Recycling
Collect & Sort
Composting
Feedstock
Monomer
Plastic Products
Plastic Wastes
Landfill
Oil & gas
Biomass
Organic wastes
Closing the carbon loop by entering the natural carbon cycle
(biodegradable and bio-based plastics)

From Linear to Circular Economy
Is Bio-Economy the Future?

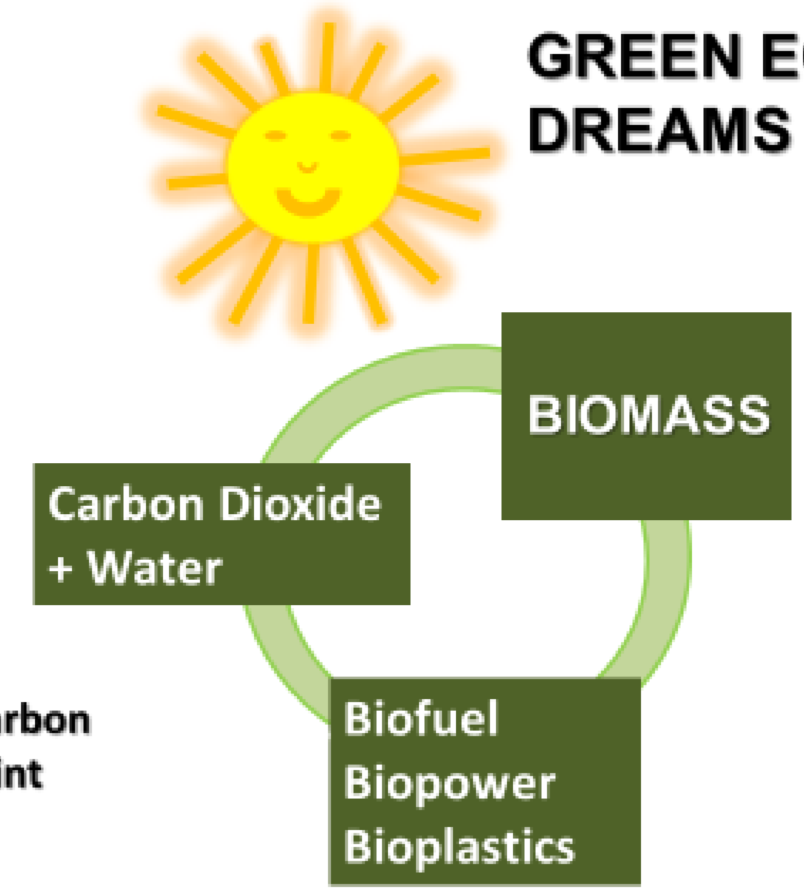
LINEAR ECONOMY



Throw-away
culture

CIRCULAR ECONOMY

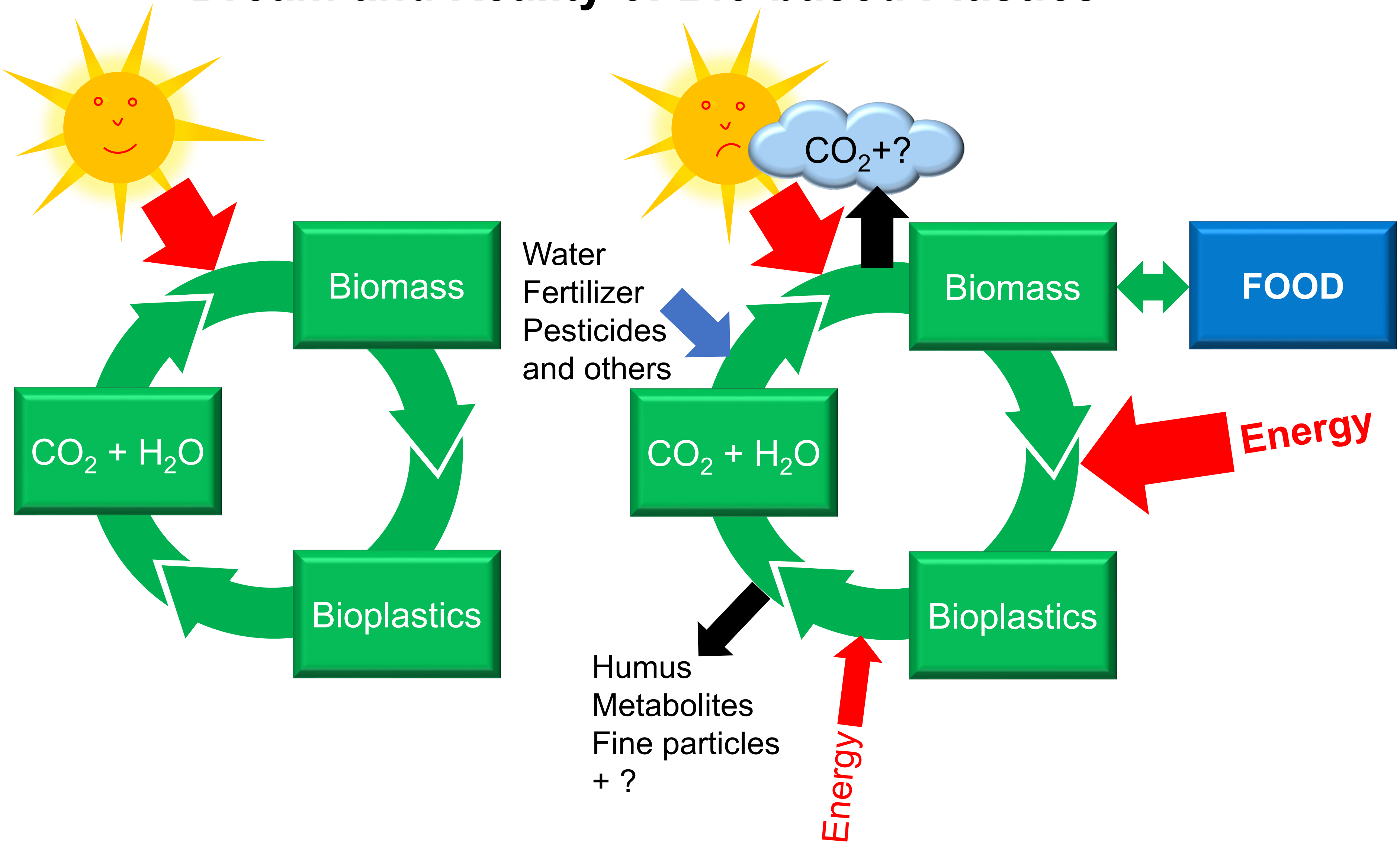
GREEN ECONOMY:
DREAMS



Low carbon
footptint

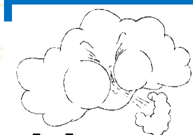
R. Mülhaupt, Macromol. Chem. Phys. 2013, 214, 159-174, Green Polymer Chemistry and Bio-based Plastics: Dream and reality

Dream and Reality of Bio-based Plastics



C. Schirmeister, R. Mülhaupt, Macromol. Rapid Commun 2022

From Linear to Circular Economy
Is Bio-Economy the Future?

Renewable resources

Wood plastics compounds (WPC)
Plant fiber composites
Natural rubber

Bio-based monomers and polymers

Bioethanol, lactic acid, 1.3-propanediol, succinic acid, polyols,…

Polyester, e.g., polylactic acid (PLA), polyhydroxyalkanoate (PHB),....


www.bridgestone.at



Biotechnology
Bio-refinery

The battle of the bag: Paper or polyethylene ?
=> Avoid single use!!!

http://www.letstalkplastics.com/facts/plastic-bags-versus-paper-bags

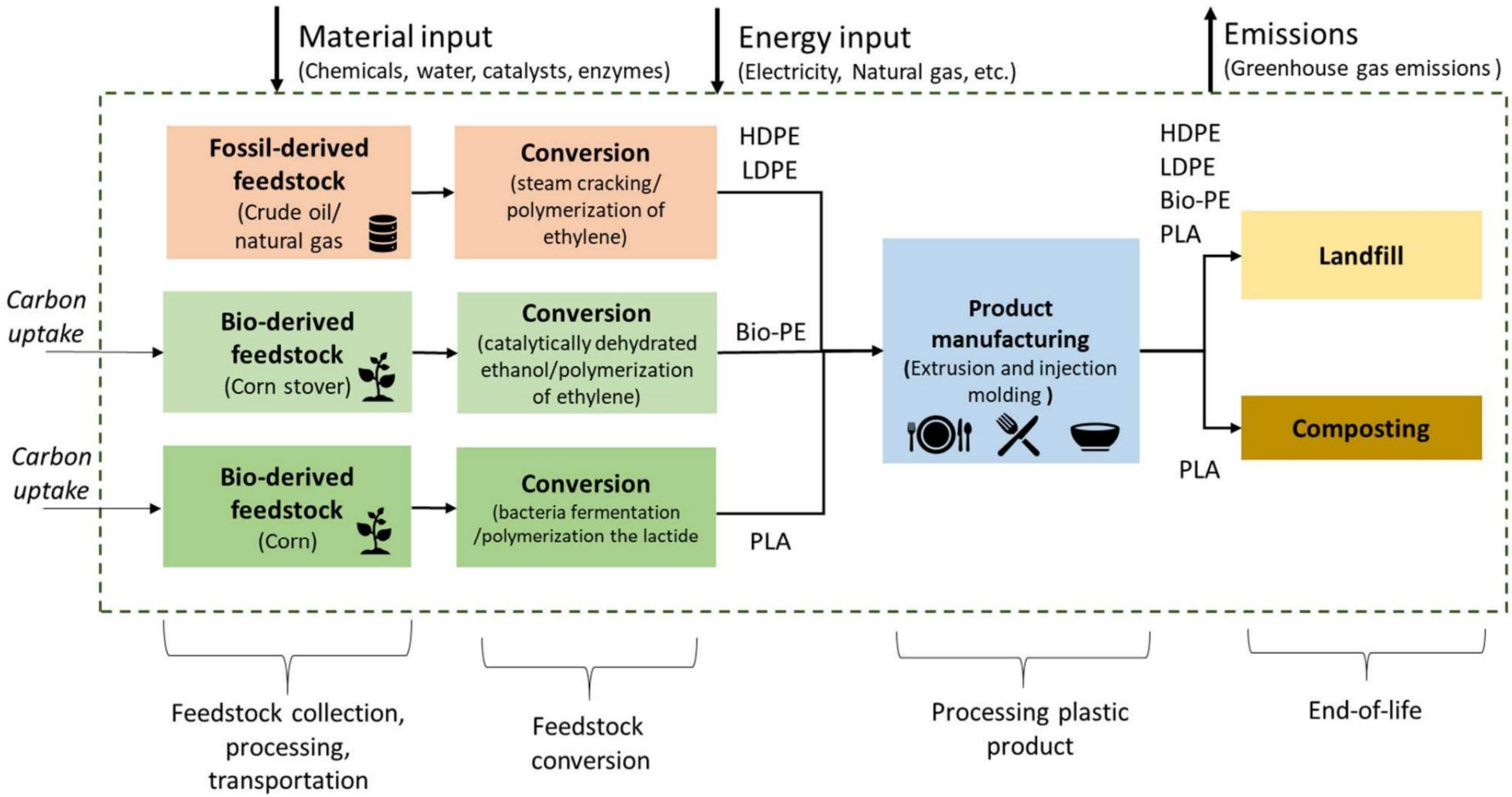
https://www.bbc.com/news/business-47027792

Paper

Cellophane

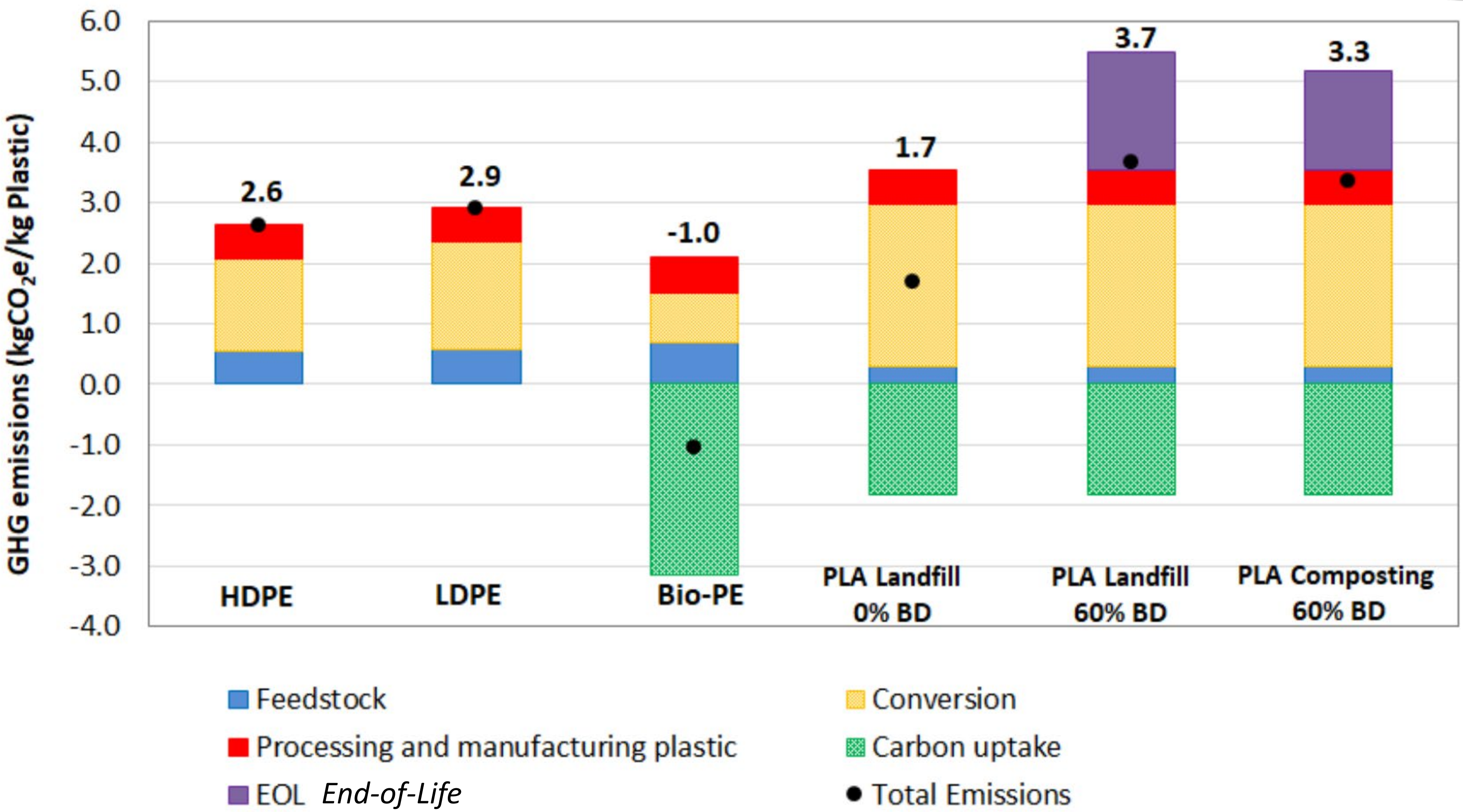
LLDPE

Life Cycle Assessment
PLA vs HDPE vs bioHDPE



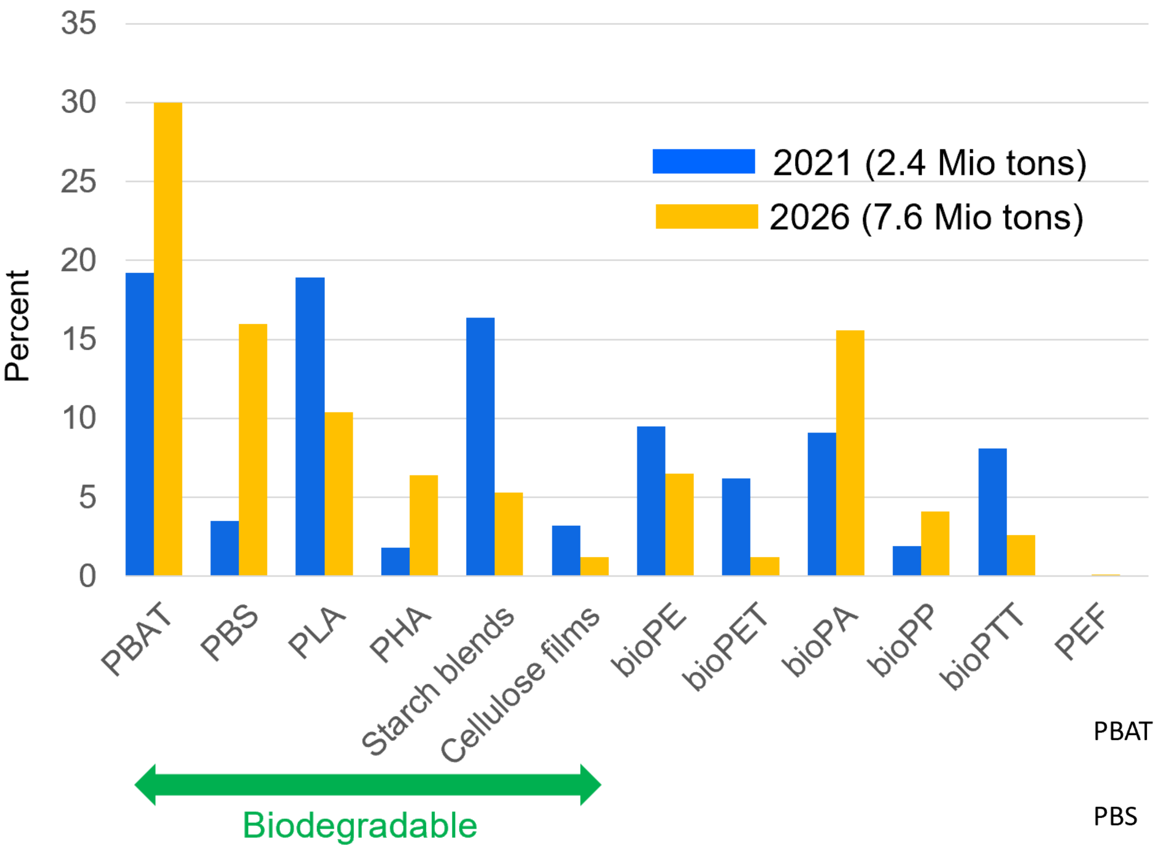
P. T. Benavides, U. Lee, O. Zare-Mehrjerdi, *Journal of Cleaner Production* 2020, *277*, 124010. Life Cycle Greenhouse Gas Emissions and Energy Use of Polylactic Acid, BioDerived Polyethylene, and Fossil-Derived Polyethylene

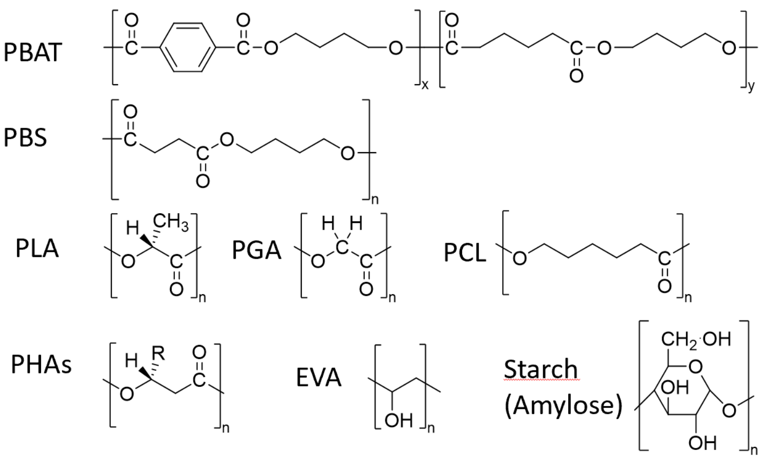
Life Cycle Assessment
PLA vs HDPE vs bioHDPE



P. T. Benavides, U. Lee, O. Zare-Mehrjerdi, *Journal of Cleaner Production* 2020, *277*, 124010. Life Cycle Greenhouse Gas Emissions and Energy Use of Polylactic Acid, BioDerived Polyethylene, and Fossil-Derived Polyethylene

Biodegradable and non-biodegradable bio-based plastics





C. Schirmeister, R. Mülhaupt,
Macromol Rapid Commun 2022

Biodegradation is not the holy grail !

PLA Biodegradation by composting at 60 °C, but no degradation in cold sea water

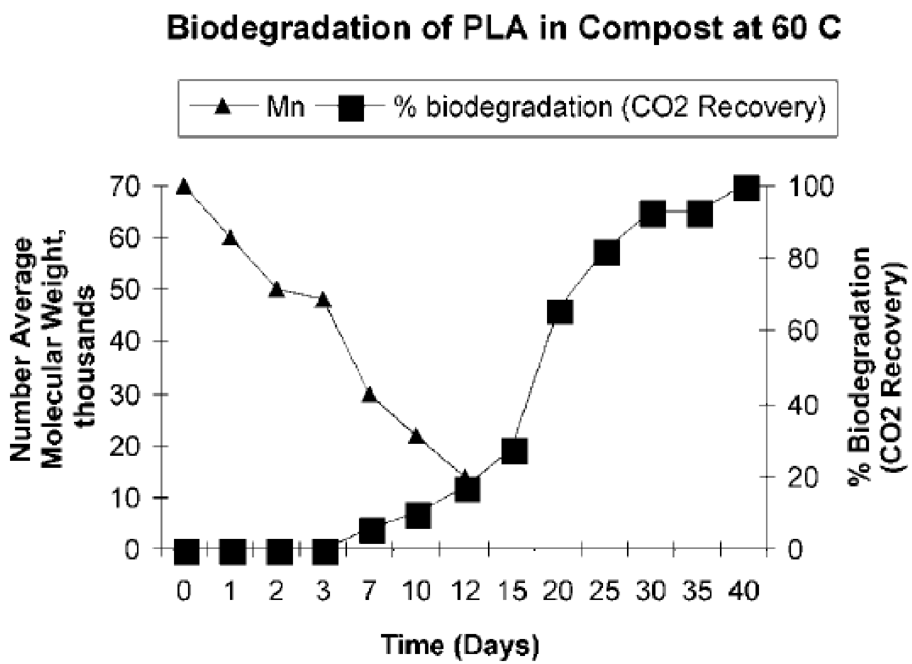
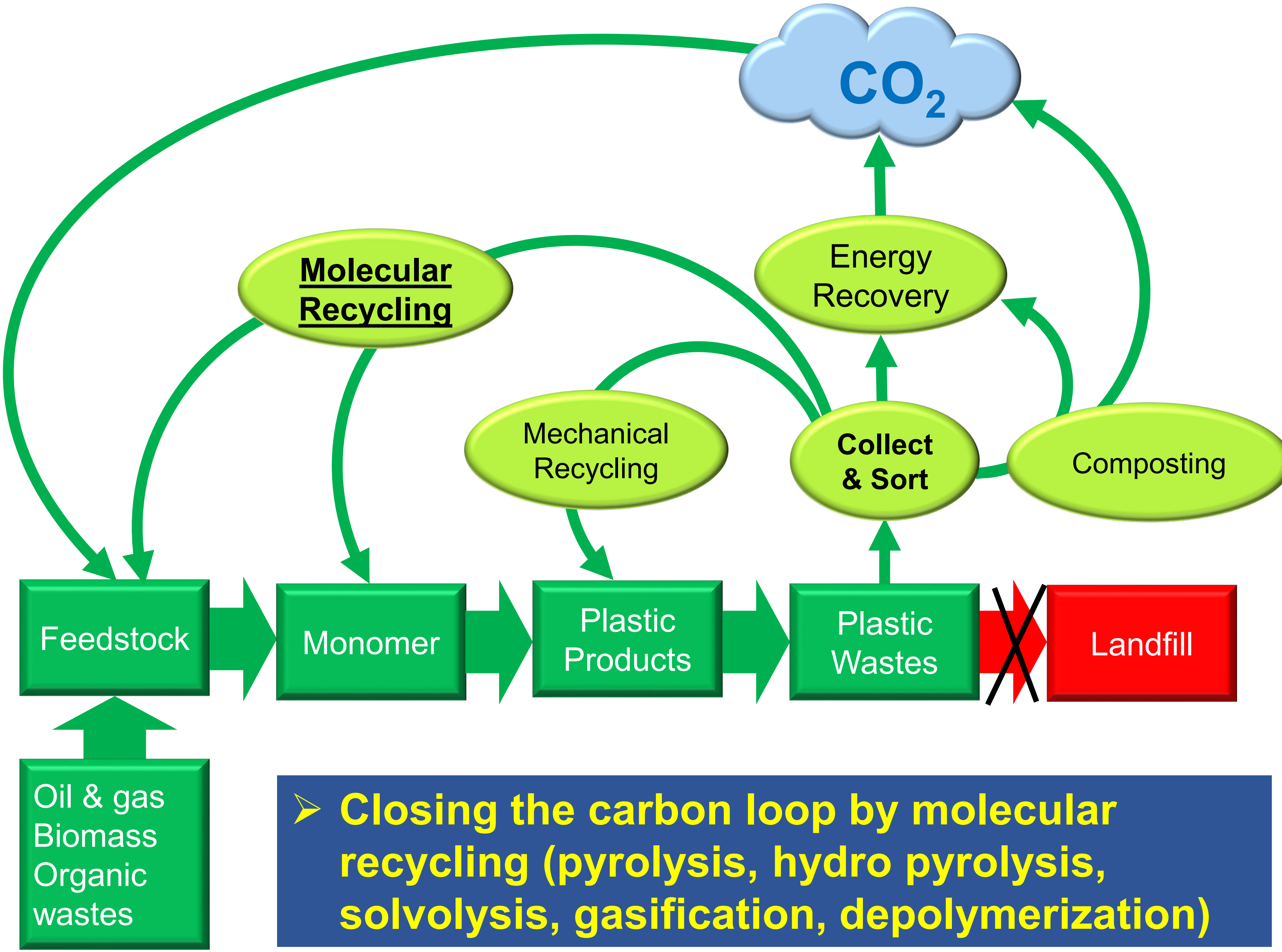


Fig. 6. Degradation of PLA at 60 °C.

R.E, Drumright, P.R. Gruber, D.E. Henton,
Adv. Mater. 2000, 12, 1841-1846, Poly Lacticacid Technology
G.-X. Wang, D. Huang, J-H. Ji, C. Völker, F.R. Wurm, Adv. Sci. 2021, *8*, 200112
Seawater-Degradable Polymers – Fighting the Marine Plastic Pollution

Biodegradation is not the solution of the global plastics littering problem

- Biodegradation is climate dependent
- No/low degradation in water
- Bioerosion = fine particles = hazardous micro plastics!
- Breeding ground for spores,…
- Throwaway of biopolymers is counterproductive regarding recycling


CO2
Molecular Recycling
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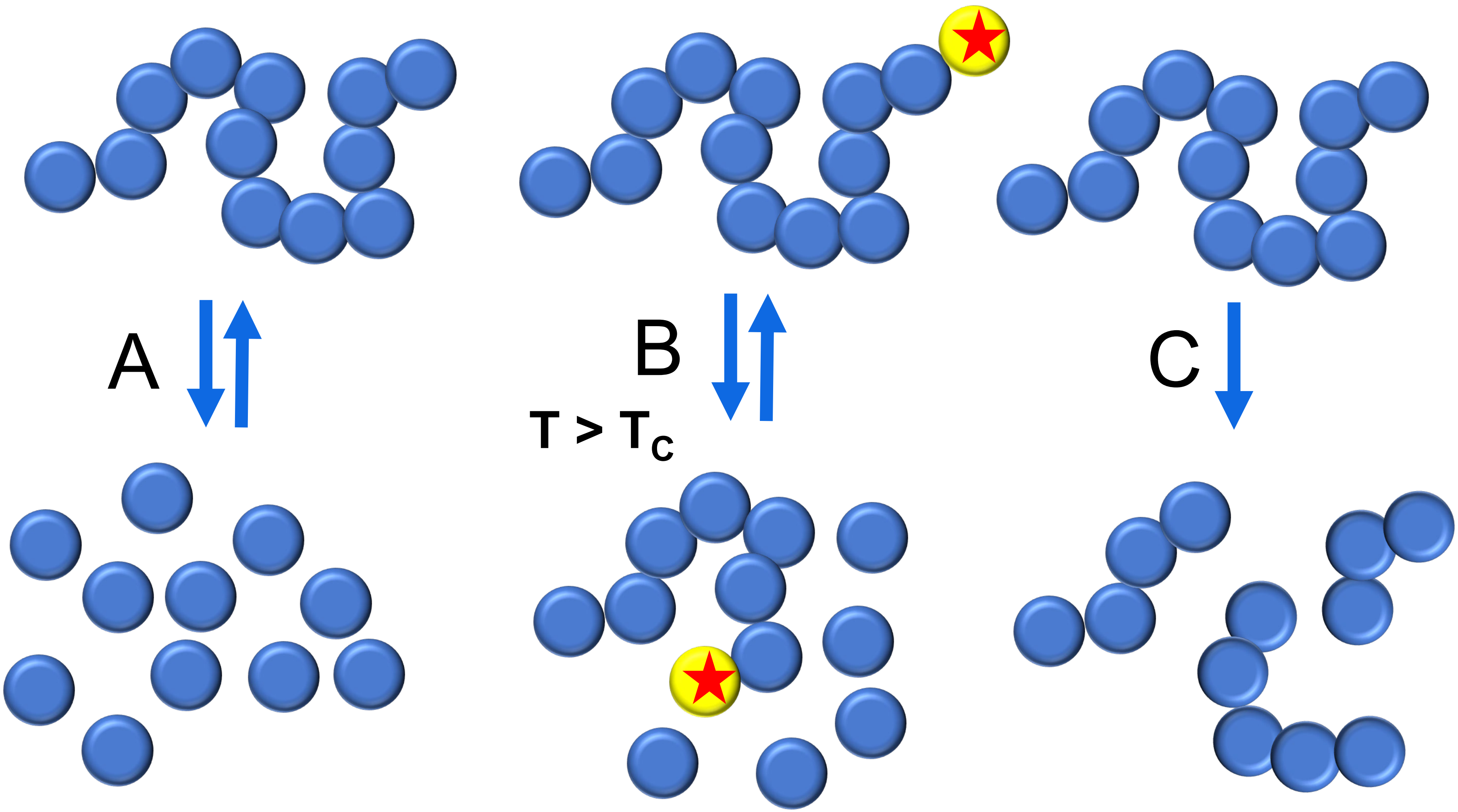
wastes
Closing the carbon loop by molecular recycling (pyrolysis, hydro pyrolysis, solvolysis, gasification, depolymerization)

Depolymerization and Fragmentation (Thermolysis, Glycolysis, Hydrolysis,…)



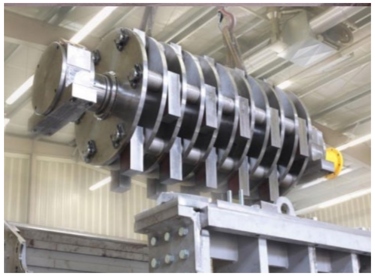
Molecular Recycling and Feedstock Recovery: Pyrolysis and Hyropyrolysis

Table 1. Recovery of oil and gas by non-catalytic polymer thermolysis.

Polymer	Temperature [°C]	Gas [wt%]	Oil [wt%]	Residue [wt%]	Others [wt%]
Polyethylene	760	55.8	42.4	1.8 C	—
Polypropylene	740	49.6	48.8	1.6 C	—
Polystyrene	580	9.9	24.6	0.6	64.9 styrene
Polyester	768	50.8	40.0	7.1	2.1 H_2O
ABS	740	6.9	90.8	1.1	1.2 HCN
Polycarbonate	710	26.5	46.4	24.6	2.5 H_2O
Polymethylmethacrylate	450	1.25	1.4	0.15	97.2 MMA
Polyvinylchloride	740	6.8	28.1	8.8	56.3 HCl
Phenol/Formaldehyde	780	14.4	28.1	49.5	8.0 H_2O
SBR	740	25.1	31.9	42.8	0.2 H_2S
Lignin	500	3.4	29.9	49.3	17.4 H_2O
Cellulose (from bark)	700	47.1	23.0	18.6 C	11.3 H_2O

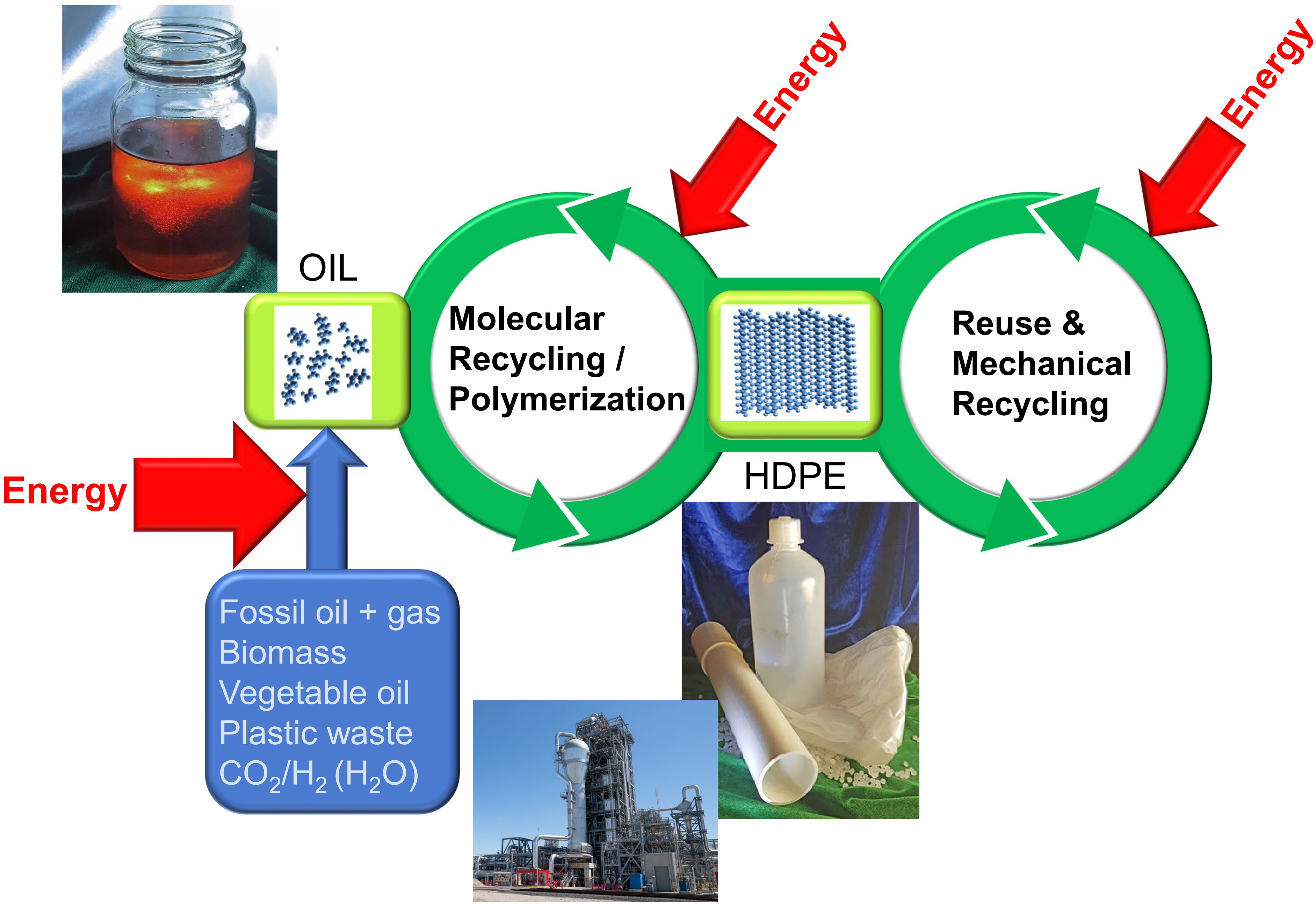
Data from W. Kaminsky, University of Hamburg *Recycling von Kunststoffen* (Eds: W. Kaminsky, H. Sinn in G. Menges, W. Michaeli, M. Bittner by (W. Kaminsky, H. Sinn in G. Menges, W. Michaeli, M. Bittner, Eds.), Carl Hanser Publishers, Munich **1992**, p. 248; ABS, poly(acrylonitrile-co-styrene-co-butadiene); MMA, methyl methacrylate monomer; SBR, poly(styrene-co-butadiene) rubber.

Catalytic degradation < 400 °C
e.g. ChemCycling™ (BASF)



e.g. Recenso / Carboliq
Catalytic tribochemical conversion (CTC)
https://www.pu-bw.de/wp-content/uploads/2017/05/open-house-PU_TP-Mesatex_26-04-2017.pdf

Shell IH² Technology
Hydropyrolysis
Turning forestry & agricultural residues, aquatic plants & (ligno) cellulosic fractions of municipal waste into fuels

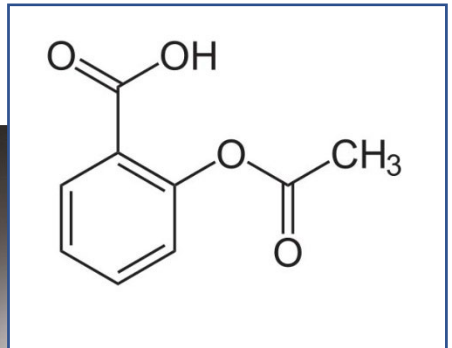


OIL
Energy
Energy
Energy
Molecular
Recycling /
Polymerization
Reuse &
Mechanical
Recycling
HDPE
Fossil oil + gas
Biomass
Vegetable oil
Plastic waste
CO_2/H_2 (H_2O)

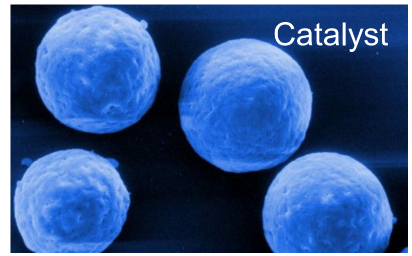
What do Aspirin and Polyethylene have in common ?

Both molecules were discovered in 1898!

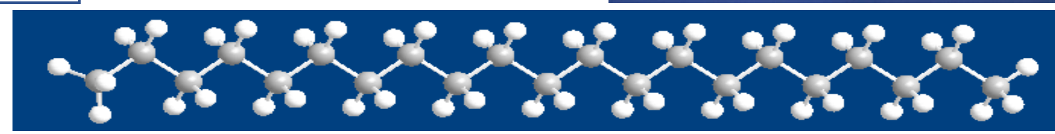
Aspirin™



Since 1898 the same product, same process, same company



Polyethylene



On-going polyolefin innovations:

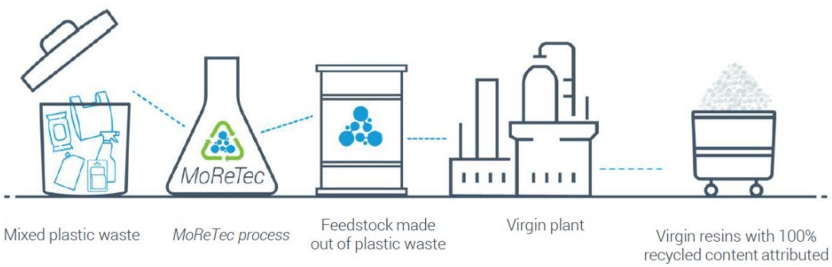
1934 ICI High Pressure LDPE (200°C/2000 bar)
1953 Ziegler- and Phillips Low Pressure-PE by catalysis (80°C/10 bar)
1970 High mileage supported catalysts, no by-products, gas phase polymerization
1980 Single-site catalysts
1990 Reactor granule technology
2000 Bio-based PE and PP
2020 Polyolefins from renewable carbon

Circulen^{TM} from LyondellBasell

https://www.lyondellbasell.com/circulen/

circulen recover by lyondellbasell

Polymers made from plastic wastes through a mechanical recycling process



circulen revive by lyondellbasell

Polymers made by converting plastic waste into feedstock to produce new polymers using a molecular recycling process

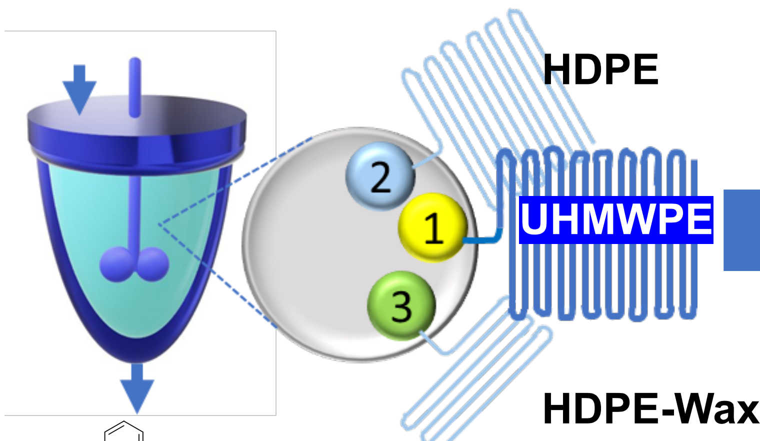
MoReTec Pilot Plant in Ferrara

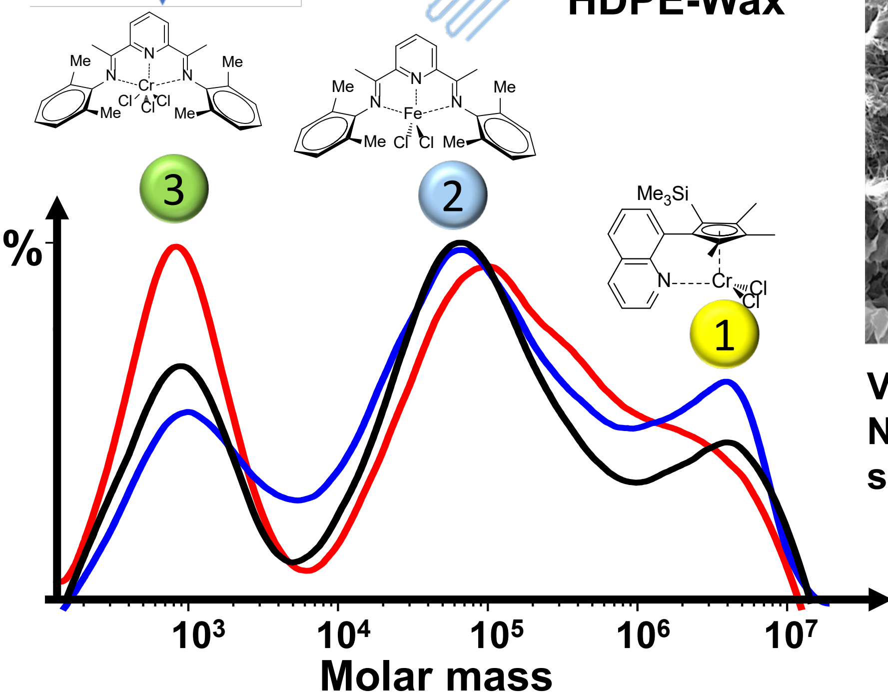
lyondellbasell

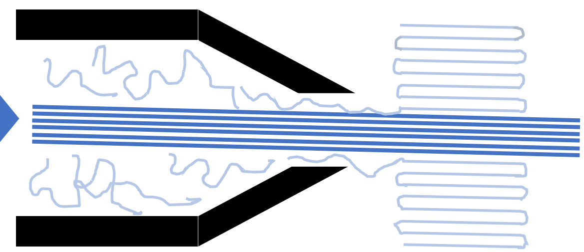
circulen renew by lyondellbasell

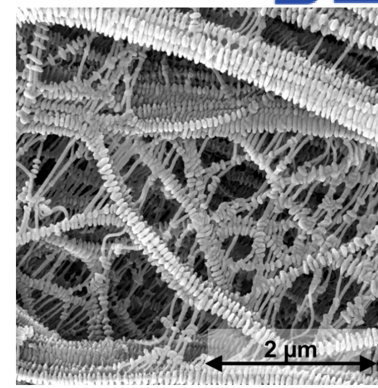
Polymers made from renewable feedstocks such as used cooking oil

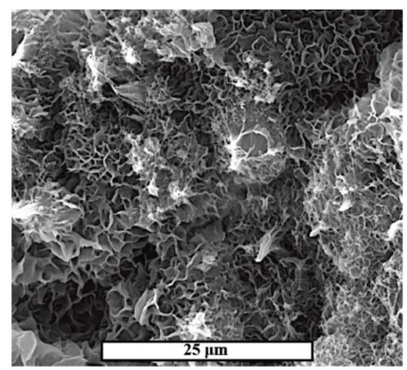
1D/2D Nanostructure formation via catalytic olefin polymerization



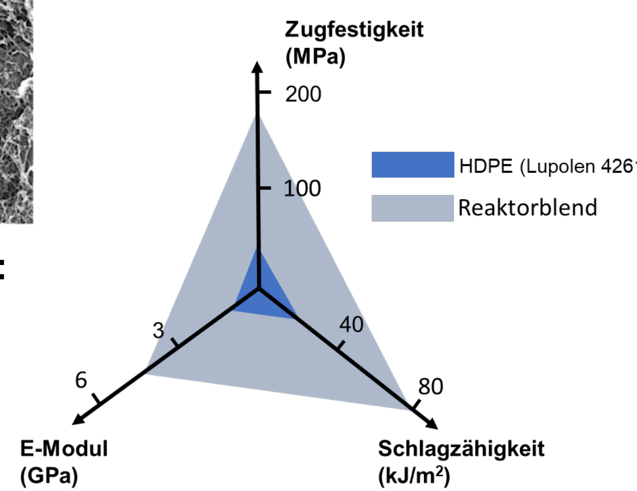






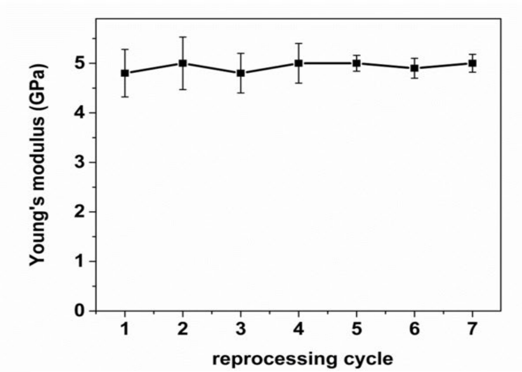


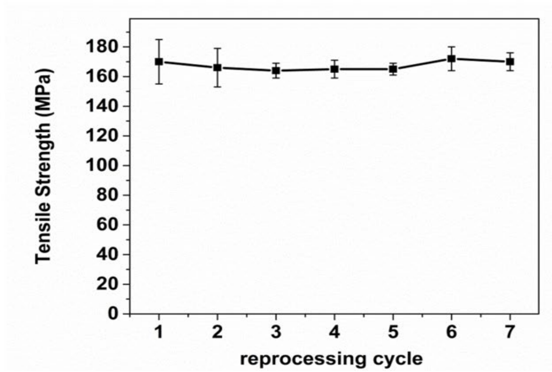
Virgin reactor blend: Nanophase separated UHMWPE

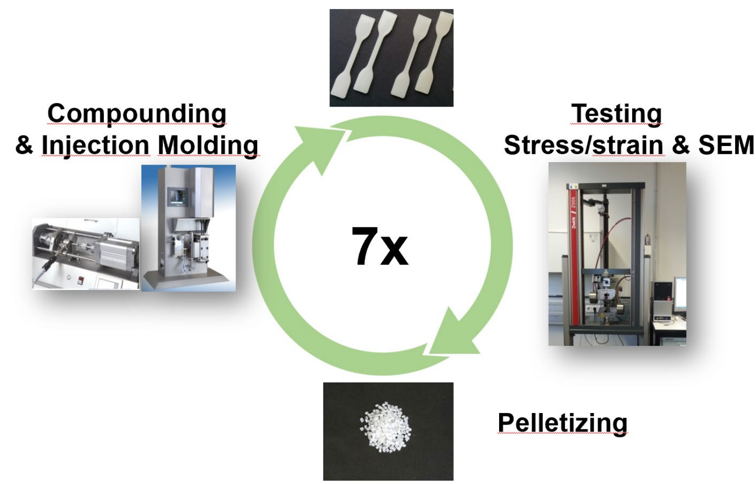


All-PE composites recycled by remolding

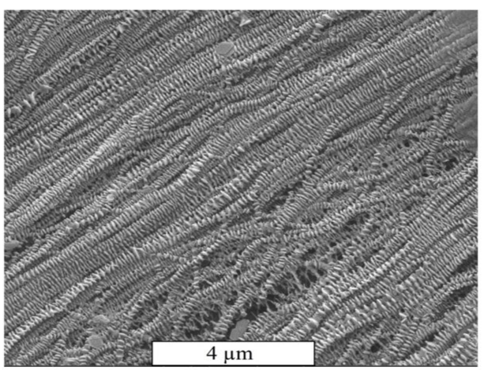
The same nanostructures & properties after 7 times recycling by re-molding



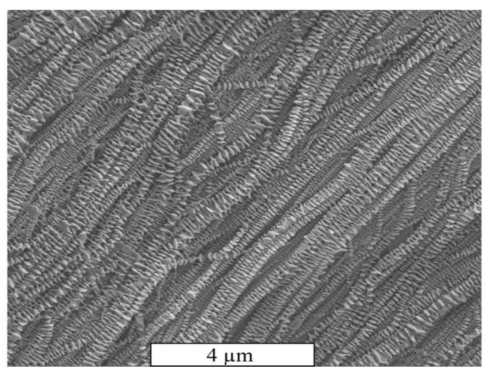




After first molding

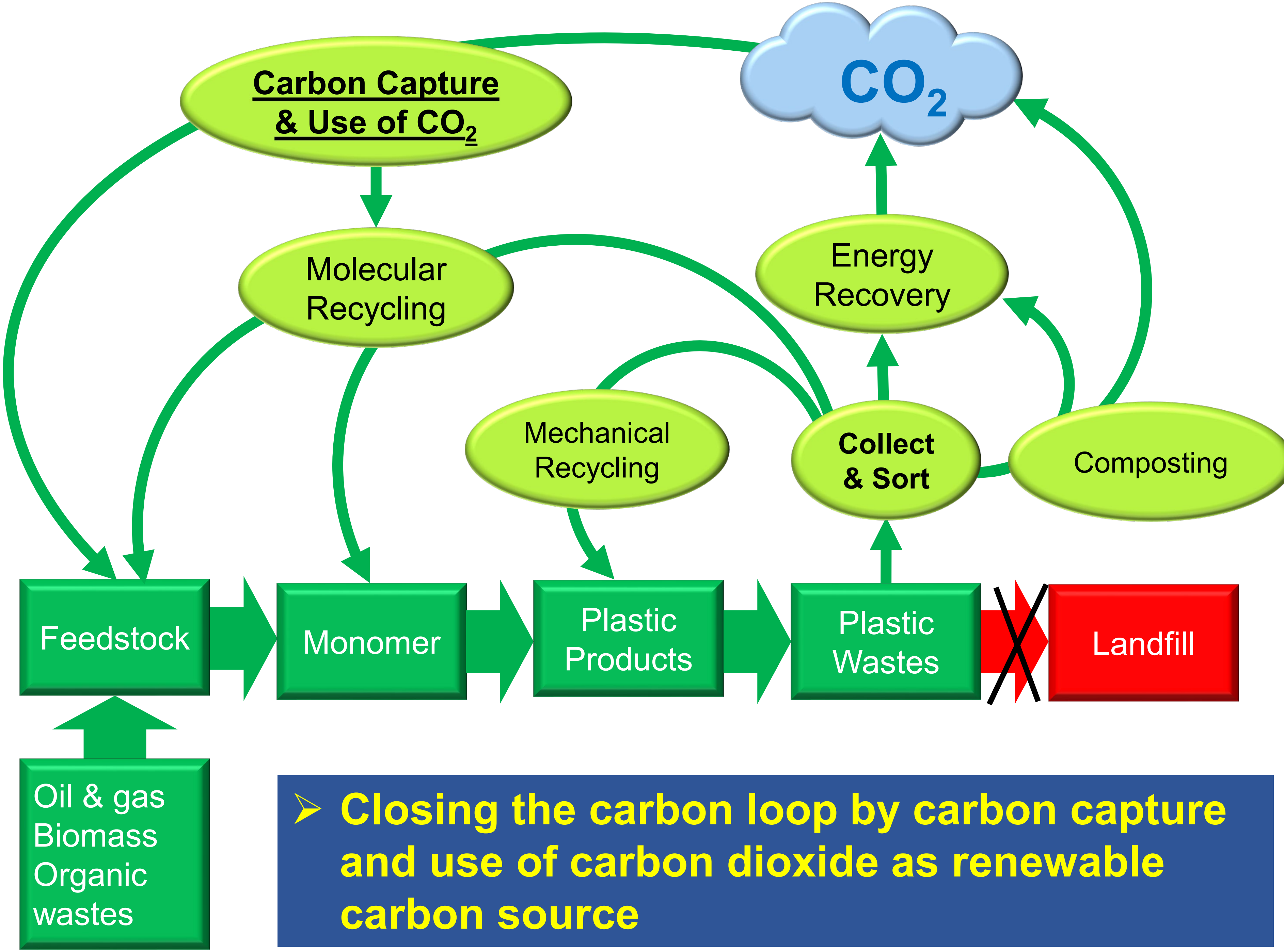


After 7 times re-molding



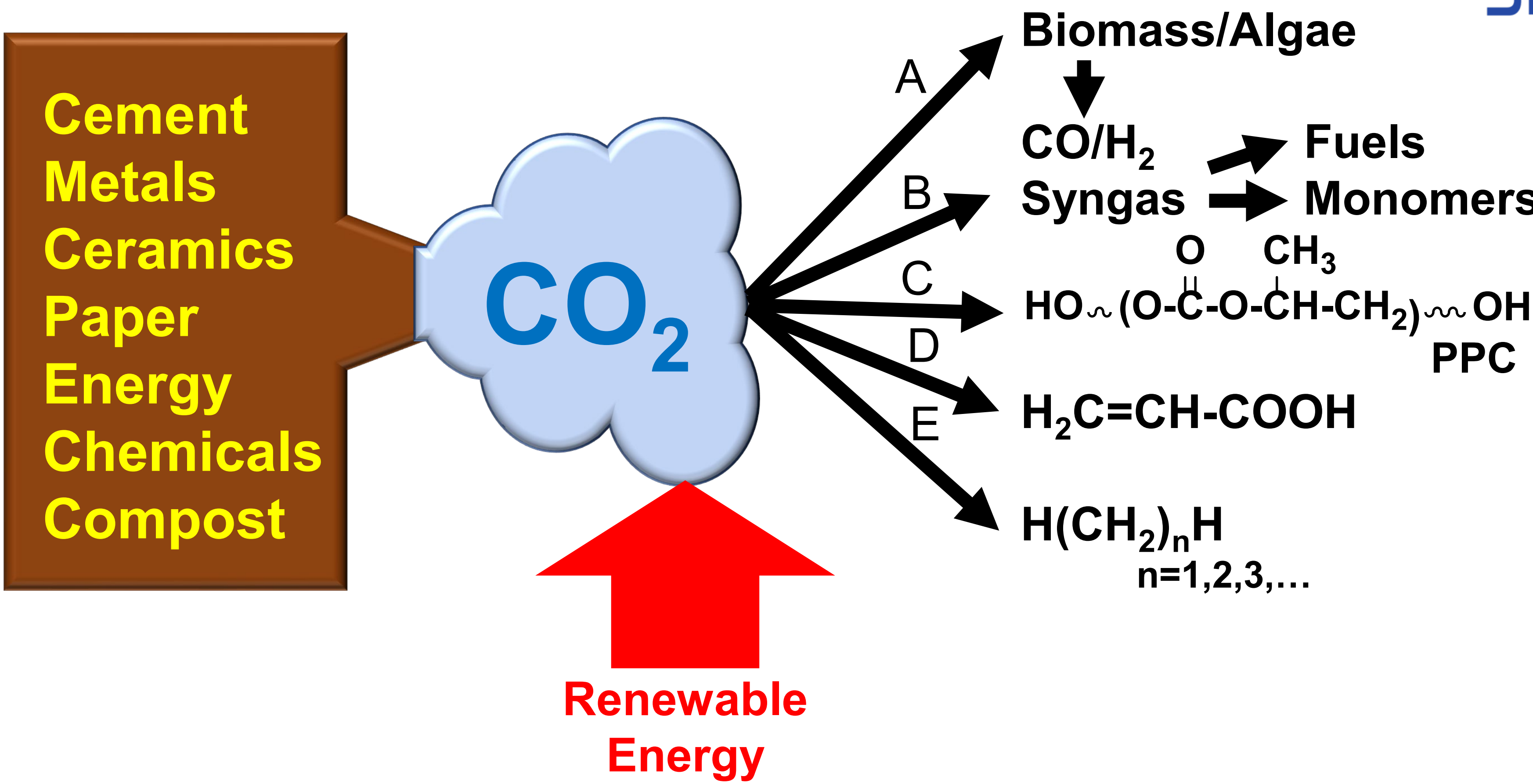
T. Hees, F. Zhong, M. Stürzel, R. Mülhaupt, Macromol. Rapid Commun. 2019, 40, 1800608, Tailoring Hydrocarbon Polymers and All-Hydrocarbon Composites for Circular Economy

F. Zhong, R. Thomann, R. Mülhaupt, *Macromolecular Materials and Engineering.* **2018**, *303*, 1800022 Processing-Nanostructure-Property Relationships of All-Polyethylene Composites Reinforced by Flow-Induced Oriented Crystallization of UHMWPE



Carbon Capture & Use of CO_2
CO_2
Molecular Recycling
Energy Recovery
Mechanical Recycling
Collect & Sort
Composting
Feedstock
Monomer
Plastic Products
Plastic Wastes
Landfill
Oil & gas
Biomass
Organic wastes
➢ Closing the carbon loop by carbon capture and use of carbon dioxide as renewable carbon source

Feedstocks and polymers from CO_2 and H_2O via CO_2 fixation



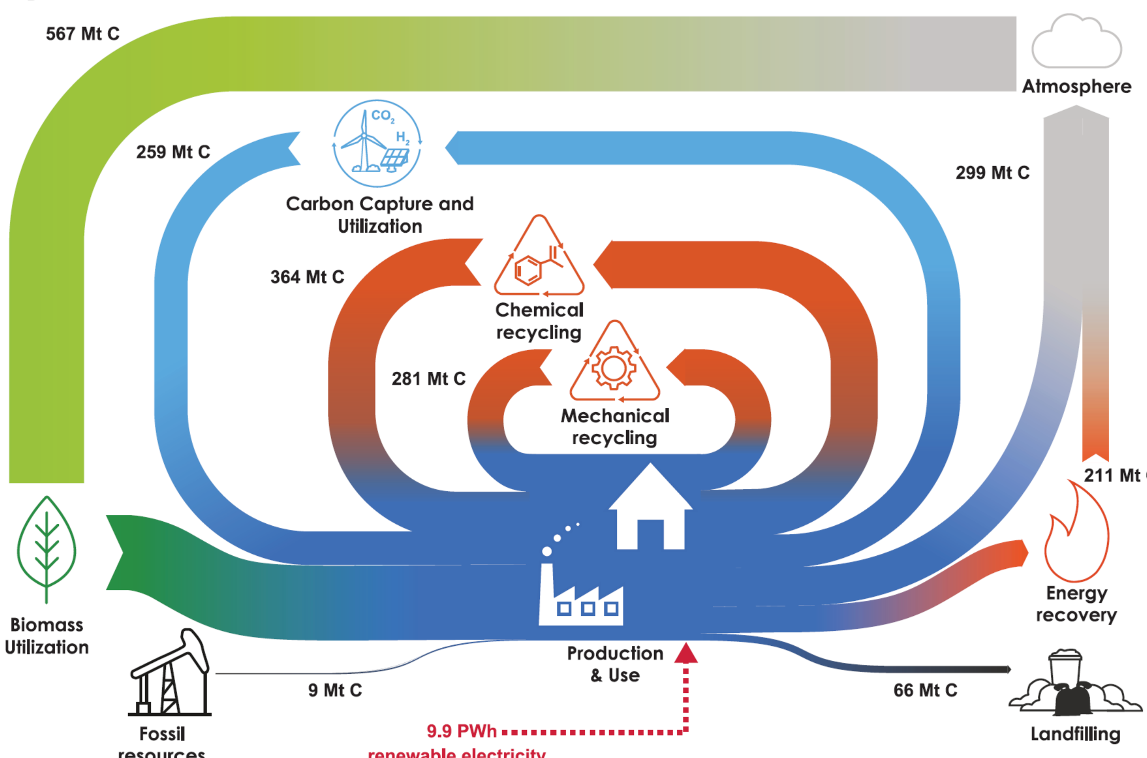
Renewable carbon for circular economy and net-zero greenhouse gas emission

Achieving net-zero greenhouse gas emission plastics by a circular carbon economy

Raoul Meys*, Arne Kätelhön, Marvin Bachmann, Benedikt Winter, Christian Zibunas, Sangwon Suh, André Bardow*, Science 2021, 374, 71–76

A net-zero emission plastics can be achieved by combining biomass and carbon dioxide (CO_2) utilization with an effective recycling rate of 70% while saving 34 to 53% of energy.

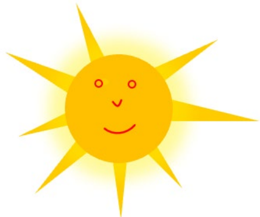
D



The future solar refinery: Hydrocarbons from carbon dioxide

$CO_2/H_2O \xrightarrow{\text{1 Year}} \text{Biomass} \xrightarrow{\text{300,000,000 Years}} \text{Oil/Gas} \xrightarrow{\text{Days}} \text{Hydrocarbon}$

? $CO_2/H_2O \xrightarrow{\text{< 1 h !!!}} \text{Hydrocarbon}$



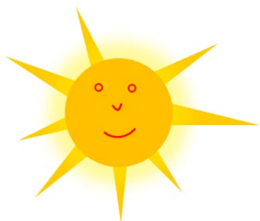
The solar refinery: Sustainable hydrocarbons from CO_2

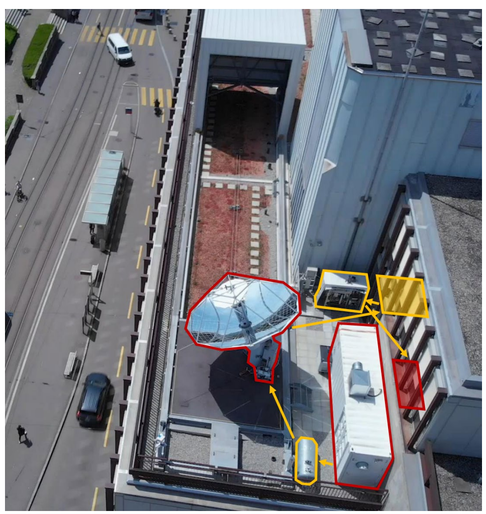
1 Year — *300,000,000 Years* — *Days*

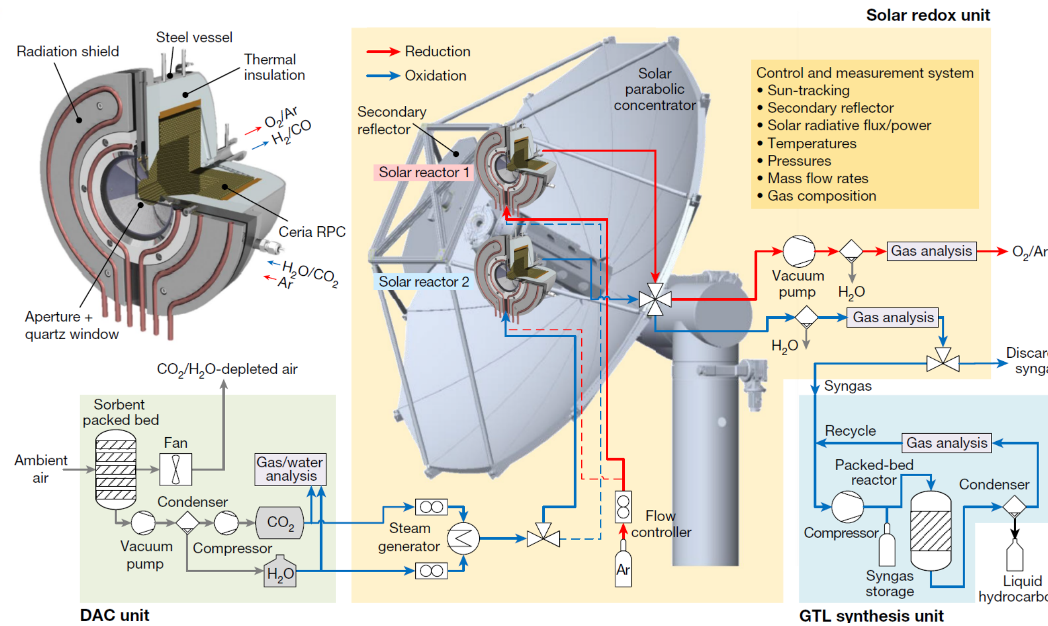
CO_2/H_2O → Biomass → Oil/Gas → Hydrocarbon

CO_2/H_2O ↓ Hydrocarbon

< 1 h !!!







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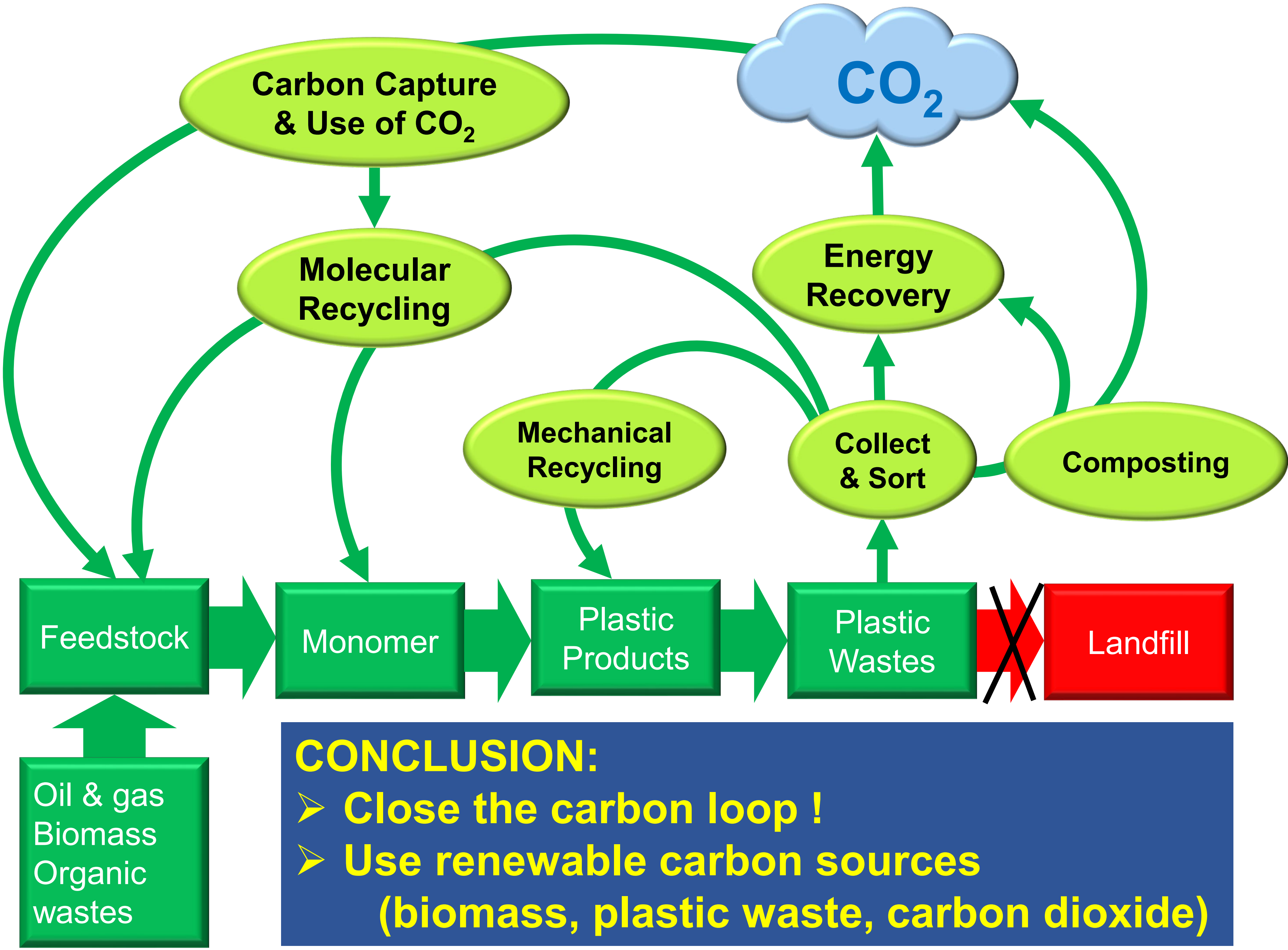
https://www.ises.org/sites/default/files/webinars/Presentation%20Remo%20Sch%C3%A4ppi_Solar%20Fuel%20Production%20from%20Ambient%20Air%20in%20a%20Modular%20Solar%20Concentrator-Reactor%20System.pdf



Carbon Capture & Use of CO_2
CO_2
Molecular Recycling
Energy Recovery
Mechanical Recycling
Collect & Sort
Composting
Feedstock
Monomer
Plastic Products
Plastic Wastes
Landfill
Oil & gas
Biomass
Organic wastes
CONCLUSION:
➢ Close the carbon loop !
➢ Use renewable carbon sources
(biomass, plastic waste, carbon dioxide)

Conclusion

- Move away from linear economy and fossil resources to circular economy and renewable carbon (plastic waste, cabon dioxide and biomass).
- Plastics do not need to be be reinvented, but their full potential must be further exploited!
- Bio degradation is not the holy grail and greenwashing is not a solution!
- Carbon loops are not 100% closed and are no *Perpetuum Mobile* – renewable energy required!
- Polyolefins for sustainability and better life !

C. Schirmeister. R. Mülhaupt. Macromol. Rapid Com 2022