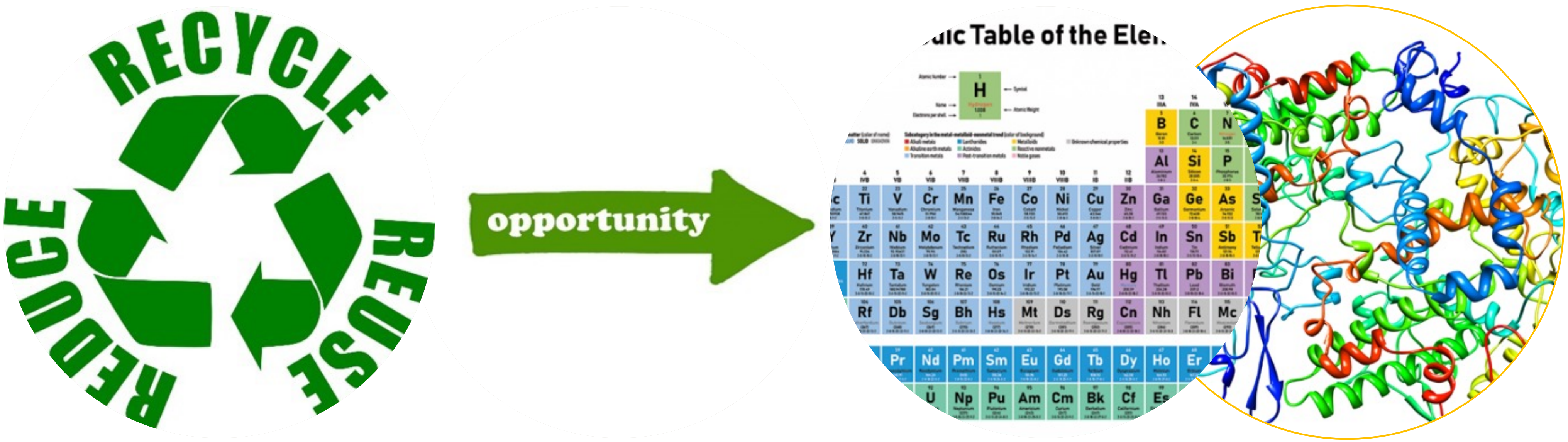
(Bio)Chemical Recycling of Polycondensation Polymers

Depolymerization of polymer back to monomers: opportunities for chemicals & enzymes

Dr. Shanmugam Thiyagarajan, 14th October 2021
Wageningen Food & Biobased Research, The Netherlands



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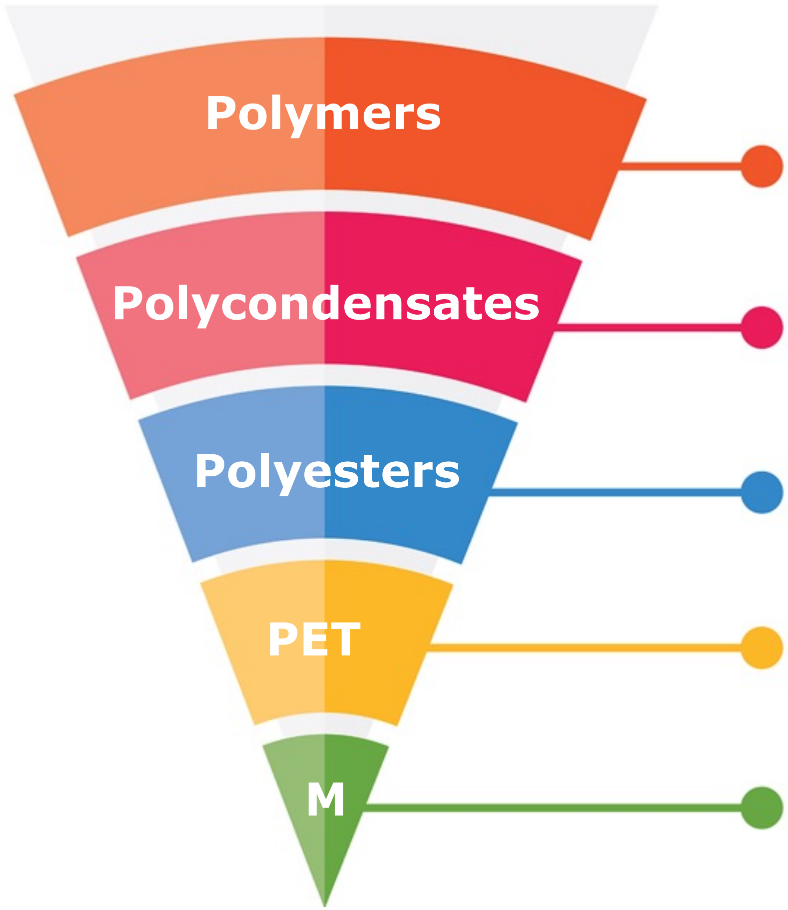
WU: 12,973 BSc/MSc-students; 2,196 PhD; 3,544 faculty and staff

WR: 3,316 staff; Revenue in 2020: € 355 million

Depolymerization potential of polymers

- Polyolefins
  - Polyethylene (PE), Polypropylene (PP)...
    - carbon-carbon (-C-C-) bonds are strong, harsh condition required to breakdown these polymers
    - monomer recovery: difficult, often in lower percentages
- Polycondensates
  - Polyesters, Polyamides...
    - ester (-COO-)/amide (-CONH-) bonds are labile, can breakdown at moderate conditions (comparatively)
    - monomer recovery >90%, relatively in high selectivity

Choice of polycondensation polymers



Production volume will continue to raise (in demand) because of expanding property and application range

Polycondensation polymers can more effectively depolymerized/recycled than other polymers

Renewable polyesters can be produced more efficiently from biomass (or CO_2)

Potential to replace other functional polymers (properties and performance yet to be tuned)

p-Terephthalic acid (p-TA) & ethylene glycol (EG)

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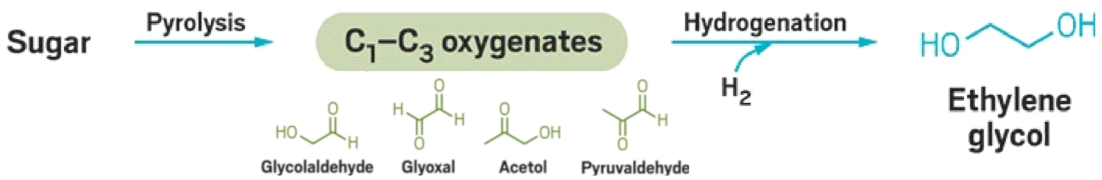
EG (MEG) from biomass

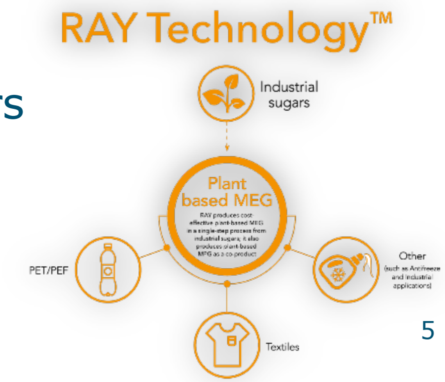
Haldor Topsoe process (and Braskem)



Conventional sugar-to-ethylene glycol approach

Avantium Ray Technology

One-step hydrogenolysis process to produce MEG from plant-based sugars (maximum theoretical yield 100% and practical yield >70%)



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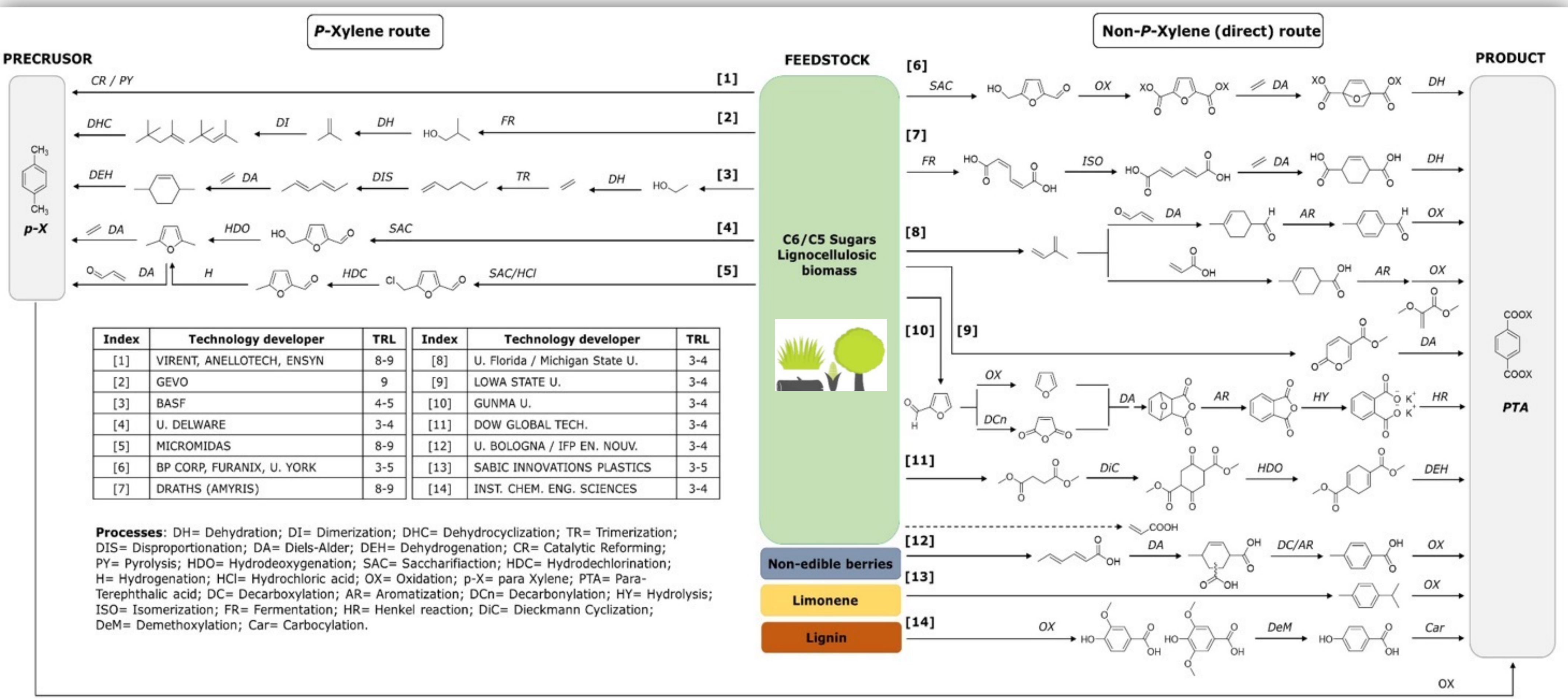
www.avantium.com; www.braskem.com.br

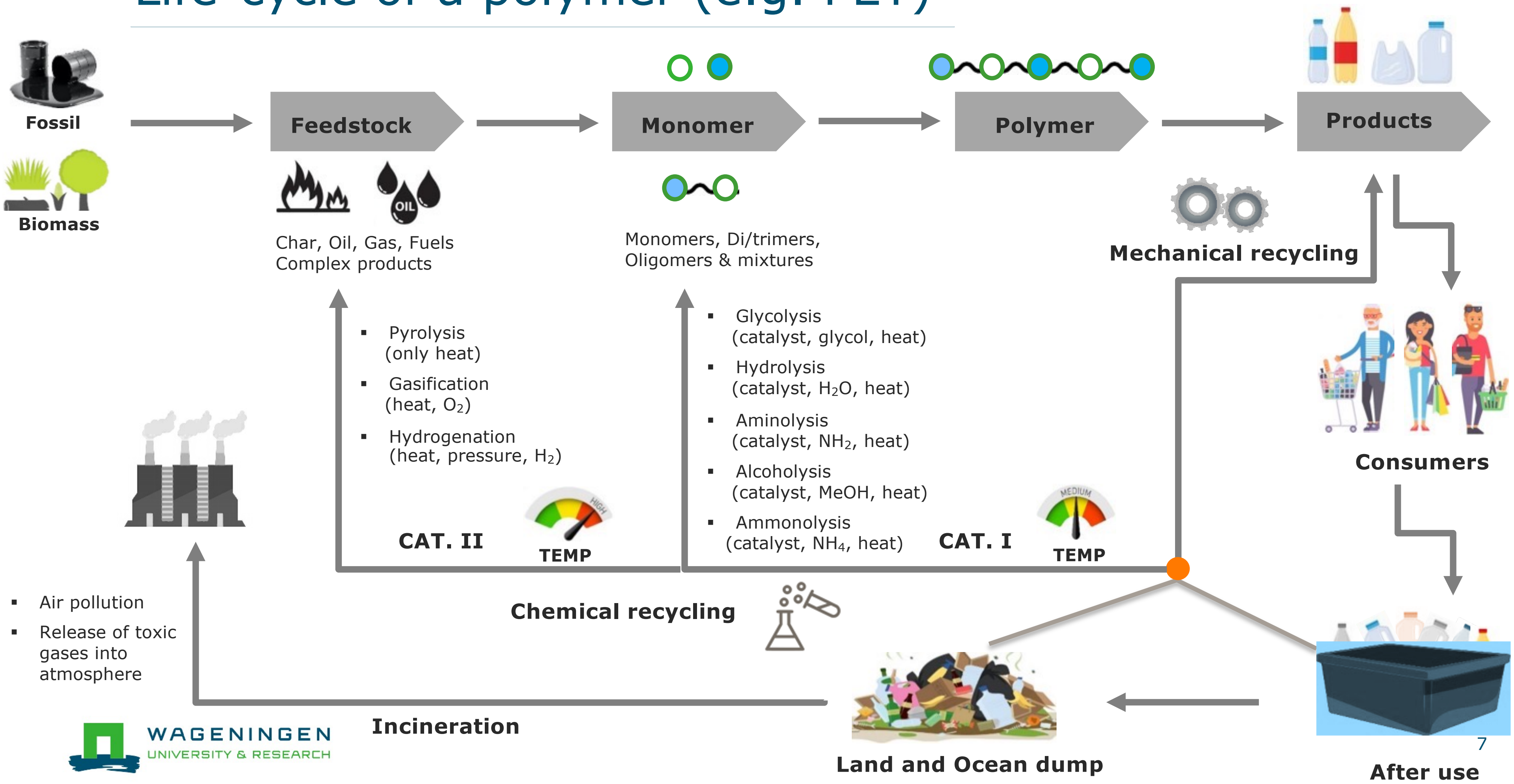
PTA from biomass



Index	Technology developer	TRL	Index	Technology developer	TRL
[1]	VIRENT, ANELLOTECH, ENSYN	8-9	[8]	U. Florida / Michigan State U.	3-4
[2]	GEVO	9	[9]	LOWA STATE U.	3-4
[3]	BASF	4-5	[10]	GUNMA U.	3-4
[4]	U. DELWARE	3-4	[11]	DOW GLOBAL TECH.	3-4
[5]	MICROMIDAS	8-9	[12]	U. BOLOGNA / IFP EN. NOUV.	3-4
[6]	BP CORP, FURANIX, U. YORK	3-5	[13]	SABIC INNOVATIONS PLASTICS	3-5
[7]	DRATHS (AMYRIS)	8-9	[14]	INST. CHEM. ENG. SCIENCES	3-4

Processes: DH= Dehydration; DI= Dimerization; DHC= Dehydrocyclization; TR= Trimerization; DIS= Disproportionation; DA= Diels-Alder; DEH= Dehydrogenation; CR= Catalytic Reforming; PY= Pyrolysis; HDO= Hydrodeoxygenation; SAC= Saccharifiaction; HDC= Hydrodechlorination; H= Hydrogenation; HCl= Hydrochloric acid; OX= Oxidation; p-X= para Xylene; PTA= Para-Terephthalic acid; DC= Decarboxylation; AR= Aromatization; DCn= Decarbonylation; HY= Hydrolysis; ISO= Isomerization; FR= Fermentation; HR= Henkel reaction; DiC= Dieckmann Cyclization; DeM= Demethoxylation; Car= Carbocylation.

Life-cycle of a polymer (e.g. PET)



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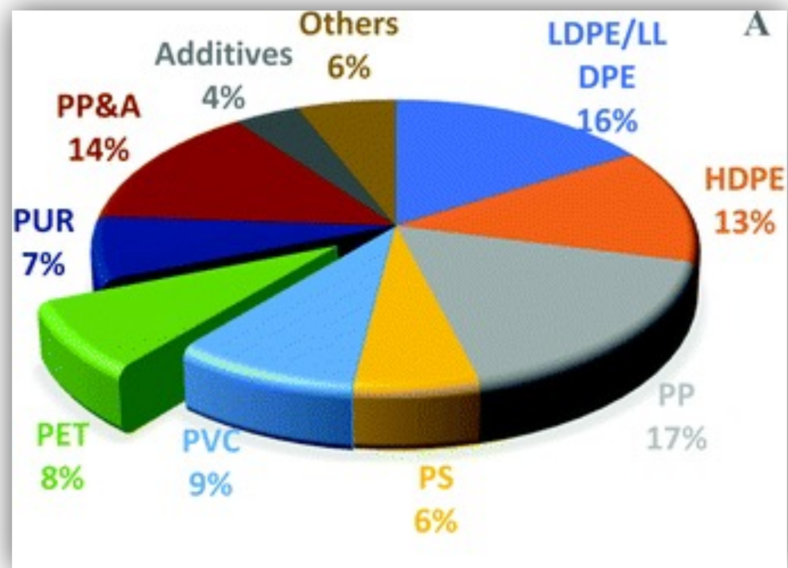
Contents

- (Bio)-Chemical recycling of:
    - Polyesters >>> PET
- Processes includes:
    - Hydrolysis
    - Alcoholysis
    - Glycolysis
    - Aminolysis and Ammonolysis
    - Enzymatic hydrolysis
- Commercial status of chemical and enzymatic recycling technology

Polyethylene terephthalate (PET)

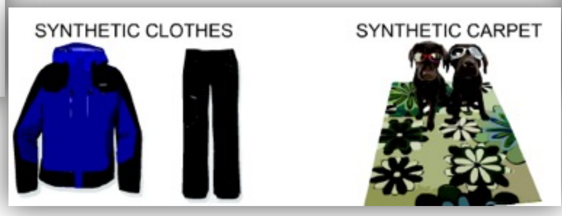
- Global polymeric material production was 388 MTon in 2019
- Polyethylene terephthalate (PET) produced via polycondensation reaction
    - PET production volumes accounted for 8% (32 Mtons)



plasticsinsight.com.

Polyethylene terephthalate (PET)

- Polyethylene terephthalate (PET) received significant attention among various commercially available polyesters
  - Production: raw material available in larger volumes and inexpensive
  - Properties: high strength to weight ratio, transparency, durable
  - End of life: Potential for recycling
- Application areas includes (but not limited to) bottle, (food) packaging, and fabrics etc...



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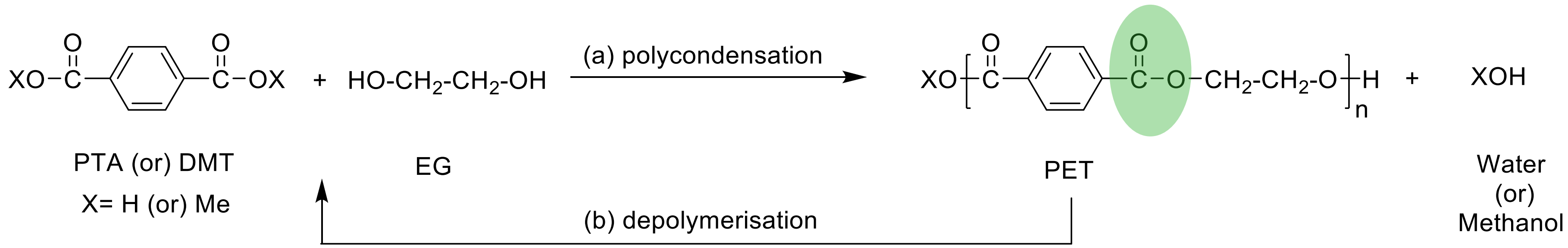
https://3devo.com

Synthesis of Polyethylene terephthalate (PET)

- Dimethyl terephthalate (DMT) (or) terephthalic acid (PTA) and ethylene glycol (EG) are the key monomers for PET production



- (a) Condensation reaction between monomers in the presence of transesterification catalyst yields polymer
- (b) Ester bond in polyester offers opportunity to breakdown (suitable condition) resulting in starting monomers (and/or oligomers)

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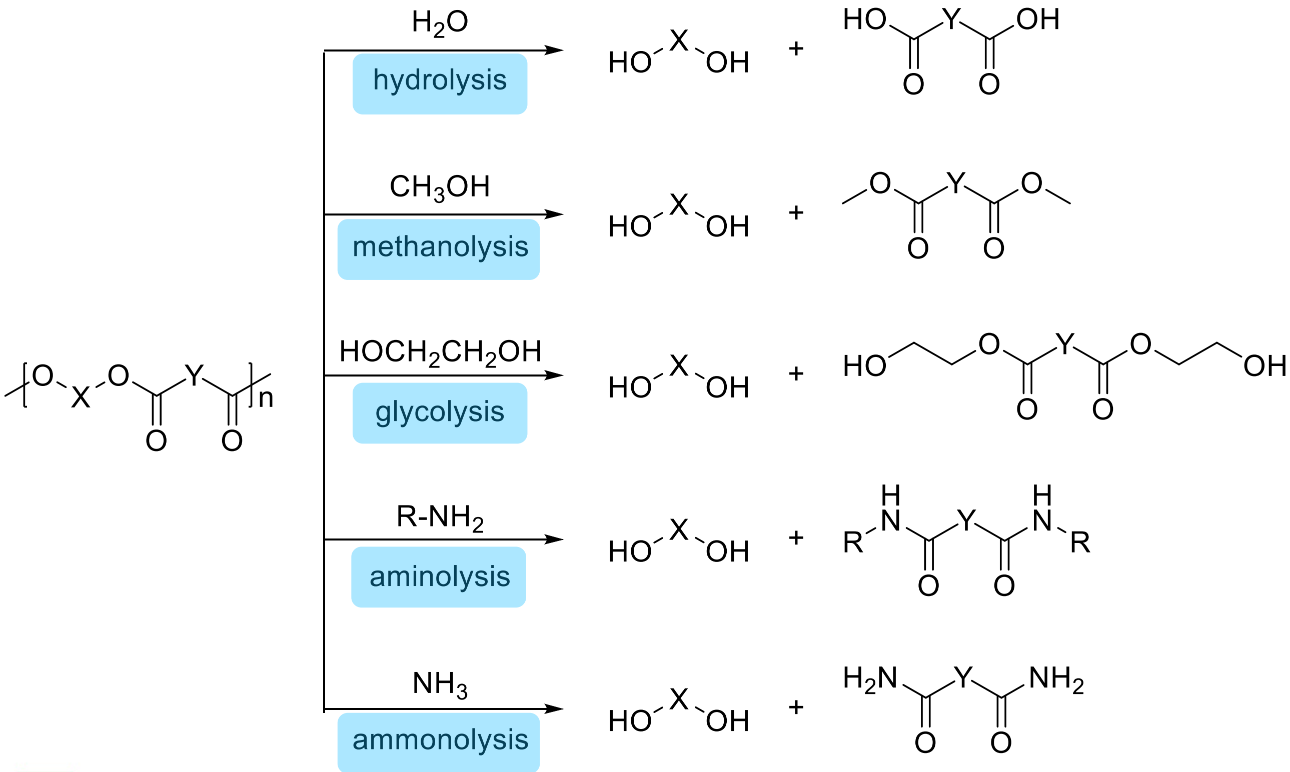
Depolymerisation using solvolysis processes

- Solvolysis of PET demonstrated successfully using different solvents either presence/absence of catalyst



Acidic (90 ºC), neutral (200-300 ºC), or alkaline (250 ºC), catalyst

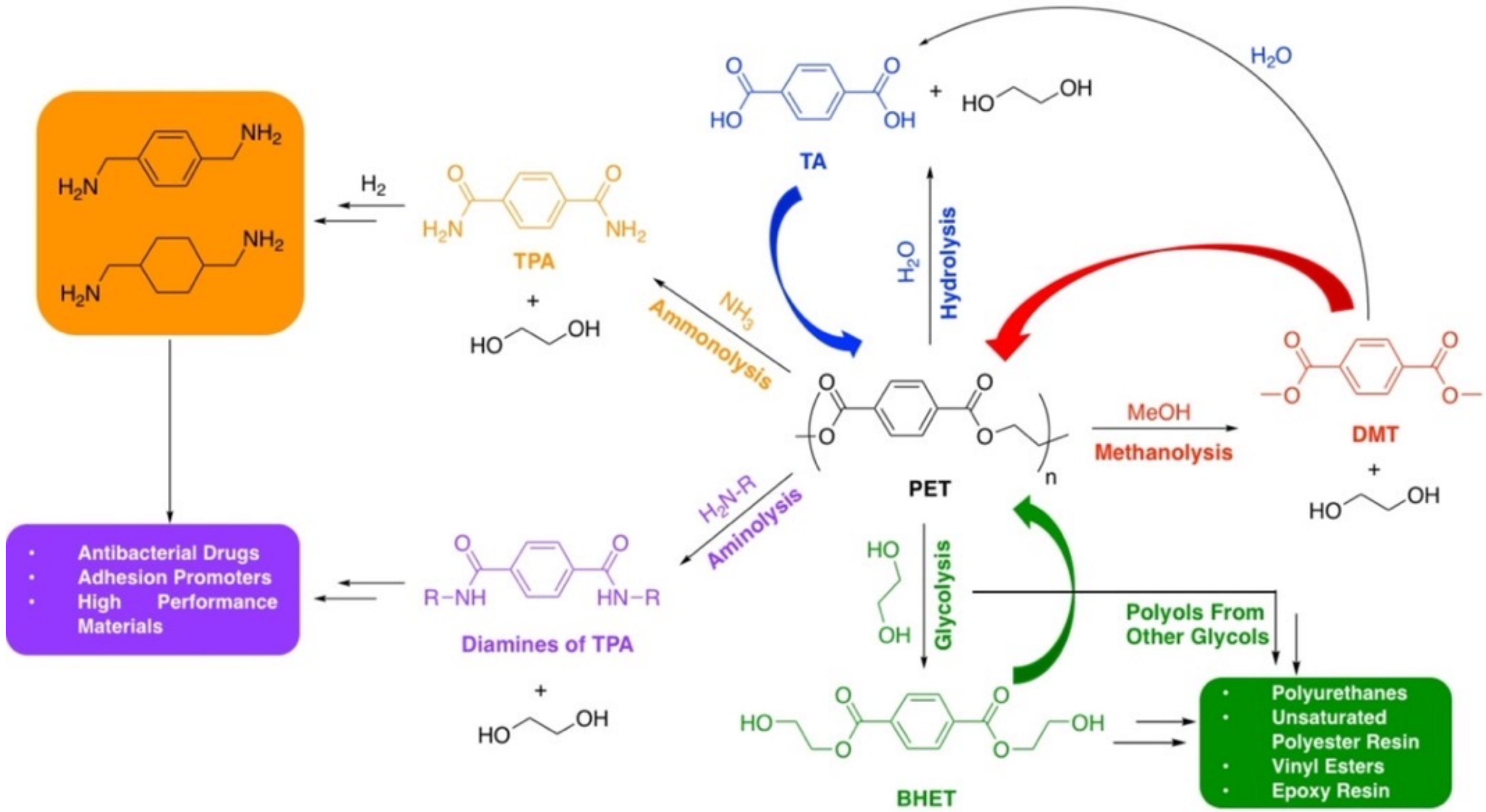
Simple alcohols (MeOH/EtOH), 180-280 ºC, catalyst

Glycol (ethylene, diethylene or triethylene), 180-240 ºC, catalyst

Amines (methyl, ethyl, propyl, butyl), 20-100 ºC, catalyst

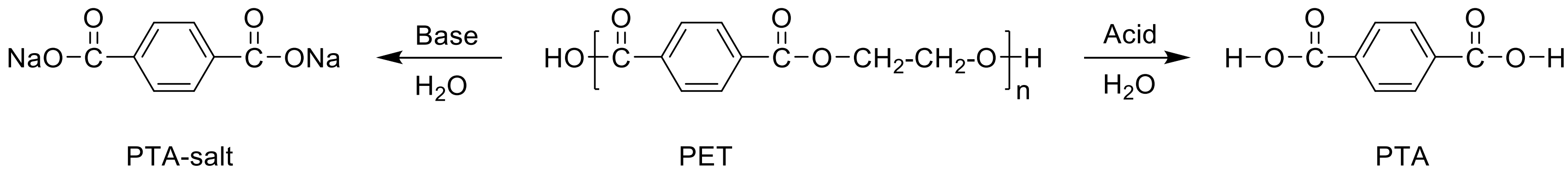
Ammonia, pressure, 120-180 ºC, catalyst

Applications of products recycled from PET



Jack Payne et al., ChemSusChem, 2021, doi.org/10.1002/cssc.202100400

Hydrolysis (Acid, Base & Neutral) of PET



Type	Reagents	Catalyst
Acid	Sulfuric acid, Nitric acid, Phosphoric acid	None
Base	Sodium hydroxide, Potassium hydroxide	Trioctyl methylammonium bromide, Tetrabutyl ammonium bromide, Tetrabutyl ammonium iodide
Neutral	Water	Zinc/Sodium acetate, Hydrotalcite, Potassium hydroxide, Organophosphotungstic catalyst, zeolites

- Each process have their own merits and demerits depending on the operating conditions

Hydrolysis (Acid, Base & Neutral) of PET

- Overview of selected conditions developed for efficient depolymerization of PET back to monomers

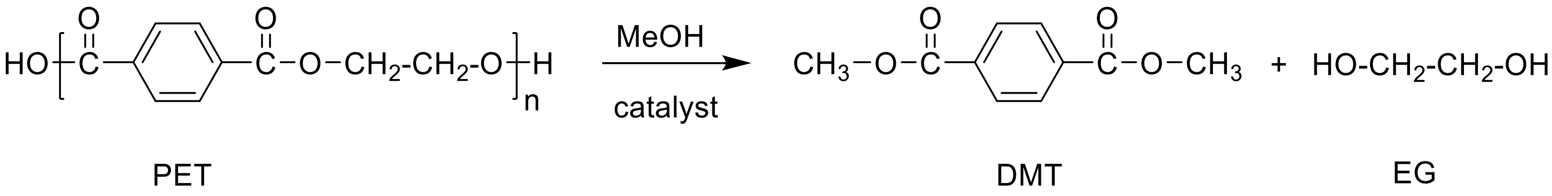
Technology developer	Starting material	Technology	Conditions						No. of steps[1]	Recovered		TRL[2]	Criteria[3]		
			Solvent	Reagent	Catalyst	Time (h)	Temp. (ºC)	Pressure (bar)		Monomer[4]	Yield (%)		C[5]	P[6]	R[7]
Tohoku University - Japan	c-PET[8]	Acid Hydrolysis	H_2O	Sulfuric acid	-	1-6	150	ATM[9]	1	PTA[10]	100	3-4	+/-	+	+/-
Aristotle University - Greece	c-PET[8]	Base Hydrolysis	H_2O	Sodium Hydroxide	-	1-2	200	ATM[9]	2	PTA[10]	98	3-4	+/-	+	+/-
Al-Mustansiriyah University - Iraq	c-PET[8]	Base Hydrolysis	H_2O	Sodium Hydroxide	Tetrabutyl ammonium bromide	1-2	200	ATM[9]	2	PTA[10]	98	3-4	+/-	+	+/-
NIAIST-Japan	PET[11]	Neutral Hydrolysis	H_2O	H_2O	-	0.5-1	420	480	1	PTA[10]	90	3-4	+	+	+
Zhejiang University of Technology - China	c-PET[8]	Netural Hydrolysis	H_2O	H_2O	$Zn(OAc)_2$	0.5-1	220-300	32	1	PTA[10]	91	3-4	+	+	+/-

1. Number of steps to obtain final monomer back; 2. TRL: Technology readiness levels according to EU definitions, estimated by the authors based on publicly available information; 3. The symbols in the criteria section (estimated by the authors based on publicly available information) are defined as; +: high (or) attractive; -: low (or) less attractive; +/-: average (or) not convincing; 4. Type of monomer obtained from the process; 5. Reaction conditions and possible scale-up options; 6. Purity of monomer(s) obtained in the process; 7. Recycling/reusing possibilities of solvents/reagents/catalysts used in the process; 8. Commercial PET sample (Mn 30 Kda or higher); 9. Atmospheric pressure; 10. P-Terephthalic acid; 11. Post-consumer PET waste fraction (mixed PET fraction), pre-treated by extrusion to obtain amorphous PET.

Hydrolysis (Acid, Base & Neutral) of PET

- Though near quantitative yields achieved, some drawbacks that hampers large scale processes
- Acid hydrolysis
    - Severe corrosion of the reactors
    - Loss of recovered monomers (e.g. over oxd. of EG to Oxalic acid)
    - High costs for down-stream processing (DSP)
- Base hydrolysis
    - Often operated at higher T, Inorganic salts formation
    - High costs for down-stream processing (DSP)
- Neutral hydrolysis
    - Monomer (PTA) purity significantly low

Alcoholysis of PET



- Directly yields monomers (DMT and EG), easily recovered by distillation, recrystallization/sublimation
- Organometallic catalysts (or) metal catalyst typically used[1]
  - $Zn(OAc)_2$, $Mg(OAc)_2$, $Co(OAc)_2$, $Al(O\text{-}i\text{-}Pr)_3$, PbO_2, ZnO (NPs)
- Ionic liquids ([Bmim]Cl) and DES (ChCl·ZnAc) were also demonstrated using supercritical ethanol and methanol
  - DMT yields achieved up to 97.7% at higher temperatures (>200 °C)

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Sinha, V., et al., J. Polym. Environ. 2010, 18 (1), 8-25; Wang, H. et al., Green Chemistry 2009, 11 (10), 1568-1575; L. Bartolome, M. I., et al., Recent developments in the chemical recycling of PET," in Material Recycling—Trends and Perspectives. 2012.; Kim, B.-K. et al., J. Appl. Polym. Sci. 2001, 81 (9), 2102-2108

Alcoholysis of PET

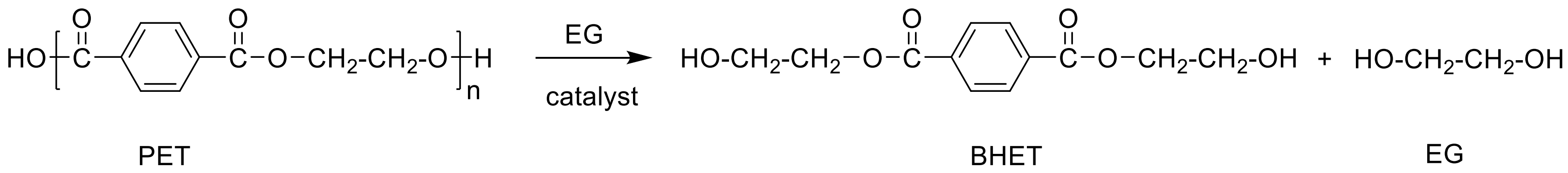
- Overview of selected conditions developed for efficient depolymerization of PET back to DMT and EG

Technology developer	Starting material	Technology	Conditions						No. of steps[1]	Recovered		TRL[2]	Criteria[3]		
			Solvent	Reagent	Catalyst	Time (h)	Temp. (°C)	Pressure (bar)		Monomer[4]	Yield (%)		C[5]	P[6]	R[7]
Imam Khomeini Int. University - Iran	c-PET[8]	Alcoholysis	Butanol	Butanol	KOH	N.D.[12]	100	ATM[9]	2	PTA[10]	96	3-4	+/-	+	+/-
Imam Khomeini Int. University - Iran	c-PET[8]	Alcoholysis	Pentanol	Pentanol	KOH	N.D.[12]	100	ATM[9]	2	PTA[10]	96	3-4	+/-	+	+/-
Kumamoto University - Japan	c-PET[8]	Methanolysis	Methanol	Methanol	-	0-1.5	300	147	1	DMT[13]	98	3-4	+	+	+
Chinese Academy of Sciences- China	c-PET[8]	Methanolysis	Methanol	Methanol	$Zn(OAc)_2$	0.5-1	250-270	110	1	DMT[13]	95	3-4	+	+	+/-

1. Number of steps to obtain final monomer back; 2. TRL: Technology readiness levels according to EU definitions, estimated by the authors based on publicly available information; 3. The symbols in the criteria section (estimated by the authors based on publicly available information) are defined as; +: high (or) attractive; -: low (or) less attractive; +/-: average (or) not convincing; 4. Type of monomer obtained from the process; 5. Reaction conditions and possible scale-up options; 6. Purity of monomer(s) obtained in the process; 7. Recycling/reusing possibilities of solvents/reagents/catalysts used in the process; 8. Commercial PET sample (Mn 30 Kda or higher); 9. Atmospheric pressure; 10. P-Terephthalic acid; 12. Not described; 13. Dimethyl terephthalate.

Glycolysis of PET

- Process of depolymerizing PET chains using glycols at temperature between 180-240 °C



- BHET (α,ω-dihydroxy molecule) and glycolates obtained as end-product
    - BHET used as monomer for PET synthesis
    - Glycolates in unsaturated polyester resins, vinyl esters, plasticizers, polyurethanes and epoxy resin etc...

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Glycolysis of PET

- Glycols investigated
  - Ethylene glycol (EG), diethylene glycol (DEG), propylene glycol (PG), dipropylene glycol (DPG), 1,4-butanediol (BD)
  - Triethylene glycol (TEG), poly(ethylene glycol) neopentyl glycol (NPG)
- Catalysts explored: transesterification catalyst, metal salts, metal oxides, ionic liquids (acid, base and neutral), hydrotalcites, deep eutectic solvents (DES), zeolites, organic base, Polyoxometalates (POMs), Urea/metal salt mixtures, popular examples includes:
  - $Zn(OAc)_2$, $Mn(OAc)_2$, $Co(OAc)_2$
  - $NaHCO_3$, Na_2SO_4, K_2SO_4,
  - Tetrabutoxy titanium, Titanium isopropoxide

Glycolysis of PET

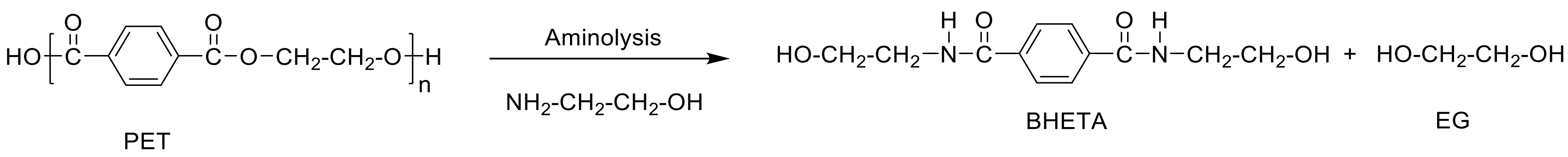
- Overview of selected conditions developed for efficient depolymerization of PET back to BHET monomer

Technology developer	Starting material	Technology	Conditions						No. of steps[1]	Recovered		TRL[2]	Criteria[3]		
			Solvent	Reagent	Catalyst	Time (h)	Temp. (ºC)	Pressure (bar)		Monomer[4]	Yield (%)		C[5]	P[6]	R[7]
UFRGS-Brazil	c-PET[8]	Glycolysis	Ethylene glycol	Ethylene glycol	$Zn(OAc)_2$	2	196	ATM[9]	1	BHET[14]	83	3-4	+	+	+/-
Henan Normal University - China	c-PET[8]	Glycolysis	Ethylene glycol	Ethylene glycol	$Zn(OAc)_2$	1-5	196	ATM[9]	1	BHET[14]	86	3-4	+	+	+/-
Institute of Process Engineerin g -China	c-PET[8]	Glycolysis	Ethylene glycol	Ethylene glycol	$Bmim_2(CoCl_4)$	1.5	175	ATM[9]	1	BHET[14]	96	3-4	+	+	+/-

1. Number of steps to obtain final monomer back; 2. TRL: Technology readiness levels according to EU definitions, estimated by the authors based on publicly available information; 3. The symbols in the criteria section (estimated by the authors based on publicly available information) are defined as; +: high (or) attractive; -: low (or) less attractive; +/-: average (or) not convincing; 4. Type of monomer obtained from the process; 5. Reaction conditions and possible scale-up options; 6. Purity of monomer(s) obtained in the process; 7. Recycling/reusing possibilities of solvents/reagents/catalysts used in the process; 8. Commercial PET sample (Mn 30 Kda or higher); 9. Atmospheric pressure; 10. P-Terephthalic acid; 12. Not described; 13. Dimethyl terephthalate; 14. Bis(2-hydroxyethyl) terephthalate.

Aminolysis of PET

- Depolymerization of PET using amine solvent results in thermodynamically stable terephthalic acid amide



- Catalyst investigated
  - Cetyl ammonium bromide (CAMBr), DBTO, $Zn(OAc)_2$, $Na(OAc)_{2,}$ K_2SO_4
- Solvents/Reagent
  - Ethanol amine, methyl amine, diethanol amine, triethanol amine, ethylene diamine, triethylene tetra-amine, triethylene penta-amine

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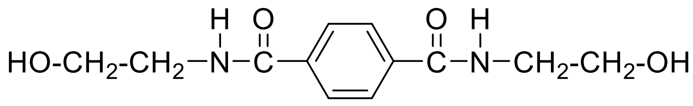
Aminolysis of PET

- Potential application explored for BHETA includes:
  - novel polyurethanes, unsaturated polyester resins, bisoxazoline synthesis, and non-ionic polymeric surfactants
  - additives in concrete mixture
  - antibacterial chemicals

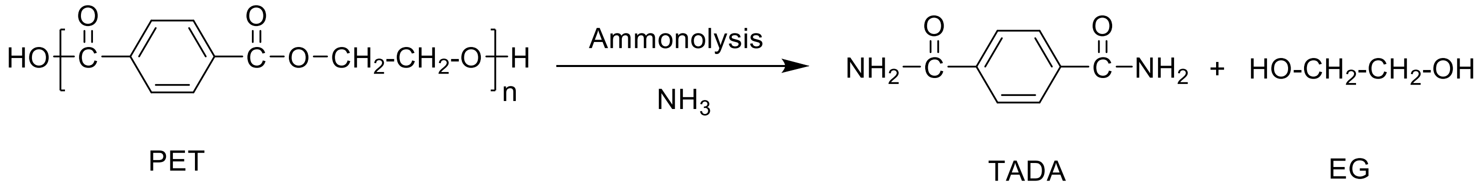


BHETA

Technology developer	Starting material	Technology	Conditions						No. of steps[1]	Recovered		TRL[2]	Criteria[3]		
			Solvent	Reagent	Catalyst	Time (h)	Temp. (ºC)	Pressure (bar)		Monomer[4]	Yield (%)		C[5]	P[6]	R[7]
Institute of Chemical Technology -India	c-PET[8]	Aminolysis	Acetic acid	Ethanol amine	Sodium acetate	0-0.5	172	ATM[9]	1	BHETA[17]	91	3-4	+/-	+	-

Ammonolysis of PET

- PET depolymerization in the presence of ammonia at (higher) temperature is called ammonolysis

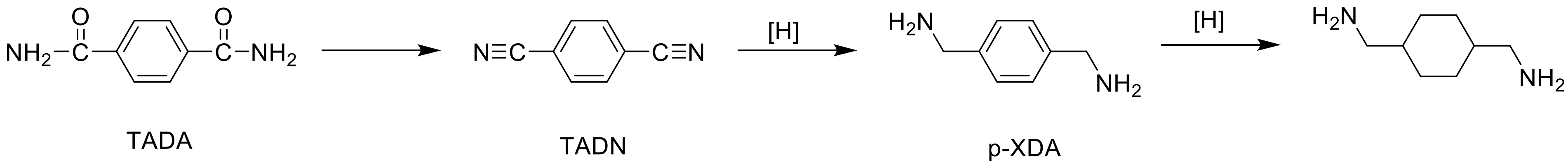


Technology developer	Starting material	Technology	Conditions						No. of steps[1]	Recovered		TRL[2]	**Criteria[3]**		
			Solvent	Reagent	Catalyst	Time (h)	Temp. (°C)	Pressure (bar)		Monomer [4]	Yield (%)		C[5]	P[6]	R[7]
Charan Singh University-India	c-PET[8]	Ammonolysis	-	NH_4	$Zn(OAc)_2$	360	RT[18]	ATM[9]	1	PTA diamide[19]	>90	3-4	+/-	+/-	-

- Operating conditions:
  - 70-180 °C, 2-20 bar NH_3, Cetyl ammonium bromide (CAMBr), $Zn(OAc)_2$

Ammonolysis of PET

- Up to 90% terephthaldiamide (TADA) is obtained with >99% purity



- TADA can be used to produce terephthalonitrile (TADN), a precursor for either p-xylenediamine (p-XDA) or 1,4-bis(aminomethyl)cyclohexane, (for polyamide synthesis)

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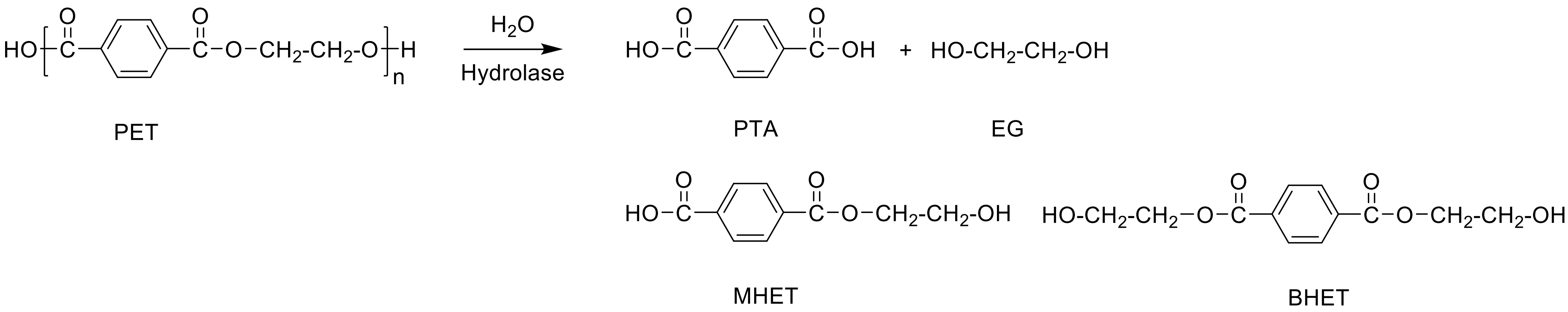
Enzymatic hydrolysis of PET

- Enzymatic hydrolysis are advantageous
    - Environmentally friendly, mild reaction conditions (<100 ^{o}C); ATM pressure
- Amylases, cellulases, xylanases, pectinases, chitinases and cutinases are well-known examples of hydrolytic enzymes that breakdown naturally-occurring bio-polymers
- Lately, these enzymes proven for the depolymerisation of polycondensation polymers, for e.g. PET
- Carbios (French biotech company) front-runners in this technology, holding various patents and commercialized PET degradation using enzymes
- Main challenge: limited to amorphous or low-crystallinity materials (<10%)

www.cazy.org; www.carbios.fr.; E. Barnard, Green Chem., 2021, 23, 3765.

Enzymatic hydrolysis of PET

- Depending on enzyme and reaction conditions, one or more products are formed in typical enzymatic hydrolysis reaction



- MHET found to inhibit enzyme activity (T-*fusca* polyester hydrolase) and needs second enzyme addition to break down further to proceed the reaction

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Type of Enzyme	Microorganism	Materials	Temperature (°C)	Product
Cbotu_EstA	*Clostridium botulinum* ATCC3502	PET film	50	TPA,MHET
Lipases	*Candida cylindracea*	PET nanoparticels	40	1,2-Ethandiol, TPA
Tcur0390	*Thermomonospora curvata* DSM43183	PET nanoparticels	50	NA
Hydrolase TfH	*Thermobifida fusca* DSM43793	PET pellete	44–55	TPA, EG
TfCut1	*Thermobifida fusca* KW3	PET nanospheres	55–65	HEB, MHET, BHET, Benzoic acid
Tha_Cut1	*Thermobifida alba* DSM43185	PET	50	TPA, Benzoic acid, HEB, MHET
MHETase and PETase	*Ideonella sakaiensis*	PET	30	MHET
BsEstB	*Bacillus subtilis* 4P3-11	PET	40–45	TPA, Benzoic acid, MHET
LCC cutinase	*Leaf-branch compost*	Amorphous PET	50–70	MHET, TPA, Benzoic acid
Polymer polyhydrox-yalkanoate	*Pseudomonas*	PET	70	EG,TPA
Hydroxyalkanoyloxy-alkanoate	*Pseudomonas*	PET	70	EG,TPA
Thc_Cut2	*T. cellulosilytica*	PET films	50	MHET, TPA, BA, HEB
Arg29Asn	*Mutant The_Cut2*	PET films	50	MHET, TPA, BA, HEB
Lipases	*Aspergillus oryzae* CCUG 33812	PET fabric	55	BHET,TPA
Gln65Glu	*Mutant The_Cut2*	PET films	50	MHET, TPA, BA, HEB
TfCut2	*Thermobifida fusca* KW3	PET films	60	MHET
Thh_Est-esterase	*Thermobifida halotolerans*	3PET model substrate	50	MHET,TPA, BA, HEB

Overview of enzymatic degradation of PET

- Longer reaction time required for completion (10-96 h)
- Operated up to 70°C
- Various PET grades investigated
- Yield up to 97% demonstrated (mixture of monomers)

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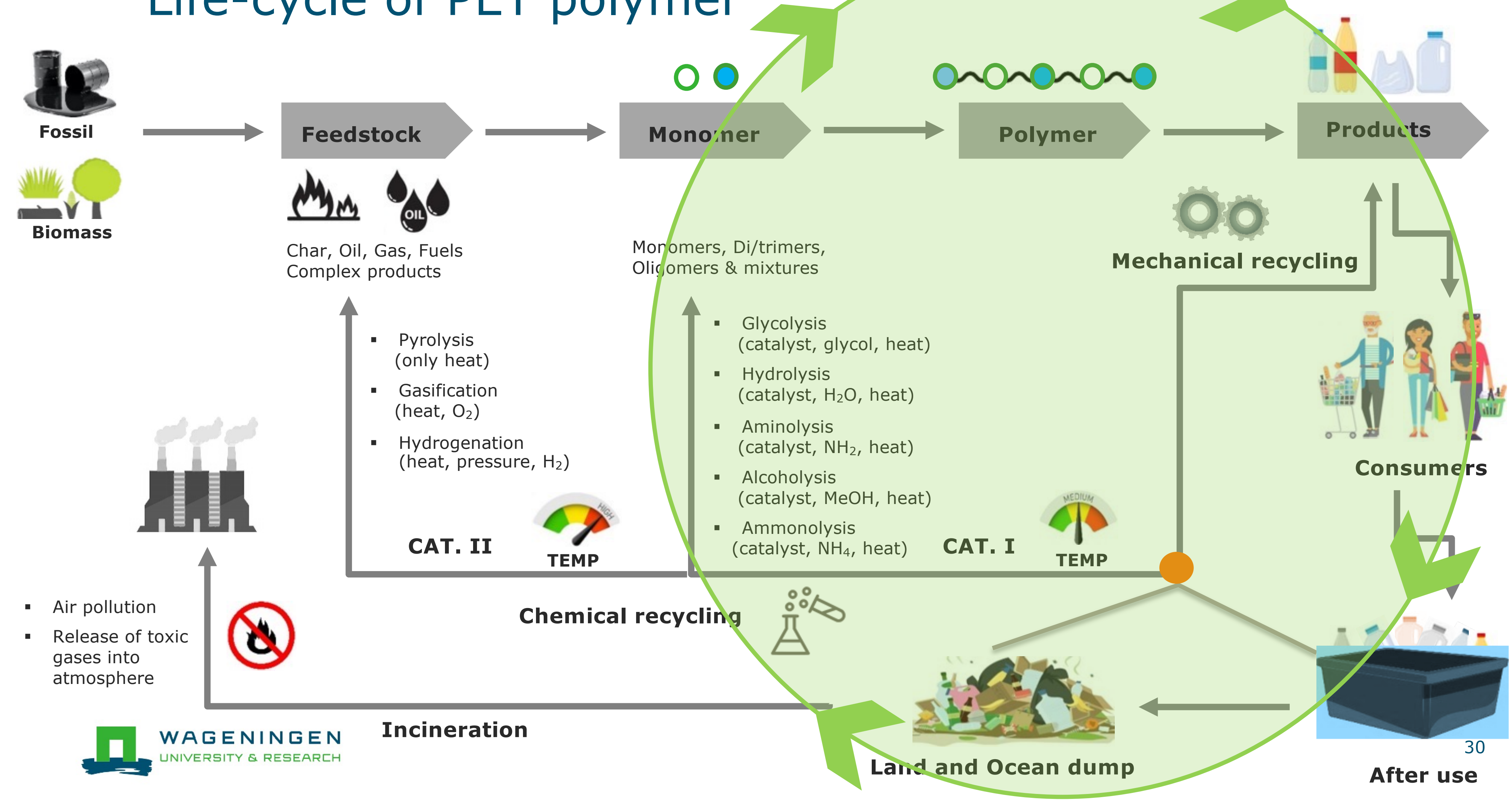
Damayanti et al., 2021, https://doi.org/10.3390/polym13091475

Overview of chemical companies in PET recycling

Company	Type of PET plastic	Technology	Catalyst/Reagent/Medium	Monomer/product	Development stage	Processing capacity
Gr3n (DEMETO) -SW	Bottle grades, packaging, textile	Alkaline hydrolysis	Microwave, base	PTA[1]	Pilot plant	60 kg/h
Eastman	Bottle grade, scrap from various products	Glycolysis/ Methanolysis	N.I.A.[2]	BHET[3]/DMT[4]	Pilot plant	N.I.A.[2]
Loop	Low value material, fibre, carpet, scraps, ocean debris	Methanolysis	N.I.A.[2]	DMT[4]	Early commercial	N.I.A.[2]
IBM (VolCat) - USA	Bottle grade, packaging, scrap from various products	Glycolysis	DBU[5] (IBM)	BHET[3]	Early stage towards pilot plant	N.I.A.[2]
Garbo (ChemPET) - IT	Bottle grade, multi-layer packages, fibres, textiles	Glycolysis	N.I.A.[2]	BHET[3]	Pilot plant	1000 t/year
Ioniqa Technologies - NL	Bottle grades, textiles, multi-layer packages	Glycolysis	Magnetite, $[Bmim][FeCl_4]$	BHET[3]	commercial Pilot plant	10 kt/year
Jeplan (BRING)	Bottle grade, fibre, textiles	Glycolysis	Sodium Methylate, Carbon[6]	BHET[3]	Pilot plant	20-25 kt/year
PerPETual – UK/IN	Bottle grades	Glycolysis	N.I.A.[2]	Low MW oligomers	Commercial plant	~2 million plastic bottles per day
Resinate Materials Group (Recyolysis)	Bottle grade, scrap from various products, PETG	Glycolysis	N.I.A.[2]	Polyester Polyol[7]	Pilot plant	200 metric ton and 4,500 metric ton
Carbios - FR	Bottle grades, textile, fibres	Enzymatic	Engineered PET-depolymerase	PTA[1]	Pilot plant under construction	N.I.A.[2]
BP (Infinia)	Bottle, unrecyclable scrap from various products	Hydrolysis	N.I.A.[2]	PTA[1]	Early stage of Pilot plant	N.I.A.[2]
Poseidon Plastics	Scrap from various products	Glycolysis	N.I.A.[2]	BHET[3]	Pilot plant	1000 t/year

Life-cycle of PET polymer



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Thank you for your attention!

To explore the potential of nature to improve the quality of life

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