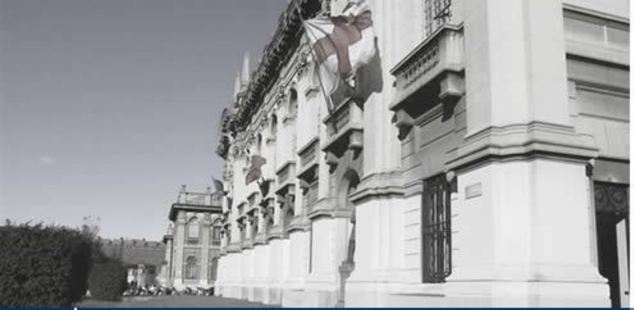

School of Industrial and Information Engineering

Course 096125 (095857)

Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

How Mitigate the Environmental Impact of Plastics.

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Dipartimento CMIC “Giulio Natta”

http://iscamap.chem.polimi.it/citterio/education/course-topics/

Introduction.

The word plastic is derived from the Greek (plastikos) meaning capable of being shaped or molded.

- *Plastics are a range of synthetic or semi-synthetic polymerization products that can be molded into a permanent object having the property of* ***plasticity***.

Properties of Plastics

Resistant	Durable	Insulator	Easy to produce	Inexpensive

About 330 million tones of plastic is produced each year.

Plastics: Pollution and Recycle.

Relevant part of Plastics are building up in landfill or reach the see!!!

How to solve the problem:

1) **Increase plastic recycling**

   and/or

2) **Use biodegradable plastics**

   and/or

3) **Use less plastics**
4) **Ban of same plastics.**

EN13432 Standard

From December 2009 plastic bags were eliminated from retail trade in Italy and EU.

Resin Identification Coding System

Plastic Wastes and Recycling Code.

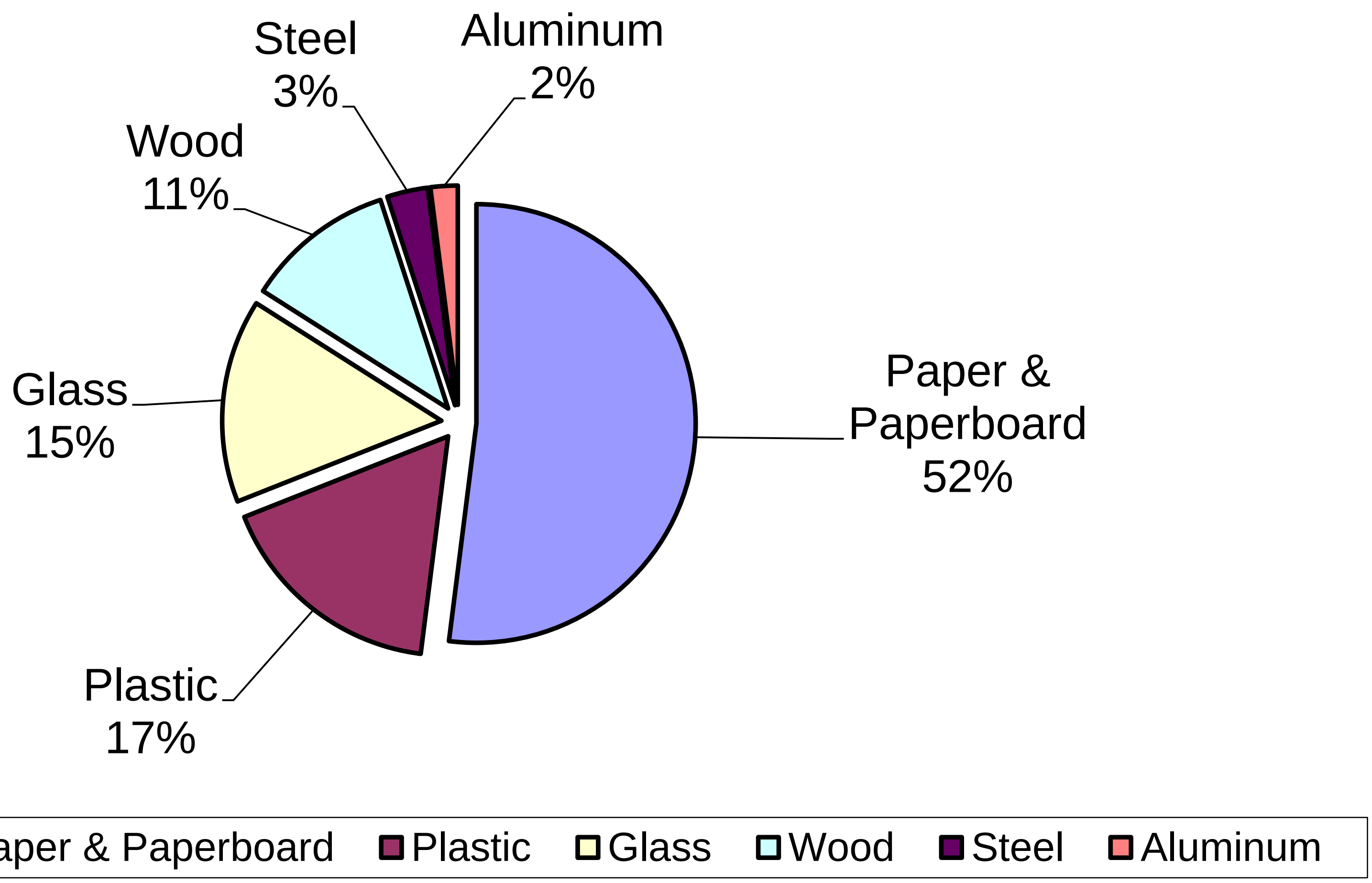
1 PETE	2 HDPE	3 PVC	4 LDPE	5 PP	6 PS	7 OTHER
polyethylene terephthalate	high-density polyethylene	polyvinyl chloride	low-density polyethylene	polypropylene	polystyrene	other plastics, including acrylic, polycarbonate, polyactic fibers, nylon, fiberglass
soft drink bottles, mineral water, fruit juice containers and cooking oil	milk jugs, cleaning agents, laundry detergents, bleaching agents, shampoo bottles, washing and shower soaps	trays for sweets, fruit, plastic packing (bubble foil) and food foils to wrap the foodstuff	crushed bottles, shopping bags, highly-resistant sacks and most of the wrappings	furniture, consumers, luggage, toys as well as bumpers, lining and external borders of the cars	toys, hard packing, refrigerator trays, cosmetic bags, costume jewellery, audio cassettes, CD cases, vending cups	an example of one type is a polycarbonate used for CD production and baby feeding bottles

Plastic Use: The Advantages and Limits.

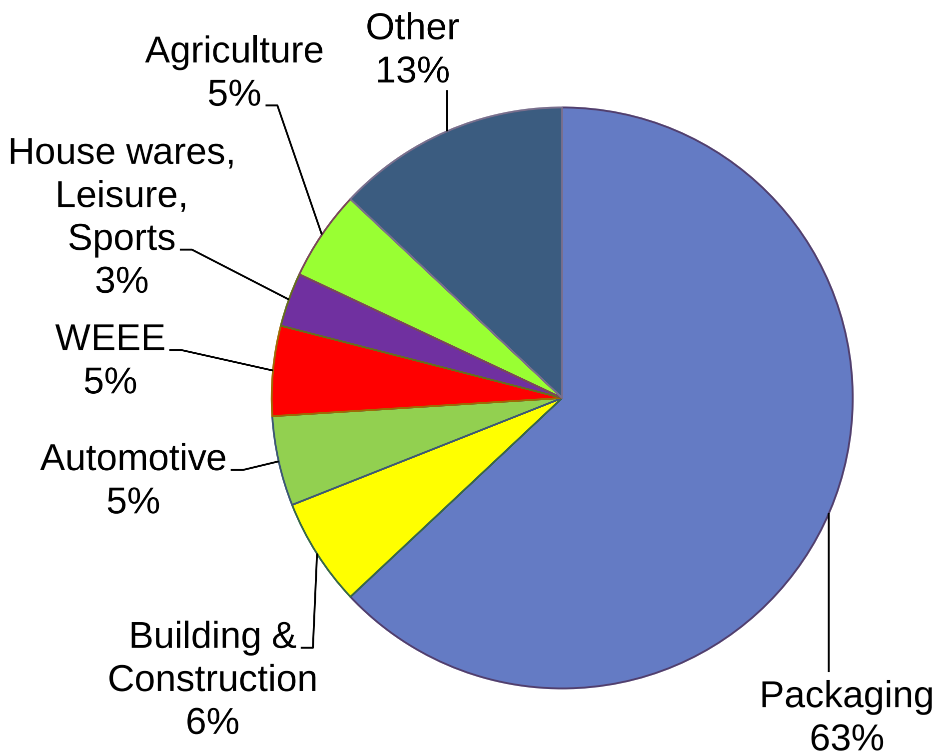
- The energy requirements for PE bags is lower than paper
- Plastics have several environmental advantages
  - i.e. fuel saving in cars owing to the lower weight
- Big convenience owing to adaptability to various needs
- Substitution of plastics ⇒ big increase in package weight, cost, volume, energy consumed, but…..
- High environmental impact (not degradable) and micro-plastics!

Municipal Solid Waste - Material Type.

Container and Packaging MSW Data, 2007 (U.S. EPA 2008)



Plastic Wastes.



> 25% of wastes in landfill are plastics (low degradation time > 50 years)

Even additives of plastic are a problem

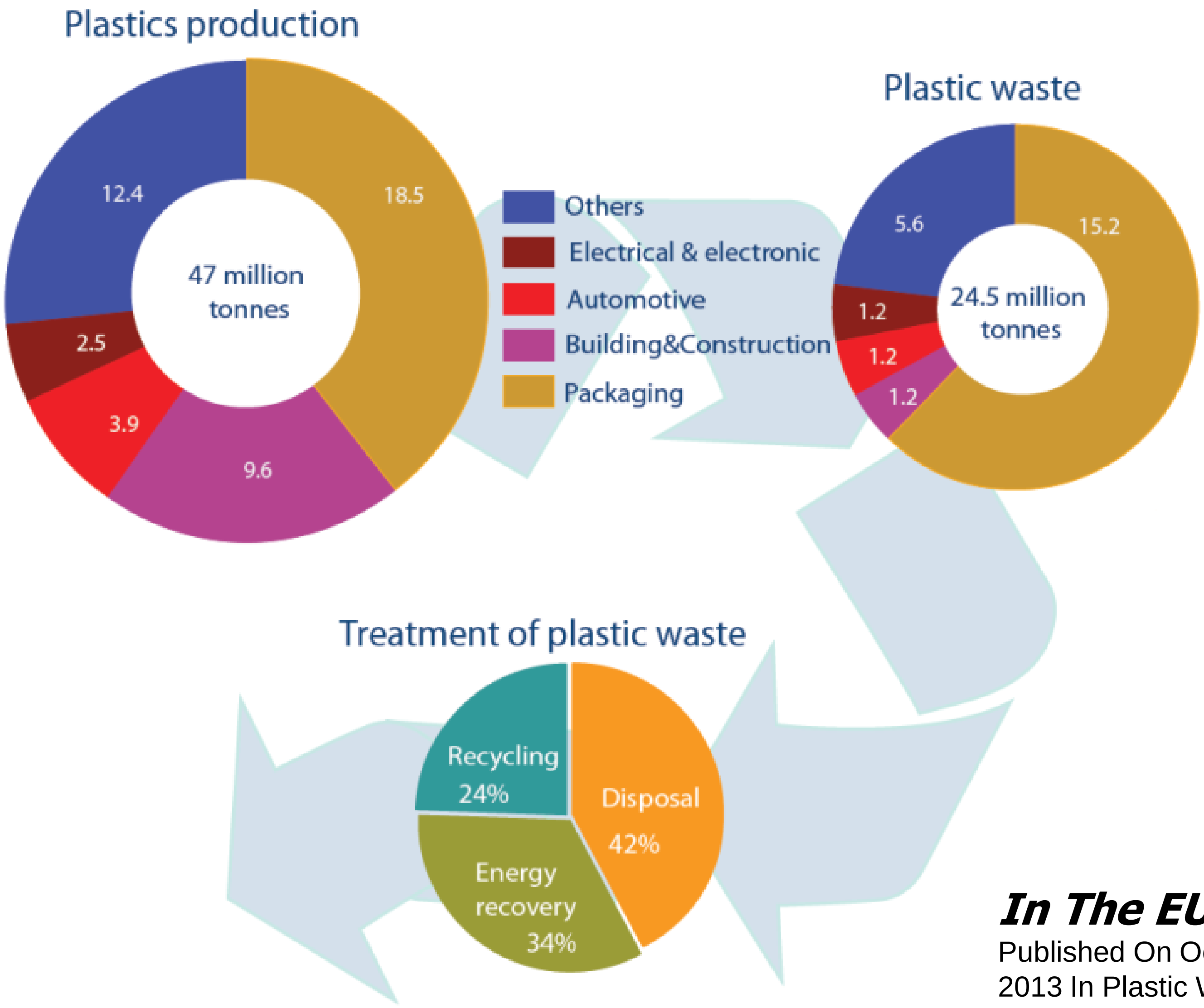
- i.e. responsible of 28% of all cadmium present

Low density increases the collection difficulties

- 20,000 bottle = 1t of recycled plastic

Waste definition: D.LGS. 152/2006 (T.U. ambiente) Art. 183

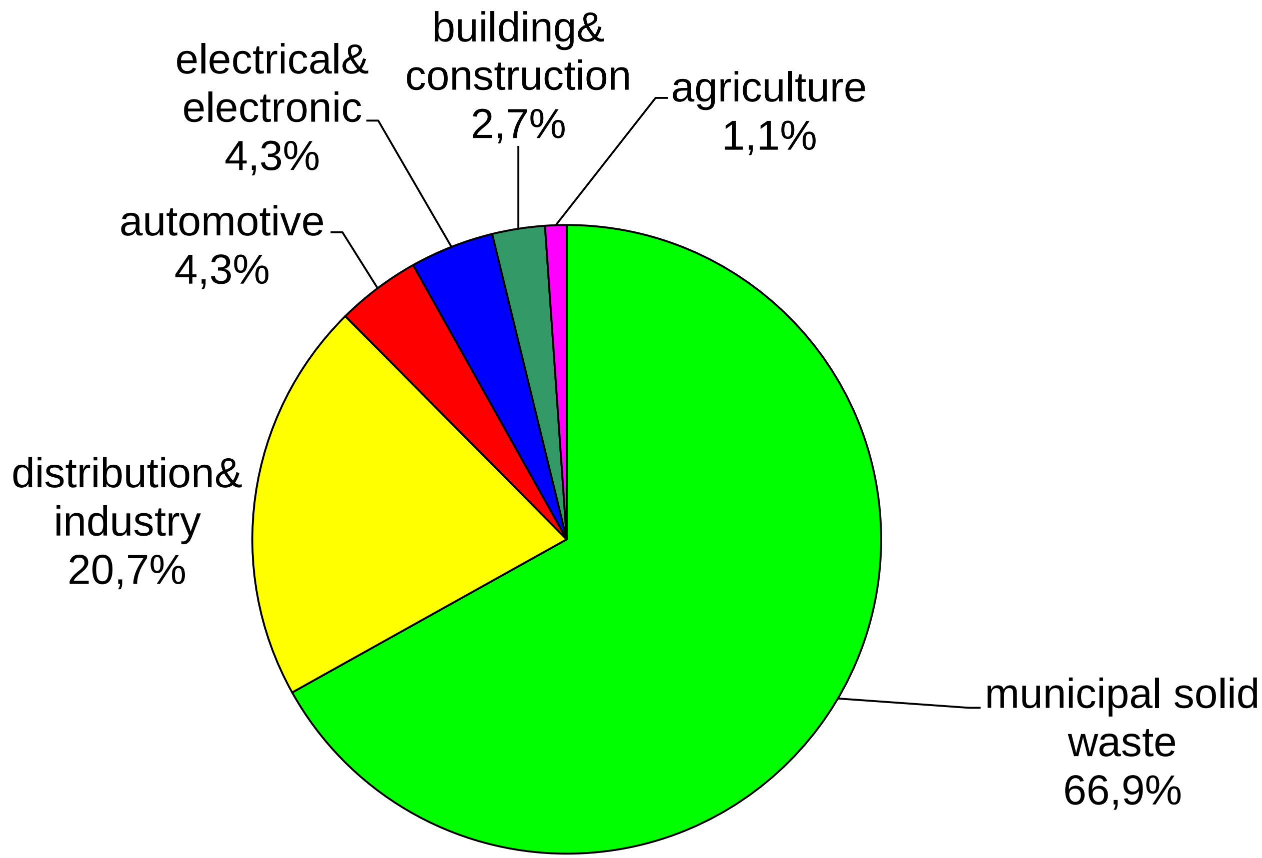
Plastics Production, Plastic Waste Generation By Industry And Plastic Waste Treatment By Method.



In The EU, 2011

Published On October 31, 2013 In Plastic Waste

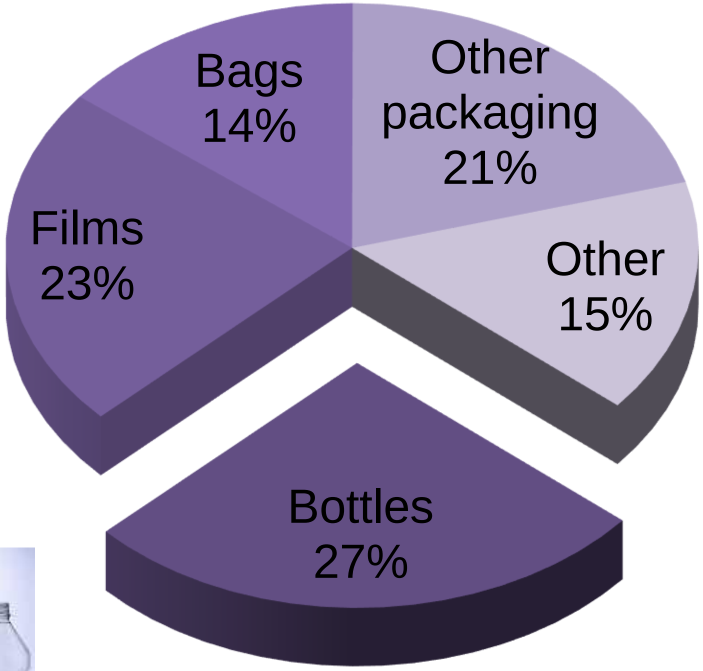
Total Plastic Wastes Collected after Use by Sector (2001) (weight %).



Europa Total: 24.500.000 tons (~ 50%)

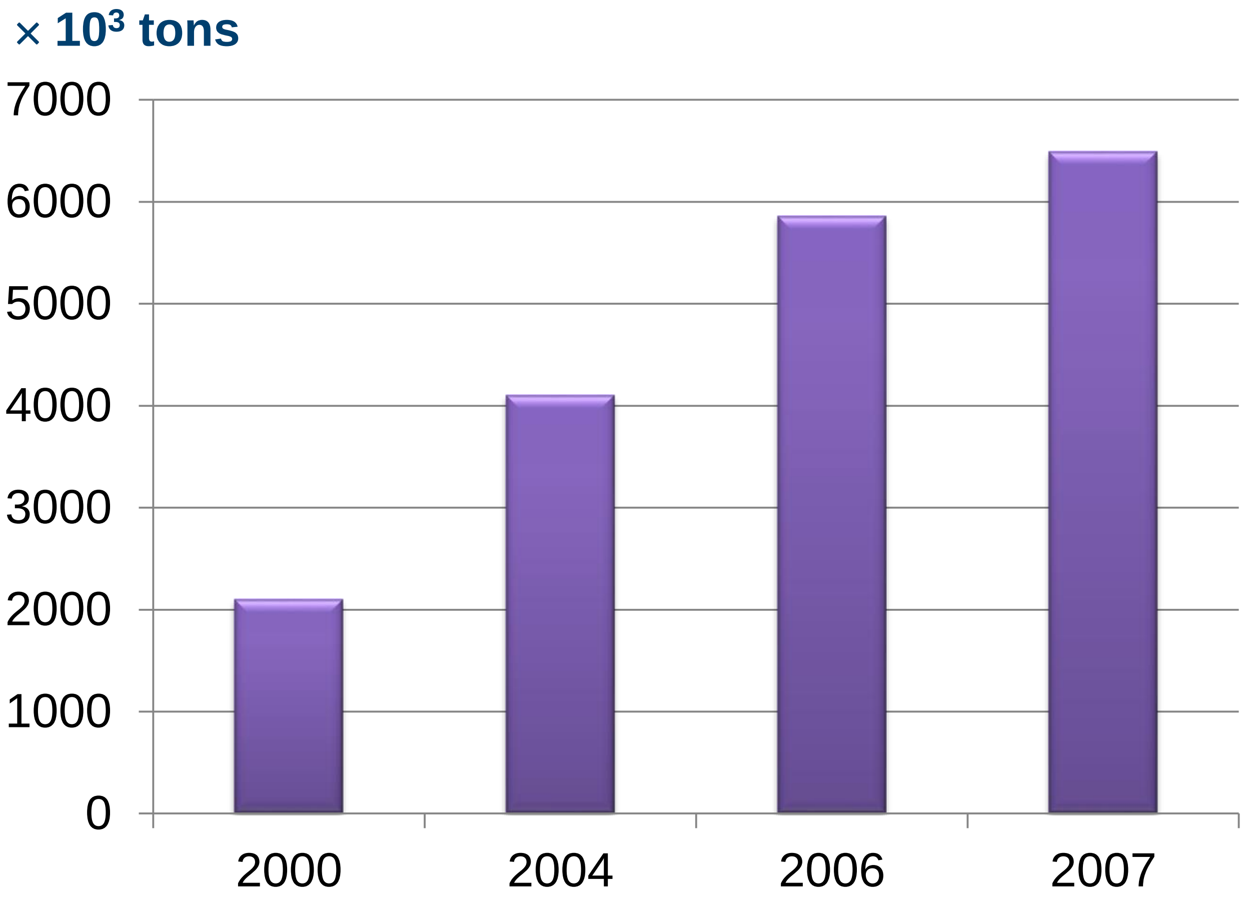
Plastics in the Household Waste Stream.

HDPE



PET

Chinese Plastic Waste Imports ($\times 10^3$ tons).



Source: Ascon GmbH, CPPI

- ***No more imported from 2015!!!***

Municipal Waste.

Municipal waste are (IT - art. 184 comma 2):

1. Domestic waste, even bulky, produced from local and places used for residential dwelling;
2. Not dangerous wastes produced from local and places used for the one different from the N° 1 similar to municipal waste for quantity and quality;
3. Wastes coming from street sweeping;
4. Of any kind or origin placed on street and public areas or on street and private areas still subject to public use or on beaches, sea and lake and on the banks of rivers;
5. vegetables coming from green areas, i.e. gardens, parks and cemeteries;
6. from exhumations and estumulatios and other waste from cemetery different from the ones of point 2), 3) and 5).

Waste Heterogeneity and Hazard.

Heterogeneity:

- The CER Code provides 900 different types of waste (of which 408 are classified as dangerous waste)
- Product characteristics and different physical states
- Each year are synthetized about 2000 new substances, new materials, and new products
- Wastes composed by different materials
- Ex. plastics: complex polymeric materials (thousand of different types) with different characteristic involving all sectors both as products and as package

Hazard:

- Substances classified hazardous are more than 6000
- CER 408 waste type classified hazardous or contaminated by different substances
- Also in municipal waste there are hazardous wastes which, when not separated, contaminate the overall material.

Special Wastes.

Special Waste are (art. 184 comma 3):

a) Wastes from farm and agro-industrial activities;
b) Wastes arising from activity of demolition/construction of buildings and hazardous wastes resulting from excavation activities;
c) Wastes from industrial manufacturing (except the petroleum coke used as fuel for production use);
d) Wastes from craftsmanship;
e) Wastes from commercial activity;
f) Wastes from service activity;
g) Wastes arising from recovery activity and waste disposal, from sludge produced by water purification and other treatment of water/wastewater and fume reduction;
h) Wastes arising from hospital activity;
i) deteriorated and obsolete machinery and equipment;
j) motor vehicles, trailers and the like out of use and parts thereof;
k) The fuel produced from waste (CDR - fuel derived from carbon wastes).

Recycling Classification.

Recycling

- Collection: plastics are labeled with a number
- Coding for plastics
  - 1 PET (polyethylenterephthalat)
  - 2 HDPE (high density polyethylene)
  - 3 Vinyl/PVC (polyvinylchloride)
  - 4 LDPE (Low density polyethylene)
  - 5 PP (Polypropylene)
  - 6 PS (Polystyrene)
  - 7 Others

- Treatment/Selection
  - Best economic is obtained when materials are selected
  - Plastics are mainly selected visually. However, plant for automatic selection based on visible/IR light adsorption are known and used.
- Definitions
  - *Post consumer Material:* Plastics collected by public organizations and processed in pellets for reuse.
  - *Post industrial Materials*: Plastics collected by firms (as scrap, splatter, waste, flakes, or packaging)

Plastics are too Valuable to Throw Away!

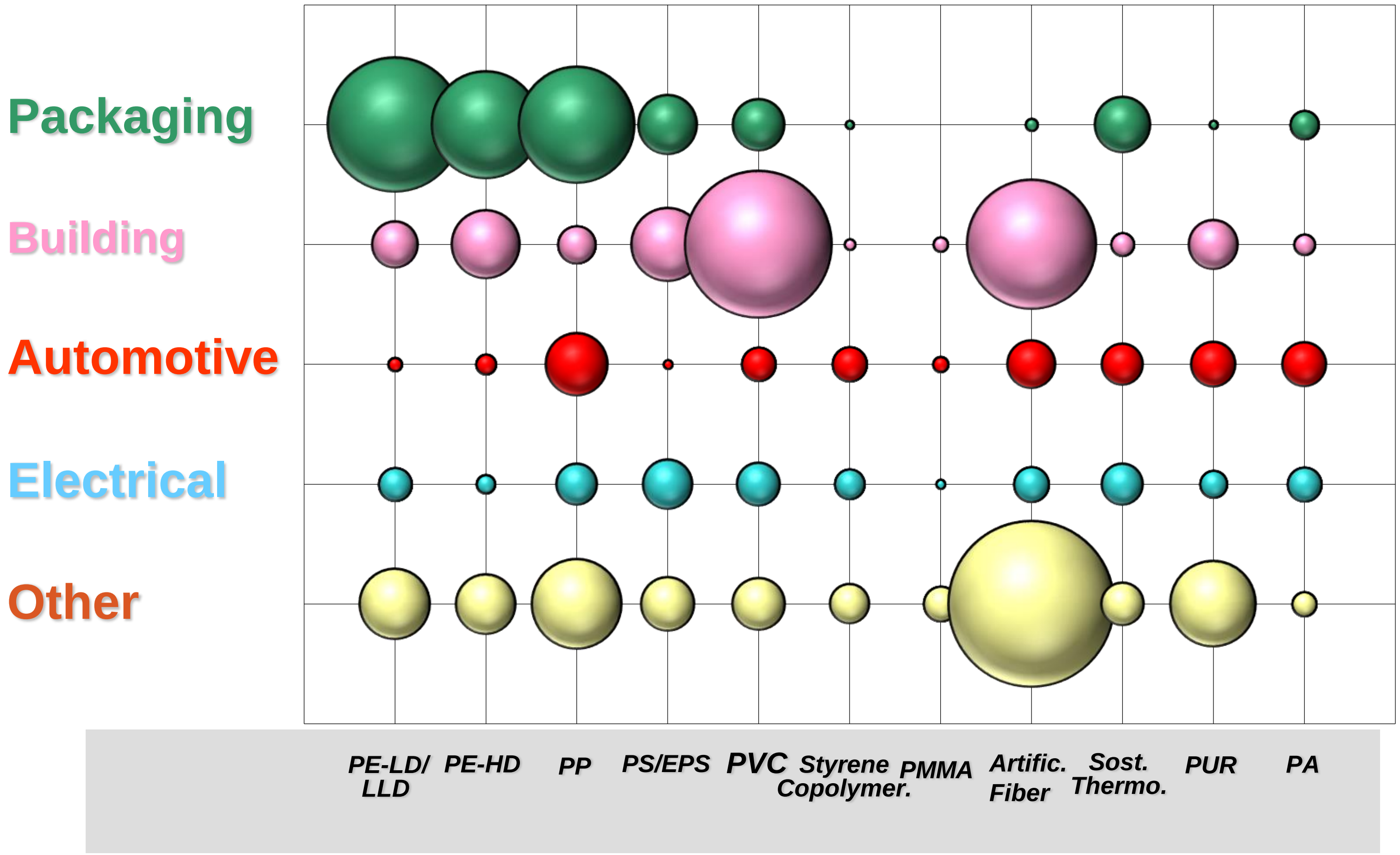
Turning waste into a resource is a goal the European plastics industry is committed to achieve to improve Europe's resource efficiency.

This goal is impossible to achieve with 38% of plastics waste still going to landfill.

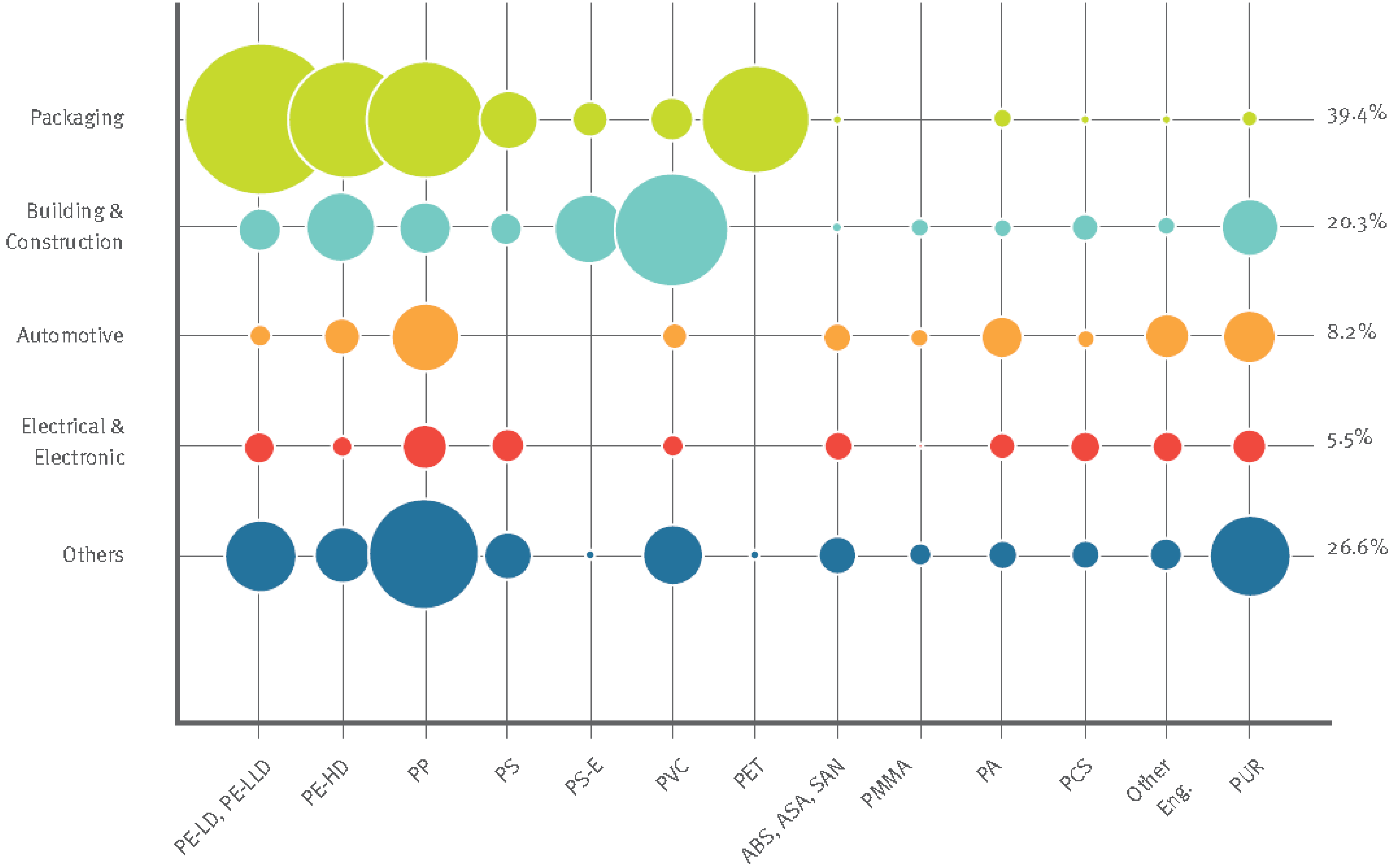
As such, landfill is a major hurdle that must be eliminated for such an ambitious goal to be reached.

Recycling and energy recovery are both complementary and necessary to achieve the **zero plastics to landfill by 2020 goal**.

Plastic Applications by Sectors and Type (2002).

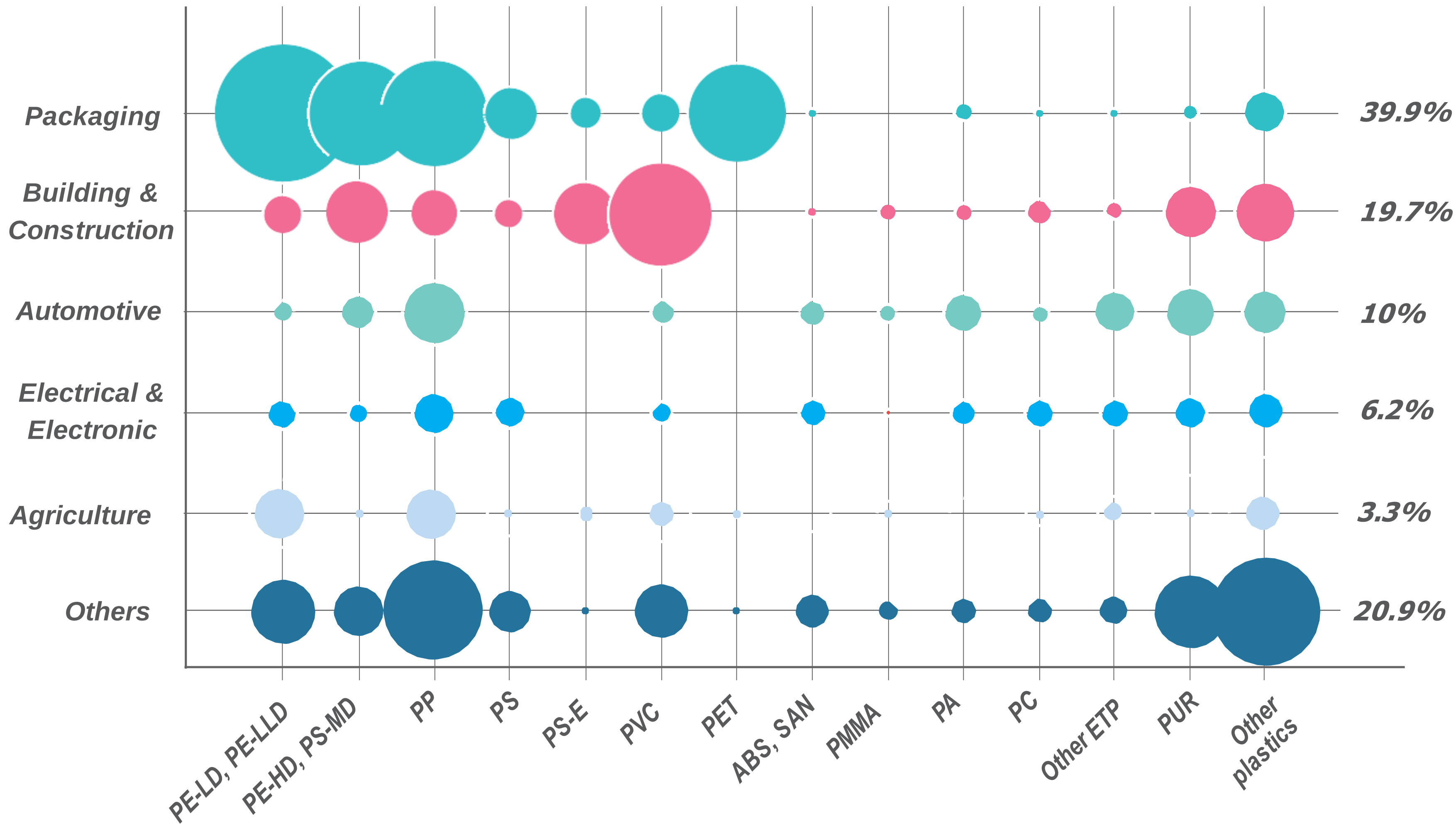


Plastics Demand by Market (2013).



Source: PlasticsEurope (PEMRG) / Consultic / ECEBD

European plastics converter demand by segments and polymer types (2016).



Source: PlasticsEurope (PEMRG) / Conversio Market & Strategy GmbH

Plastics Identification System (ISO 1043-1).

Plastic		Filler	
>ABS<	Acrylonitrile/butadiene/styrene	GF	Glass Fiber
>ABS-FR<	Flame-retardant ABS	GB	Glass bead
>EP<	Epoxy	MP	Mineral powder
>PA<	Nylon (polyamide)	CF	Carbon fiber
>PA6<	Nylon 6		
>PA66<	Nylon 6/6		
>PBT<	Polybutylene terephthalate		
>PC<	Polycarbonate		
>PE<	Polyethylene		
>PE-LLD<	Linear low-density polyethylene		
>PE-LMD<	Low-medium den.polyethylene		
>PE-HD<	High density polyethylene		
>PET<	Polyethylene terephthalate		
>PS<	Polystyrene		
>PS-HI<	High impact polystyrene		
>PVC<	Polyvinyl chloride		
>SAN<	Styrene/acrylonitrile		
>SI<	Silicone		

Materials Compatibility.

- The mingling of different polymers in the recycled stream makes recycling of plastics difficult.
- There is a need for separating plastic components into appropriate categories based on composition.

Design consideration:

- Use as few different types of materials as possible
- Ensure all materials can be easily separated from the primary plastics
- More than one type of plastics used should be compatible with one another.

Materials Compatibility Chart.

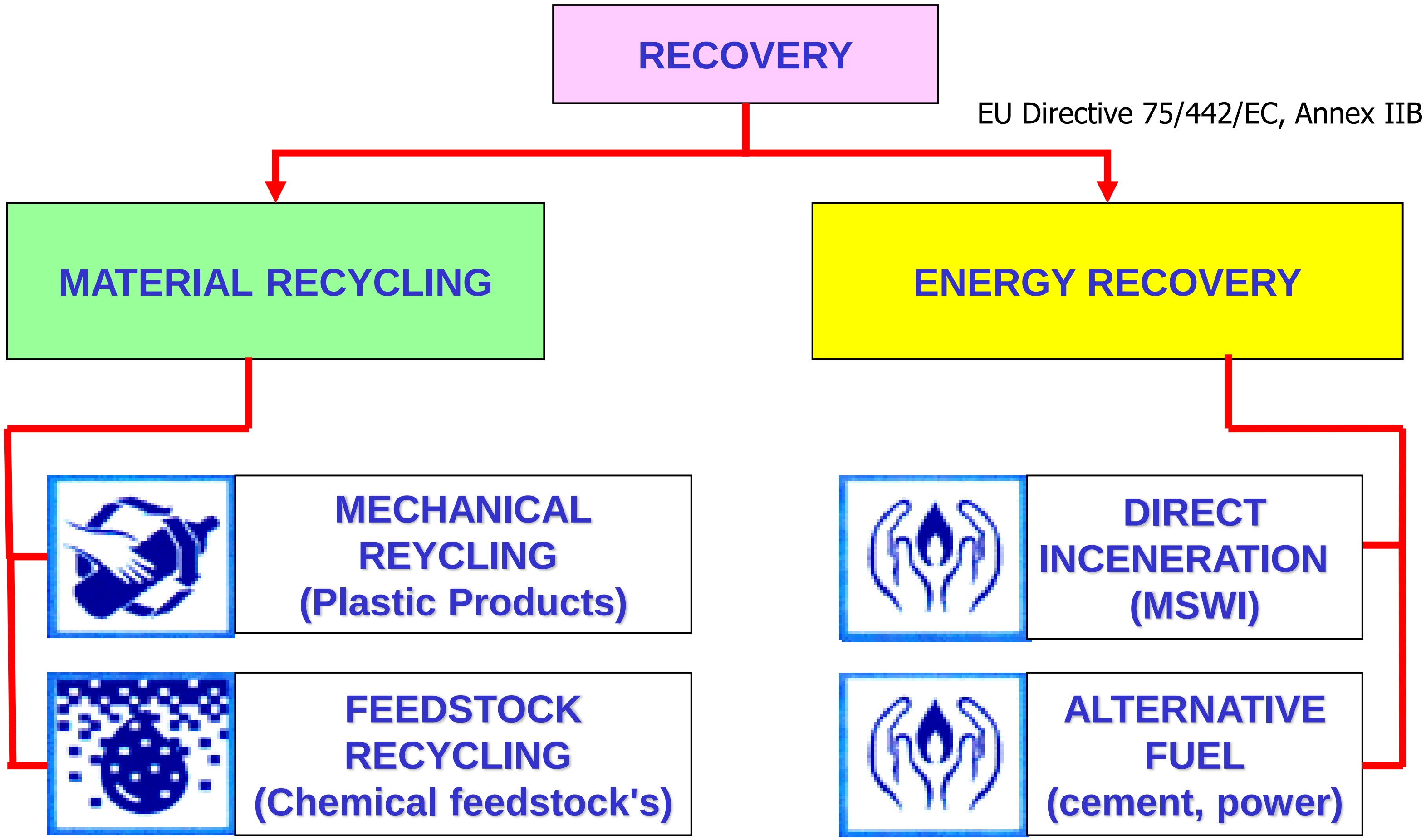
polyolefin

Matrix Material	Additive											
	PE	PVC	PS	PC	PP	PA	POM	SAN	ABS	PBTP	PETP	PMMA
PE	■	□	□	□	■	□	□	□	□	□	□	□
PVC	□	■	□	□	□	□	□	■	●	□	□	■
PS	□	□	■	□	□	□	□	□	□	□	□	□
PC	□	⊙	□	■	□	□	□	■	■	■	■	■
PP	■	□	□	□	■	□	□	□	□	□	□	□
PA	□	□	⊙	□	□	■	□	□	□	⊙	⊙	□
POM	□	□	□	□	□	□	■	□	□	⊙	□	□
SAM	□	■	□	■	□	□	□	■	■	□	□	■
ABS	□	⊙	□	■	□	□	⊙	□	■	⊙	⊙	■
PBTP	□	□	□	■	□	⊙	□	□	⊙	■	□	□
PETP	□	□	⊙	■	□	⊙	□	□	⊙	□	■	□
PMMA	□	■	⊙	■	□	□	⊙	■	■	□	□	■

Key: ■ Compatible ● Compatible with limitations □ Compatible only in small amounts
⊙ Non compatible

Source : Adapted from Bras e Rosen, 1997.

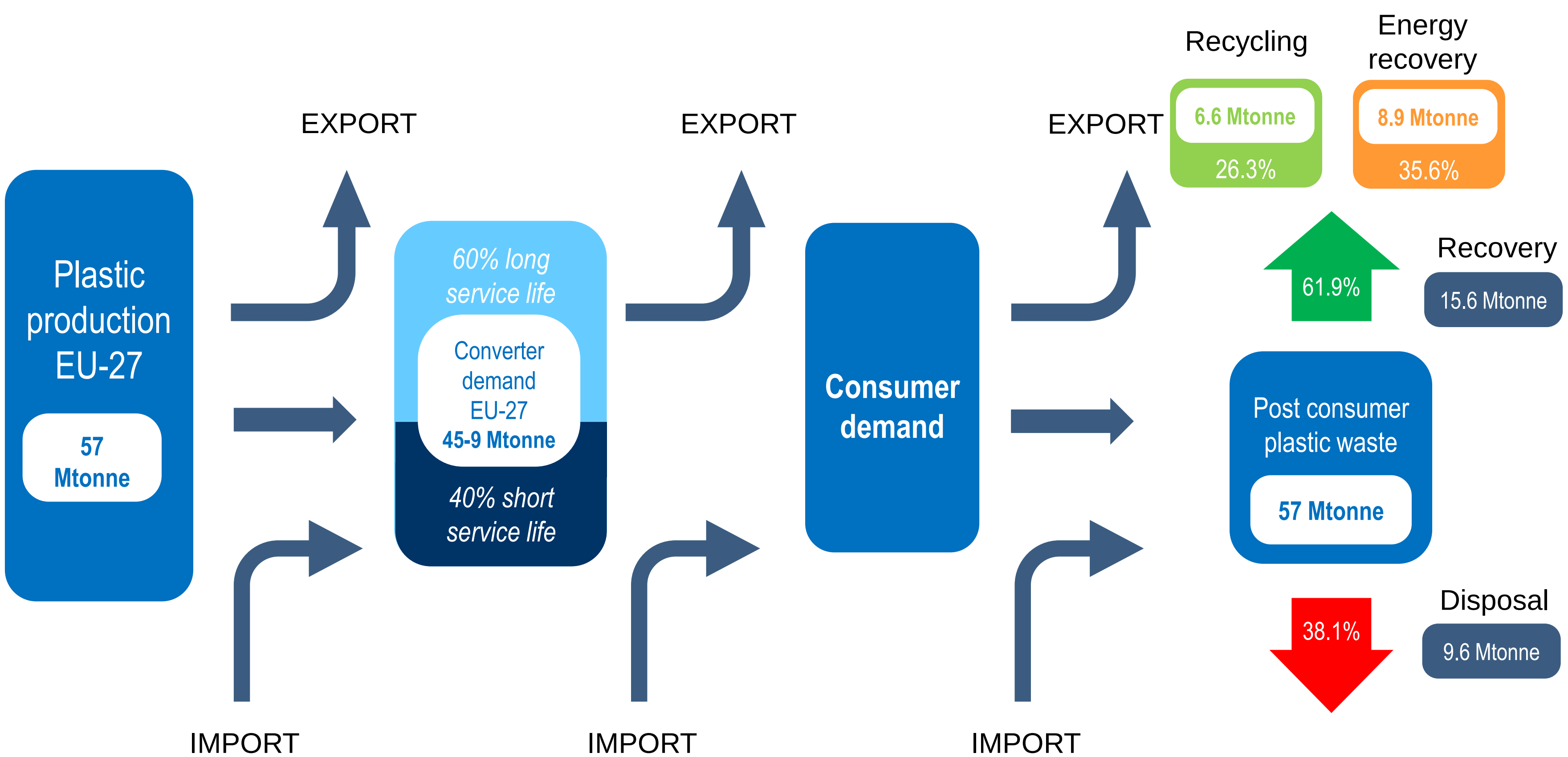
Options for Plastics Recovery.



"Cycle-of-Life" of a Polymer.

- Selection/design of the polymer
- Synthesis of monomer
- Polymerization
- Post-polymerization manufacture and/or polymer blends
- Use
- Post-use
  - Recycle,
  - Energy recovery
  - Disposal (Landfill)

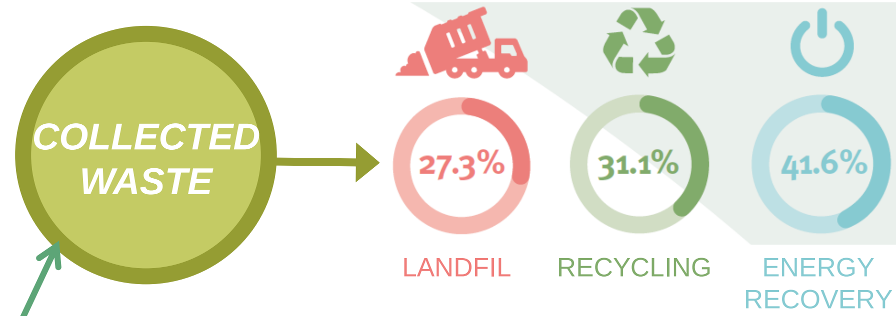
Life Cycle of Plastics in 2012 (EU-27+N/CH).

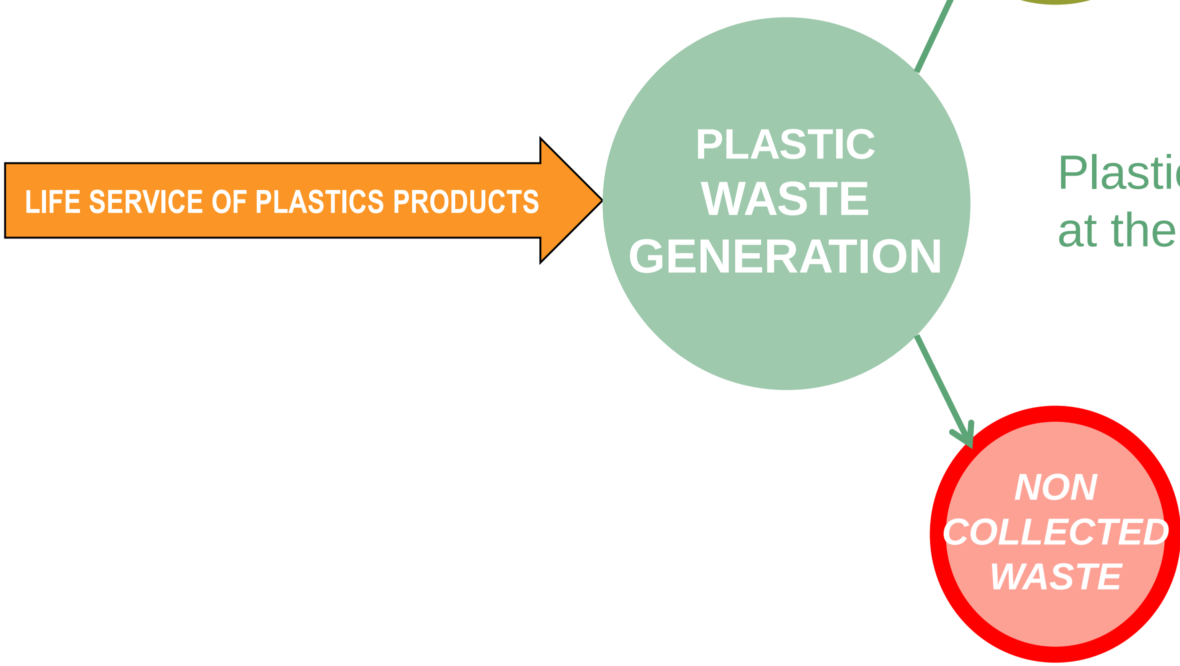


Plastics Products Cycle- The End of Life

_EU - 2016_

The service life of plastics products goes from less than 1 year to 50 years or more



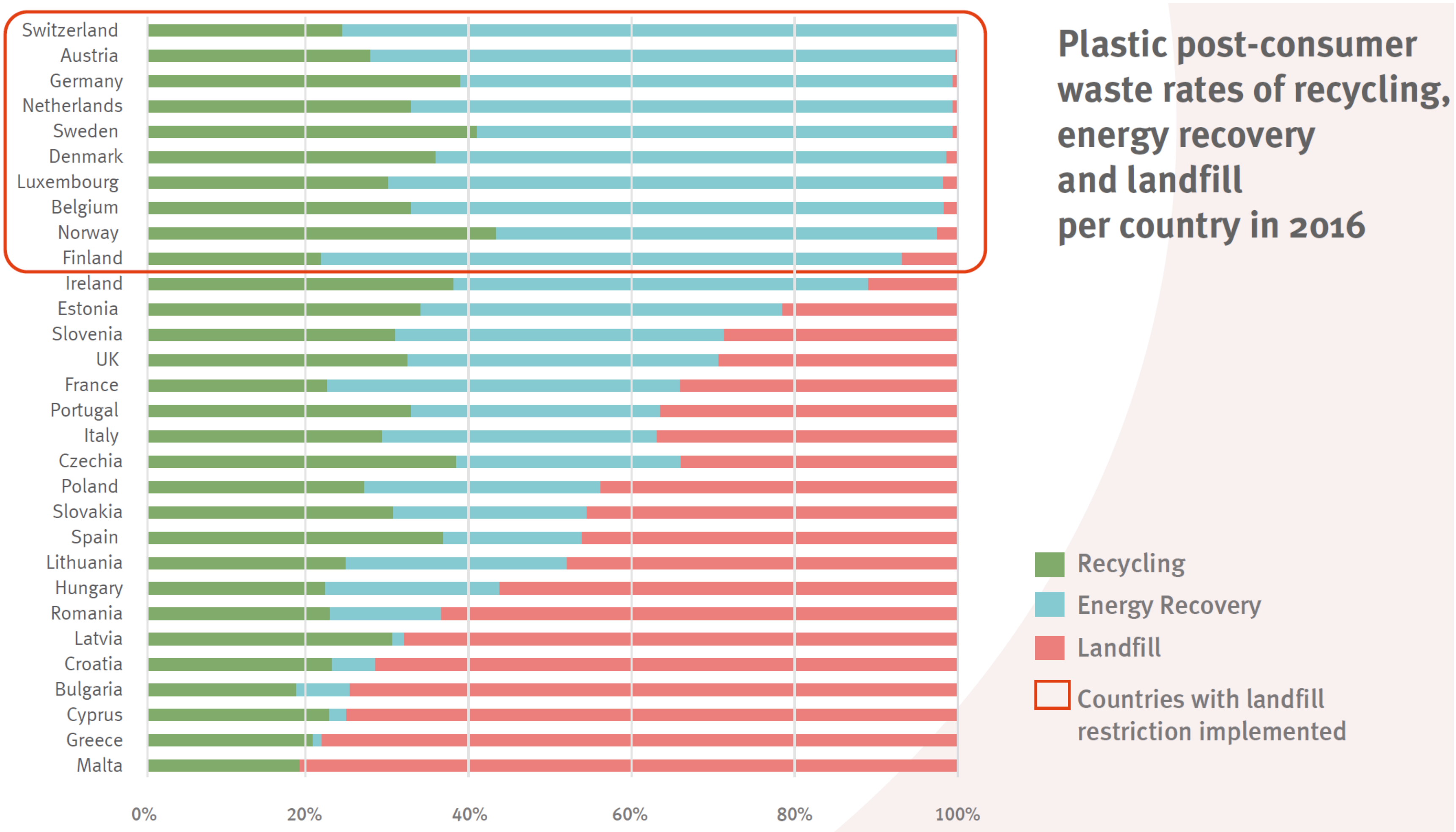


Plastics become waste at the end of their service life

The ratio on collected and non collected plastics depends on countries

Fom production to waste, different plastic products have different life cycles and this is why the volume of collected waste cannot match, in a single year, the volume of production or consumption.

Landfill Bans Foster Higher Recycling Rates

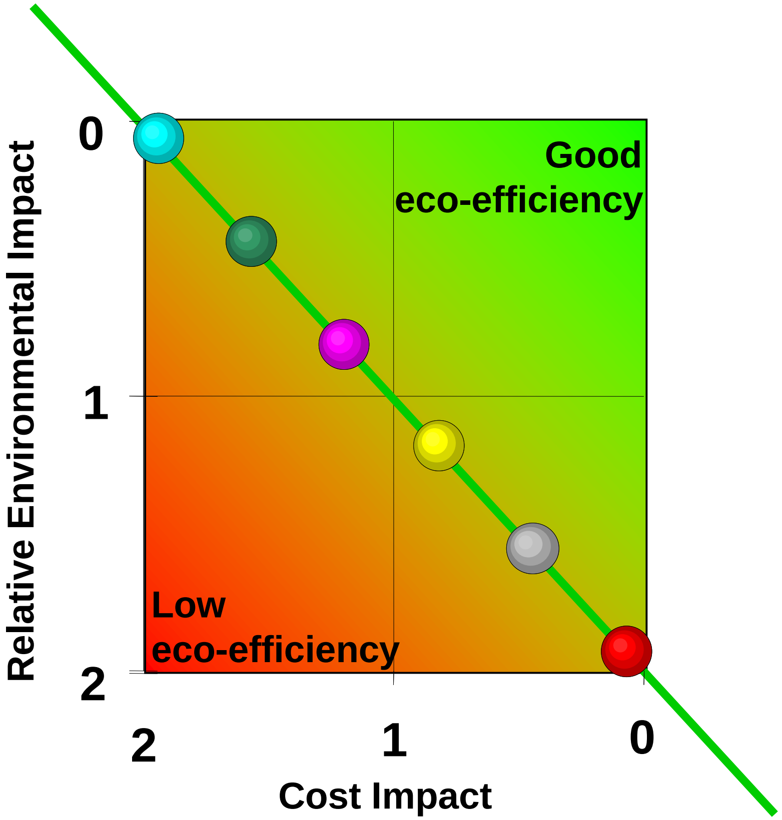


Eco-Efficiency Concept.

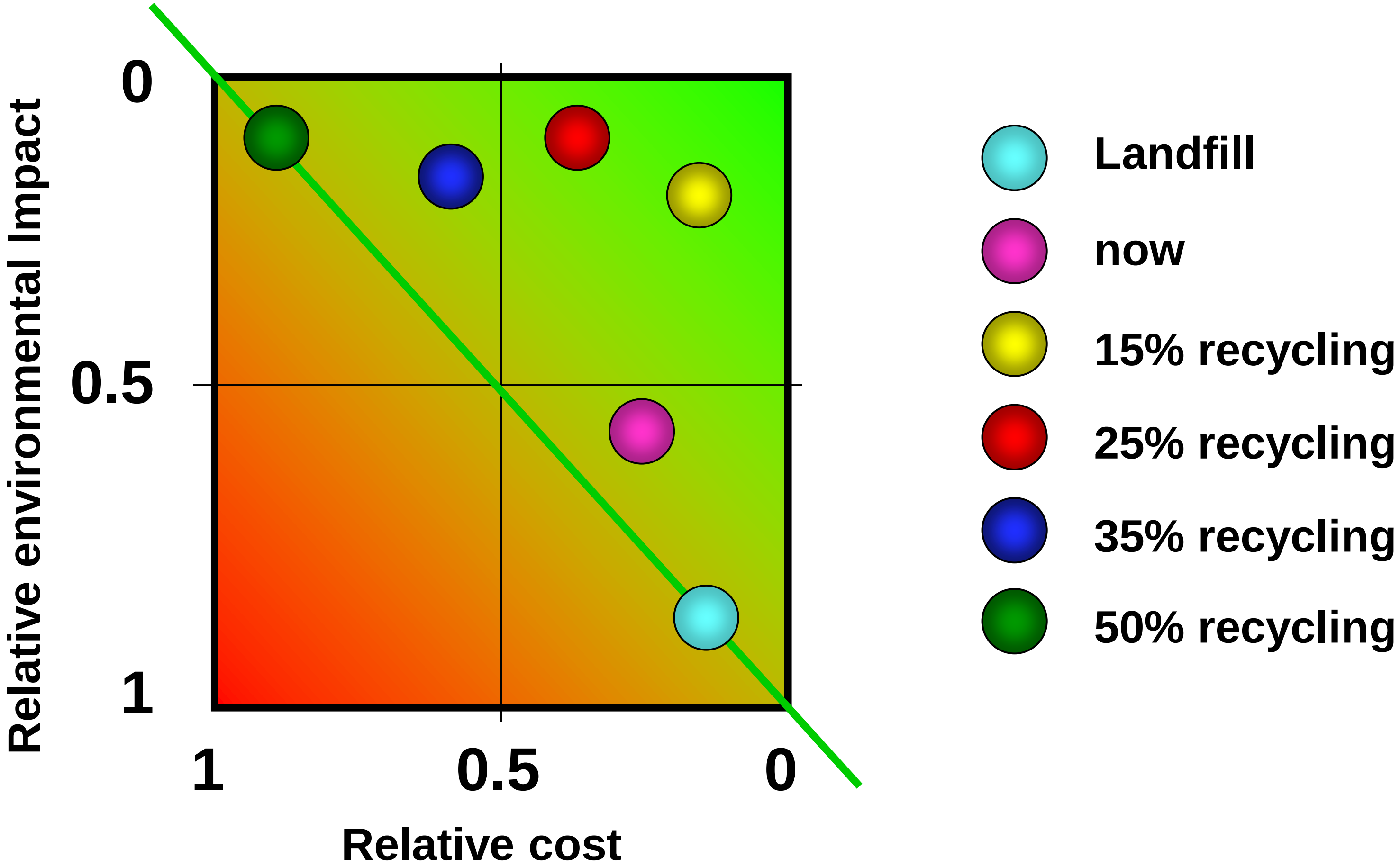
Full LCA part aggregated:

- **Energy**
- **Raw Materials**
- **Emission**
- **Tox & risk potential**

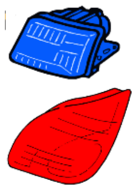
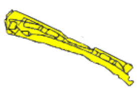
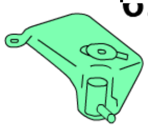
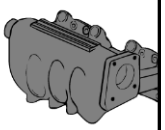
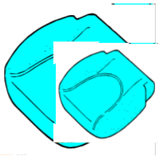
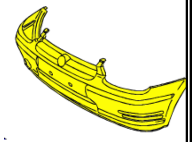
Pilot trials, working facilities



Eco-efficiency of Packaging Waste Management Options (European Context).

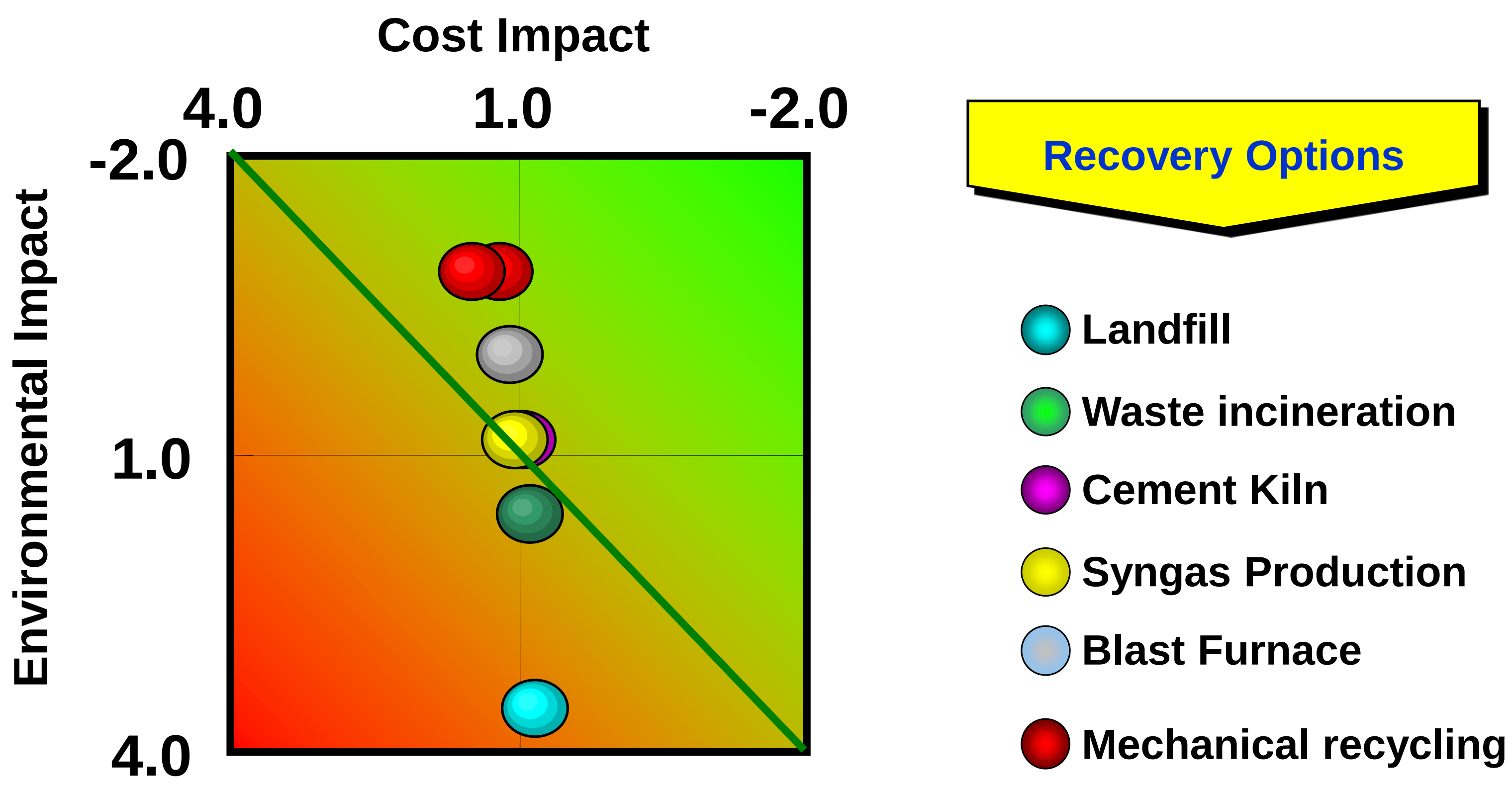


Selected Automotive Applications.

Size	small	medium					big
Part	Mirror Housing (finisher) 	Lamp 	Air system 	Washfluid Tank+liq u.   (lid)	Intake manifold 	Seat cushion 	Bumper 
Plastics	ABS Group (ind. Total mirror)	PC Group (incl. Total lamp)	PP Group (incl. dashboard)	PE Single part	PA Single part	PUR Single part	PP

- Big, medium and small parts
- Individual parts or in assembly
- Different types of plastic

Eco-Efficiency: Recovery of a Bumper (PP).



*) assuming 100 % recycled is used in the same application = **ideal case**

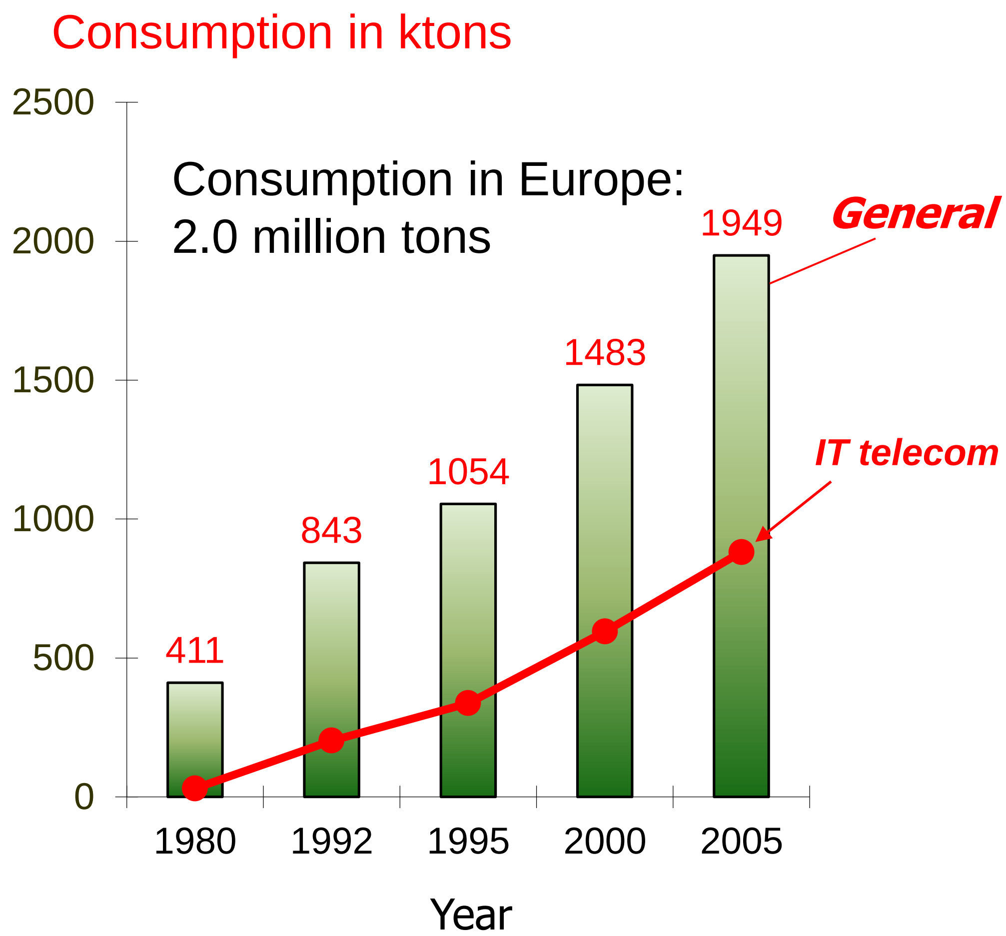
Eco PowerMate PC of NEC.

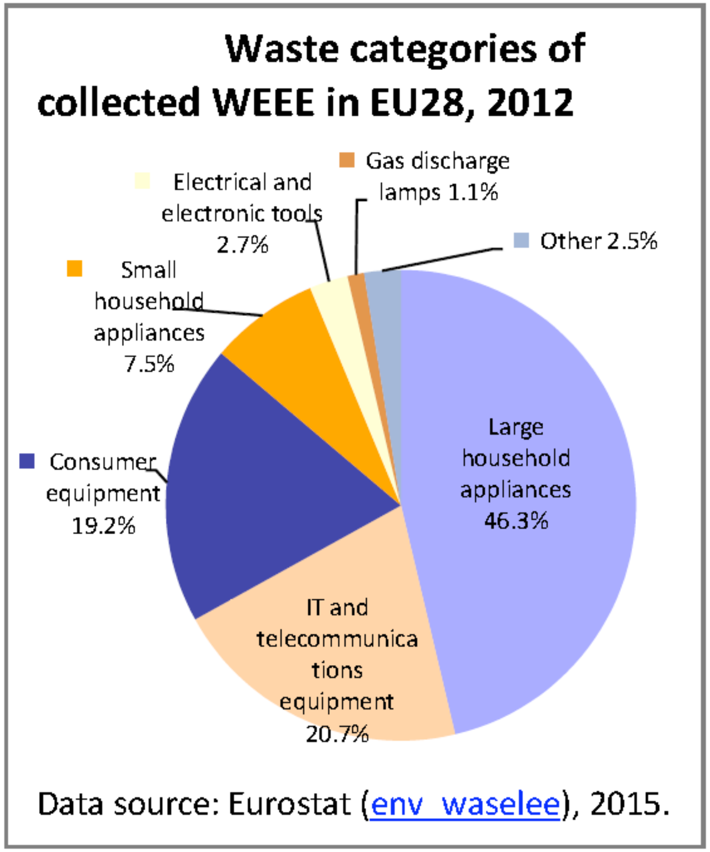
- 100% recycled plastic
- Virtually no dangerous material
- Use 1/3 of typical energy for a PC
- Equipped with a 900MHz Crusoe processor, 20GB hard disk, and 15-in.monitor.

E-Paper, E-Ink, E-Newpaper.

- E-Ink – available in different format
- 160 pixels/inch; variable dimensions
- Readiness and flexibility similar to paper
- Luminosity 5x and uses 99% less power than a LCD.

Plastics in Electrical & Electronic – Significant Increase.





Recycling: European Definition (Directive 75/442/EC on Waste, Annex IIB).

Includes: Mechanical recycling

Feedstock recycling

Chemical recycling

Non included: **energy recovery**

Case	Recycling	With energy recovery	Landfill	Pyrolysis
1(PE)	+++	++	+	
1(PET)	+++	++	+	
2(MIX1)	+++	++	+	++
2(MIX2)	++	++	+	+++
2(MIX3)	+++	++	+	++
2(MIX4)	++	++	+	+++
3(PE)	+++	++	+	
3(PP)	+++	++	+	
3(PS)	++	+++	+	
3(PET)	+++	++	+	
3(PVC)	+++	++	+	

xxx	best option
xx	intermediary option
x	worst option
	Option not assessed

Packaging & Packaging Waste Directive 94/62/EC (proposal amendment 2013/0371 (COD)).

	94/62/EC	Revision (2)	Revision (3)
Deadline	30 June 01	31 Dec 08	4 Nov 13
Overall recov	50-65%	Min 60%	
Overall recycl	25-45%	Min 55-80%	
Glass recycl	Min. 15%	Min. 60%	
Paper recycl	Min. 15%	Min. 60%	
Metals recycl	Min. 15%	Min. 50%	
Plastics recycl	Min. 15%	Min. 22.5%*	Reduction light plastic
Wood recycl	-	Min 15%	

*22.5 % by weight for plastics, counting exclusively material that is recycled back into plastics
**60% recovery of packaging plastics (lightweight plastics)

Difficult Materials to Recycle.

Thermosetting Plastics (epoxide, polyimides, polyesters)

- The recycling of thermosetting plastics is more difficult because these materials cannot be easily remolded or reformed.
- Some thermosetting are milled and then added to pure material before reworking as filler materials.

Rubber (natural or synthetic BN, SBR, etc.)

- When vulcanized, it becomes an highly crosslinked material.
- Contains further a variety of other fillers and additives.
- Most waste rubber are end use tires, which are not biodegradables.
- Waste tire can be used as fuel in some industrial applications, but they generate polluting emissions.

Composite Materials based on Plastics.

- A composite is a combination of two or more different materials that results in a superior (often stronger) product.

The Recycling Process.

Primary Processing

Plant internal recycling

Secondary or physical processing (mechanical recycle)

- Milling and washing
- Refusing and reforming

Tertiary or chemical processing (chemical recycle)

- Depolymerization
- Purification of regenerated chemicals

Cannot be used substances which are not normed !

Complex technologies are required for Plastic recycle:

- Complete identification of plastics (codes or analytical!)
- Method of Label removal, metal covering, adhesives, or insulating foam (if recycled)
- Separation of rubber and other elastomers from plastics with similar density
- Separation of metal sheets
- Identification and removal of potentially dangerous materials (battery, mercury relays, soldering alloy based on beryllium copper and lead)
- Control of plastic additives and fillers.

Plastic Selection by Sector.

Packaging Commerc.	Packaging Industry	post consumer house	Automotive	Electrical electronic	Agriculture	Building

COLLECTING AND RECYCLING SYSTEMS

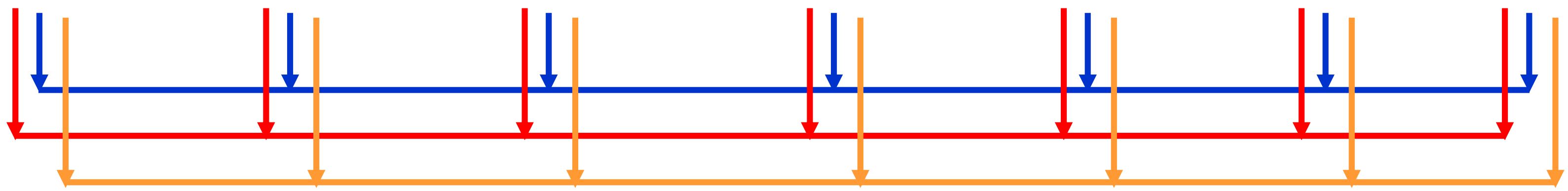
- Energy recovery
- Selected materials recycling
- Mixed material recycling

Integrated Flow in Plastic Waste Recovery.

- **Depending on use**

COLLECTION AND CLASSIFICATION

Packaging Commerc.	Packaging Industry	post consumer house	Automotive	Electrical electronic	Agriculture	Building



- **Depending on material**

Recycling of mixed materials

Recycle of selected materials

Energy recovery

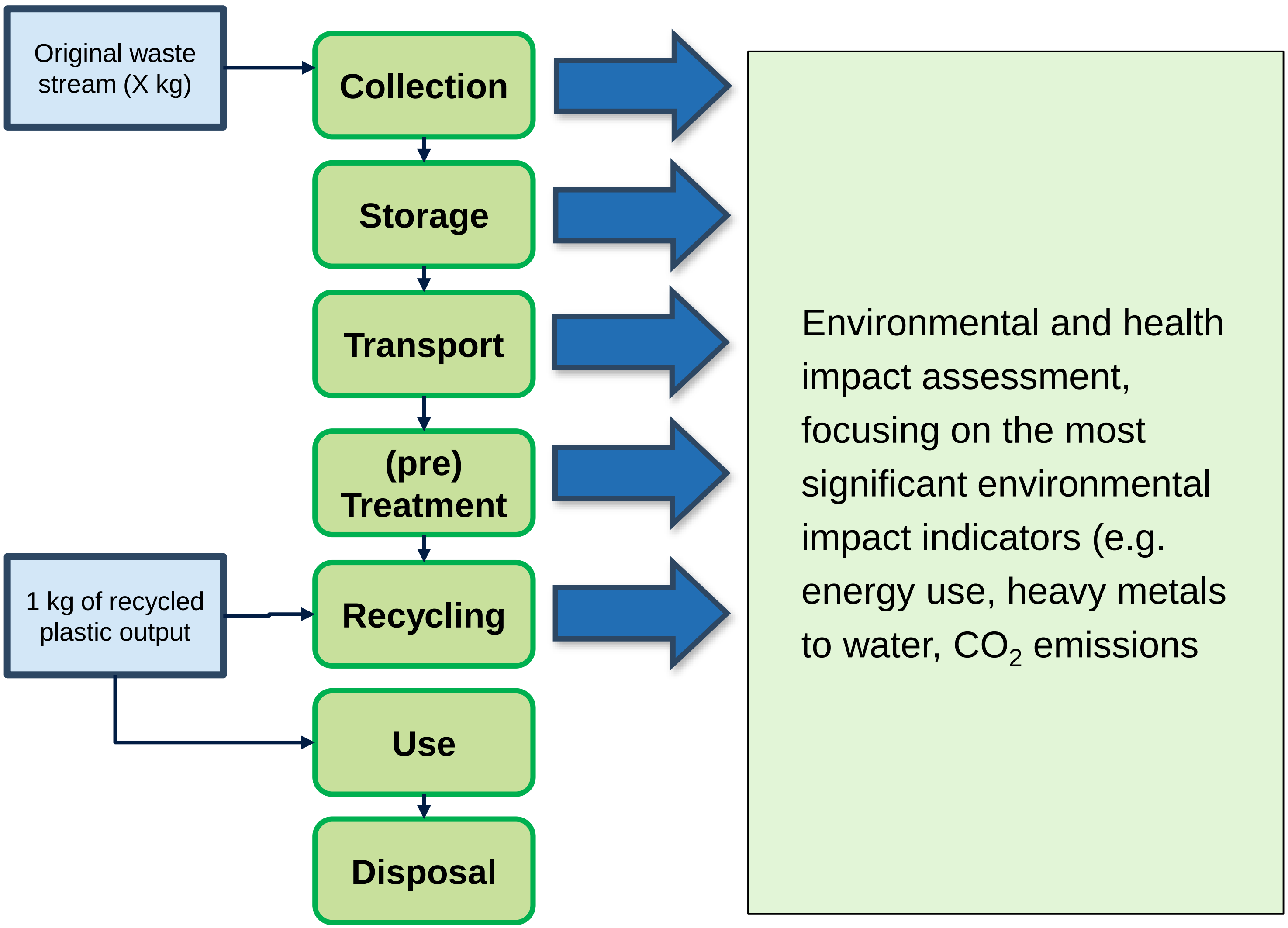
RECYCLING FROM

Plastics related to use sector

TO

Plastics focused on materials

Environmental Impact of Plastic Recycling.



Contribution to the reduction (-) or increase (+) of GWP compared to landfill (kg_{CO2eq} per kg).

Scenario	Collection/sorting	Treatment	Process	Landfill	Total
Bottle recycling	0.1	0.54	-1,27	-0,31	-0.95
Film recycling	0.1	*	-0.48	-0.36	-0.74

Impact category	Unit	Bottle to bottle recycling, UK	Bottle recycling, UK	Bottle recycling, China
High-density polyethylene (HDPE)				
Abiotic depletion	kg Sb eq	0.242	0.326	0.345
Climate change	kg CO_2 eq	31.5	32.9	35.9
Photo-oxidation	kg C_2H_4 eq	0.01	0.0352	0.0395
Eutrophication	kg PO_4^{3} eq	0.0116	0.0051	0.011
Acidification	kg SO_2 eq	0.0671	-0.0513	0.0109
Human toxicity	kg 1.4-DB eq	3.66	3.51	5.24
Freshwater ecotoxicity	kg 1.4-DB eq	0.523	0.732	0.763
Polyethylene terepthalate (PET)				
Abiotic depletion	kg Sb eq	0.445	0.573	0.606
Climate change	kg CO_2 eq	54.1	68.3	73.5
Photo-oxidation	kg C_2H_4 eq	0.026	0.0455	0.0528
Eutrophication	kg PO_4^{3-} eq	0.0222	0.0655	0.0754
Acidification	kg SO_2 eq	0.131	-0.00779	0.0973
Human toxicity	kg 1.4-DB eq	7.15	17.4	20.4
Freshwater ecotoxicity	kg 1.4-DB eq	1.16	2.73	2.78

Vollni V., Schmied M. (2000) Assessment of plastic recovery options.

«Consorzi di Filiera».

Italian Legislation have introduced eight «Consorzi di filiera» with reference to specific commercial **categories.**

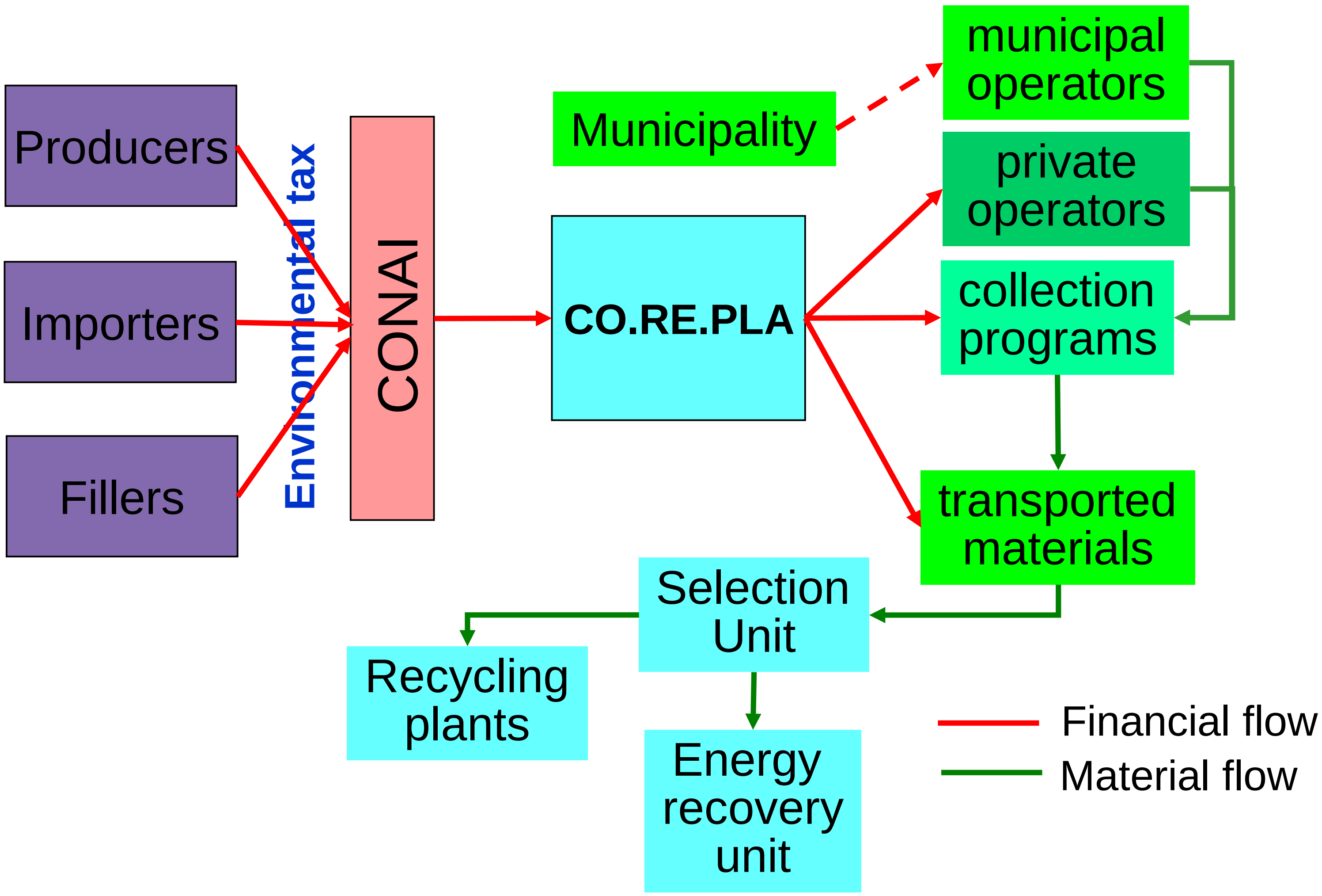
CNA	Consorzio nazionale acciaio *www.cna.it*
CIAL	Consorzio imballaggi alluminio *www.cial.it*
COMIECO	Consorzio recupero e riciclo degli imballaggi a base cellulosica w*ww.comieco.it*
RILEGNO	Consorzio nazionale recupero e riciclaggio degli imballaggi di legno *www.rilegno.it*
COREPLA	Consorzio nazionale per il recupero degli imballaggi di plastica *www.corepla.it*
COREVE	Consorzio recupero vetro *www.coreve*
COBAT	Consorzio recupero batterie *www.cobat*
COOU	Consorzio obbligatorio oli usati *www.coou*

Italian Initiative.

CO.RE.PLA is a national consortium for collection, recycling, and recovery of plastic package wastes. Start in 1997 to coordinate the following processes:

- Plastic waste collected by municipal services
- Collection of secondary and tertiary plastic containers
- Selection of types of used packages
- Recycle and recover wastes from collected packages.
- Organize the sale of plastic recycled.

Recycling System Organization (It).



Consortium Composition and Headquarters.

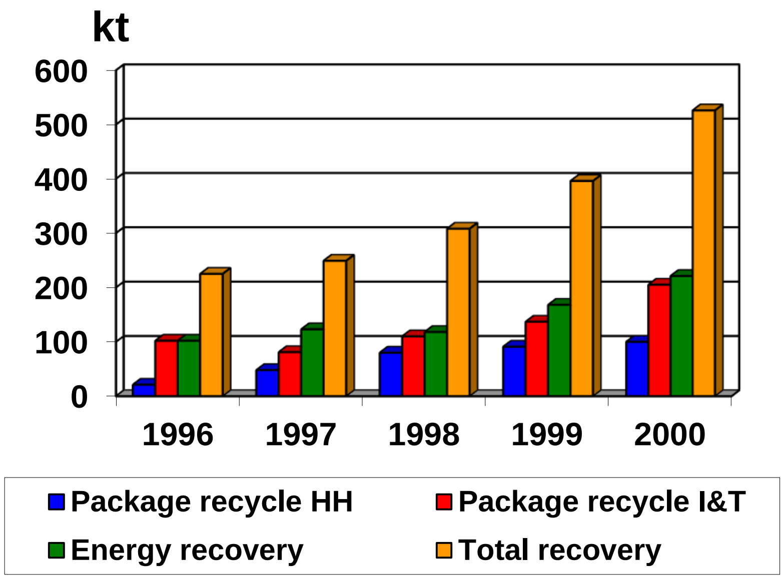
CATEGORY	MEMBER NUMBER	% SECTOR
FEEDSTOCK PRODUCTORS	97	91
PACKAGING PRODUCTORS	1902	86
PACKAGING USERS	26	35
RECYCLING COMPANIES	45	80

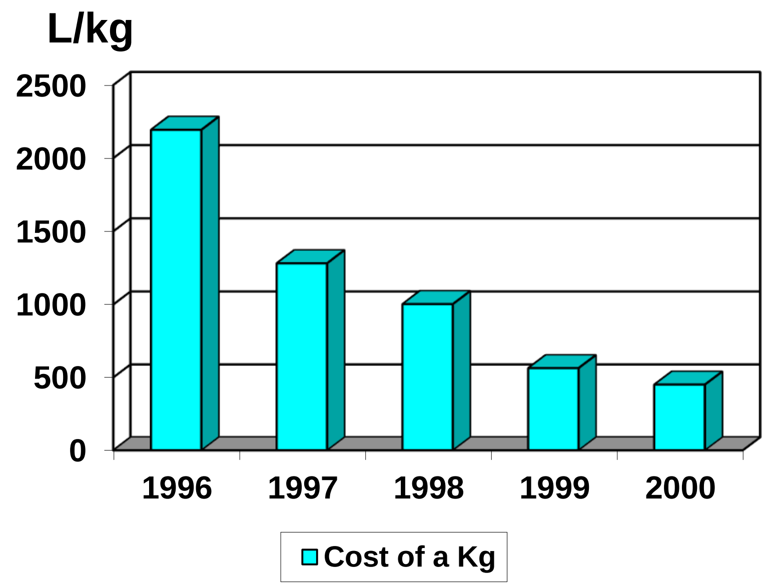
18 Selection centers

47 Collection centers

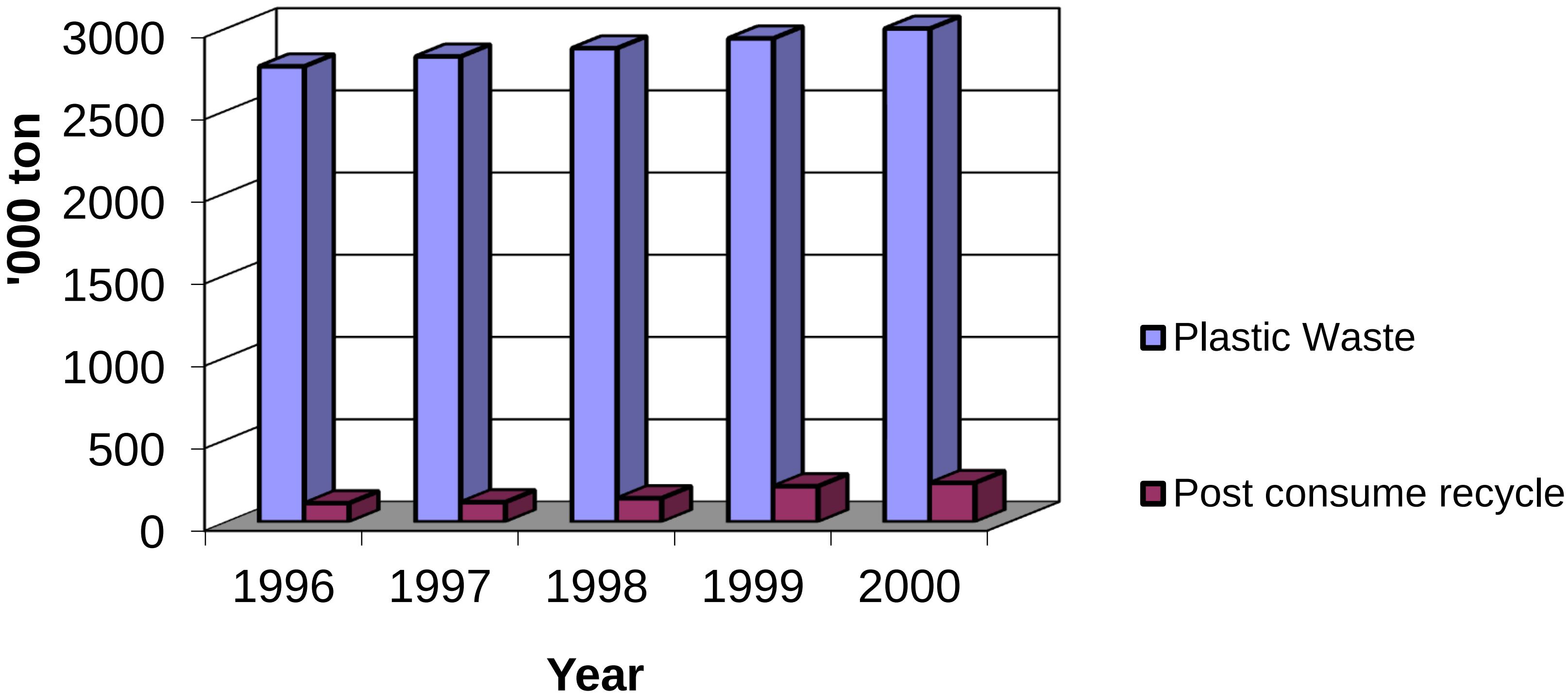
A grid of 50 centers for secondary and tertiary packaging of plastic.

Amount and Costs of Recycling.

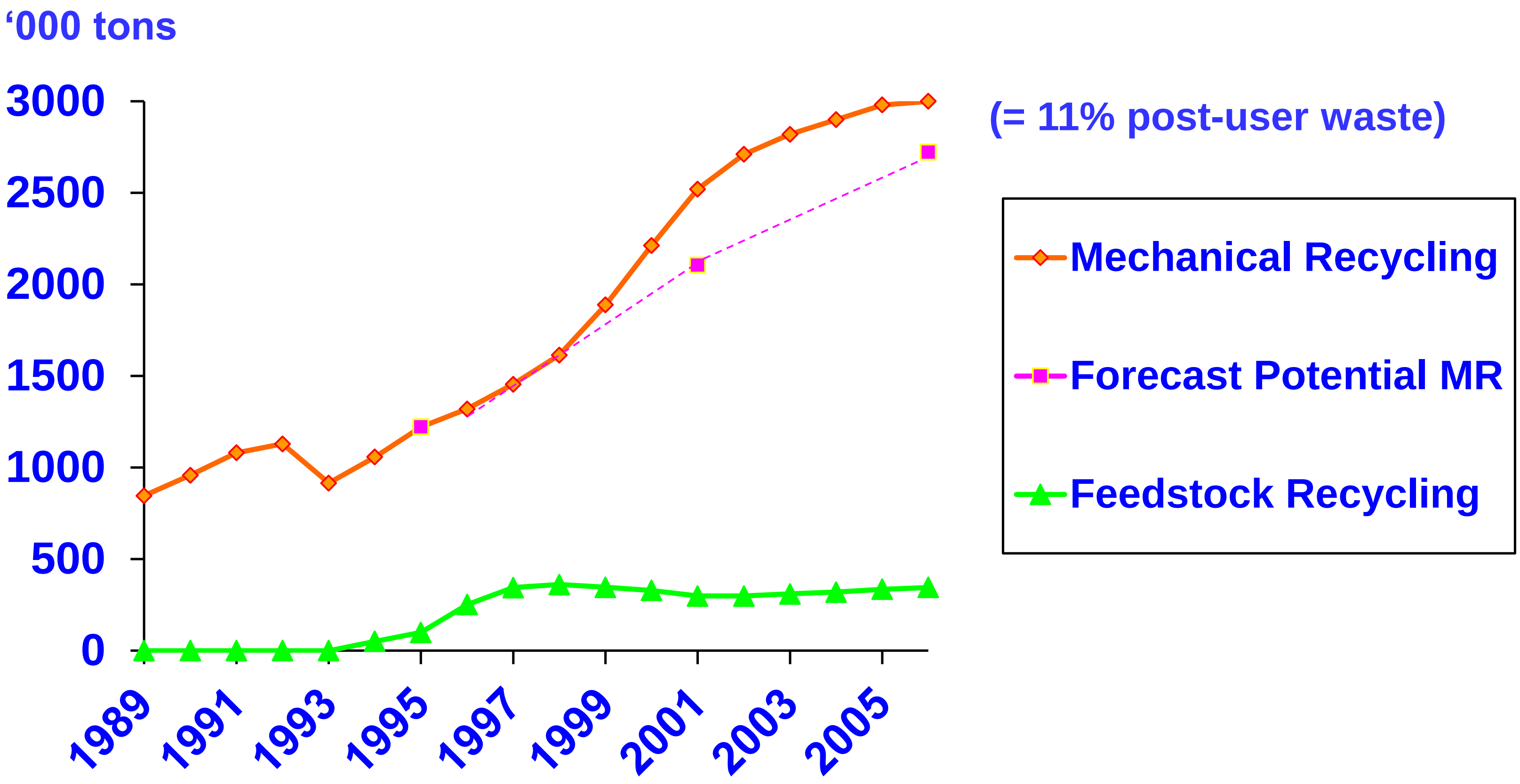




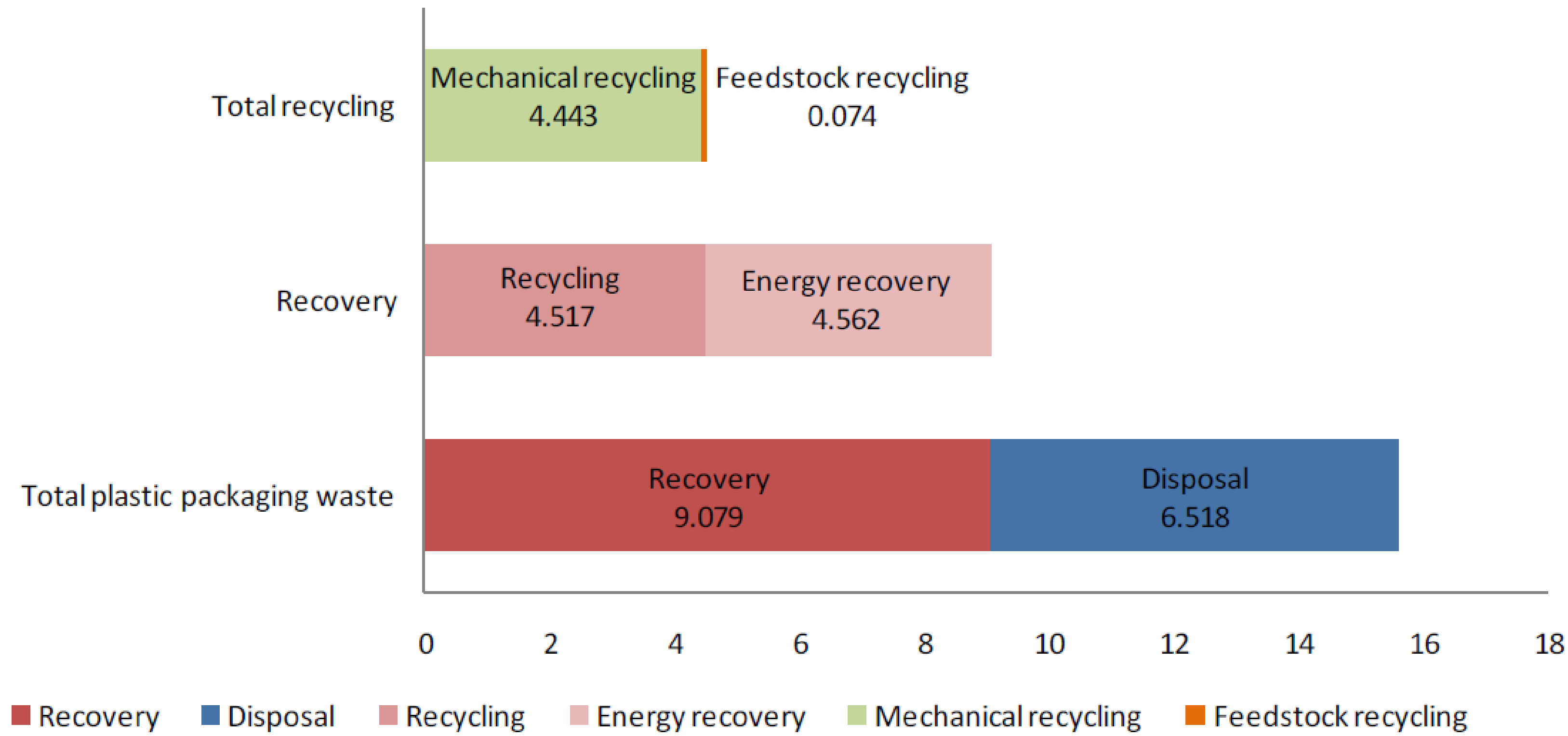
Plastic Recycling.



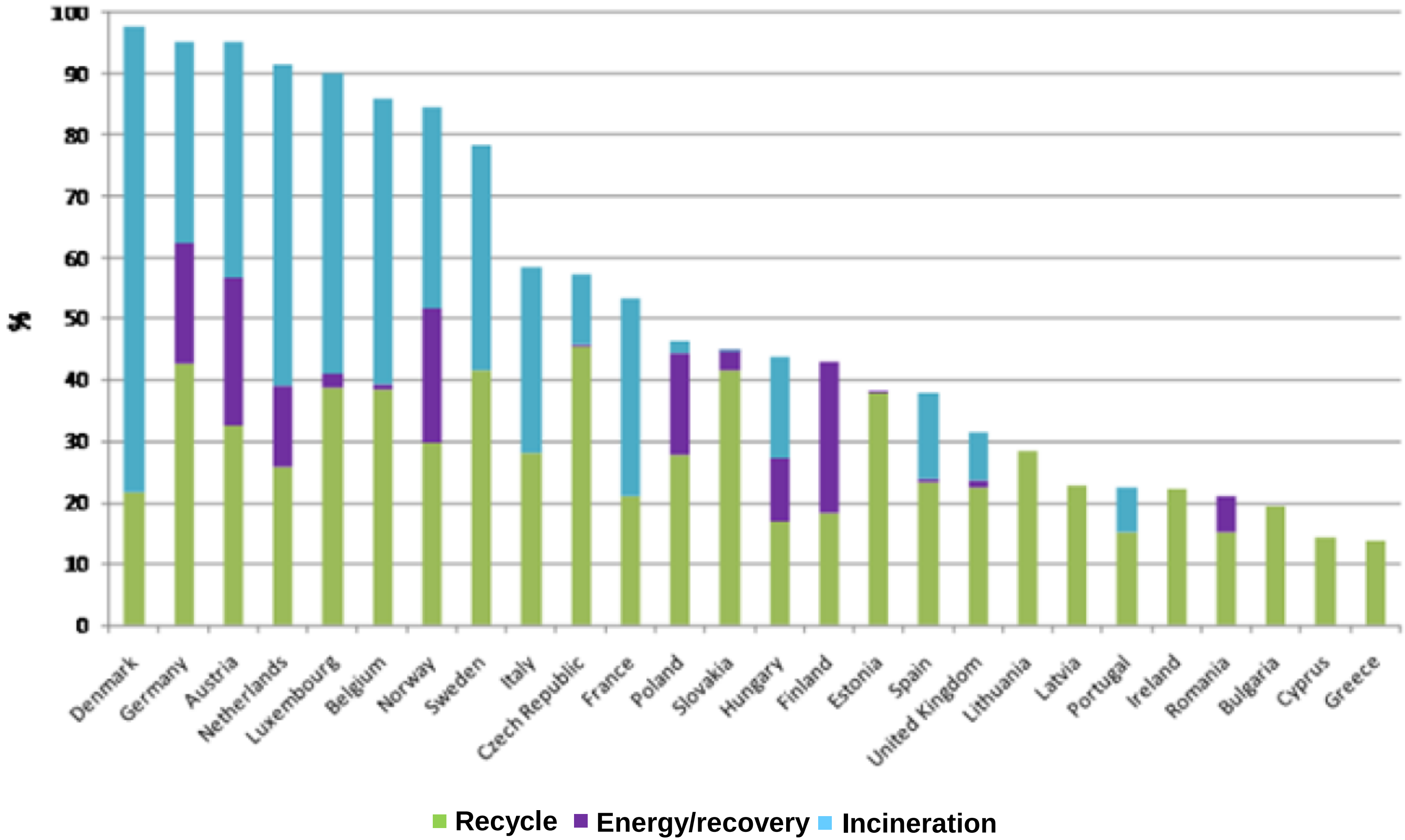
Recycling Progress in UE.



Treatment of Total Plastic Packaging Waste in EU-27 (Mt) (2008).



Treatment of Total Plastic Packaging Waste by EU-27, 2007-9 (%).



Practical Development in the Recovery of Plastic Wastes

- Automatic Selection (labeling/identification)
- Integral Treatment MSW
- Identification of best practices for mechanical recycling*
- Carbon substitute (plastics/paper)
- Recycling Processes with Solvent (PVC, PO)
- Recycle as monomer (PET, nylon)
- Recycle of other materials (PVC, mixed)

The Recycling of Plastics is Carried out in a Five Step Process.

Step 0 - Plastics collection

This is done through roadside collections, special recycling bins and directly from industries that use a lot of plastic.

Step 1 - Manual and/or mechanical sorting

At this stage nails and stones are removed, and the plastic is sorted into three types: PET, HDPE and 'other'.

Step 2 - Chipping

The sorted plastic is cut into small pieces ready to be melted down.

Step 3 - Washing

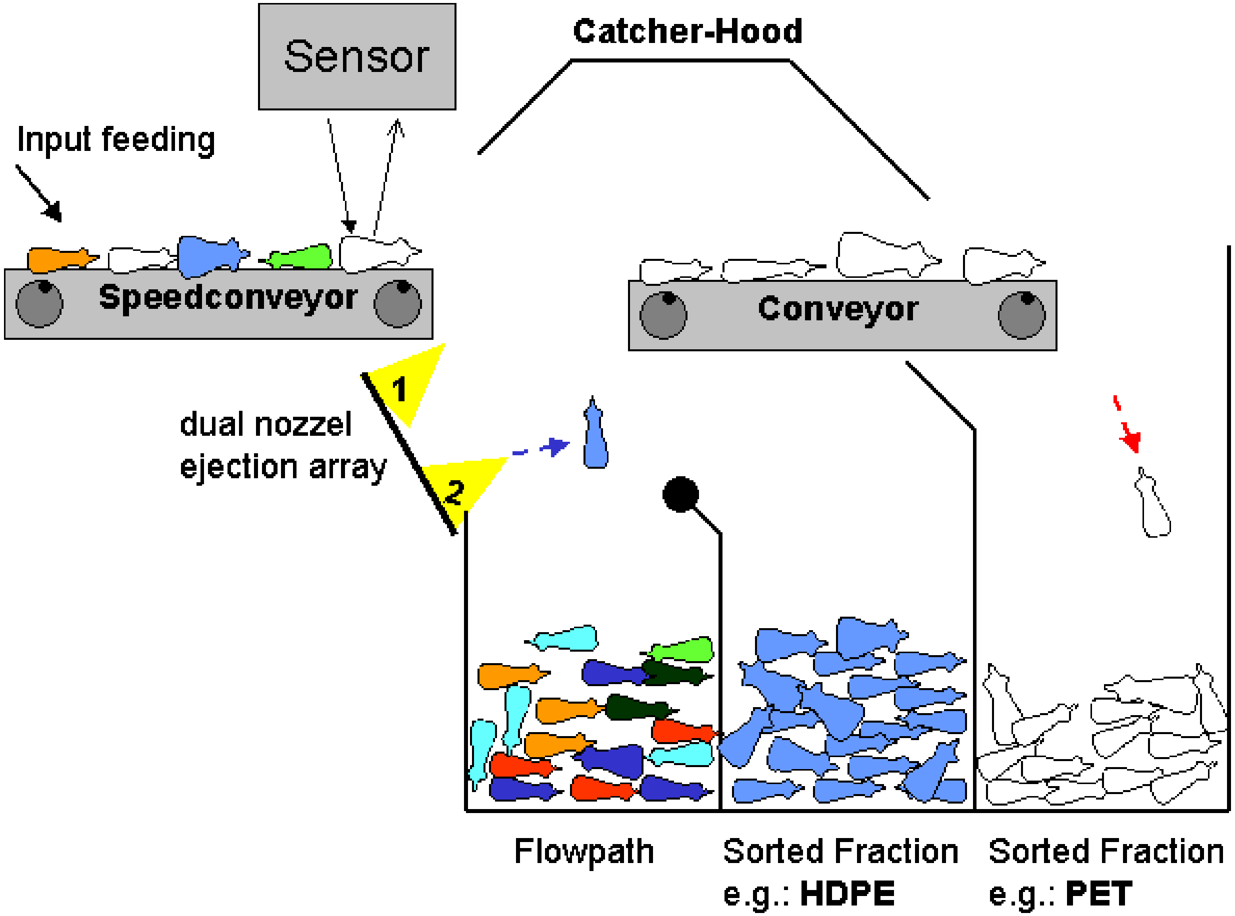
This stage removes contaminants such as paper labels, dirt and remnants of the product originally contained in the plastic.

Step 4 - Pelleting

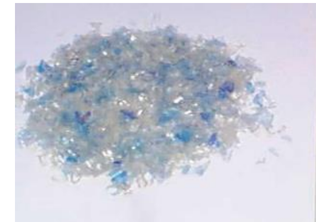
The plastic is then melted and extruded into small pellets ready for reuse.

Step 5 – Packaging. Recycled plastic is put into containers for packaging and labeled with information on type of material, density and melt index.

Sorting by Optical Sensor.



Steps for “Bottle to Bottle”.



Collection/ Sorting → ***Baled Bottle*** → ***Grinding Washing*** → ***Flake***

Flake → ***Cleaning Process*** → ***BTB Pellet***

Features of Mechanical Recycling.

Different plastics not compatible

Properties can deteriorate

Closed loop recycling is limited:

PVC windows	⇨	windows
PET bottles	⇨	fiber applications
PP bumpers	⇨	plant pots
PE food contact film	⇨	garbage bags
PE film	⇨	pipes
PP closures	⇨	non-critical car parts

Mechanical Recycling.

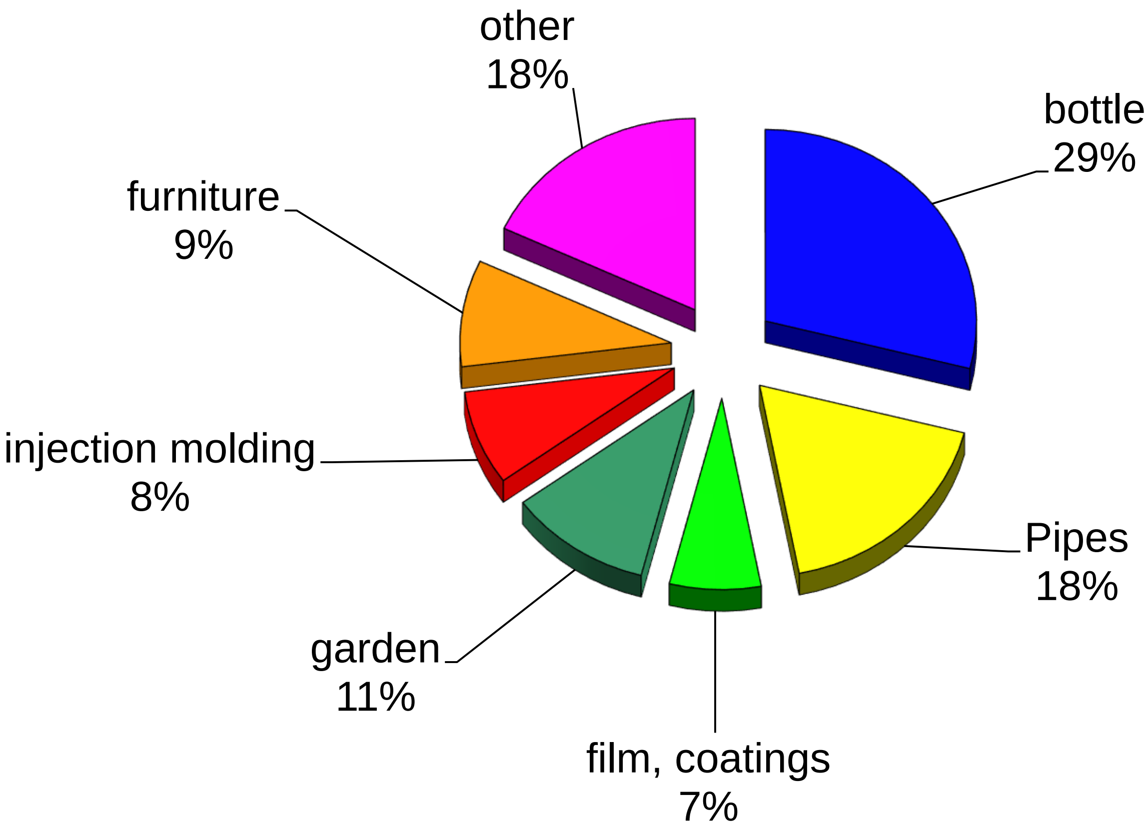
Potential limitations:

- Processing specifications
- Color, odor, food contact considerations
- Substitution ratio
- Price vs. virgin material

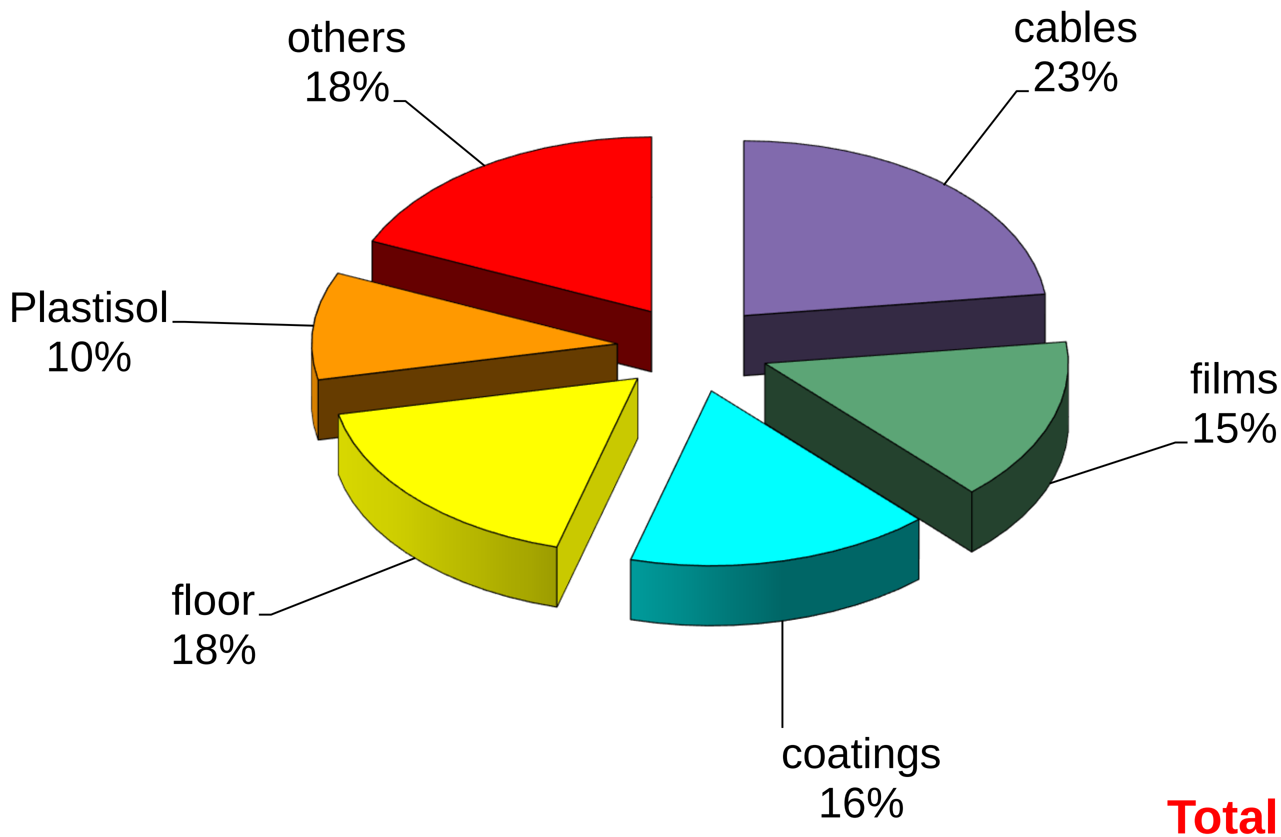
Future trends:

- Improved sorting technologies
- Vinyloop process
- Other solvent processes
- Wood composites

Final Uses of Recycled HDPE Bottles.



Market of PVC Composites (Kton/anno – 2017).

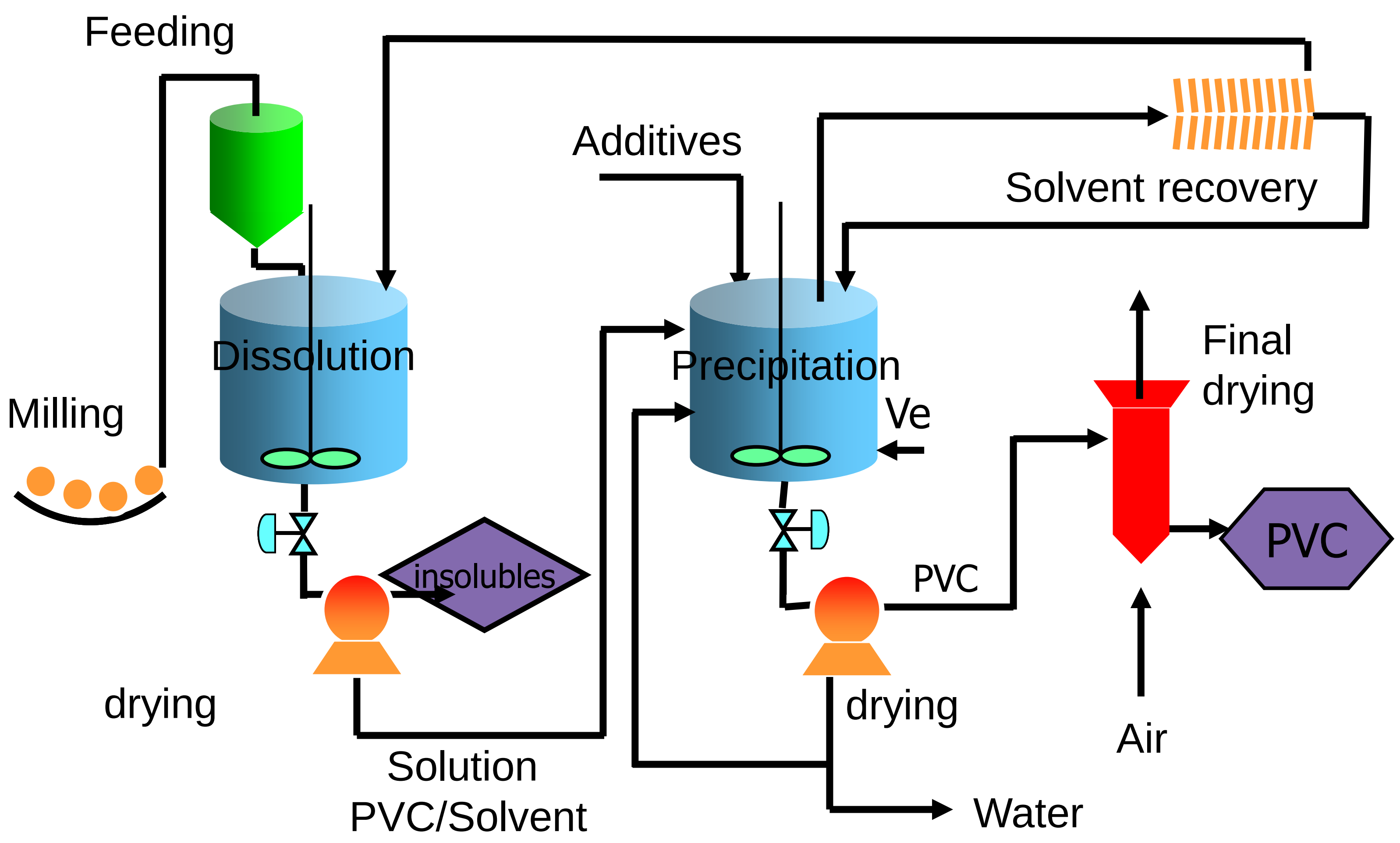


Total:
4091 Kton
composites/year

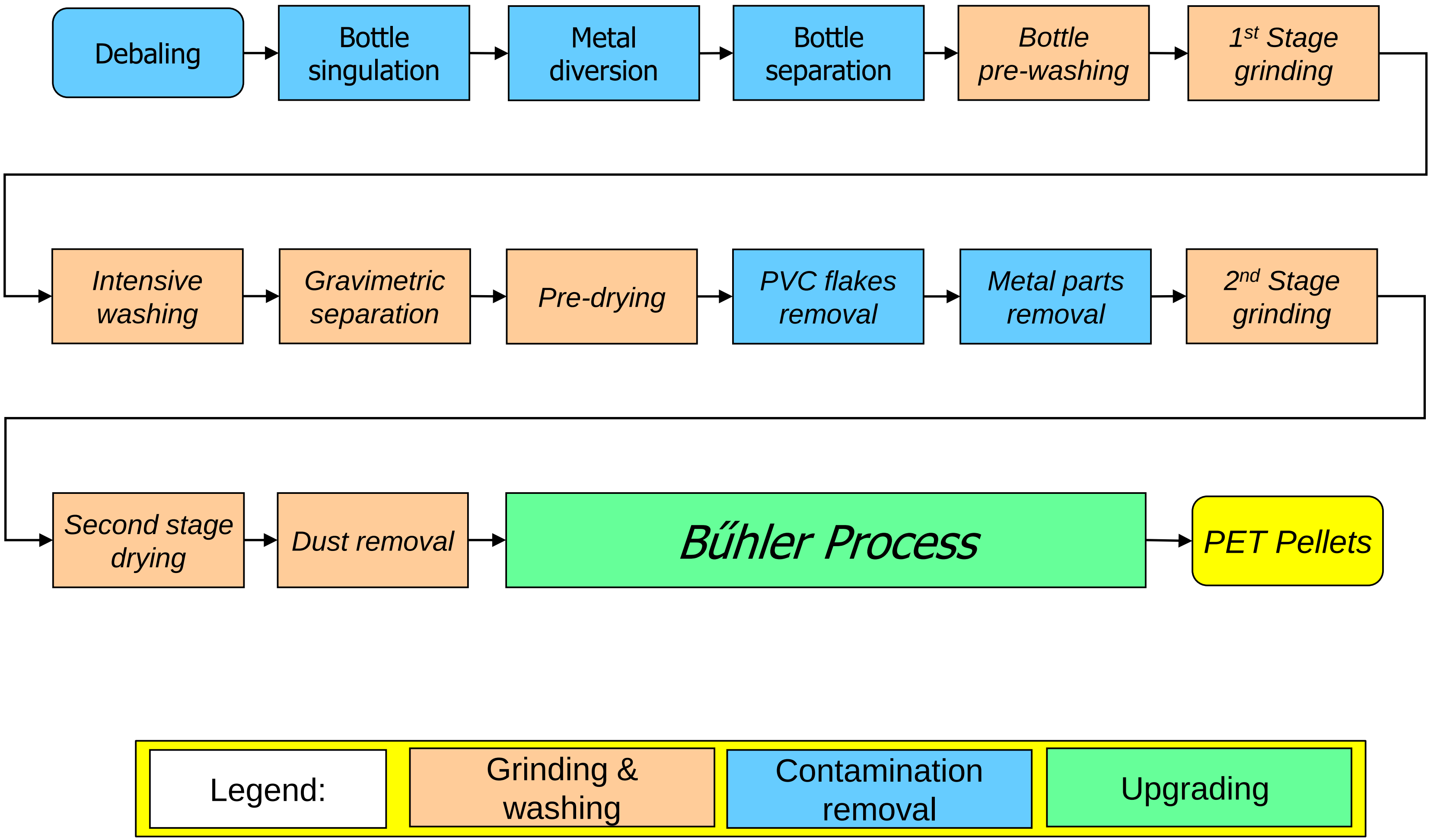
Basics of PVC Recycle.

- The process of PVC Mechanical Recycle uses a solvent to separate PVC from fibers or other materials
- The process operates in a close cycle
- Batch process
  - Dissolution
  - PVC precipitation
  - Solvent recycle
- PVC Recovering as PVC Composites able to be Converted in final products.

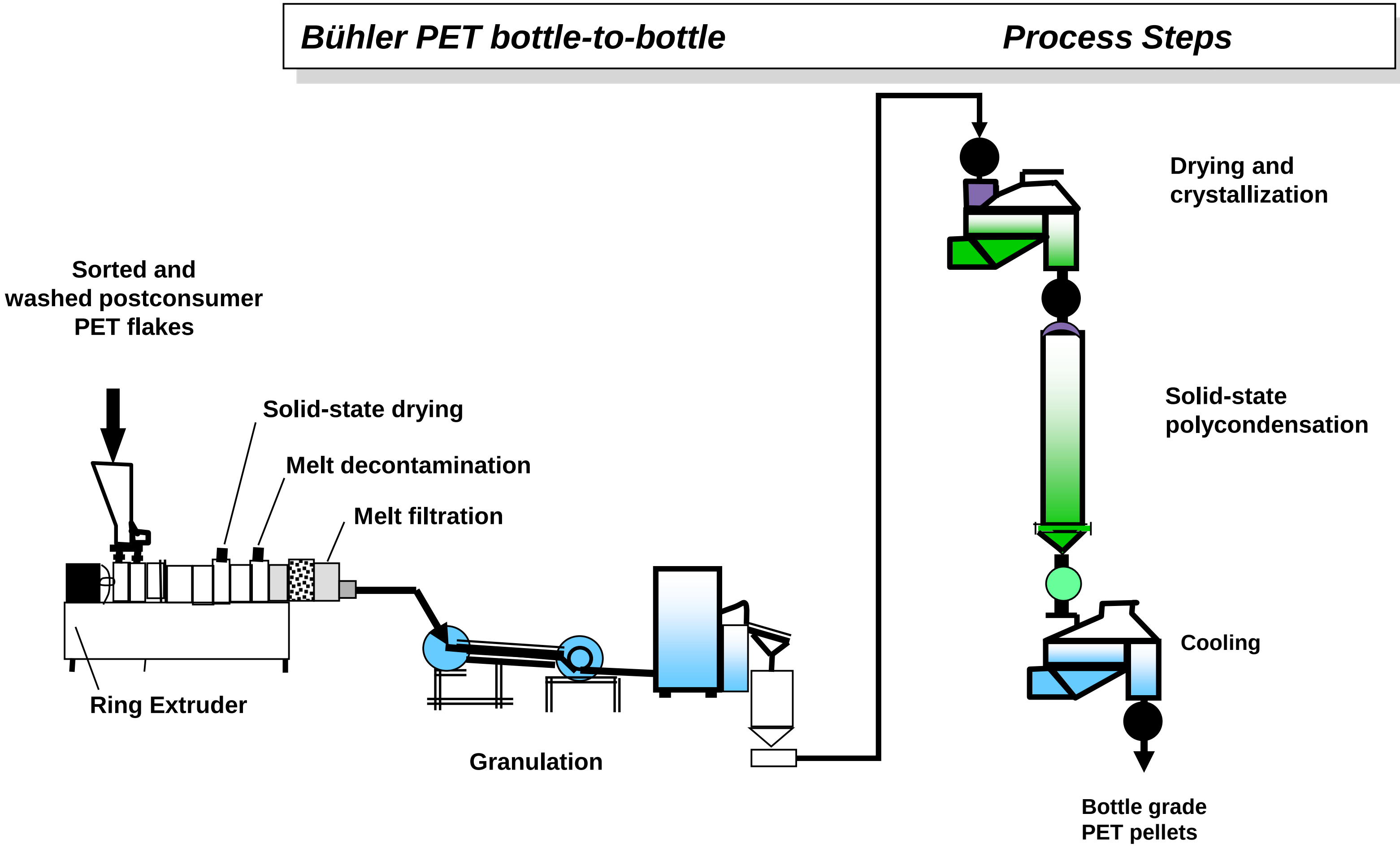
Summary of PVC Recycling Process.



Steps in the PVC Recycling Process.

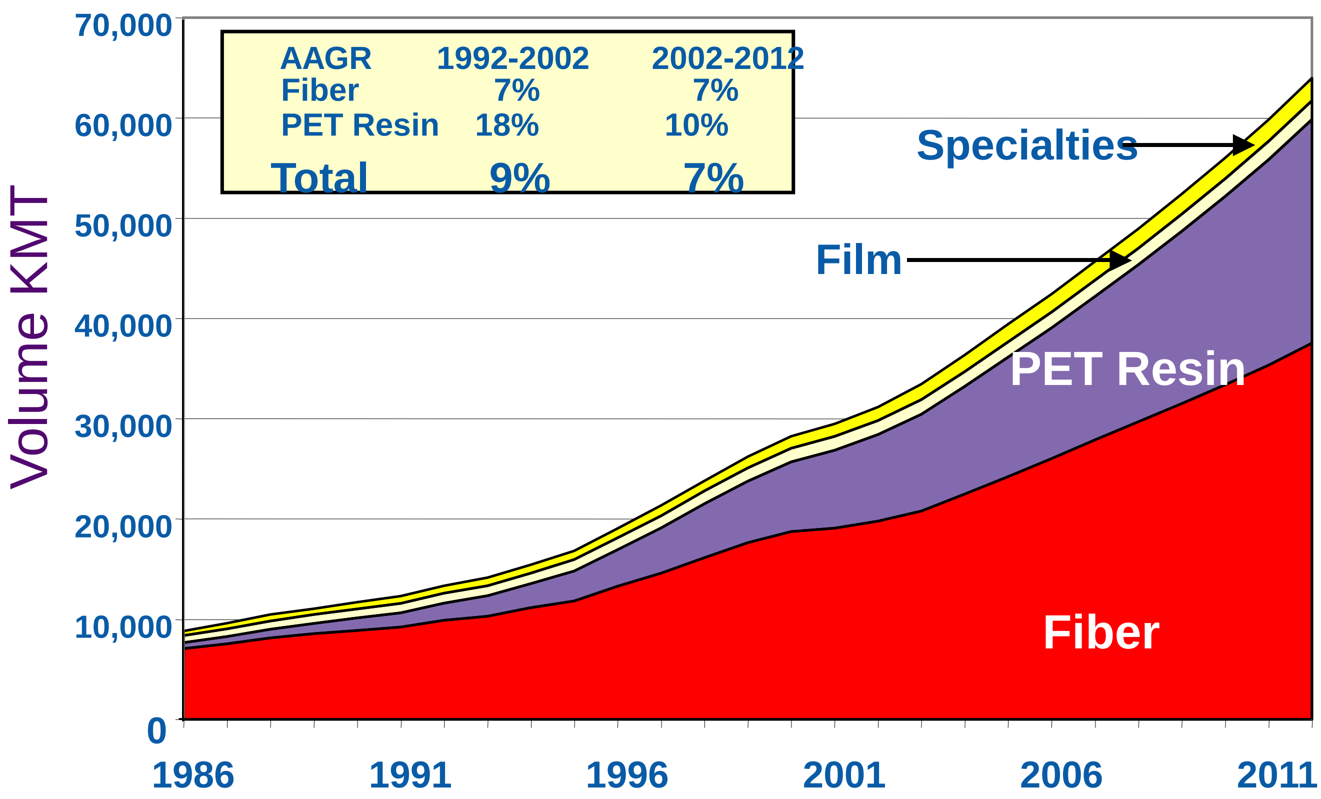


Bülher Process.



In the Ring Extruder the material is initially degassed in the solid-state

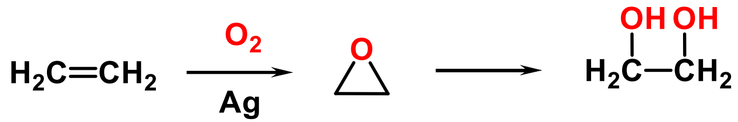
World Polyester Demand.



Raw Materials for PET Monomers

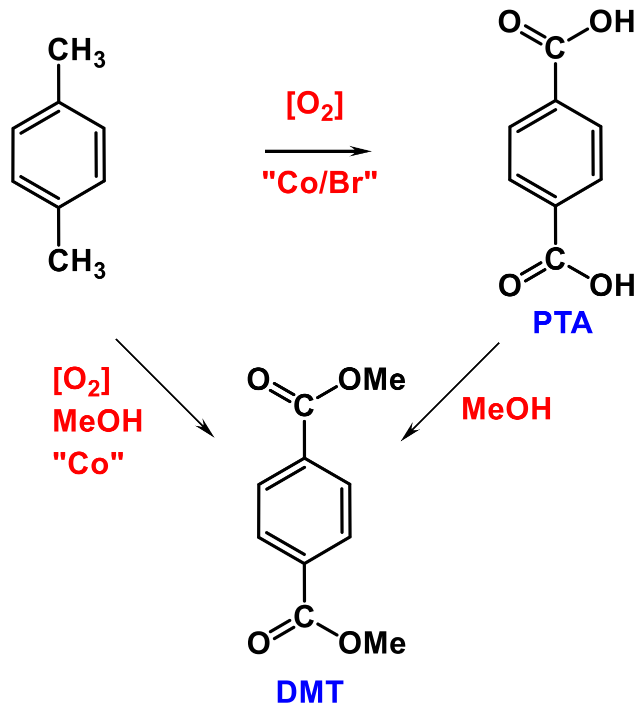
Temperature 175-225 ºC.
Pressure 1500-3000 kPa (15-30 Atm)

Production of Ethylene Glycol (EG)



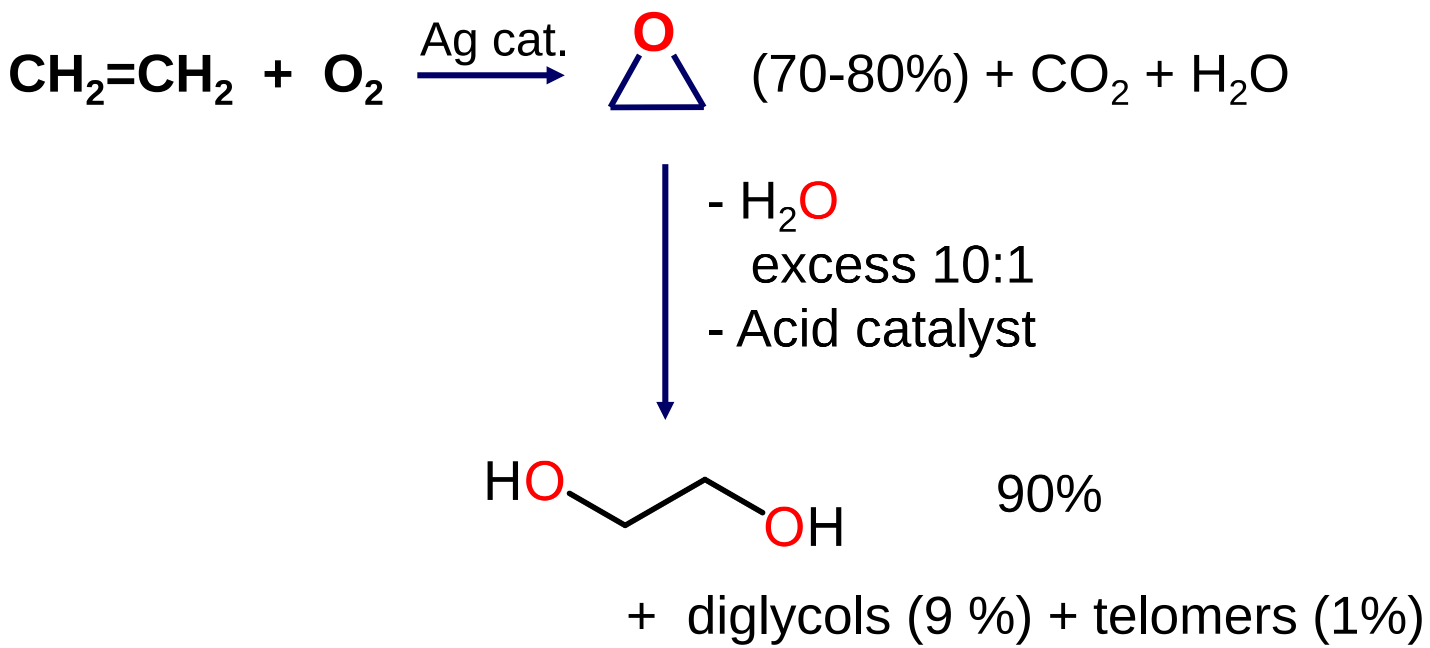
Temperature 150-200ºC.
Pressure 500 psi (ca.. 35 bar)

Production of PTA and DMT



PTA = terephthalic acid
DTM = methyl terephthalate

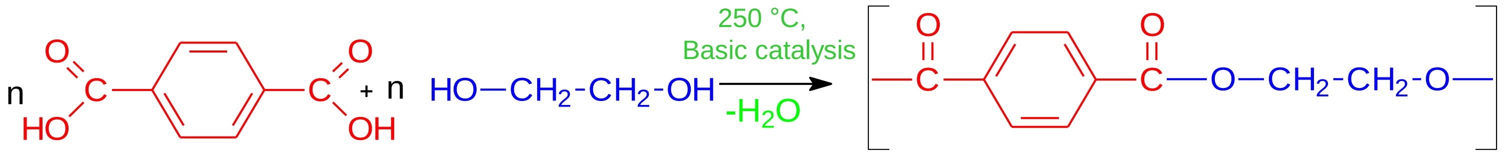
Production of EG Monomer.



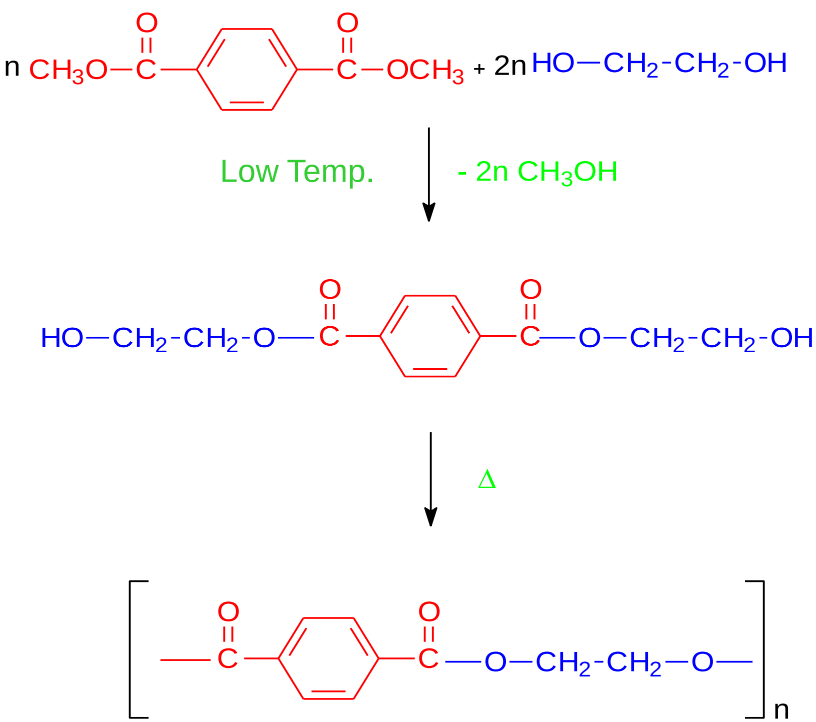
Oxygen is used in the first stage, both reactions are exothermic; EO is recovered from water, then distilled. The crude glycol mixture is further fractionated.

Polyester Chemistry - Esterification of PET.

Step growing polymerization - *Polycondensation*

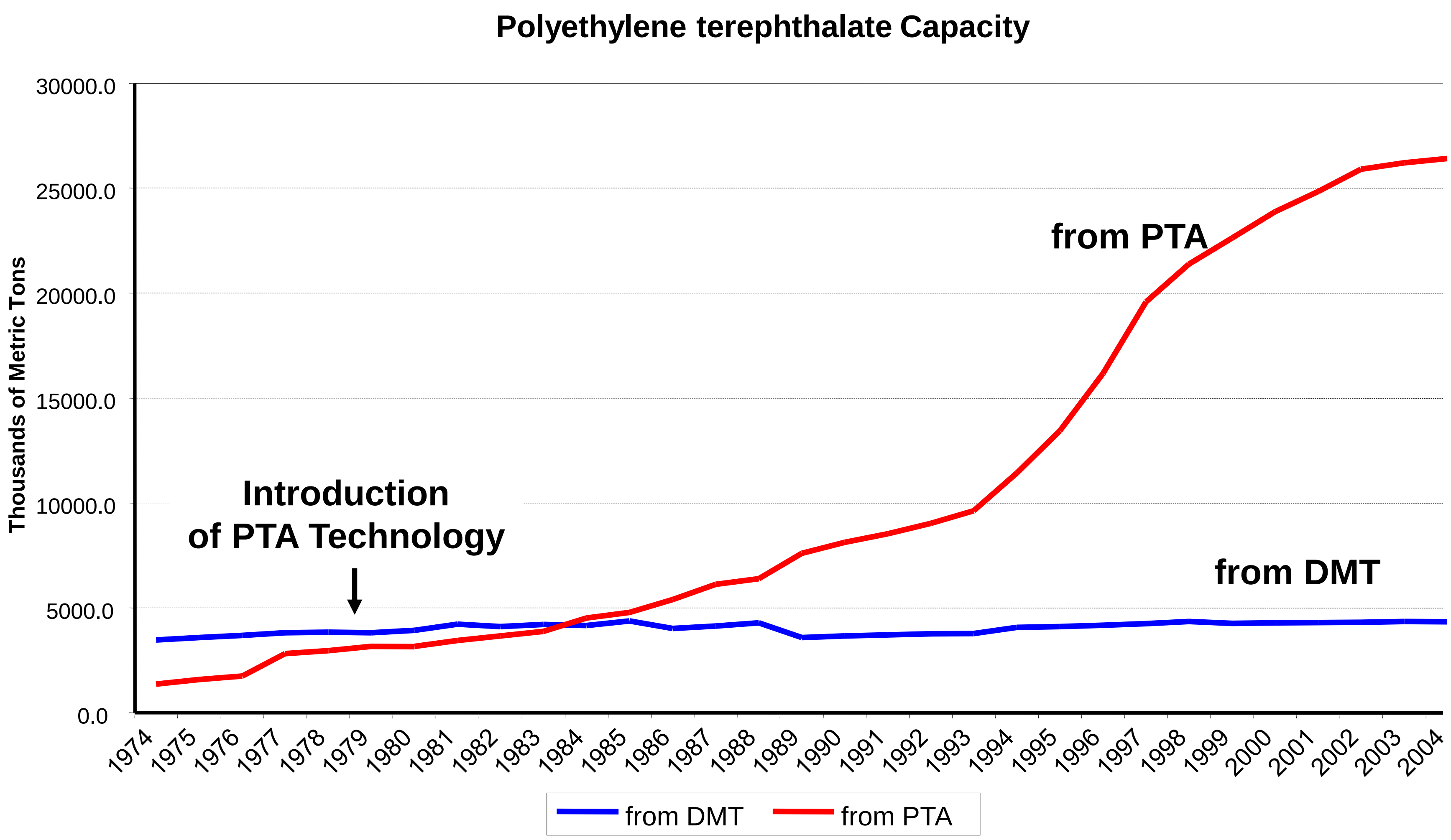


Interexchange between Esters - *Transesterification*

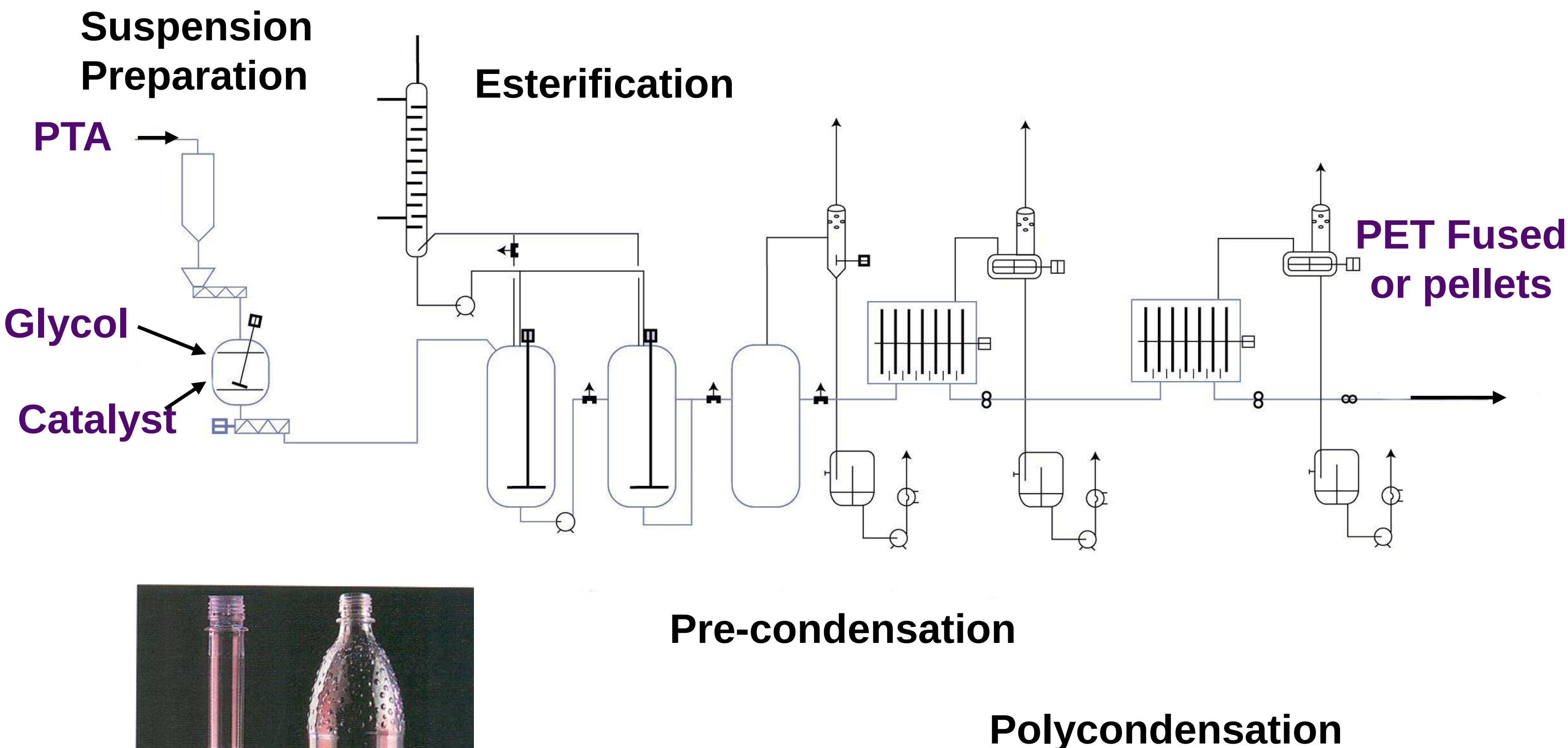


Relevant use of energy, low emissions: ~ 0.7 – 3.9 g/kg product; most emissions are reduced through optimization of cooling towers.

PTA Technology Preferred (Amoco).



PET Manufacture Process.

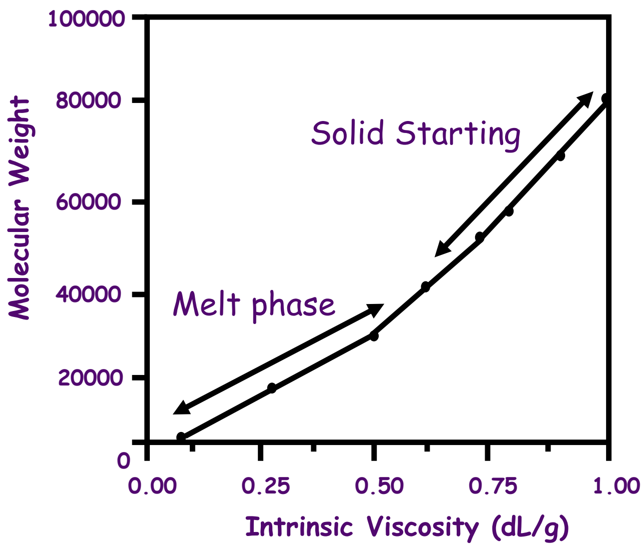


Intrinsic Viscosity (IV) and Molecular Weight (MW).

IV	Grade ofl PET	MW
0.50	**Fibre Grade**	**29,000**
0.60	**Filament Grade**	**36,000**
0.70	**Bottle Grade (Low IV)**	**47,000**
0.80	**Bottle Grade (Med IV)**	**57,000**
0.90	**Bottle Grade (High IV)**	**67,000**
1.0	**Tyre Cord Grade**	**78,000**

Higher IV

- Increases strength (pressure containers)
- Increases stress crack resistance (pressure containers)
- Reduces crystallization rate (clear preforms)



Chemical Recycling of PET.

Three main routes to the chemical recycling of PET :

Glycolysis

The conditions used are more «mild» than methanolysis or hydrolysis, but is less effective to treat waste colored and/or mixed materials. The products are commonly oligomers which can be used to make fresh PET, or as precursor of polyurethane foams or unsaturated polyesters.

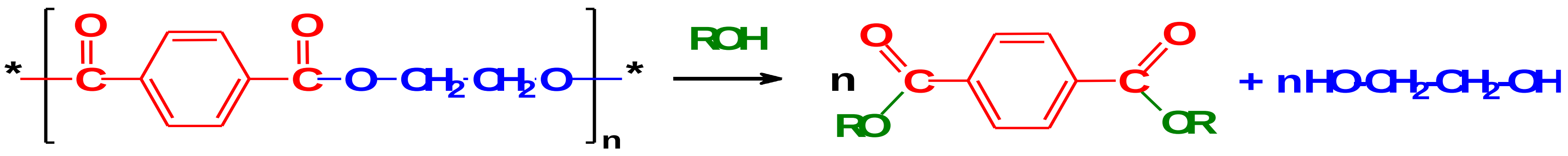
Hydrolysis

Need drastic conditions, in particular as concerns T and P owing to the low wettability of PET. When carried out in basic media (saponification), the reaction is easier and allow to obtain salts of terephthalic acid from which PTA can be recovered by acidification. High capital investments are needed because of the high number of operations and the drastic conditions of the process, which however allows to treat colored and/or mixed wastes.

Methanolysis

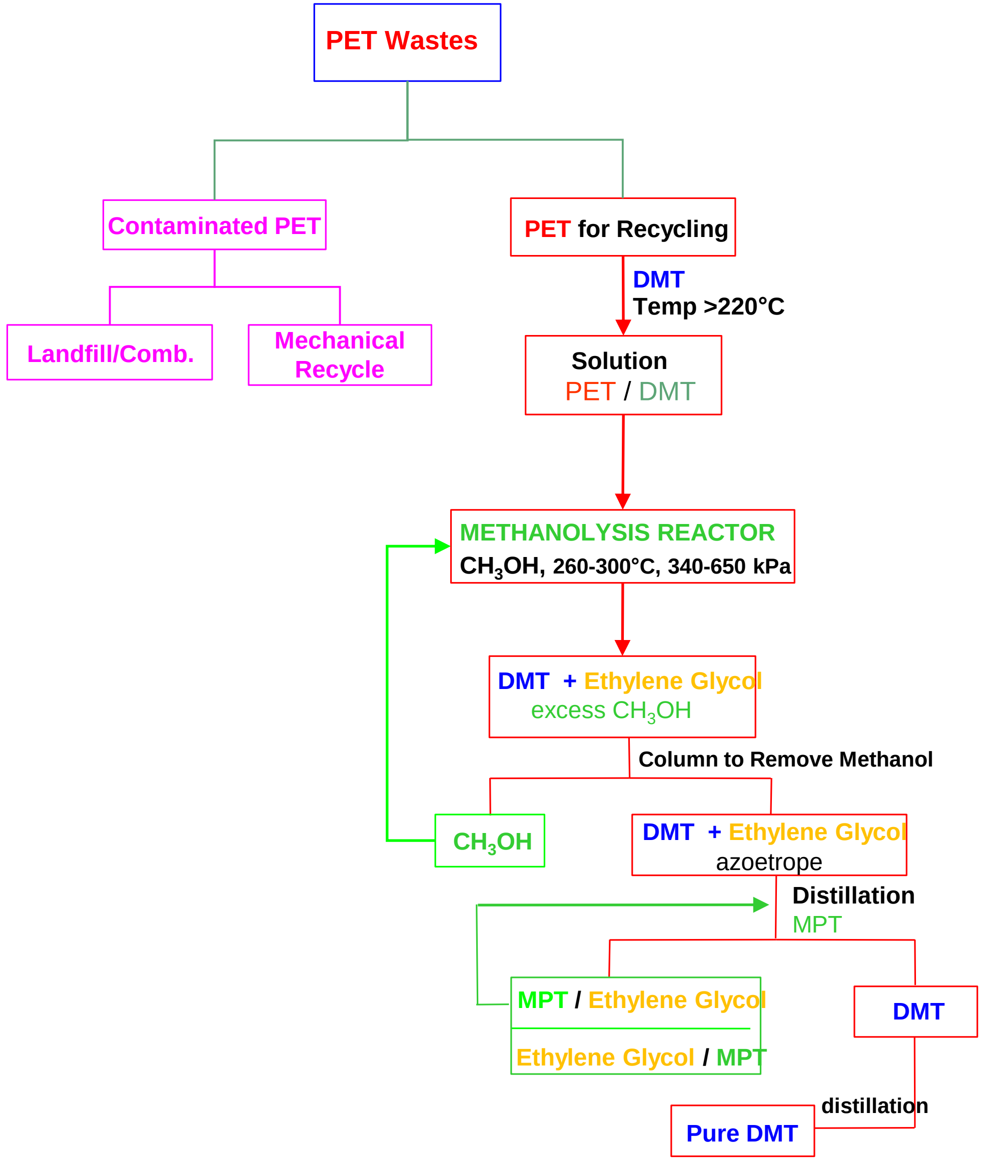
Consists in a transesterification (commonly base catalyzed) and need drastic operative conditions. dimethylterephthalate (DMT) is the final product, useful in the direct preparation of PET, and can treat colored or mixed samples.

Polyester Regeneration.

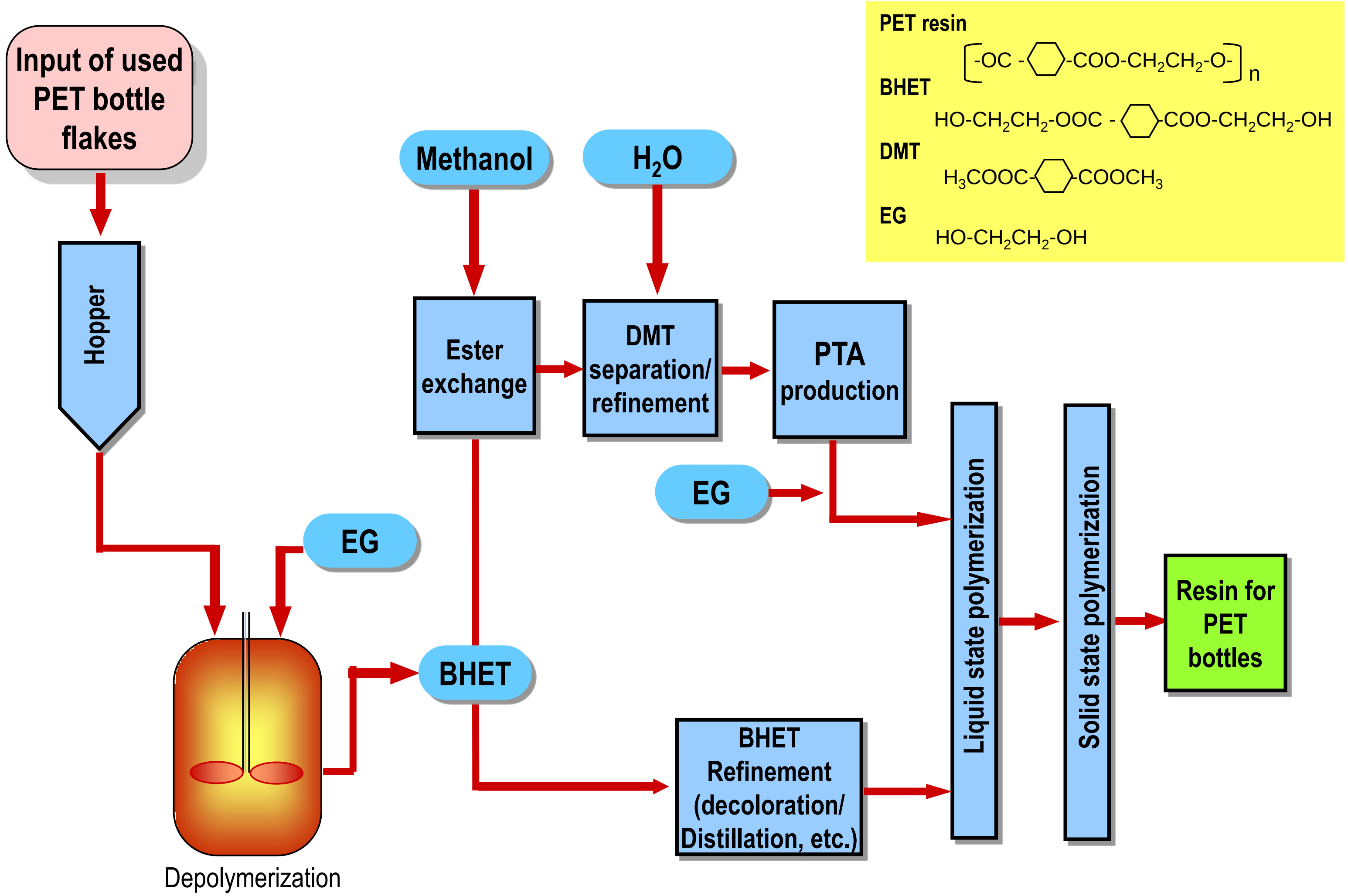


Glycolysis	R = CH_2CH_2OH	100-180°C	100-200 kPa
Hydrolysis	R = OH	160-350°C	340-1000 kPa
Methanolysis	R = CH_3	260-300°C	340-650 kPa

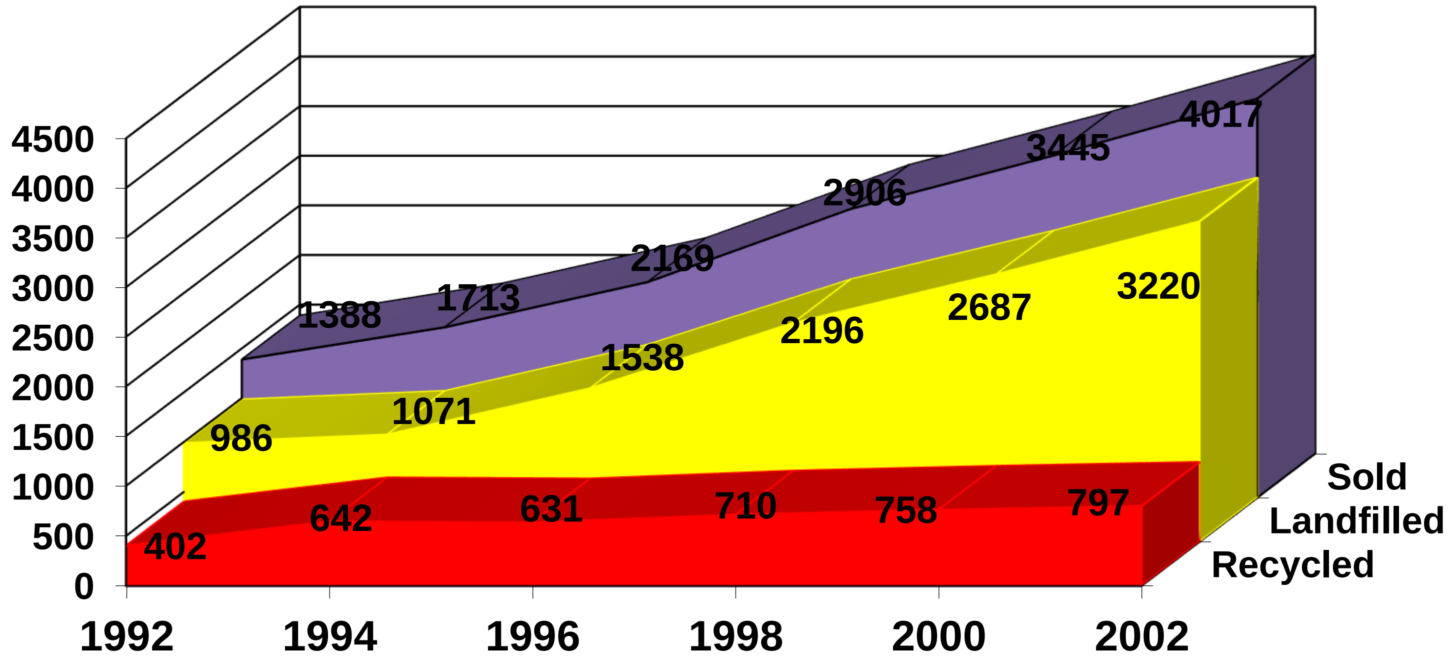
Petretec Process (Dupont) for Polyester Regeneration.



Teijin e Aies Co. Processes.

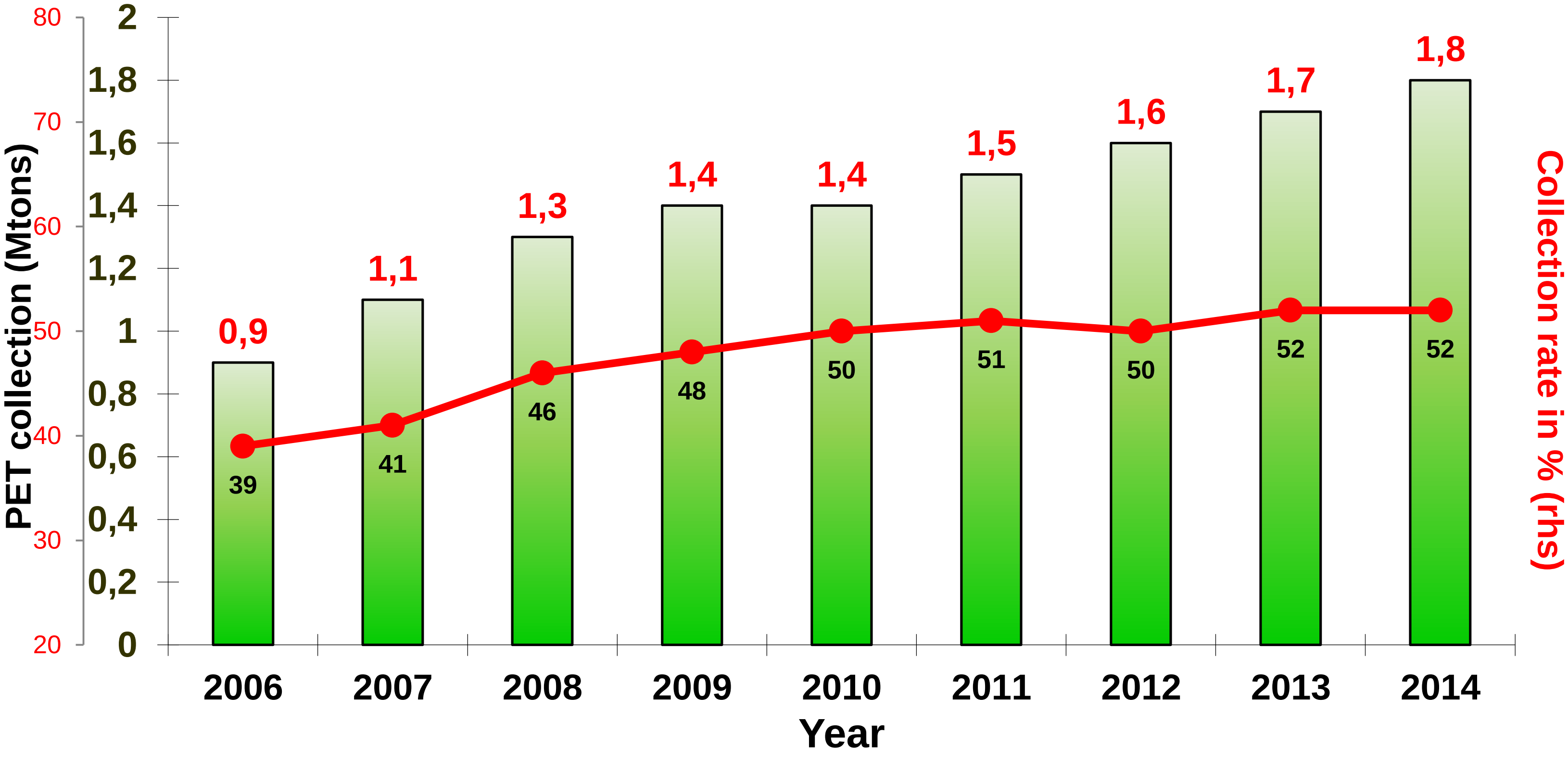


Difference between PET Sales and Recycling (1992-2002).

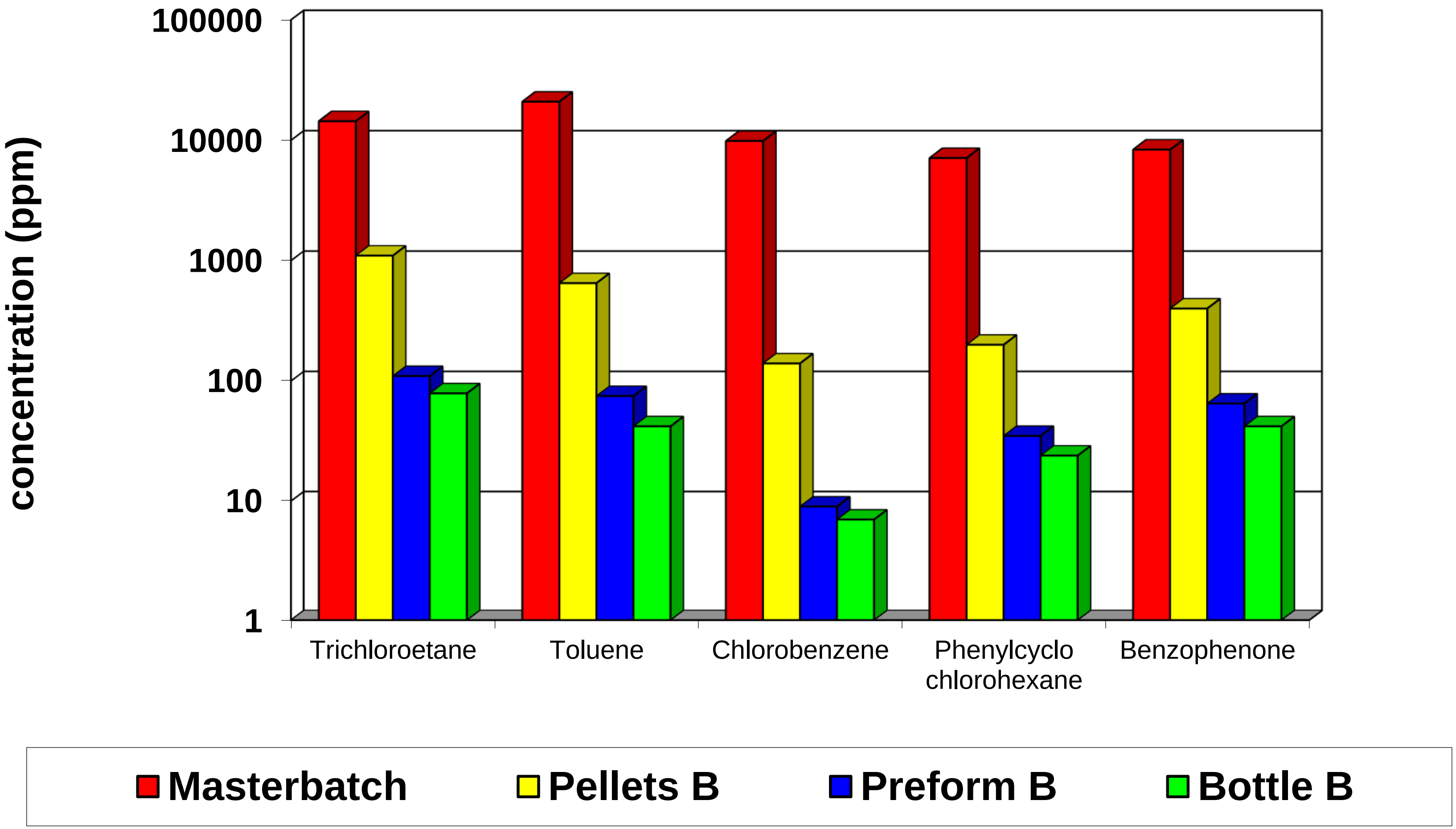


Source: "2002 National Post-Consumer Plastics Recycling Report." R.W. Beck, Inc. for the American Plastics Council. 2003.

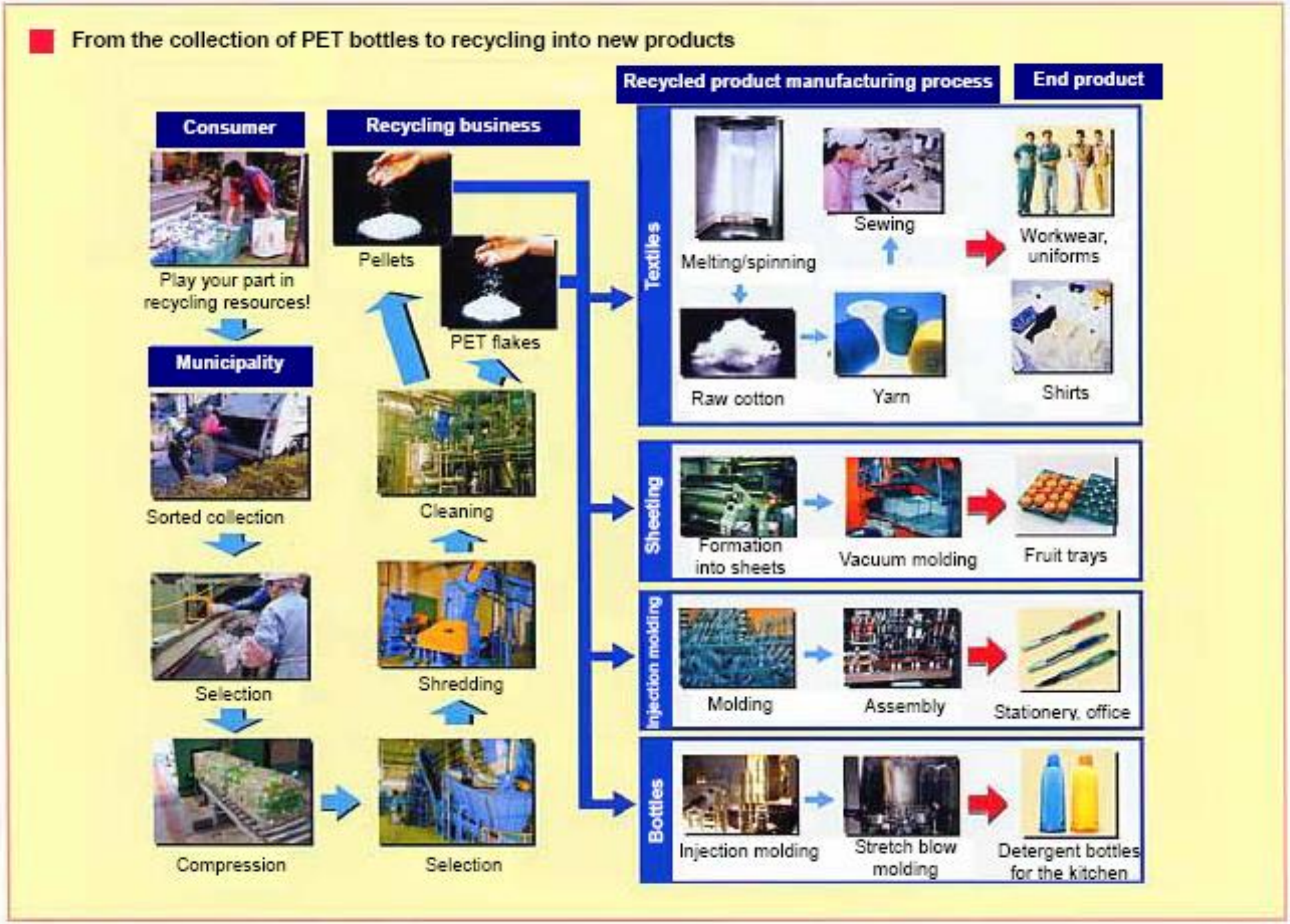
Post-Consumer PET Bottle Collection in Europe.



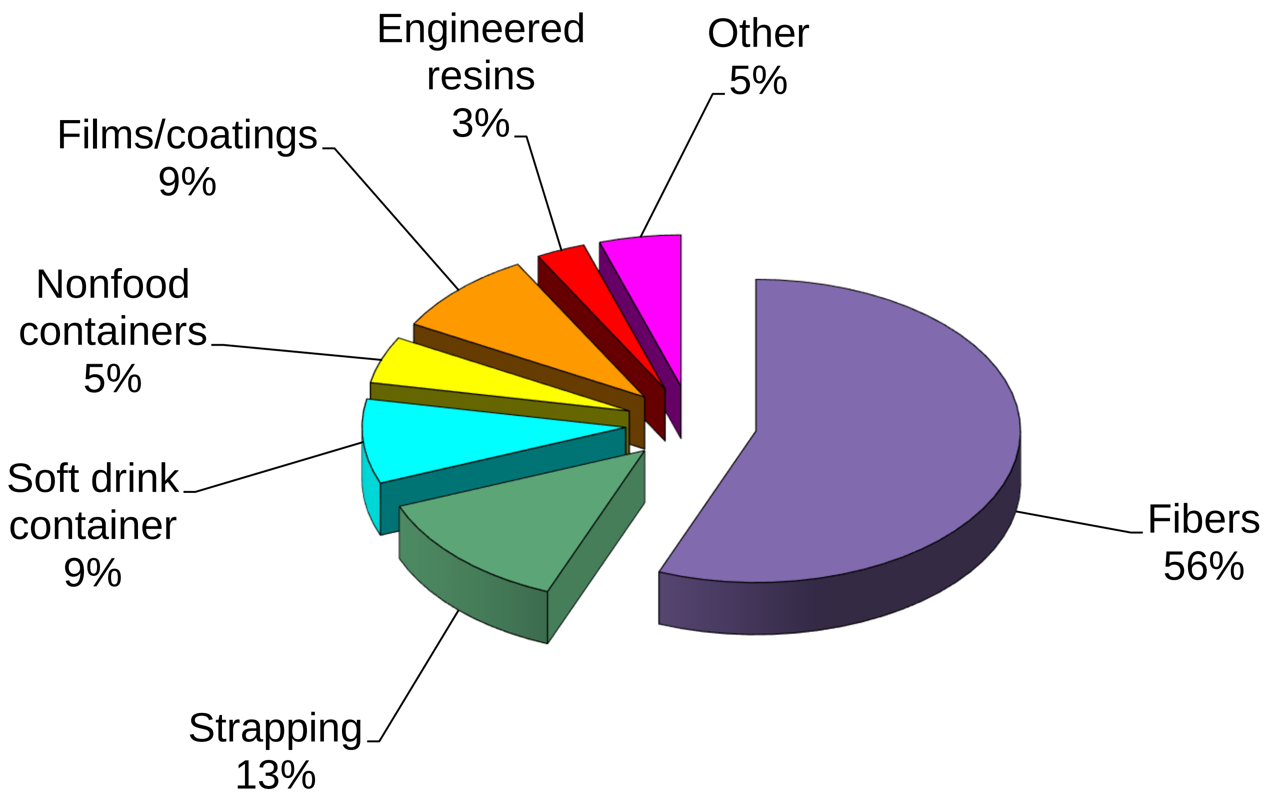
Decontamination at Flakes Level.



Bottle PET Recycling into New Products.



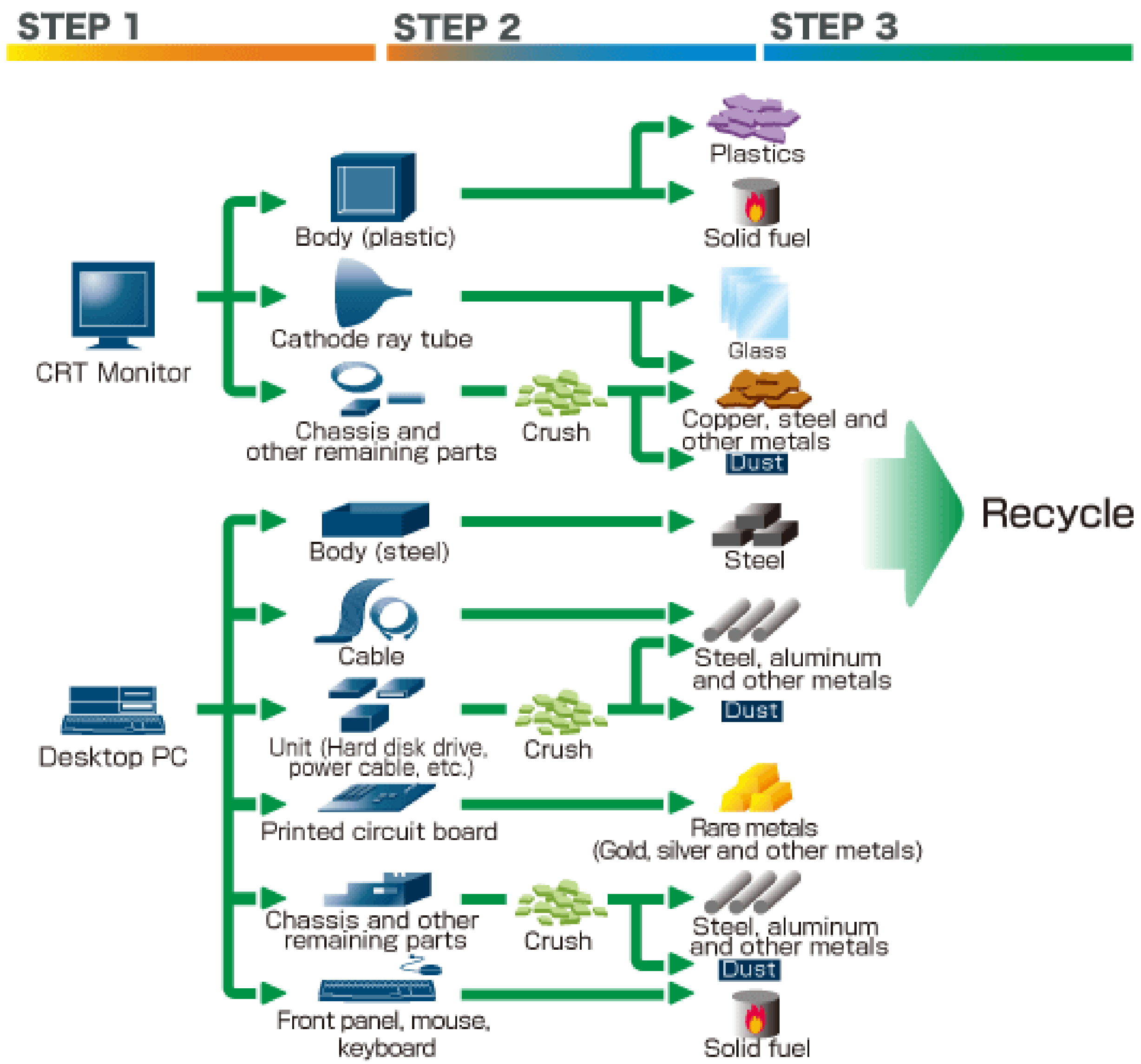
Final Uses of PET Recycled from Bottles for Food.



Energy saving: PET/RPET = 24

Products Made with Recycled PET.

How Plastics in Computers are Recycled.



The Future of Plastic Recycling.

- Quality of the raw material
- Single stream collection
- Long term vision
- Reliable partners and long term contracts
- Transparancy
- Sustainability
- Markets will become more volatile, but the world needs more secondary fibres
- End of waste directive
- Fair Trade and Free Trade
- Quality Standards.

School of Industrial and Information Engineering

Course 096125 (095857)

Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO





Biodegradable Plastics.

Prof. Attilio Citterio

Dipartimento CMIC "Giulio Natta"

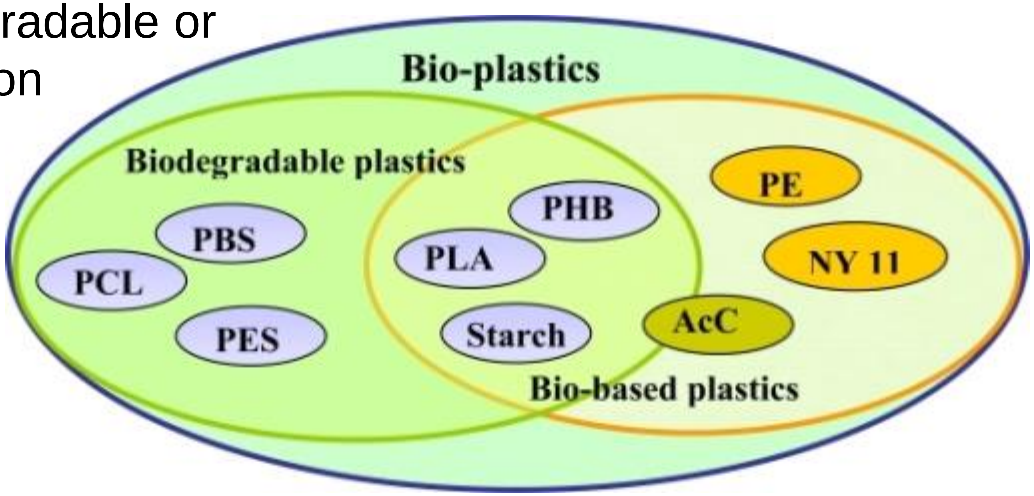
http://iscamap.chem.polimi.it/citterio/education/course-topics/

Bio-plastics and Biodegradable Plastics.

The word "bio-plastics" is often used confusingly. However, bio-plastics consist of either biodegradable plastics (i.e., plastics produced from fossil materials) or bio-based plastics (i.e., plastics synthesized from biomass or renewable resources).

The inter-relationship between biodegradable plastics and bio-based plastics is shown in Figure 1. Polycaprolactone (PCL), and poly(butylene succinate) (PBS) are petroleum based, but they can be degraded by microorganisms. On the other hand, poly(hydroxybutyrate) (PHB), poly(lactide) (PLA) and starch blends are produced from biomass or renewable resources, and are thus biodegradable. Despite the fact that polyethylene (PE) and Nylon 11 (NY11) can be produced from biomass or renewable resources, they are non-biodegradable. Acetyl cellulose (AcC) is either biodegradable or non-biodegradable depending on the degree of acetylation.

Starch, cellulose, chitosan and other polymers from nature are classified as natural polymers.

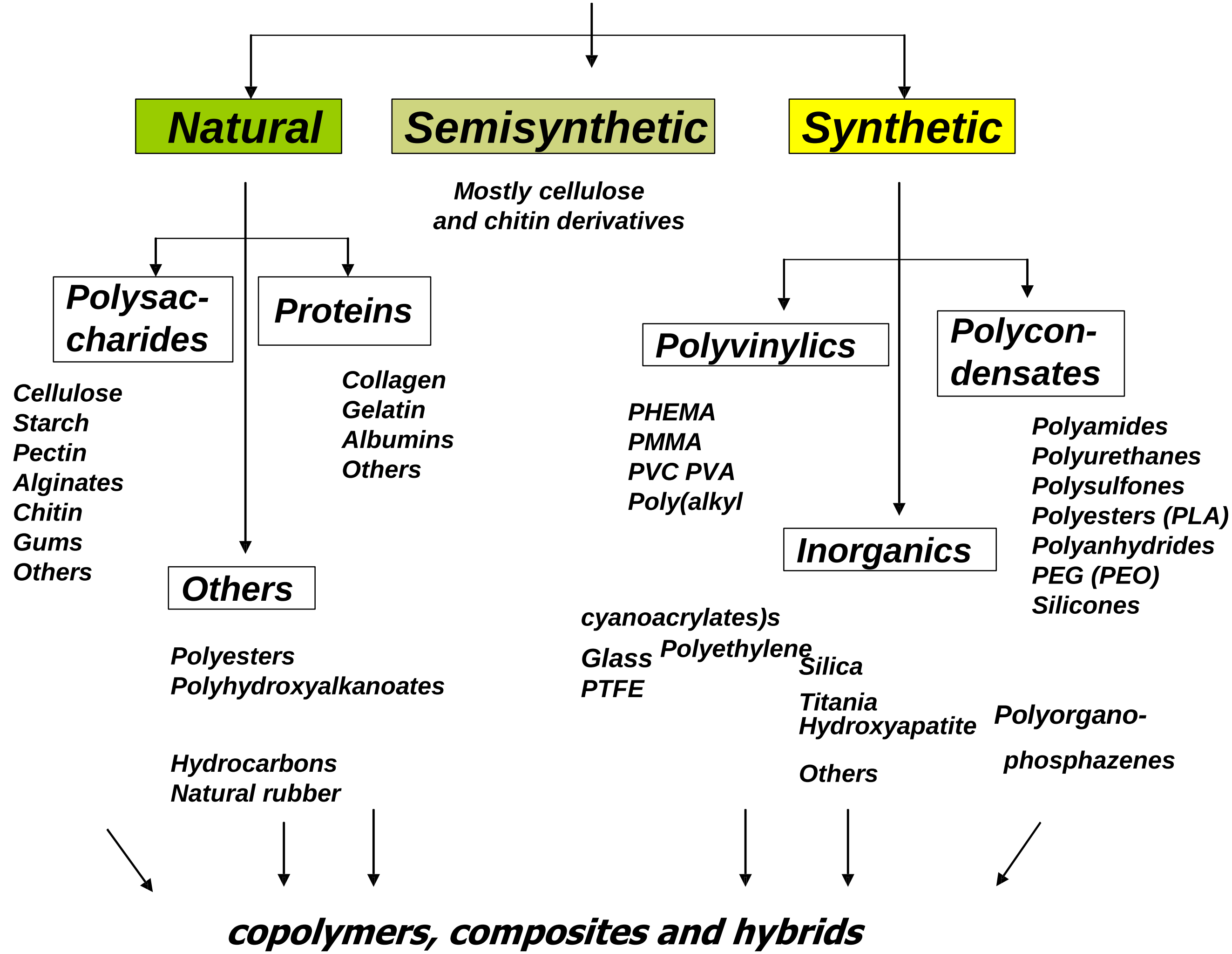


Biodegradable Plastics.

Several types of plastics are biodegradable:

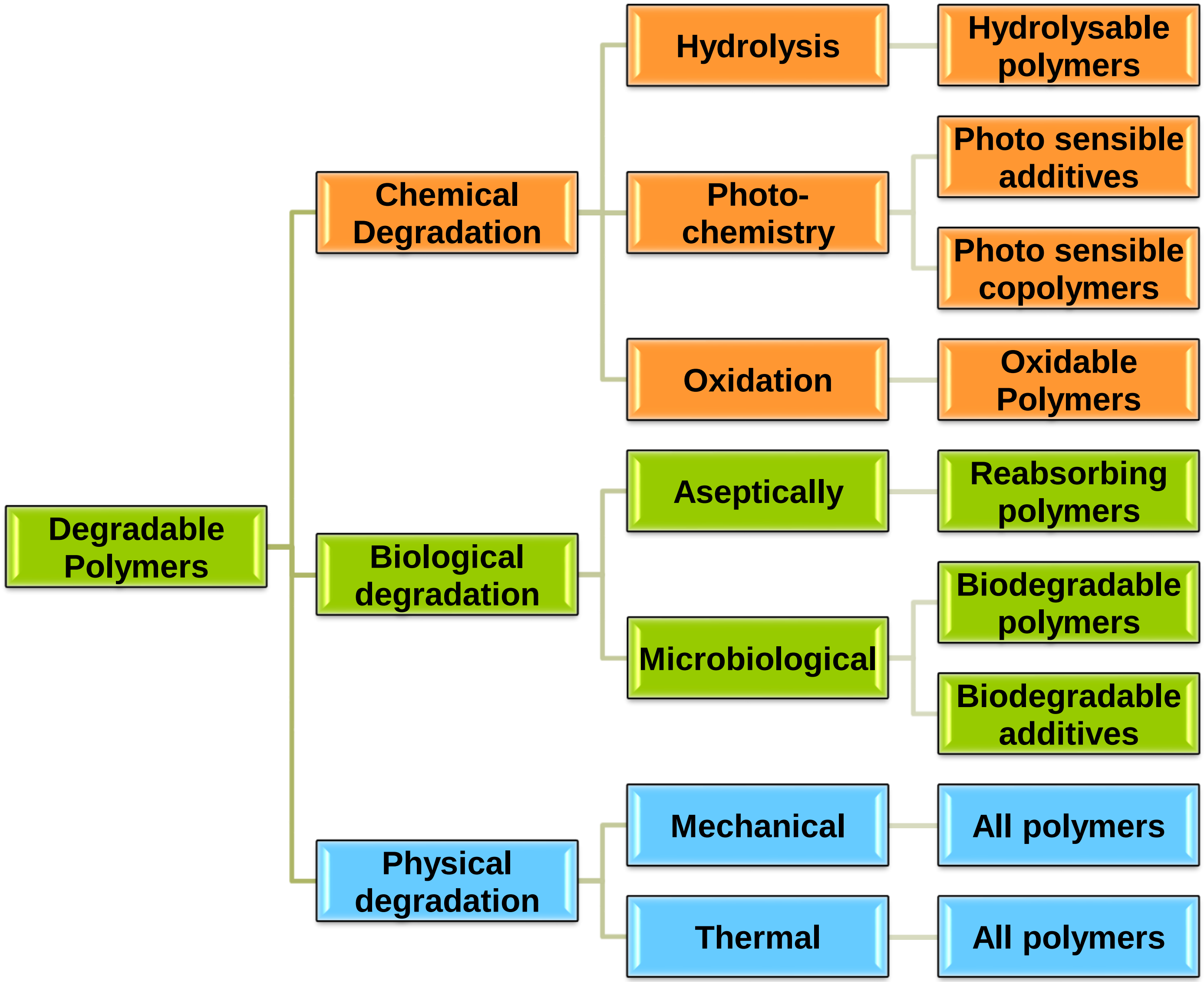
1. Biopolymers (polymers made by living organisms or from natural precursors) having bonds breakable by biological systems)
   - Polyhydroxyalkanoates, polyaminoacids, polyglycerols, etc.
2. Photodegradable Plastics (chemical stability and material durability) is reduced by additives or via appropriate preparative methods).
3. Synthetic biodegradable plastics : prepared by inclusion of starch, cellulose, etc., on synthetic polymer during manufacture

Polymeric Biomaterials Used for Bioapplications.

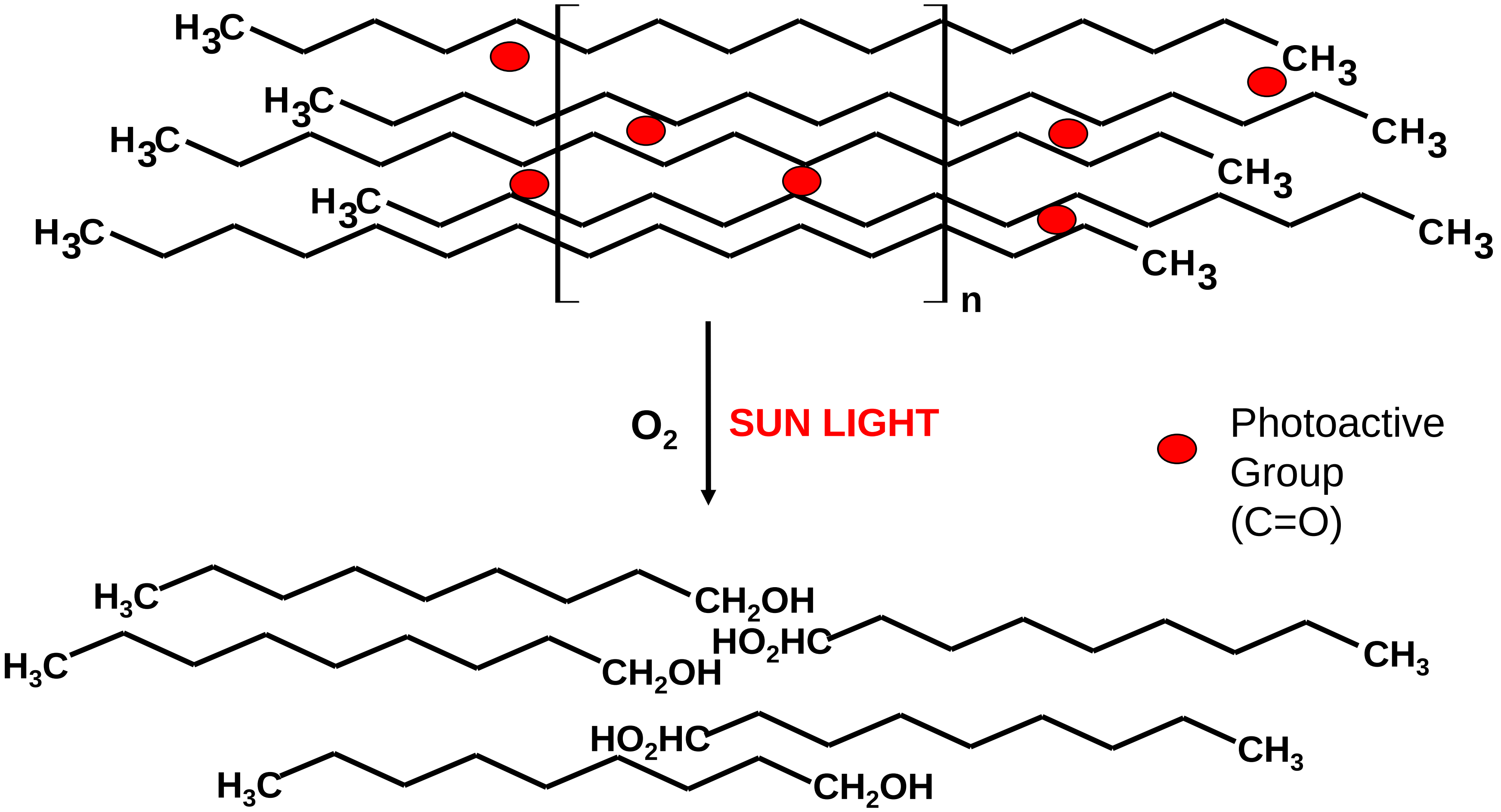


Classification according to polymer type from: Arshady, R., Introduction to Polymeric Biomaterials. Citrus Books: London, 2003.

Chemo- Bio- and Physico-Degradation of Plastic Materials.

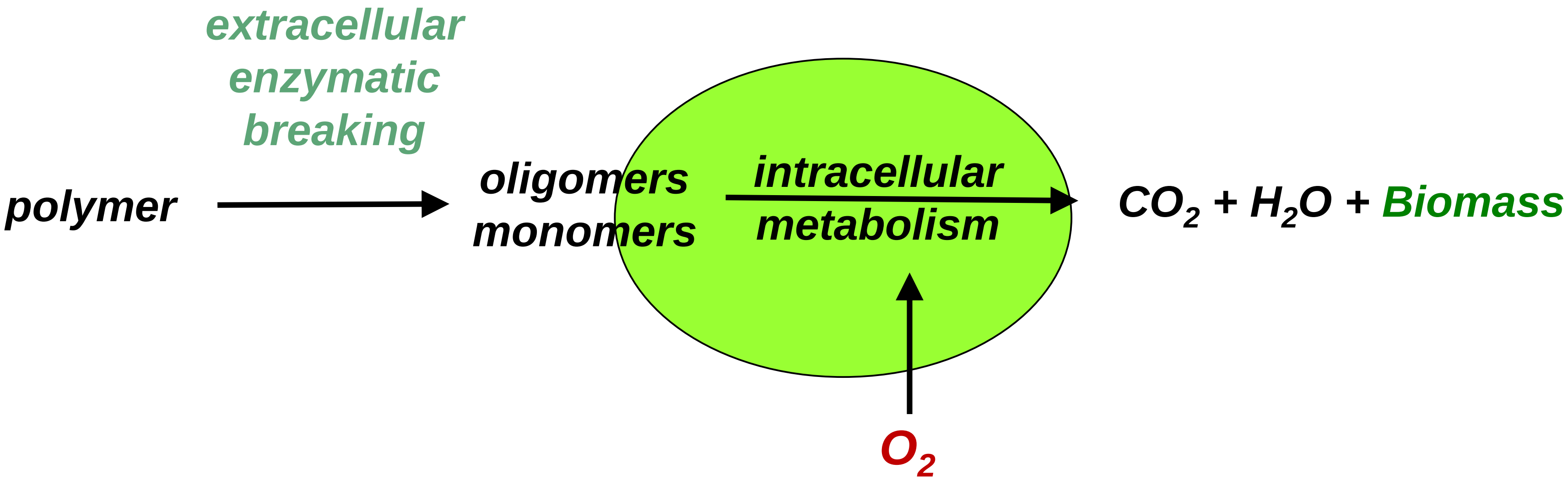


Photodegradable Polyethylene.



Biodegradation Mechanism.

To cell level



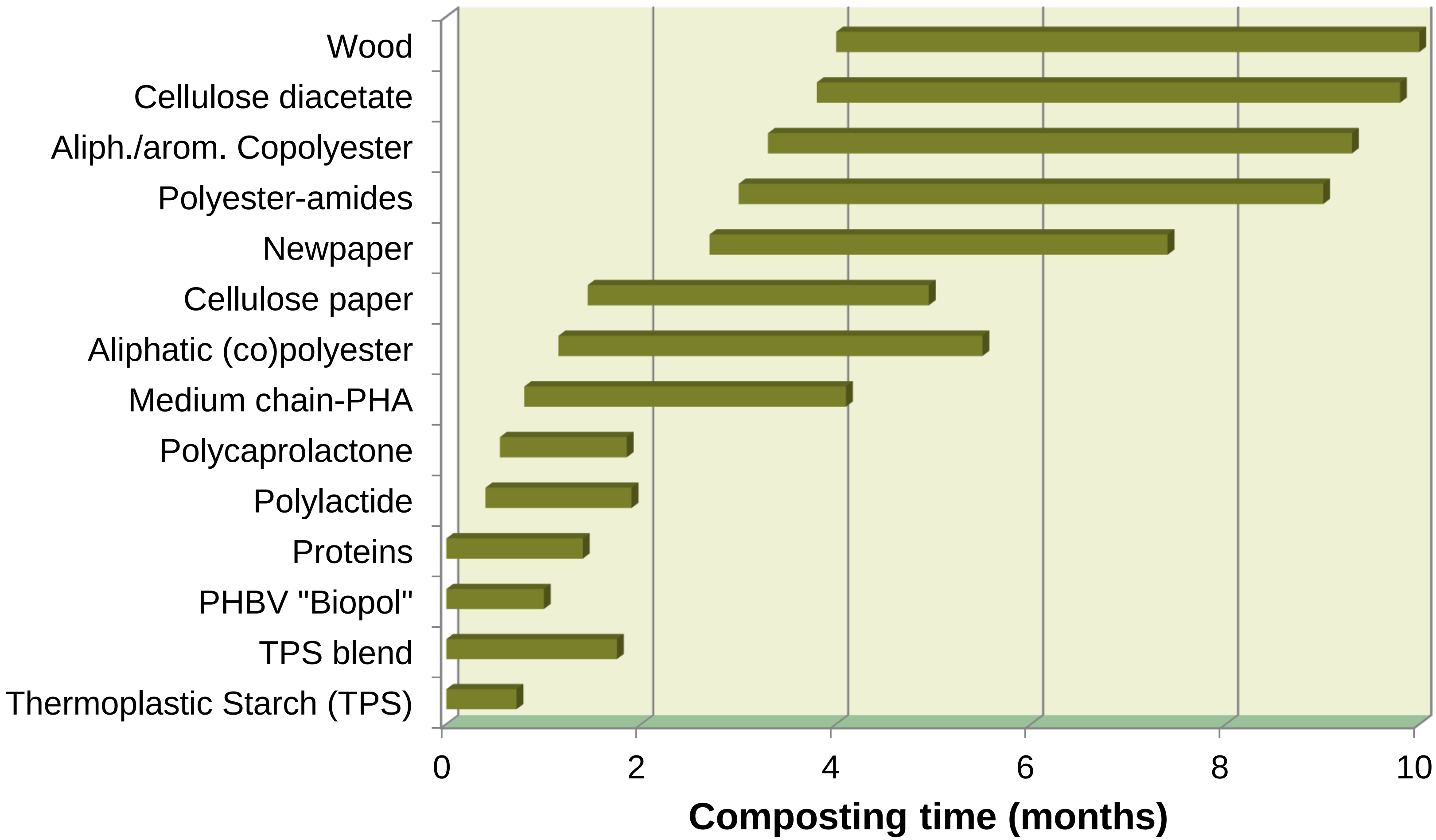
Endocellular enzymes can react only with molecules that are penetrated in the cell: small or long hydro-soluble molecules.

Tests and Norms Related to Biodegradation.

The only norm which actually refers to biodegradation is NF EN 13342. Four Criteria of acceptance are indicated:

- **Composition: maximum amount of volatile solids and heavy metals**
- **Biodegradability: > 90% of reference substance amount evaluated simultaneously, this must shows a biodegradation >70% in 45 days**
- **Time of test limited to 6 month**
- **Disintegration: less than 10% of residues of >2 mm size in 3 month**
- **Quality of final compound: performance >90% of starting**

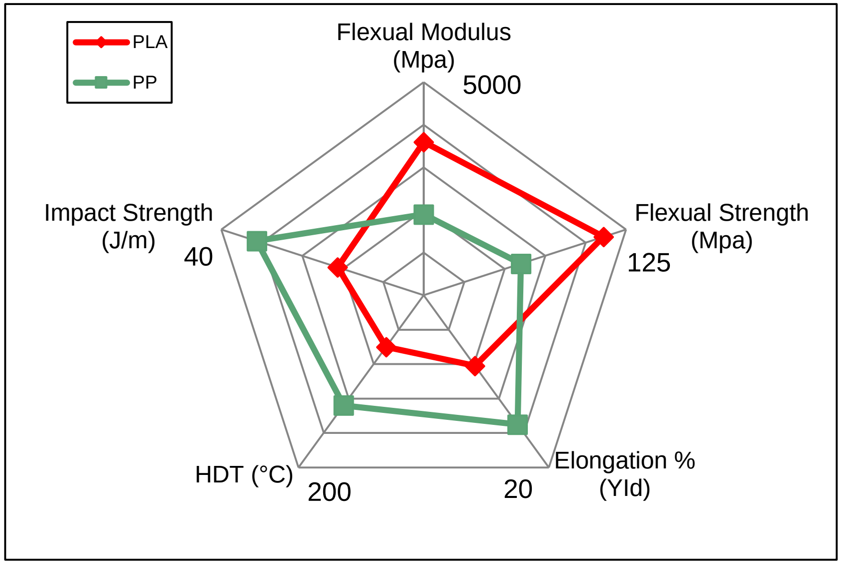
Biodegradable End of Life. Composting?



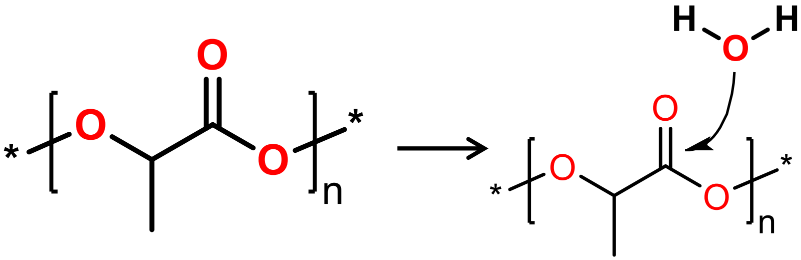
Differences between PLA and PP.

Compared with common petroleum-based polymers such as polypropylene (PP), advantages of PLA include high strength and high modulus, in addition to being a biodegradable renewable resource. Disadvantages of PLA include low resistance to conditions of high heat and humidity, low heat distortion temperature (HDT), low flexibility, and long mold cycle time.

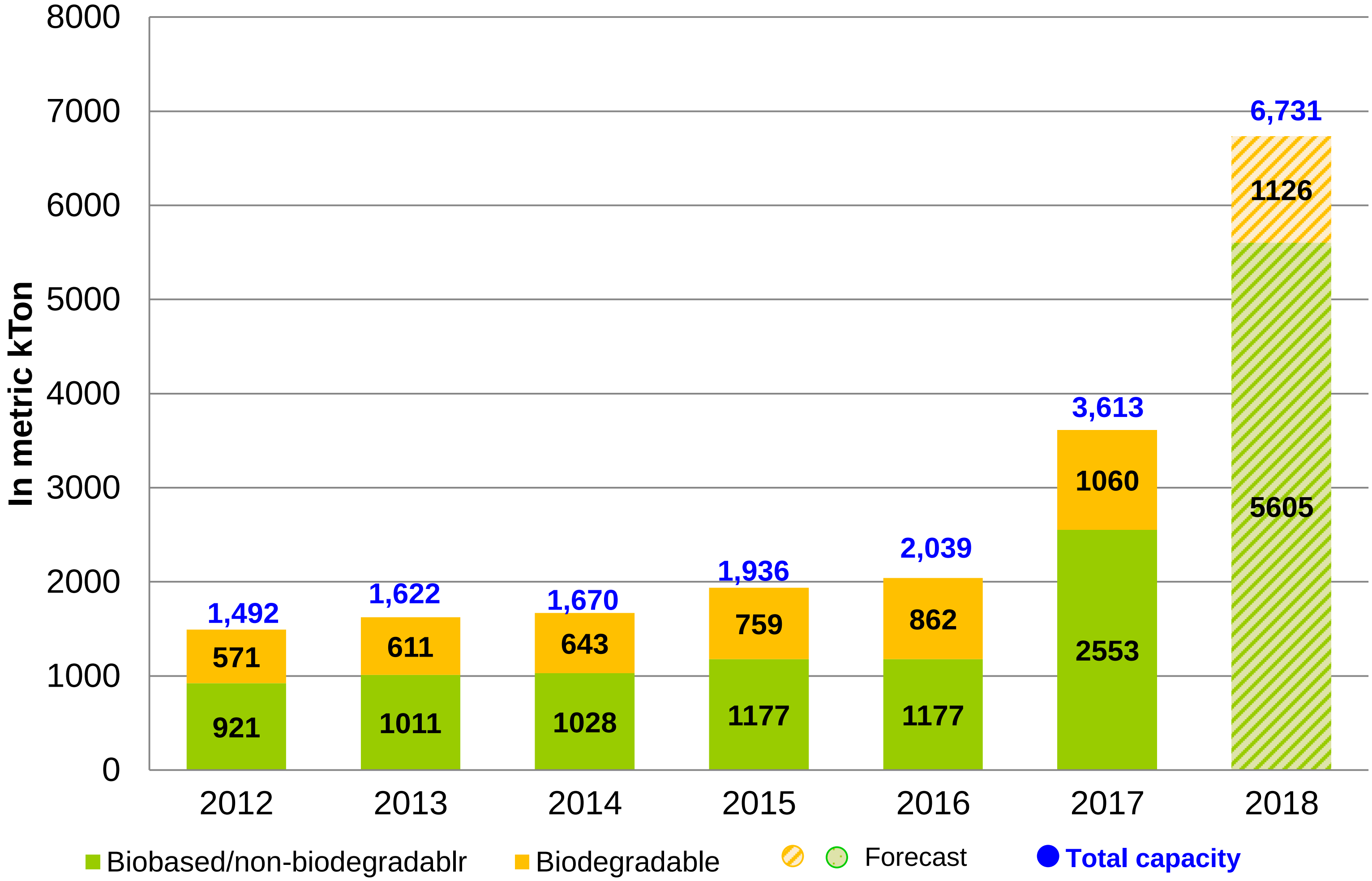
A main focus of research is to improve durability of PLA, mainly related to fast hydrolysis under high humidity conditions.



PLA possesses higher strength than PP, but inferior heat resistance and impact strength.

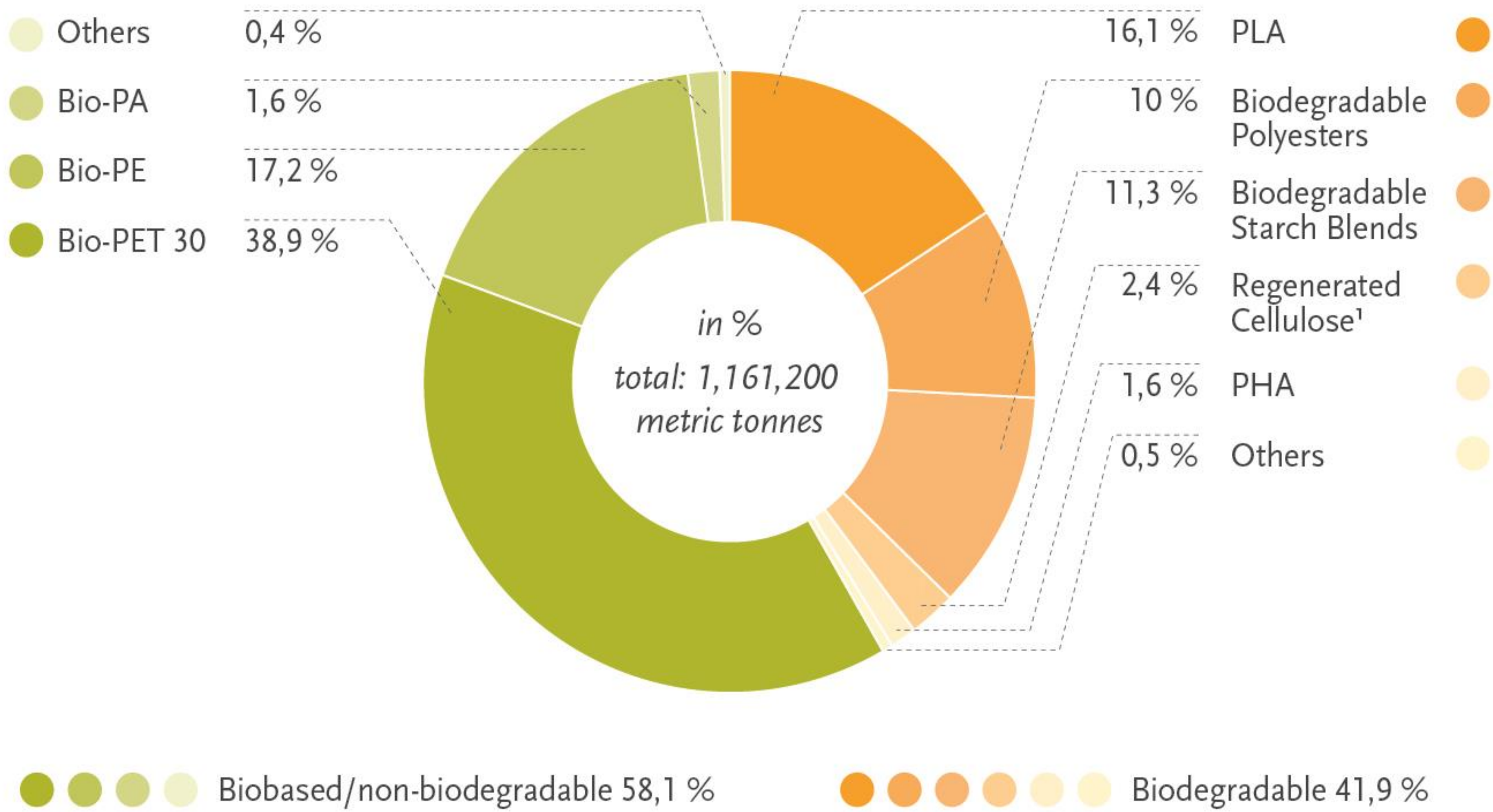


Global Production Capacity of Bioplastics.

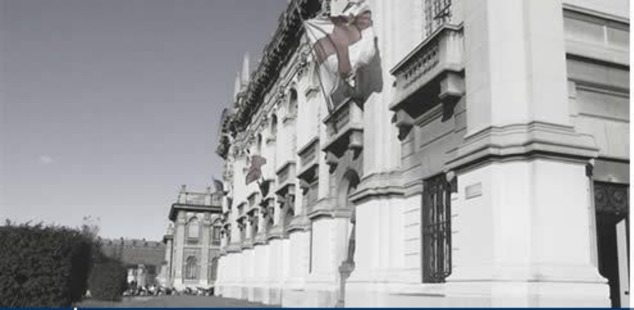


Source: Bioplastic EU

Capacity Bioplastic Production in 2011 by types.



Source: Bioplastic EU



School of Industrial and Information Engineering
Course 089017
Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

Thermal Poly(aspartate) as a Biodegradable Alternative to Poly(acrylate).

Prof. Attilio Citterio
Dipartimento CMIC "Giulio Natta"
http://iscamap.chem.polimi.it/citterio/education/course-topics/

Scale Build Up in Industrial Water Handling Processes.

Scale consists of insoluble inorganic compounds such as calcium carbonate, calcium sulfate, and barium sulfate.

Scaling induces:

- reduced water flow though pipes,
- reduced heat transfer in boilers and condensers,
- pump failures

Antiscalants.

- Prevent scale formation entirely or
- Permit the scale to be deposited in such a way that it is easily removed by the fluid flowing along the pipe or heat transfer surface.
- Antiscalants complex with the cations present in water to prevent formation of the insoluble inorganic solids.

Per es.:

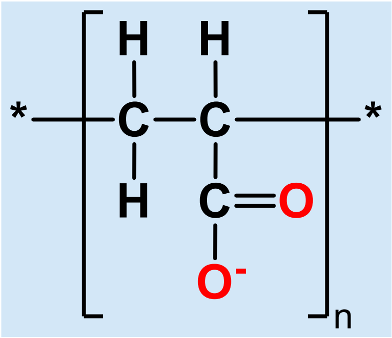
$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftarrows CaCO_3(s)\downarrow$$

$$Ca^{2+}(aq) + EDTA^{4-}(aq) \rightleftarrows [CaEDTA]^{2-}(aq)$$

Polyacrylate (PAC).

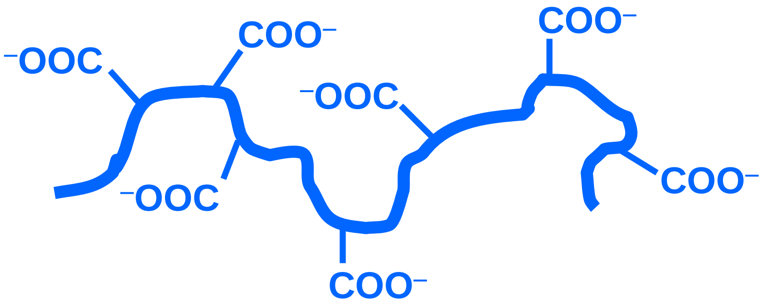
Polyacrylate (PAC) is one of the most common scale inhibitors.

- PAC is a polyanion, i.e. a polyelectrolyte.

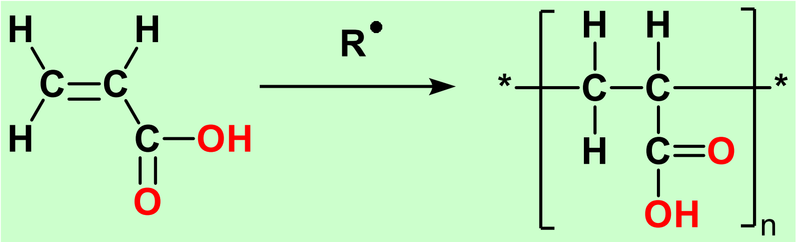


<u>Polyelectrolytes</u>:

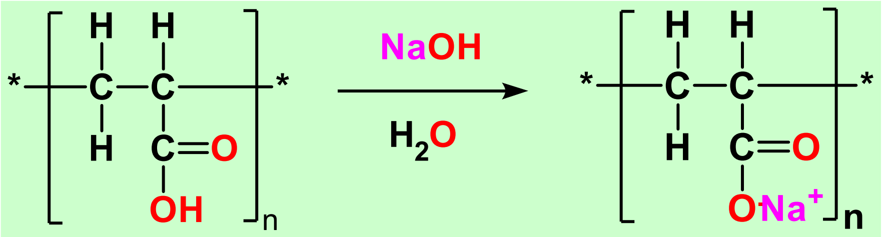
- **Are polymers with bound positive or negative charges**
- **Are also called macroions or polyions**
- **Can be polyanions or polycations**
- **Are generally water soluble polymers if their structure is linear**



Synthesis of Polyacrylic Acid and Conversion to Polyacrylate.



- Radical Initiation
- PM controlled by termination agents by atom transfer (weak C-H, S-H or O-H bonds, ethers, alcohols, tiols, etc.)

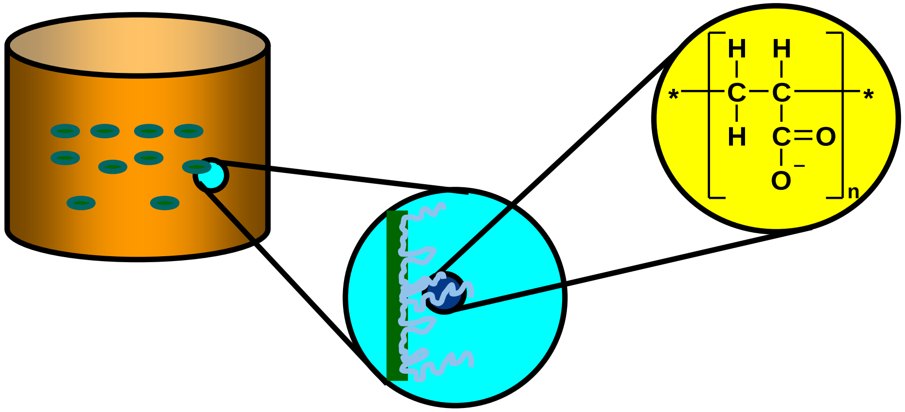


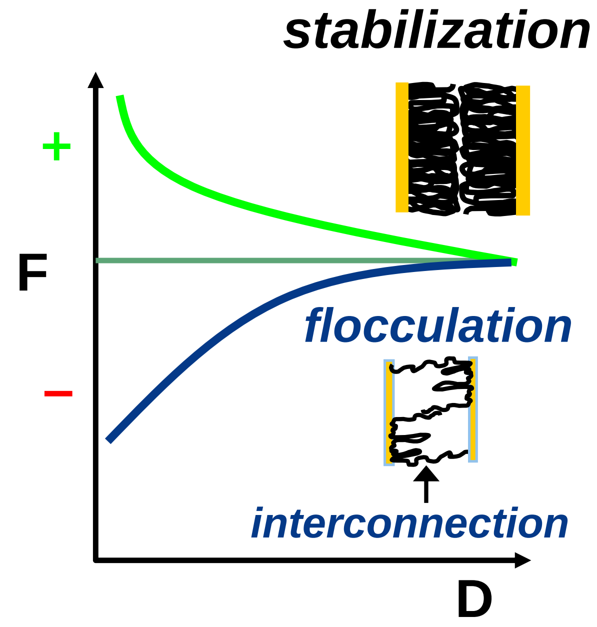
- Crosslinking (through a tridimensional lattice) slow down the H^+/Na^+ exchange

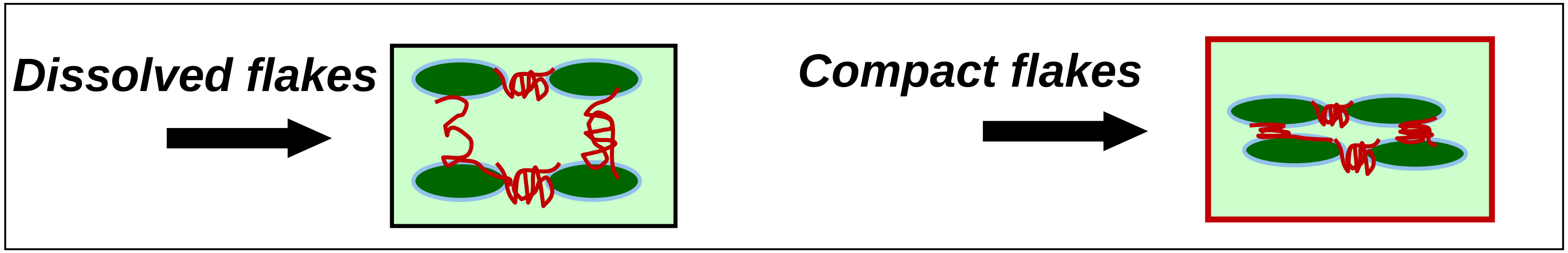
PAC as an Antiscalant or Dispersant.

- Polymeric antiscalants are generally low molecular weight polymers.
- Polymeric dispersants consist of higher molecular weight fractions.
- Dispersants do not stop the formation of scale, but instead are able to keep the scale particles suspended in the bulk fluid by imparting a negative charge to the particles.
- PAC comprises 5% of many laundry detergent formulations because of its dispersant properties.

Polyelectrolytes – Particle Interaction.

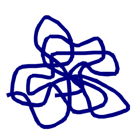




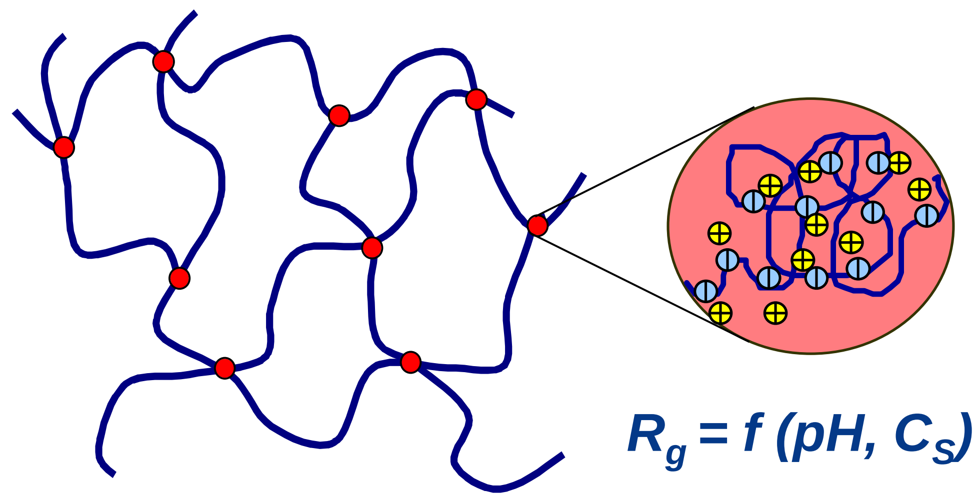


Crosslinked PAC.

- A crosslinked form of the sodium salt of polyacrylic acid is used as a superabsorbent material in diapers and other personal hygiene products.
- Crosslinked PAC has a great affinity for water, but is unable to dissolve and will instead swell in aqueous solution.
- Because of the presence of the charged groups on the polymer chain of a polyelectrolyte, the polymer will be highly expanded in aqueous solution.



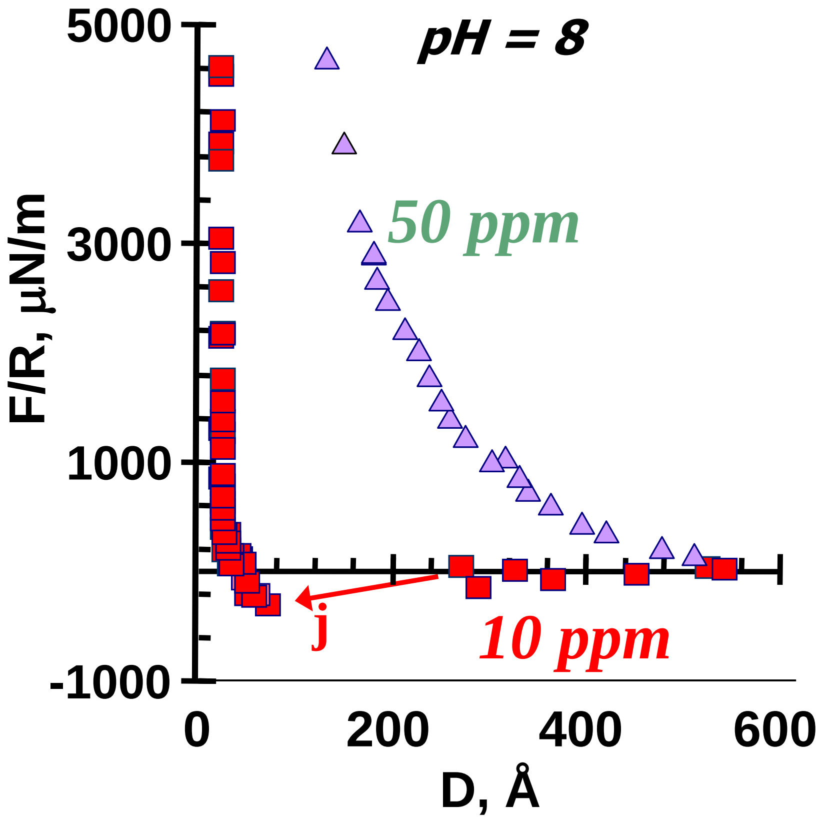
Dry crosslinked polymer

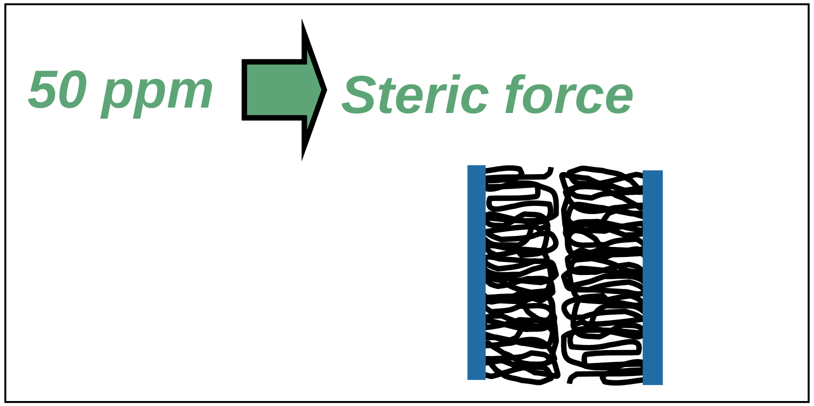


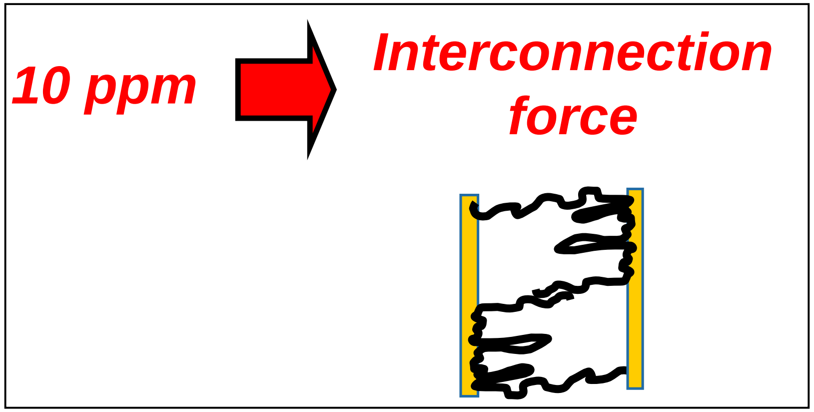
$$R_g = f\,(pH, C_S)$$

Crosslinked swelled polymer

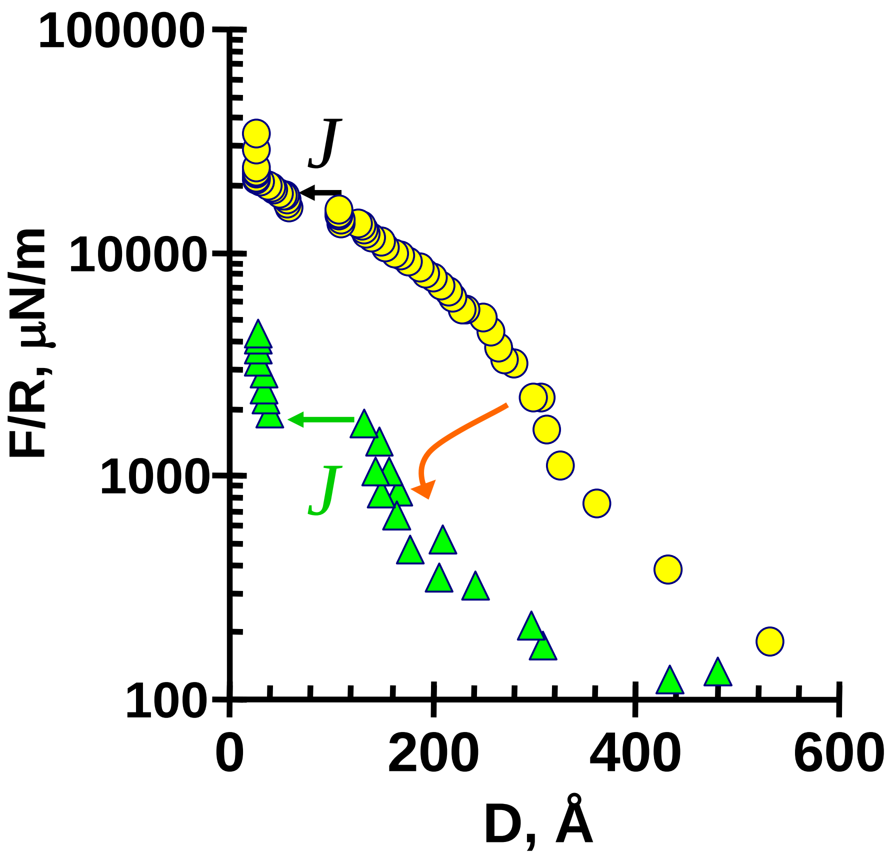
Forces on Mica Surface
(Mg^{2+}, pH = 8, PAA = 10-50 ppm).

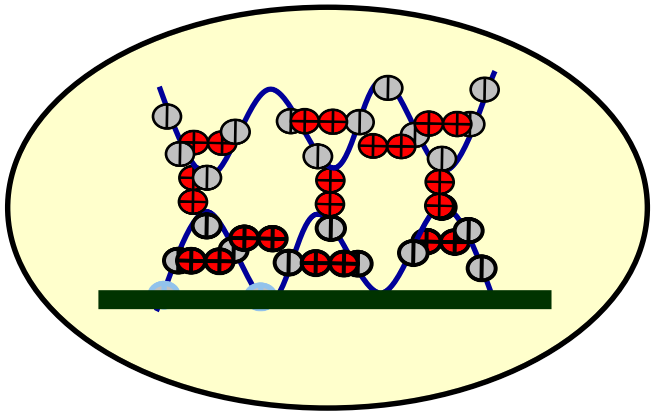


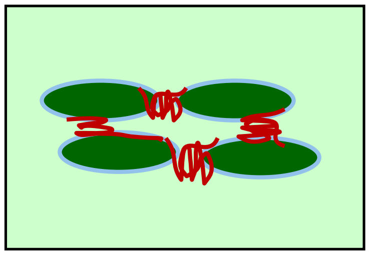




Forces on Mica Surface
(Ca^{2+}, pH = 8, PAA 10 ppm).







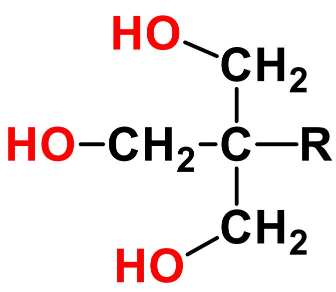
Compact flakes

Crosslinking Agents.

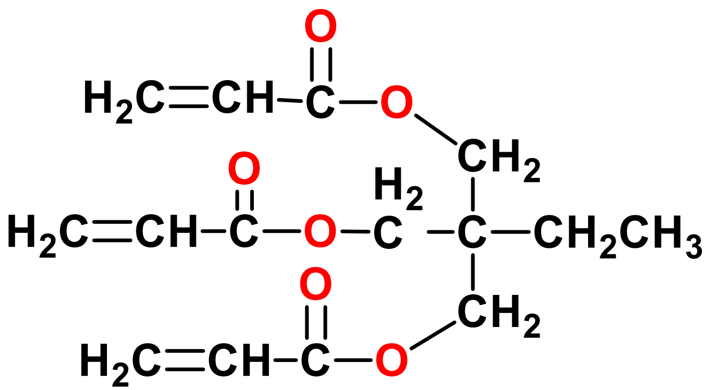
Low molecular weight compounds having more reactive centers (almost 3) able to form a tridimensional knot in the lattice of polymer.

Typical are:

- polyalcohols (polyols : tri and tetra OH) for polycondensation reaction to give polyesters
- polyol acrylates (for radical polymerization - crosslinking agents)



R = H,
R = alkyl
R = CH_2OH



Trimethylolpropane triacrylate

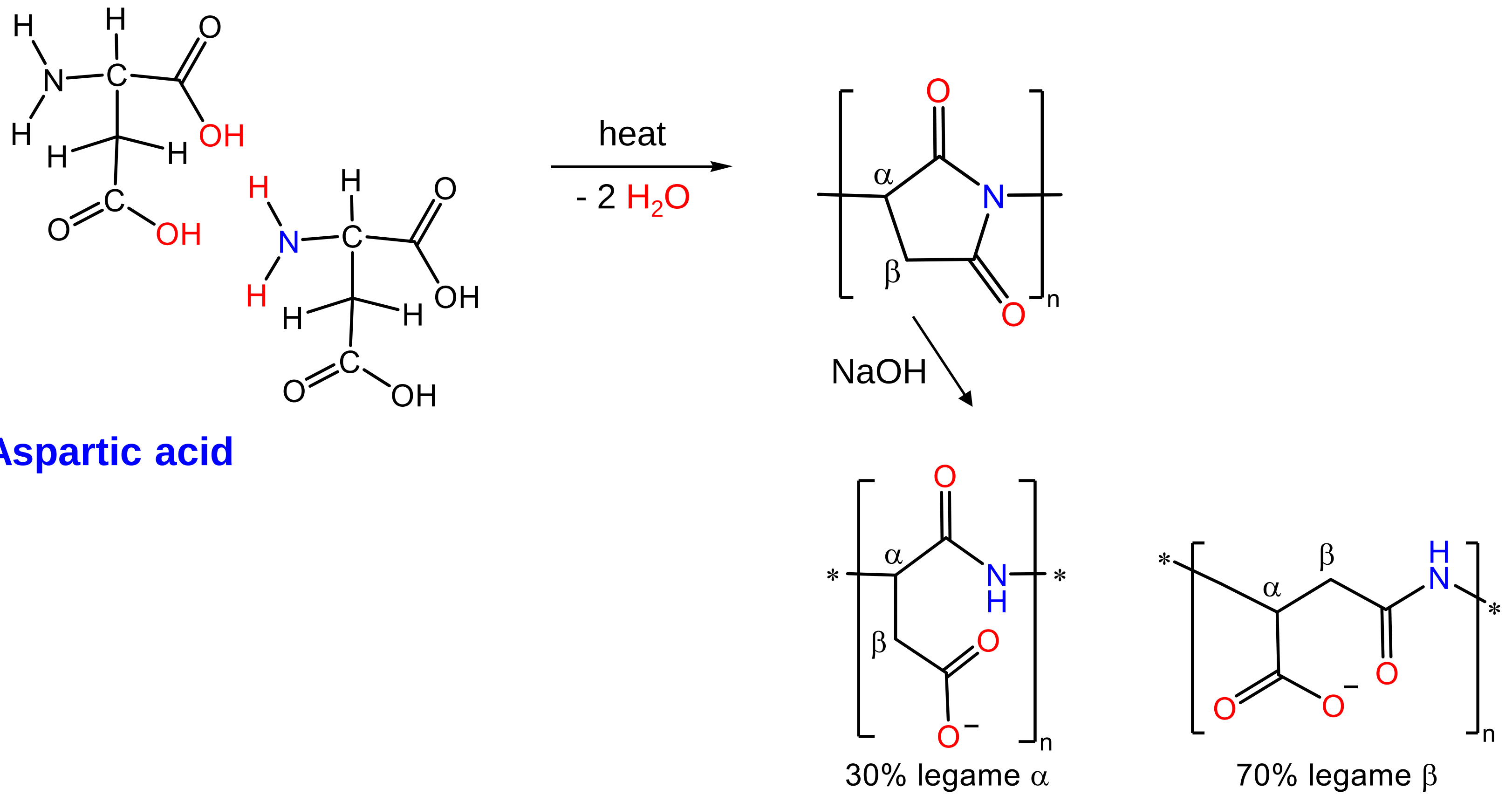
PAC and the Environment.

- PAC is nontoxic and environmentally benign, but it is not biodegradable.
- Because it is widely used for many applications, it poses an environmental problem from a landfill perspective.
- When PAC is used as an antiscalant or a dispersant, it becomes part of wastewater.
- PAC is nonvolatile and not biodegradable, so the only way to remove it from the water is to precipitate it as an insoluble sludge.
- The sludge must then be landfilled.

Substitute: Thermal Polyaspartate.

- The Donlar Corporation developed an economic way to produce thermal polyaspartate (TPA) in high yield and with little or no waste products.
- Polyaspartate is a biopolymer synthesized from L-aspartic acid, a natural amino acid.
- Polyaspartate has similar properties to the polyacrylates and so it can be used as a dispersant, or an antiscalant, or a superabsorber.
- Polyaspartate is biodegradable.

Synthesis of Thermal Polyaspartate.



Aspartic acid

Polyaspartate

TPA as Alternative to Polyacrylates.

TPA is marketed and sold as:

- a corrosion and scale inhibitor,
- a dispersing agent,
- a waste water additive,
- a superabsorber, and also as
- an agricultural polymer. *(As an agricultural polymer, TPA is used to enhance fertilizer uptake by plants. Less fertilizer is added to the soil and the environmental impact from fertilizer run-off is reduced*).