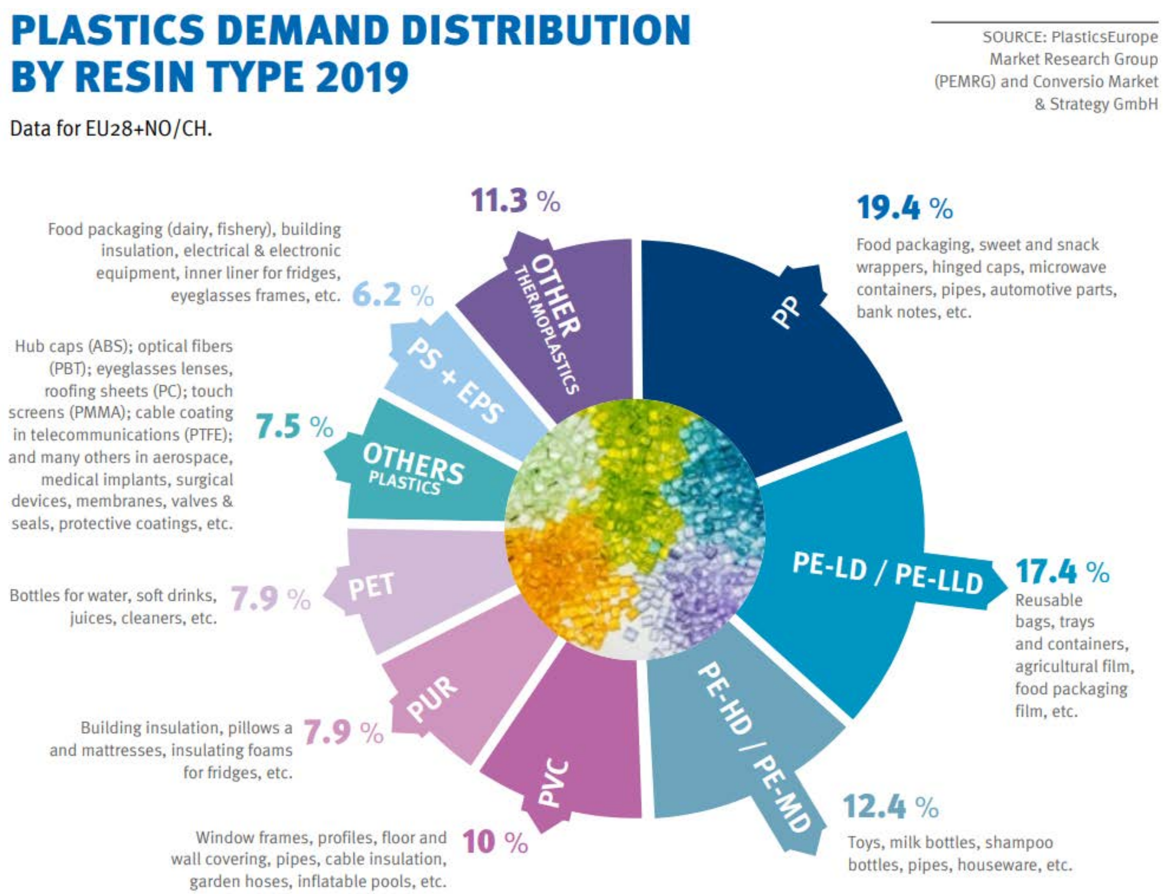
TECHDAY 8 SETTEMBRE

Chemical Recycling: properties of the obtained materials

08/09/2021

Plasmix

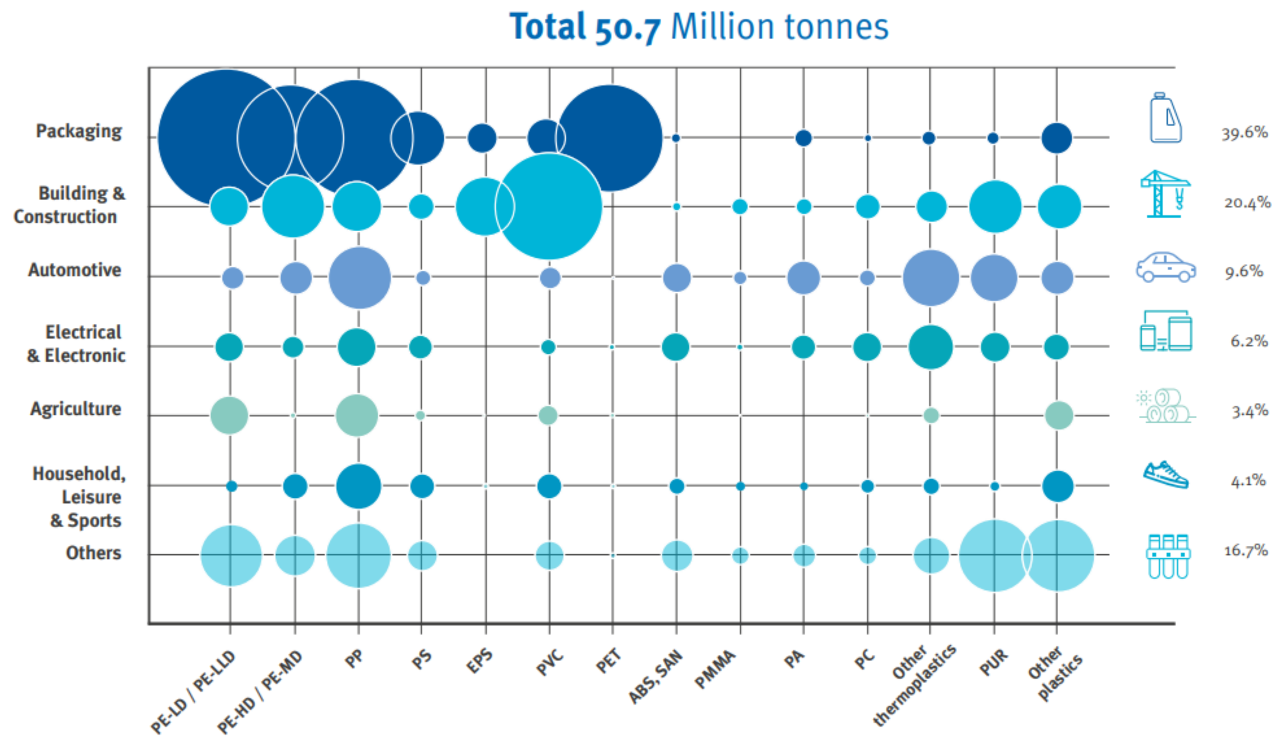

PLASTICS DEMAND DISTRIBUTION BY RESIN TYPE 2019
Data for EU28+NO/CH.
SOURCE: PlasticsEurope Market Research Group (PEMRG) and Conversio Market & Strategy GmbH
19.4 %
PP
Food packaging, sweet and snack wrappers, hinged caps, microwave containers, pipes, automotive parts, bank notes, etc.
17.4 %
PE-LD / PE-LLD
Reusable bags, trays and containers, agricultural film, food packaging film, etc.
12.4 %
PE-HD / PE-MD
Toys, milk bottles, shampoo bottles, pipes, houseware, etc.
10 %
PVC
Window frames, profiles, floor and wall covering, pipes, cable insulation, garden hoses, inflatable pools, etc.
7.9 %
PUR
Building insulation, pillows and mattresses, insulating foams for fridges, etc.
7.9 %
PET
Bottles for water, soft drinks, juices, cleaners, etc.
7.5 %
OTHERS PLASTICS
Hub caps (ABS); optical fibers (PBT); eyeglasses lenses, roofing sheets (PC); touch screens (PMMA); cable coating in telecommunications (PTFE); and many others in aerospace, medical implants, surgical devices, membranes, valves & seals, protective coatings, etc.
6.2 %
PS + EPS
Food packaging (dairy, fishery), building insulation, electrical & electronic equipment, inner liner for fridges, eyeglasses frames, etc.
11.3 %
OTHER THERMOPLASTICS

Plastic Demand

SOURCE: PlasticsEurope Market Research Group (PEMRG) and Conversio Market & Strategy GmbH

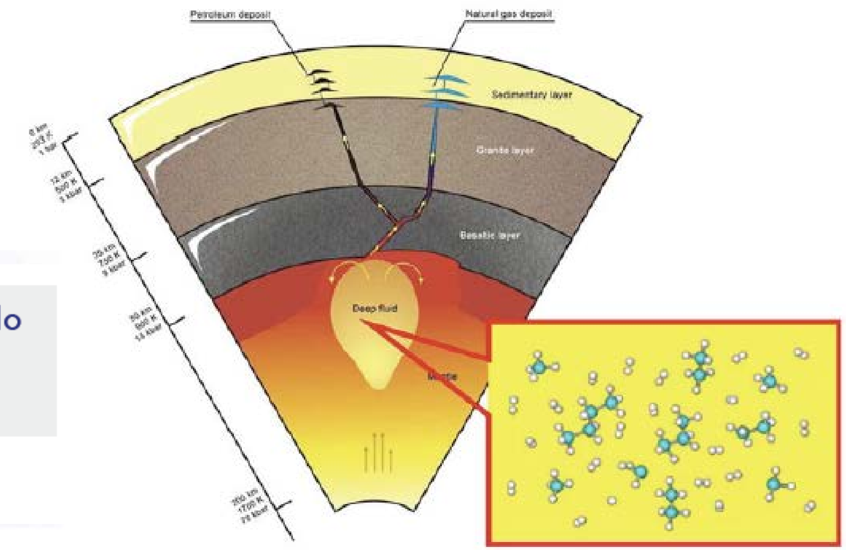
PLASTICS DEMAND BY SEGMENT AND POLYMER TYPE IN 2019

Data for EU28+NO/CH.



WHY RENEWABLE?

Performed in laboratory at 1500°C and 5.7Gpa. (PNAS, 2004).

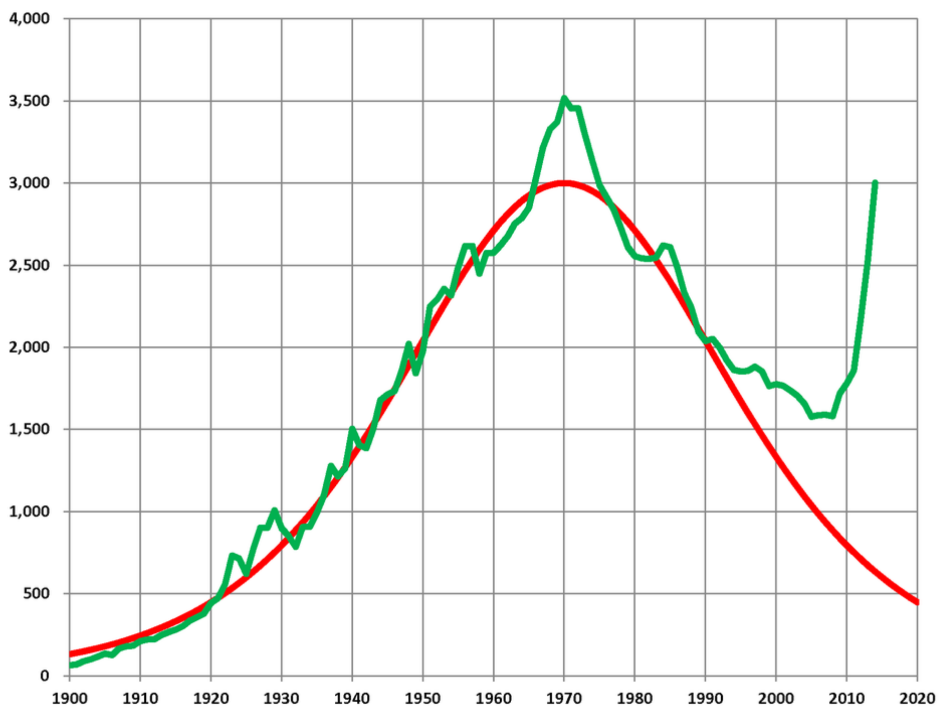


Heretic idea: oil and natural gas in the ground have nothing to do with biology (*Thomas Gold)* and their inorganic formation is still filling the reservoirs.

$$CaCO_3 + 12FeO + H_2O \rightarrow CaO + 4Fe_3O_4 + CH_4$$

Abiogenic petroleum origin is a term used to describe a number of different hypotheses which propose that petroleum and natural gas are formed by inorganic means rather than by the decomposition of organisms.

END OF OIL?



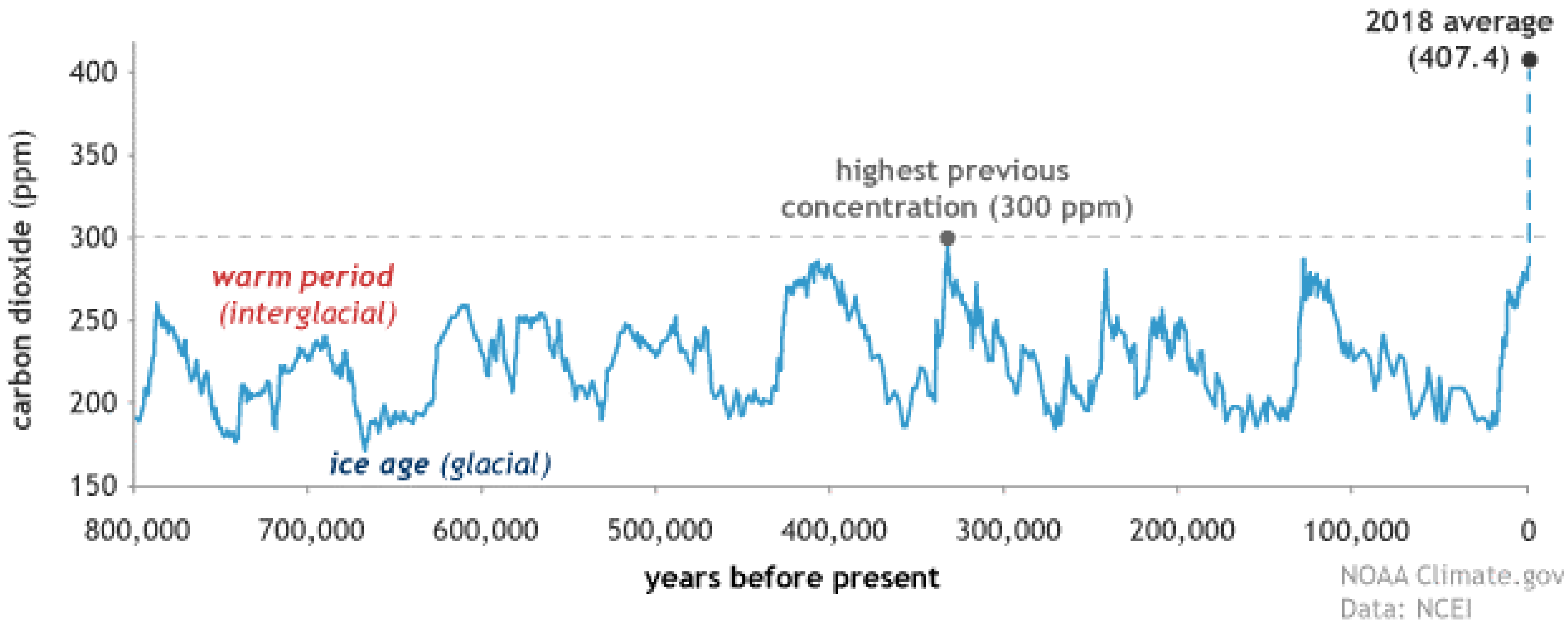
We are approaching the end of easily accessible oil and some experts claim that the era of the cheap oil may be ending.

The so called unconventional oil are more carbon laden and higher in toxic impurities. They tend to be heavy, complex and locked up deep in the earth, tightly trapped between or bound to sand, tar and reck.

They can be processed into petroleum products but impure feedstock requires large energy input to upgrade.

WHY RENEWABLE? **Because of Pollution**

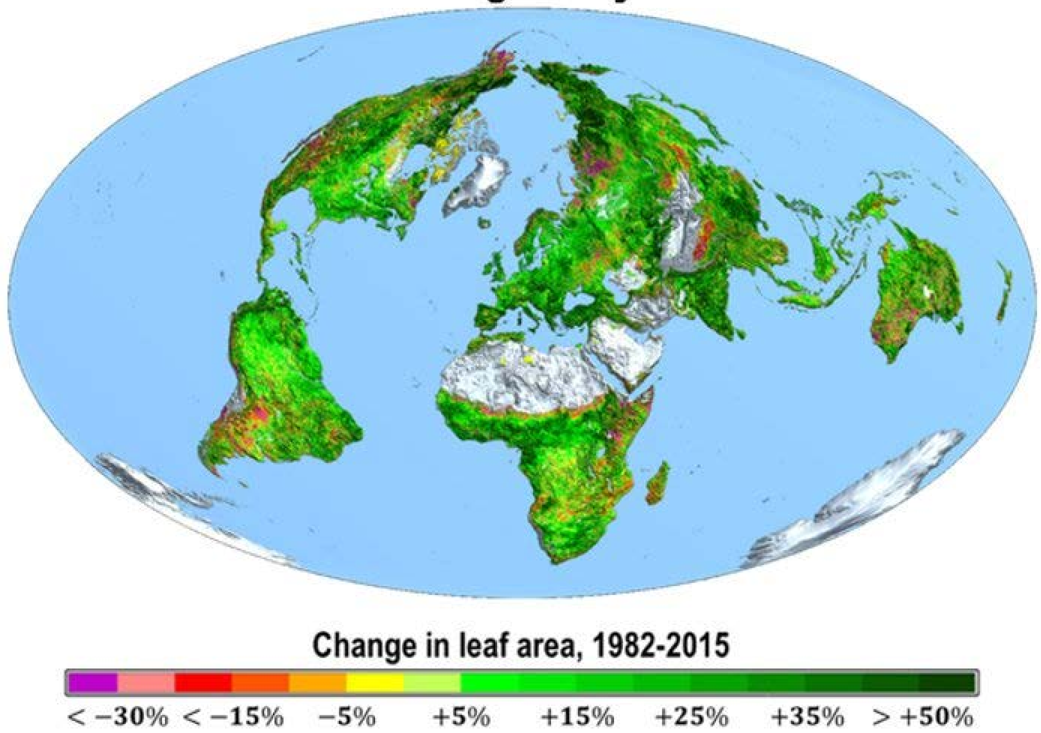
CO_2 during ice ages and warm periods for the past 800,000 years



Is this dangerous for our planet?

The Truth:

Significant "greening" of the Earth - vegetation is increasing in up to 50% of the planet and decreasing in only 4%

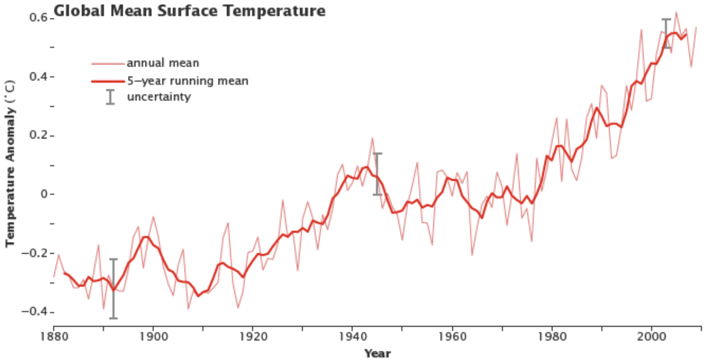


Modified from Zhu Z, et al. (2016) Greening of the Earth and its drivers, Nature Climate Change 6, 791–795 Permission R Myeni

Nature climate change 6, 791-795 2016, «greening of the Earth and its drivers»

The Truth: It Happens Like in Our Reactors

- CO_2 released is growing and growing → 40 Gt/year
- Temperature of the atmosphere is increasing →



As it happens in our polymerization reactions:

- Reaction rate of Photosynthesis is increasing more and more!!!

> Vegetation structural change since 1981 significantly enhanced the terrestrial carbon sink

Nature Communications, volume 10, Article number: 4259 (2019)

WHAT WE CAN DO?

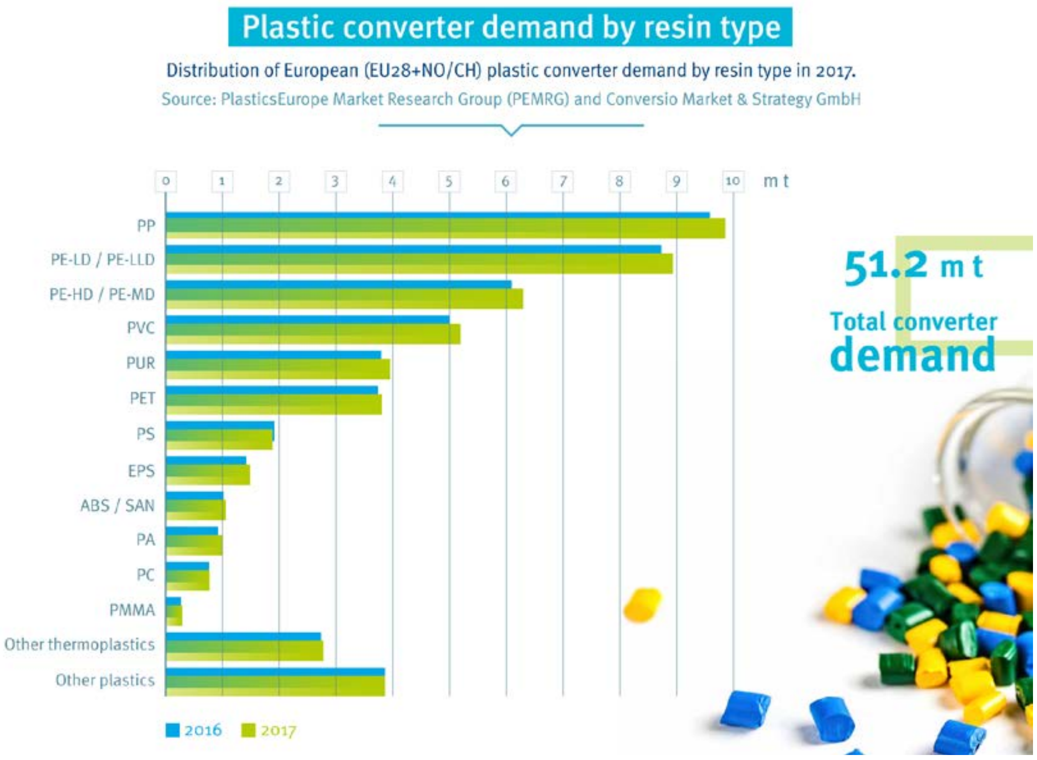
OIL PRODUCTION: 93 MBbl/day → MORE THAN 170 t/second

- Oil →

ROAD	50.1%	
Petrochemicals	14.3%	→ 4% goes into Plastic
Residential	9.2%	
Aviation	7.8%	
Marine	3.4%	
Electircity Generation	2.3%	
Domestic	1.7%	
Other Uses	11.2%	

IEA, «Production of crude oil including lease condensate», 31.3.19

Something More About Plastic



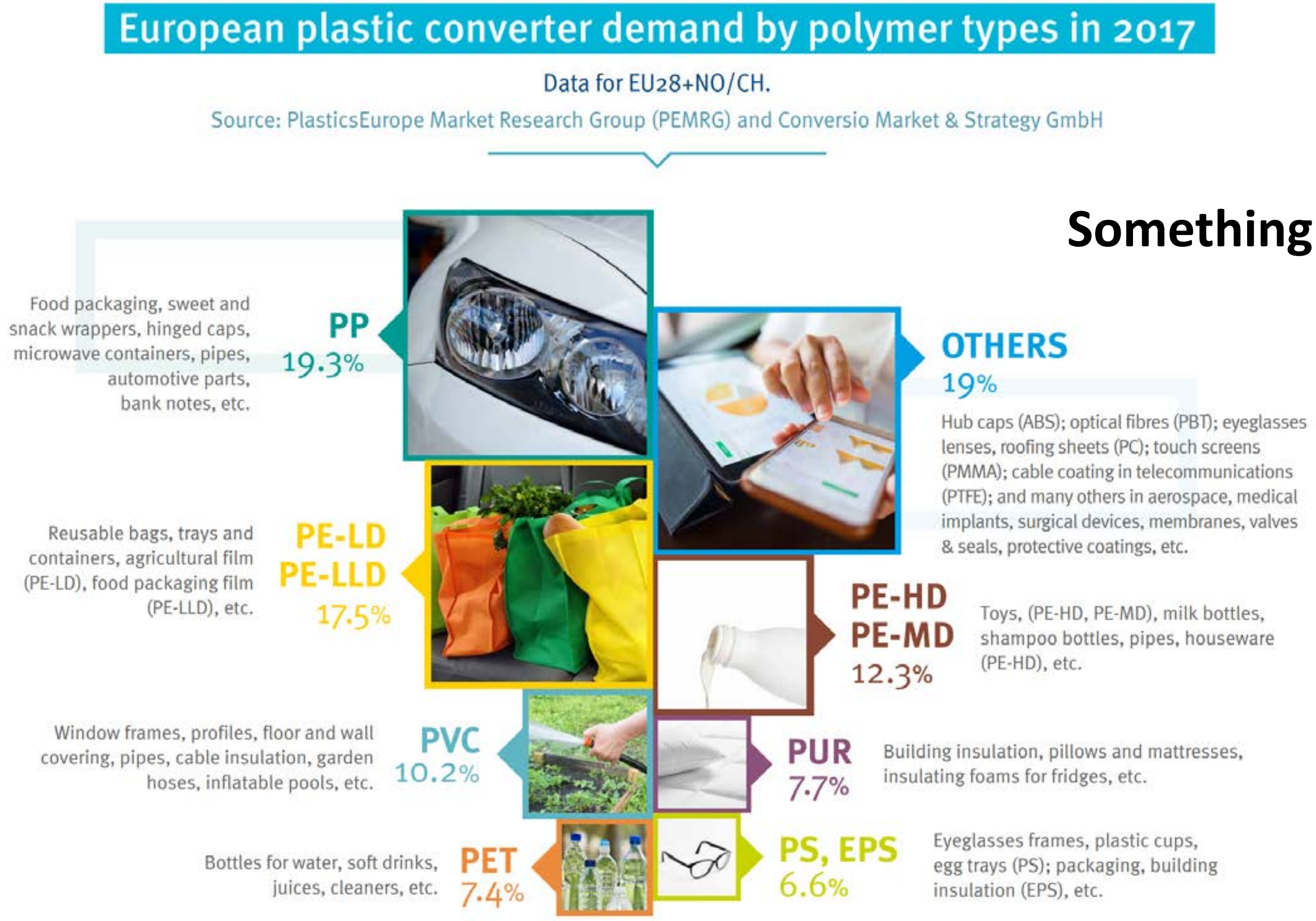
PLASTIC PRODUCTION: 348 Mt/year

PP	68 Mt
LDPE	64 Mt
PP&A films	59 Mt
HDPE	52 Mt
PVC	38 Mt
PET	33 Mt
PUR	27 Mt
PS	25 Mt
Additives	25 Mt
Others	16 Mt

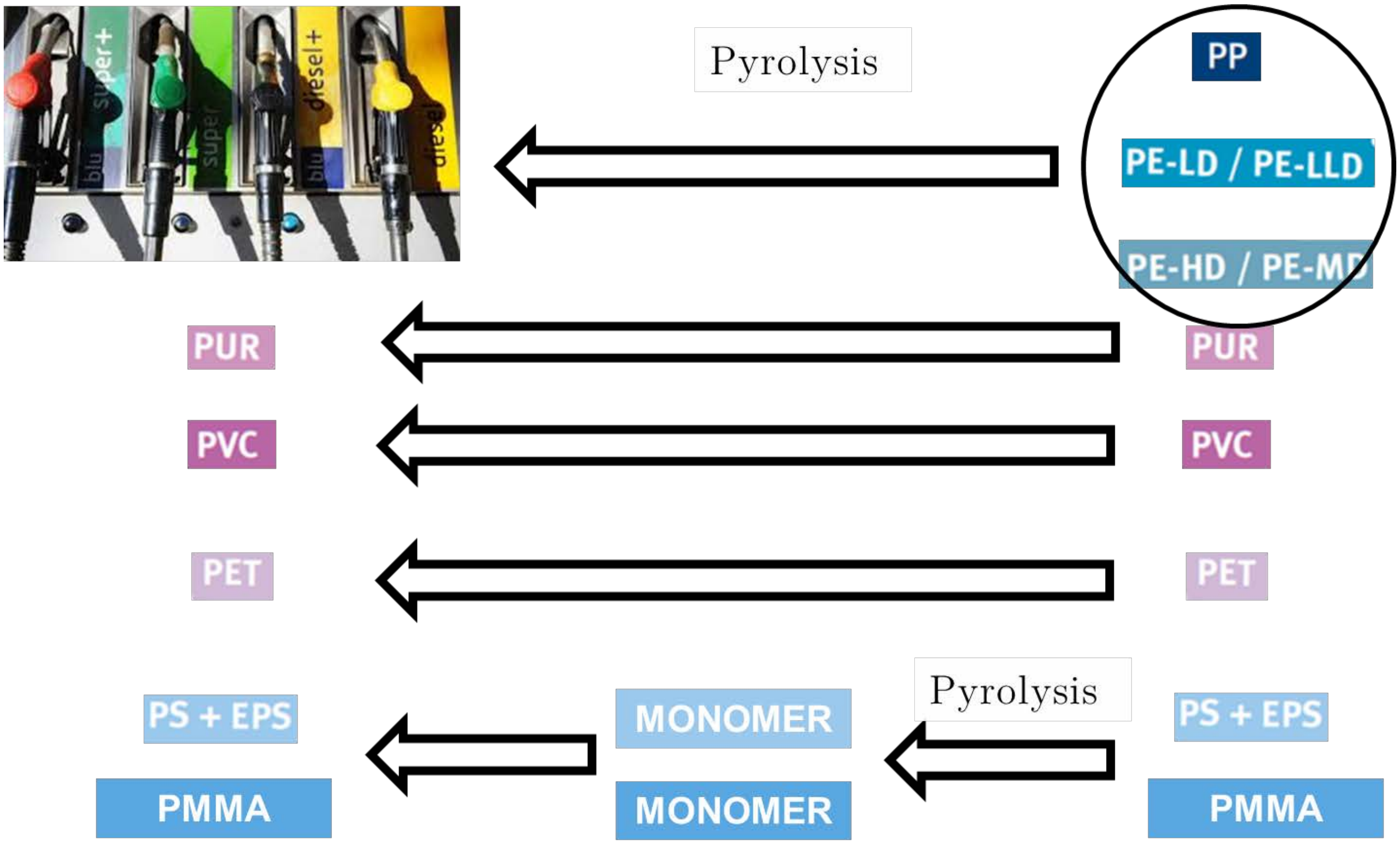
https://www.plasticseurope.org/application/files/6315/4510/9658/Plastics_the_facts_2018_AF_web.pdf

Something more about Plastic

Something More About Plastic



Chemical Recycling



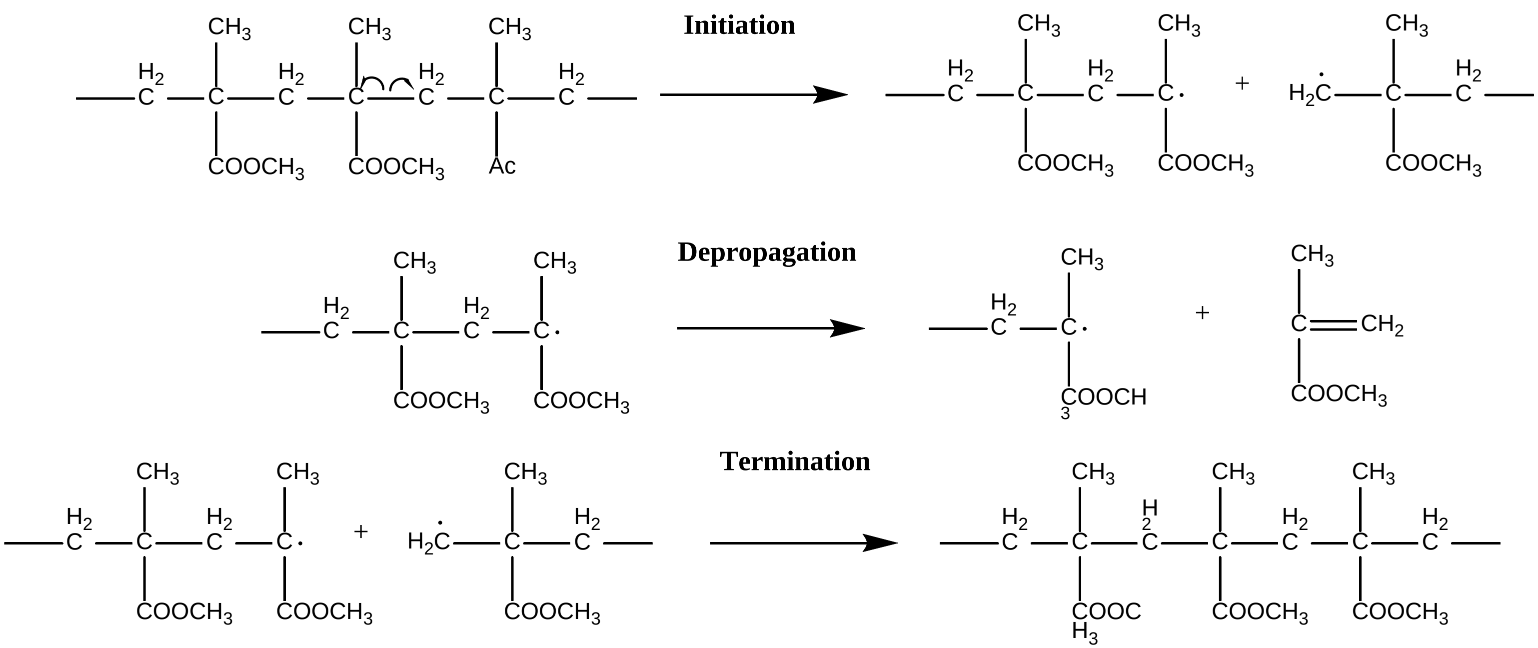
Styrene-Acrylics, an example of Chemical Recycling

Due to the results shown in table, the pyrolysis technique can be a promising system for the depolymerisation of PMMA and PS thanks to relatively low Temperature and high monomer recovery

Feed	Pyrolysis temperature, °C	Gas, wt %	Oil, wt %	Residue, wt %	Others, wt %
Polyethylene (PE)	760	55.8	42.4	1.8 C	
Polypropylene (PP)	740	49.6	48.8	1.6 C	
Polystyrene (PS)	580	9.9	24.6	0.6	64.9 styrene
Mixture PE – PP – PS	750	52.0	46.6	1.4	
Polyester (PETP)	768	50.8	40.0	7.1	2.1 H_2O
Polyurethane (PUR)	760	37.9	56.3	0.5	5.0 H_2O 0.3 HCN
Polyamide (PA-G)	760	39.2	56.8	0.6	3.4 HCN
Polycarbonate (PC)	710	26.5	46.4	24.6	2.5 H_2O
Poly(methyl methacrylate) (PMMA)	450	1.25	1.4	0.15 C	97.2 MMA
Poly(vinyl chloride) (PVC)	740	6.8	28.1	8.8	56.3 HCl
Polytetrafluoroethylene (PTFE)	760	89.3	10.4	0.3	
Medical syringes	720	56.3	36.4	5.8	1.5 steel
Plastic from household separation	787	43.6	26.4	25.4	4.6 H_2O
Plastic from car shredding	733	29.9	26.7	27.6	14.0 metals 1.8 H_2O
Ethylene – propylene – diene rubber (EPDM rubber)	700	32.3	19.2	47.5	1.0 H_2O
Styrene – butadiene rubber (SB rubber)	740	25.1	31.9	42.8	0.2 H_2S
Scrap tires	700	22.4	27.1	39.0	11.5 steel
Lignin	500	3.4	29.9	49.3	17.4 H_2O
Cellulose (wood)	700	47.1	23.0	18.6 C	11.3 H_2O
Sewage sludge	600	34.3	27.7	33.2	4.8 H_2O

PMMA Recycling

The thermal decomposition of PMMA can be industrially performed in an **extrusion system, in a lead bath or in a fluid bed**.



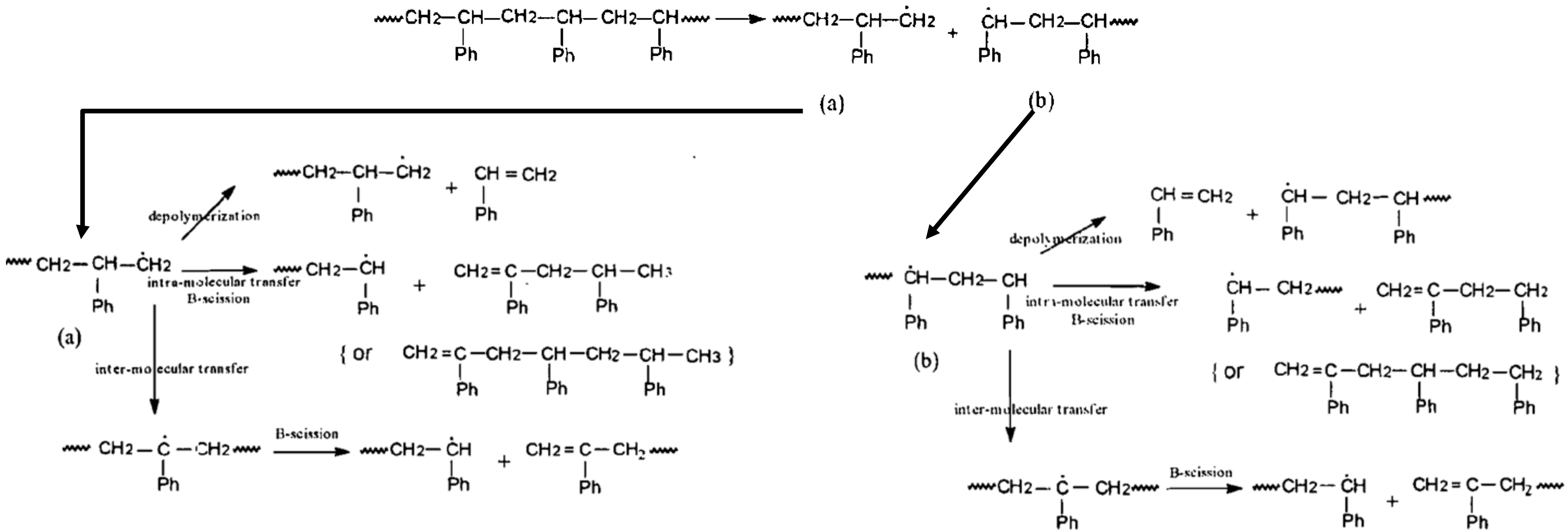
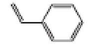
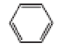
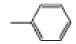
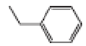
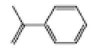
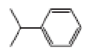
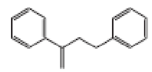
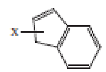
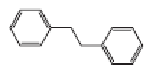
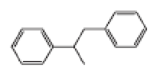
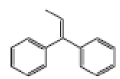
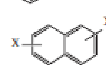
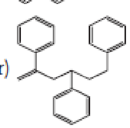
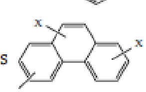


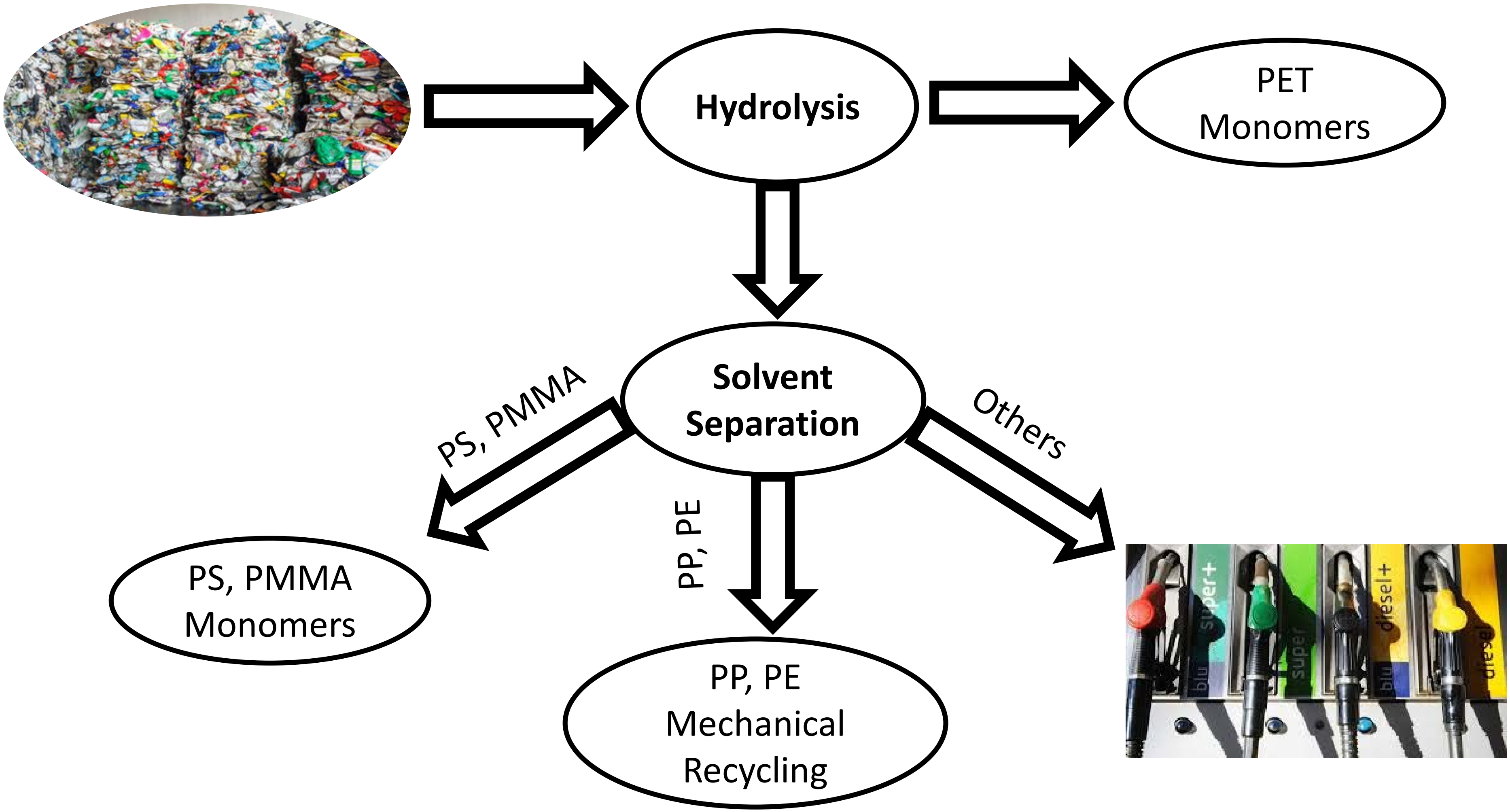
Table 4. The activation energies and preexponential constants of the pyrolysis products of PS

Parameter	E_{act}(kJ/mol)	k_0(sec^{-1})	R
monomer	77.3	3.64×10^4	0.997
dimer	67.1	5.13×10^3	0.990
trimer	62.4	2.11×10^3	0.995
G1	77.0	3.45×10^4	0.998
G2	63.7	2.92×10^3	0.990
G3	58.4	9.60×10^2	0.993
total products	71.3	1.16×10^4	0.998

PS Recycling

Compounds, chemical formula	Thermal (PS1)	Catalytic BaO (PS2)	Catalytic FCC (PS3)	Plastic container (PS4)	Plastic glass (EPS) (PS5)
Styrene (monomer) 	63.9	69.6	45.1	53.3	70.0
Benzene 	–	–	1.9	–	0.1
Toluene 	2.0	2.4	3.1	5.6	2.5
Ethylbenzene 	0.5	1.1	–	1.9	1.5
α-Methylstyrene 	2.1	2.6	6.3	5.9	2.3
Xylene 	–	–	16.8	–	–
Cumene 	–	–	1.7	0.2	0.3
2,4-Diphenyl-1-butene (dimer) 	14.0	18.4	1.9	11.9	9.0
Indane, Indene, etc. 	2.0	0.3	5.0	2.5	0.2
1,2-Diphenylethane 	2.2	0.7	0.9	2.1	0.8
1-Methyl-1,2-diphenylethane 	1.1	0.4	0.5	1.4	0.4
1,3-Diphenylpropane 	0.6	0.6	0.5	2.8	0.8
1,1′-Diphenylpropene 	0.7	0.4	1.1	–	0.7
Naphthalene and derivatives 	0.1	–	1.2	–	–
2,4,6-Triphenyl-1-hexene (trimer) 	2.2	1.8	0.3	3.5	5.0
Phenanthrene and derivatives 	0.2	–	4.7	0.4	0.3
Other aromatic compounds	8.4	1.7	9.0	8.5	6.1

Chemical Separation



Prof. Davide Moscatelli
Dept. Chemistry Materials and Chemical Engineering G. Natta
Building 6
Piazza Leonardo Da Vinci 32, 20133 Milano
davide.moscatelli@polimi.it
02.2399.3135
+39.328.9072138