MMA two

Second Generation MethylMethAcrylate

Concepts of chemical recycling: part 2
Scale-up and industrial implementation

Jean-Luc DUBOIS

ARKEMA
INNOVATIVE CHEMISTRY

Virtual Workshop on Polymer Recycling

Sept 15th 2020

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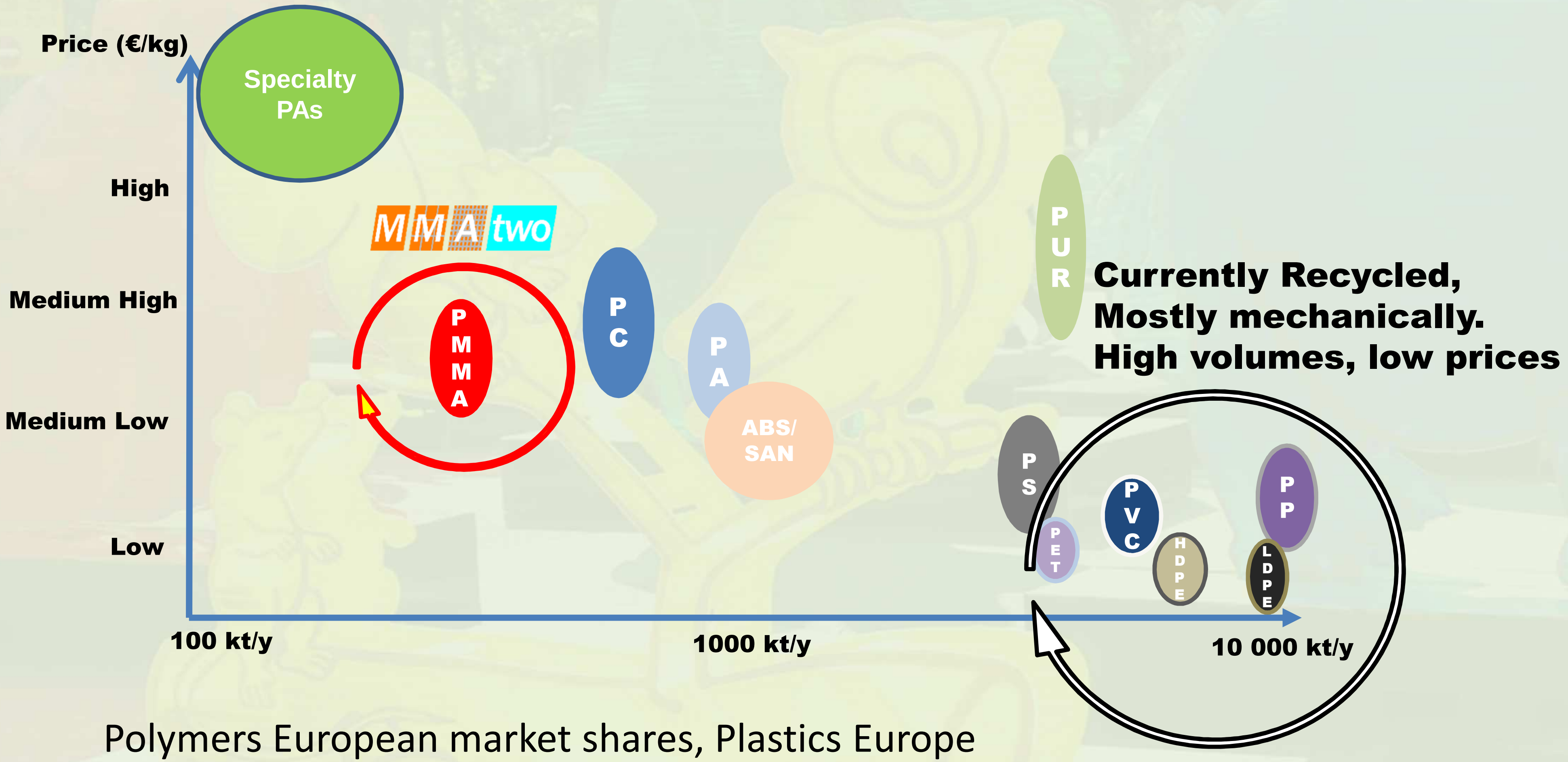
Polymers are not all born equal for recycling

Challenges and Incentives for PMMA Recycling

Comparison with other Polymers

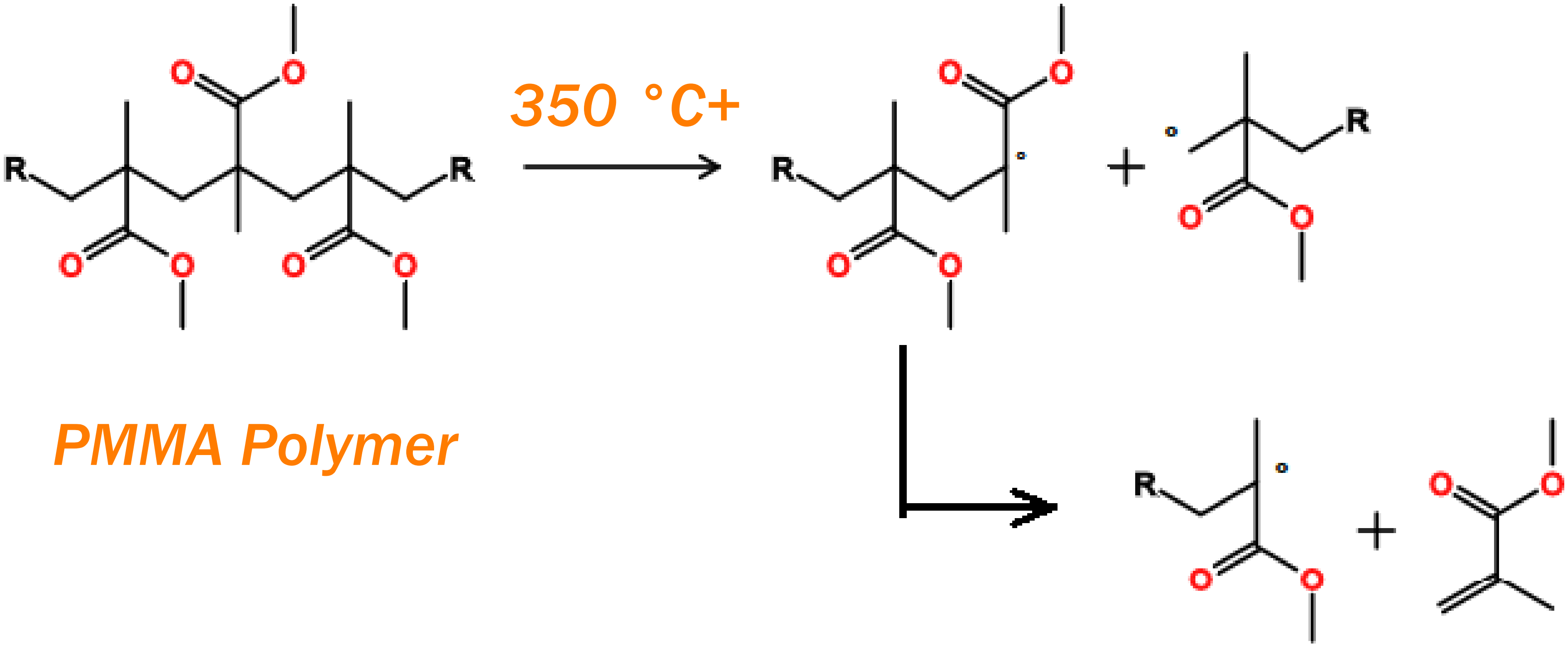
PMMA: high value, but low volume



Polymers European market shares, Plastics Europe
Plastics converter demand by resin type (2016)

Source: JL DUBOIS –November 20th 2018

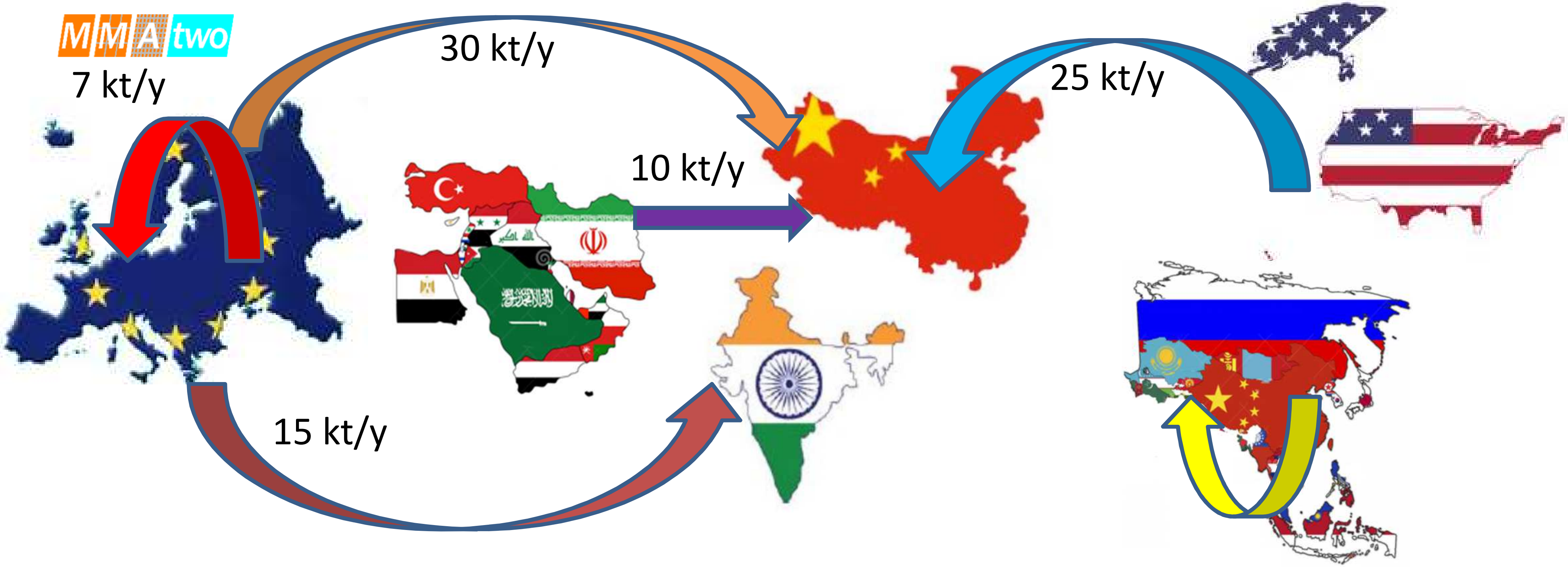
PMMA Thermal depolymerization process
Radical Unzipping Mechanism



PMMA Polymer

MMA, Monomer

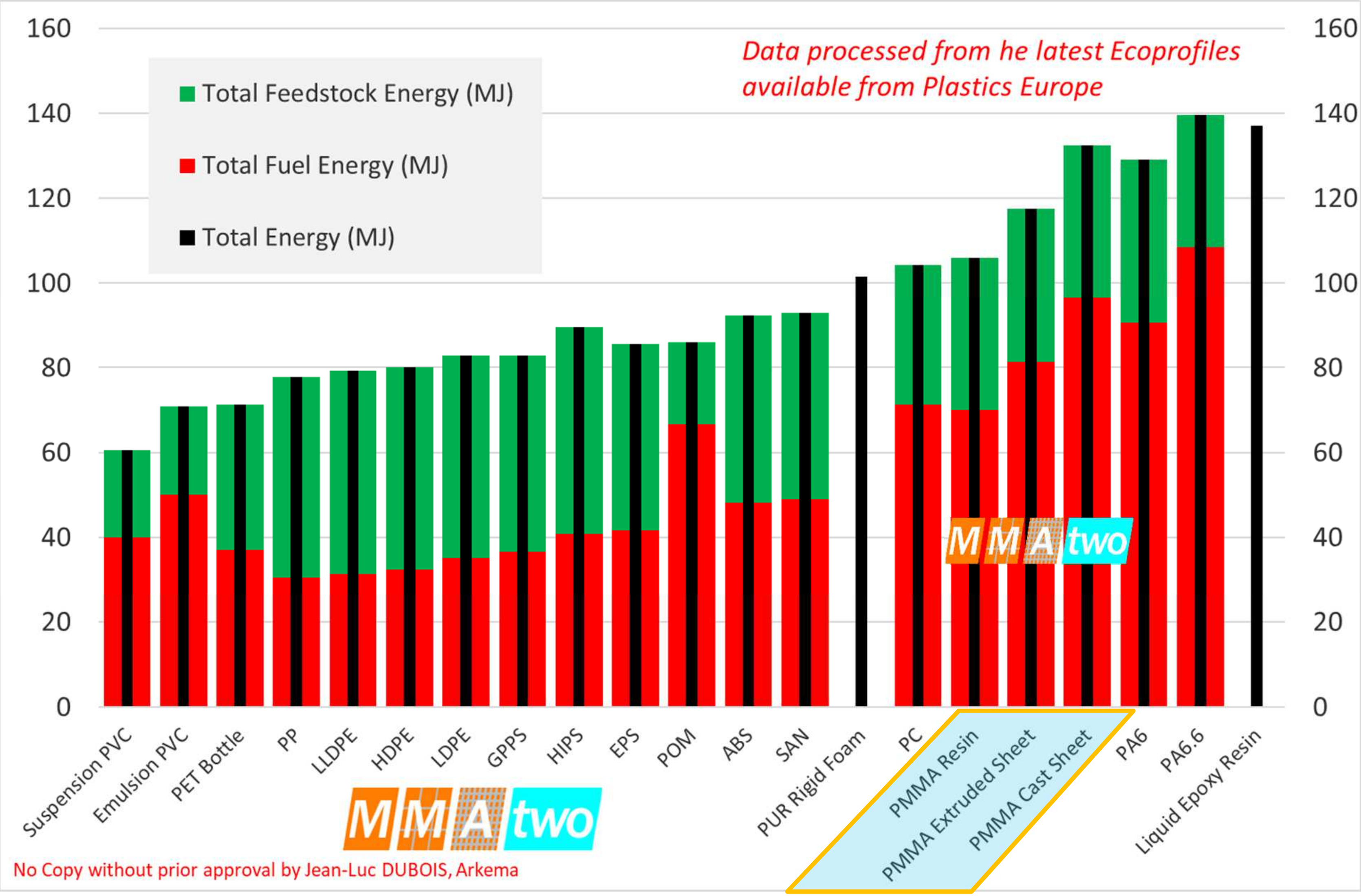
2019 PMMA scraps trade for depolymerization



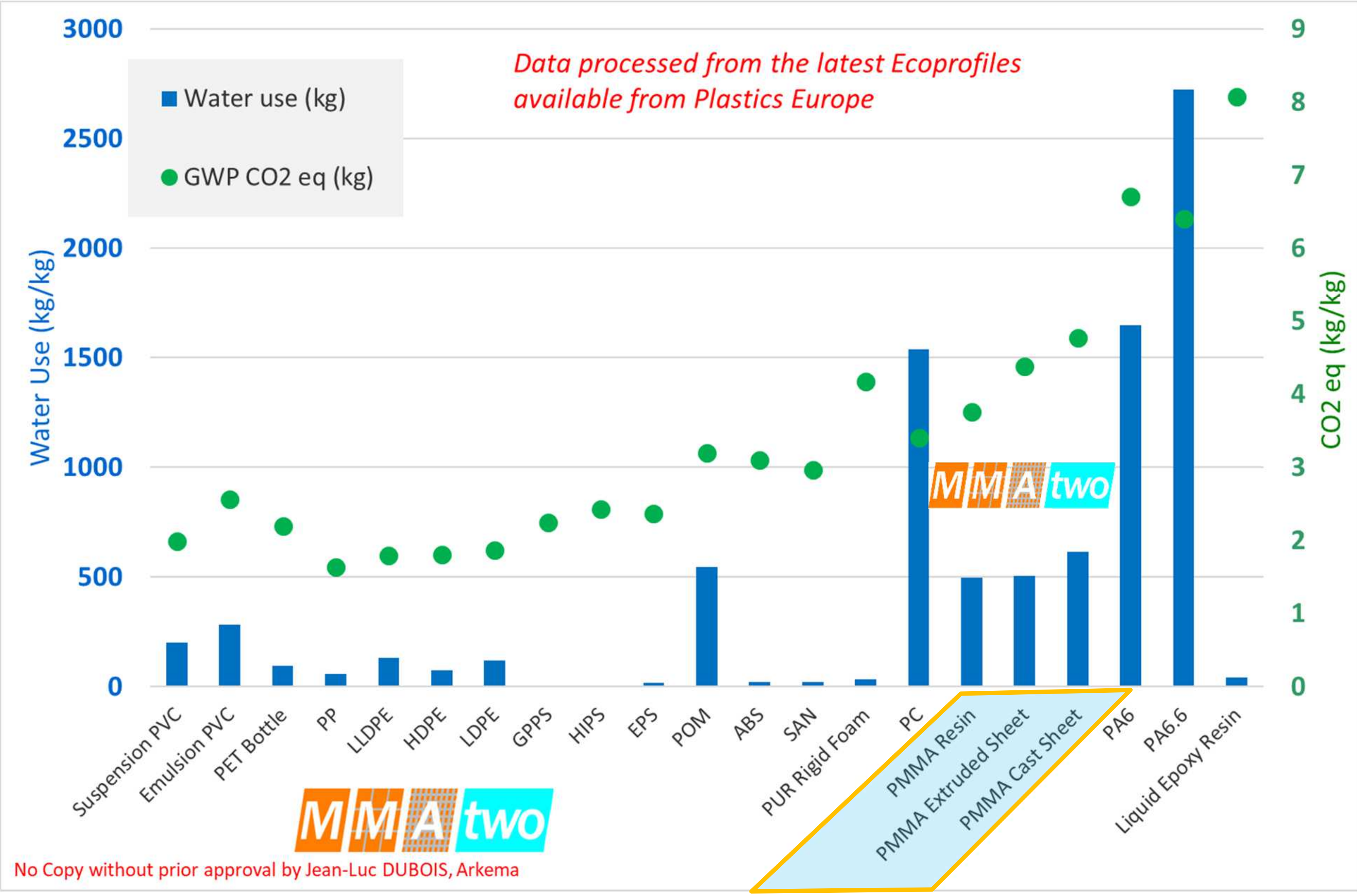
To be further refined during the MMAtwo project
(Data collected from Customs, Traders, Recyclers)

200 kt/y prior to the import ban
100 kt/t after
(Source: Japan Chemical Daily, May 2019)

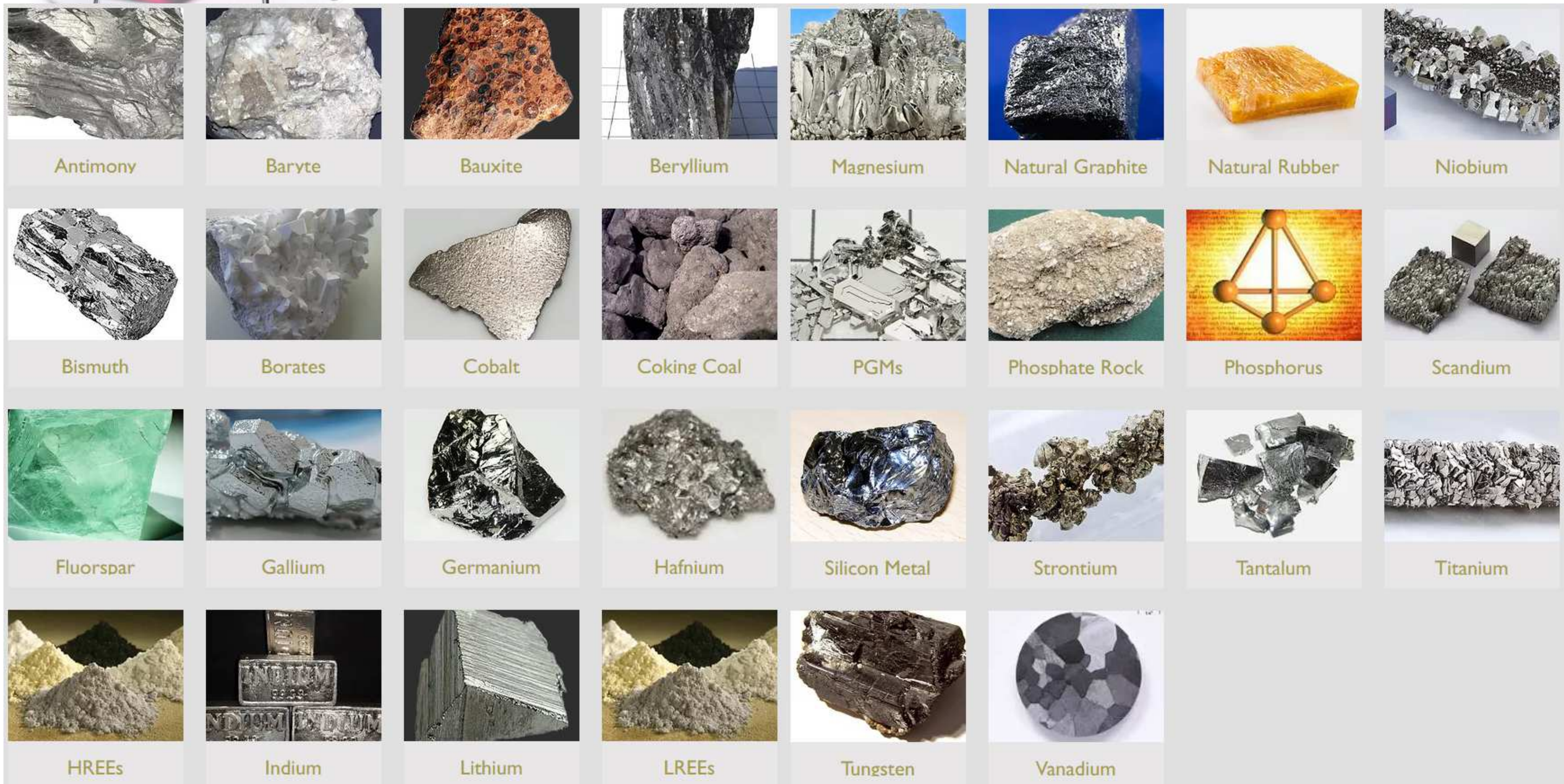
Energy Consumption in Polymers production



Water consumption and CO_2 eq emissions

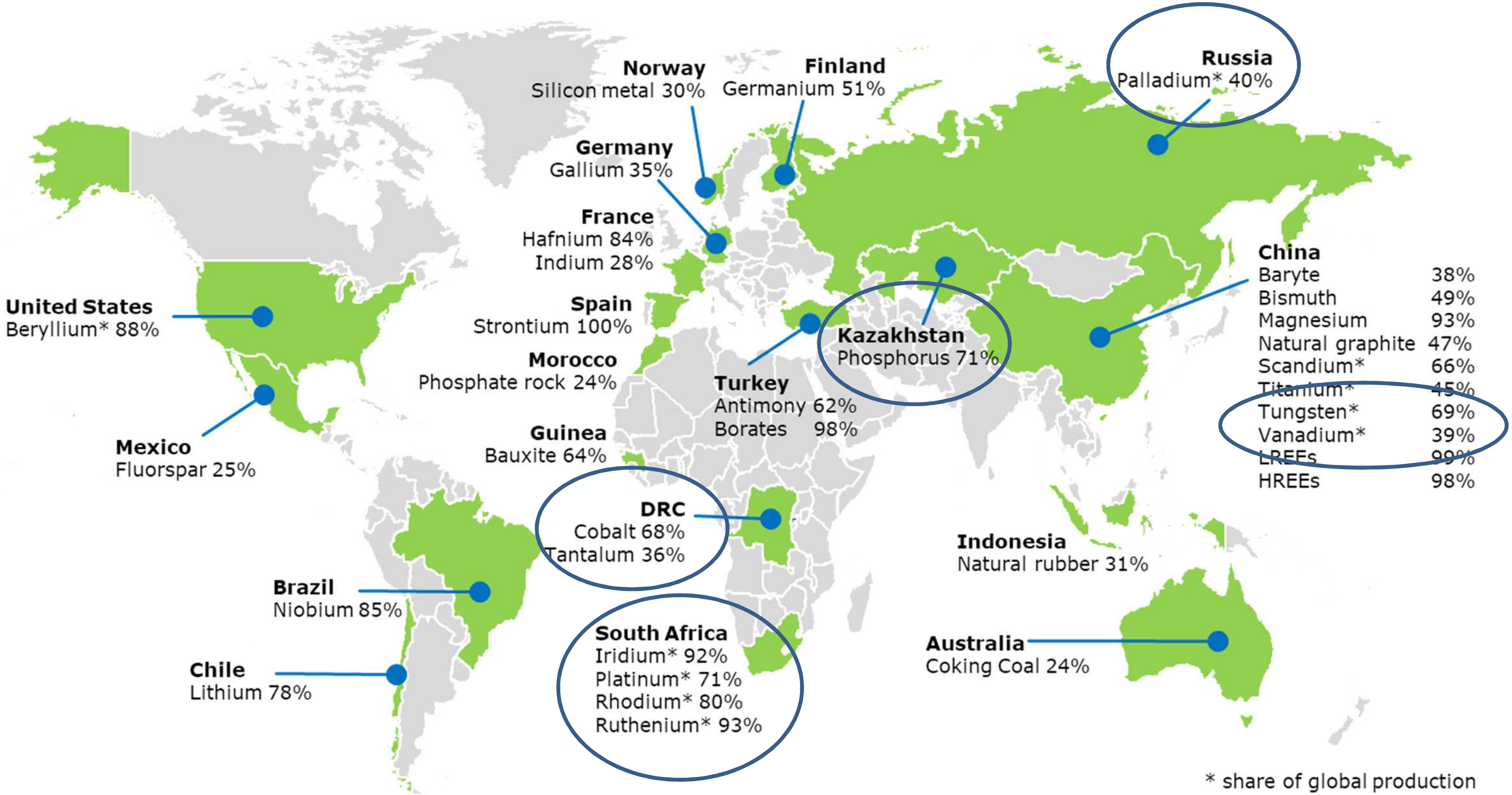


Incentive for Recycling Critical Raw Materials



https://www.crmalliance.eu/critical-raw-materials

Critical raw materials



https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en

C3 (Acetone) Route to MMA: Synthesis process used in EU

(based on MMA eco-profile)

2020 Critical Raw Materials (mg/kg MMA C3 route)			
Antimony	**Gallium**	**Phosphate rock**	
1.88 E-5	1.6 E-6		
Baryte	**Germanium**	**Phosphorus**	**Heavy Rare Earth Elements**
2298		**139**	Europium: 3.06 E-3
Bauxite	**Hafnium**	**Scandium**	
Beryllium	**Indium**	**Silicon metal**	**Light Rare Earth Elements**
	1 E-03	2.45 10-6	**Lanthanum: 0.366**
Bismuth	**Lithium**	**Strontium**	**Cerium: 1.22**
	1.14 E-6		**Neodymium: 0.202**
Borate	**Magnesium**	**Tantalum**	Samarium: 1.53 10-2
0.0048	6.73E-03	1.53 E-3	
Cobalt	**Natural Graphite**	**Titanium**	**Platinum Group Metals**
5.75 E-4		8.11 E-3	Palladium: 1.84 10-3
Coking Coal	**Natural Rubber**	**Tungsten**	**Platinum: 0.307**
			Rhodium: 1.12 10-3
Fluorspar	**Niobium**	**Vanadium**	Rhenium: 7.67 10-6
93.5		**20.8**	Ruthenium: 6.95 10-6

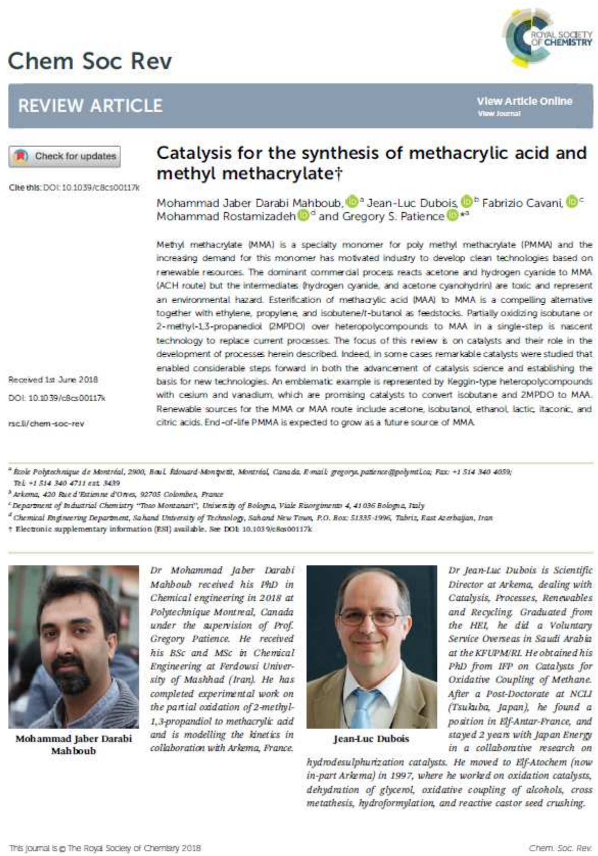
MMA C2 and C4 routes: Catalysts used

C4 Routes:

Isobutene Oxidation: Mo-Bi-Fe-Ni-Co-P-W-O…
Methacrolein Oxidation: P-Mo-V-Cu-Cs-O…
Methacrolein Oxyesterification: Pd-Pb or Au-Ni

C2 Routes:

MethoxyCarbonylation of ethylene: Pd, P
Hydroformylation: Rh, P
Aldolization: Cs-Zr-X
Oxyesterification: Pd-Pb, Au-Ni
Methacrolein Oxidation: P-Mo-V-Cu-Cs-O…



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Catalysis for the synthesis of methacrylic acid and methyl methacrylate†

Mohammad Jaber Darabi Mahboub,[a] Jean-Luc Dubois,[b] Fabrizio Cavani,[c] Mohammad Rostamizadeh[d] and Gregory S. Patience*[a]

Methyl methacrylate (MMA) is a specialty monomer for poly methyl methacrylate (PMMA) and the increasing demand for this monomer has motivated industry to develop clean technologies based on renewable resources. The dominant commercial process reacts acetone and hydrogen cyanide to MMA (ACH route) but the intermediates (hydrogen cyanide, and acetone cyanohydrin) are toxic and represent an environmental hazard. Esterification of methacrylic acid (MAA) to MMA is a compelling alternative together with ethylene, propylene, and isobutene/t-butanol as feedstocks. Partially oxidizing isobutane or 2-methyl-1,3-propanediol (2MPDO) over heteropolycompounds to MAA in a single-step is nascent technology to replace current processes. The focus of this review is on catalysts and their role in the development of processes herein described. Indeed, in some cases remarkable catalysts were studied that enabled considerable steps forward in both the advancement of catalysis science and establishing the basis for new technologies. An emblematic example is represented by Keggin-type heteropolycompounds with cesium and vanadium, which are promising catalysts to convert isobutane and 2MPDO to MAA. Renewable sources for the MMA or MAA route include acetone, isobutanol, ethanol, lactic, itaconic, and citric acids. End-of-life PMMA is expected to grow as a future source of MMA.

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Dr Mohammad Jaber Darabi Mahboub received his PhD in Chemical engineering in 2018 at Polytechnique Montreal, Canada under the supervision of Prof. Gregory Patience. He received his BSc and MSc in Chemical Engineering at Ferdowsi University of Mashhad (Iran). He has completed experimental work on the partial oxidation of 2-methyl-1,3-propandiol to methacrylic acid and is modelling the kinetics in collaboration with Arkema, France.

Jean-Luc Dubois

Dr Jean-Luc Dubois is Scientific Director at Arkema, dealing with Catalysis, Processes, Renewables and Recycling. Graduated from the HEI, he did a Voluntary Service Overseas in Saudi Arabia at the KFUPM/RI. He obtained his PhD from IFP on Catalysts for Oxidative Coupling of Methane. After a Post-Doctorate at NCLI (Tsukuba, Japan), he found a position in Elf-Antar-France, and stayed 2 years with Japan Energy in a collaborative research on hydrodesulphurization catalysts. He moved to Elf-Atochem (now in-part Arkema) in 1997, where he worked on oxidation catalysts, dehydration of glycerol, oxidative coupling of alcohols, cross metathesis, hydroformylation, and reactive castor seed crushing.

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Catalysis for the synthesis of methacrylic acid and methyl methacrylate.
•Mohammad Jaber Darabi Mahboub, Jean-Luc Dubois, F. Cavani, Mohammad Rostamizadeh, Gregory S. Patience

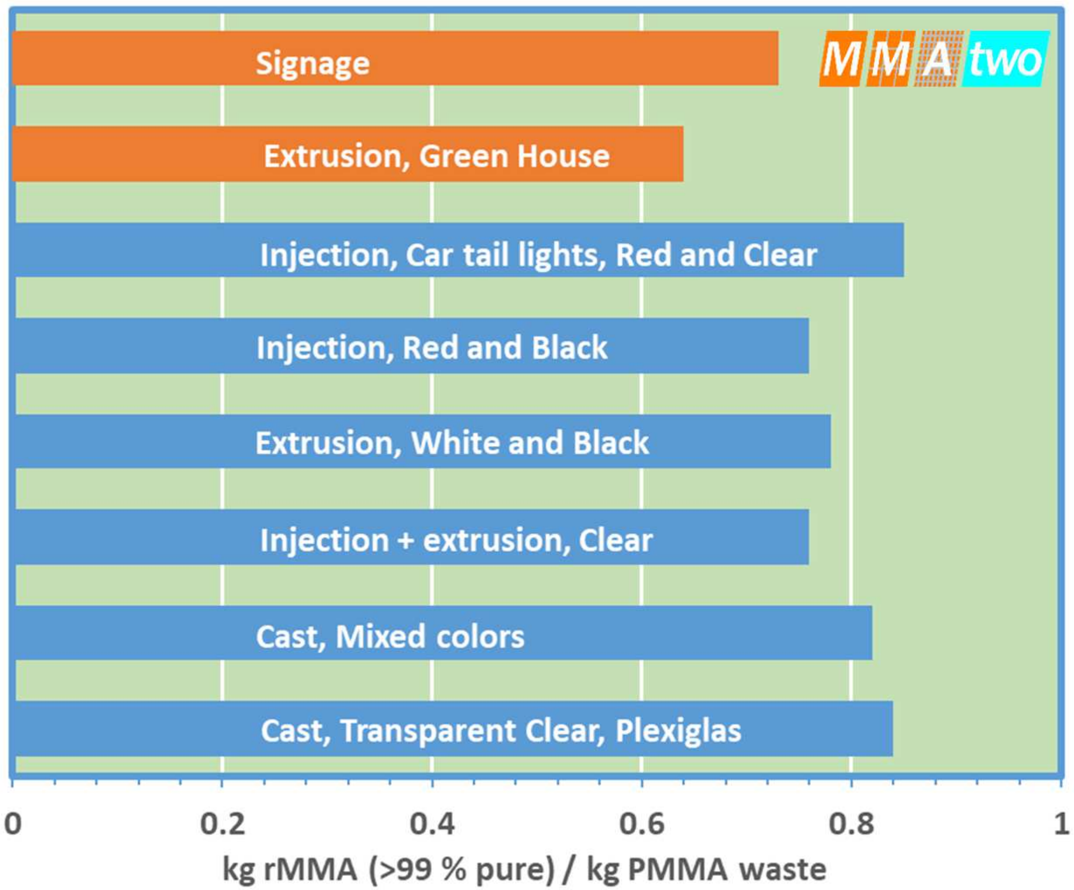
https://doi.org/10.1039/C8CS00117K

Mass Balance: Plastic to Monomer/Polymer (data from MMAtwo)

© ARKEMA Speichim processing

The crude MMA samples obtained at bench scale were further purified by **Speichim** to above 99 % purity grade.
The mass yield of high purity monomer from PMMA waste ranges from 64 to 85 wt %. All PMMA wastes were successfully converted to high quality monomer.

Source: MMAtwo Newsletter N° 2
Available on MMAtwo website



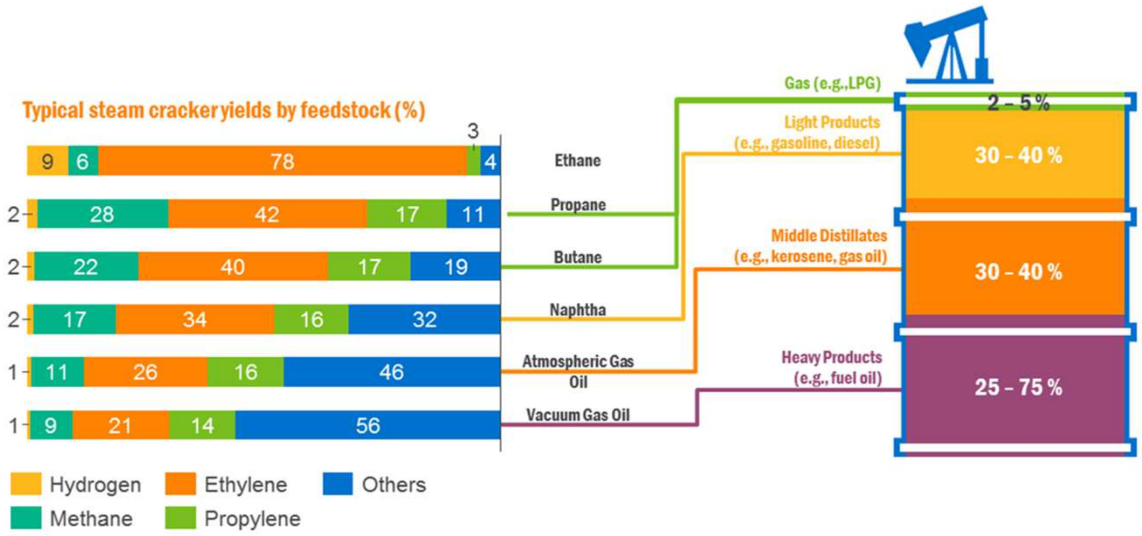
Orange: Post-Consumer, Blue: Post Industrial

Mass Balance Incentive: Plastic to Polymer Yield

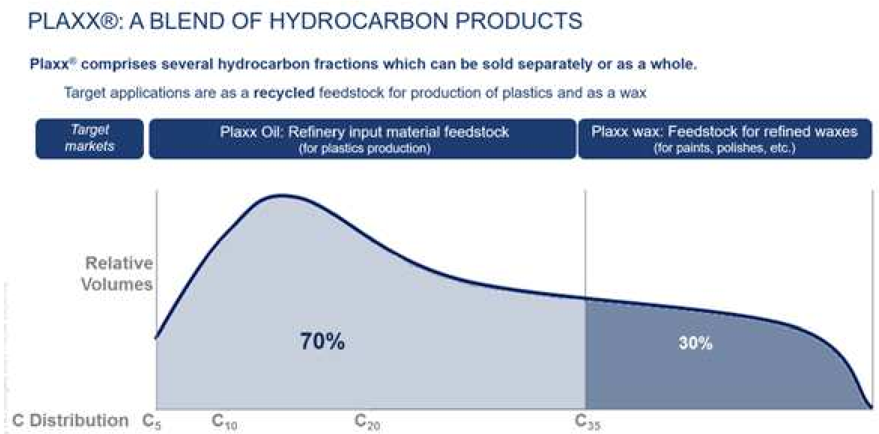
PMMA Case study: **64 to 85 wt % yield**

Polyolefins Case study: Process

- Pyrolysis of pure or mixed polyolefins to liquids (yield about 75 wt %)
- A part of the liquid is Naphtha like (about 70 wt %)
- Yield of a Naphtha Steam Cracker to Ethylene: e.g. 32 %, and to Propylene: 16 %.
- Global yield PE to PE = 75 % * 70 % * 32 % = 17 wt %; and
- Global yield Mixed Polyolefins to Mixed Polyolefins = 75 % * 70 % * 50 % = 26 wt %



https://www.nexant.com/resources/crude-oil-chemicals-back-fundamentals



Source: Recycling Technologies

Impact : environment & people GHG emissions and Non-Renewable Energy consumption estimates (MMAtwo project targets)

	Hypothesis	GHG emissions	Non-renewable energy
Waste collection	500 km average distance	0.147 kg CO_2 eq /kg rMMA	2.358 MJp/kg waste
Sorting, washing	Similar to other plastics	0.028 kg CO_2 eq /kg waste	0.335 MJp/kg collected waste
Grinding	Similar to other plastics	0.118 kg CO_2 eq /kg rMMA	1.426 MJp/kg rMMA
Depolymerization	5 MJ/kg crude rMMA @ 80% yield after distillation	0.413 kg CO_2 eq /kg rMMA	5.974 MJp/kg rMMA
Purification	50% self sufficiency by burning lights and heavies	0.500 kg CO_2 eq /kg rMMA	7.240 MJp/kg rMMA
TOTAL		1.205 kg CO_2-eq/kg rMMA **i.e. -65% vs. virgin MMA** (3.470 kg CO_2-eq/kg)	17.333 MJp/kg rMMA **i.e. -77% vs. virgin MMA** (74 MJp/kg)

Review of PMMA depolymerization technologies

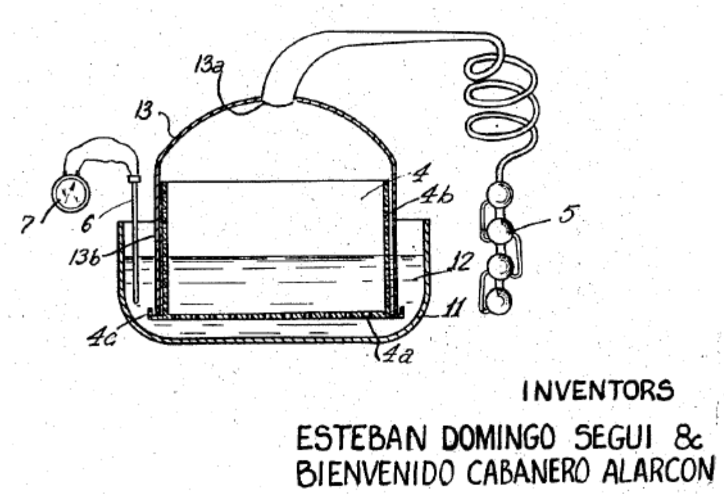
PMMA depolymerization technologies
Dry Distillation technologies -
Still in use in many countries

In 1936, Daniel Strain from DuPont, patented (US2030901) the depolymerization of PMMA in a distillation unit equipped with a condenser (so-called Dry distillation method). An 88 % yield was obtained and the recovered MMA could be repolymerized. Other patents on the purification of the recovered MMA followed.

Low Capex

Product quality
High Opex

PMMA depolymerization technologies Molten metal bath process

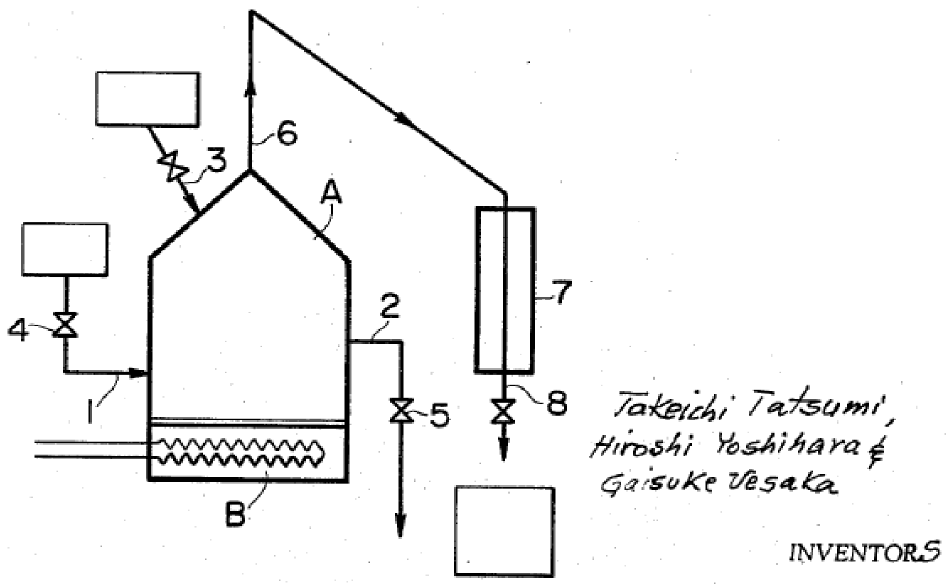


STATE OF THE ART TECHNOLOGY
Molten-Lead bath process Technology
Figure extracted from US Patent 2 858 255, (1958), E. Domingo Segui and B. Cabanero Alarcon.

Proven technology.
High track record with high quality wastes.
Still in use in Europe

Generate solid residues contaminated with the metal

Other molten metals and salts…



Other metals and metal salts (ex **US 3 886 202**, (1975) assigned to Denshi Kagaku KK, T. Tatsumi, H. Yoshihara, G. Uesaka) have been proposed to replace lead, but lead still offers the best performance.
Examples illustrate the process with Lithium chloride-Potassium chloride salts as heat transfer medium.

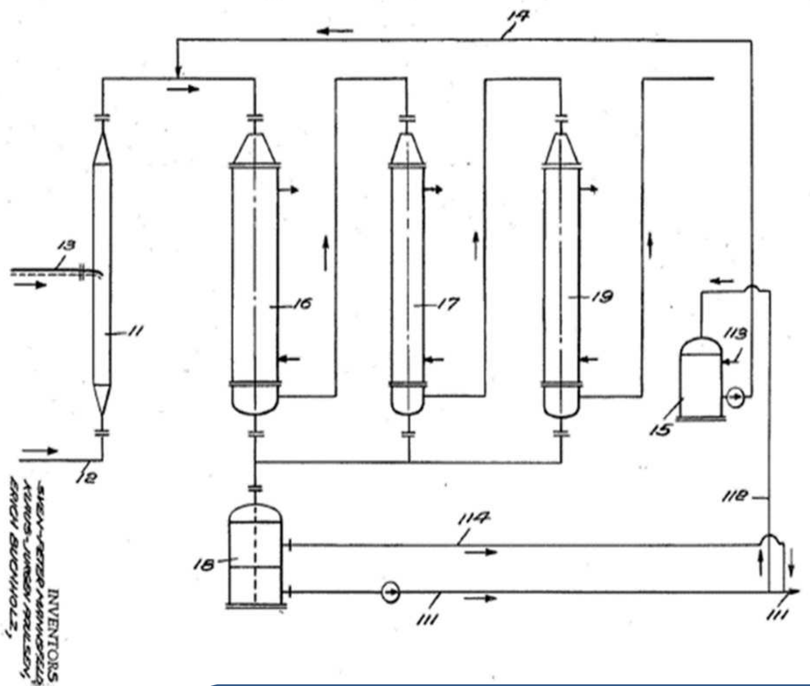
PMMA depolymerization technologies
High Boiler solvent

Depolymerization in the presence of a high boiler solvent US 2470361, Isador Miller and Arthur L Beiser. In a practical example as much **high boiler solvent as PMMA are heated together under vacuum from 200 to 340 °C**. Both solvent and MMA are condensed and MMA is distilled at atmospheric pressure. Solvent and remaining MMA are reused of a subsequent batch. This process has the disadvantage that some impurities will accumulate in the solvent, and that solid residues from the PMMA will be contaminated with solvents, leading to significant losses.

Might be interesting for mixed streams

High Energy consumption
Generate solid residues contaminated with the solvent

PMMA depolymerization technologies: Super heated steam



MMA is not soluble in water, easy separation

High Energy consumption

Flowsheet of the Superheated steam process, **US Patent US3494958**. Ground polymer below centimeter size is used in the process and superheated steam is used as heat carrier. The teaching of this patent is that the monomer would be rather stable in presence of steam and would not hydrolyze easily. This would be in contradiction with other results from the other processes in absence of steam that report the presence of methanol and water among the products.

PMMA depolymerization technologies
Fluid bed processes

Fig.1.

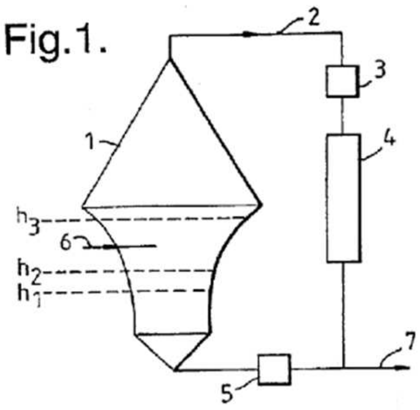
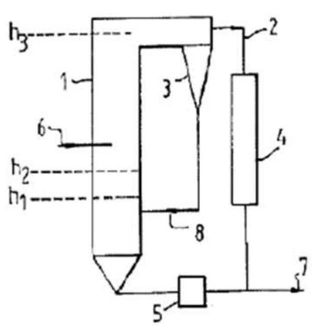
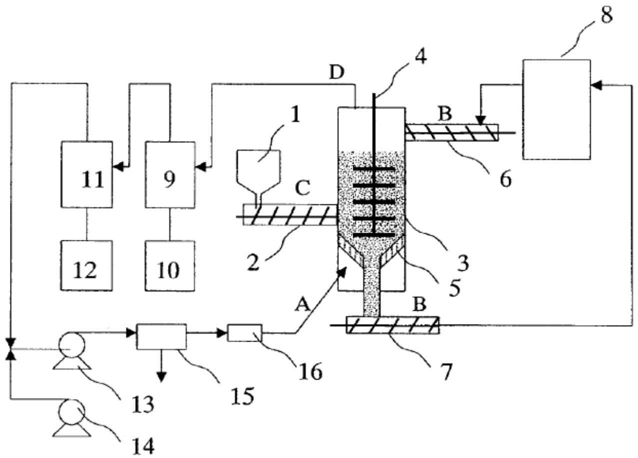


Fig.2.



The fluid bed technology was also investigated by ICI in collaboration with Mitsubishi Rayon, and later by Du Vergier **US 5 663 420** (1997), P.W. Vaughan, D.J. Highgate and Kaminsky et al. (J Anal. App. Pyrolysis 19 (1991) 311-318). In this endothermic process, the heat transfer medium is a hot sand bath which is circulated to be reheated in a separate capacity. Any remaining polymer is also burned before being returned to the reactor. The PMMA scraps are injected in the fluid bed and depolymerize when in contact with the hot sand. The carbonaceous materials produced and the PMMA residues are withdrawn with the sand and burned while reheating the sand which is returned to the reactor.

FIG. 6

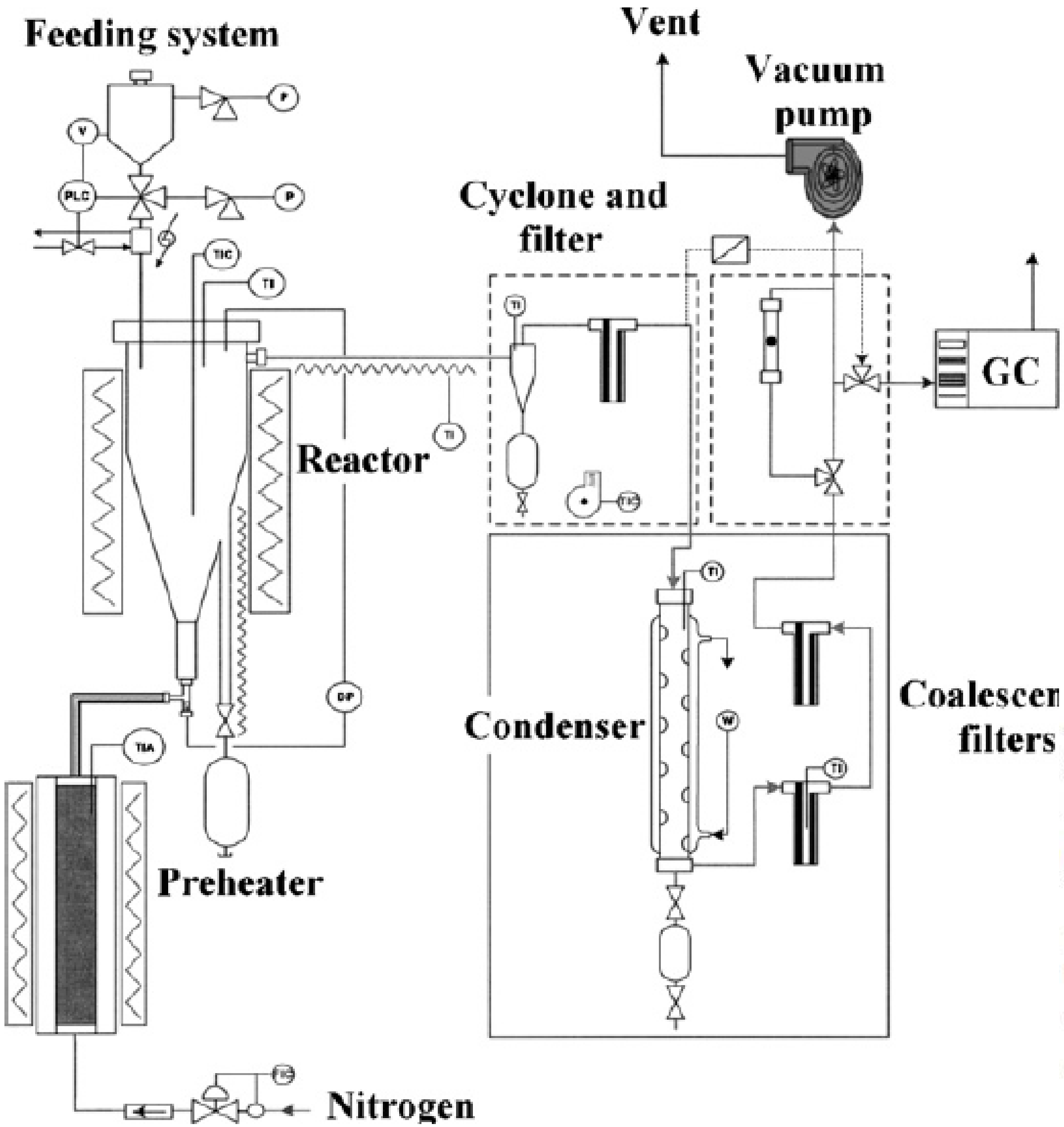


Mitsubishi Rayon has been operating a fluidized bed pilot unit of 2000 t/y capacity, maybe according to its **US Patent 8 304 573** (2012) A Sasaki, N. Kikuya, T. Ookubo, M. Hayashida (and **EP2157075B1**). Some details on the process have also been reported in conferences

Heat transfer

High Energy consumption
Reactor unstability

Spouted bed



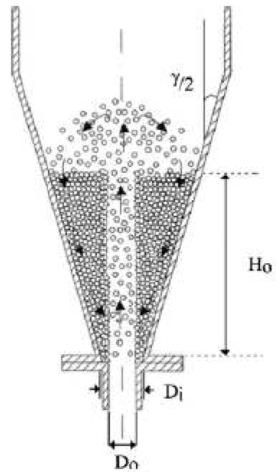


Fig. 2. Dimensions of the reactor and solid movement in a conical spouted bed reactor.

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Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

ELSEVIER

Recycling poly-(methyl methacrylate) by pyrolysis in a conical spouted bed reactor

Gartzen Lopez, Maite Artetxe, Maider Amutio, Gorka Elordi, Roberto Aguado, Martin Olazar*, Javier Bilbao

University of the Basque Country, Department of Chemical Engineering, P.O. Box 644-E48080, Bilbao, Spain

PMMA depolymerization technologies
Rotary kiln vs Auger Screw

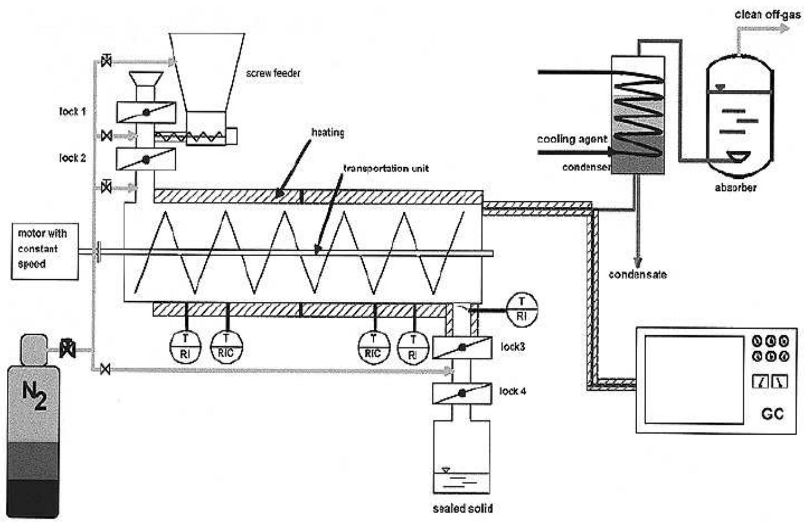


Figure 10. Laboratory tube reactor with internal mass transport.

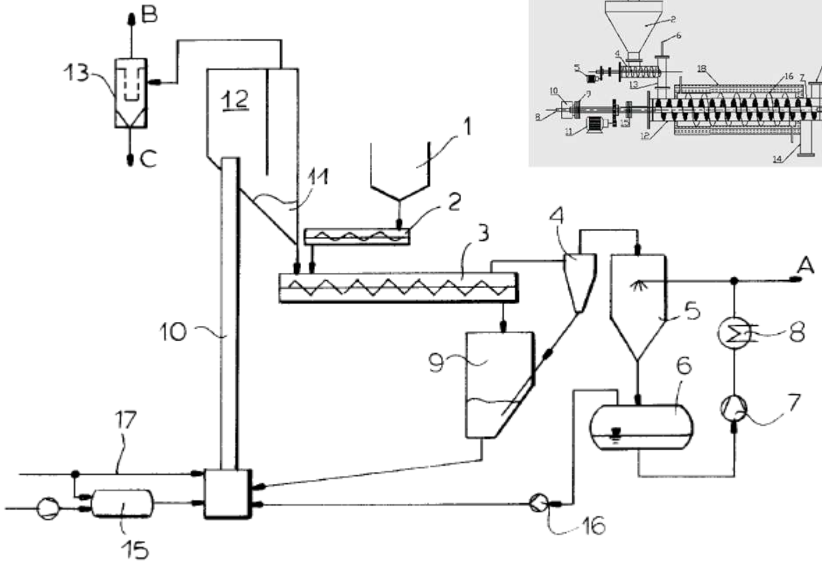
Emig et al. compared the fluid bed technology and the "extruder" type technology, such as developed by Rohm with high sand to polymer mass ratios, and recommend to investigate a rotary kiln reactor.
"Chemical Recycling of Polymer Materials", Frank Sasse and Gerhard Emig, in Chem. Eng. Technol., 21 (1998) 10

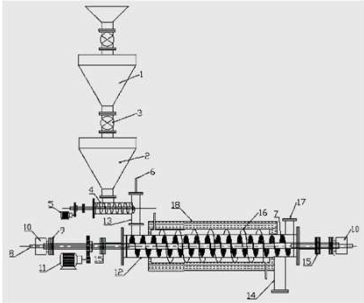
The **dry distillation is probably the oldest process**: British Patent GB460009 (1937) assigned to Rohm and Haas and US Patent 2 030 901, assigned to DuPont, 1936 – D.E. Strain. GB460 009 describes a process where PMMA is heated with hot sand over several hours. Char material remains in the sand and small amount of methanol and water are produced.. In the former case, the PMMA is contacted with sand and heated for several hours

Simple technology

Additional heat transfer medium.
Scale-up

PMMA depolymerization technologies Conveyor (Auger Screw) and Paddle reactors





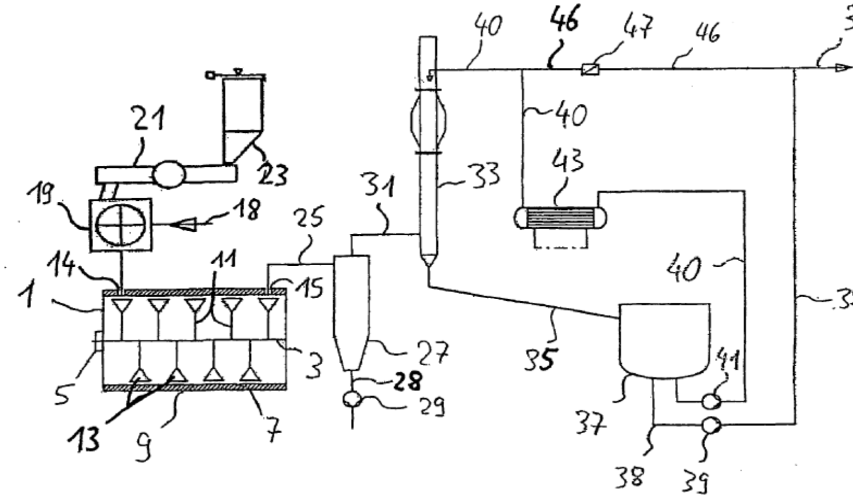
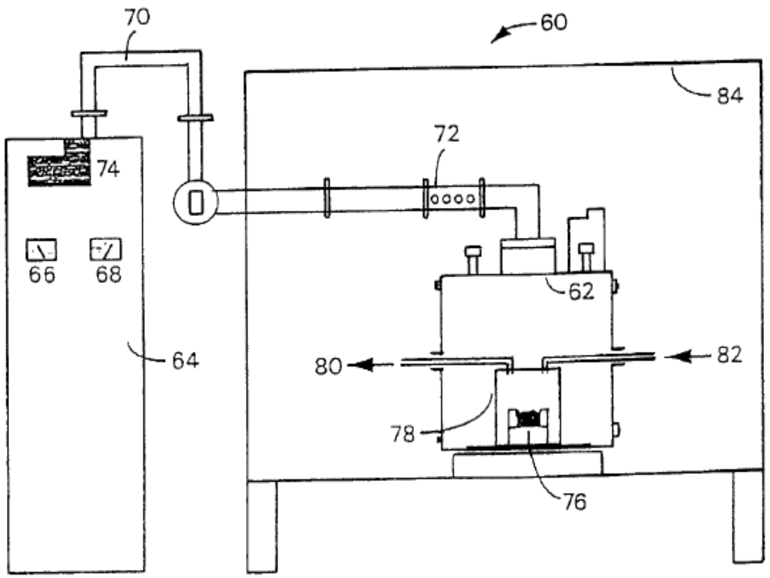


Fig. 1

Metallgesellscahft Aktiengesellschaft and Rohm GmbH Chemische Fabrik, investigated a process combining a circulation of hot sand as heat carrier (to reheat the sand) and a conveyor where the polymerization takes place. **US 6 469 203** (2002) H.-J. Weiss, J. Schmalfeld, U. Zenter, T. Groschang, U. Gropp, W. Fuss, R. Goedecke, E. Schöla.

Figure from **US patent application 2006/205845** assigned to Roehm GmbH, Egbert Schola and Mojmir Ruzicka. According to this process the PMMA scraps are fed in a paddle-reactor (rotating paddles) and a hot solid medium is placed in the capacity to transfer heat from external part of the reactor to the PMMA. The vapors are continuously removed and fine particles are trapped.

PMMA depolymerization technologies
Microwaves processes



US6160031 (2000) assigned to AECI described a depolymerization process using microwaves. As the depolymerization takes place at high temperature close to the self-ignition temperature, the reaction has to be carried out in a controlled environment. No specific effect of microwaves were demonstrated besides the heating effect, which make microwave an expensive way of heating polymers.

Direct Heat transfer

Lack of proven track record
Scale-up issues

Recent announcement:

Agilyx

Lucite International

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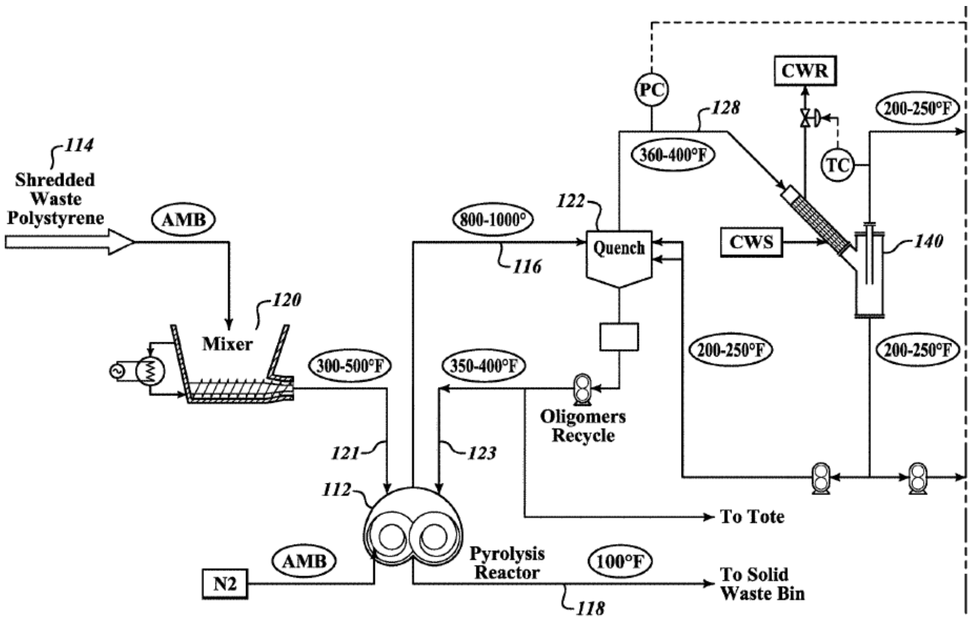
Press Release

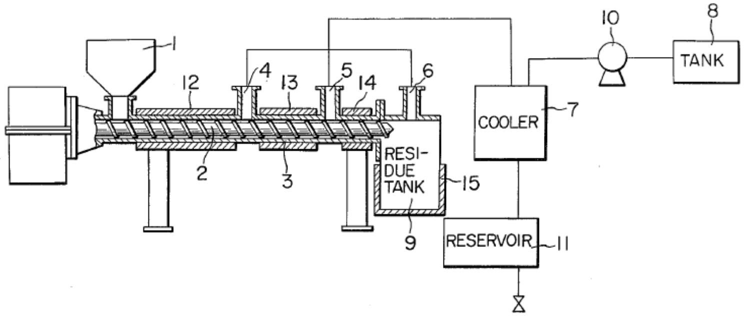
Lucite International and Mitsubishi Chemical Corporation increase the pace on a Circular Economy for PMMA with Agilyx Corporation

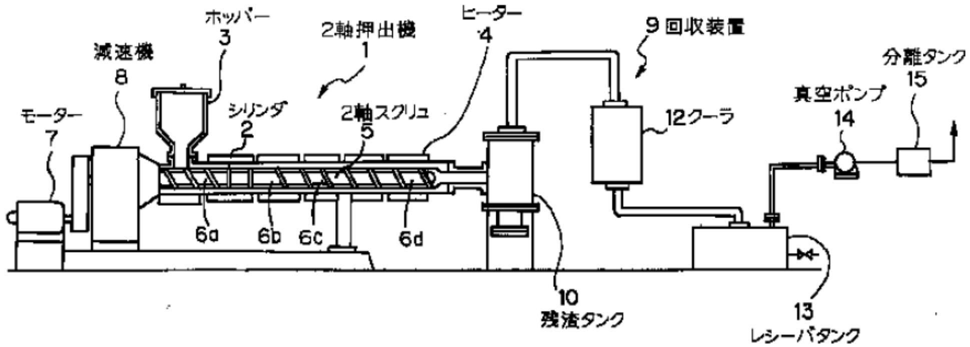
5th May 2020

Lucite International (LI), together with Agilyx Corporation (Agilyx), is working to deliver a significant contribution to the Circular Economy for PMMA (initially in Europe) with the support of LI's parent company, Mitsubishi Chemical Corporation (MCC).



PMMA depolymerization technologies Screw/extruder processes



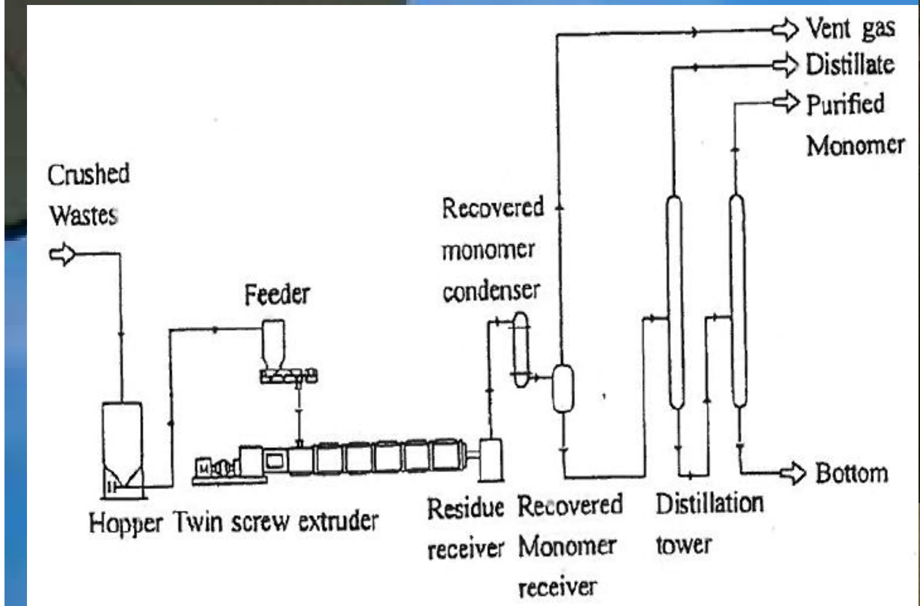


The reactive extrusion-depolymerization is illustrated in a number of patents, including US 3 959 357 (1976) assigned to **Japan Steel Works**, H. Tokushige, A. Kosaki, T. Sakai. This process uses single or twin screw extruder, and heat is provided internally and externally. The monomer produced by the depolymerization is discharged through venting orifices and condensed externally.

SELECTED TECHNOLOGY

In a more recent patent (priority 1997), **Japan Steel Works** describes another extruder type equipment, JP3410343, in which the depolymerized products is discharged at the end of the screw and solid residues are collected separately.

MMAtwo twin-screw in JSWEurope



JSW and Kosui Chemical (a small Japanese PMMA producer) developed a depolymerization process using a twin screw extruder technology in 1995. The MMA is produced at high temperature (400-500°C) from the electric heater and shearing from the mixing screw in the twin-screw extruder. The produced MMA is captured at the end of the twin screw extruder, cooled in a heat exchanger and purified. **The PMMA depolymerization unit at Kosui chemical was operated about 5 years**.

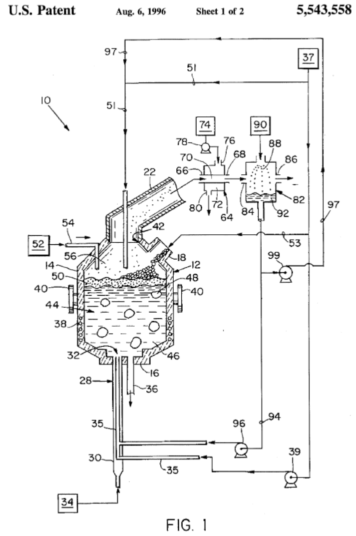
MMAtwo Pilot plant in operation

MMAtwo first depolymerization pilot tests completed (June 2020)

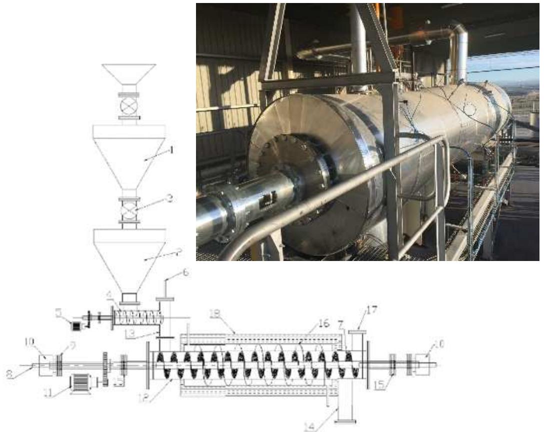
Recycled Methyl Methacrylate through PMMA depolymerization

Dry Distillation Still reactor

Rotating Drum reactor



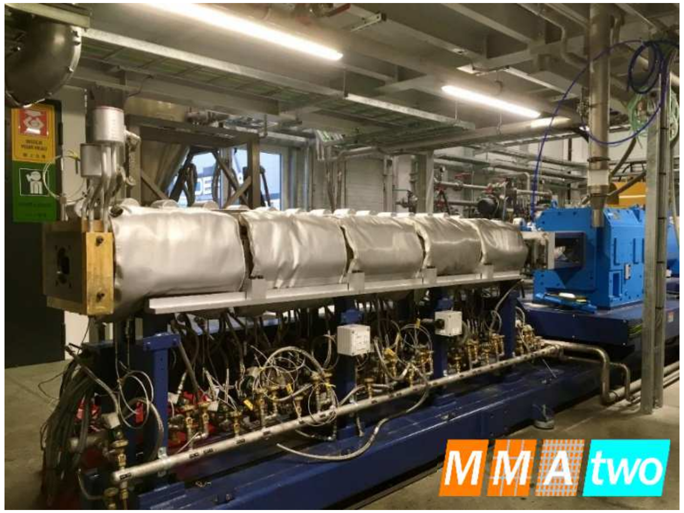
Molten Metal reactor

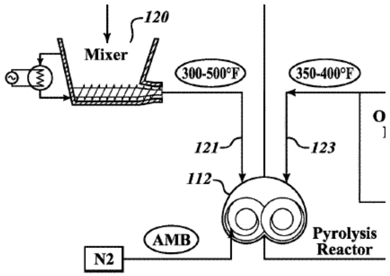


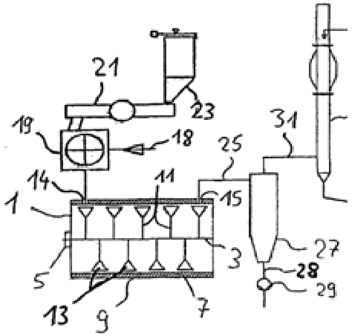
Auger reactor

(w or w/o circulating solid)

Twin-Screw reactor







Rotating Paddle reactor

Microwave or Induction reactors (not shown)

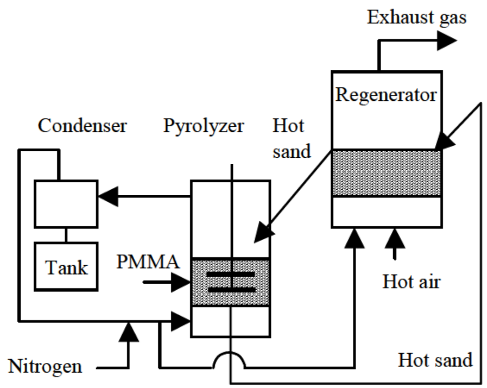


Fig.1 Apparatus

Fluid Bed reactor

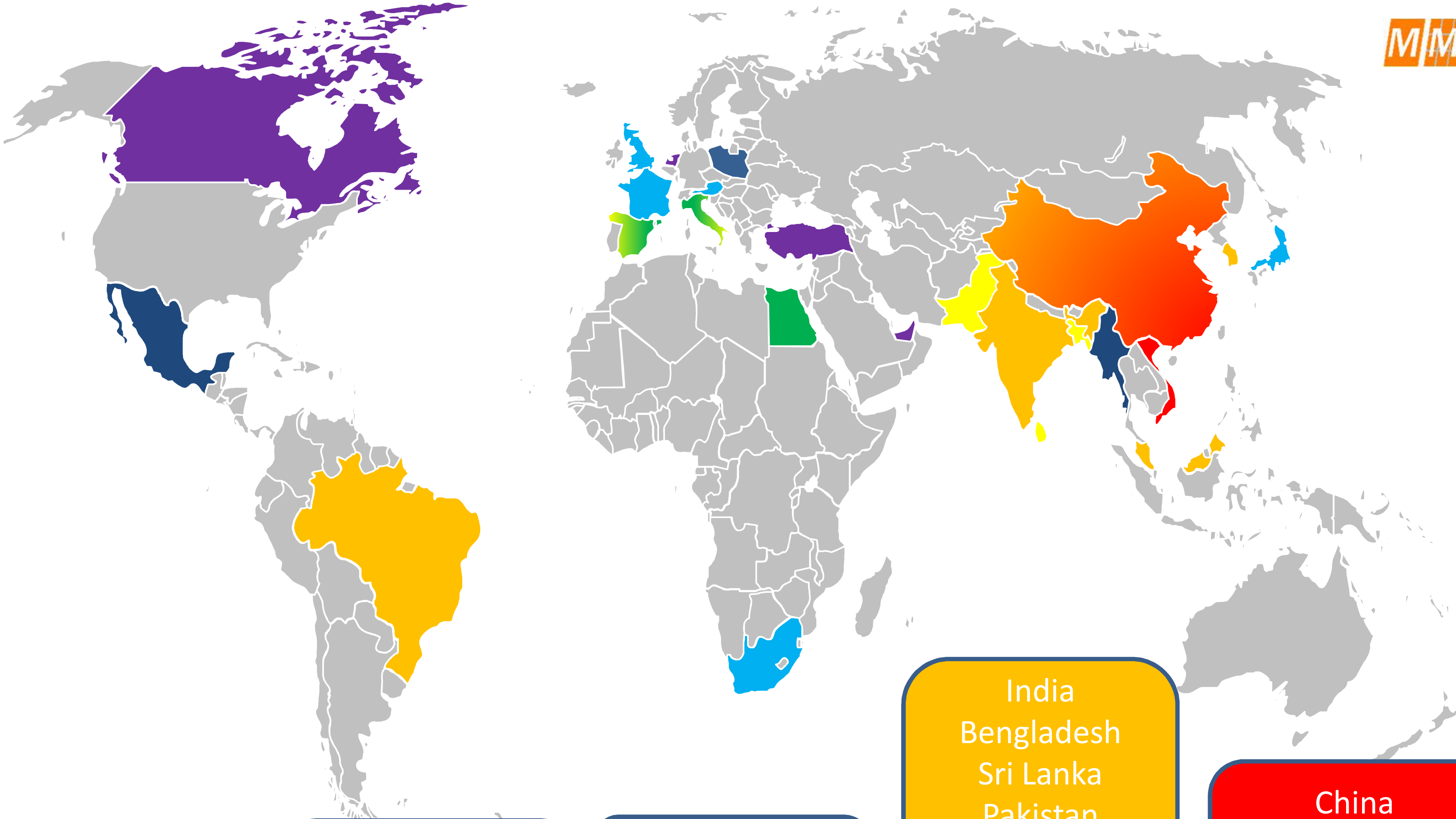
Benchmarking and survey of alternative technologies (recycled MMA) – more to come…

	M1	M2a	M2b	M3a	M3b	M4.1 & .2	MMAtwo Targets
Purity	98.0 %	99.5 % (guessed) (cast sheet grade)	99.5 % (guessed) (cast sheet grade)	**99.8 %** (claimed from cast)	97.7 % MMA + 1.8 % MA (claimed from extrusion)	**95.0 %**	(cast sheet grade)
Energy demand at Pretreatment, Grinding, Cracking and Purification	**6.80-7.17 MJ/kg**	10.5 MJ/kg	9.3 MJ/kg	25.5 MJ/kg	14.7 MJ/kg	8.15 MJ/kg	<15 MJ/kg MMA (processs energy)
Process CO_2	**0.55 kg CO_2/kg**	0.81 kg/kg	0.72 kg/kg	1.83 kg/kg	0.96 kg/kg	0.48 – 0.88 kg CO_2/kg	0.91 kg CO_2/kg

Including energy from side products burned on site

Recycled Methyl Methacrylate World Map

Closed facility	Molten metal Technology	Dry distillation Technology	Rotating Drum Technology	Unknown (yet) Technology	Possible new plant



Americas 2 000 t+ 5-10 companies	Europe 7-10 000 t 3-5 companies	Middle East 5-10 000 t 2-3 companies	India Bengladesh Sri Lanka Pakistan Malaysia 20 -30 000 t+ >30, leaders	China Vietnam 100 000 t Many, 2 leaders

Recycled MMA World Map
Prepared by Jean-Luc DUBOIS (Arkema)
with Simon Van der Heijden (Heathland)

To learn more about MMAtwo...

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Europe

MMAtwo recycling projects starts

A key next stage would be to see if the technology handles tougher, post-industrial materials

Katherine Sale London

Despite the ongoing recession caused by the pandemic, the EU-backed MMAtwo recycling project has managed to continue its research, starting up a depolymerisation unit including a first in the field pre-treatment plant, according to the project's chairman.

MMAtwo produced in June the first samples of recycled methyl methacrylate (R-MMA) in June and Jean-Luc Dubois said there had been a number of technological advancements in the project, which is set to use twin-screw depolymerisation technology.

Nearly all MMA is polymerised to make homopolymers and copolymers; the largest application is casting, moulding or extrusion of polymethyl methacrylate (PMMA) or modified polymers.

The MMAtwo project is backed with financing from the EU and led by producers and research institutions.

"There was a plant previously using this process [twin-screw depolymerisation], but that could only processed top quality MMA. We wanted something that could process everything," said Dubois, who is also scientific director at French chemicals major Arkema.

He added that several polymethyl methacrylate (PMMA) waste products (post-industrial and post-consumer) had already been depolymerised by Arkema at bench scale as high mass yields with high monomer content can be achieved with most of the grades.

This is an area where MMAtwo has seen more success than initially expected and, despite some minor delays linked to the pandemic, the project has managed to process more types of waste products than initially thought.

Despite the progress, the project remains in a pilot phase, however. It produced 700 kilograms of R-MMA in June during the first test.

Next - partnering, testing

The next stage would be to conduct further runs, with partnering MMA producers taking part in the project using the samples in production.

PMMA samples have been produced from batch and they have been compared to virgin material.

Most samples within the range can cope with odour issues and behave the same way as virgin product in terms of performance, when put under accelerated aging tests.

A key next stage would be to see if the technology can handle tougher, post-industrial materials, which may contain copolymers or inorganics such as screens from computers or televisions.

A good opportunity to come from the recent coronavirus-pandemic is the widespread investment in PMMA sheets, used as protective shields in hospitals, restaurants as well as shops, said Dubois.

The material is ideal for recycling due to the use of pure, transparent acrylic sheet, according to Dubois.

Waste collection

Collection of waste is still a major objective for the project, which is looking at the potential to establish a comprehensive infrastructure across the 27 countries in the EU.

"For any business, your lifeline is your feedstock - all revenue is based on what you can collect and convert," said Simon van der Heijden, co-founder of plastics recycling firm Heathland, part of MMAtwo, and coordinator of the project.

The project has successfully identified the multiple waste streams in the EU, and is currently collecting 9,000 tonnes across the bloc, an amount expected to increase considerably as the project continues; end-of-life product remains the main challenge.

"End of life is more hidden, and harder to collect efficiently," added Van der Heijden.

He added that the pre-treatment process being tested by Heathland has become one of the project's milestones this year, and a "first of its kind" in Europe.

WP2, PMMA depolymerization to crude rMMA

Source: ARKEMA

Jean-Luc Dubois
Chairman, MMAtwo

"It needs to be driven by consumers - the more they ask for it the more it will drive the change. If they want ... R-MMA then they need to show up"

"All PMMA that is depolymerised needs to be pre-treated; however, to do this automatically is new – waste collection and straight into pre-treatment, into suitable feedstock to depolymerise. Innovative separation technology and automated," he said.

The two key areas that will gather momentum in the market for recycled MMA are: government targets and the price of the product versus virgin monomer.

EU legal framework

Despite this being a partially funded EU project, there is no legislation currently in place for this sector. Much of the government targets are related to packaging, and so impact products such as polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET).

"PE/PP worldwide production is more than 10 times that of PMMA, it's easier to collect and [it is a] lower-value material," said Dubois.

"You consume a lot of energy to depolymerise PE... You don't save that much energy. But you do when you produce and recycle PMMA; it is a material harder to collect but its value is higher

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement N° 820687.