Les Mardis de la Chimie Durable

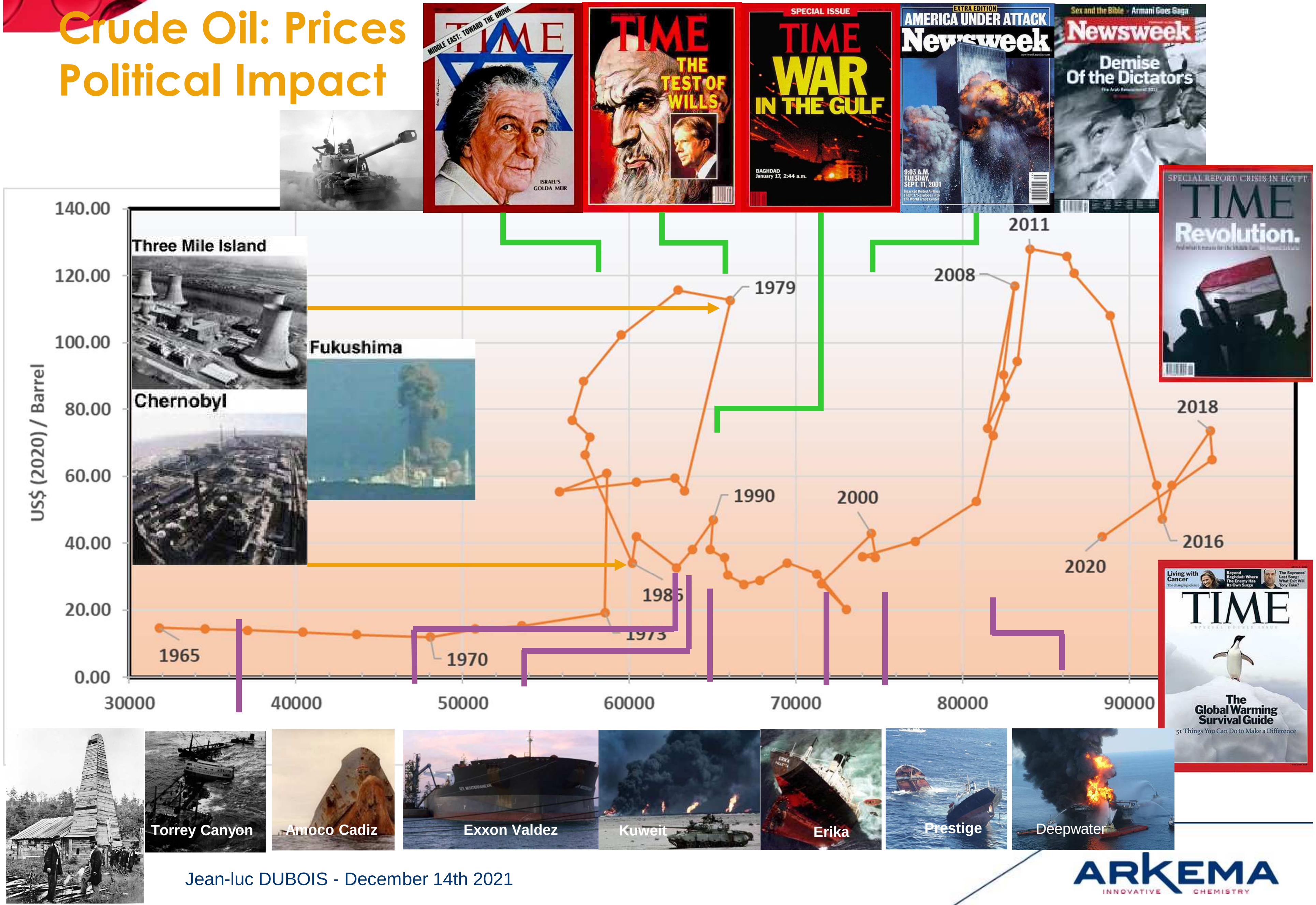
Présentation de travaux en chimie durable
Spéciale « Industrie* »
4ème édition en wébinaire
14 décembre 2021, 9h45-12h

Chimie Durable: conversion de biomasse, recyclage et conversion du CO_2. Exemples et challenges

Jean-Luc Dubois
(Directeur Scientifique, Arkema)

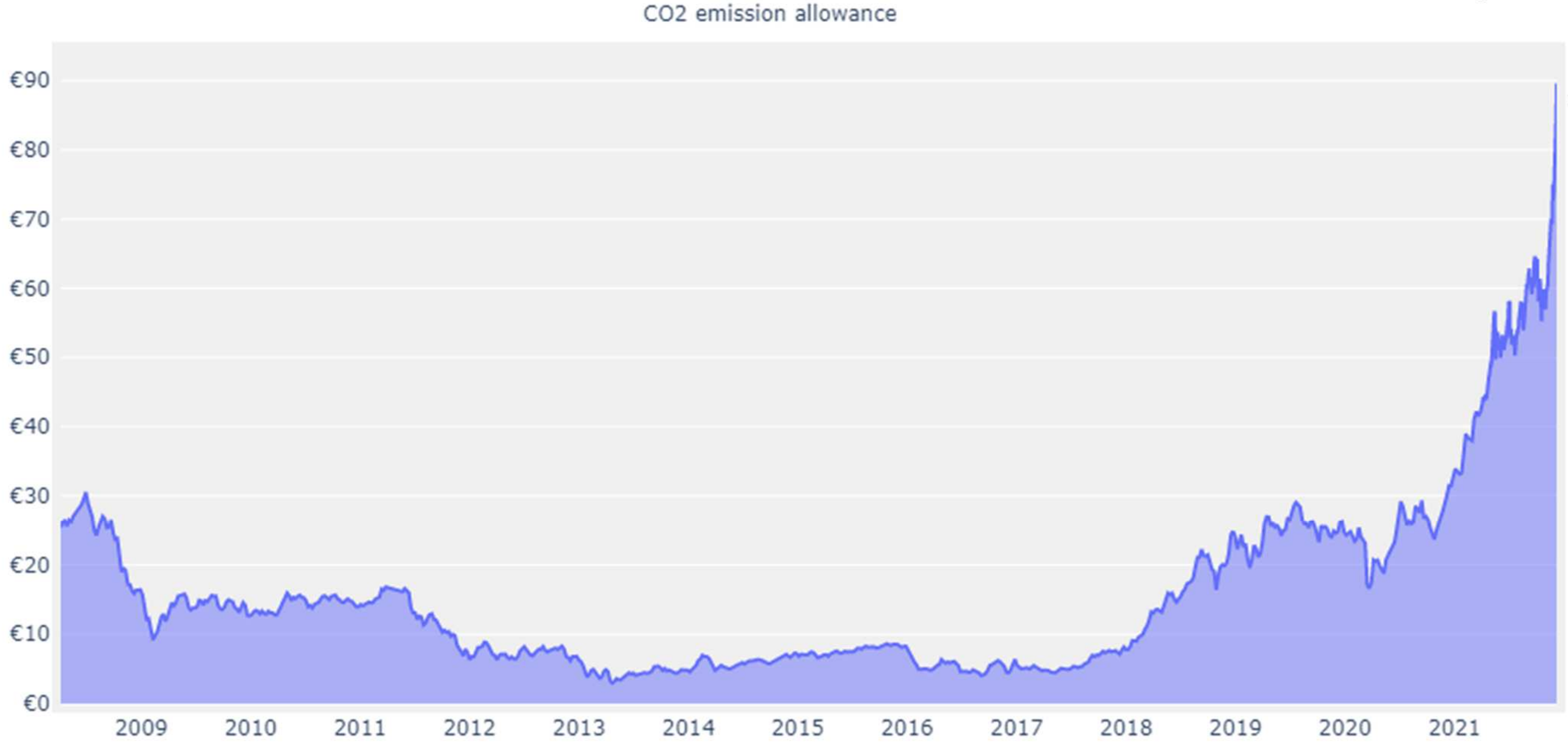
Crude Oil: Prices Political Impact

Crude oil production costs less than 30$/bl in middle east, and most of it less than 60 $/bl



Jean-luc DUBOIS - December 14th 2021

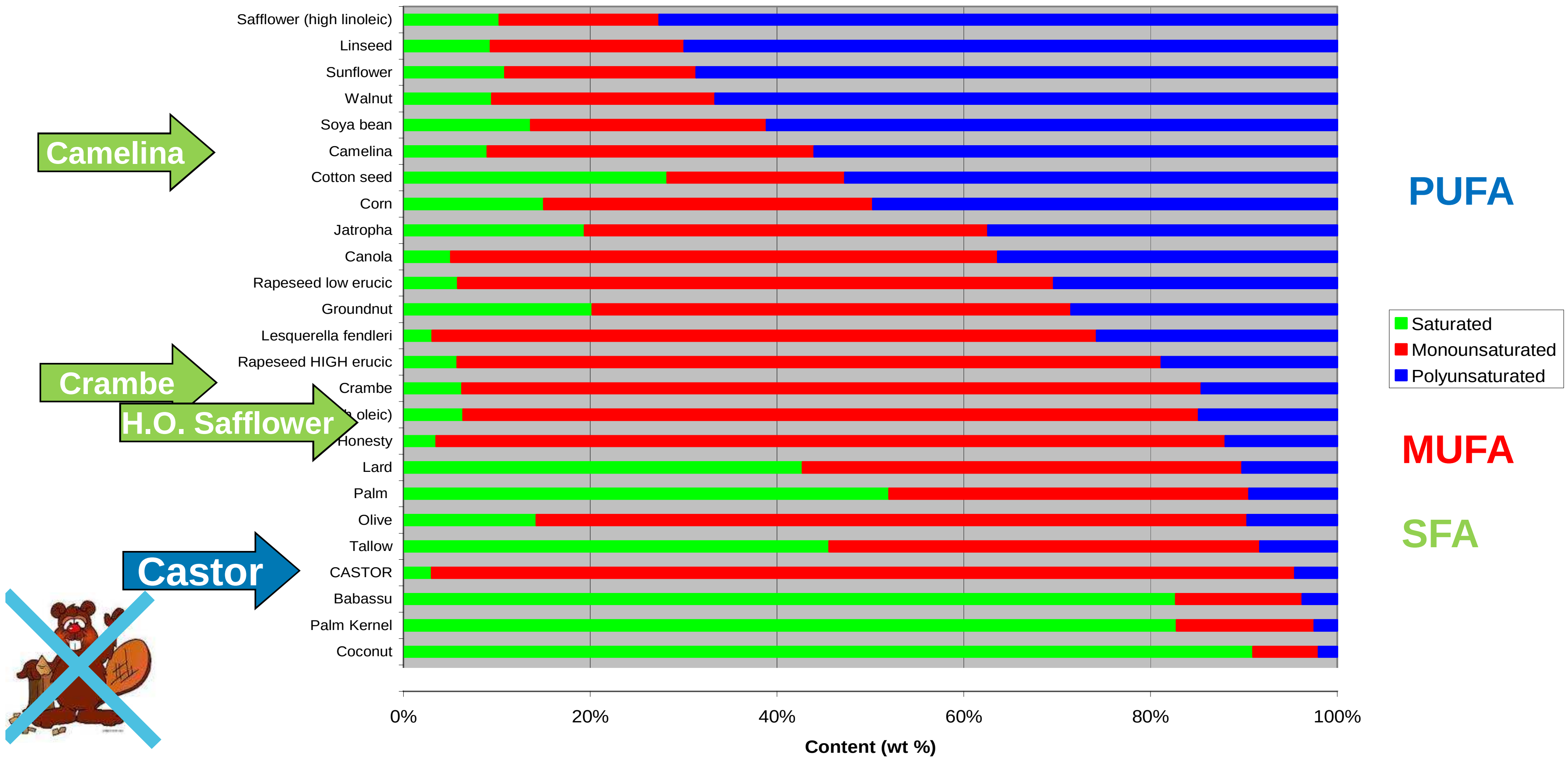
CO2 emission allowance €/tonne



→ 100€/t CO_2 ➔ about 50 $/bl more on crude oil price

Fatty Acid Profile

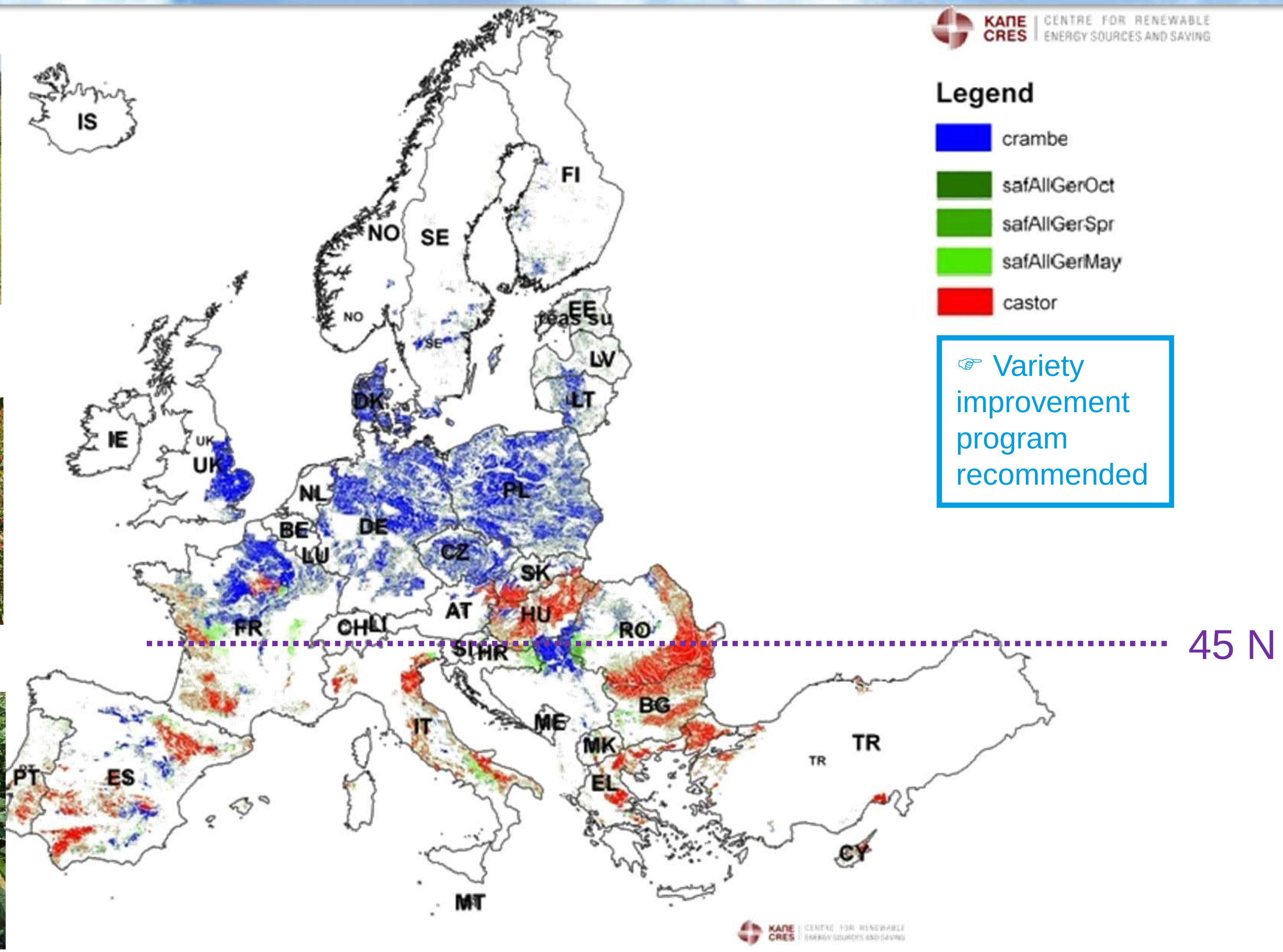
Source: « Lexicon of Lipid Nutrition », Pure Appl. Chem., Vol 73, N°4, PP 685-744, 2001 and Oleon datasheets + internal data



CRAMBE

SAFFLOWER

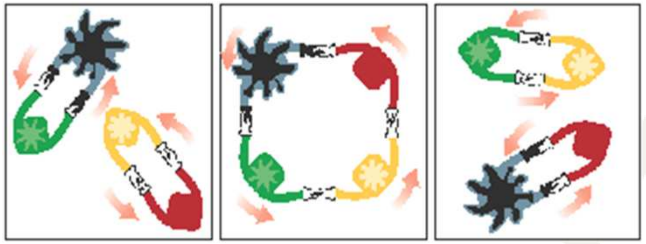
CASTOR



Data are missing for IS, IE, North-West Italy, Sicily, Sardigna, Corsica, Southern Greece, TR
Contribution from Myrsini Christou and Giannis Eleftheriadis (CRES)

The world is our inspiration

Metathesis of Vegetable Oils for Aminoacids production



ALTERNATIVE MONOMERS ROUTE

Castor Oil

Marseille
MeOH, Cracking, HBr, NH_3

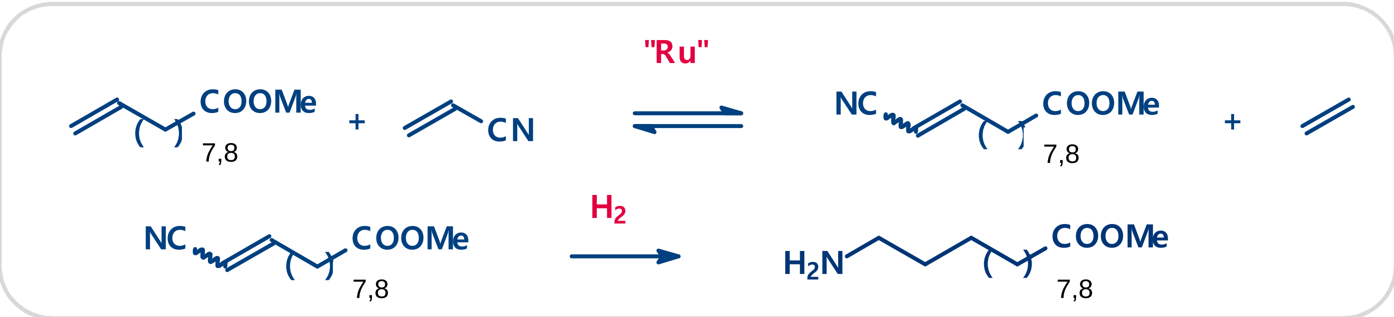
PA11

RILSAN BY ARKEMA

Palm, rapeseed, castor…

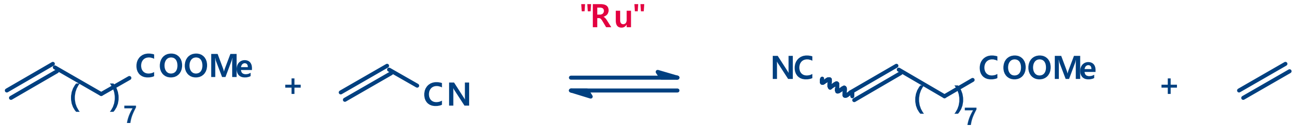
Metathesis technology

2 steps

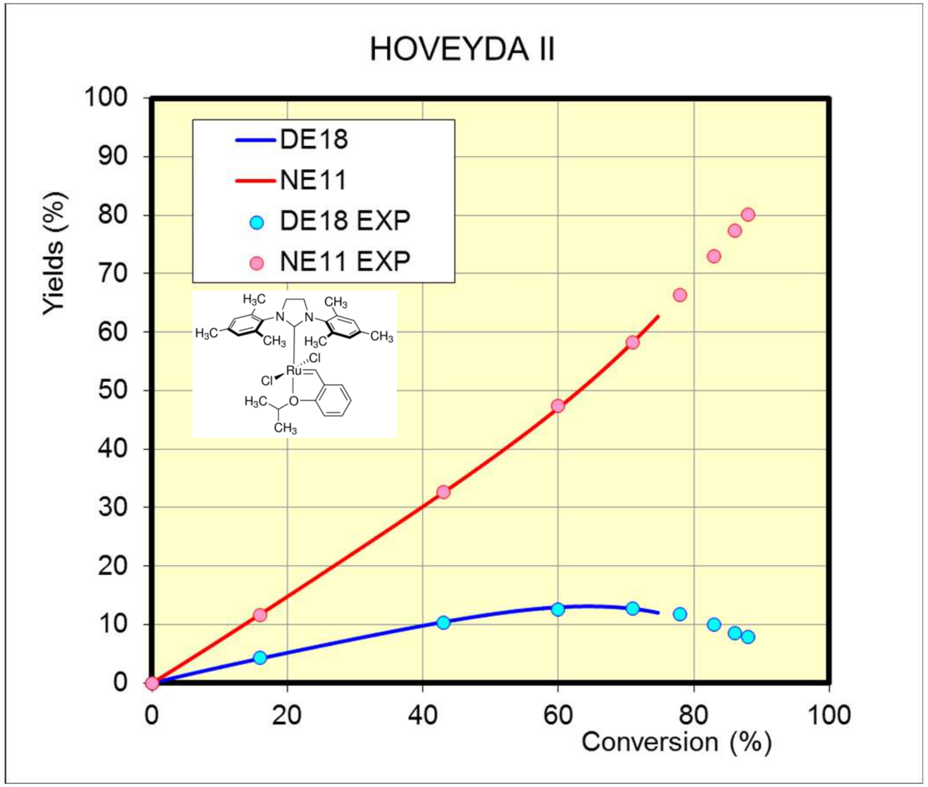


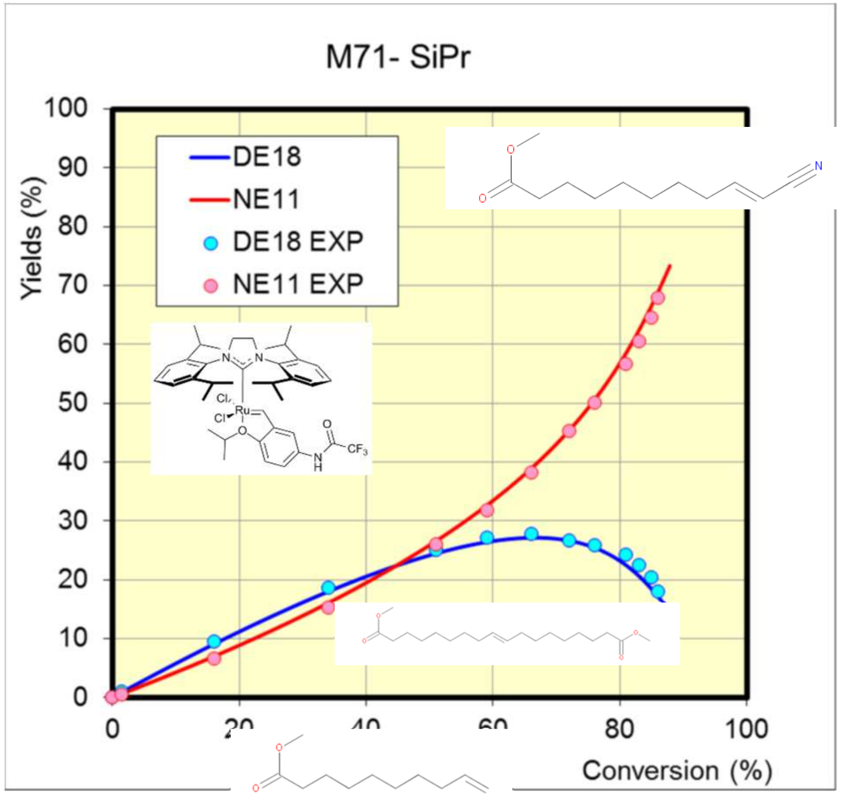
PA11
PA12

KINETIC MODELIZATION, SIPR VERSUS SIMES



Conditions: continuous catalyst addition (100 and 30 ppm), half acrylonitrile at start of reaction and continuous addition, Toluene solvent, reflux condition, 10 wt % 9-methyl decenoate in Toluene





In general, SiPr catalysts are more active and SiMes Catalysts are more selective

Castor based PA12 sample
Made with Arkema's Methyl-10-undecenoate.

COSMOS: Camelina and crambe Oil crops as Sources for Medium-chain Oils for Specialty oleochemicals

WP2 & 3


Camelina


Crambe

WP4

Long-chain fatty acids

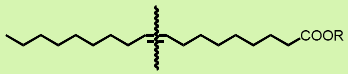
(Refined) Oils → Fatty acids
(Refined) Oils → Fatty esters

WP5

Co-products → Glucosinolates, Insect oils, Insect proteins

WP6

Chemical and Biotechnological chain scission



Application tests

Medium-chain fatty acids

C10-C14
Palm kernel & coconut markets

High-value Products

- Bio-plastics
- Lubricants
- Surfactants
- Flavours
- Fragrances
- Bio-pesticides
- Food/Feed

Vegetable Oils Fatty Acids Profiles

CX:n (X=chain length, n=number of unsaturation or C=C bonds)

Oil	C8:0	C10:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1
Rapeseed					4.5	2	57.5	23	11	0.6	2.3		
Soybean					9.0	4.5	25	49.5	11				
Palm Kernel	3.5	3.0	50.5	15.5	9.0	2.0	14.5	2.5		0.5			
Coconut	8	7	48	16	9	2	7	2					
Camelina					6	2	15	18	35	1	19		1
HEAR					2.5	2	17	18			10	1	45
Crambe					2.4	0.8	17.9	8.3	5.7	0.5	4.2	2.1	55.9

Need solutions to make short fatty acids from European crops

Catalysis in Cosmos

Long Chains Fatty Acids
Camelina & Crambe
C16-C22

Oil
Refined Oil
Fatty Esters Acids

Hydrogenation Upstream

Metathesis

Oxidative Cleavage

Hydrogenation Downstream

Applications Tests

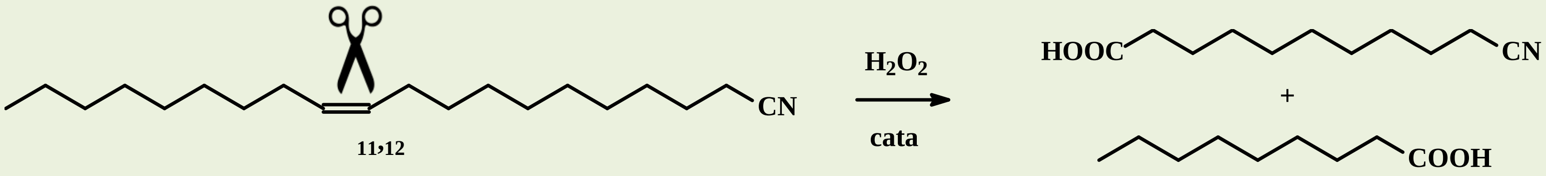
Medium Chain Fatty Acids
C10-C14
Palm kernel & coconut markets

High Value Products

- Bio-plastics
- Lubricants
- Surfactants
- Flavors & Fragrances
- Bio-pesticides
- Food-feed

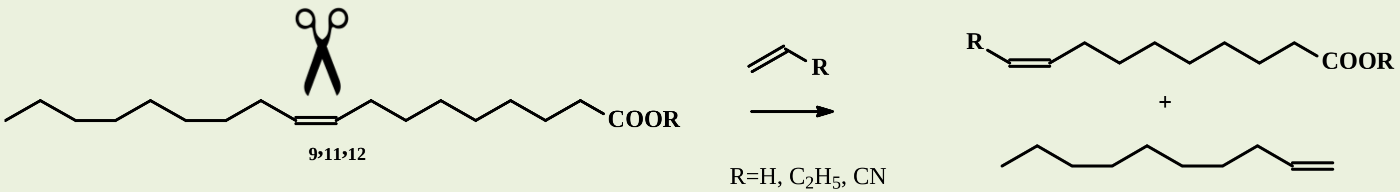
Fatty Acids conversions and applications

- Oxidative cleavage of MUFA:



gondoic nitrile (C20:1)

- Cross-metathesis (ethenolysis, butenolysis, acrylonitrile):



9-CARBONS DIACID: AZELAIC ACID

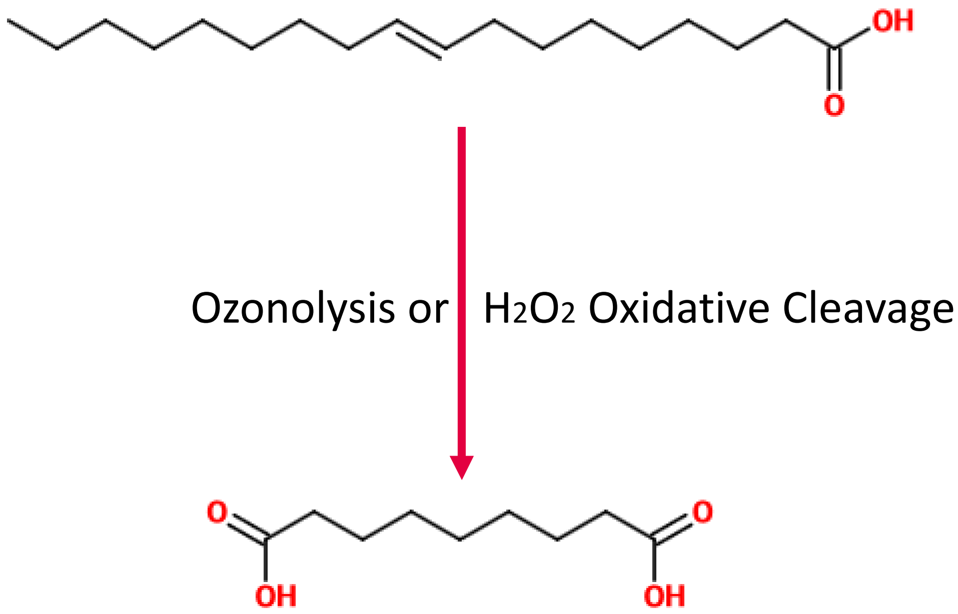
CRODA

CRODA SIPO

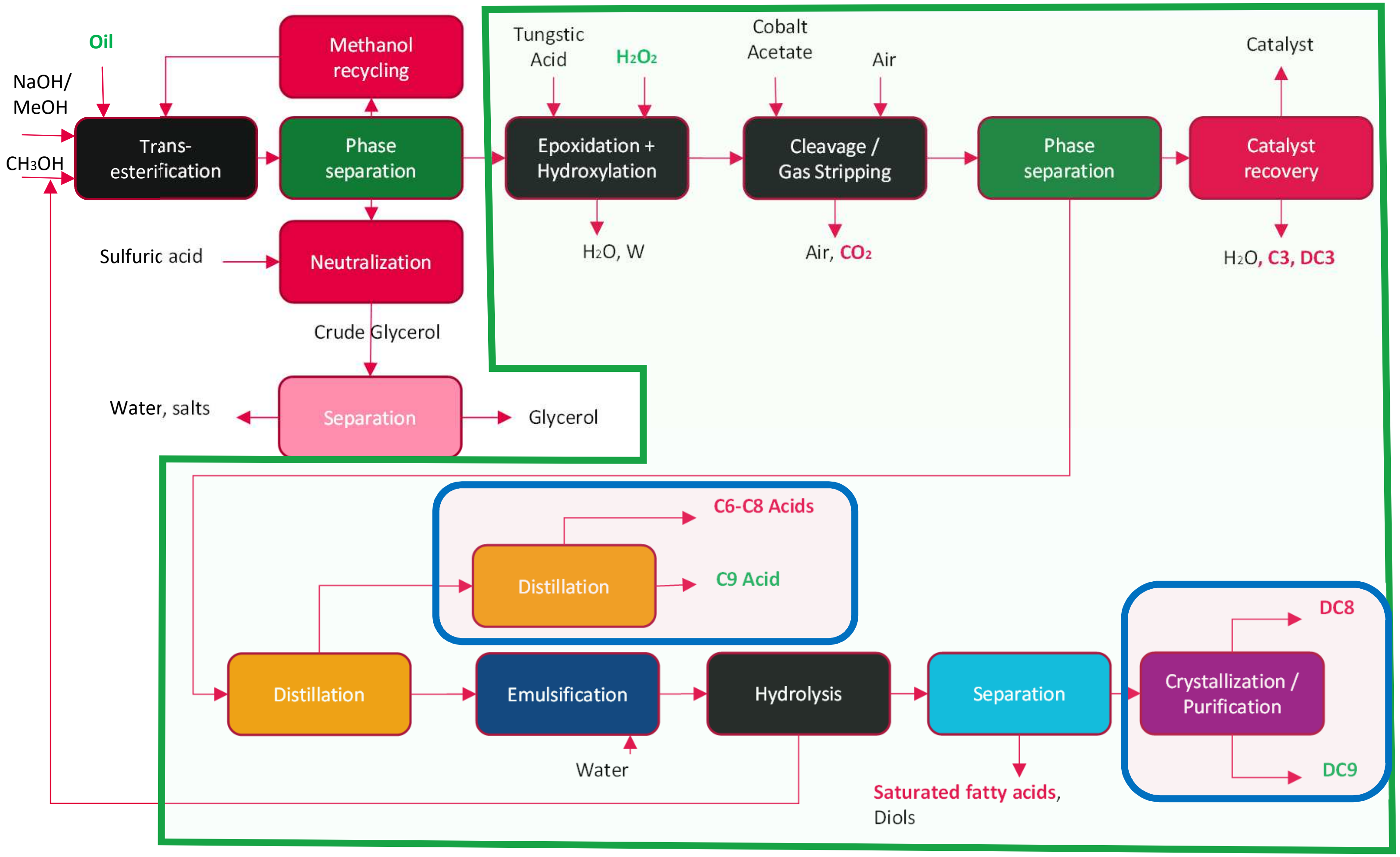
Emery Oleochemicals

NOVAMONT

MATRICA

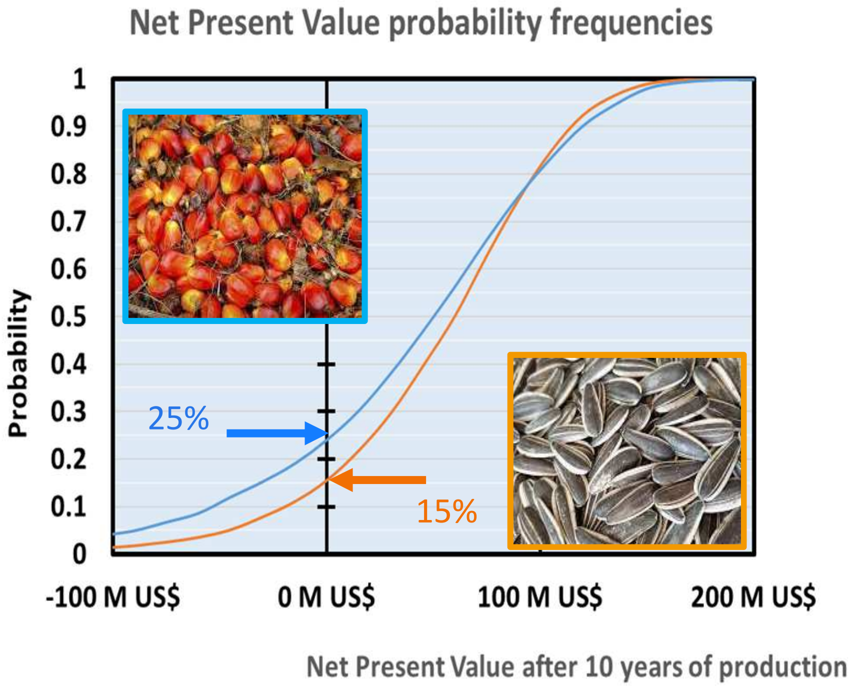


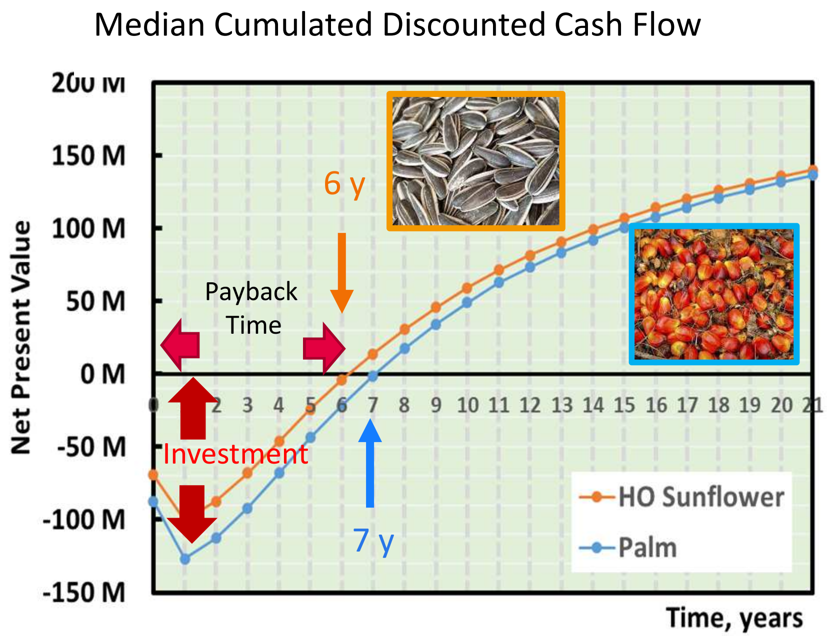
PROCESS BLOCK DIAGRAM: 3 SCENARIOS
FROM THE OIL, FROM THE ESTER, WITHOUT FINAL PURIFICATIONS



COSMOS
ADDING VALUE TO CAMELINA AND CRAMBE OIL

NET PRESENT VALUE, PAYBACK TIME, RISK ANALYSIS





- **Net Present Value: Probability to make more money than a reference case at 10 % internal return.**
- **Payback time: time needed to cover Investment costs**

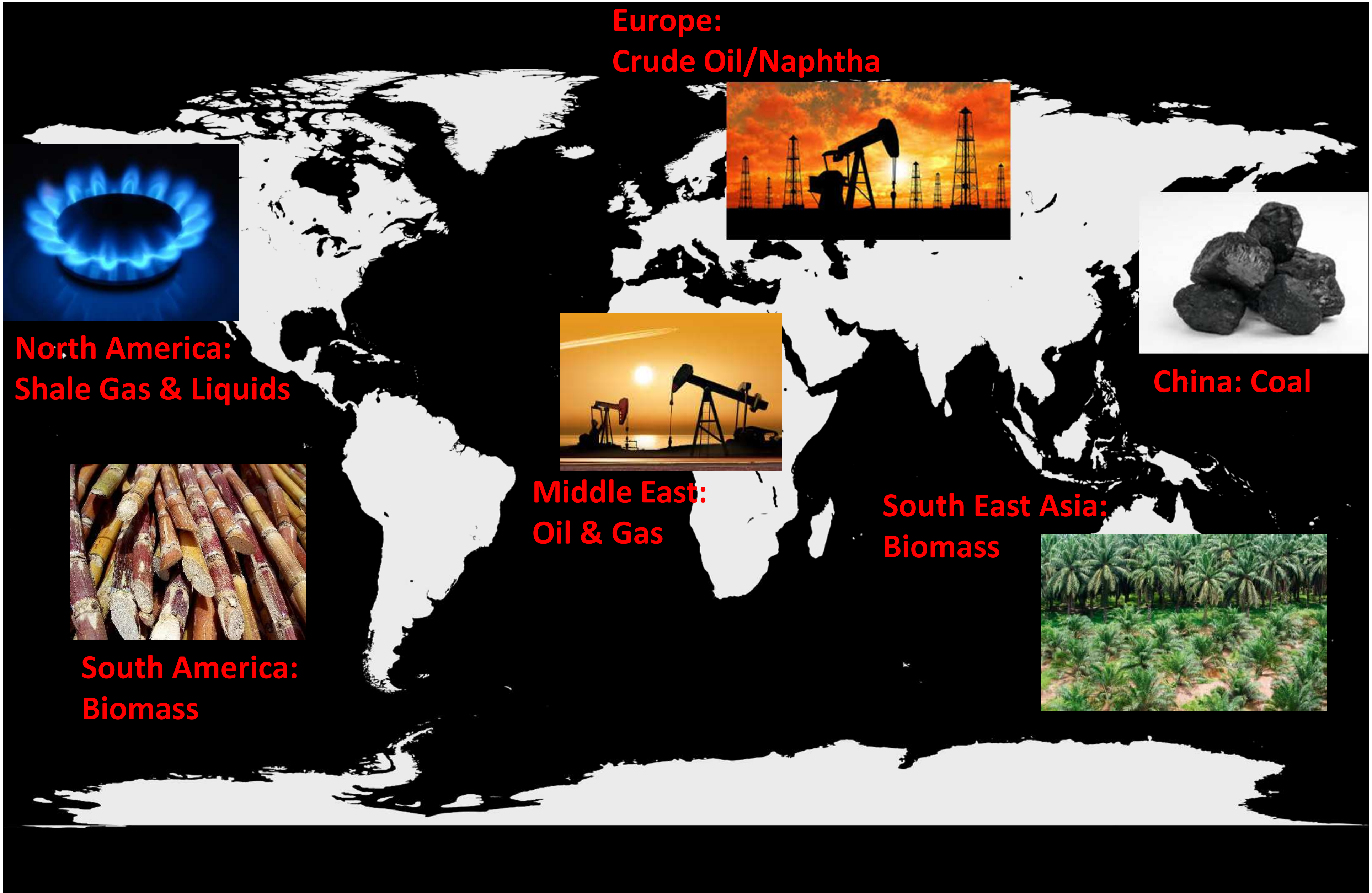
- **High Oleic Sunflower Oil, although taken at higher price, is a less risky option. But still requires much time for Payback (Risk on Capital).**

COSMOS
ADDING VALUE TO CAMELINA AND CRAMBE OIL

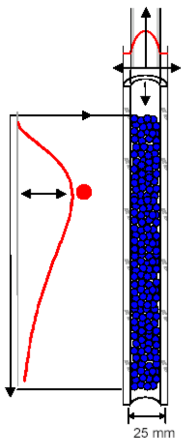
ARKEMA
INNOVATIVE CHEMISTRY

Alternative routes to Acrylic Acid

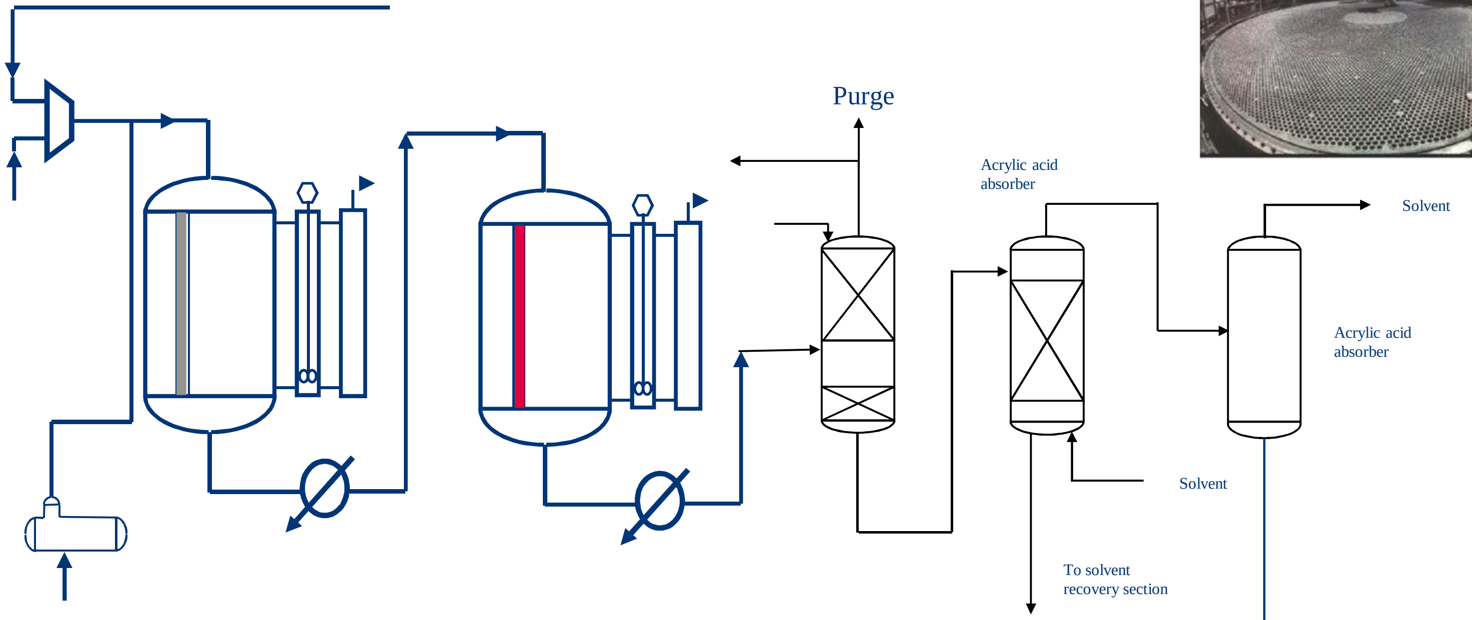
Process selection may depend on local feedstock availability.

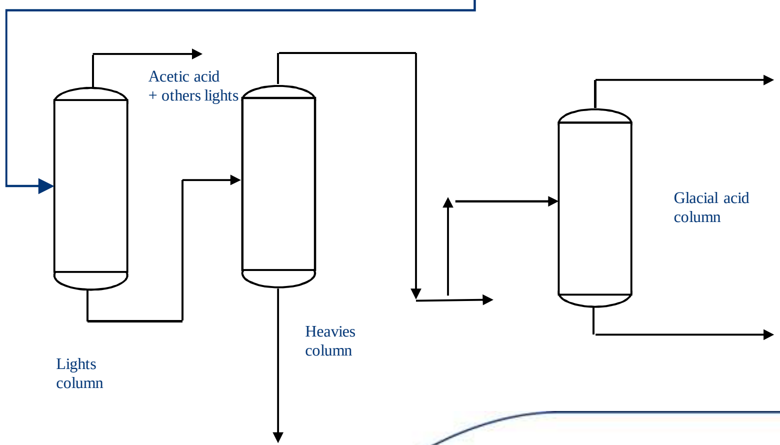


Conventionnal Propylene oxidation process
Multitubular Fixed Bed Reactors



Hot spot





Acrolein reactor fabrication

Number of tubes: > 27.000

Weight: 350 MT

Acrylic acid reactor

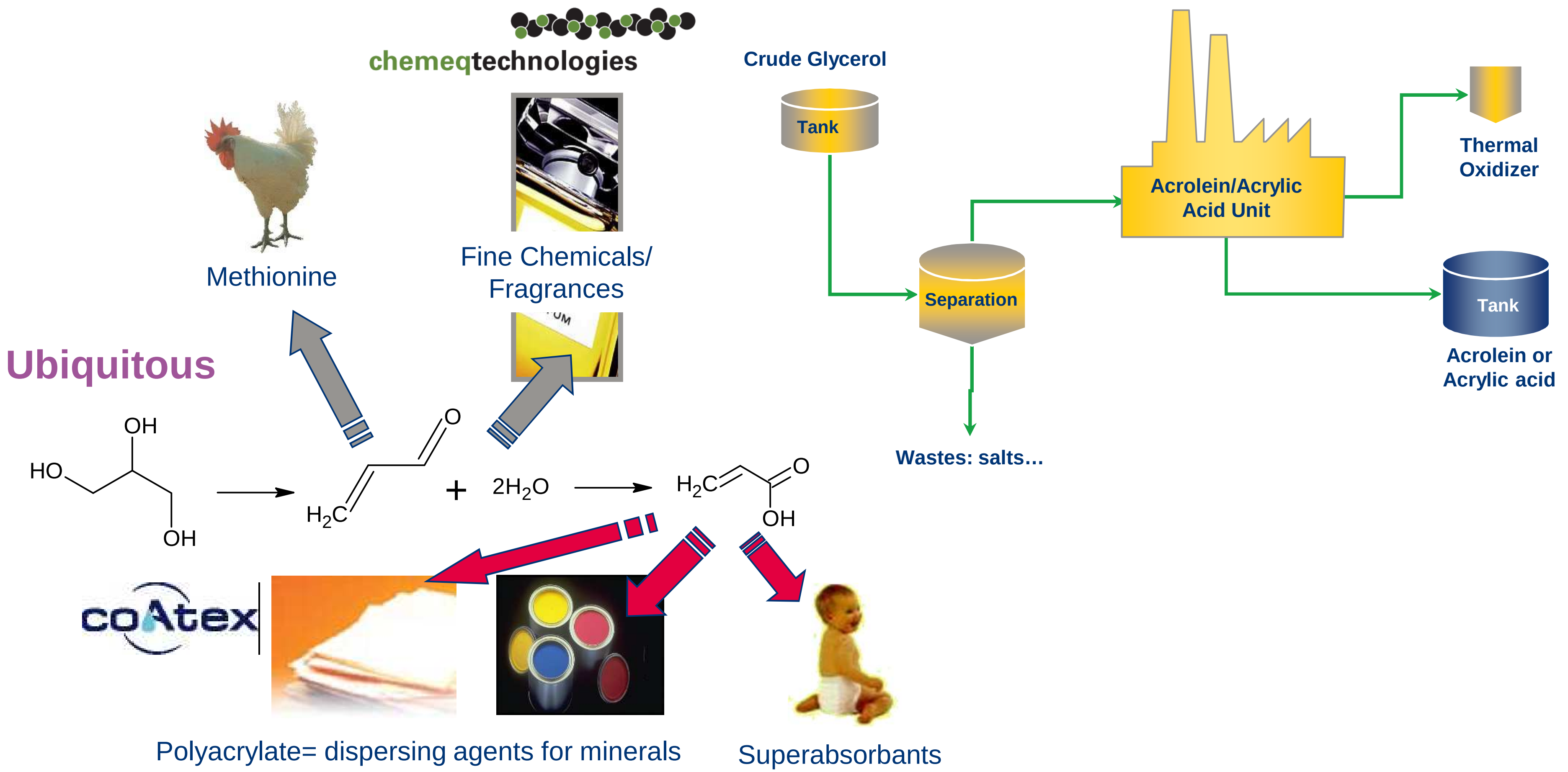
Number of tubes > 27.000

Weight: 570 MT

Multitubular fixed bed reactors @ dwe.com

Acrolein/ Acrylic Acid: ARKEMA's Project

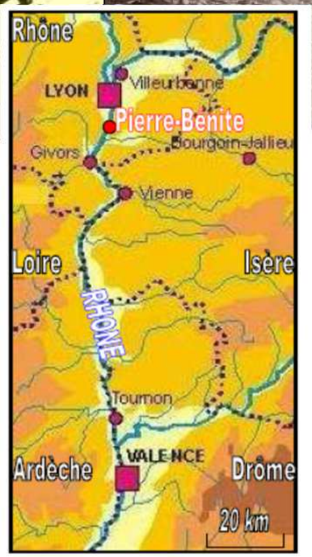
- **Double internal dehydration of Glycerol leads to Acrolein, further oxidized to Acrylic acid**



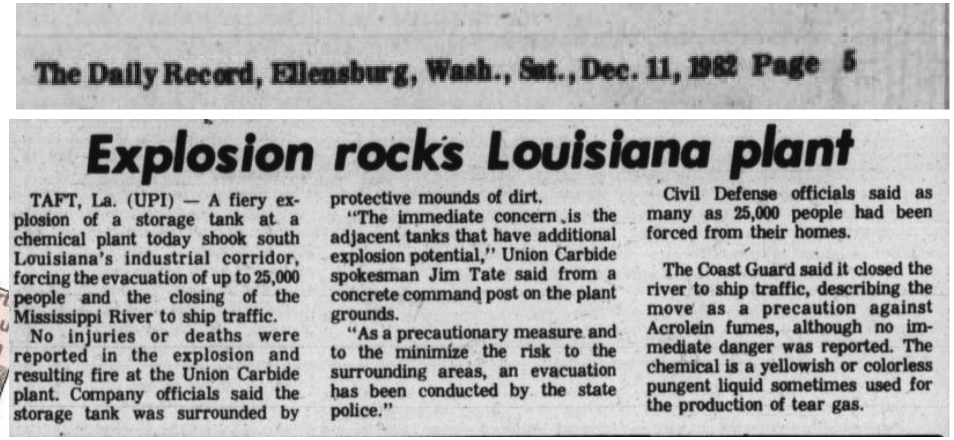
ARKEMA INNOVATIVE CHEMISTRY

Environmentally Friendly Process: Avoid scenarios of past accidents

- Target: develop a new process for on-site Acrolein production to avoid storage and transportation of a highly toxic Chemical.
- Pierre Bénite, France. July 10, 1976.
- Taft, USA/ December 10, 1982.



Major contamination of the Rhône River, during clean-up of a train tank
367 Tons dead fish



The Daily Record, Ellensburg, Wash., Sat., Dec. 11, 1982 Page 5

Explosion rocks Louisiana plant

TAFT, La. (UPI) — A fiery explosion of a storage tank at a chemical plant today shook south Louisiana's industrial corridor, forcing the evacuation of up to 25,000 people and the closing of the Mississippi River to ship traffic.

No injuries or deaths were reported in the explosion and resulting fire at the Union Carbide plant. Company officials said the storage tank was surrounded by protective mounds of dirt.

"The immediate concern is the adjacent tanks that have additional explosion potential," Union Carbide spokesman Jim Tate said from a concrete command post on the plant grounds.

"As a precautionary measure and to the minimize the risk to the surrounding areas, an evacuation has been conducted by the state police."

Civil Defense officials said as many as 25,000 people had been forced from their homes.

The Coast Guard said it closed the river to ship traffic, describing the move as a precaution against Acrolein fumes, although no immediate danger was reported. The chemical is a yellowish or colorless pungent liquid sometimes used for the production of tear gas.

17,000 Louisiana Residents Return Home as Site of Blast Is Declared Safe Aerial view of the wreckage of tanks after an explosion and fire Saturday at the Union Carbide chemical plant in Taft, La. Residents within a five-mile radius of the site were evacuated because of the fear of toxic fumes from the fire. They were permitted to return home yes-terday. River traffic near the plant, situated on the banks of the Mississippi River 30 miles west of New Orleans, was halted until fire burned itself out. The chemical in the tanks was acrolein, which is used to make algaecides, animal food supplements and tear gas.

The New York Times

Explosion of a Storage facility
17000 people evacuated

ARKEMA
The world is our inspiration

Alternative Routes to Acrolein & Acrylic Acid

ARKEMA **Mixed alcohol direct oxidation via acrolein (2010-)**

Cross metathesis (ethenolysis) of Fumaric or Muconic acids (2000s)

Carbonylation of Ethylene Oxide via Propiolactone (mid 2000s-)

Via Fermentation to 3-Hydroxypropionic acid /PHP (mid 2000s-)

ARKEMA **Glycerol oxydehydration via acrolein (early 2000s-)**

ARKEMA Propane direct oxidation (1990-early 2000s)

ARKEMA Propane – Ballast/Inert gas (1987-)

Lactic acid dehydration (1950s-)

Gas to olefins
(via syngas and CH_3OH)

Methanol to olefins/propylene

Propane dehydrogenation to propylene

Propylene oxidation (2 steps), 1970s ARKEMA

Propylene Oxidation (1 step)

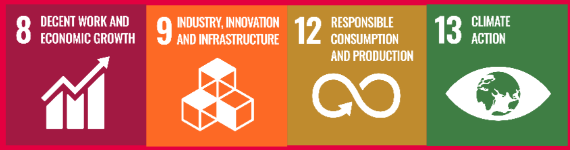
Acrylonitrile Hydrolysis

Acetic acid to ketene+Formaldehyde, to propiolactone, 1960s (not commercialized)

High T, High P, Reppe process, 1956 (Nickel free)

Reppe Chemistry, Acetylen+CO,+ROH 1954

Ethylene Cyanohydrin process, 1927



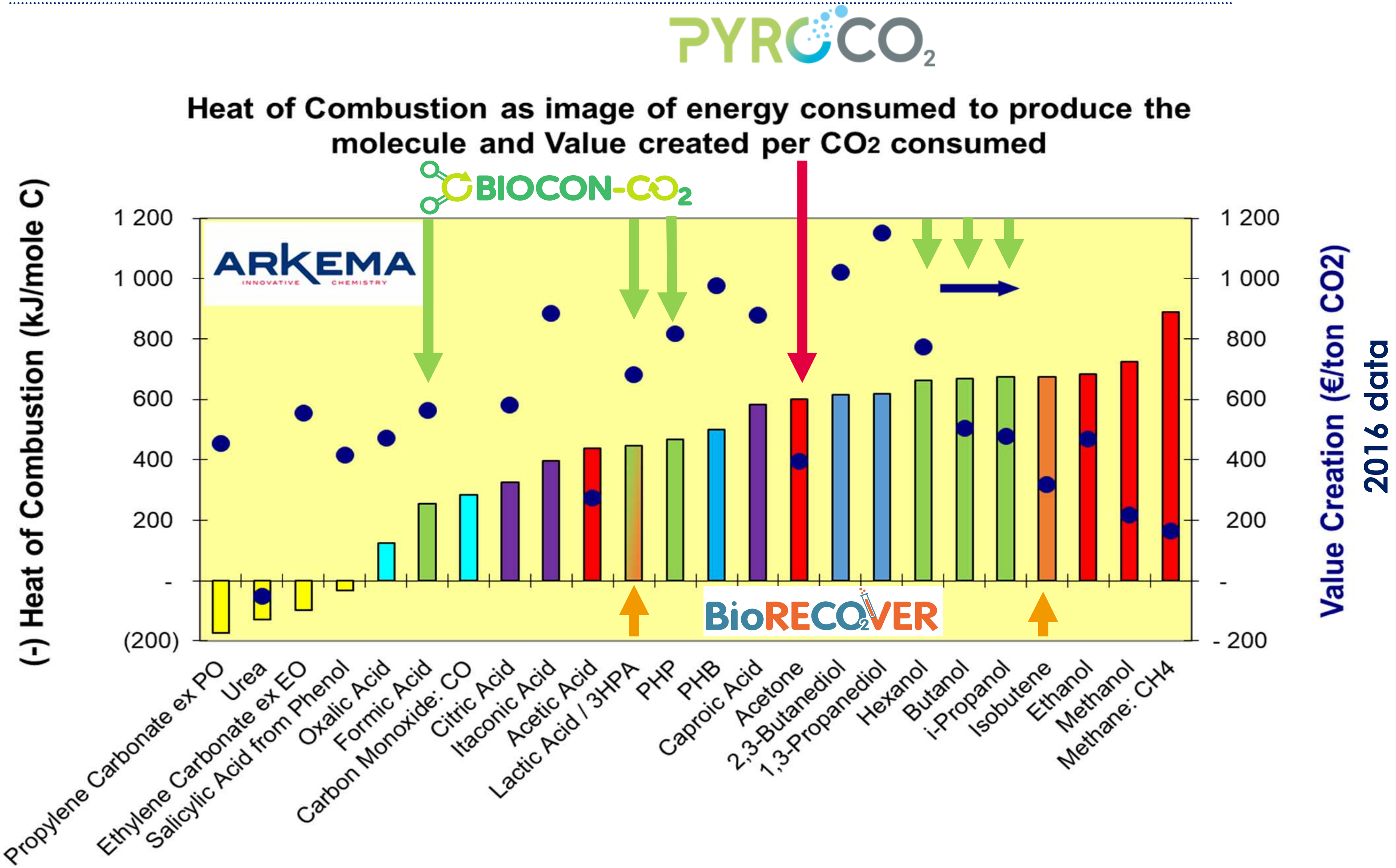
CO_2 GAS FERMENTATION

OPPORTUNITIES AND TECHNICAL CHALLENGES

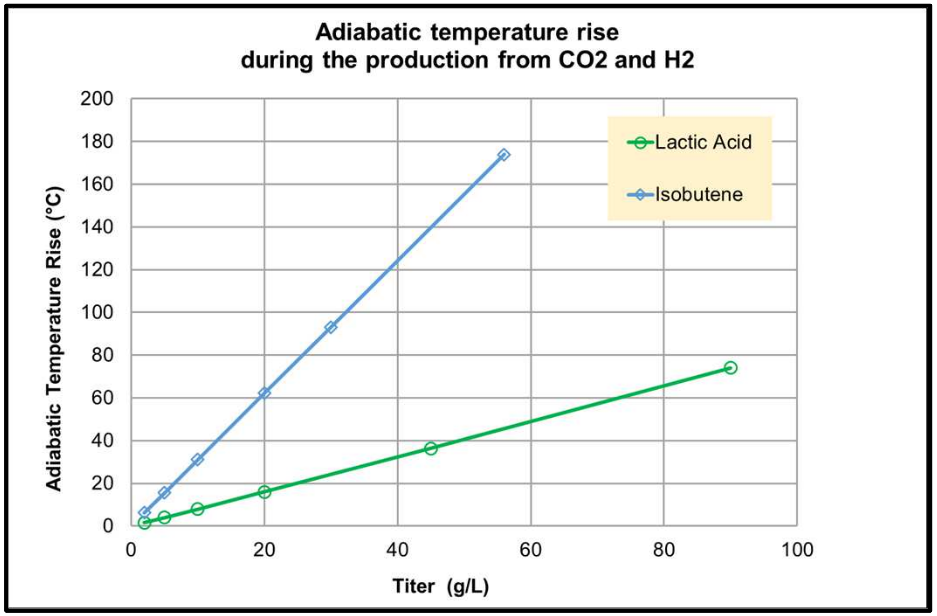
JEAN-LUC DUBOIS
SCIENTIFIC DIRECTOR
ARKEMA

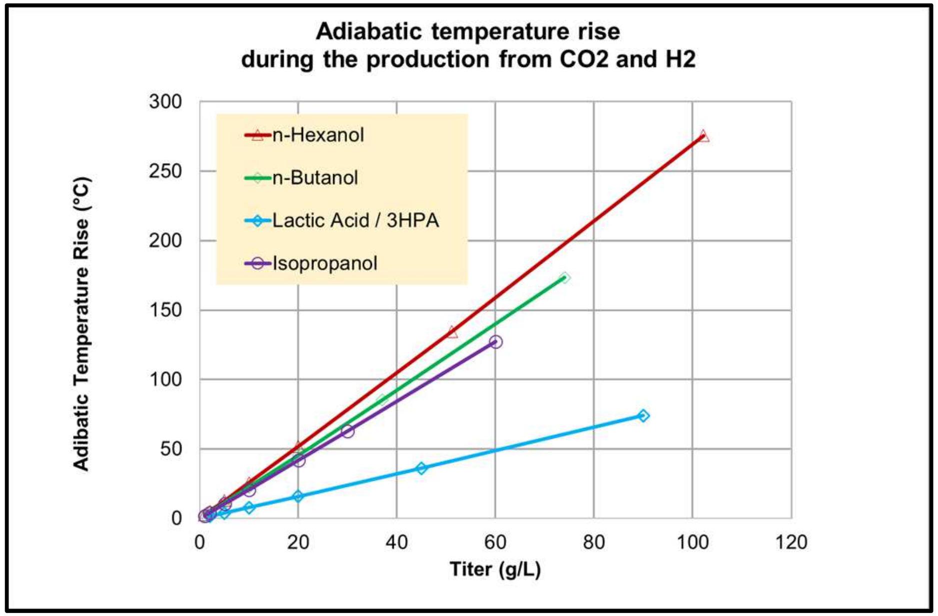
ARKEMA
INNOVATIVE CHEMISTRY

TARGET PRODUCT SELECTION: VALUE CREATION AND ENERGY CONSUMPTION



HEAT MANAGEMENT: ADIABATIC TEMPERATURE RISE





- Probably impossible to reach more than 10-20 g/L without external cooling
- Low Titers = High Capital Cost
- 100 kt/year of lactic acid = energy loss of 93 900 MWh/year = equivalent of the energy consumed by more than 14 000 Europeans in their households.

MMA two

Second Generation MethylMethAcrylate

Process Intensification in PMMA recycling

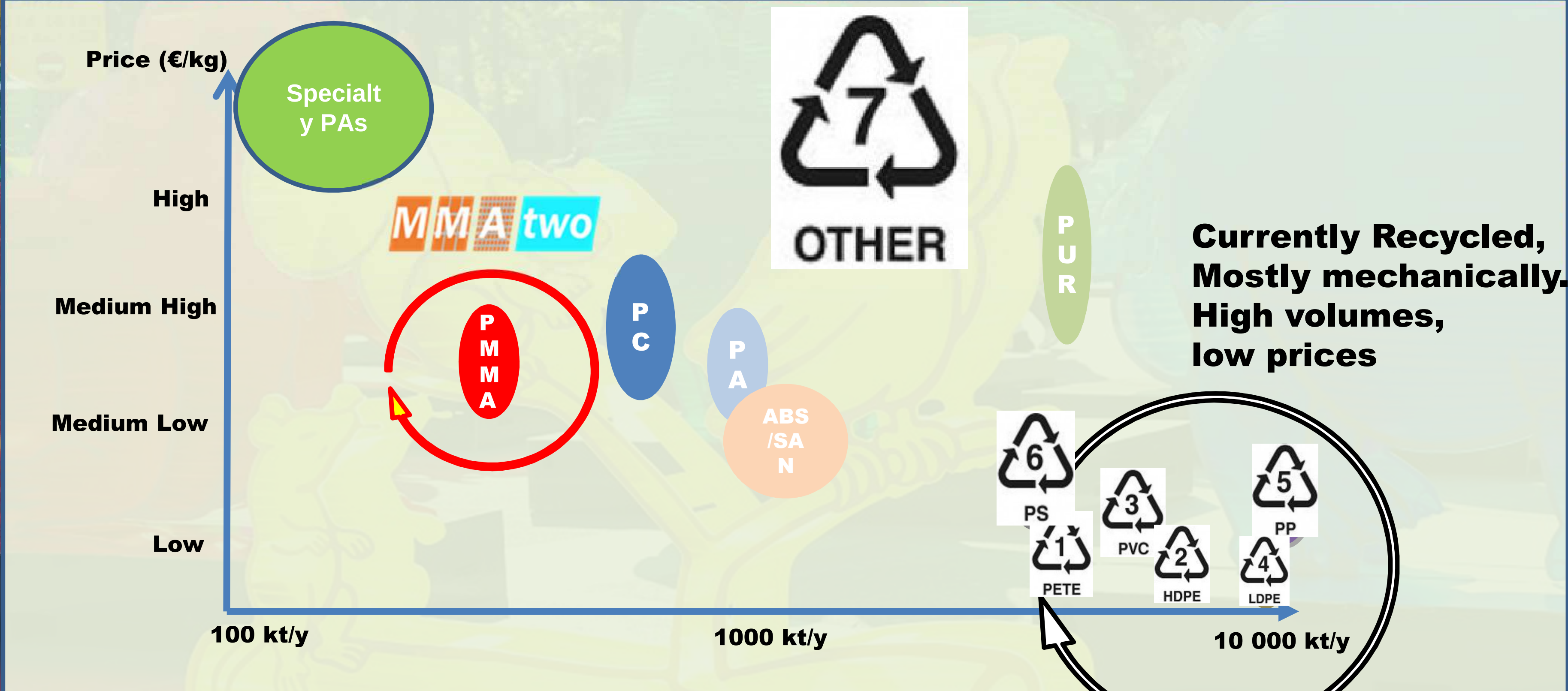
Jean-Luc DUBOIS

ARKEMA
INNOVATIVE CHEMISTRY

Plastic Recycling
December 14h
2021

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

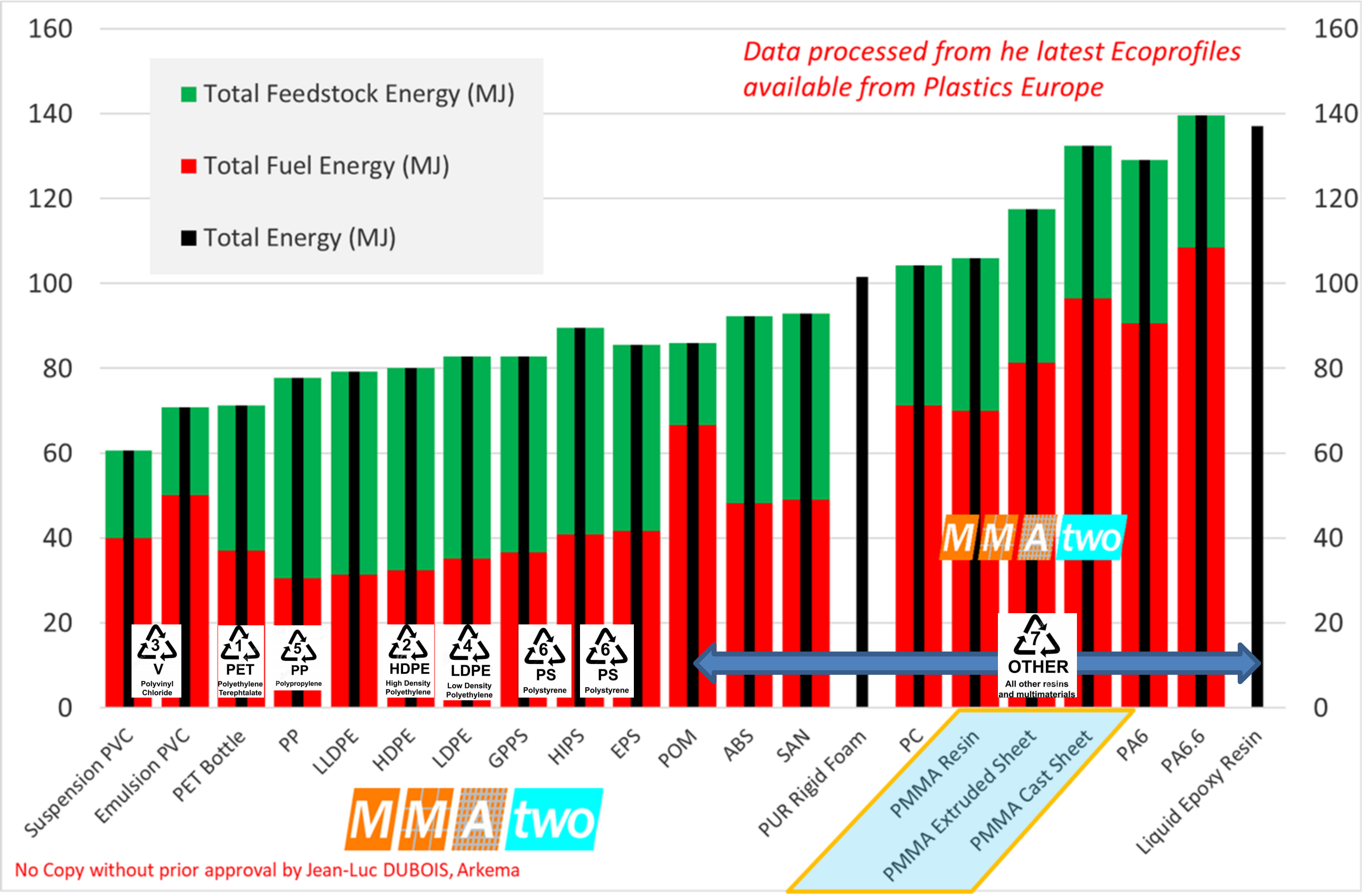
PMMA: high value, but low volume



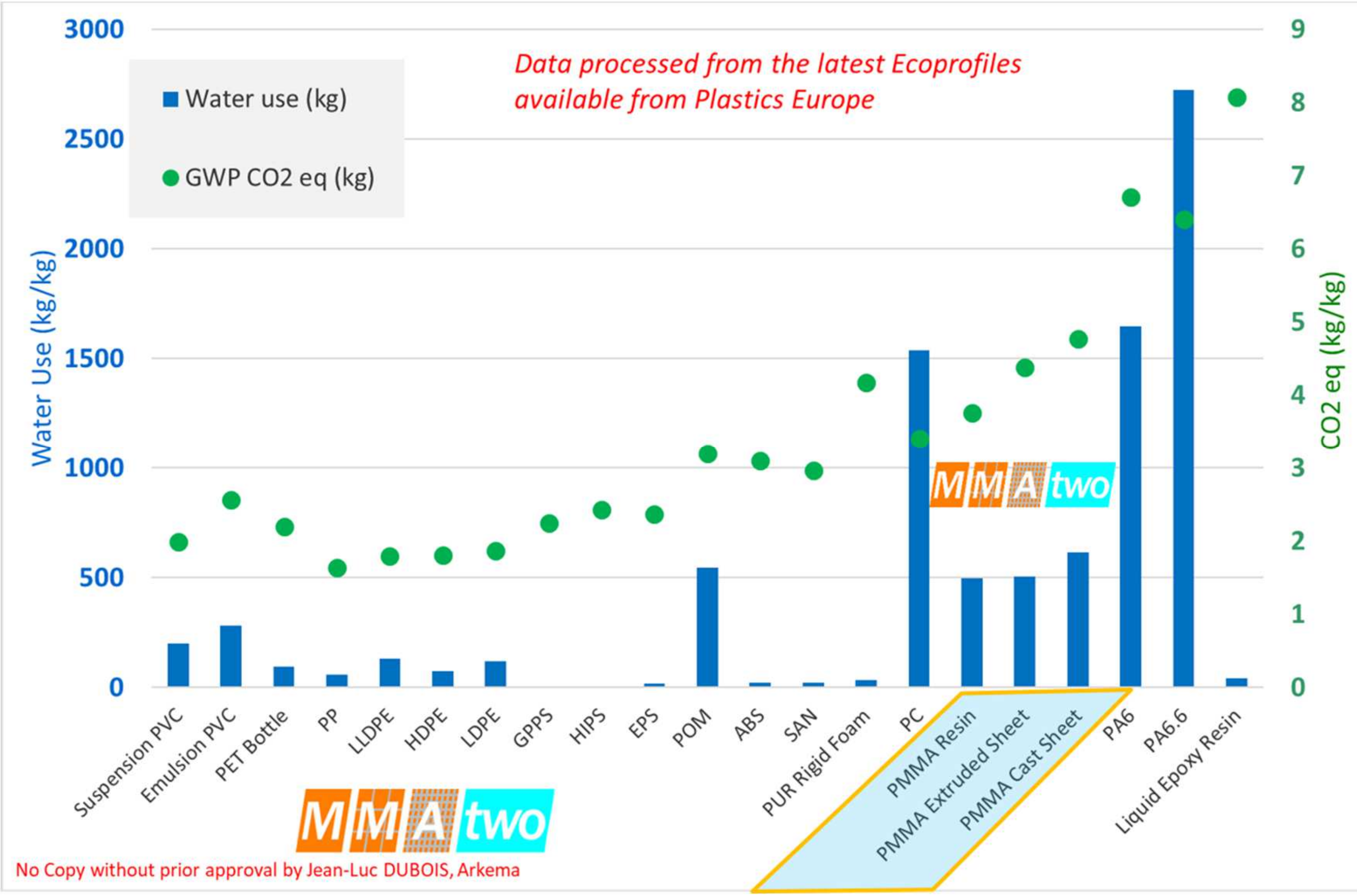
Polymers European market shares, Plastics Europe
Plastics converter demand by resin type (2016)

Source: JL DUBOIS –November 20th 2018

Energy Consumption in Polymers production:
High demand for technical polymers



Water consumption and CO_2 eq emissions



Dry Distillation Still reactor

Rotating Drum reactor

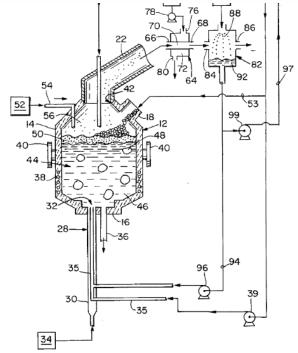
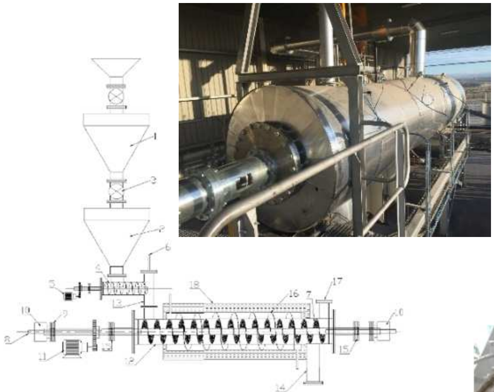


FIG. 1

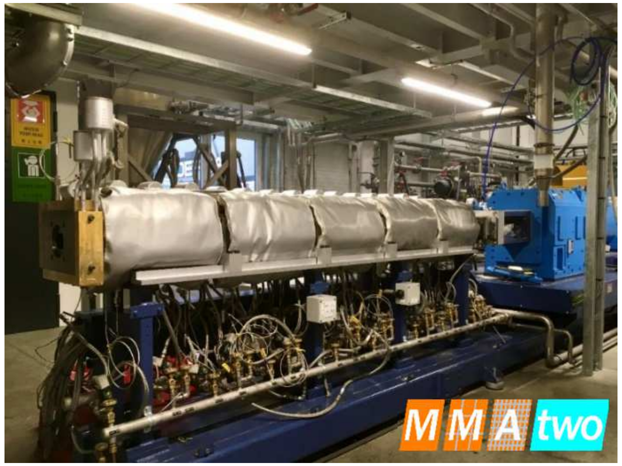
Molten Metal reactor

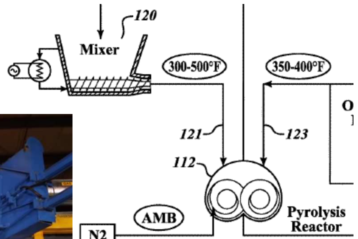
Twin-Screw reactor

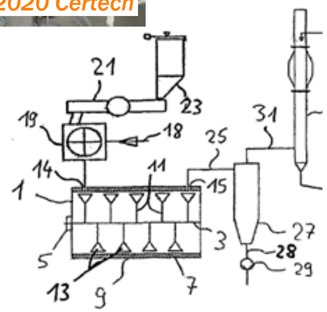


Auger reactor

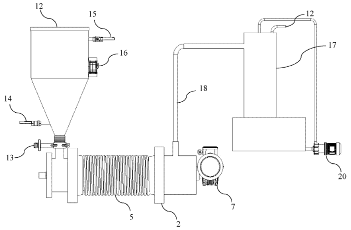
(w or w/o circulating solid)







Rotating Paddle reactor



Microwave & Induction reactors

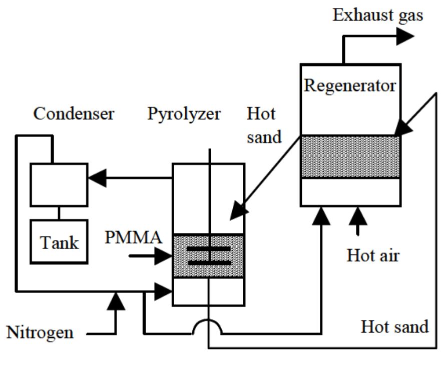
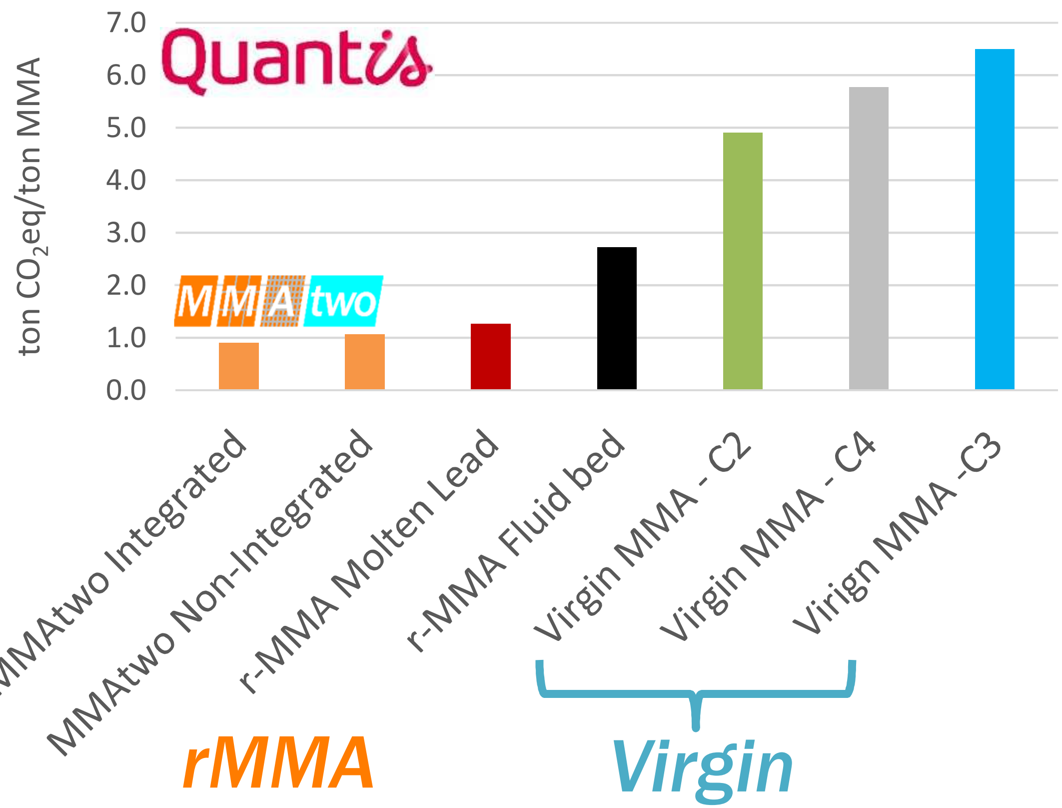


Fig.1 Apparatus

Fluid Bed reactor

LCA: M36 Main results

Benchmarking with virgin technologies



Main Results

- Compared to virgin production, there is a large impact reduction (more than -75%) depending on the technology
- Comprared to other recycling technologies, the impact reduction ranges between -20% to -60%
- More recycling processes to come soon

Data sets:

Virgin MMA: C2 route (3), C3 route (3), C4 route (3)
R-MMA: Lead Bath (3+1); Fluid Bed (2),
Rotating Drum (3), Dry Distillation (5), Stirred Tank (3)
Dry Distillation with biomass as energy Source (3)

Chain of Custody: Options

Chain of Custody:

Customer demand

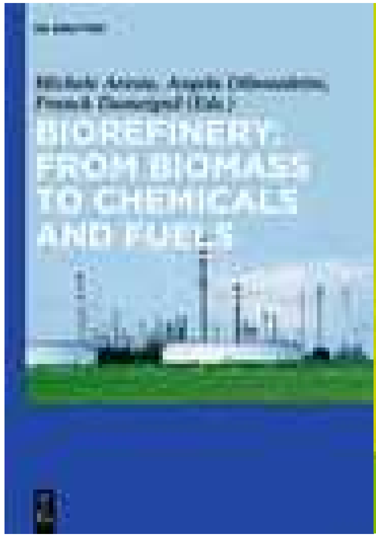
01	Identity Preserved, Dedicated plant	Regenerated MMA 100 %	MMA two
02	Segregated, Single plant Batchwise	Regenerated MMA 100 %	Virgin MMA
03	Controlled Blending, Mixed stream, single product	Regenerated MMA 50%	
04	Mass Balance, Mixed streams. Allocation, Physical link	Regenerated MMA 25%	Regenerated MMA 75 %
05	Book & Claim Credits and Products follow different path		

« Green Notes for Green Chemistry »

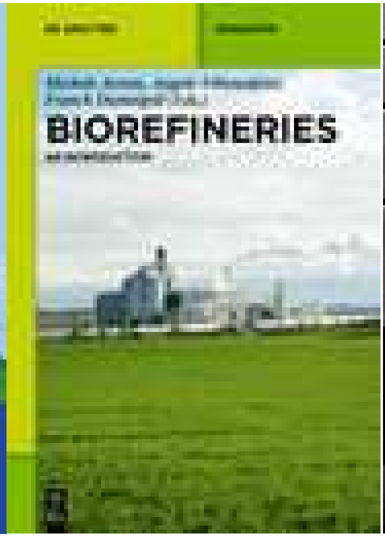
- Development of « Green » chemistry requires to set the conditions to make money
- Use all parts of the crops
- Develop Safer processes
- Renewable chemicals with improved Life Cycle Analysis
- Renewable (bio-based) ≠ biodegradable ≠ non-toxic
- High value polymers offer more opportunities for recycling

The world is our inspiration

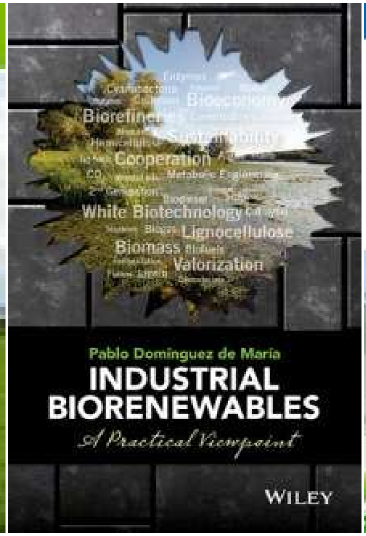
TO LEARN MORE:
SEE MY CONTRIBUTIONS TO THE FOLLOWING BOOKS



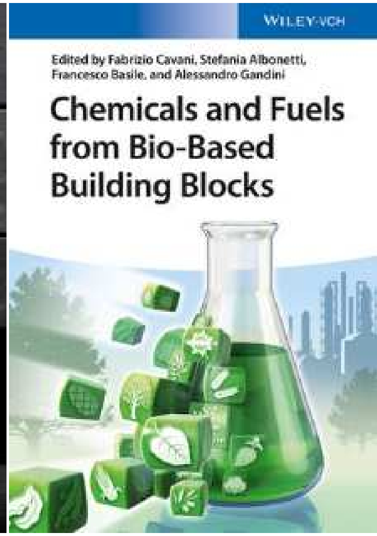
Chapter 2:
Refinery of the future: feedstock, processes, products
(2012)



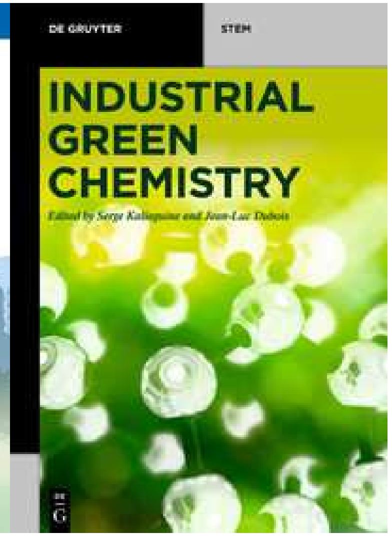
Chapter 10:
Oil chemistry: chemicals, polymers, and fuels
(2015)



Chapter:
Castor Reactive Seed Crushing Process to Promote Castor Cultivation
(2016)



Chapter:
Arkema's Integrated Plant-based Factories
(2016)



Chapter 2
Alternative routes to more sustainable acrylonitrile: biosourced acrylonitrile.
Chapter 4 Fatty nitrile esters hydrogenation for biosourced polyamide polymers.

Thank you for your attention