

Les Substances Naturelles :

La Panacée ?

Mercredi 27 Novembre 2019



Fondation de la Maison de la Chimie

RESSOURCES RENOUVELABLES POUR LES PRODUITS D'ARKEMA D'AUJOURD'HUI ET DEMAIN.

Jean-Luc DUBOIS, Directeur Scientifique





**A GLOBAL GROWTH
COMPANY, LEADER IN
ITS ACTIVITIES**



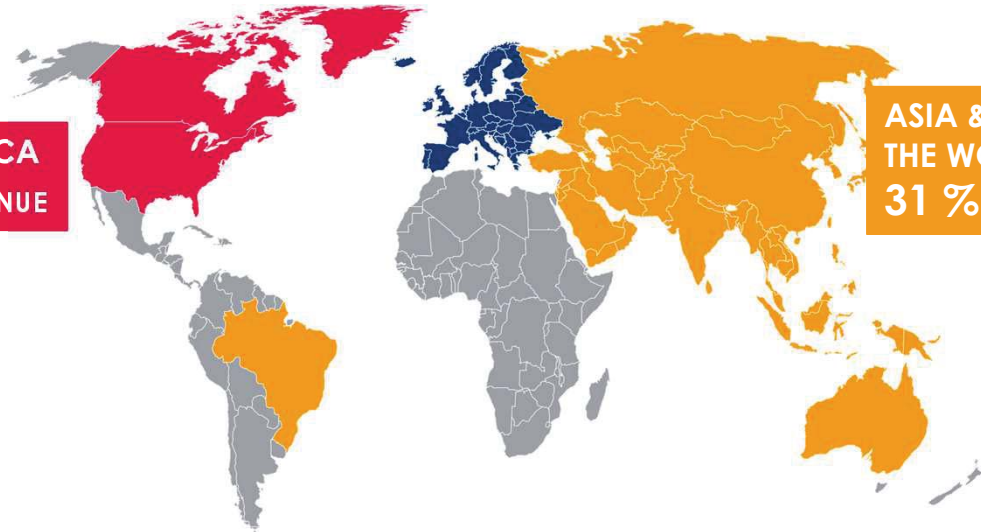
2018 SALES: €8.8 bn



**N° 1 to 3 IN THE WORLD IN OUR MAIN BUSINESSES
(90% of sales)**

**EUROPE
38 % OF REVENUE**

**NORTH AMERICA
31 % OF REVENUE**



**ASIA & REST OF
THE WORLD
31 % OF REVENUE**



OUR DNA: INNOVATIVE CHEMISTRY



FROM 2012 TO 2018,
IN THE TOP 100
GLOBAL INNOVATORS

- 
- ❖ **244** patents filed in 2018,
60% relating to sustainable development issues
 - ❖ **1,600** researchers, **60** R&D partnerships
 - ❖ **~3 %** of Group sales allocated to R&D
 - ❖ **1** incubator dedicated to breakthrough innovations



6 RESEARCH PLATFORMS DEDICATED TO SUSTAINABLE DEVELOPMENT



New energies

Materials to develop solar power, wind power, and electric batteries

e.g. Kynar® PVDF, Elium® liquid resin



Biosourced materials

Solutions to replace fossil resources as raw materials

e.g. Rilsan® polyamide 11, Pebax® Rnew® elastomer, Sarbio® advanced liquid resins



Water treatment

Materials for **water filtration applications**

e.g. Kynar® PVDF



Home efficiency and insulation

Solutions to reduce energy consumption of buildings

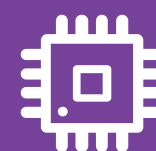
e.g. Bostik® sealant



Lightweight materials

Materials for composites and 3D Printing

e.g. Sartomer® resins, Kepstan® PEKK polymer, Rilsan® polyamide 11



Consumer electronics

Solutions to bring electronics within everyone's reach

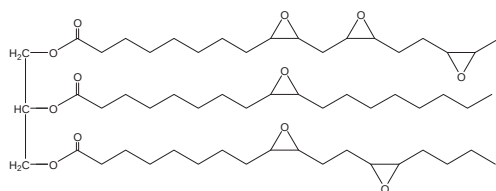
e.g. Piezotech® fluoropolymer

THREE BUSINESS SEGMENTS



High Performance Materials

- Technical polymers (**Specialty polyamides** and Fluoropolymers)
- Adsorption/Filtration (CECA)
- Organic Peroxides / **additives**
- **Specialty Adhesives (Bostik)**
- **Sartomer (Photocure resins)**



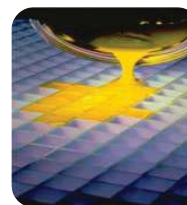
Industrial Specialties

- **Thiochemicals**
- Fluorogases
- **Altuglas International**
- Hydrogen peroxide

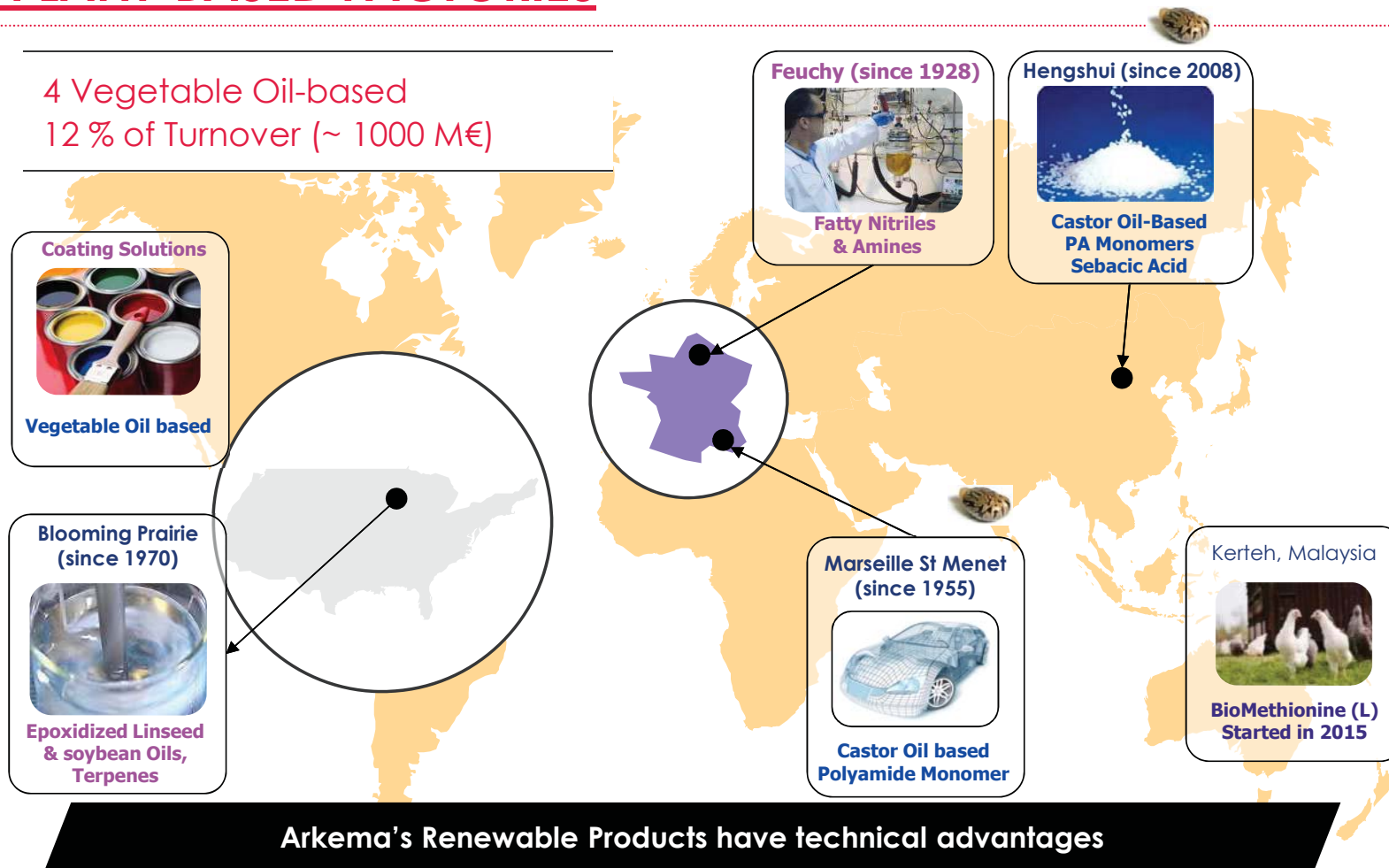


Coating Solutions

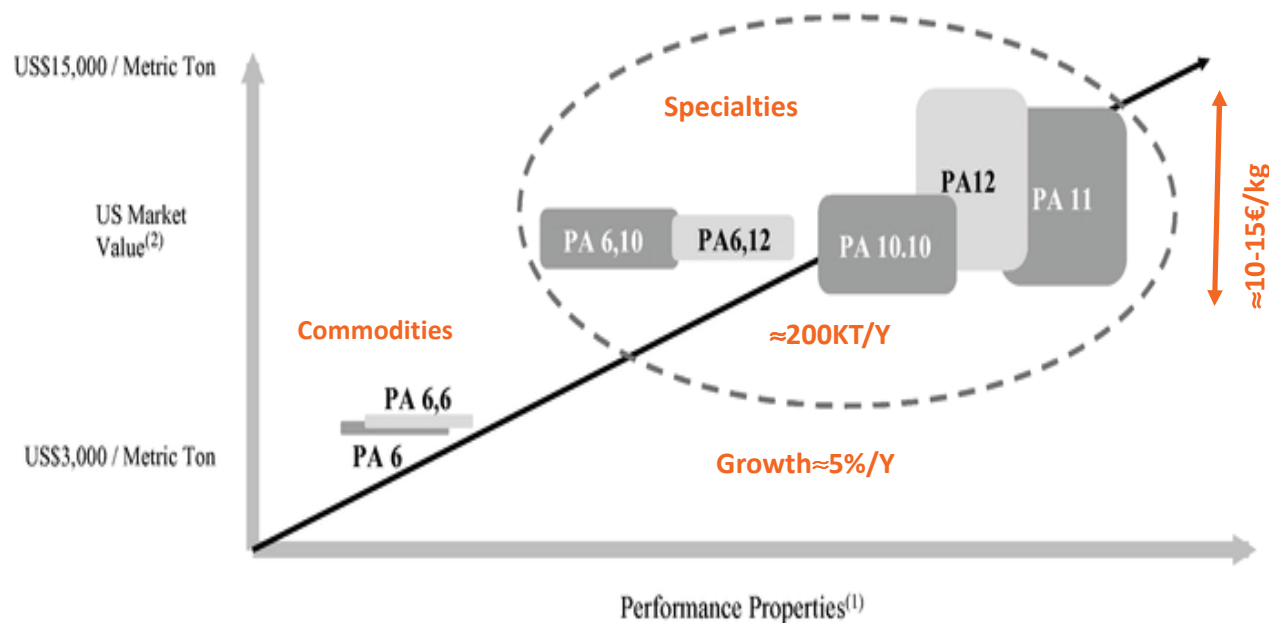
- **Acrylic monomers**
- **Coating resins**
- **Coatex (rheology additives)**



ARKEMA'S PLANT-BASED FACTORIES



POLYAMIDES MARKET



Source: Cathay Industrial Biotech Ltd., IPO F1 form, July 19th 2011

ARKEMA
INNOVATIVE CHEMISTRY

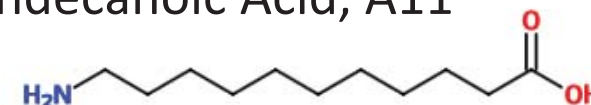
EVONIK
INDUSTRIES

UBE
UBE INDUSTRIES, LTD.

EMS
EMS-GRIVORY

C10-C11-C12 monomers

Amino-Undecanoic Acid, A11



main end-markets

Transportation

Fuel lines
Air brake systems



Energy

Flexible pipes for deep
off shore oil recovery



Consumer goods

Sport (shoes, ski boots,
etc.)
Cosmetics



Industrial coatings

Powder coating
Adhesives (hot melt)

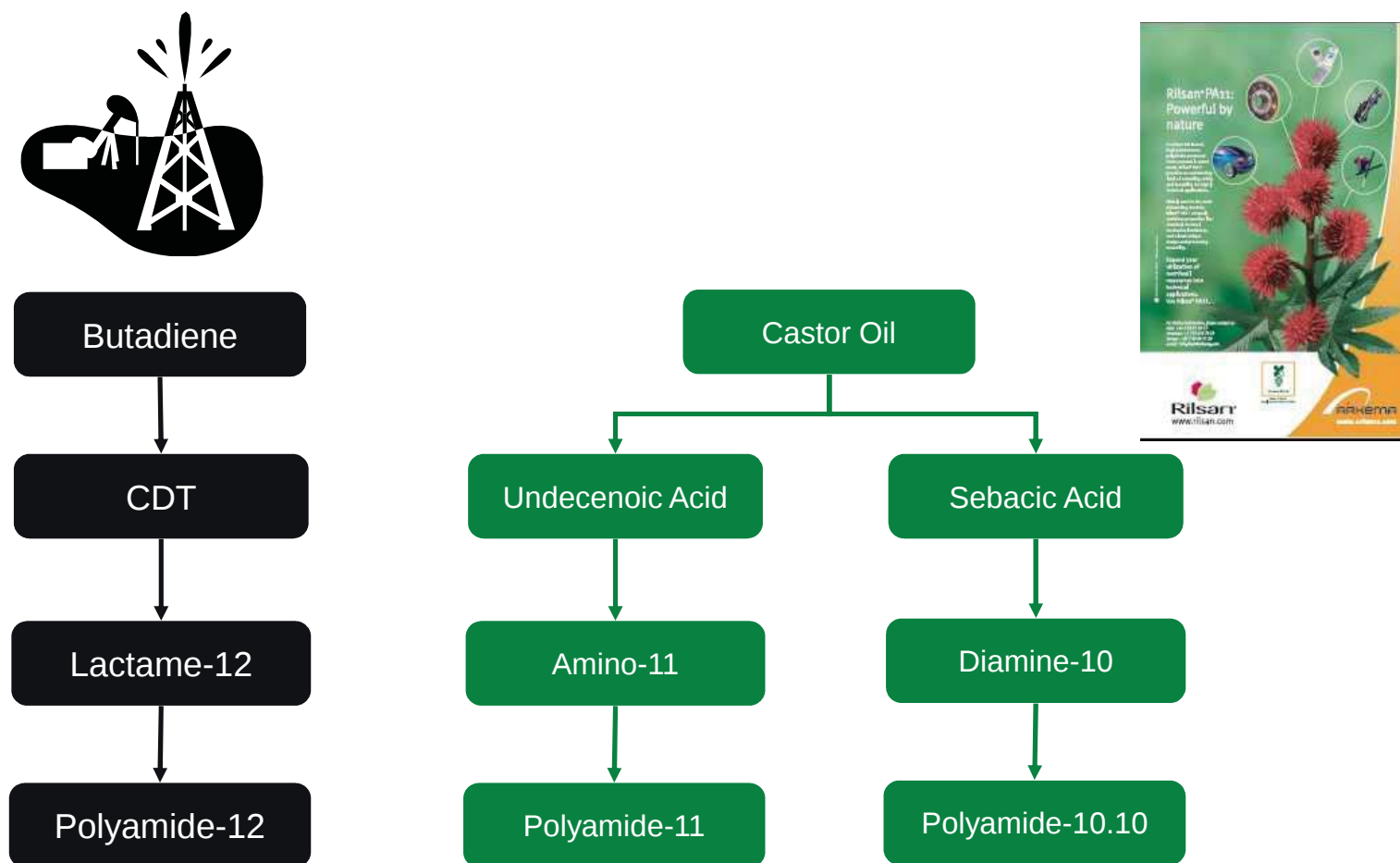


Electronics

Covers for laptops and
mobile devices

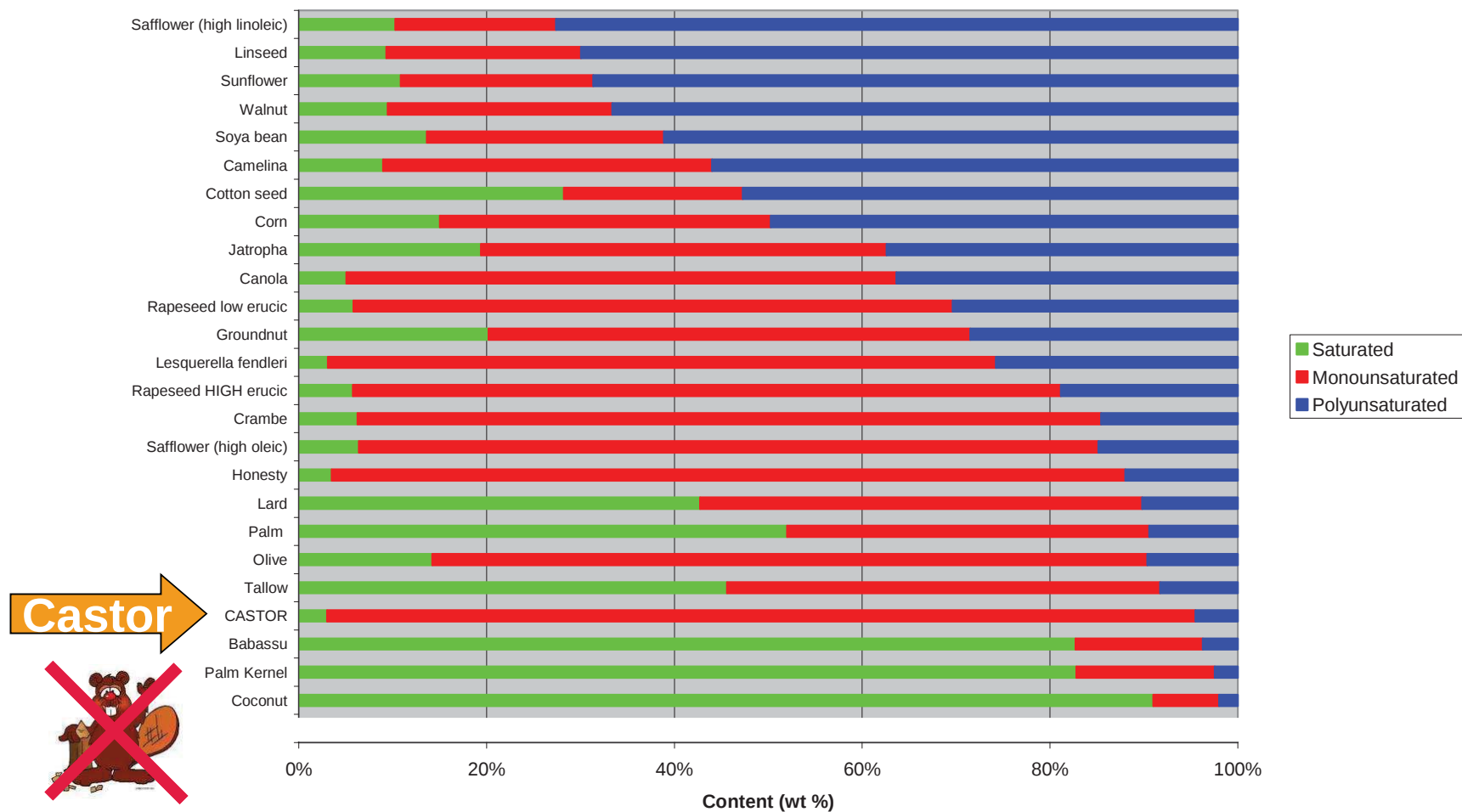


ARKEMA'S RENEWABLE LONG CHAIN POLYAMIDES



FATTY ACID PROFILE

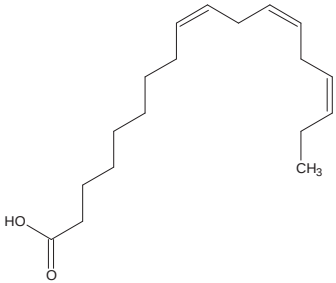
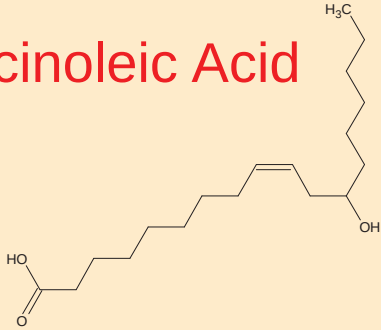
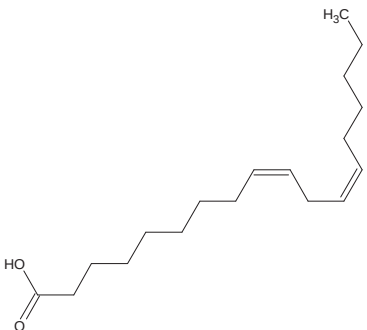
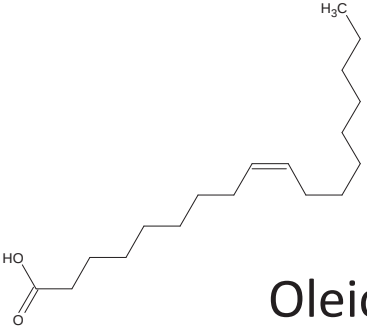
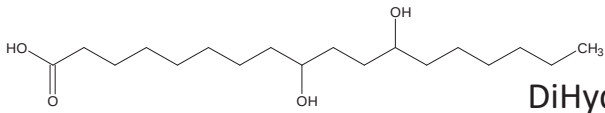
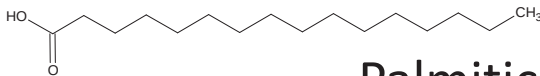
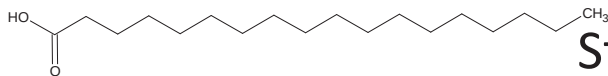
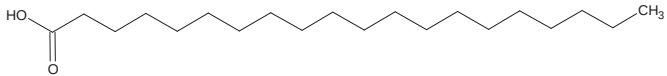
SOURCE: « LEXICON OF LIPID NUTRITION », PURE APPL. CHEM., VOL 73, N°4, PP 685-744, 2001 AND OLEON DATASHEETS + INTERNAL DATA



Castor

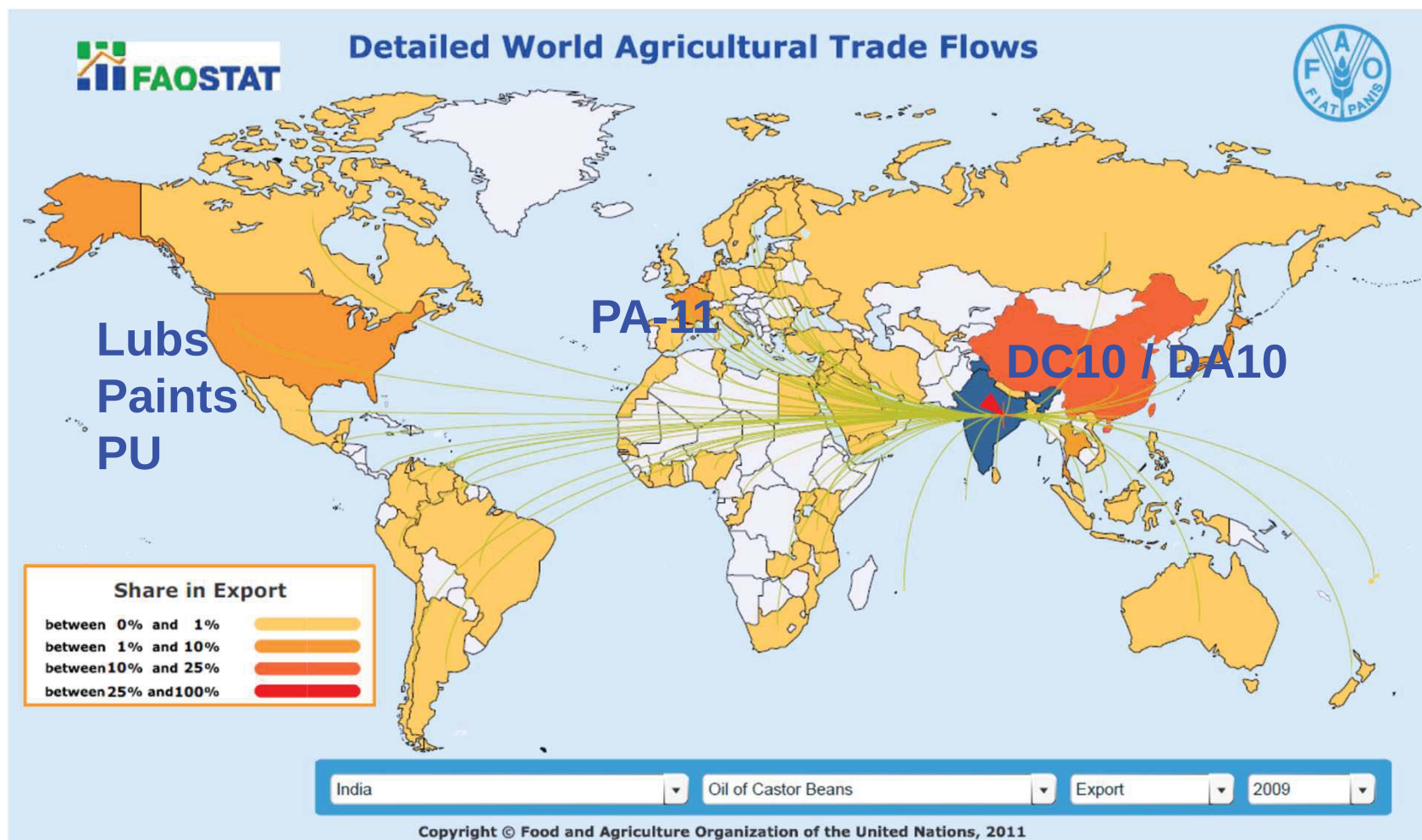


CASTOR OIL: RICH IN RICINOLEIC ACID

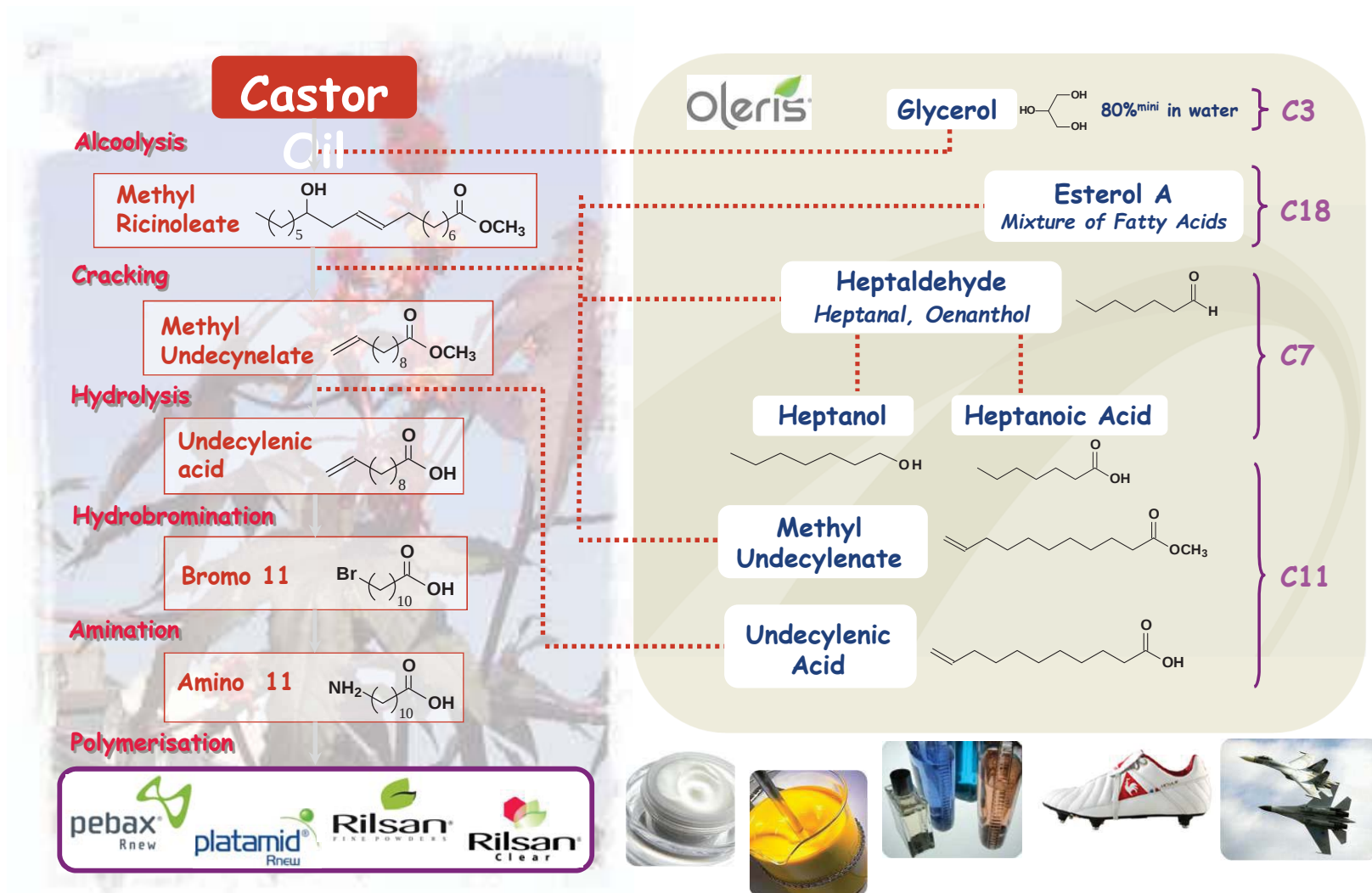
 Linolenic	0.5 - 1.0 %	 Ricinoleic Acid	85.0 – 95.0 %
 Linoleic	1.0 – 5.0 %	 Oleic	2.0 – 6.0 %
 DiHydroxyStearic	0.3 -0.7 %	 Palmitic	0.5 - 1.0 %
 Stearic	0.5 -1.0 %		0.3 %

Other minor fatty acid: lesquerolic acid, ...

CASTOR OIL TRADE EXPORT FROM INDIA AND MAJOR APPLICATIONS PER REGION



ARKEMA ST-MENET PLANT'S PROCESS FLOW



HENGSHUI, CHINA CASTOR OIL-BASED



CASTOR OIL, ALKALINE CLEAVAGE: SINGLE STEP REACTION SEQUENCE

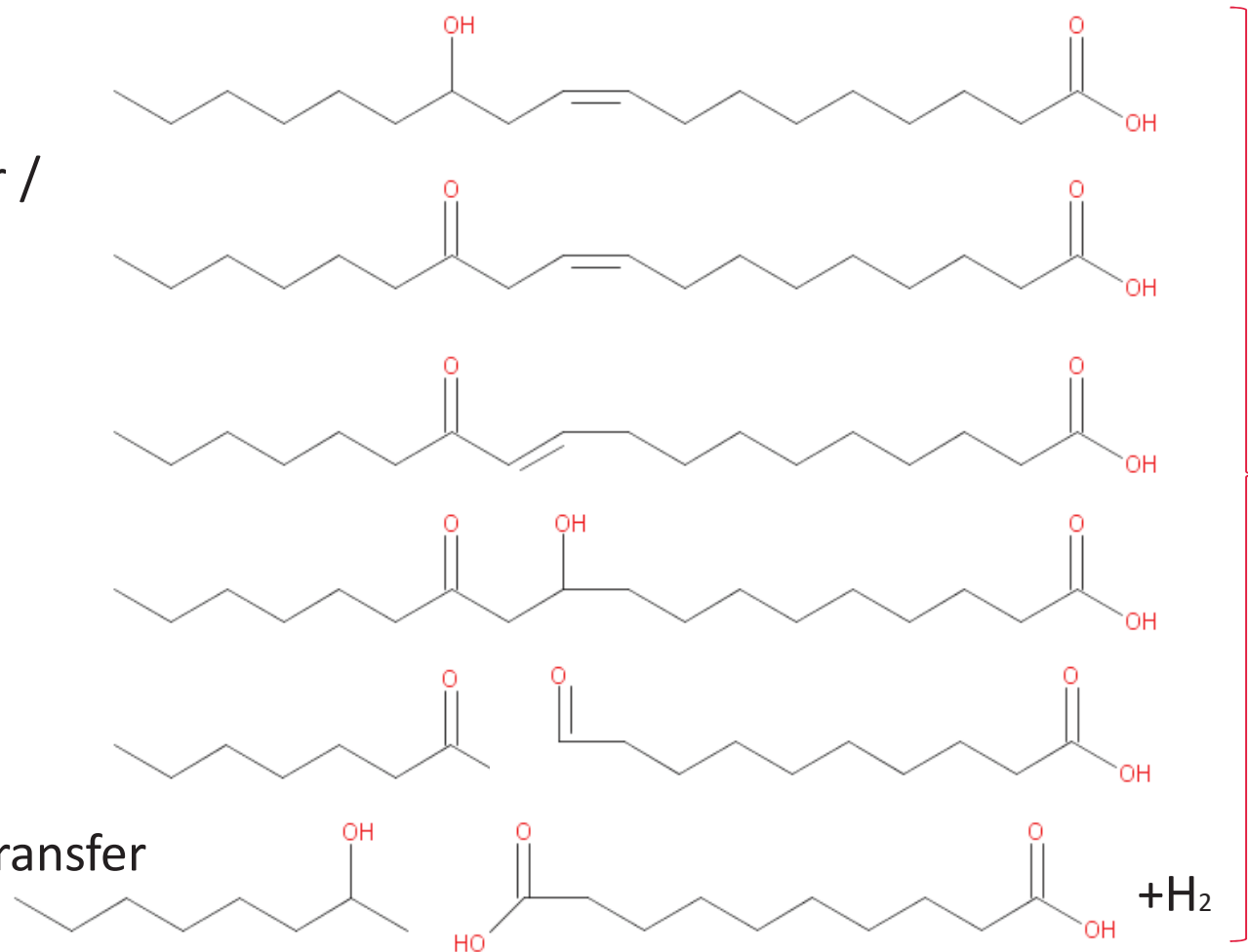
Hydrogen transfer /
Dehydrogenation

Isomerization

Hydration

Retro-aldolization

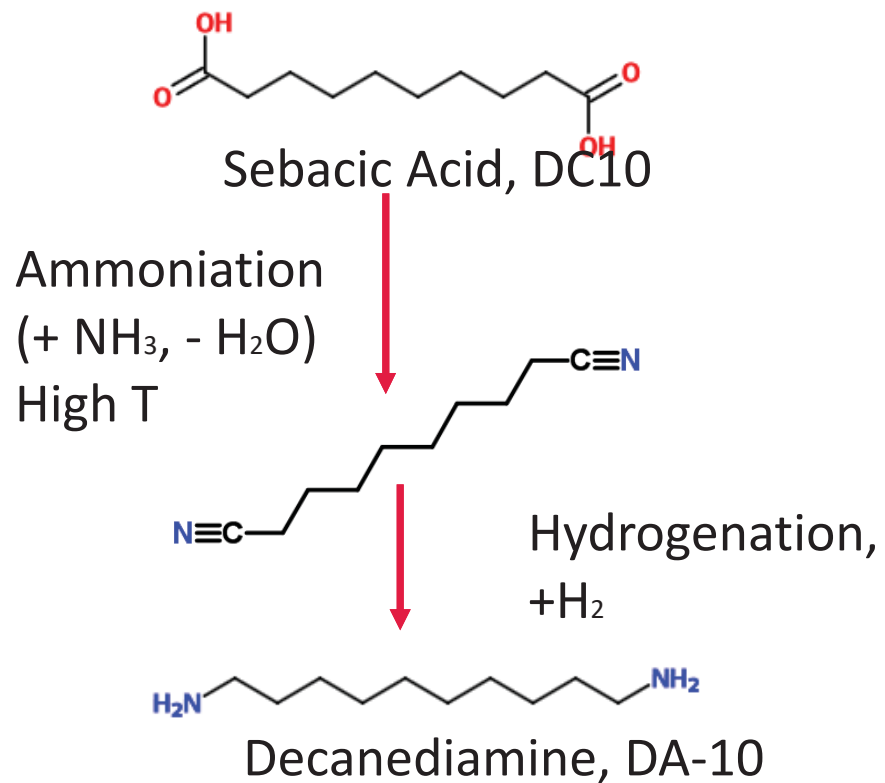
Oxidation +
Hydrogenation / H transfer



(Na⁺, OH⁻)

+H₂

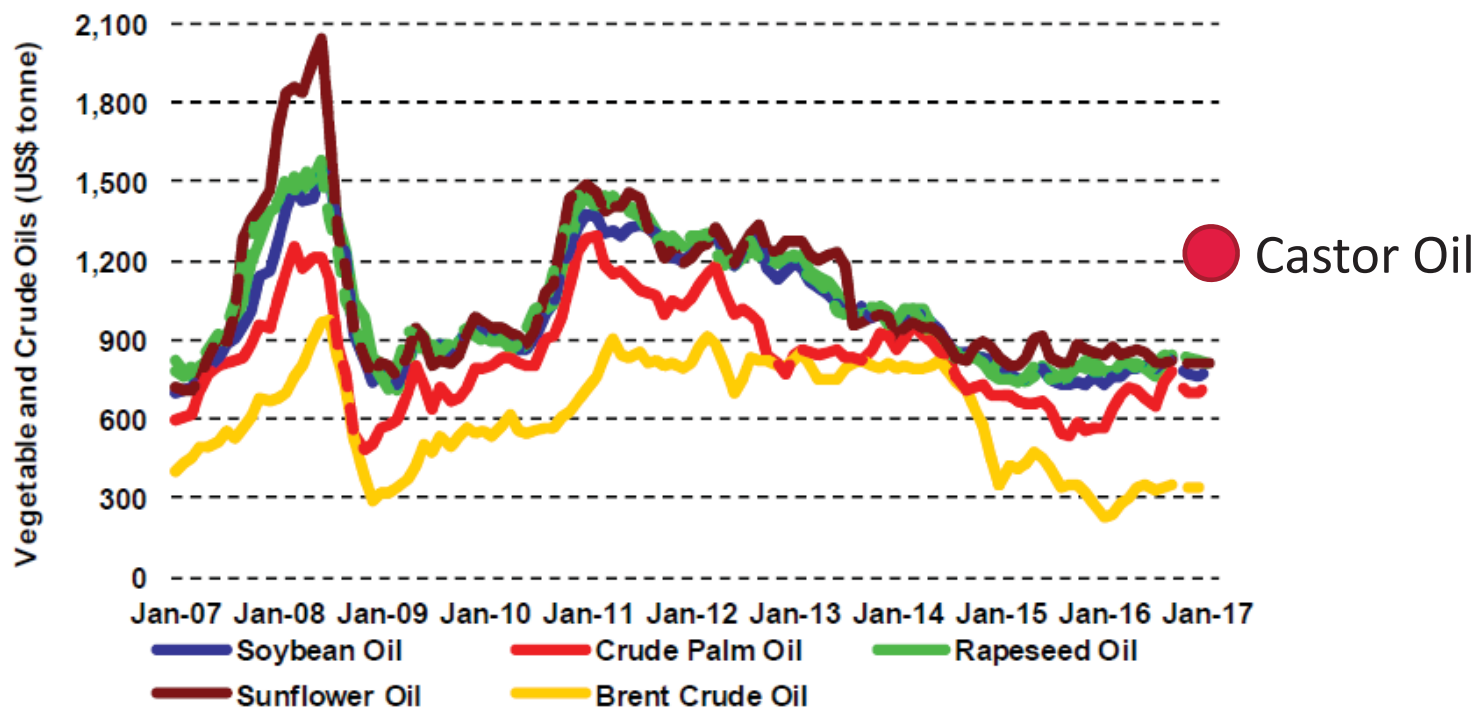
C10-DIAMINE



Note: Sebacic acid can also be converted to the diol by hydrogenation

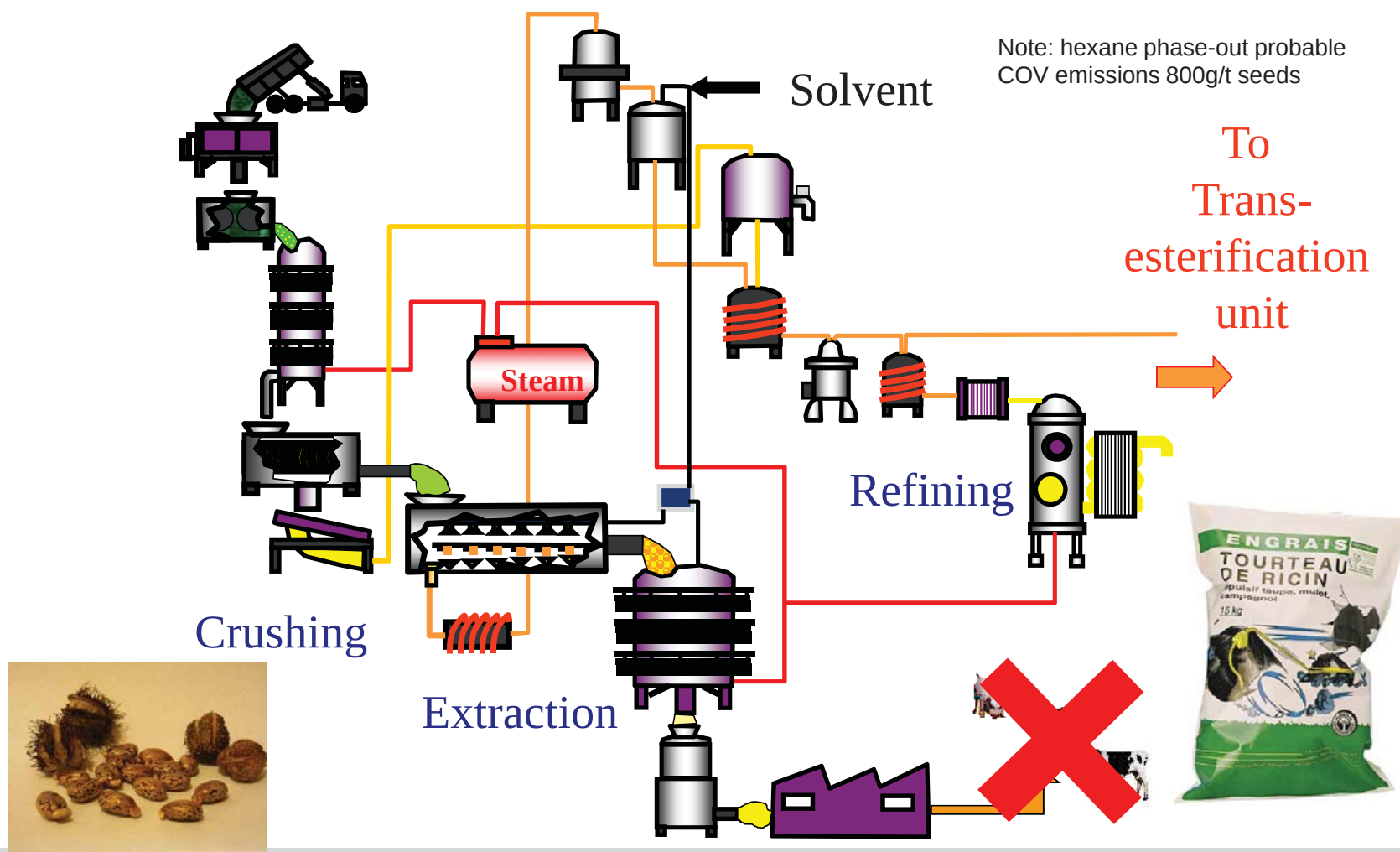
PRICES OF VEGETABLE OILS

EU vegetable oil prices since 2007, with six month forecasts (NW EU ports)

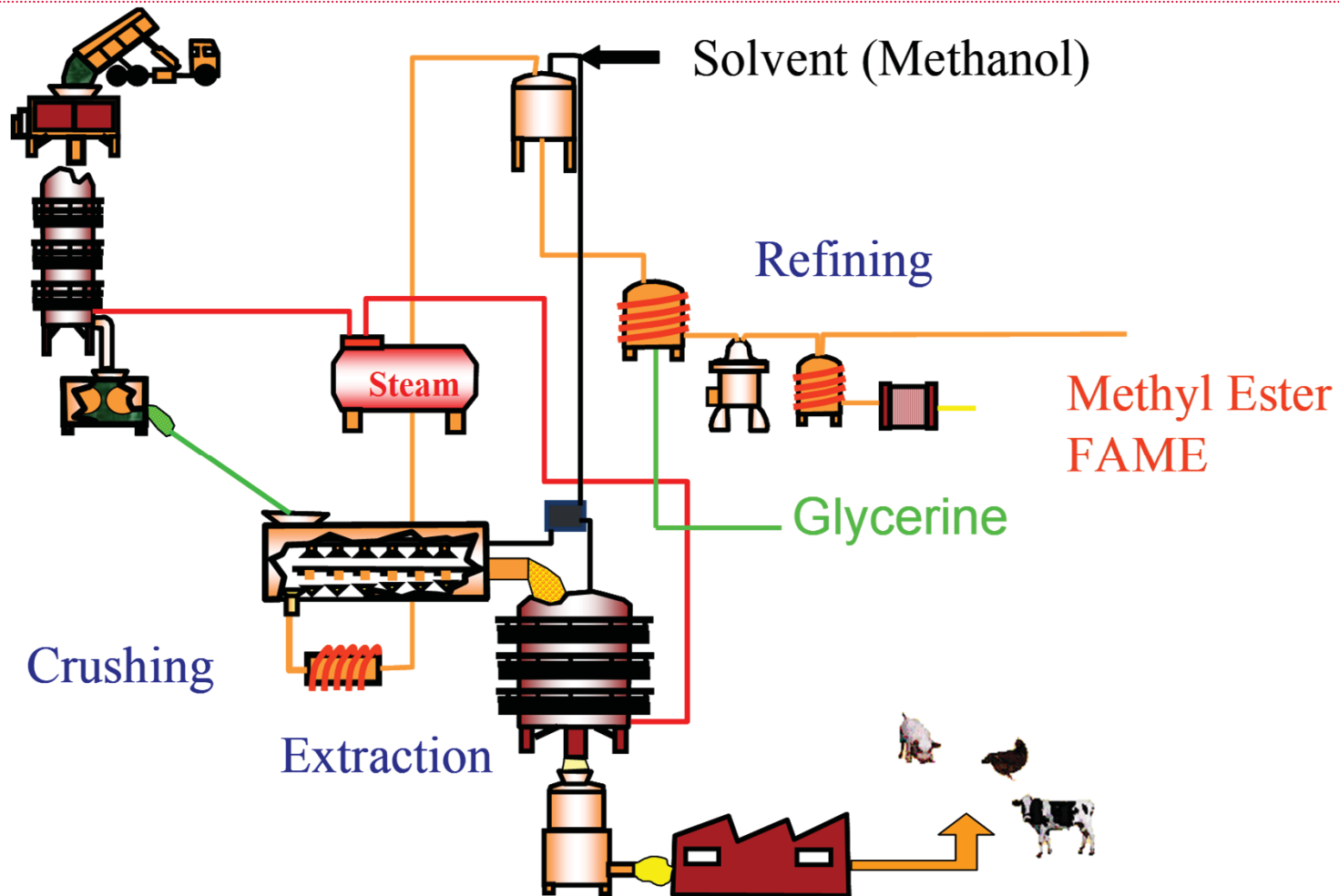


Source: LMC international

CONVENTIONAL PROCESS TO PRODUCE CASTOR OIL AND ITS METHYL ESTER



REACTIVE SEED CRUSHING PROCESS



THE TRIPLE EFFECT

- 
- ✓ **Reduce CAPEX**
 - ✓ Smaller number of pieces of equipment
 - ✓ **Reduce OPEX**
 - ✓ Reduce maintenance, labor and processing cost
 - ✓ **Detoxify**
 - ✓ Reduced toxicity of the Seed Meal

Also contributed to this work

- ADEME financial support to project RICHARB
- Jacques BARBIER, Antoine PICCIRILLI, Julien MAGNE (Valagro)

WO2010/076527, Jean-Luc DUBOIS, Julien MAGNE, Jacques BARBIER, Antoine PICCIRILLI
WO2010/084276, Jean-Luc DUBOIS, Antoine PICCIRILLI, Jacques BARBIER, Julien MAGNE
WO2011/092430, (Jatropha seeds) Jean-Luc DUBOIS, Juline MAGNE, Anoine PICCIRILLI

...

ALTERNATIVE MONOMERS ROUTE



Castor Oil

Marseille
MeOH, Cracking, HBr, NH₃



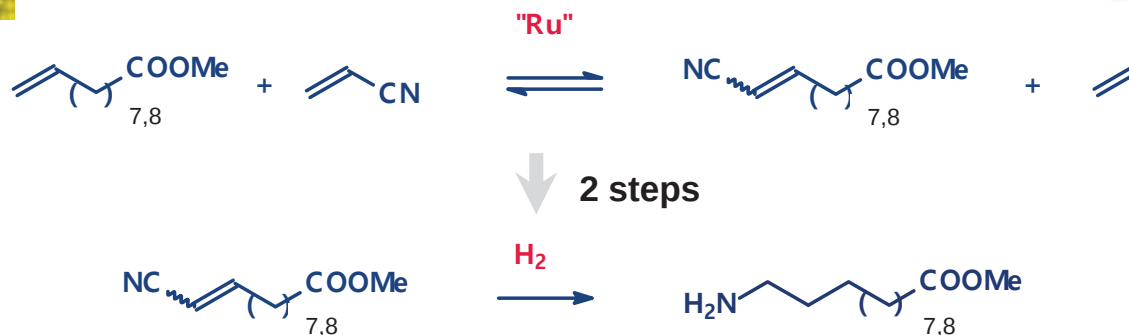
PA11



Palm, Rapeseed,
HOSO based C10:1
Castor based C11:1

Metathesis technology

RILSAN
BY ARKEMA



PA11
PA12

CASTOR BASED PA12 SAMPLE MADE WITH ARKEMA'S METHYL-10-UNDECENOATE.



RESULTS FROM EUROBIOREF PROJECT



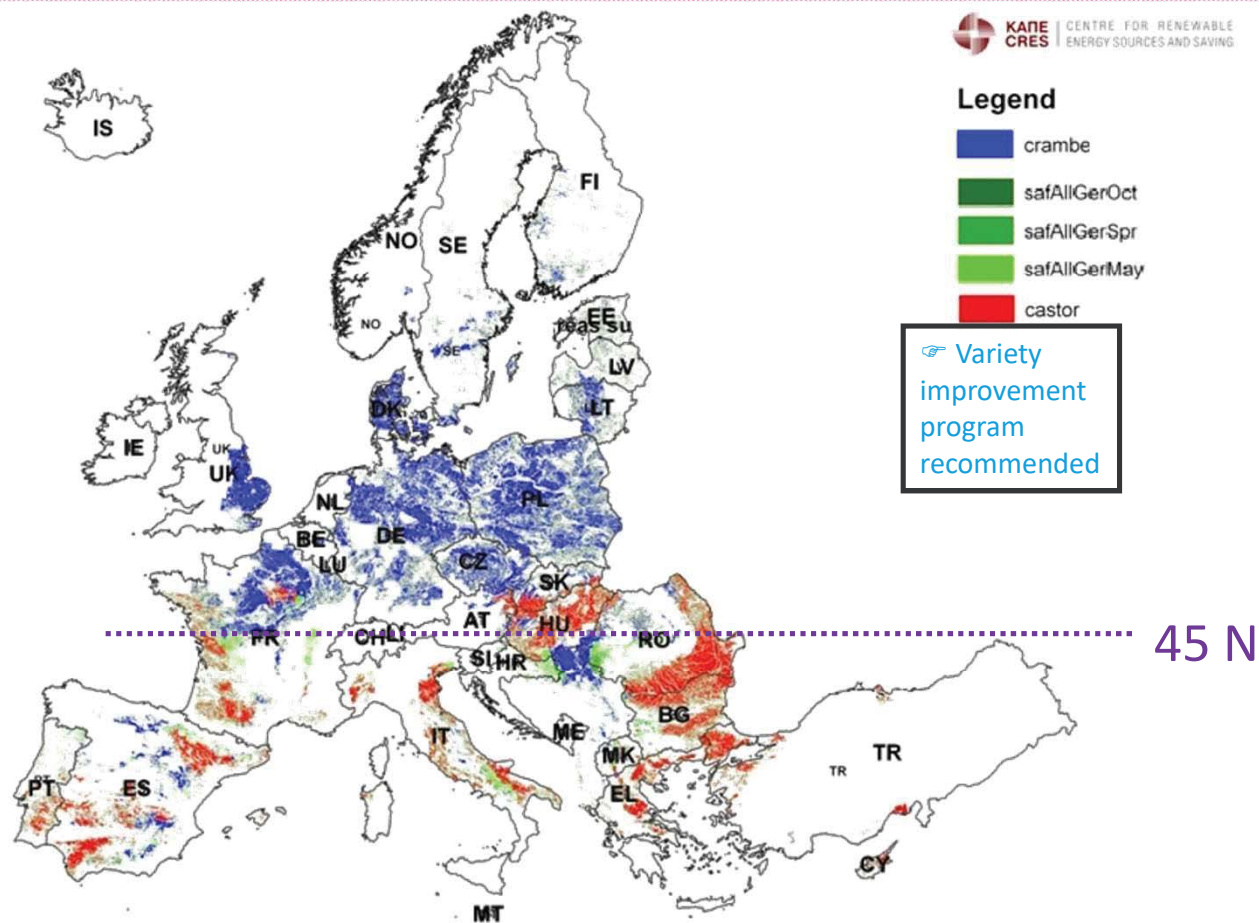
CRAMBE



SAFFLOWER

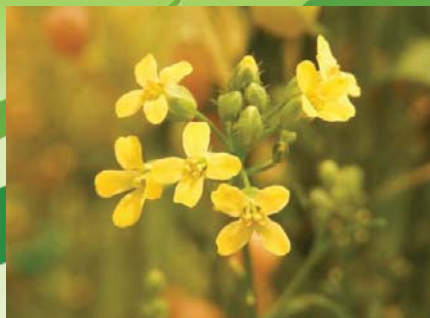


CASTOR



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





Camelina sativa



Crambe abyssinica

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

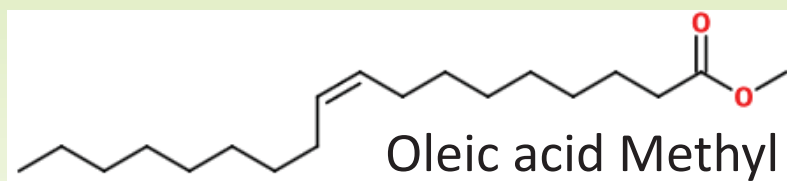


Funded by the Horizon 2020
Framework Programme of
the European Union

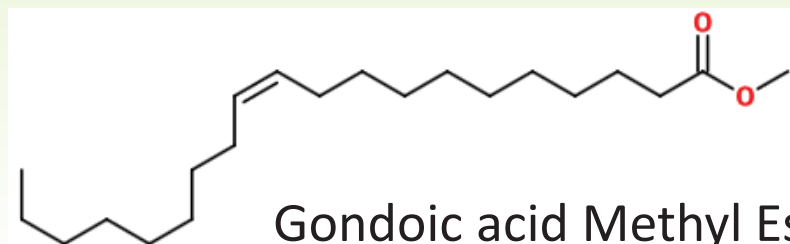


Other Fatty acids, from selected vegetable oils

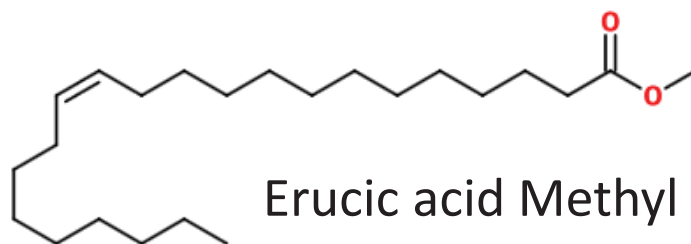
Routes to other monomer chain length



Oleic acid Methyl Ester, C18:1, delta-9



Gondoic acid Methyl Ester, C20:1, delta-11



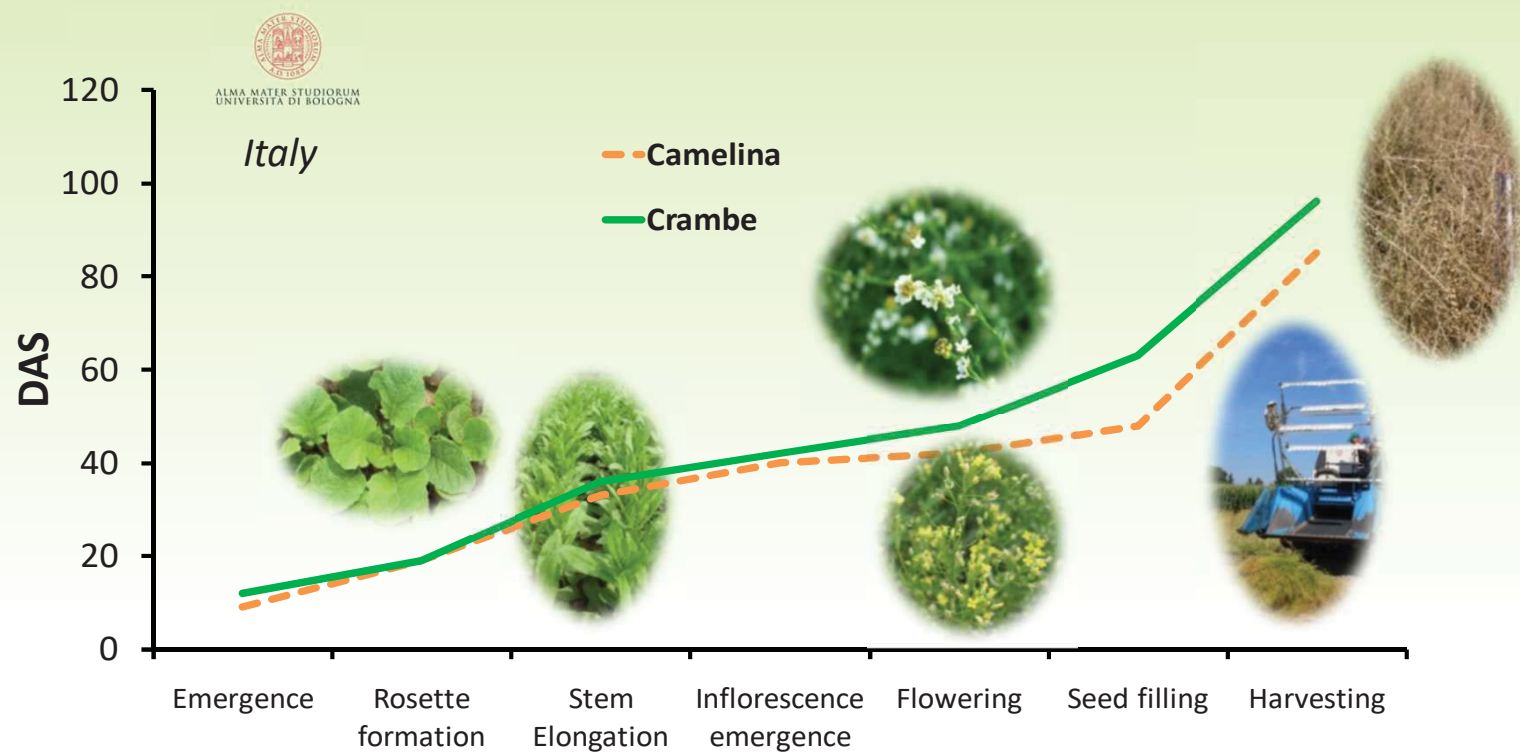
Erucic acid Methyl Ester, C22:1, delta-13



Funded by the Horizon 2020
Framework Programme of
the European Union

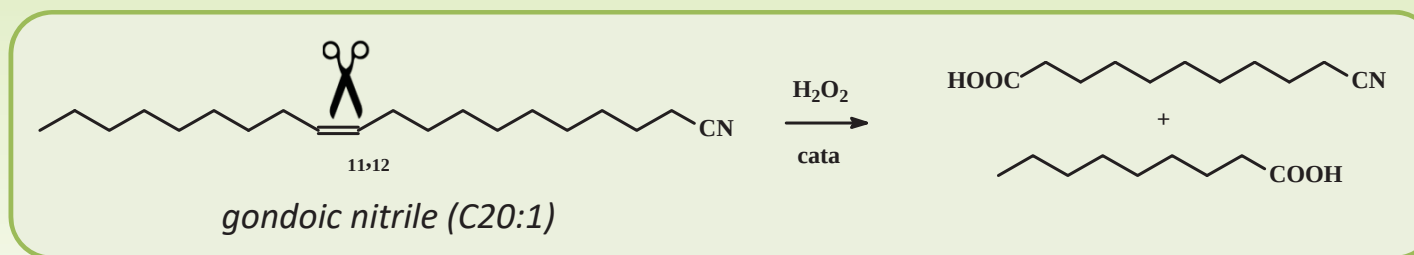


Cultivation strategies



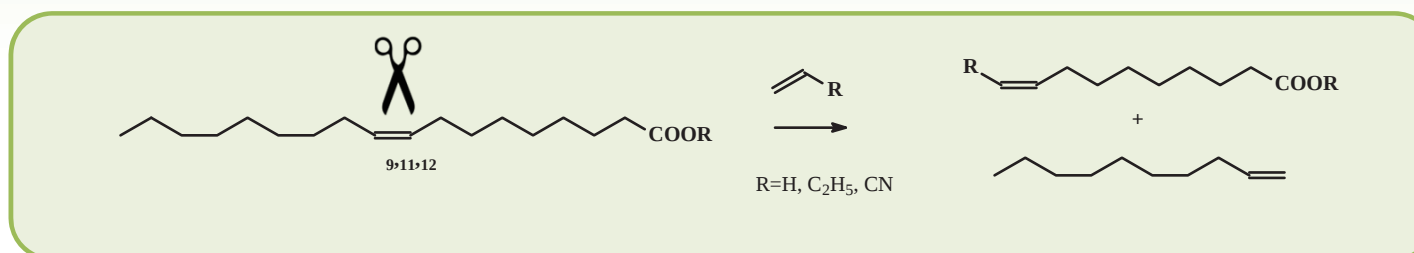
Fatty Acids conversions and applications

- Oxidative cleavage of MUFA:



ARKEMA
INNOVATIVE CHEMISTRY

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



Apeiron
synthesis

ARKEMA
INNOVATIVE CHEMISTRY



COSMOS Final Results

Video:

<https://www.youtube.com/watch?v=H53KW4CYxG4>

Brochure:

http://cosmosh2020.eu/media/2019/09/19-08-30-COSMOS__Project_achievements_web.pdf.



ALKYD RESINS

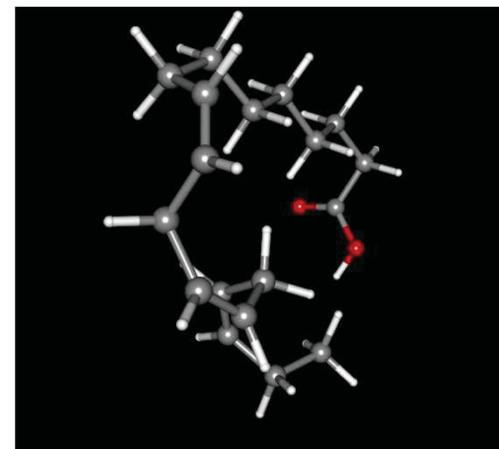


❖ Major application: Paints and Varnishes

❖ Process: esterification with polyols.

❖ Technical requirements:

- Siccative property (self drying)



❖ What does it mean in terms of appropriate fatty acid

- PolyUnsaturated Fatty Acids (PUFA). Linolenic acid (C18:3); Linoleic (C18:2)
- Dehydrated Castor oil (conjugated linoleic acid C18:2),
- Hydroxystearic acid (C18:0, OH)

❖ Appropriate vegetable oils:

- Linseed oil, High Linolenic safflower oil, Camelina, Castor.

POLYAMIDE



❖ Major application: Specialty Polymers

❖ Processes: Oil dependant

- Transesterification, thermal cleavage, hydrolysis, hydrobromination, ammonolysis → Castor Oil to Polyamide 11
- Hydrolysis, alkaline cleavage, acidification (sebacic acid-DC10)/ ammoniation, hydrogenation (DA10) → Castor oil to Polyamide 10.10

❖ Technical requirements:

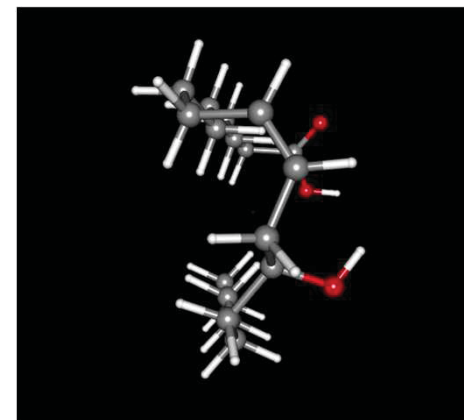
- Hydroxyfatty acid, with chain $R'-(CH_2)_n-CH=CH-CH_2-CHOH-R$

❖ What does it mean in terms of appropriate fatty acid

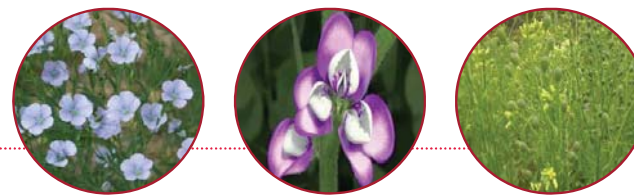
- Ricinoleic acid (C18:1, OH); Lesquerolic acid (C20:1, OH)

❖ Appropriate vegetable oils:

- Castor oil, Lesquerella oil



EPOXYDIZED OILS



❖ **Major application: Secondary plasticizers, polyols**

❖ **Process: epoxidation with peracids**

- Oil + peracetic or performic acid → epoxidized oil

❖ **Technical requirements:**

- High number of epoxide functions

❖ **What does it mean in terms of appropriate fatty acid**

- Linolenic acid (C18:3), Linoleic acid (C18:2)

❖ **Appropriate vegetable oils:**

- Linseed oil, Soybean oil, Camelina oil

OXIDATIVE CLEAVAGE (OZONE O₃/H₂O₂) PRODUCTS

❖ Major application:

- Azelaic (DC9) and Brassylic (DC13) acids → Diacids, lubricants, plasticizers, monomers; flavor and Fragrances.
- Pelargonic acid (C9): Herbicide

❖ Process: Ozonolysis or H₂O₂ cleavage

- Fatty acid + O₃ → Diacid + Monoacid (e.g.: oleic → Azelaic (DC9) + Pelargonic)
- Fatty acid / Fatty ester / Fatty Nitrile + H₂O₂ → Diacid/nitrile-acid + monoacid
- Reductive Ozonolysis → Aldehyde production (Fragrances)

❖ Technical requirements:

- Chain length selectivity → affects polymer crystallinity
- Extremely low monofunctional content → affects chain length

❖ What does it mean in terms of appropriate fatty acid

- MonoUnsaturated Fatty Acid (MUFA): Oleic acid (C18:1);
- Gondoic acid (C20:1); Erucic acid (C22:1)

❖ Appropriate vegetable oils:

- HO sunflower, HO safflower, HO Camelina, Crambe, HEAR, ... HO Cardoon... Beef tallow, animal fats.

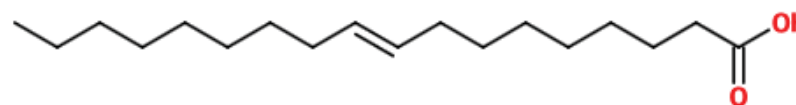


SELECTED CASE STUDY: OXIDATIVE CLEAVAGE

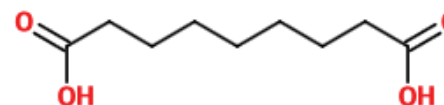
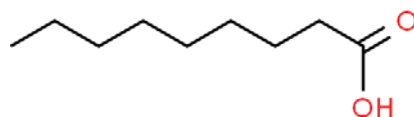
❖ 9-Carbons diacid: Azelaic acid

❖ 9-Carbons monoacid: Pelargonic acid

CRODA
CRODA SIPO

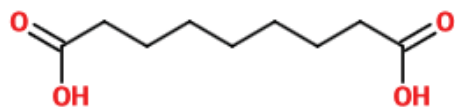


Ozonolysis or H₂O₂ Oxidative Cleavage



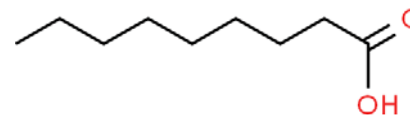
❖ → Main Products: Pelargonic acid (C9), Azelaic acid (DC9)

MAIN MARKETS



❖ Azelaic Acid (DC9)

- Monomers
- Plasticizers
- Lubricants



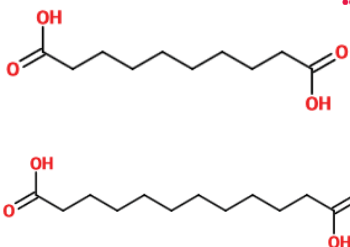
❖ Pelargonic acid (C9)

- Lubricants
- Herbicides



Competes with (tropical oils):

- Sebacid acid (DC10) ex castor oil,
- Dodecanedioic acid (DC12), if biobased ex Palm Kernel and Coconut oil



Competes with (tropical oils):

- Heptanoic (biobased from castor oil) – C7
- Octanoic (caprylic) and Decanoic (Capric) – C8/C10 (biobased from palm kernel/coconut oils)

HERBICIDES: GLYPHOSATE ALTERNATIVES

✓ *Les résultats de notre essai*

+++ Très bon 20 à 17
 ++ Bon 16,5 à 13
 + Acceptable 12,5 à 10
 - Insuffisant 9,5 à 7
 -- Très insuffisant 6,5 à 0

Les pourcentages entre parenthèses expriment le poids de chaque critère dans la notation finale.

	 Bayer Jardin Natria Désherbant polyvalent	 Solabiol Désherbant cours, allées, terrasses	 Fertiligène Désherbant jardin, cours et allées	 Clairland Désherbant tous jardins Express	 Roundup Désherbant action rapide, formule biocontrôle Speed	 Roundup Désherbant jardin, effets visibles sous 6 h
• Conditionnement	1 l	1 l	0,9 l	0,9 l	1,2 l	1 l
• Prix indicatif	8,90 €	5,50 €	20 €	25 €	5,90 €	Produit interdit de vente ⁽²⁾
• Prix indicatif au litre	8,90 €	5,50 €	22 €	28 €	5 €	
• Substance active	Acide caprylique + acide caprique	Acide caprylique + acide caprique	Acide acétique	Acide pélargonique	Acide acétique	Glyphosate + acide pélargonique
Performances (40 %)	+	+	-	++	--	++
• Sur plantes graminées	+	-	--	+	--	+
• Sur plantes adventices	+	+	-	++	--	++
• Sur plantes à feuilles larges	+	+	--	+	--	+
Biotoxicité (30 %)	+++	++	-	+	-	--
Avis sur la composition (30 %)	+	+	++	--	++	--
NOTE GLOBALE (100 %)	12,5/20	11,5/20	8,5/20	8/20	6,5/20⁽¹⁾	Non noté

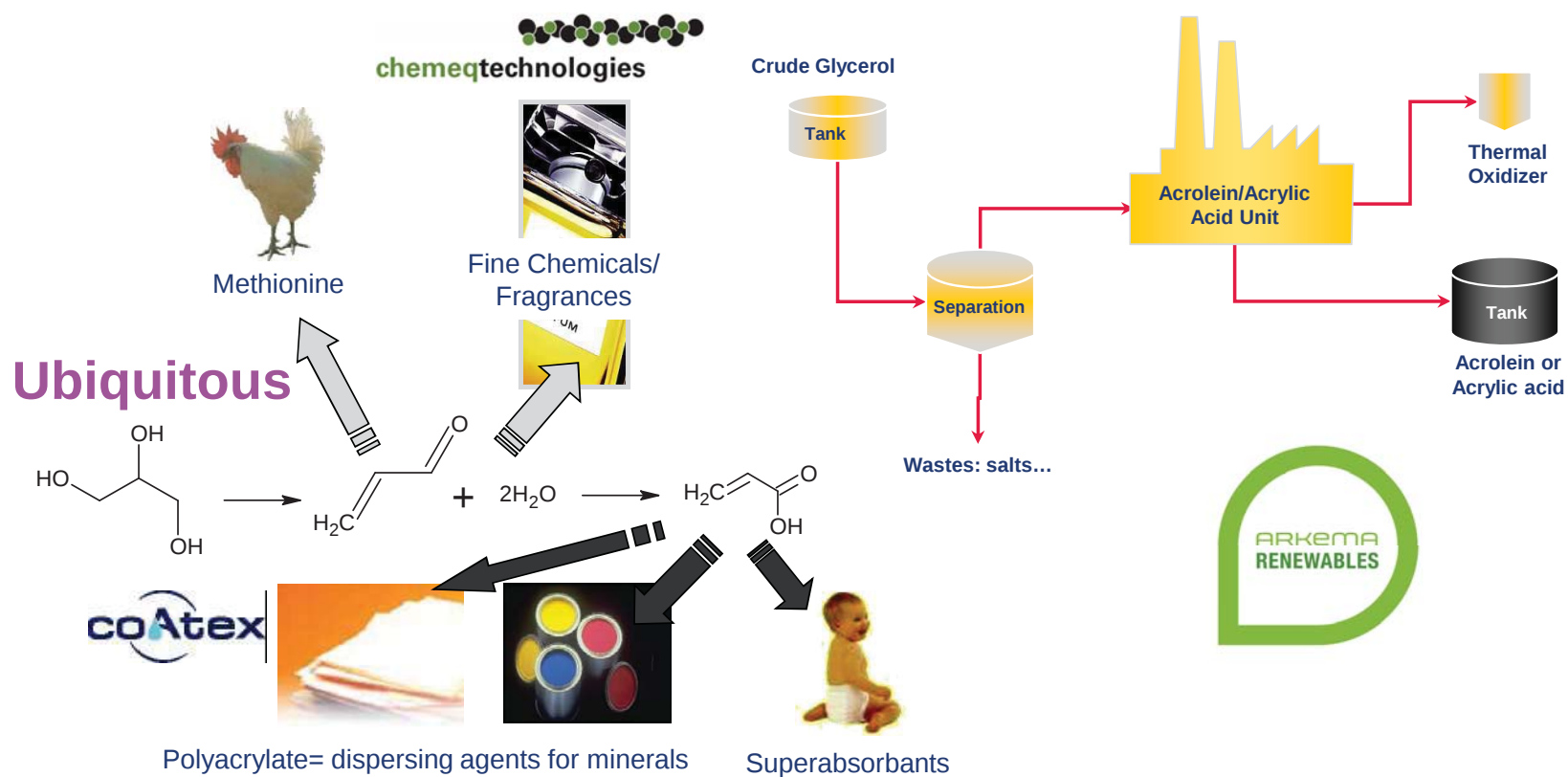
(1) L'appréciation globale ne peut être supérieure aux performances. (2) Le produit testé a été acheté avant son interdiction au prix de 20 € le bidon d'un litre.

C8+C10 C8+C10 C2 C9 C2

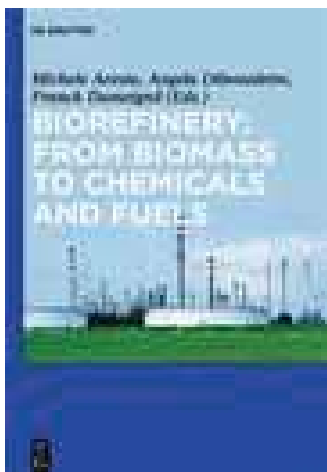
✦ Pelargonic (C9:0) competes with Caprylic (C8:0) and Capric (C10:0)

ACROLEIN/ ACRYLIC ACID: ARKEMA'S PROJECT

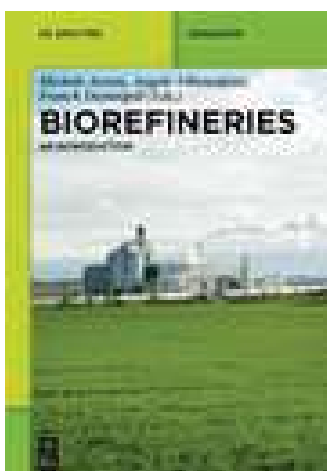
- Acrolein and Acrylic acid are currently produced from propylene (Petroleum).
- Double internal dehydration of Glycerol leads to Acrolein which is further oxidized to Acrylic acid



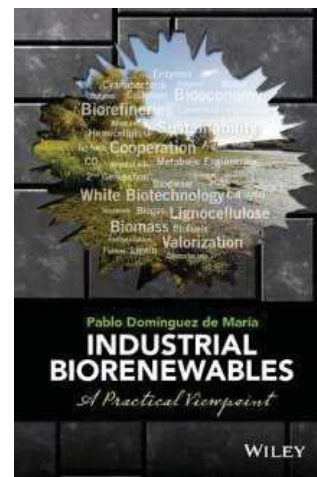
**TO LEARN MORE:
SEE MY CONTRIBUTIONS TO THE FOLLOWING BOOKS**



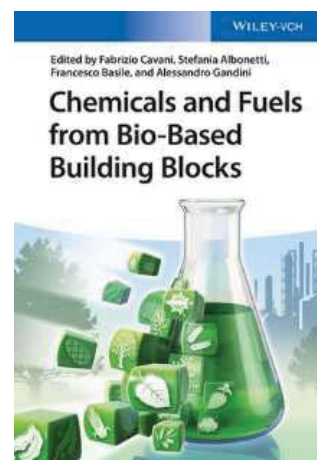
Chapter 2:
Refinery of the
future: feedstock,
processes,
products
(2012)



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



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

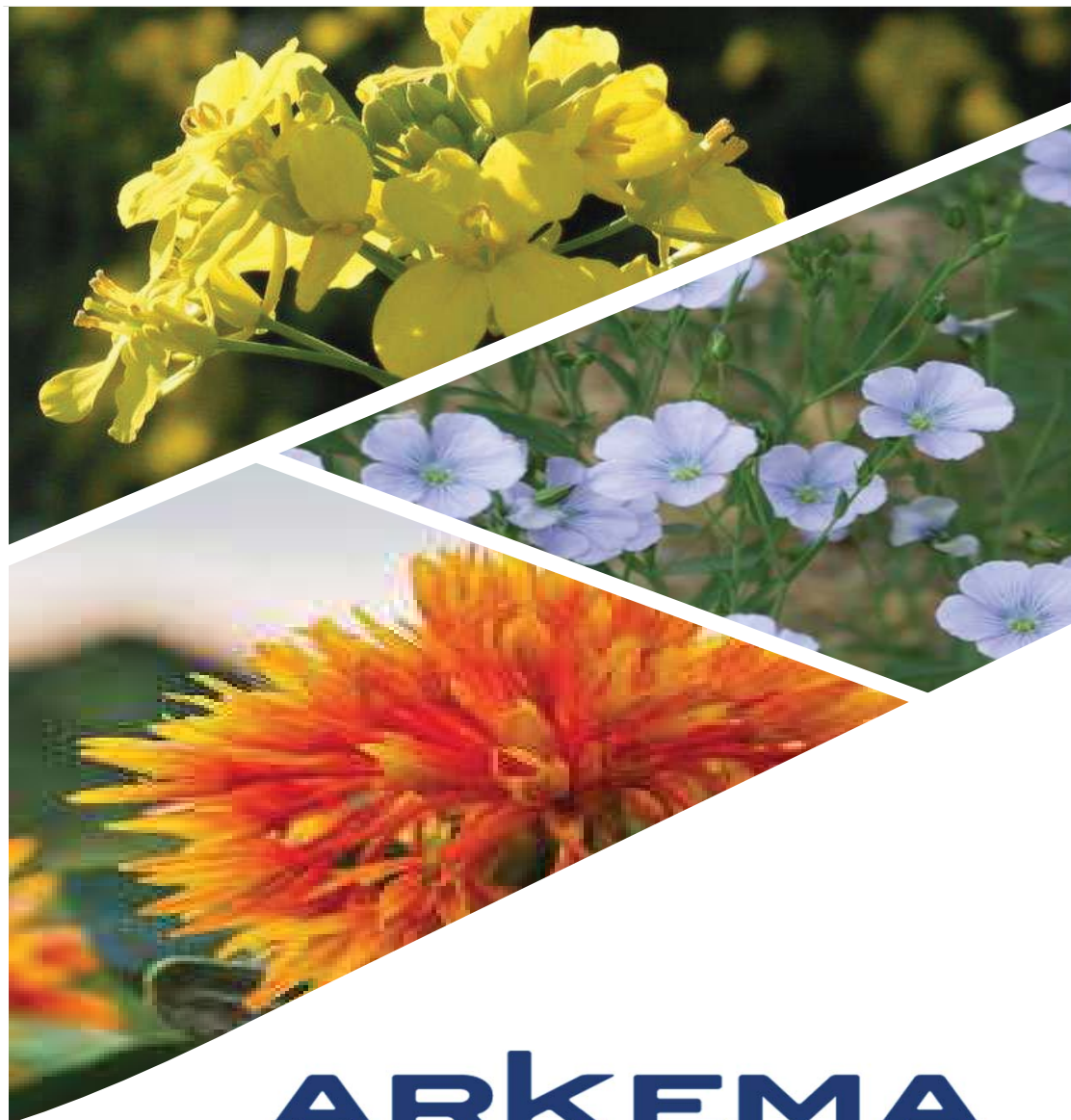


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