

# ARKEMA

Les défis de la  
Chimie

lundi 3 Octobre 2022

## Sources de carbone

pour les grands intermédiaires de la chimie organique :

NOUVELLES APPROCHES

2<sup>e</sup> Session

Nouveaux procédés  
de production de grands intermédiaires.

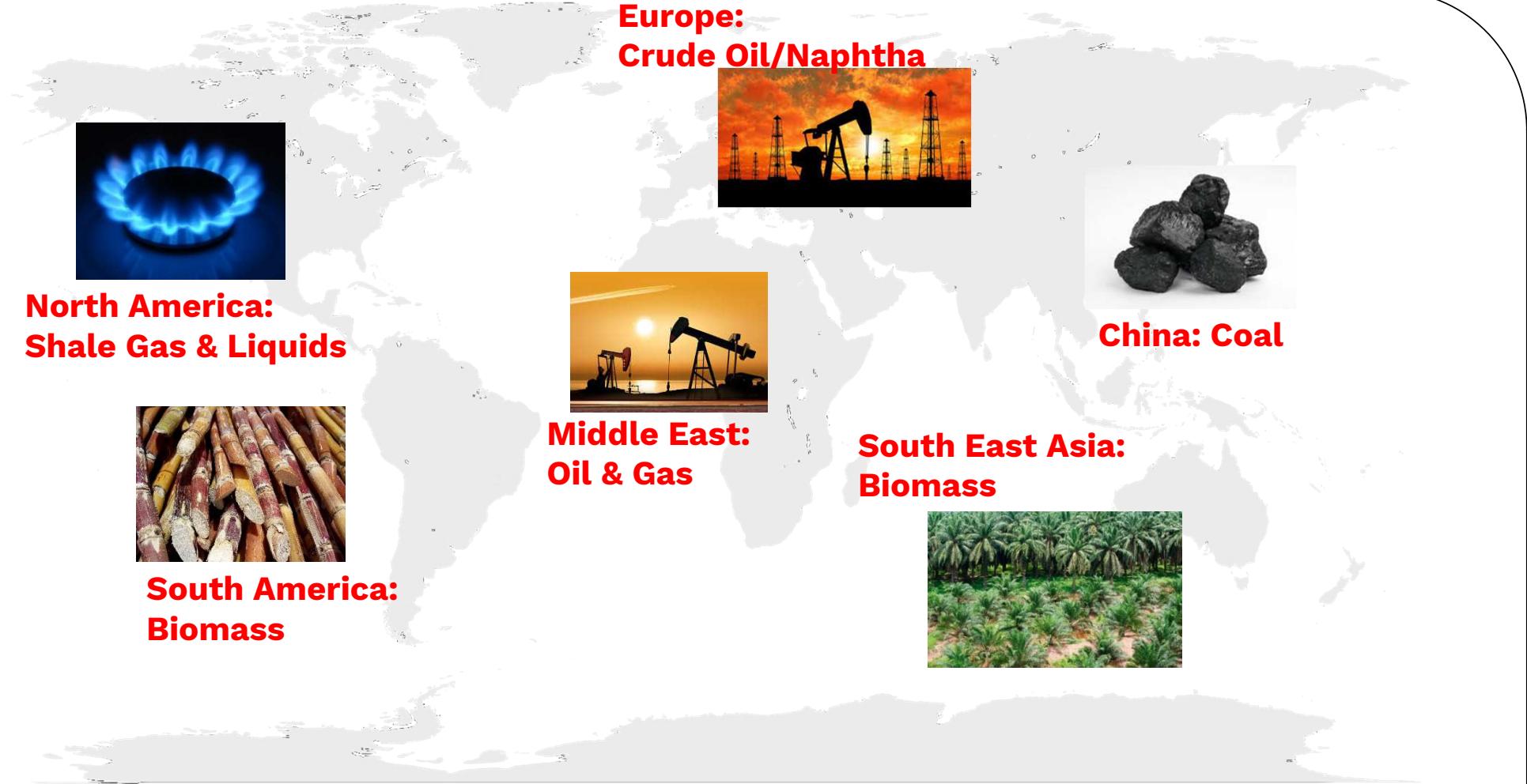
14h00 - 14h30 Les acrylates (Acrylonitrile et Acides [meth]acryliques).  
Jean-Luc DUBOIS, Directeur Scientifique • Arkema

# Les Acrylates

## Acrylonitrile et Acides (Meth)Acryliques

Jean-Luc DUBOIS

Process selection may depend on local feedstock availability.



Review

## Review on Alternative Route to Acrolein through Oxidative Coupling of Alcohols

Vincent Folliard<sup>1,\*</sup>, Jacopo de Tommaso<sup>2</sup> and Jean-Luc Dubois<sup>2,\*</sup><sup>1</sup> Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON), Univ Lyon, Université Claude Bernard Lyon1, CNRS, IRCELYON, 2 Avenue Albert Einstein CEDEX, 69626 Villeurbanne, France<sup>2</sup> Arkema France, Corporate R&D, 420 Rue d'Estienne d'Orves, 92705 Colombes, France;

jacopo.de-tommaso@arkema.com

\* Correspondence: vincent.folliard@ircelyon.univ-lyon1.fr (V.F.); jean-luc.dubois@arkema.com (J.-L.D.); Tel.: +33-472-398-511 (J.-L.D.)

## Strategy in achieving propane selective oxidation over multi-functional Mo-based oxide catalysts

Chem. Eng. Technol. 2009, 32, No. 3, 1–8

Antoine Godefroy<sup>1</sup>Gregory S. Patience<sup>1</sup>Maria Tzakova<sup>1</sup>Dominique Garrait<sup>2</sup>Jean-Luc Dubois<sup>2</sup>

### Research Article

## Reactor Technologies for Propane Partial Oxidation to Acrylic Acid

Catalysis Communications 17 (2012) 23–28



Contents lists available at SciVerse ScienceDirect

Catalysis Communications

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



### Short Communication

Influence of surface acid–base properties of zirconia and titania based catalysts on the product selectivity in gas phase dehydration of glycerol

# Acrylic Acid



## Green Chemistry

### PAPER

[View Article Online](#)  
[View Journal](#) | [View Issue](#)

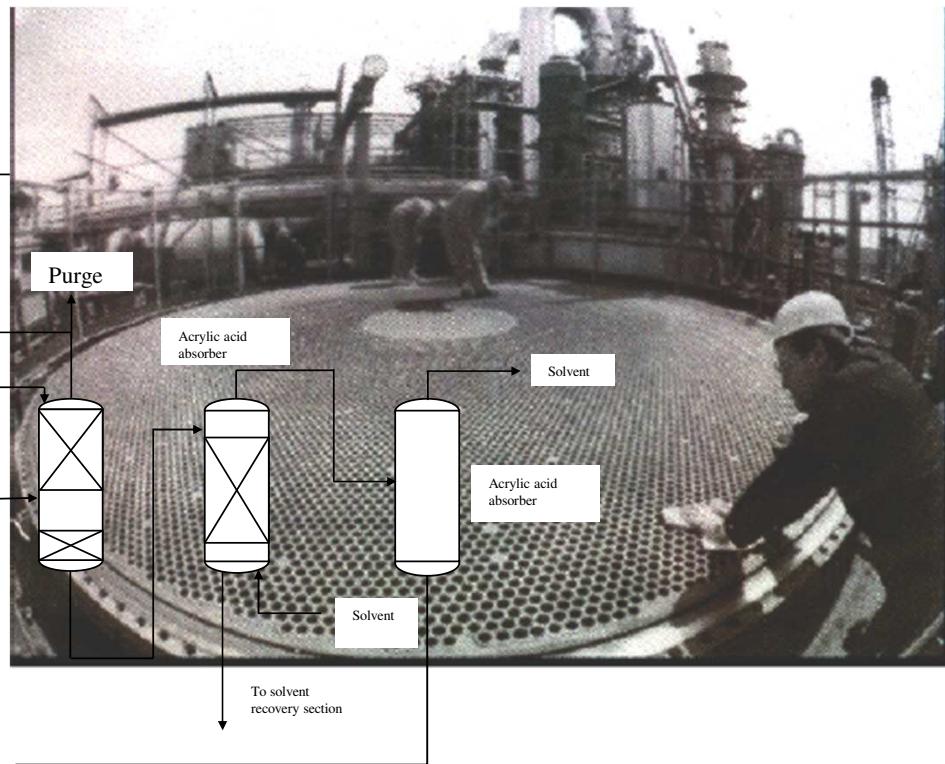
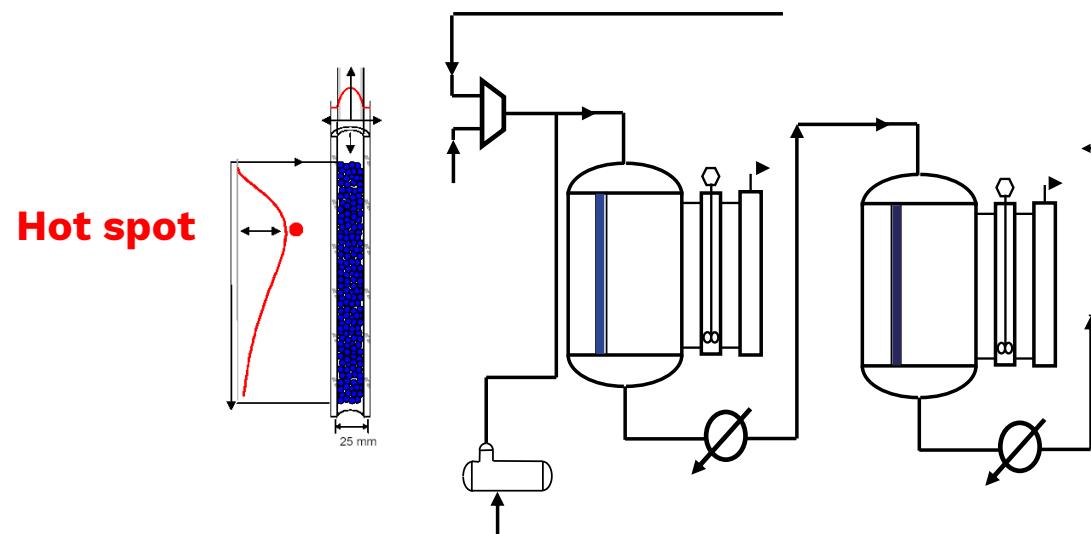
Cite this: Green Chem., 2015, 17, 343

## Glycerol as feedstock in the synthesis of chemicals: a life cycle analysis for acrolein production†

D. Cespi,<sup>a</sup> F. Passarini,<sup>\*a,b</sup> G. Mastragostino,<sup>a</sup> I. Vassura,<sup>a,b</sup> S. Larocca,<sup>c</sup> A. Iaconi,<sup>d</sup>

# Conventionnal Propylene oxidation process

## Multitubular Fixed Bed Reactors



Acrolein reactor fabrication



Number of tubes: > 27.000

Weight: 350 MT

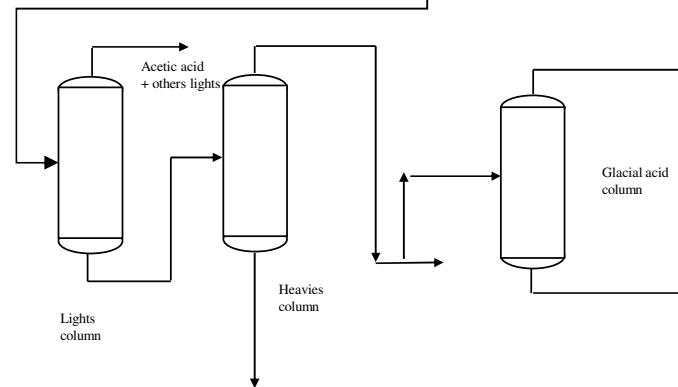
Multitubular fixed bed reactors @ dwe.com

Acrylic acid reactor

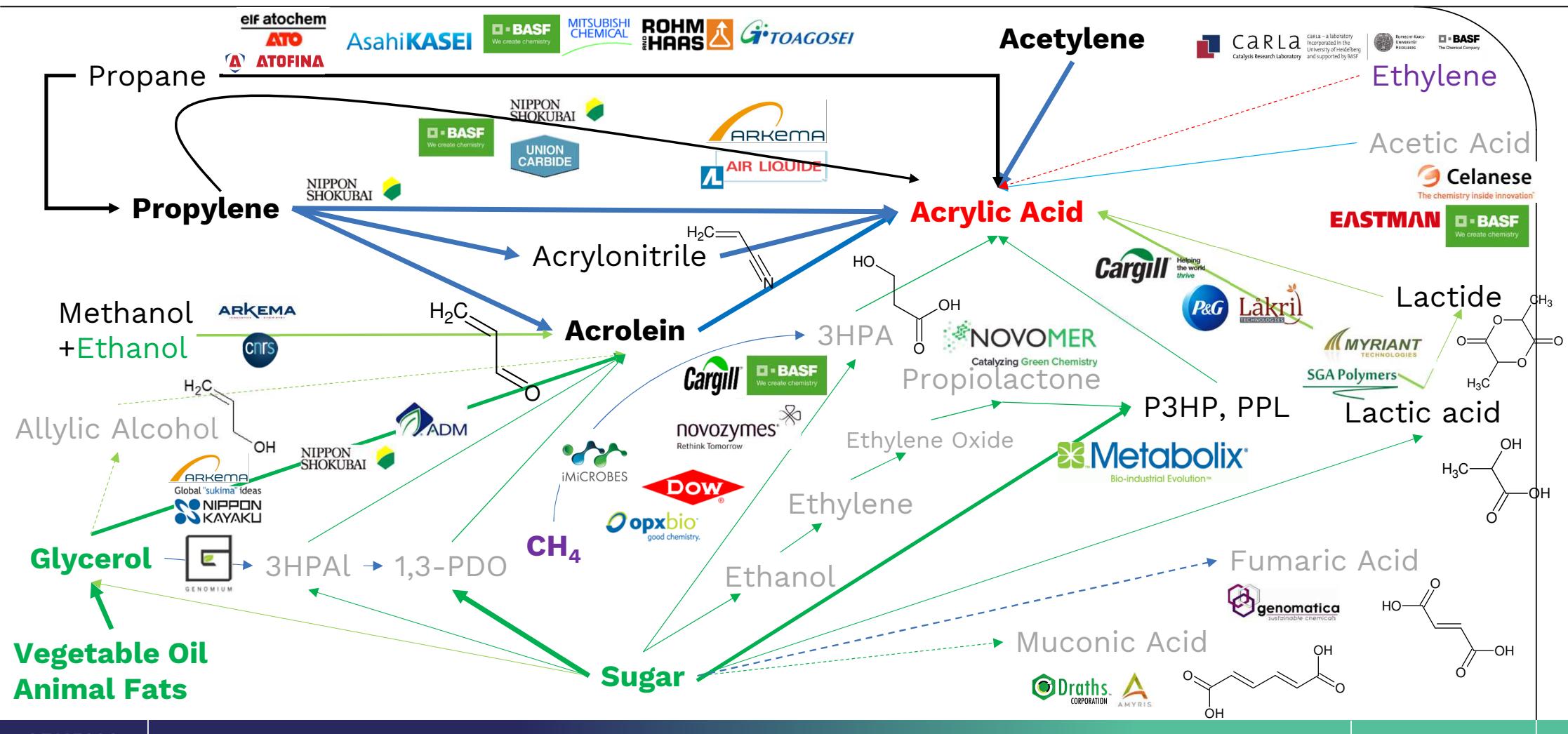
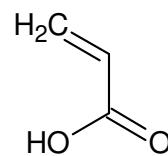


Number of tubes > 27.000

Weight: 570 MT

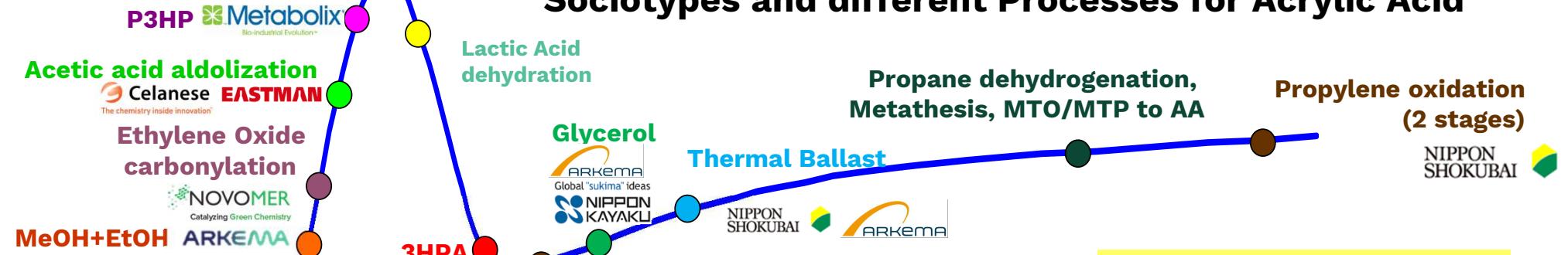


# Acrylic Acid

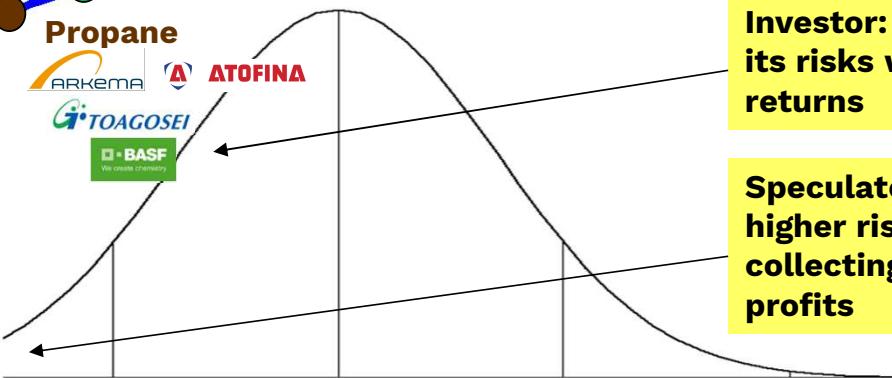


## Sociotypes and different Processes for Acrylic Acid

Expectations



Adoption rate



Sociotypes

Innovators	Early adopters	Early Majority	Late Majority	Laggards	Skeptics
Tech addicts	Visionaries (get ahead of the herd!)	Pragmatists (stick with the herd)	Conservatives Hold on!	Not in my backyard!	Skeptics No way!

TRL



Investor: Trying to minimize its risks while maximizing returns

Speculator: Willing to accept higher risks, in the hopes of collecting higher than average profits

# Acrylonitrile

DE GRUYTER

STEM

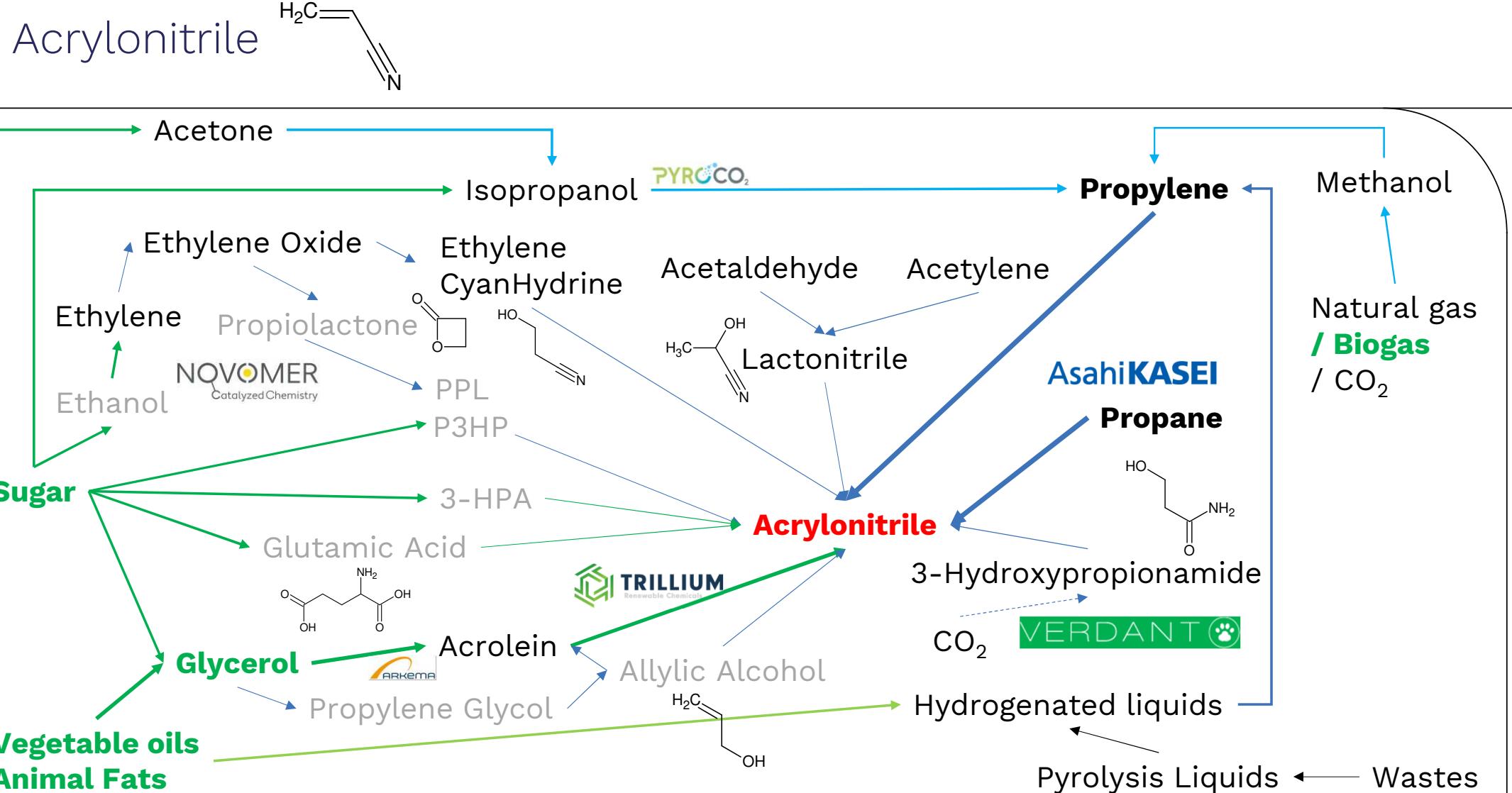
## INDUSTRIAL GREEN CHEMISTRY

*Edited by Serge Kaliaguine and Jean-Luc Dubois*

Jean-Luc Dubois and Serge Kaliaguine

**2 Alternative routes to more sustainable  
acrylonitrile: biosourced acrylonitrile**

DE  
G





Cite this: DOI: 10.1039/c8cs00117k

## Catalysis for the synthesis of methacrylic acid and methyl methacrylate†

Mohammad Jaber Darabi Mahboub,<sup>1</sup> Jean-Luc Dubois,<sup>2</sup> Fabrizio Cavani,<sup>3</sup> Mohammad Rostamizadeh,<sup>4</sup> and Gregory S. Patience<sup>1,2\*</sup>

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 reads acetone and hydrogen cyanide to MMA (AHC route) but the intermediate (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 cerium 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.

Received 1st June 2018

DOI: 10.1039/c8cs00117k

rsc.li/chem-soc-rev

<sup>1</sup> École Polytechnique de Montréal, 2900, Boulevard Édouard-Montpetit, Montréal, Canada. E-mail: gregory.patience@polymtl.ca; Fax: +1 514 340 4059; Tel: +1 514 340 4711 ext. 3439<sup>2</sup> Arkema, 420 Rue d'Etienne d'Orves, 92705 Colombes, France<sup>3</sup> Department of Industrial Chemistry "Toso Montenaro", University of Bologna, Viale Risorgimento 4, 41036 Bologna, Italy<sup>4</sup> Chemical Engineering Department, Sahand University of Technology, Sahand New Town, P.O. Box: 51335-1996, Tabriz, East Azerbaijan, Iran

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8cs00117k

# Methacrylic Acid/ Methyl ester

Mohammad Jaber Darabi  
Mahboub

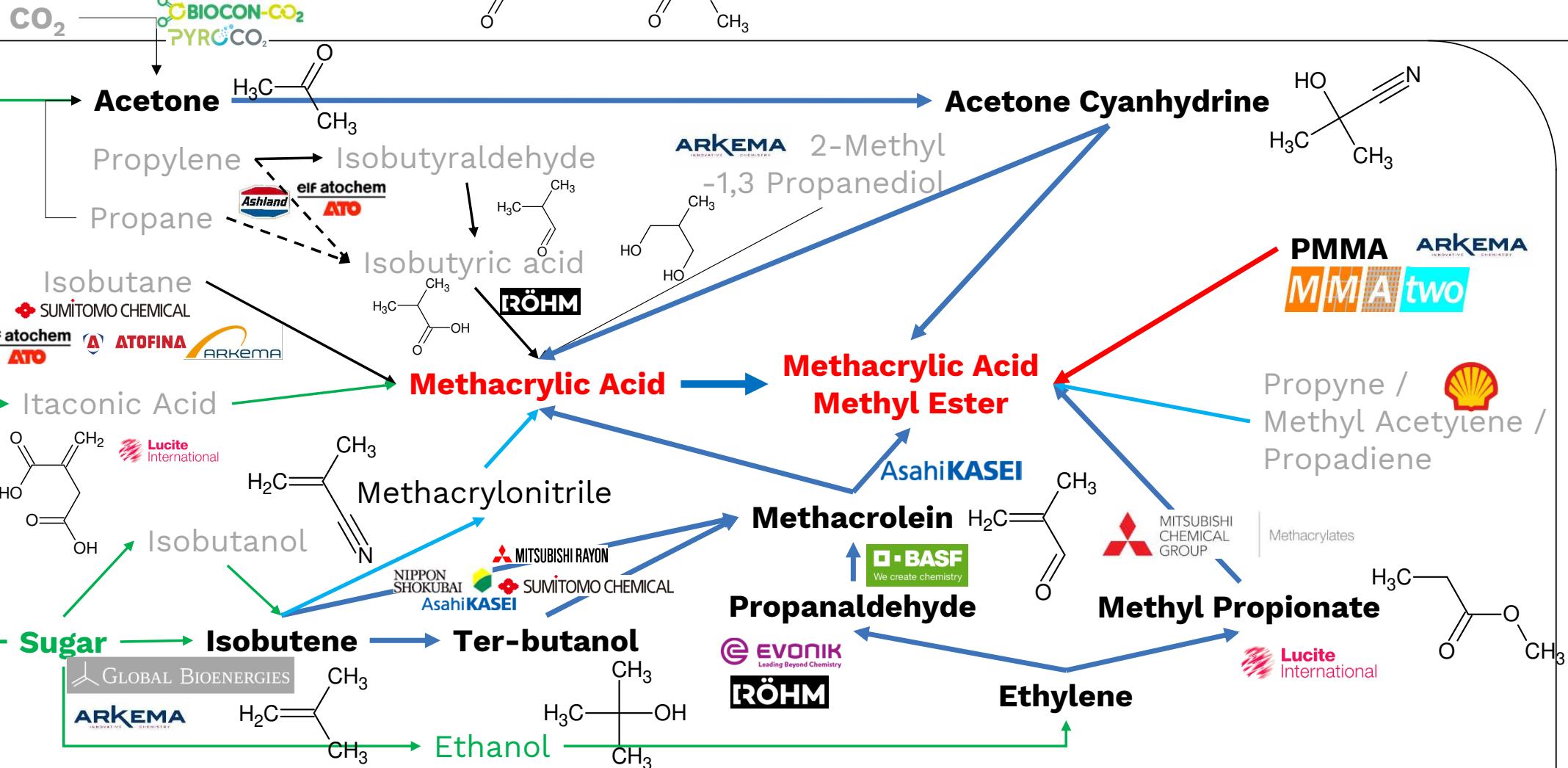
Dr Mohammad Jaber Darabi Mahboub received his PhD in Chemical engineering in 2018 at Polytechnique Montréal, Canada under the supervision of Prof. Gregory Patience. He received his BSc and MSc in Chemical Engineering at Ferdowsi University of Mashhad (Iran). He has completed experimental work on the partial oxidation of 2-methyl-1,3-propanediol 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 IPP on Catalysts for Oxidative Coupling of Methane. After a Post-Doctorate at NCLJ (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.

## Process routes



<http://www.mmatwo-footprinter.eu/> (to be updated with final results soon)



# Environmental Benefits Calculator BETA

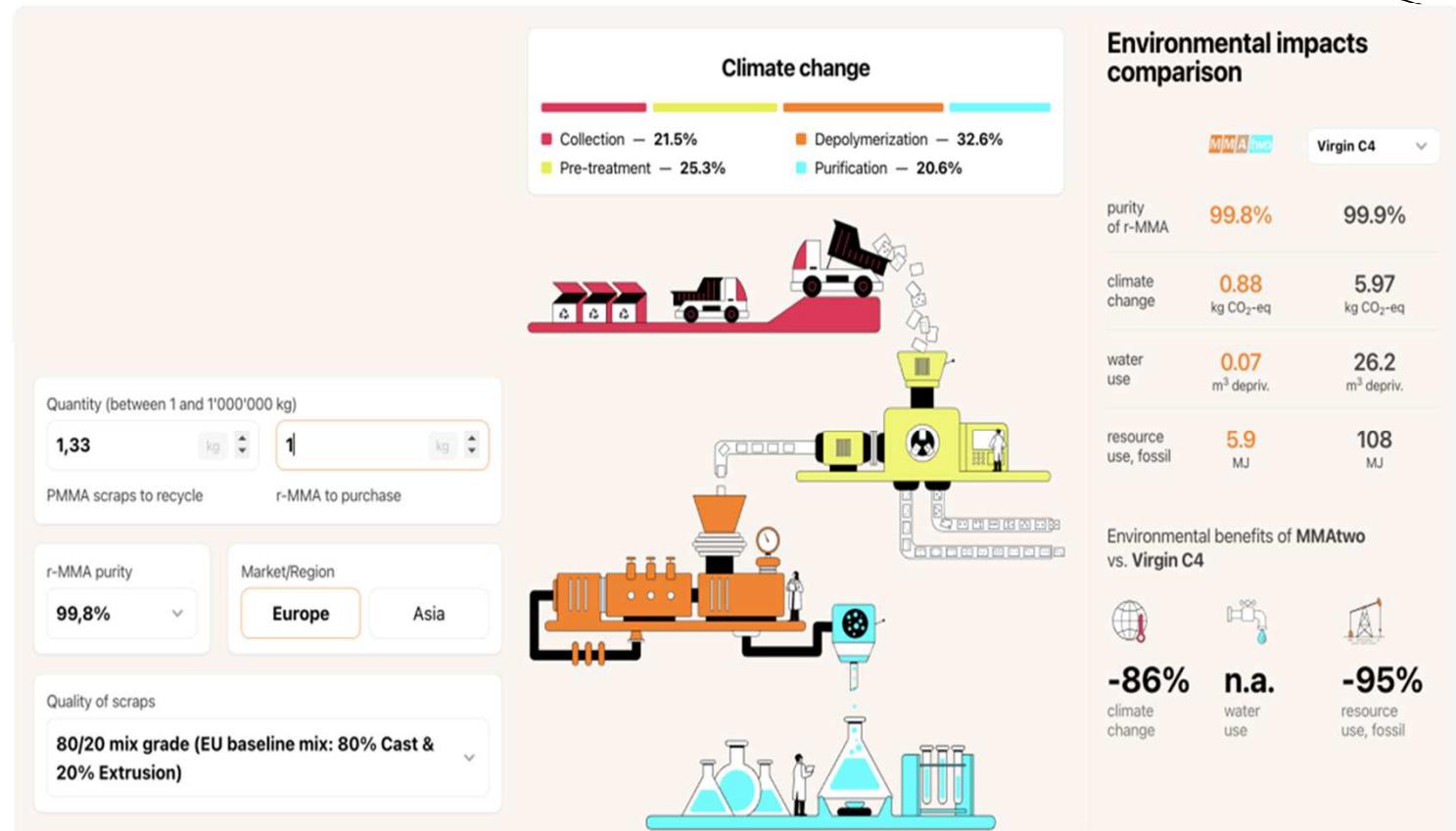
The final version will be available in September 2022.

The MMAtwo Project **aims at constructing a novel and fast growing PolyMethylMethAcrylate (PMMA) recycling value chain** based on the production of «Second Generation MethylMethAcrylate (MMA)» from post-consumer and post-industrial PMMA based products.

The technology is a cost effective and efficient recycling process with **reduced energy consumption and CO<sub>2</sub> emissions**, that aims to **reduce the utilization of primary fossil resources** in the process industry by **at least 30%**.



MMAtwo - This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 820687.



The MMAtwo project results presented reflect only the author's view. The Commission is not responsible for any use that may be made of the information it contains.

Expectations

Expectations

TRL

Isobutanol

Itaconic Acid

Lucite International

2-Methyl-1,3 PDO

ARKEMA

Propylene

Glycerol

TRILLIUM  
Renewable Chemicals

Propiolactone

NOVOMER  
Catalyzed Chemistry

3-HPA

Glutamic Acid

HydroxyPropionamide

VERDANT

1

2

3

4

5

6

7

8

9

ARKEMA

GLOBAL BIOENERGIES

ARKEMA

Altuglas

eif atochem

ATO

Ashland

ARKEMA

SUMITOMO CHEMICAL

ARKEMA

Isobutene

Isobutane

Propyne

Methacrylonitrile

Glyceral

Propiolactone

3-HPA

Glutamic Acid

HydroxyPropionamide

Isobutanol

Itaconic Acid

2-Methyl-1,3 PDO

Propylene

ARKEMA

PCMV

MADREPERLA

MMA two

PMMA

depolymerization

Ethylene (LIMA)

RÖHM

Ethylene (ALPHA)

EVONIK

Mitsubishi

Chemical

Propylene

Propane

Asahi

KASEI

# Methacrylic Acid/ Methyl MethAcrylate

BASF

We create chemistry

Ethylen

(Hydroformylation)

Lucite

International

Mitsubishi

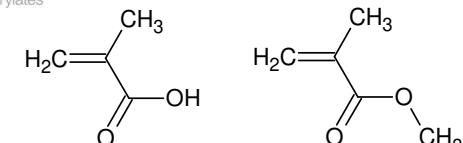
Chemical

Group

Methacrylates

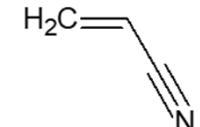
Isobutene/t-Butanol oxidation (2 stages)

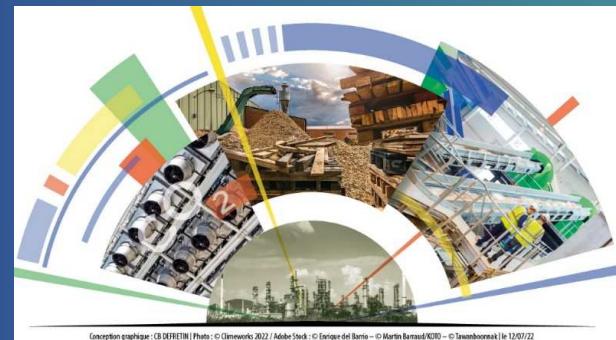
Acetone Cyanhydrine



# Acrylonitrile

Propylene





Les défis  
Chimie

Fondation de la Maison de la Chimie

## Sources de carbone

pour les grands intermédiaires de la chimie organique :

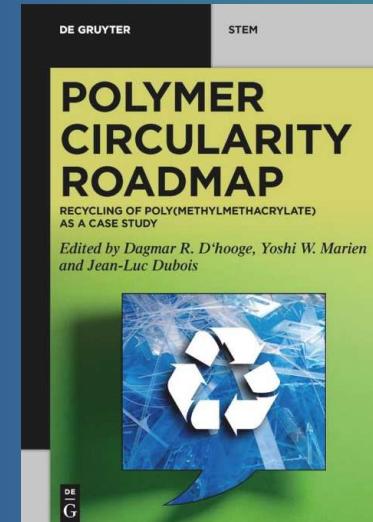
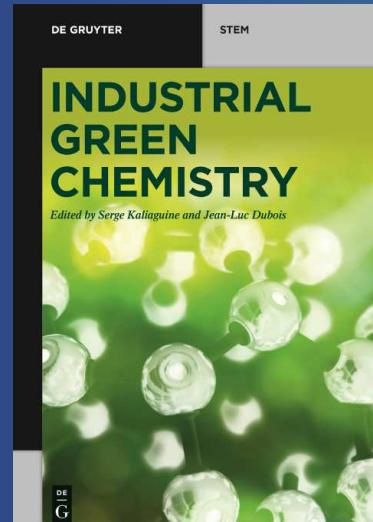
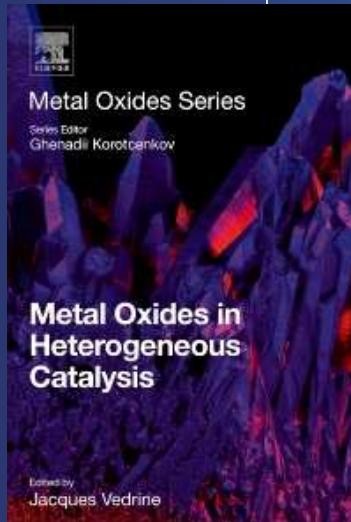
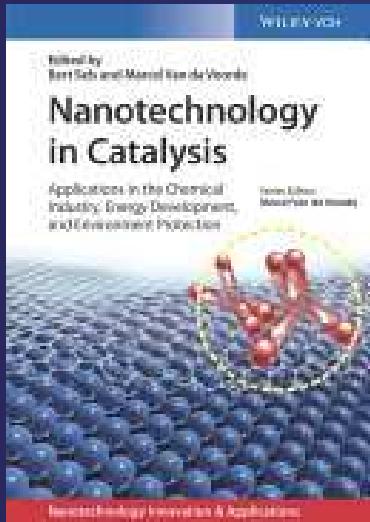
NOUVELLES APPROCHES

lundi 3 Octobre 2022

Maison de la Chimie – 28 rue Saint-Dominique 75007 PARIS

# Merci pour votre attention

## Suggestion de lectures



ARKEMA

# *Chain of Custody: Options for recycling / monomer regeneration*



## → **Identity Preserved**

- Dedicated plant 

Regenerated MMA 100 %

## → **Segregated**

- Single Plant, Batch-wise

Regenerated  
MMA 100 %

Virgin MMA

## → **Controlled Blending**

- Mixed stream, single product

Regenerated MMA 50%

## → **Mass Balance, Mixed streams**

- Allocation, Physical link

Regenerated  
MMA 75 %

Regenerated  
MMA 25%

## → **Book & Claim**

- Credits and Products follow different path