ARKEMA

4th meeting academic-industry of CNC

12/9/2024

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R&D Scientist

Factories of life: Generation and Transformation of materials and active ingredients

-

Biotechnologies: a revitalized lever for producing sustainable bio-sourced products

Plan of the presentation

→ **Biocatalysis: Expectations from Arkema?**

→ **Example #1: A process combining fermentation and enzymatic catalysis for BioMethionine production**

→ **Example #2: A drop-in approach of enzymatic catalysis using existing catalysts for ADAME® production**

→ **Take-home messages**

1

Biocatalysis: Expectations from Arkema?

21,100 passionate employees across the globe

Diversity and inclusion

2,3% of company sales allocated in R&D

17 R&D centers

1800 researchers

WOMEN AND MEN AT THE HEART OF OUR DEVELOPMENT

> **10,000** customers

Collaborations with leading brands

€9.5 bn sales

Presence in **55** countries

151 plants

Biocatalysis: Expectations from Arkema?

→ **Driver #1: To reach a cost structure in adequation with commodity or specialty chemistry markets**:

- High volume (at least several hundred of tons/y for specialties)
- Medium market prices

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→ **Driver #2: We want to develop sustainable processes for producing biosourced or recycled based products** (ex. Drop-in chemicals)

- With a low product carbon footprint (PCF)
- A good Life Cycle Assessment cradle to gate of bioprocesses developed is a critical requisite to ensure a good final PCF

For us, it's at the heart of our development.
We take concrete actions and measure our progress every step of the way.

Climate

Keeping global warming in line with the Paris Agreement.

→ 2030 target

Emissions

-48.5% *vs* 2019

≤ 2,000 kt equivalent CO_2 absolute greenhouse gas (GHG) emissions for scopes 1 & 2

-54% *vs* 2019

≤ 85,000 kt equivalent CO_2 absolute greenhouse gas (GHG) emissions for scope 3

2

Example #1: A process combining fermentation and enzymatic catalysis for BioMethionine production

Internal success-story – BioMethionine production through Joint-Venture with CJCJ

→ **Since 2015, at Kerteh (Malaysia)** Arkema's partner CheilJedang is producing methionine

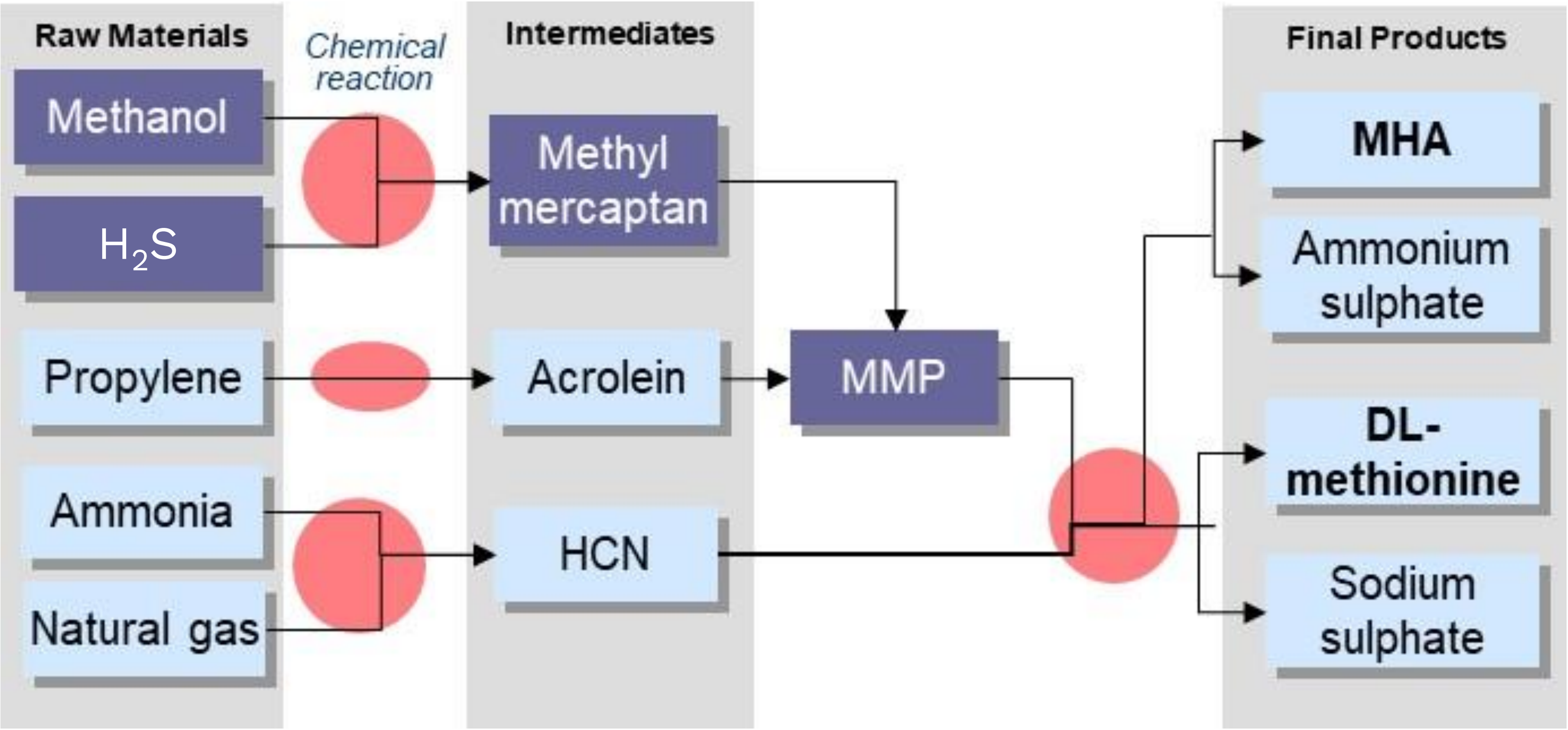
→ This process uses **methyl-mercaptan supplied by Arkema** and bio-based raw material

→ CJ CheilJedang and Arkema teams worked together for developing this new process

OCT 8, 2012 - PRESS RELEASE

Arkema and CJ officially launch the start of the construction of their Bio-Methionine and Thiochemicals complex in Malaysia

Existing chemical process of D/L-Methionine production



→ 5 steps, all chemical (**harsh conditions**)

→ **Toxic** and/or dangerous **intermediates**

→ **No stereoselectivity**

HCN : cyanhydric acid ; MMP : 3-methyl mercaptopropionaldehyde ;
MHA : methionine hydroxy analog

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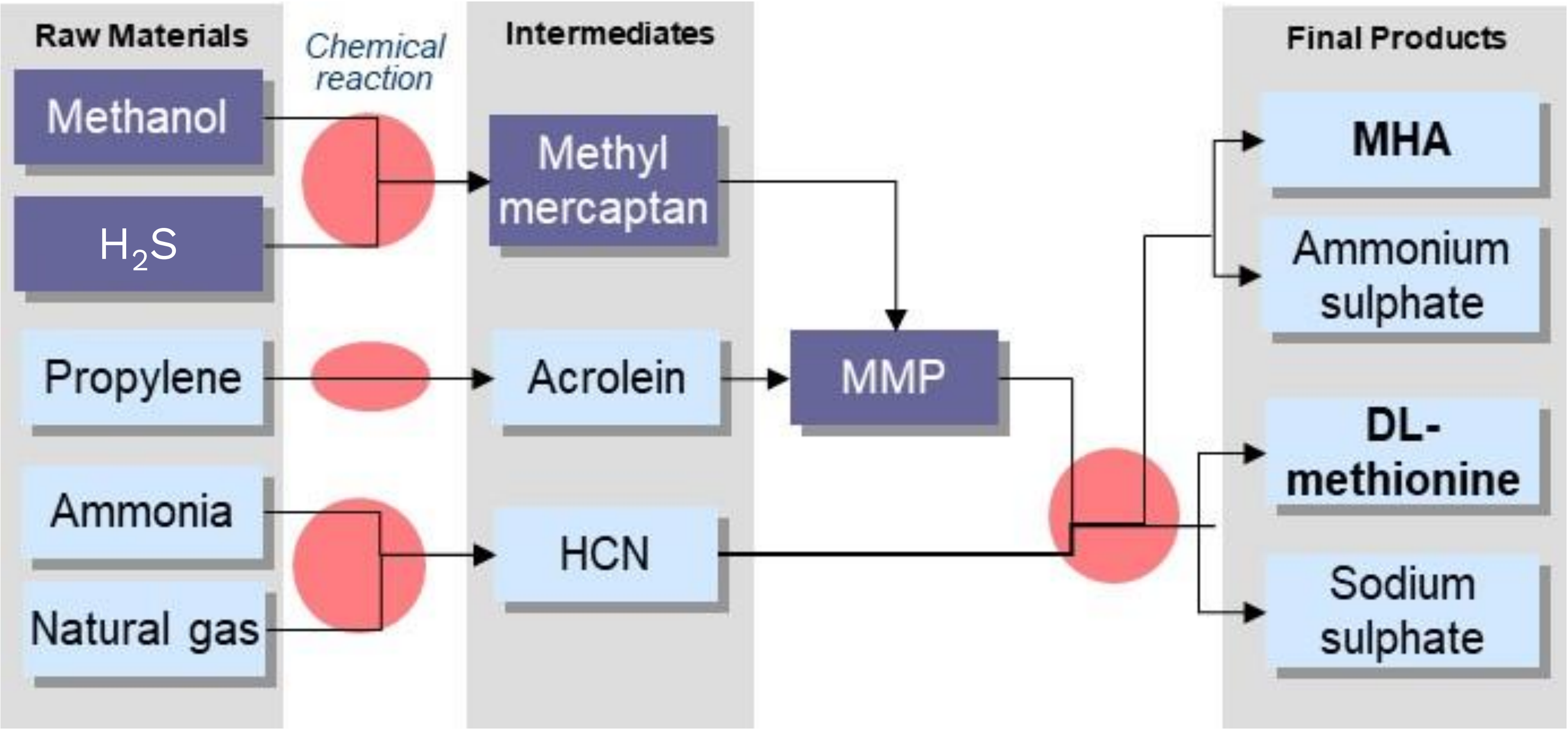

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- → 5 steps, all chemical (**harsh conditions**)
- → **Toxic** and/or dangerous **intermediates**
- → **No stereoselectivity**
- → Possibility to **obtain analog**
- → This process is **highly cost-efficient**!...
- → Possibility of **lowering PCF** through propylene mass balance

New chemo-enzymatic process for L-Methionine production

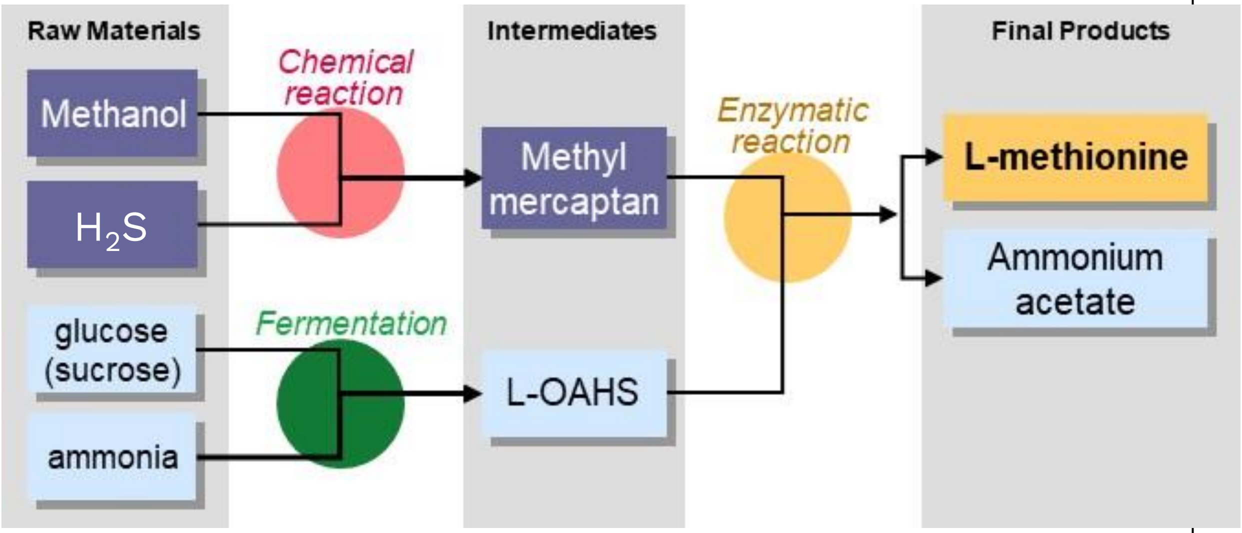
→ CJ CheilJedang/ARKEMA Plant

- **3 steps** : 1 chemical, 1 fermentation, 1 enzymatic catalysis reaction

→ **Very high volumes** (became a commodity product the last few years)

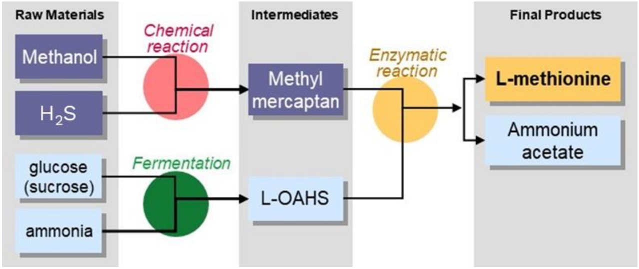
→ Performances addressed by this technology:

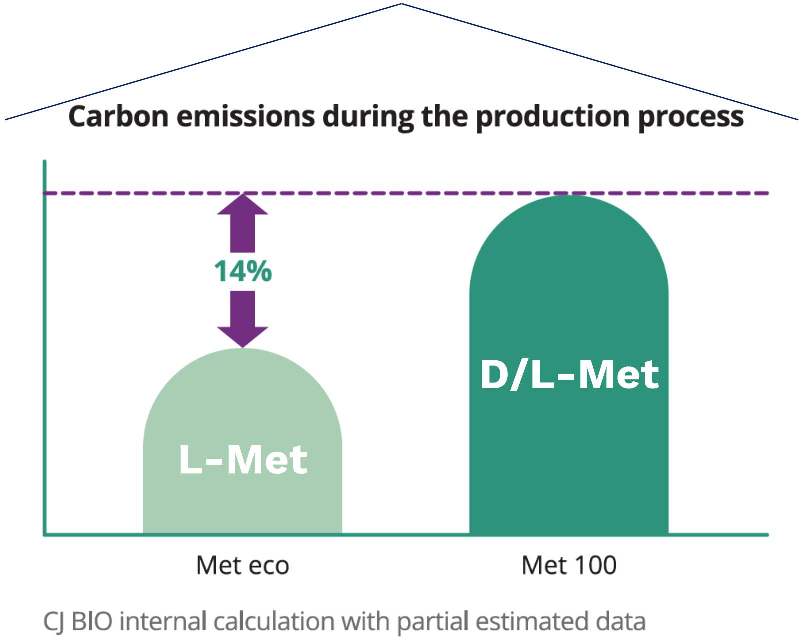
- **Good BOM from sugar, ammonia and MeSH**
- **Production cost** globally in adequation with the market targeted
- The only **stereoselective process** (enantiopure form only (levogyre)) ► product efficiency ++
- **Partially biobased product** (4 biogenic carbons (on 5) came from bioresources)



WO13029690 B1 - PREPARATION OF PROCESS OF L-METHIONINE

Carbon-efficiency of BioMethionine obtained from Biocatalysis





Bioprocess is more sustainable than chemical one

(- 14% of Greenhouse Gas emissions)

Public communication of CJ CheilJedang
Kim *et al.*, 2024 – WO 10.1016/j.jclepro.2024.142700

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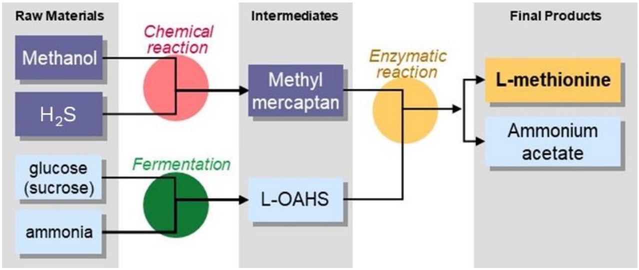

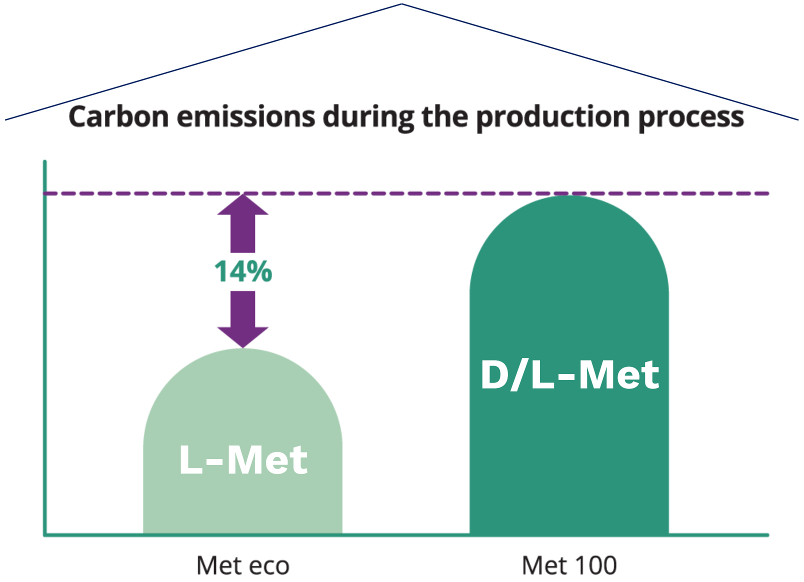

CJ BIO internal calculation with partial estimated data

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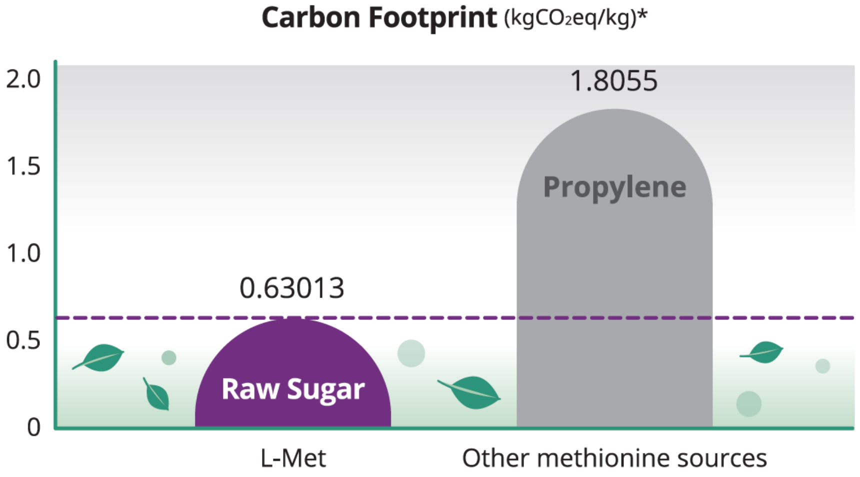
Global product carbon footprint of L-Methionine is better than D/L-Methionine

(~ 3 times less CO_2 emissions)



* CML climate change data

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Sum-up: BioMethionine process *vs.* expectations of Arkema from Biocatalysis

→ **Driver #1**: To reach a cost structure in adequation with commodity or specialty chemistry markets

→ Globally OK for BioMethionine:

- Challenge: Methionine is currently a commodity

→ Cost efficiency on BioMethionine permitted by:

- **Feedstocks**: reliable & cheap 
- **Catalyst** performances fully fine tuned 
- **Production process**: full optimization
- **Waste streams**: full valorization ► mandatory for bioprocesses cost efficiency

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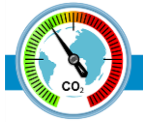
→ **Driver #2**: Develop sustainable processes for producing biosourced or recycled based products

→ OK for BioMethionine:

- Carbon emissions during production process have been optimized
- Biogenic carbon contained in raw material allows to reach a very low PCF for BioMethionine (~ 3 times lower than petrobased Methionine)



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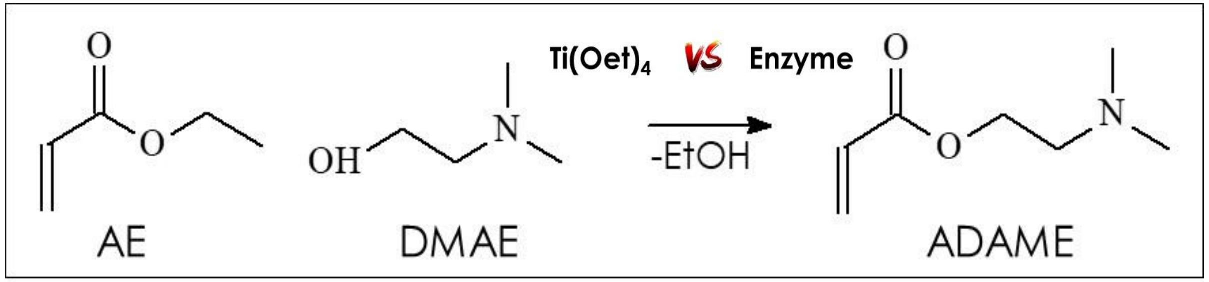
Example #2: A drop-in approach of enzymatic catalysis using existing catalysts for ADAME® production

Why replacing ethyl titanate homogeneous catalyst?

→ Dimethylaminoethyl acrylate is currently produced at Carling plant using a **homogeneous catalyst (ethyl titanate)**:



AE: Ethyl acrylate

DMAE: Dimethylaminoethanol

EtOH: Ethanol

ADAME: Dimethylaminoethyl acrylate

PTZ = Phénothiazine

$Ti(Oet)_4$ = Ethyl tinanate

Why replacing ethyl titanate homogeneous catalyst?

→ Technical data sheet for the dreamed catalyst:

CHARACTERISTICS	BENEFITS
Heterogeneous catalyst Supported enzyme	• To avoid an additional distillation column in case of new unit (currently needed for removing homogeneous catalyst) • Lower CAPEX

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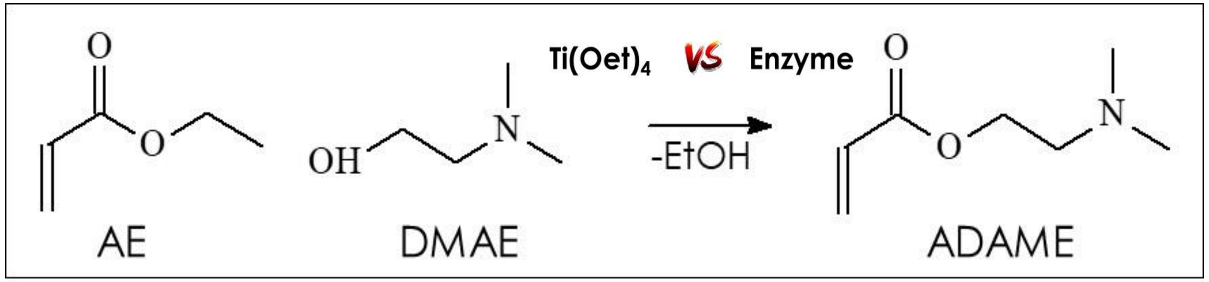

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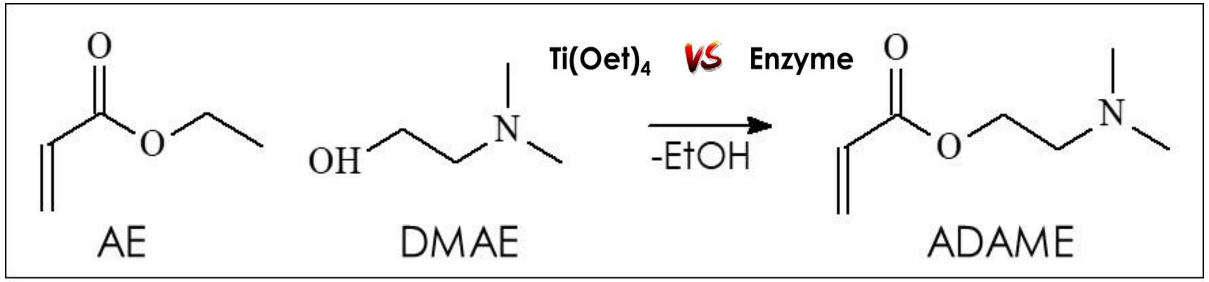

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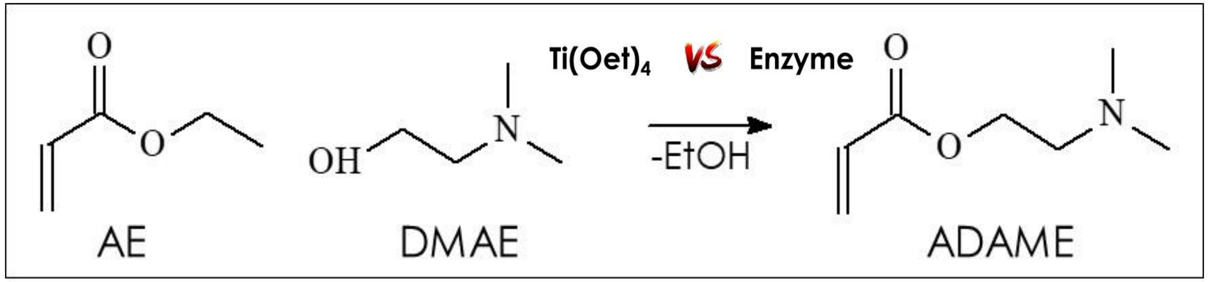

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Better selectivity Decrease of side products formation	• Lower raw material variables costs • Easier purification • Lower energy consumption for separation
Sustainable catalyst Coming from renewable resources	• Catalyst supplying ensured (even if titanate would not be limiting over coming years)

AE: Ethyl acrylate

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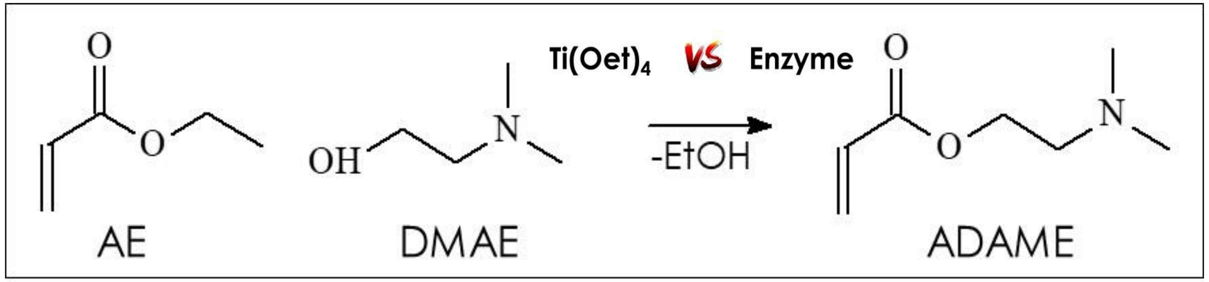
→ Several supported enzymes are available on the market: **Novonesis, Amano, Purolite**



ADAME enzymatic synthesis conditions at lab scale

(*) PTZ is an inhibitor of polymerization

Continuous synthesis with azeotrope withdrawing

- Ethyl acrylate (AE)
- Dimethylaminoethanol (DMAE)
- Phenothiazine (PTZ)

Conditions:

- Temperature = 50°C *vs.* 110°C with ethyl titanate
- Pressure = 130 mbar *vs.* 420 mbar with ethyl titanate
- Residence time = 3 hours
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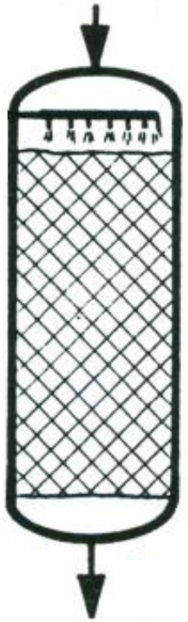

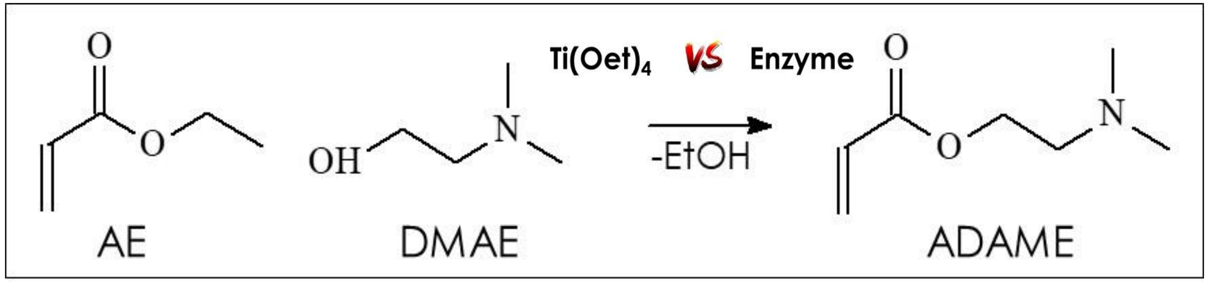

- Ethanol
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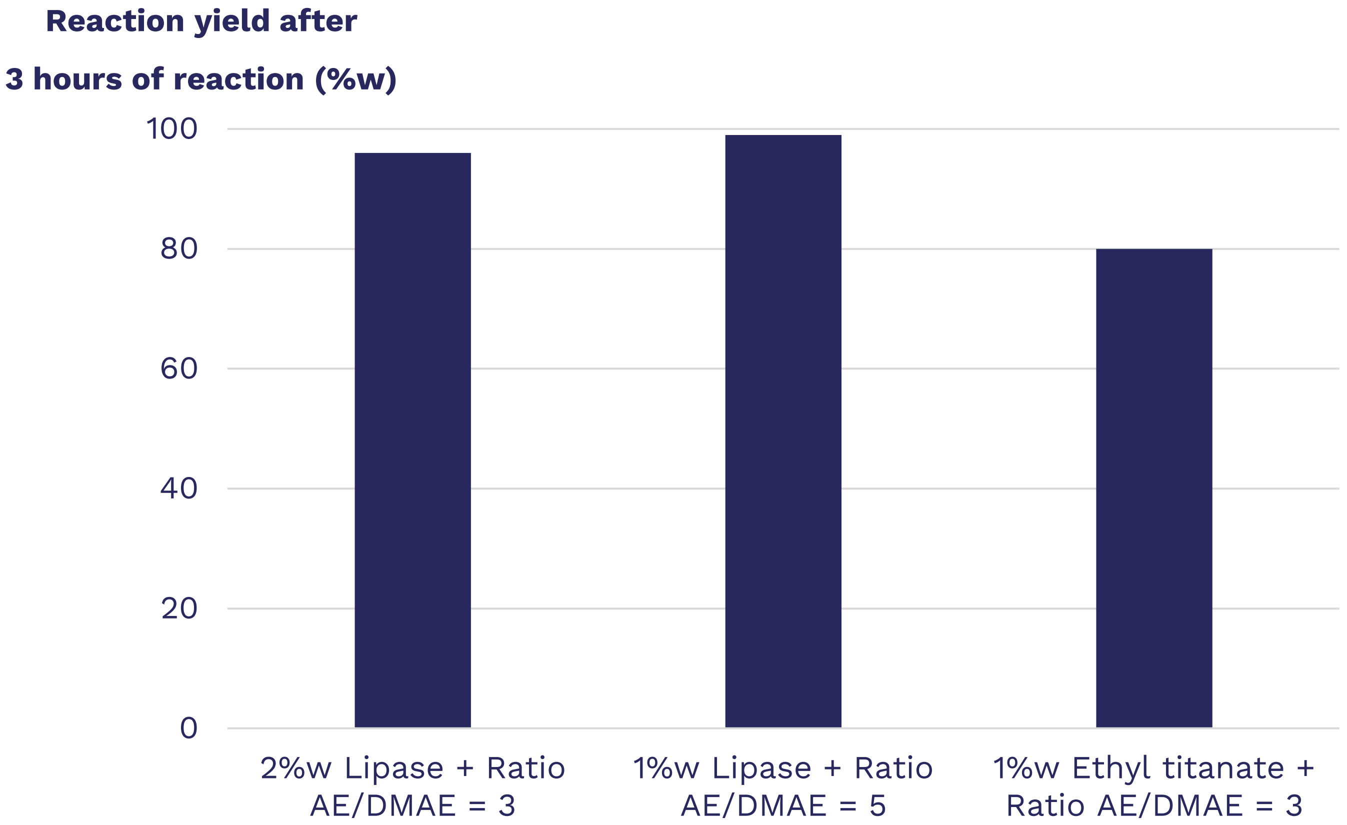
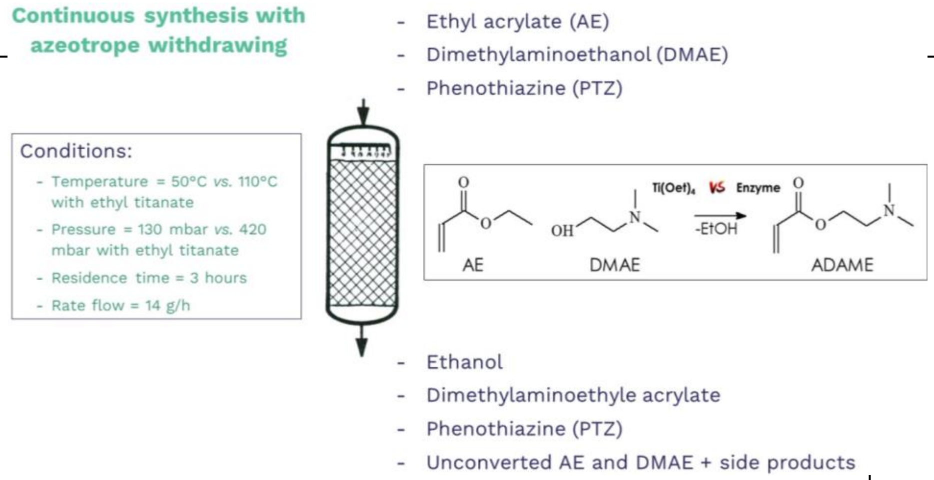
- Unconverted AE and DMAE + side products

Better kinetic and selectivity obtained with enzyme!





→ Results highlight that:

- **Enzyme kinetic is good** (better reaction yield after 3 hours of reaction at iso-weight of lipase *vs.* ethyl titanate)
- **Reaction yields up to 99%w** could be obtained after 3 hours of reaction using lipase

Property of Arkema

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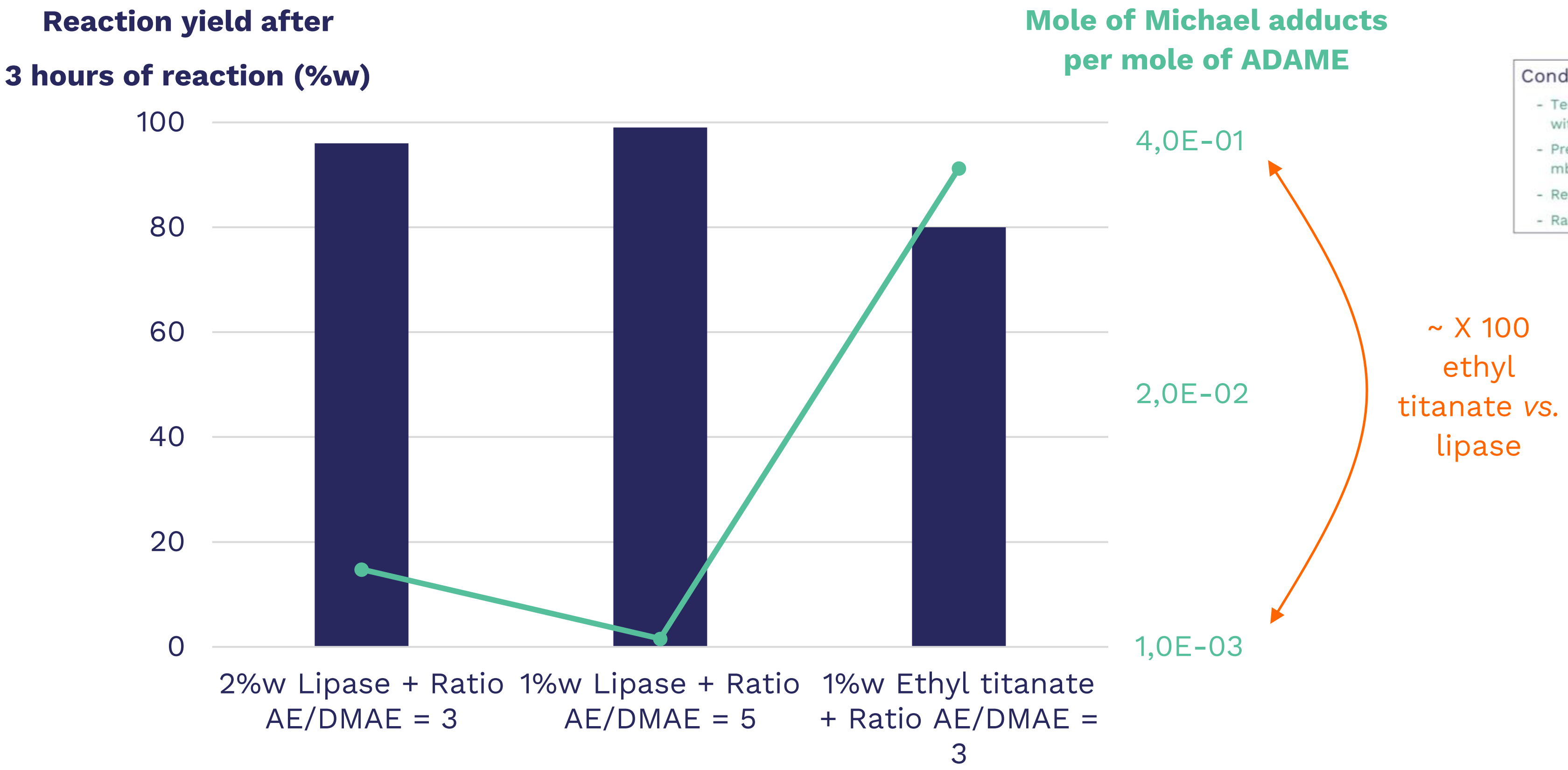

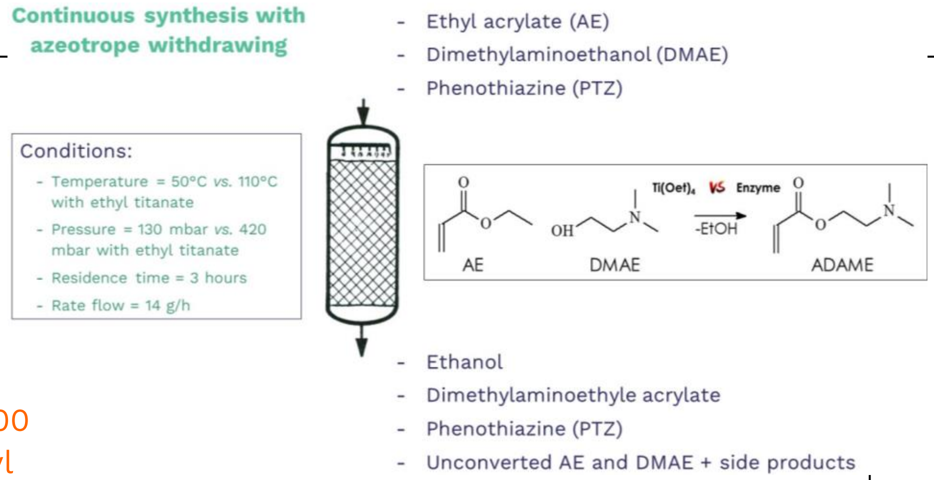

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- **100 times less** sides products are obtained *vs.* ethyl titanate (at iso-conversion for longer reaction times, still worst selectivity obtained with the chemical catalyst)

No PTZ required anymore with enzyme!

CONDITIONS	REACTION YIELDS (%w)	POLYMER IDENTIFICATION THROUGH SEC ANALYSIS (+/-)
1%w Lipase + **2000 ppm of PTZ** + Ratio AE/DMAE = 3 Reaction time = 3 hours	97	-
1%w Lipase + **200 ppm of PTZ** + Ratio AE/DMAE = 3 Reaction time = 3 hours	98	-
1%w Lipase + **0 ppm of PTZ** + Ratio AE/DMAE = 3 Reaction time = 3 hours	95	-

Continuous synthesis with azeotrope withdrawing

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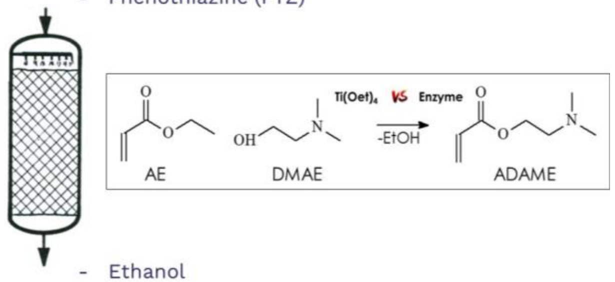

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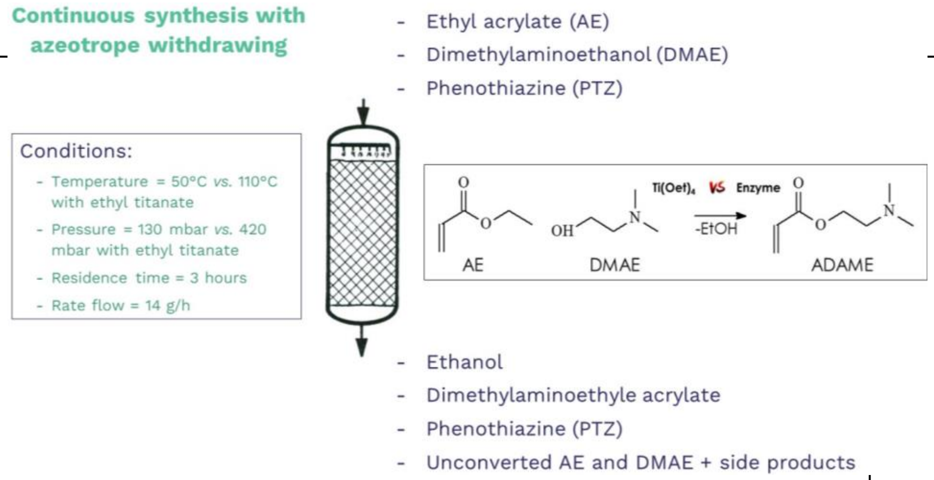

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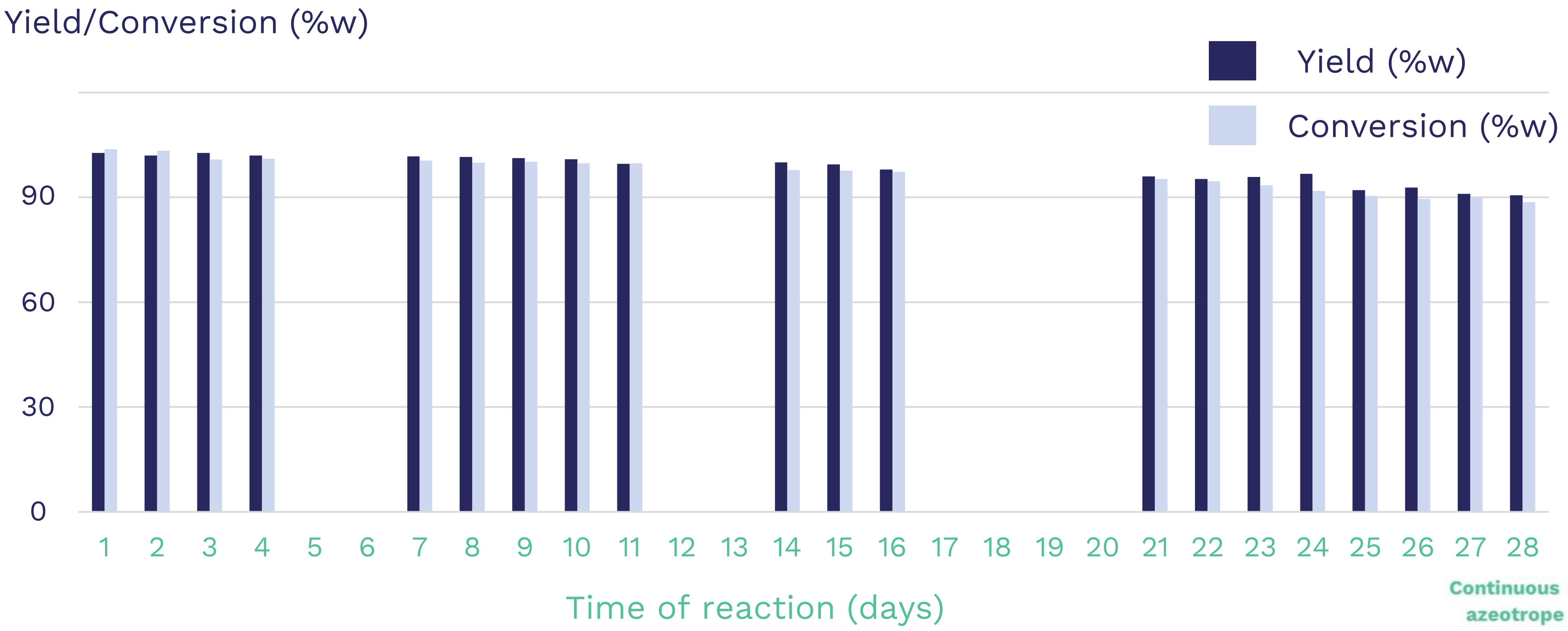
1%w Ethyl titanate+ **2000 ppm of PTZ** + Ratio AE/DMAE = 3 Reaction time = 3 hours	80	-
1%w Ethyl titanate+ **200 ppm of PTZ** + Ratio AE/DMAE = 3 Reaction time = 3 hours	73	+
1%w Ethyl titanate+ **0 ppm of PTZ** + Ratio AE/DMAE = 3 Reaction time = 3 hours	79	++

→ Results highlight that the enzymatic reaction could be achieved without PTZ (polymerization inhibitor) because realized in milder conditions (50°C *vs.* 110°C with ethyl titanate)

→ By decreasing PTZ 10 times (i.e. 200 ppm), **we decrease the impact of PTZ on variable costs**

Recycling tests of Lipase in continuous conditions



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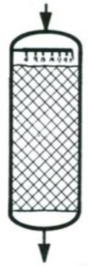

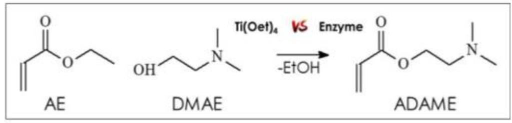

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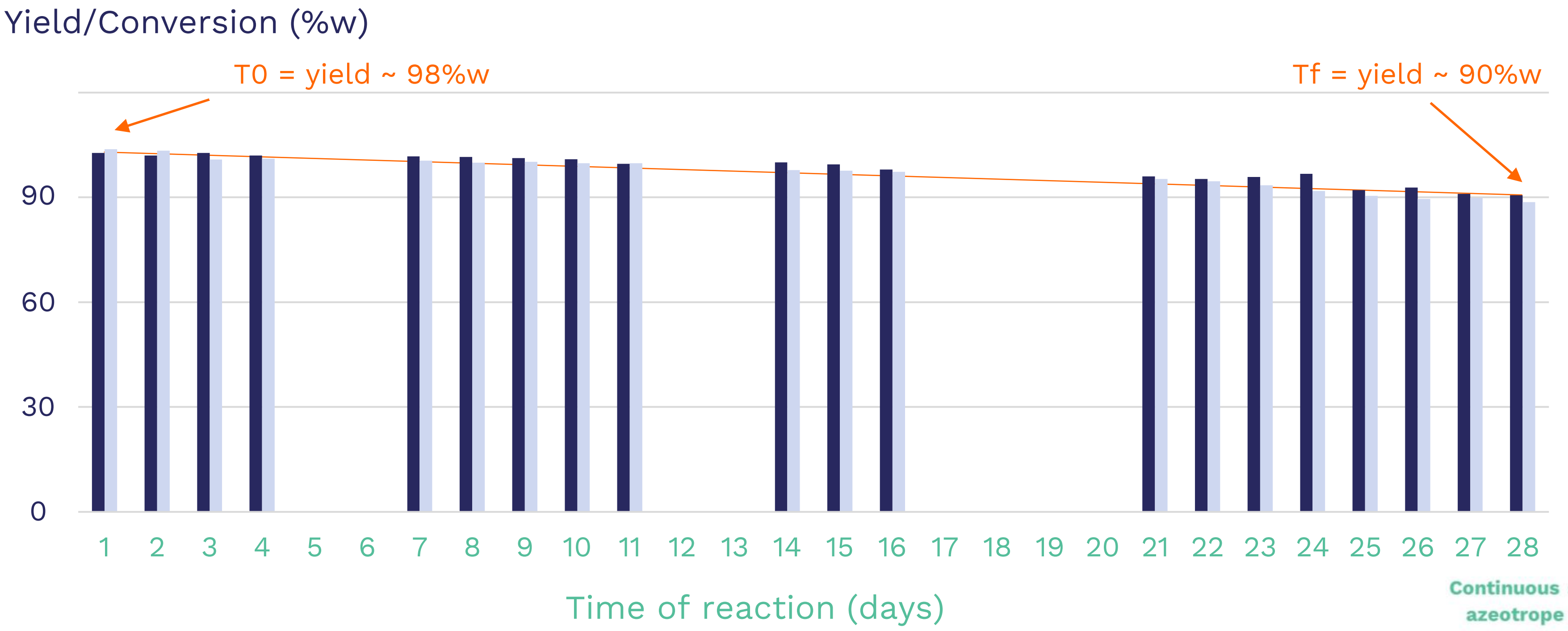

→ T_0 yield achieved corresponds to the **maximal yield** that could be theoretically reached

→ There is a **slow and continuous loss of catalyst activity**:

- Caused by slight enzyme deactivation?
- Caused by slight enzyme support destruction?

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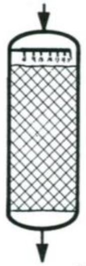

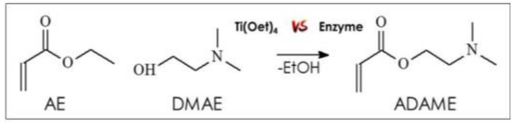

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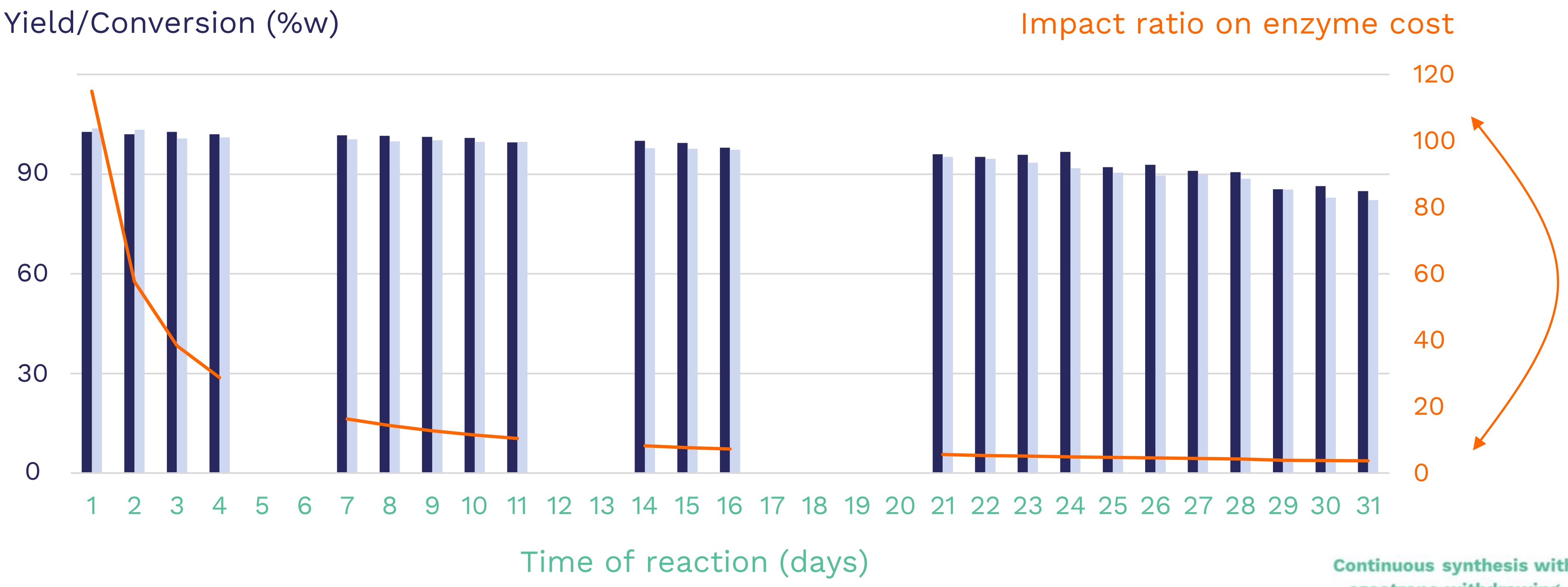

Decrease of > 100 times the impact of enzyme price on process variable costs

→ **Enzyme recycling allows to decrease the catalyst price ~ X 100** in these conditions

→ Further optimizations are needed to decrease even more the impact of catalyst on variables costs of ADAME process as impact on variable costs still **(start to be negligible)**

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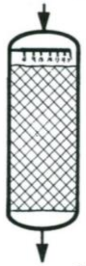

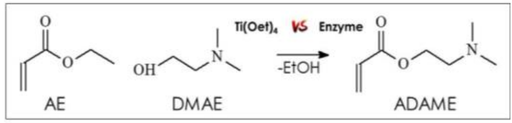

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Sum up on ADAME synthesis and perspectives

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PATENTED

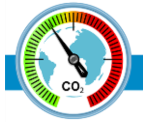
→ **Patent filed** in January 2023:

- Title: Production process of (meth)acrylic esters from amino alcohol through enzymatic transesterification

→ Next steps:

- Pursue optimizations for decreasing impact of catalyst price on process variables costs
- **Pre-industrial pilot** to validate the process performances using the best conditions
- **Opportunity for other esters** through enzymatic transesterification (**mass balance/fully biobased?**)...

Take-home messages: Develop a biocatalysis process for meeting sustainability!

→ **Bioprocesses are not necessarily sustainable (be careful about DSP steps)**: 

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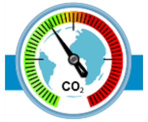
→ **Bioprocesses are not necessarily sustainable (be careful about DSP steps)**: 

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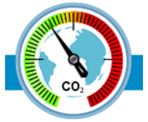
→ **Bioprocesses are not necessarily sustainable (be careful about DSP steps)**: 

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→ **Arkema firmly believes that biotechnologies will be one of key tools for industrial decarbonization in the coming years** and **is developing several projects** through collaborations and partnerships with academic and industrial groups

ARKEMA

4th meeting academic-industry of CNC

12/9/2024

Jean-Christophe LEC, PhD
R&D Scientist

Factories of life: Generation and Transformation of materials and active ingredients

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Biotechnologies: a revitalized lever for producing sustainable bio-sourced products