



*Second Generation MethylMethAcrylate*

**CONCEPTS OF PURIFICATION**

*A processing point of view*



**Certech**  
R&D partner in chemistry

**Philippe De Groot**



**Speichim  
processing**  
*Séch  global solutions*

**Fadi BOUTROS**

**MMAtwo  
workshop**

**15/09/2020**

*Thank you for citing this work with DOI*

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# Agenda

- **Presentation of partners SPEICHIM & CERTECH**
- **Techniques and methodologies used for purification and characterisation in the frame of MMAtwo project**
- **Results**

*MMAtwo workshop – 15/09/2020*



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# SPEICHIM PROCESSING

Speichim is specialized in toll purification; mainly in industrial distillation (various distillation technics) and liquid-liquid extraction which is a good help for distillation.

Solvents recovery

Fine chemicals purification

**Speichim participates in MMAtwo project** in purification of the crude MMA to obtain a virgin MMA like.

**Patented Speichim "FLOAT VALVE PLATES".**

**Our customers :**

Fine chemicals

Pharmaceutical intermediates

Agrochemicals

Petrochemicals

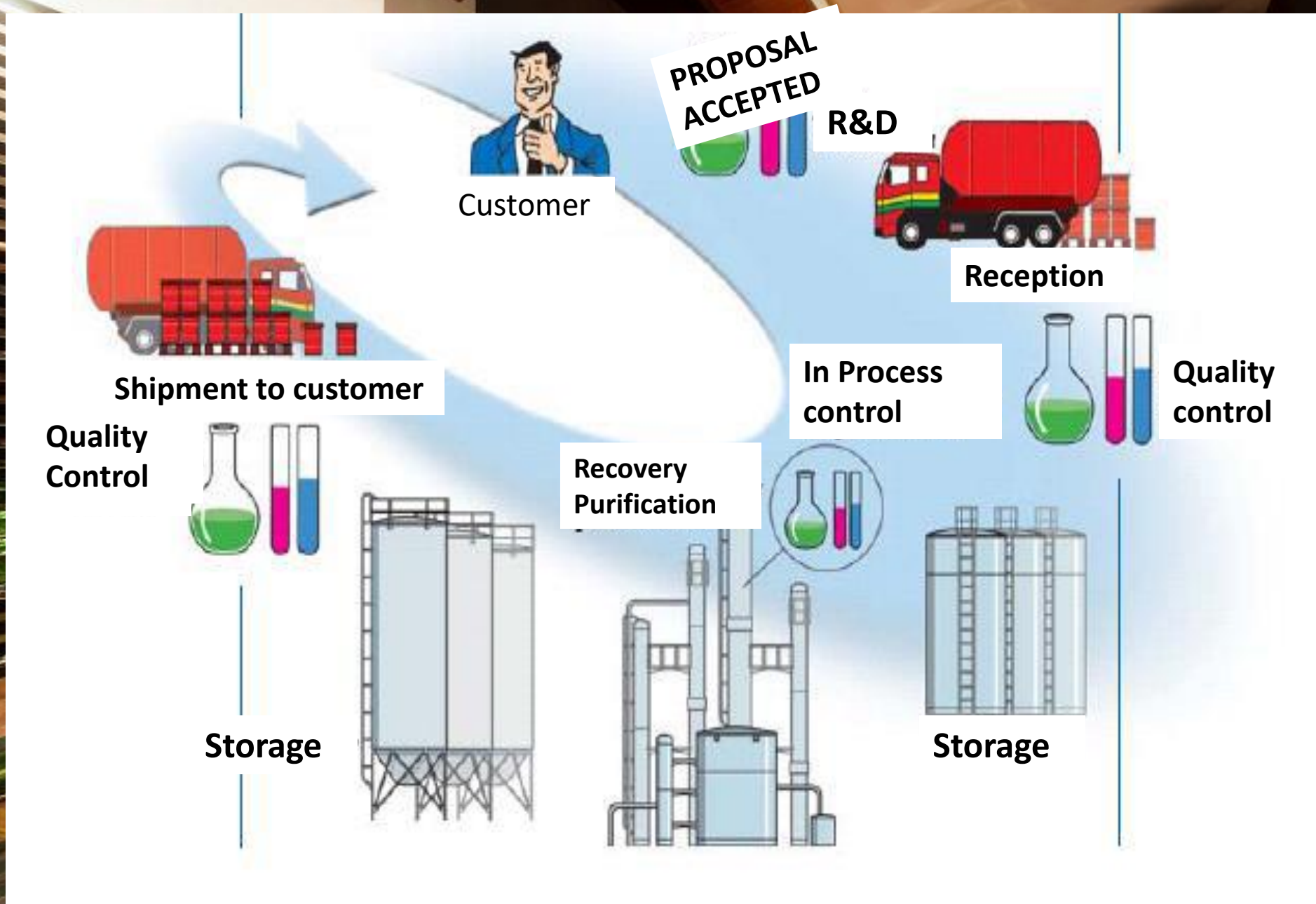
Flavour and fragrance/Cosmetics

...



**Customers mainly in Europe but also in USA, Japan, Middle East ...**

# SPEICHM ORGANIZATION





# SPEICHIM ACTIVITIES

- Working at Speichim Processing for more than 30 years
- More than 15 years as R&D Manager (mainly development)
- 300 samples/year for R&D study to propose a toll purification for our customers (theoretical studies, trials, samples to the customers for approval ...).
- We have to reply within a short period of time (days/weeks).
- A quick solution (process) should be found with acceptable price.
- We don't use systematically simulators (PROSIM, ASPEN ...).
- Why process simulators are not always helpful in our activity ?
  - Product must be present in the databases (activity coefficients ...),. The major number of fine chemicals are not included in database
  - we have to make thermodynamic measurements to check if data are correct. Thermodynamic data measurements are a heavy duty
  - We have to choose the right thermodynamic models
  - No precise design is needed as our equipments are multipurpose
  - We must know the tendency to be able to trust the simulators
  - Etc. ...
  - Long time study
- Laboratory trial is mandatory





# LABORATORY TRIAL IS A MAJOR STEP

- All our studies are confirmed by laboratory trials.
- Laboratory trials are based on Physical and chemical characteristics (when available) and on our know how.
- **GC-MS (Mass Spectrum)** is a good help to identify unknown impurities.
- **DSC (Differential Scanning Calorimetry)** : to find possible exothermic reactions
- **MSDS** : for stuff health
- **LAB TESTS** are very important to follow, corrosion, degradation, exothermic reaction, residue on evaporation (fooling), unknown products etc... **Thermodynamic cannot help.**
- The best process is the **most economical** and the **most robust**
- For very high value product, **piloting** is mandatory
- **Thermodynamic** is still mandatory for big project
- **PURIFICATION IS A FEELING WITH EXPERIENCE**



**PILOT PLANT**



# DAILY PROCESSING *versus* CONCEPTION

Conception	Daily processing
Rare (new process)	Frequent/daily
Long period of study	Short delay (fixed by the customer project/need)
Dedicated equipment (sharp conception)	Existing equipment: <ul style="list-style-type: none"> <li>• Dimensions</li> <li>• Feed plate</li> <li>• Side draw</li> </ul>
Thermodynamic measurements and process simulator	Experience and know how
Piloting	Quick laboratory trial
Optimized process and Energy recycling	<ul style="list-style-type: none"> <li>• Search for the more economic process (cost price)</li> <li>• Robust process</li> </ul>
Automation	Flexible process (managed by human) Need of qualified operators
Should be successful (can be optimized)	Successful (but still totally adjustable)
Global : process+instruments+equipments ...	Pure processing
On line analysers	Control by operators and optimization





**Certech**  
R&D partner in chemistry

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- **Research & development partner** and supplier of analytical and technological services in the fields of **environment, materials and processes**
- Quality management system according to the ISO 9001 and ISO 17025 standards
- **Recognised expert in the field of VOCs and odour**
- **Accredited by Renault and PSA**

#### **Roles in MMAtwo project:**

- . standardisation and classification of PMMA waste
- . general characterisation including **Emissions and odours from recycled methyl methacrylate and derived polymers**

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# *Batch and continuous distillation*

## Batch :

- small amounts

- More than one product to be purified from a mixture

- Longer residence time

- Intermediate fractions

## Continuous distillation

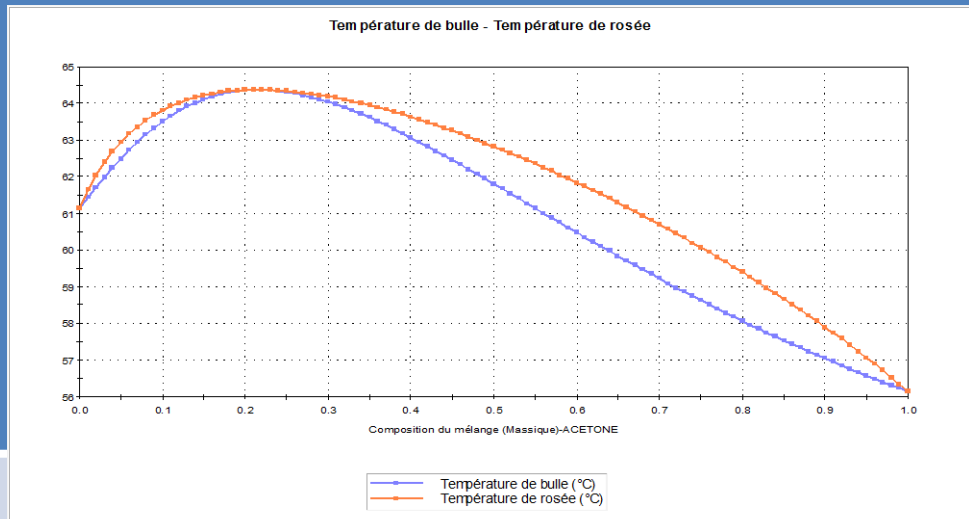
- Important streams

- Easy to follow up

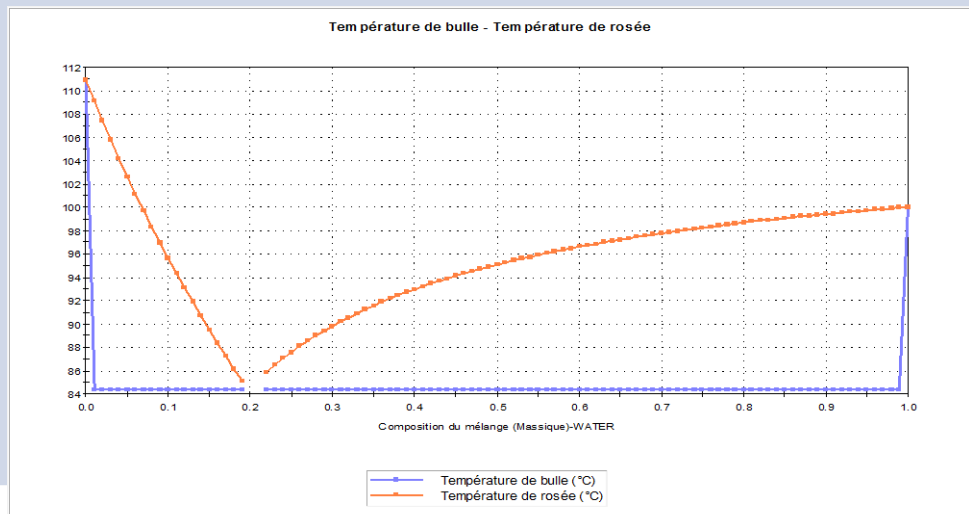
- Needs a big number of equipment

# Interests of equilibrium curves 1/2

Homogeneous  
Chloroform/acetone @ 1 atm



Heterogeneous  
water/toluene @ 1 atm

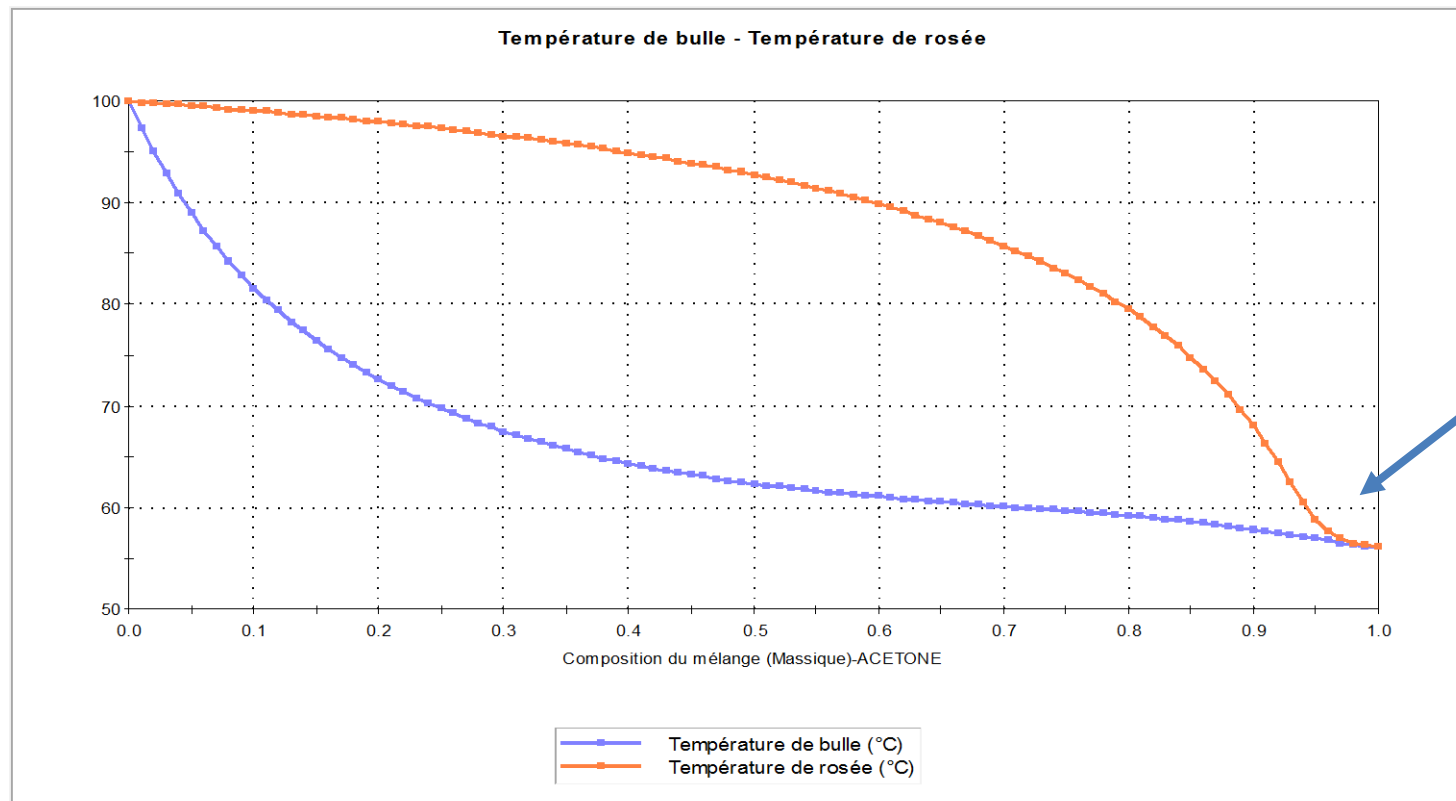






# Interests of equilibrium curves 2/2

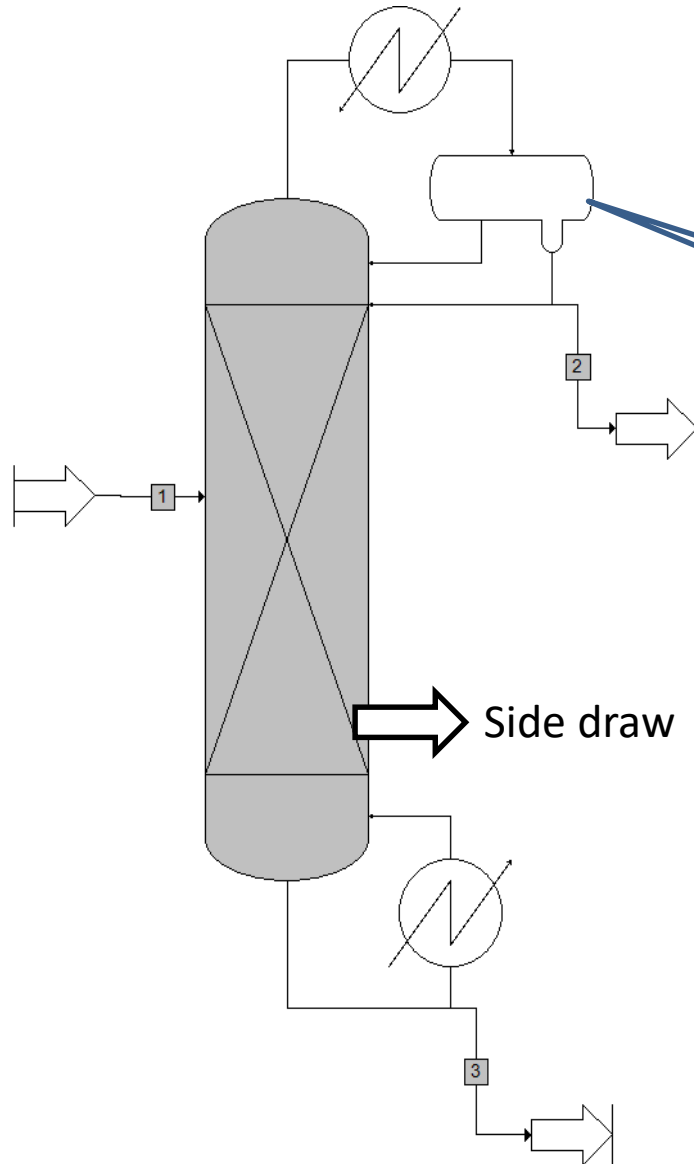
- Pinched curves



Acetone cannot be obtained with less than 2000 ppm of water

**water/acetone @ 1 atm**

# HETEROAZEOTROPIQUE

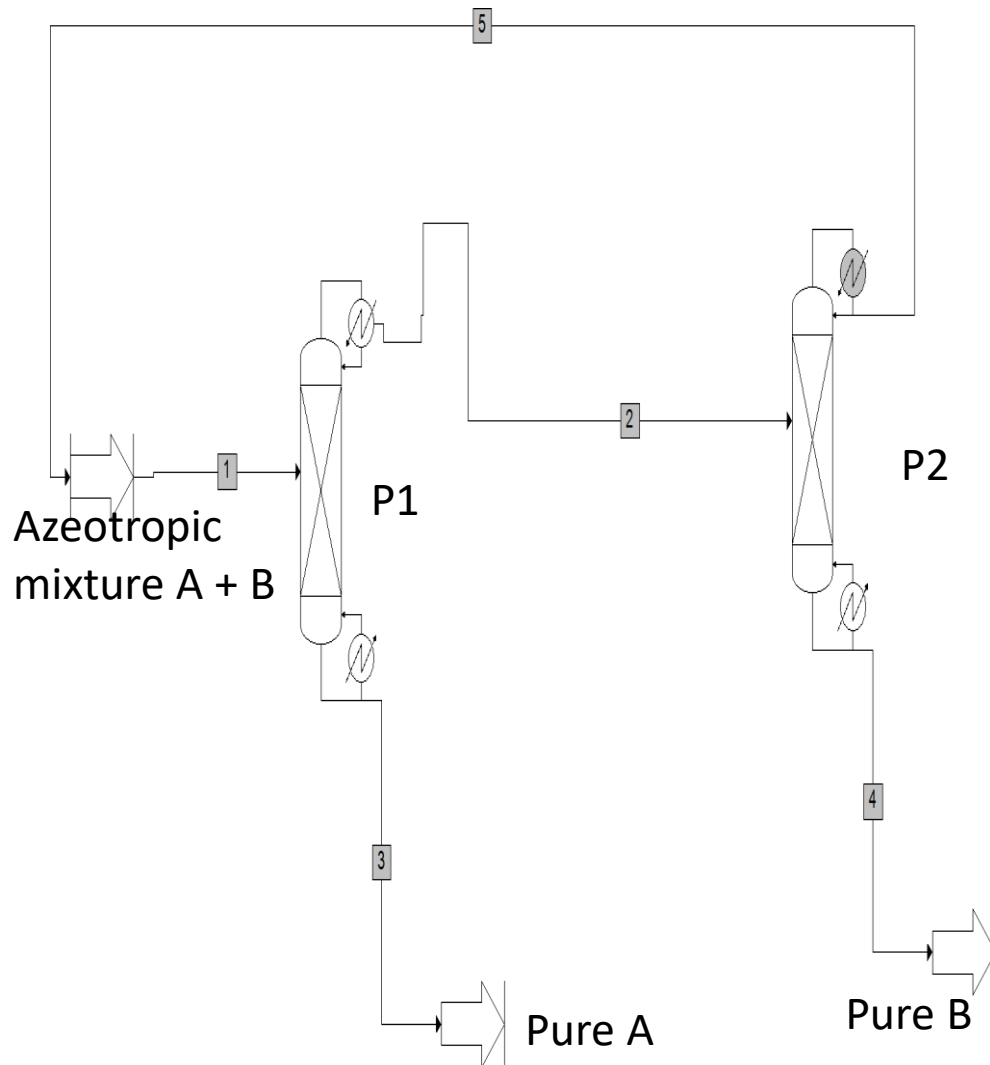


e.g : Dehydration with  
or without entrainer

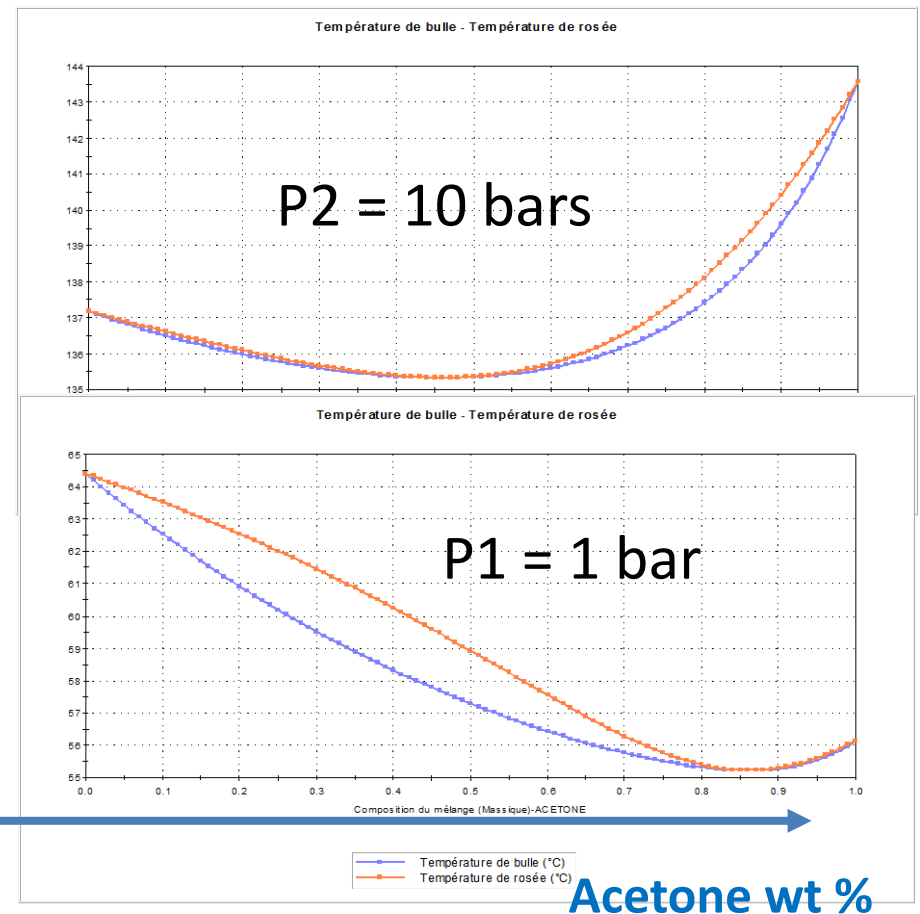


# Pressure swing

## MeOH/Acetone @ 1 AND 10 BARS



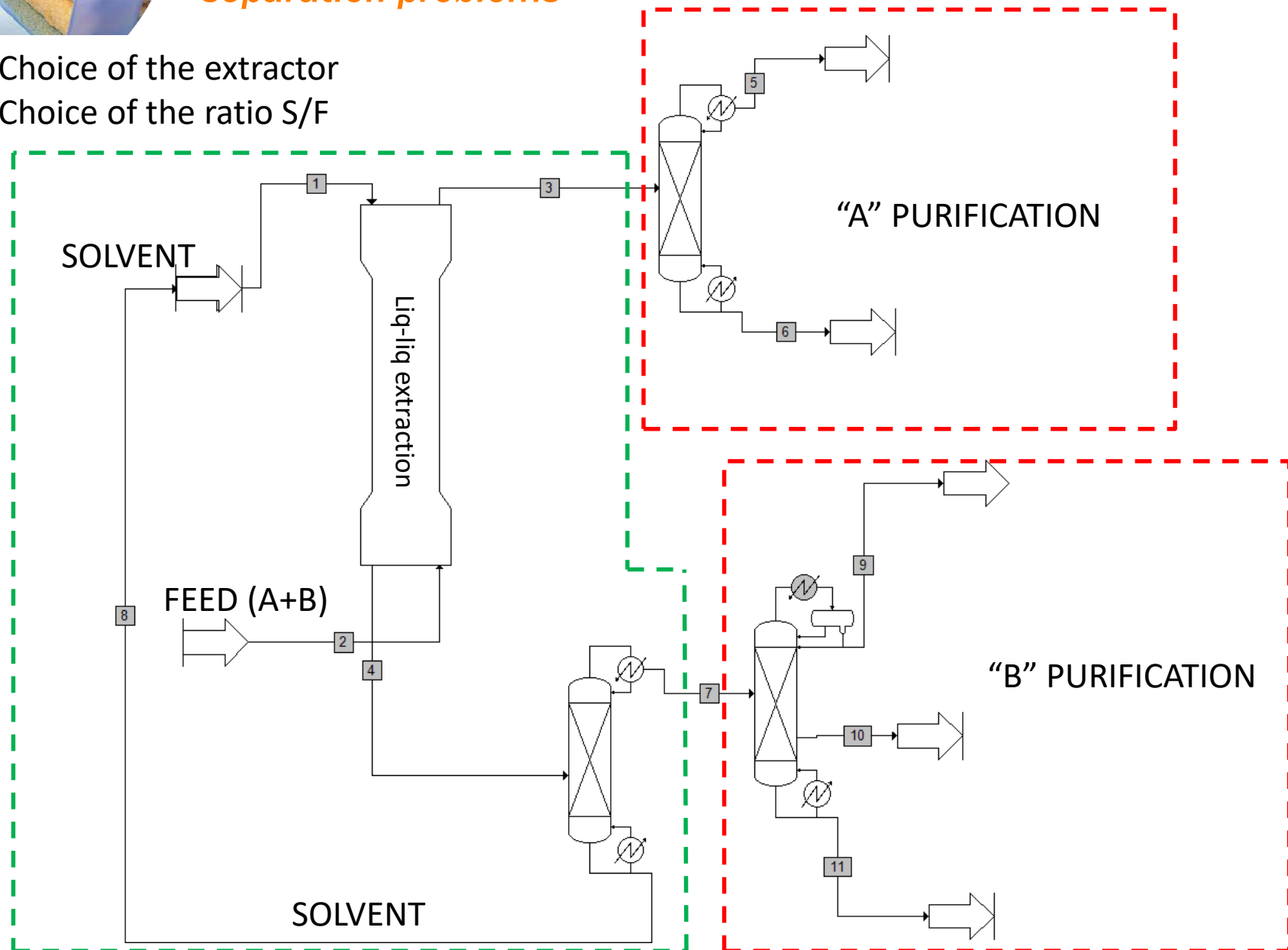
T°C





# Liquid-liquid extraction *very good help for distillation separation problems*

- Choice of the extractor
- Choice of the ratio  $S/F$





# EXTRACTIVE DISTILLATION

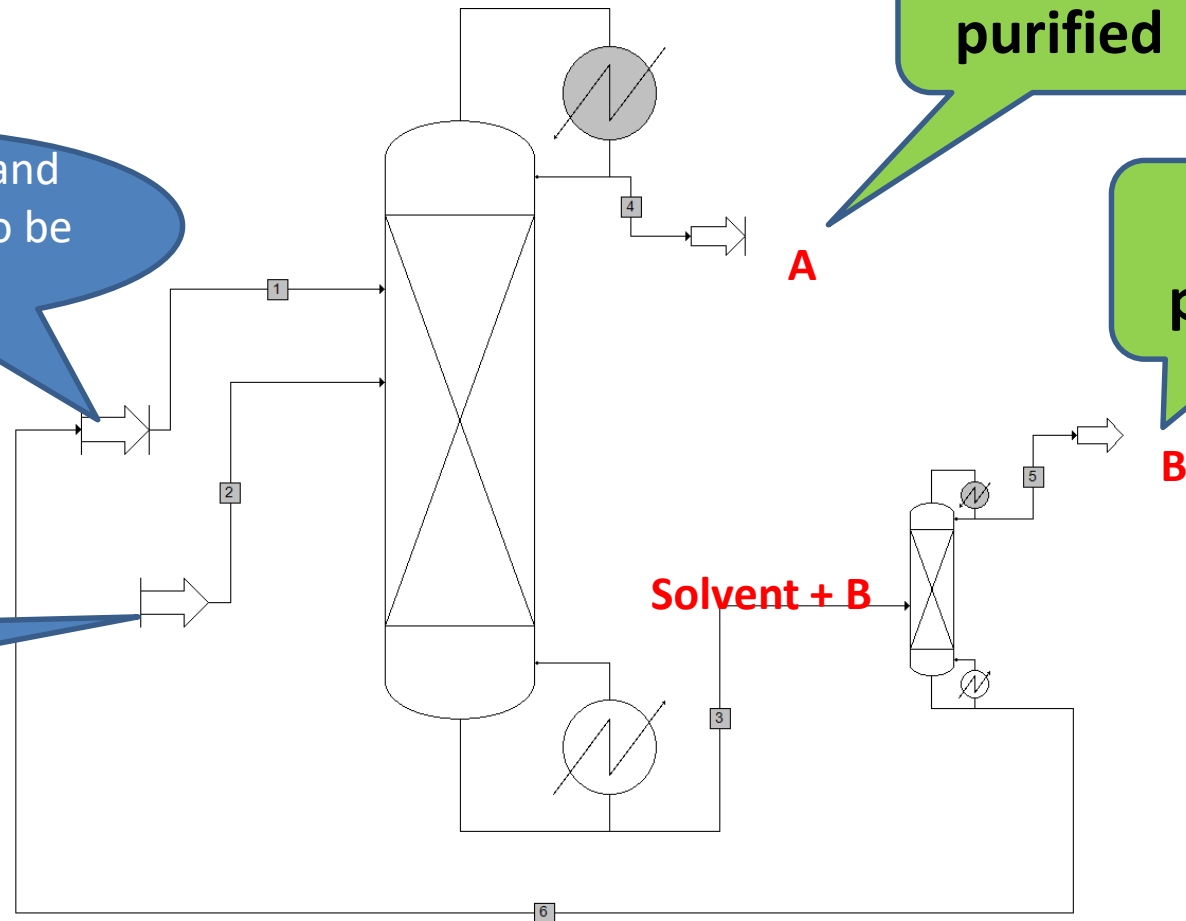
Solvent mainly used is water

Solvent, ratio and feed position to be selected

MIXTURE **A+B**  
TO BE SEPARATED

To be purified

To be purified





# MOLECULAR DISTILLATION or SHORT PATH

High boiling products (pressure < 0,01 mbar)

Thermal sensitive products (low residence time and pressure)

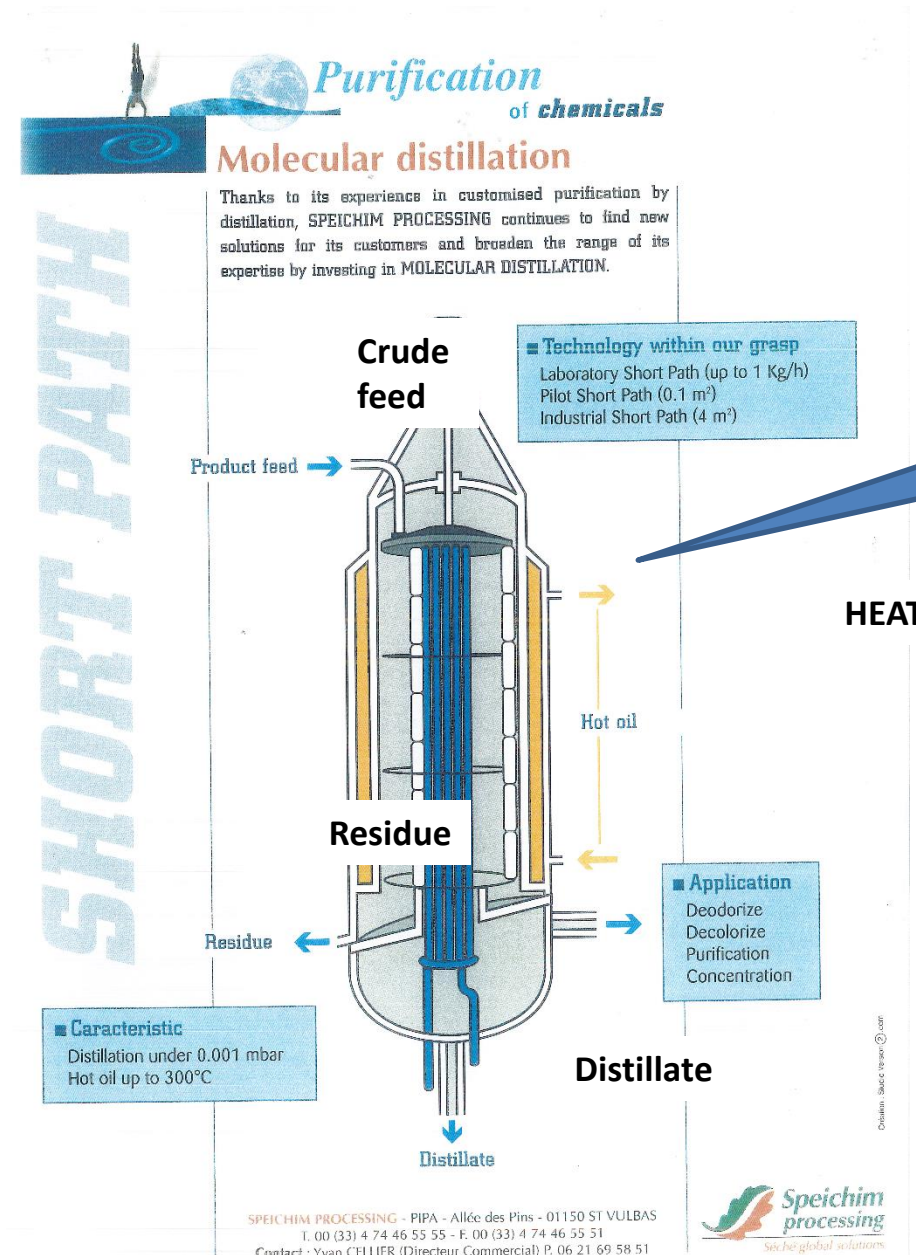
Desodorization

Decoloration

Purification

Concentration

Etc. ...





# *Other purification processes*

## Membrane (Pervaporation)

Very specific technic mainly for water removal

Little power consumption

e.g : membrane can remove water from esterification reaction to shift the equilibrium to ester side

## Reactive distillation with catalyst in the separation packing

Very good technic but equipment should be dedicated for one process

# From monomer purification to polymer emissions & odours

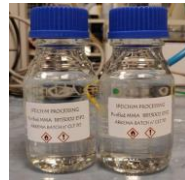


PCR / PIR  
PMMA  
Waste  
streams



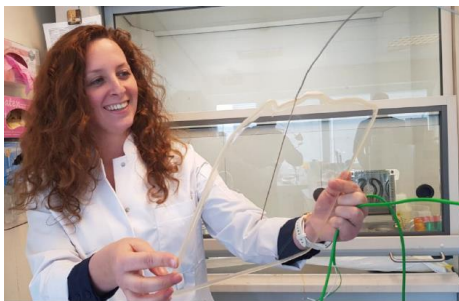
Pre-treatment  
Depolymerisation

rMMA



Purification  
Repolymerisation

rPMMA

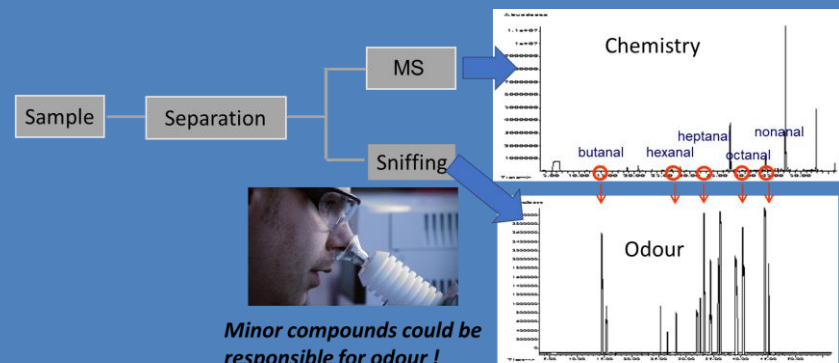


## Emissions & odour assessment

Global odour intensity & Field of Odours®  
(odorous notes)



Gas chromatography-mass spectrometry/sniffing :  
chemistry/odour correlation





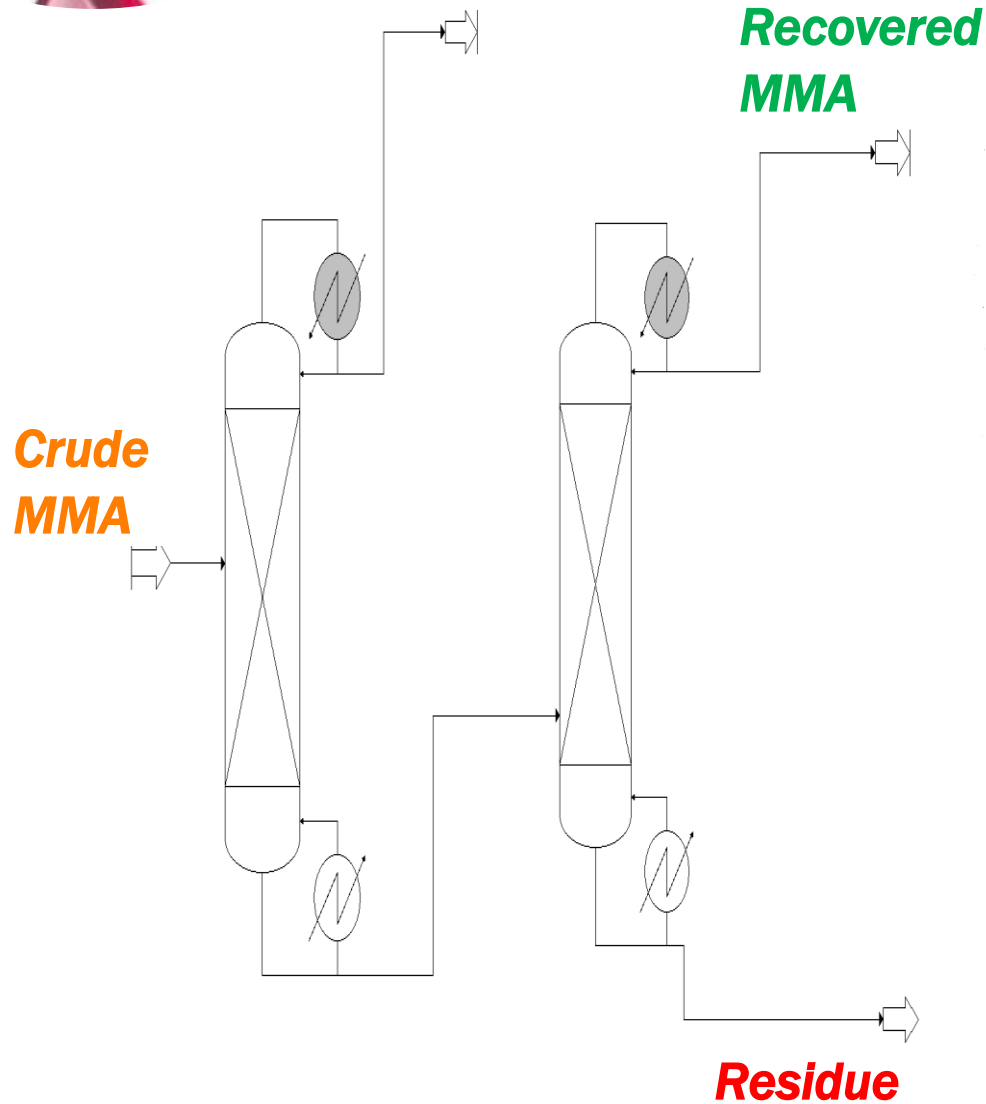


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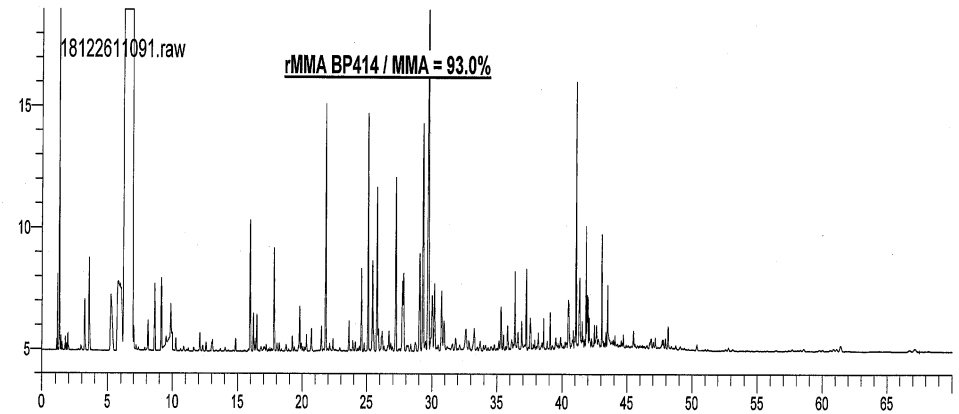
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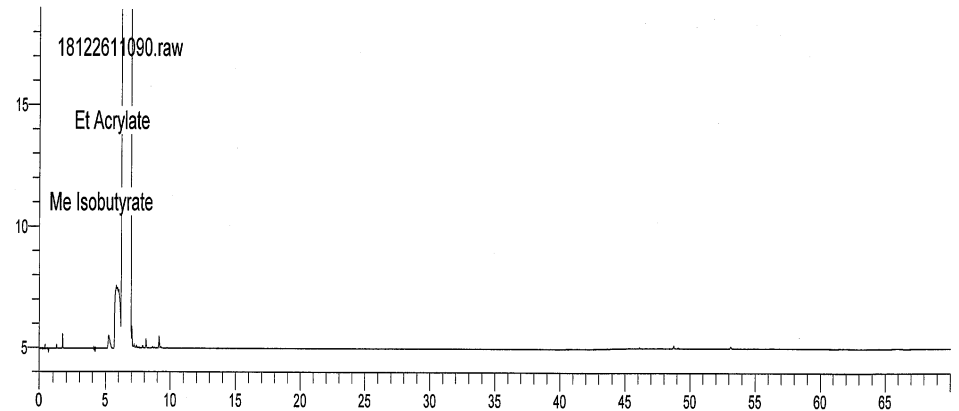
# MMAtwo : MMA purification



## Crude MMA

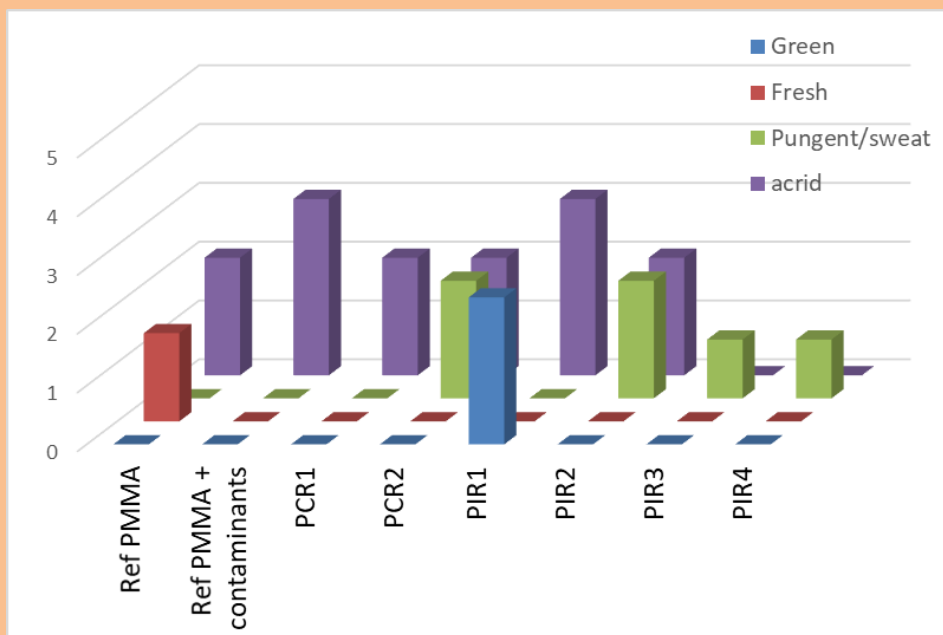
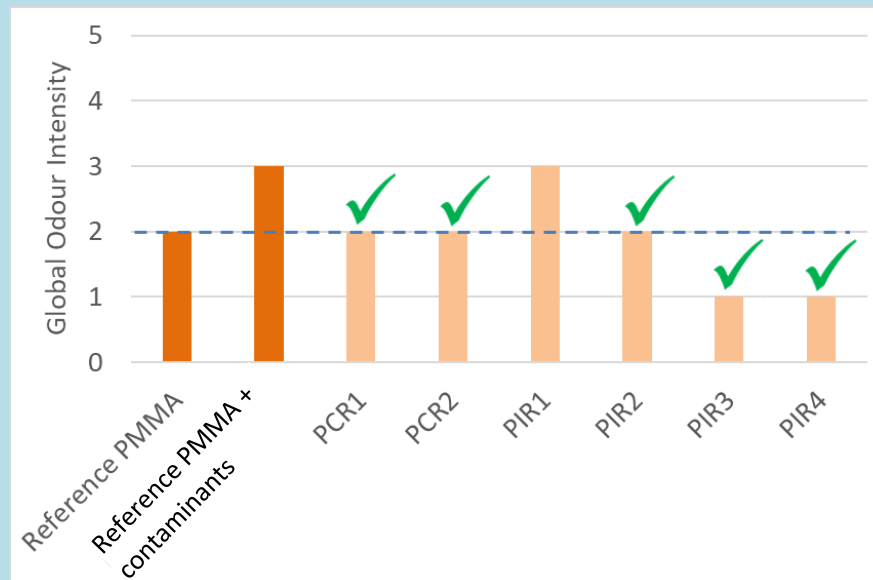


## Recovered MMA





Global odour intensity determination by human panel: 5 out of 6 rPMMA polymerised using rMMA from various sources (industrial scrap and post consumer) have a global odour intensity  $\leq$  to reference PMMA



### Field of Odours® / Odorous notes of rPMMA:

- Acrid note dominates
- More investigation needed for Pungent note



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