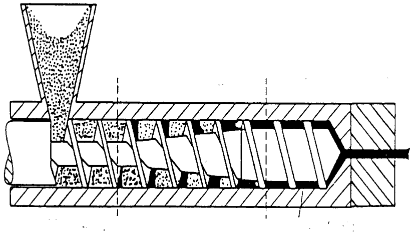
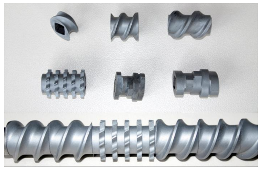
"Extrusion réactive des polymères naturels. Intensification des réactions de modification des Lignines et amidons."





Christophe Bliard

Institut de chimie moléculaire de Reims

CNRS UMR 7312

Université de Reims Champagne-Ardenne

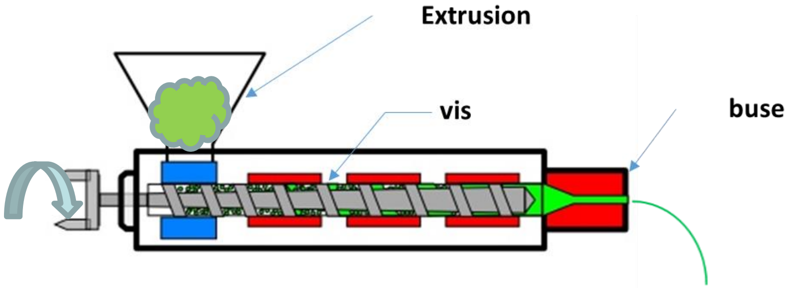
Ecole thématique Procédés durables Banyuls 08-14 sept. 2019

Plan

- Introduction
- Batch vs Extrusion Reactive
  - Comparaison des deux technologies
- L’extrusion Réactive REX
  - Fonctions d’un extrudeur ; paramètres.
- Les différentes technologies
  - Mono/ Bivis co-rot contra-rot.
  - La réaction en REX
    - Modélisation
    - L’EMS
    - Modification des Agropolymères
    - Les exemples au labo CMS
    - Régiosélectivité « Modèle de Spurlin »
    - Lignin
    - Scale-up

Extrusion réactive vs réactions en batch

A + B → C + D



Modification chimique

Réactions en batch
Pbl changement d'échelle : Mélange

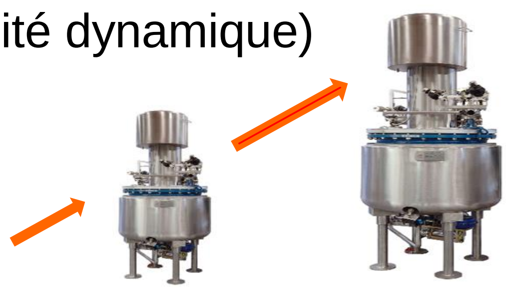
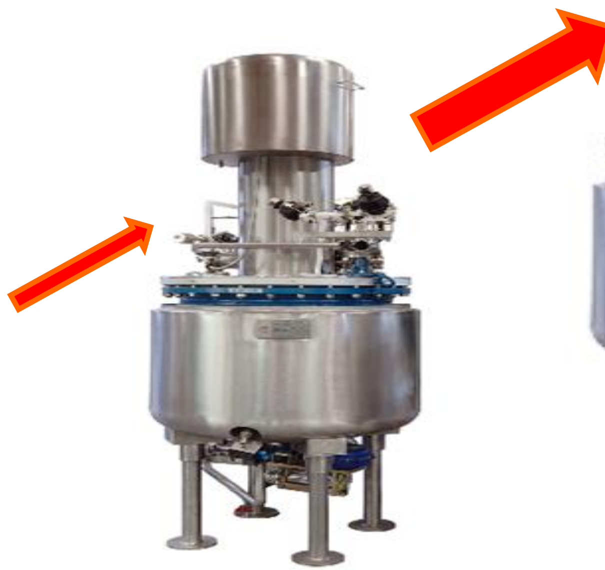
Vitesse de réaction : coefficient de diffusion (Mélange réactants)

Loi de Stokes Einstein[1]

$D=KT/(6\pi r\mu)$

$R = 1/2(V/N)^{1/3}$

(μ viscosité dynamique)


1 Einstein A. Annalen der Physik, vol. 17, no 8, 1905, p. 549–560

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Réactions en batch
Pbl changement d'échelle : sous produits

Dégradation réactifs et produits $\propto$ temps de séjour

Sous-produits ↗ temps de réaction

Qualité des produits ↘

1 Einstein A. Annalen der Physik, vol. 17, no 8, 1905, p. 549–560

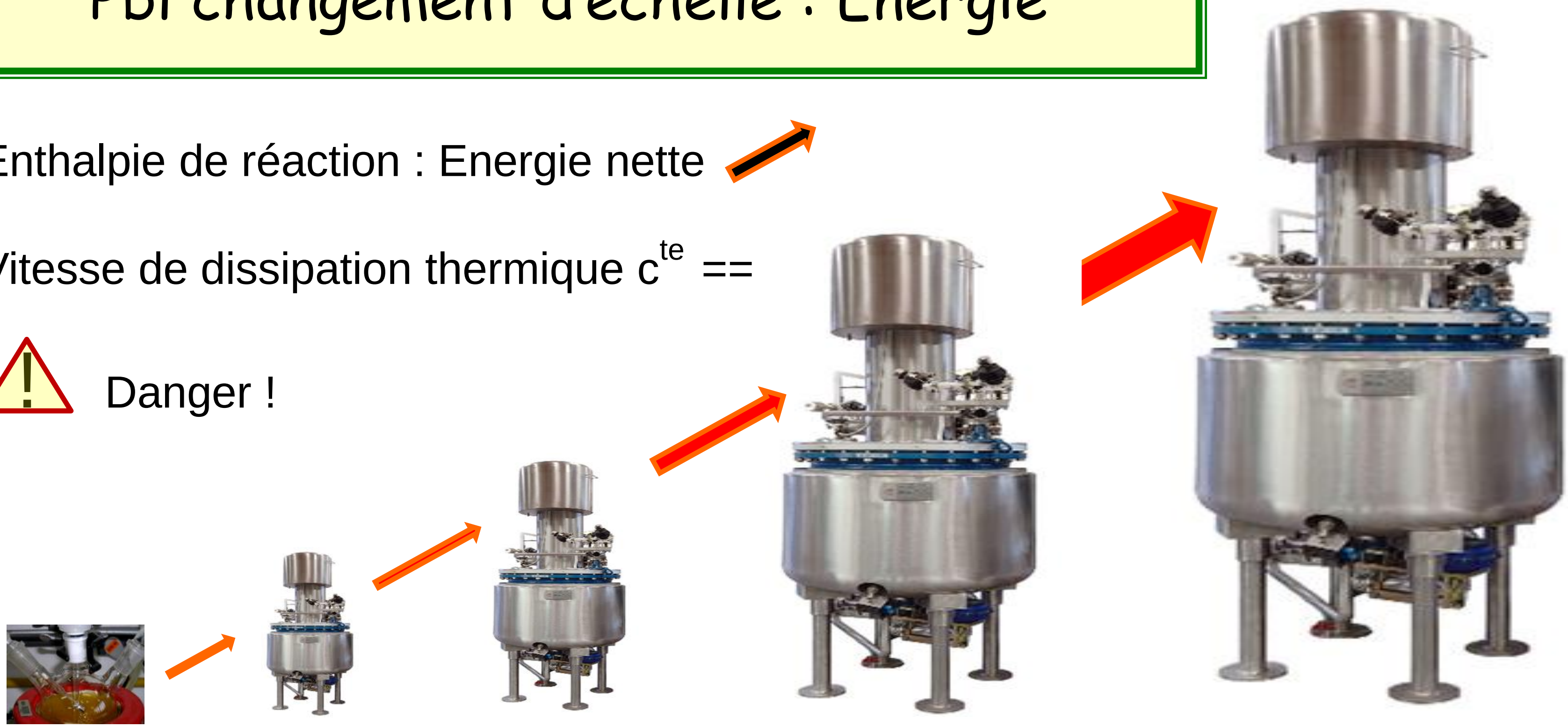
Goscinny Uderzo Pilote 1966

Réactions en batch
Pbl changement d'échelle : Energie

Enthalpie de réaction : Energie nette ↗

Vitesse de dissipation thermique c^{te} ==

⚠ Danger !



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Réactions en batch

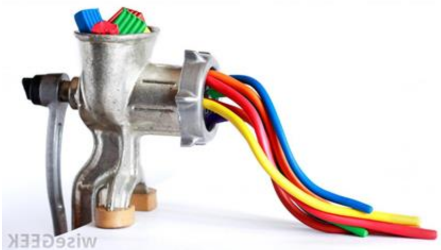
A + B → C + D (+ e + f + g)

In practice, it is fairly difficult to achieve a high **reaction efficiency (RE)** and avoid by - products formation

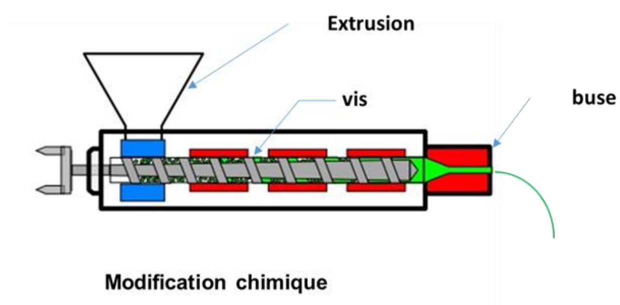
- Not good
- ➢ quantity solvent & reagents used
- ➢ low RE & Poor reaction control
- ➢ high residence time
- ➢ slow heat transfer
- ➢ by-products

- Good
- ➢ ubiquitous equipment
- ➢ well known technology

Extrusion réactive



$$A + B \rightarrow C + D + e$$



- Faster kinetics , versatile

- Specific equipment
- Viscosity constraints

- producing large amount
- High RE & good reaction control
- Short residence time
- Fast heat transfer
- Fewer by-products

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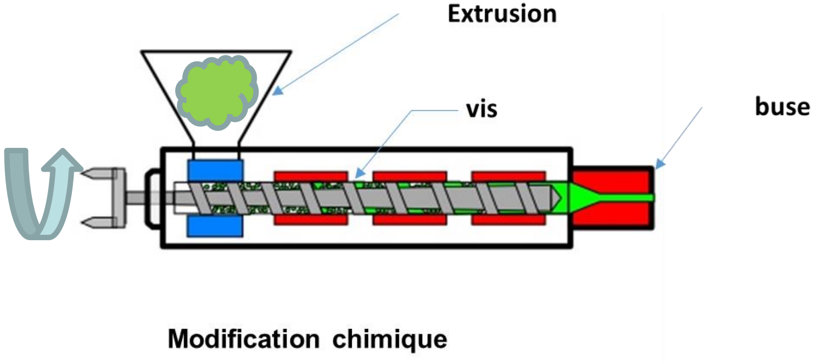
Batch vs Extrusion



Equipement traditionnel
Modulation temps de réaction
Process très répandu

Lenteur des réactions
Enthalpie réaction
Dégradations- sous produits
Consommations solvants
Effluents
!

Pas de solvants & moins d'effluents
Contrôle paramètres & qualité produits
Concentration du milieu réactionnel
Réactions + propres + rapides
Process continu

Modulation matériel ∝ quantités & réaction
Paramètres réactionnels et technologiques
Changement de paradigme

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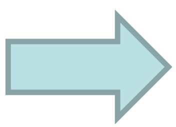
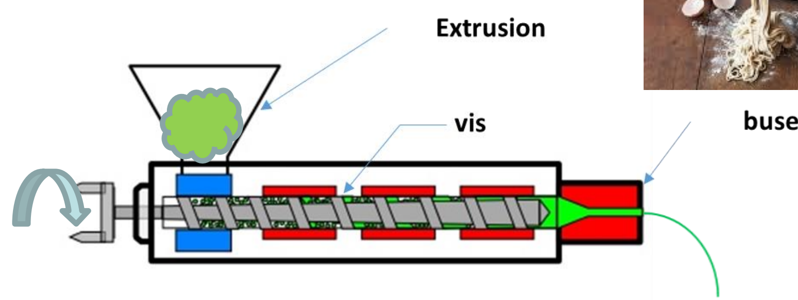
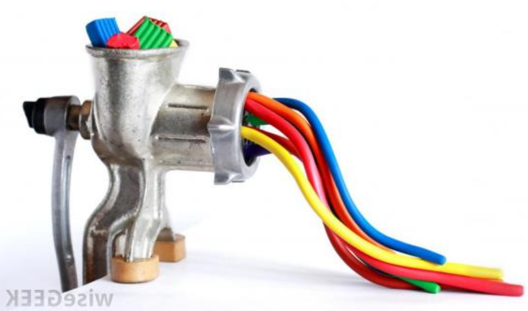
Du Batch à l' Extrusion réactive

A + B → C + D





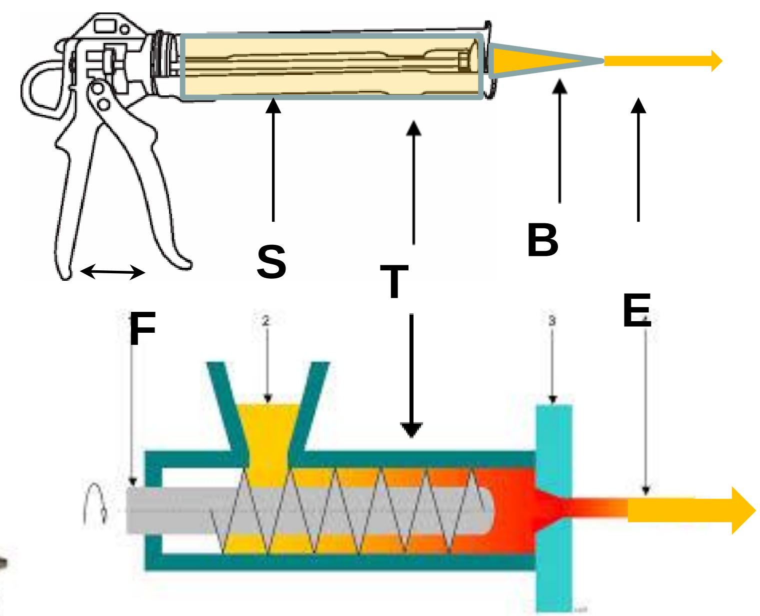
Modification chimique



L' Extrusion Réactive REX

« Le procédé de transformation des polymères, comme l'extrusion bivis, et le contrôle d'une réaction chimique dans des conditions particulières (milieux très visqueux, haute température, temps de séjour court). …. calculs d'écoulement en géométrie complexe, des cinétiques de réaction et des comportements rhéologiques évolutifs. … approche de mécanique des milieux continus. «

B. Vergnes et al., C.R. Chimie 9 (2006) 1409.



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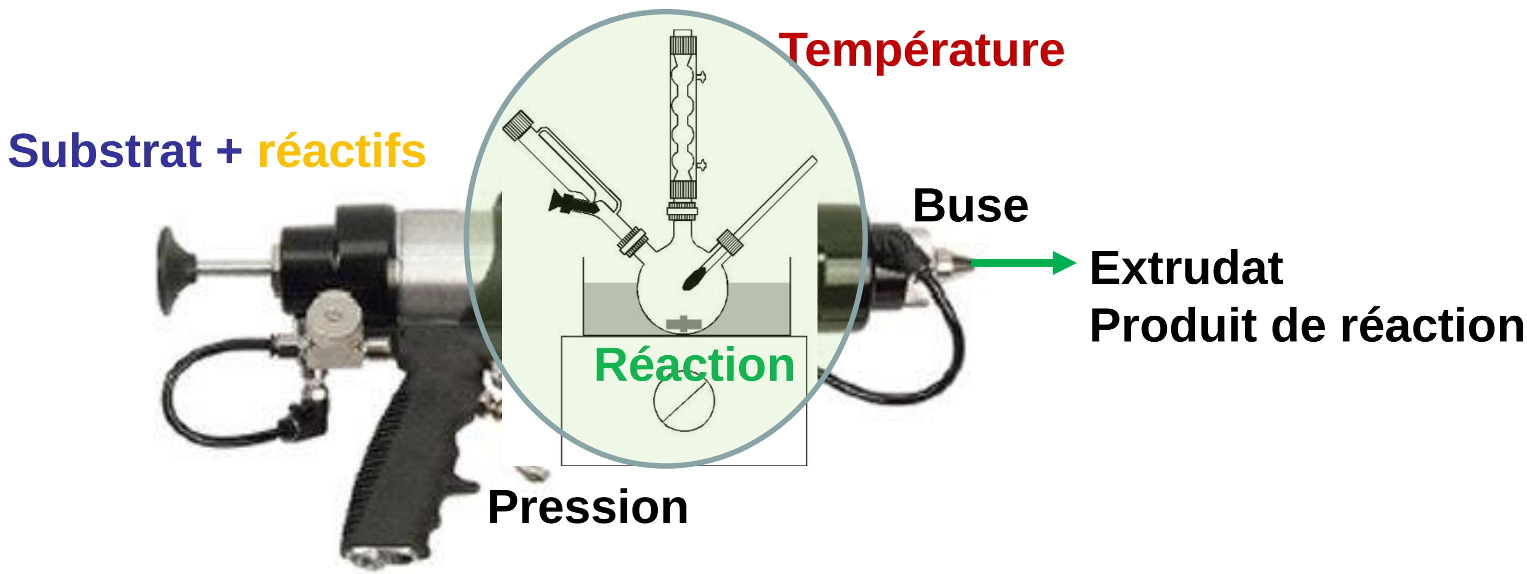
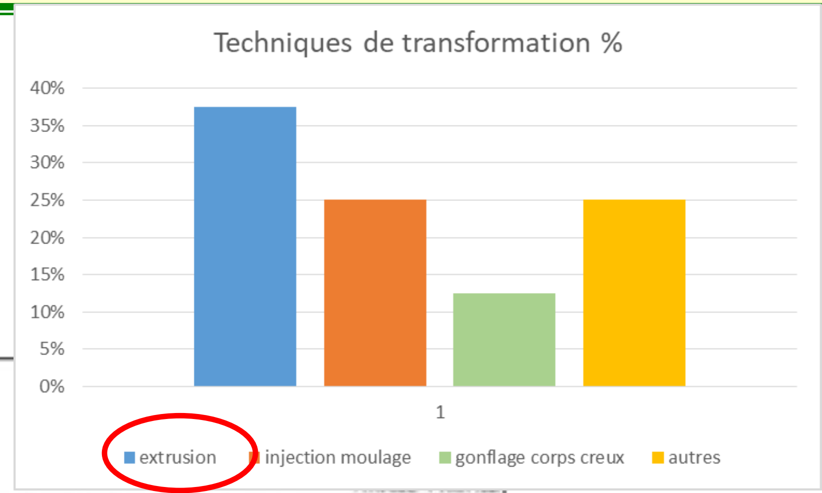
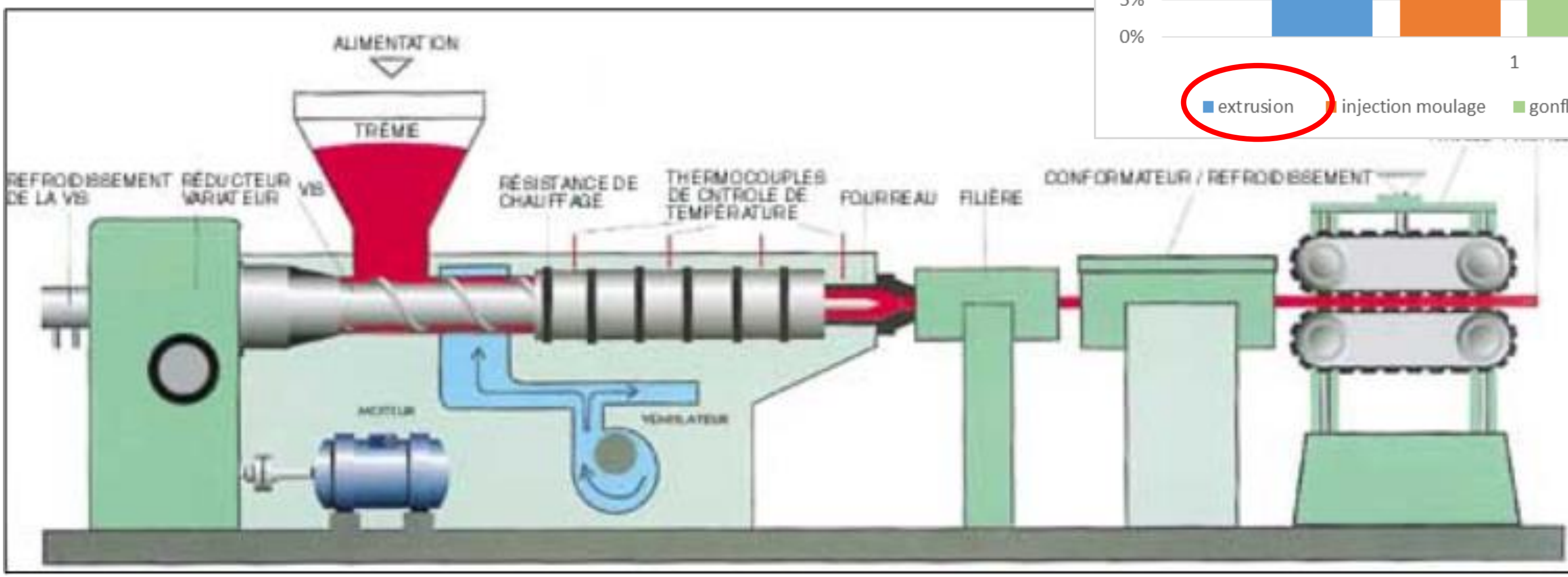
Extrusion Réactive : Réacteur en continu



L' Extrusion : Technologie majeure de transformation des matériaux polymères



Marché de transformation
des matière plastiques 300 Mt



www.plasticseurope.org

Quelques fournisseurs Industriels

Extrudeuses corotatives

Berstorff GmBH (Allemagne)
http://www.berstorff.com
Clextral (France)
http://www.clextral.com
Coperion Werner et Pfleiderer
http://www.werner-pfleiderer.de
Japan Steel Works, Ltd (Japon)
http://www.jsw.co.jp/en
Leistritz Aktiengesellschaft (Allemagne)
http://www.leistritz.com
Maris SpA (Italie)
http://www.mariscorp.com

Extrudeuses contrarotatives interpénétrées

Battenfeld Extrusionstechnik (Allemagne)
http://www.bex.battenfeld.com
Bausano Group SpA (Italie)
http//www.bausano.it
Coperion Werner et Pfleiderer
http://www.werner-pfleiderer.de
Demag Krauss Maffei (Allemagne)
http://www.bkk-dkm.de
Japan Steel Works, Ltd (Japon)
http://www.jsw.co.jp/en
Leistritz Aktiengesellschaft (Allemagne)
http://www.leistritz.com
Luigi bandera SpA (Italie)
http://www.luigibandera.com
Milacron (USA)
http://www.milacron.com
Reifenhäuser Extrusion (Allemagne)
http://www.reifenhauser.com/en

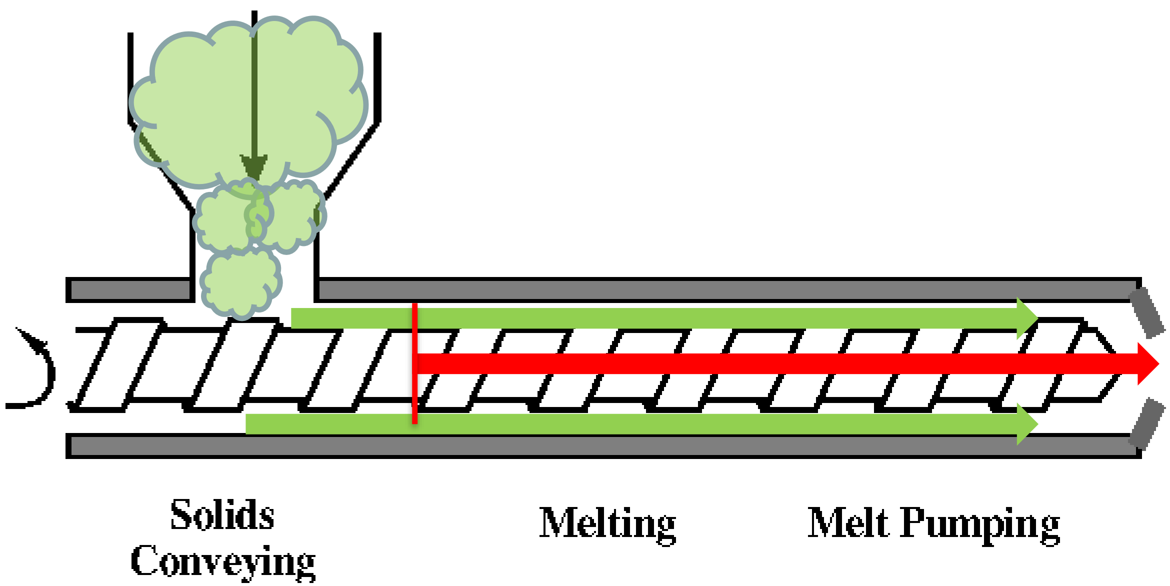
Extrudeuses contrarotatives non interpénétrées

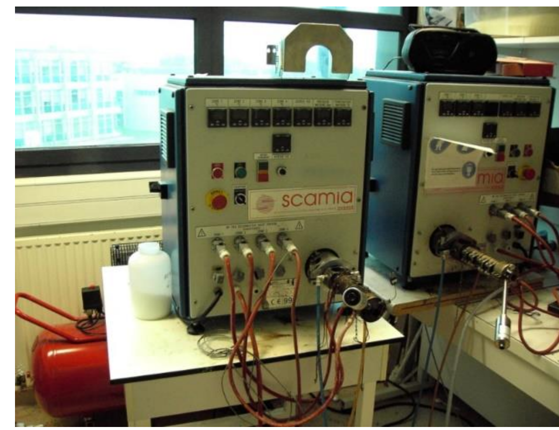
Farrel (USA)
http://www.farrel.com
Japan Steel Works, Ltd (Japon)
http://www.jsw.co.jp/en
Kobe Steel Group (Japon)
http://www.kobelco.co.jp/english
NFM Welding Engineers (USA)
http://www.nfm.net

Vergnes B., Chapet M. (2001). Procédés d'extrusion bivis, Techniques de l'Ingénieur, AM3653, 1–23.

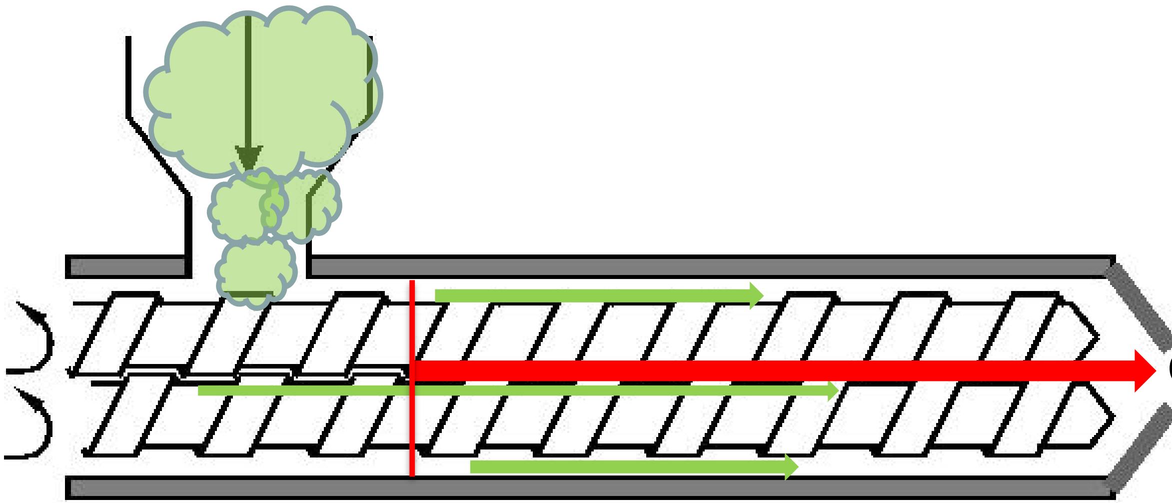
Systèmes monovis

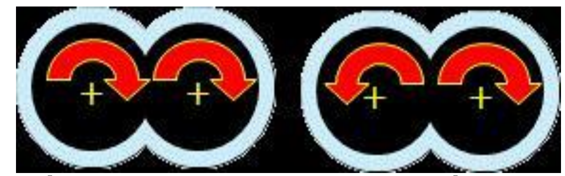
Réacteur parfaitement piston



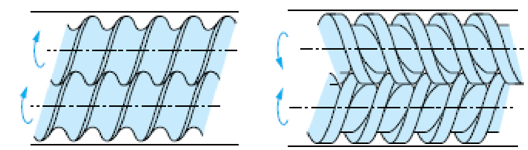


Systèmes bi-vis

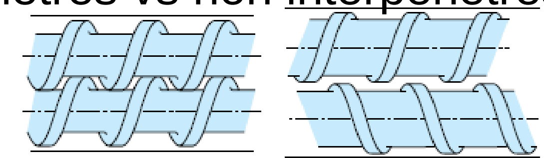




Corotatives vs contra-rotatives



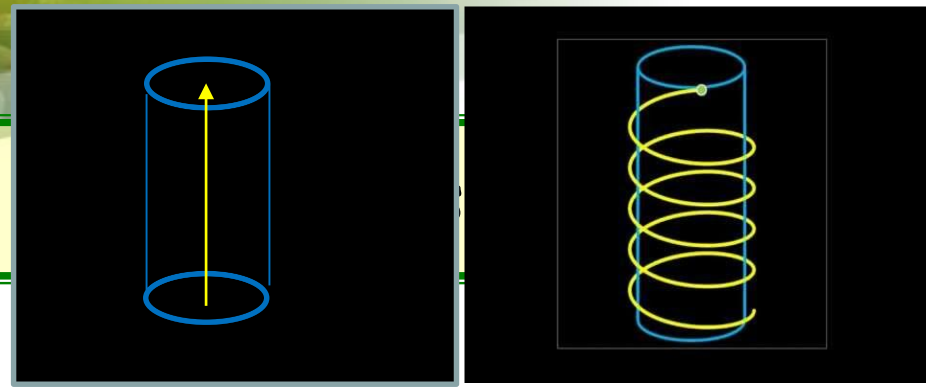
Interpénétrés vs non interpénétrés



Contra-rotative : similaire à un écoulement piston
Co-rotative : meilleur mélange des substrats

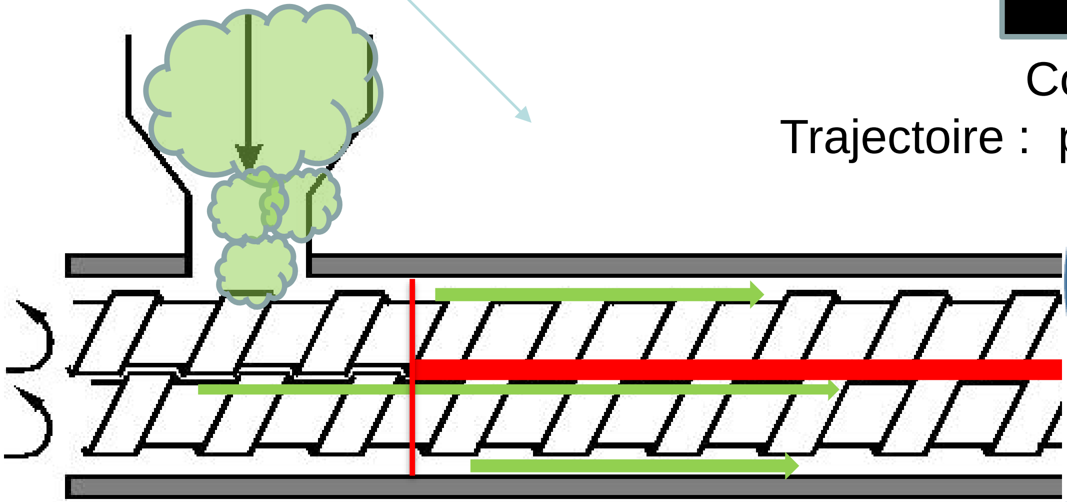
- *Vergnes B., Chapet M. (2001). Procédés d'extrusion bivis, Techniques de l'Ingénieur, AM3653, 1–23.*

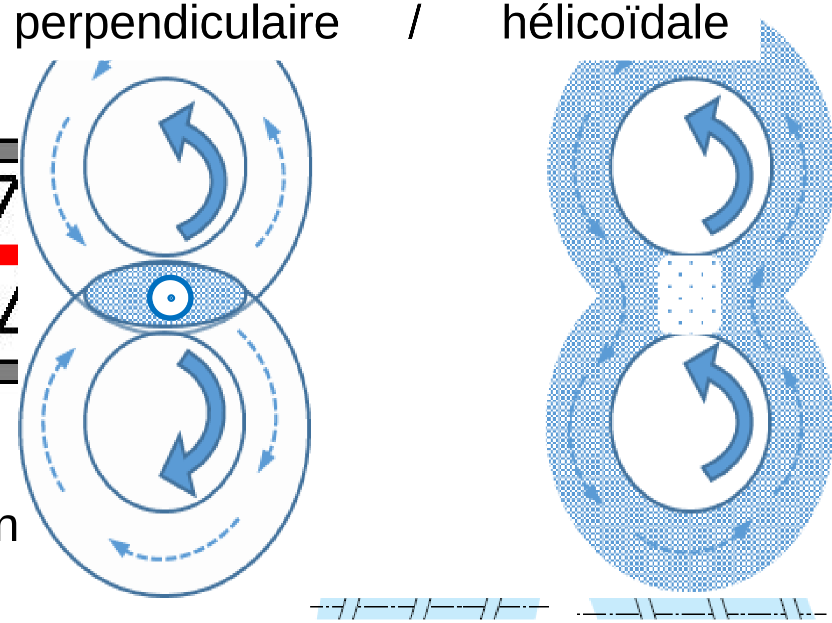
- *Milotskyi, R., Bliard, C., Venditti, R., Ayoub; A., Starch Extrudates as Sustainable Ingredients in Food and Non-Food Applications ACS Symposium Series Vol. 1304*



Contra rotative / Corotative

Trajectoire : perpendiculaire / hélicoïdale





Contra-rotative, similaire à un écoulement piston

Co-rotative meilleur mélange des substrats

- *Vergnes B., Chapet M. (2001). Procédés d'extrusion bivis, Techniques de l'Ingénieur, AM3653, 1–23.*

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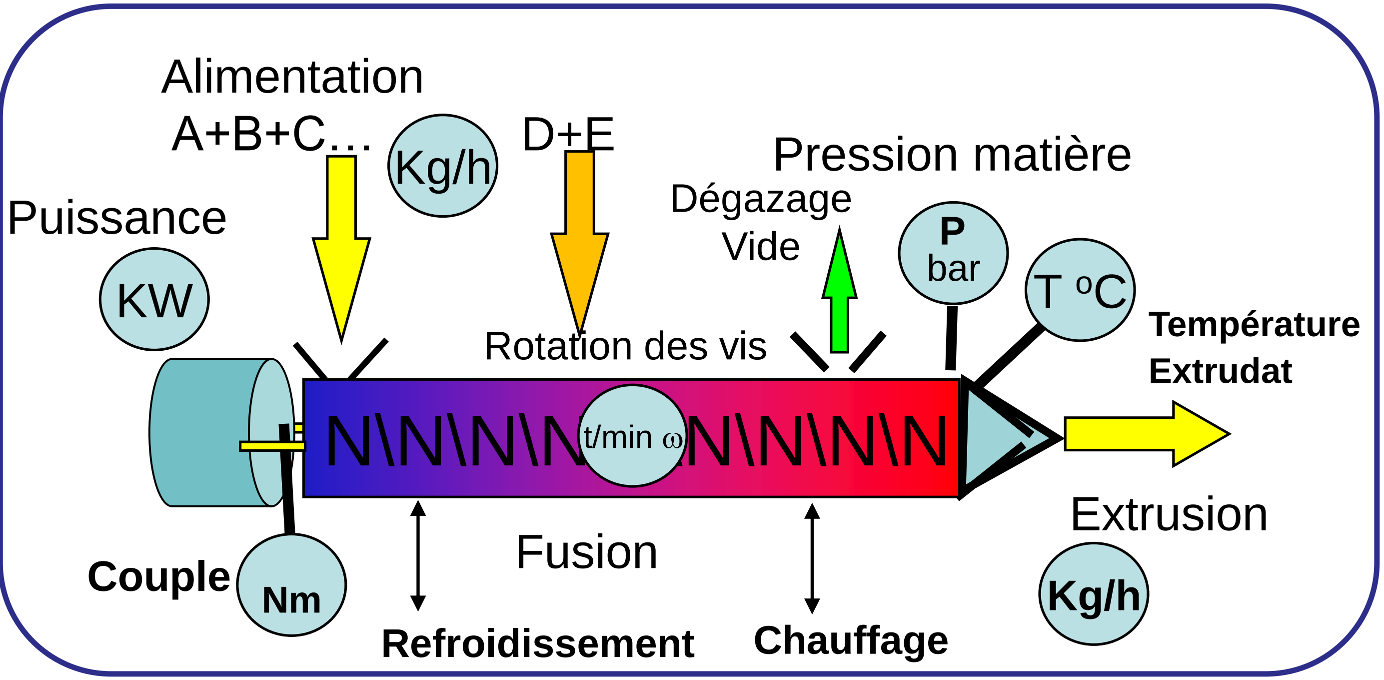
La réaction chimique en REX



<u>Extrusion Bi-Vis</u>

Intensification

Sans solvant

↗ Concentration

↗ Cinétique

↗ Sélectivité :

↗ Contrôle

des réactions

secondaires

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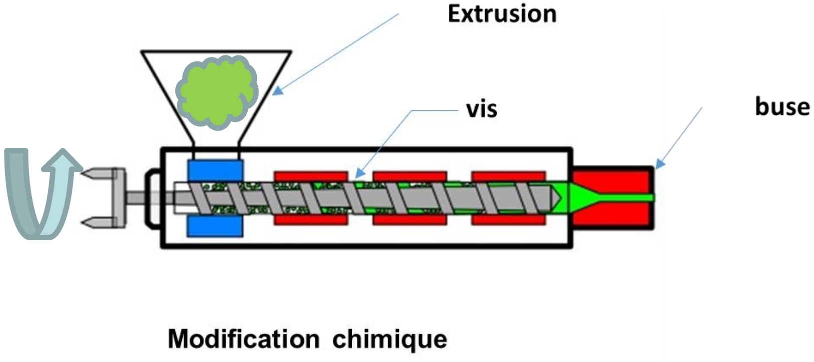


Extrusion :

Mélanges solides (solide + solides)

Mélanges biphasiques (cuisson extrusion : solide + liquides)

Mélanges plastifié (polymères + plastifiants + réactifs)

Mélanges fondus (fusion de solides)

- Pharma specific version with specific features
  - Product contact parts manufactured from Pharma grade steel
  - Removable barrel for easy cleaning
  - Barrel Setup using tri-clamps to avoid any threads
  - Removable Touch screen for Isolator applications
  - Full validation documentation available
  - Temperature range limited to 280 °C

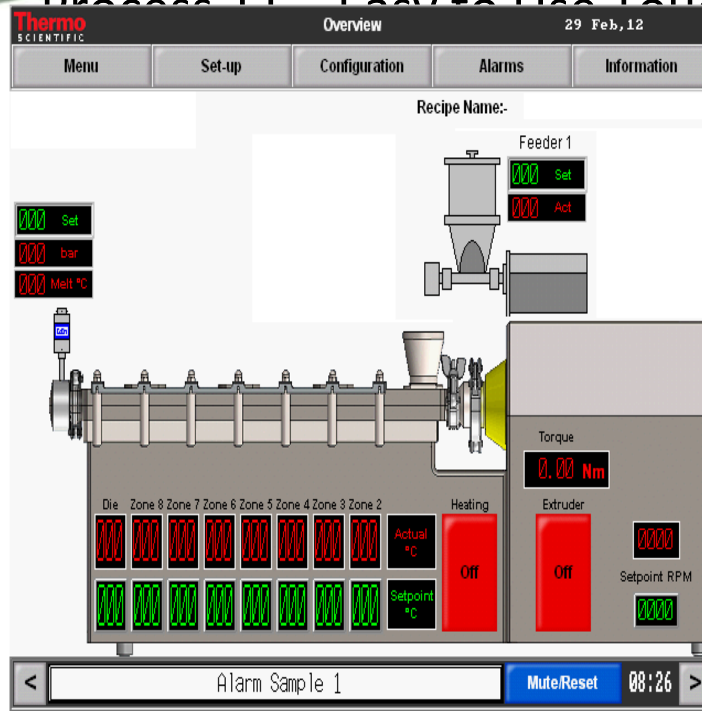
Bench-Top Design with integrated Electronics

ted Screws

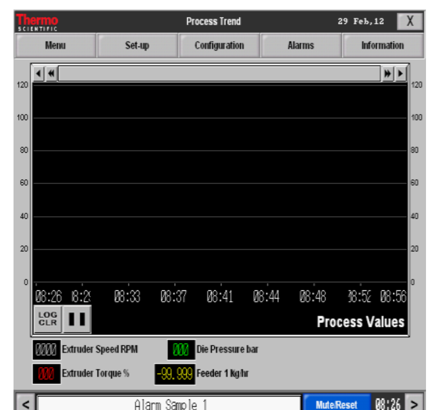
een Control


Thermo
Overview
10 Jan,12
Menu
Set-up
Configuration
Alarms
Information
Recipe Name:
Torque
0.0 Nm
Speed RPM
Setpoint RPM
Heating
Extruder
Off
Off
Mute/Reset
23:21
RUN
EMERGENCY STOP

Process 11 – Easy to Use Touchscreen

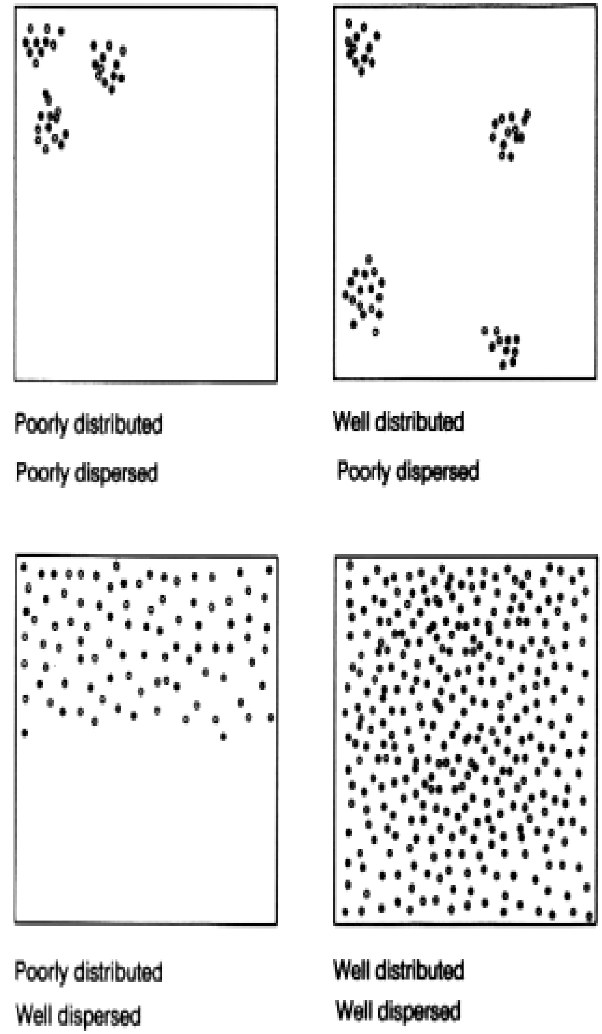


- All Set-Points:
  - Temperatures
  - Screw Speed
  - Feed rate(s)
- Processing data
  - Torque
  - Pressure
  - Melt Temperature
- Processing trend
  - M, n, p, T_M, FR vs. time
- Temperature trend
- Temperature profile
- Recipe storage
- Alarm history



Dispersive and Distributive mixing

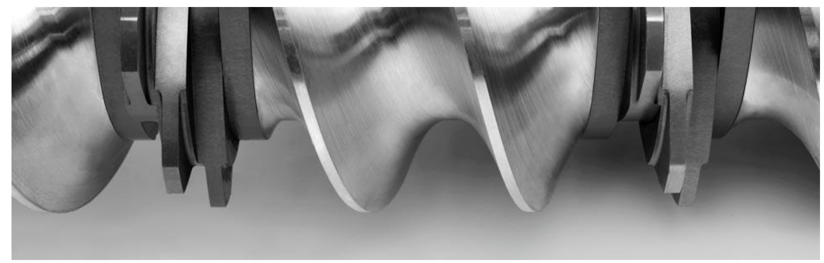
- For nearly all mixing applications a well dispersed and well distributed mixture is required.
- Distributive mixing can be achieved by splitting and reorienting the flow repeatedly
- Dispersive mixing can be achieved by passing the mixture through small regions of intense deformation.

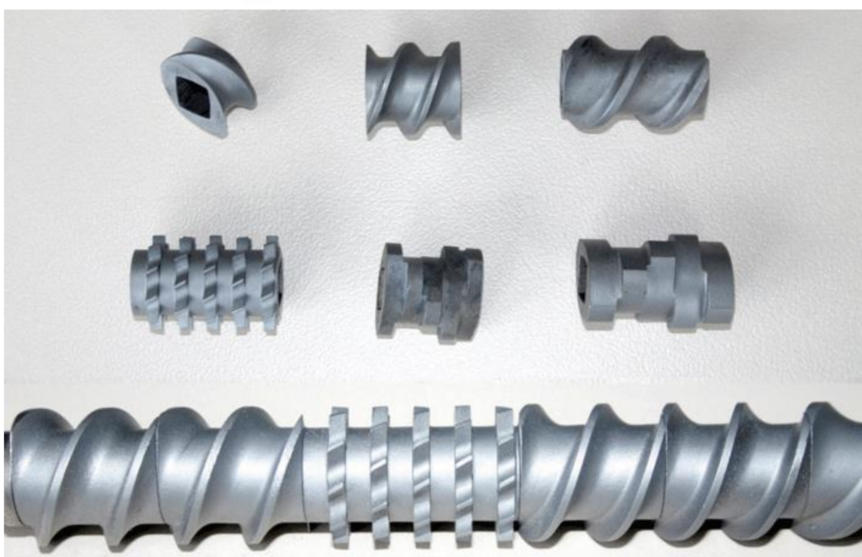


Mixing and composites, M. Kontopoulous Chee 18.2. p. 390presentation Queens University

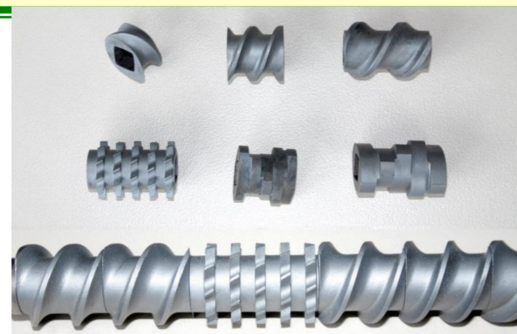
Eléments de vis modulables :

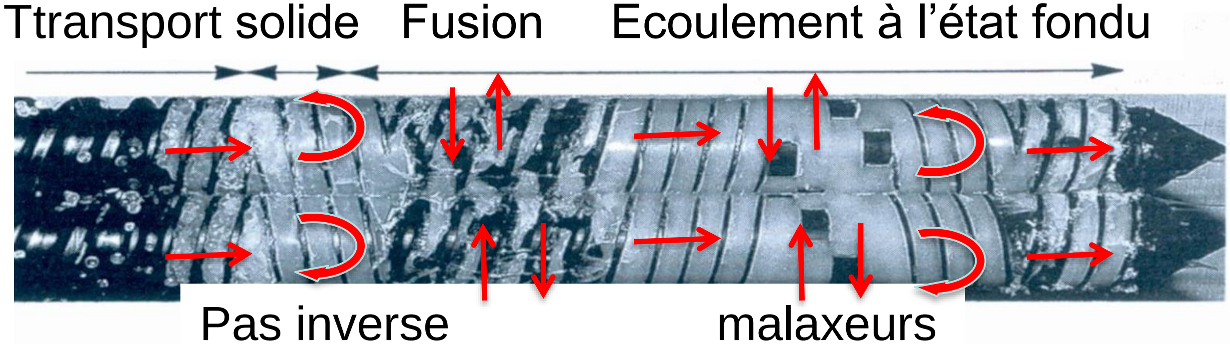
Convoyage
malaxage
contrefilets



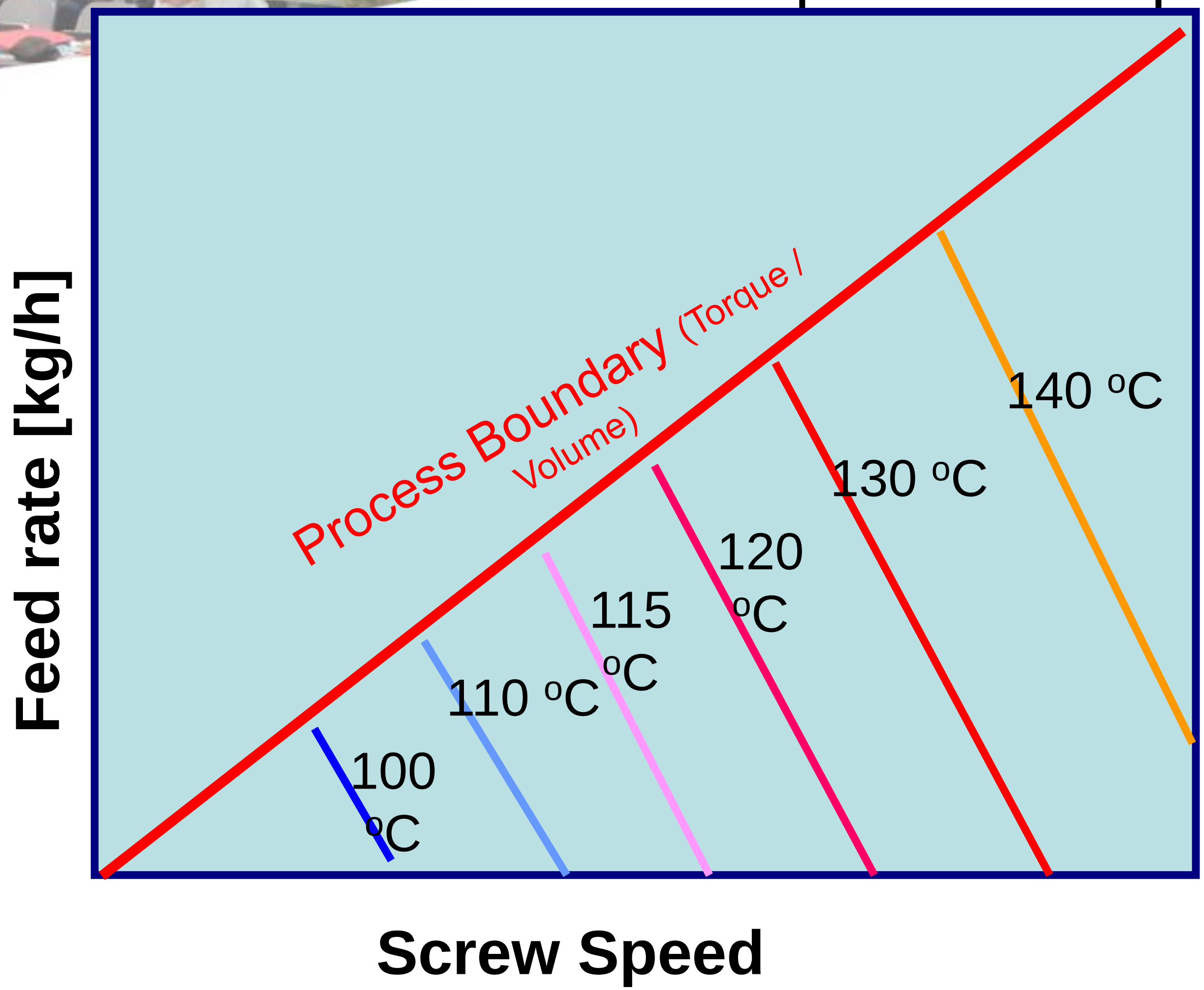


Assemblage des éléments le long de la vis



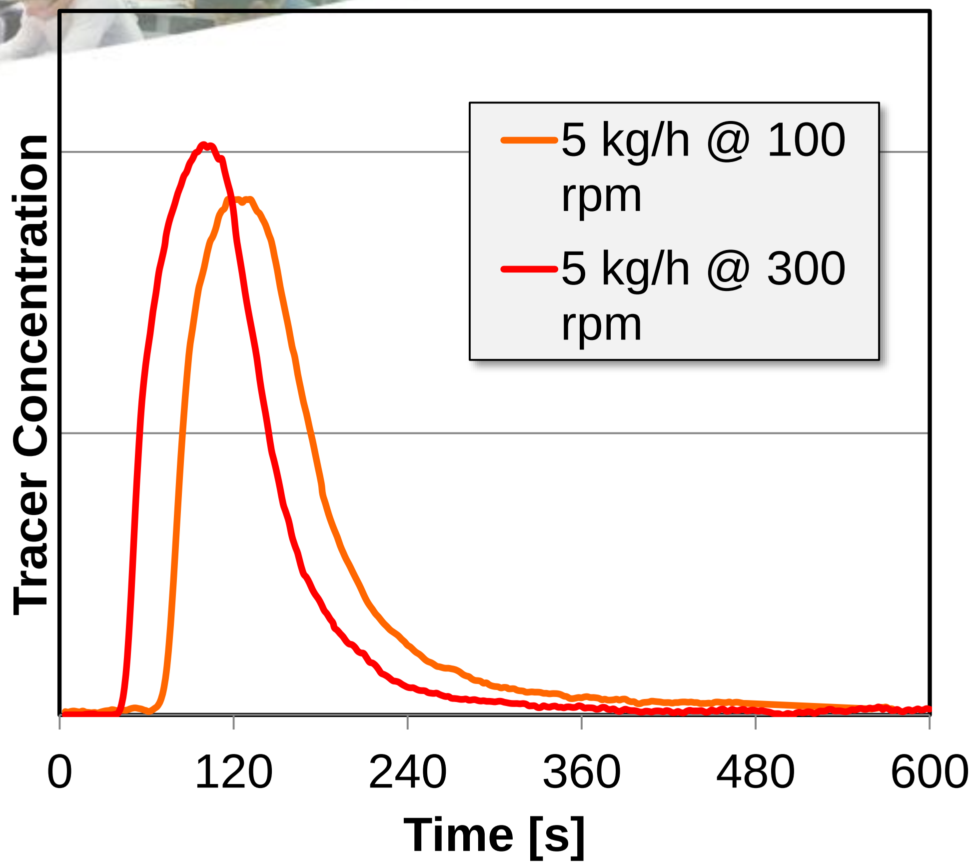


Melt Temperature Dependence



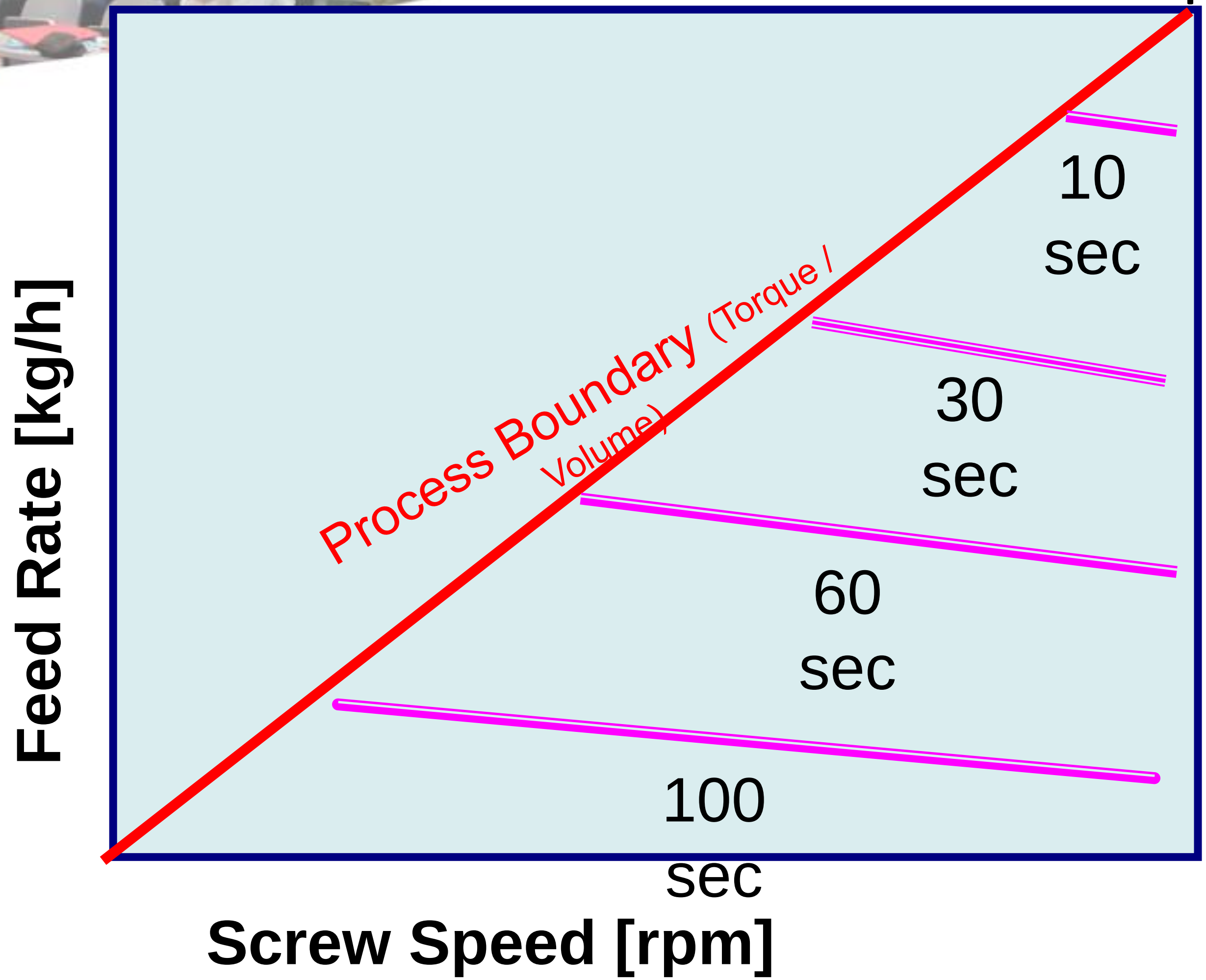
The Melt Temperature increases with increased Feed Rate and Screw Speed

Influence on Residence Time



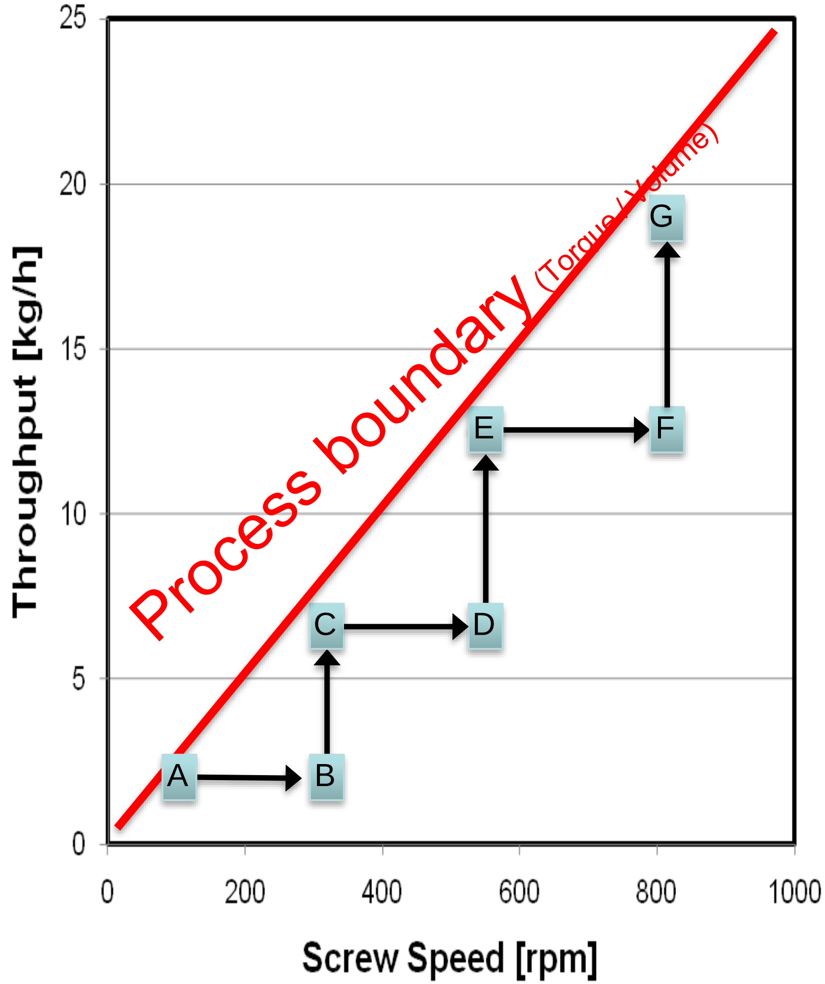
- Residence time mainly influenced by throughput
- Increased throughput reduces residence time
- Residence time less depending on screw speed

Residence Time Dependence



The Retention Time decreases with increased Feed Rate

Optimization of the Compounding Process



A Start with low screw speed and low throughput

B Increase screw speed

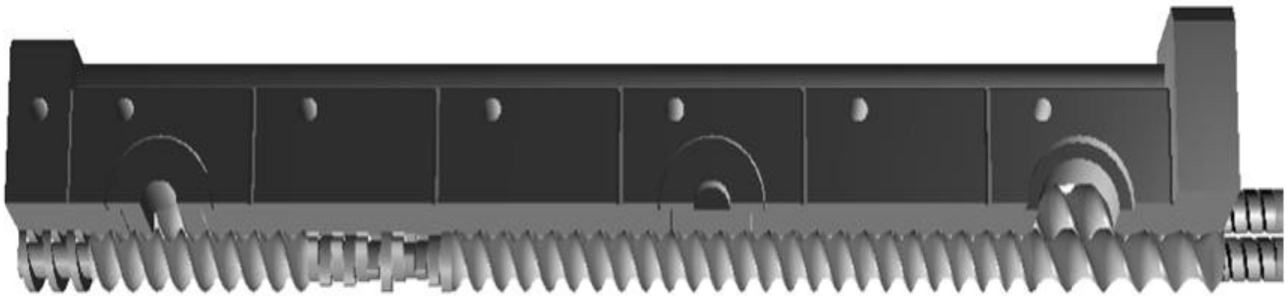
C Increase throughput (at same speed) until maximum torque is reached

D Increase Screw speed, torque decreases

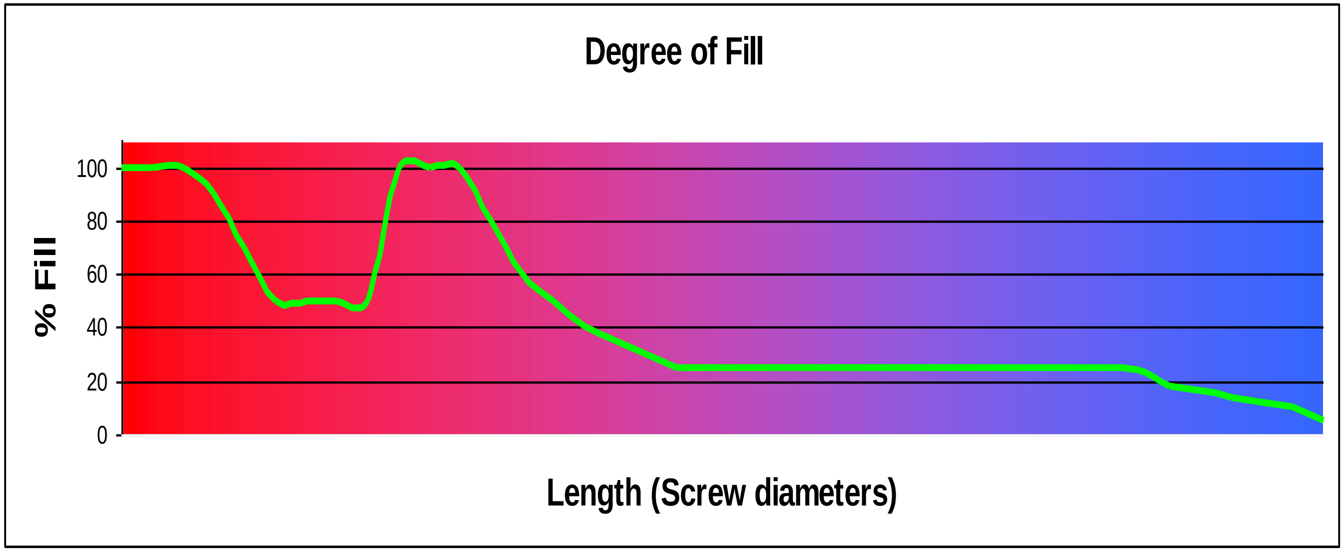
- Repeat A-D until maximum of system capacity

- Process boundary can be torque and volume limited
- Slope of boundary depends on:
  - Temperature profile
  - Screw Design
  - Material Blend

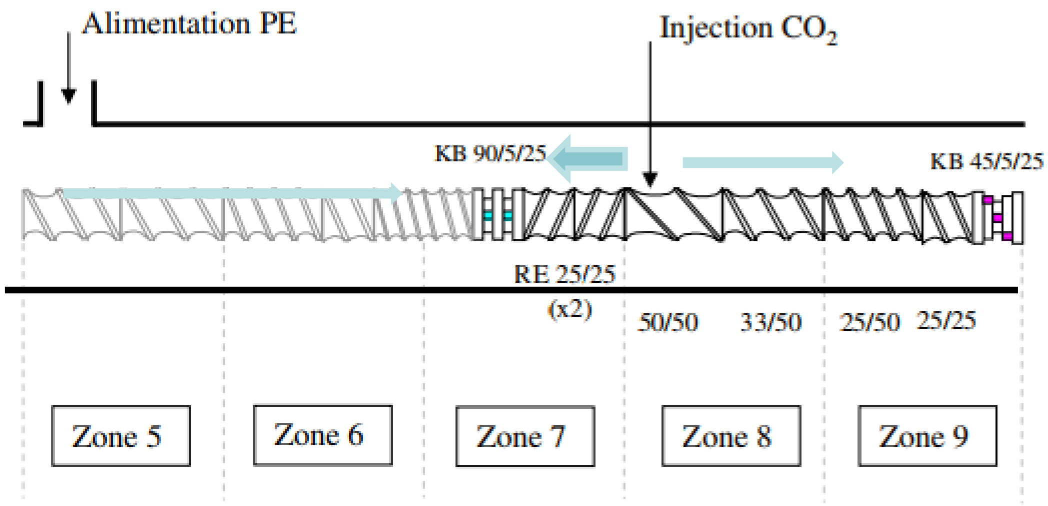
Degree of Fill along the Screws



Venting Mixing Feeding



Extrusion réactive
Injection de CO2 supercritique



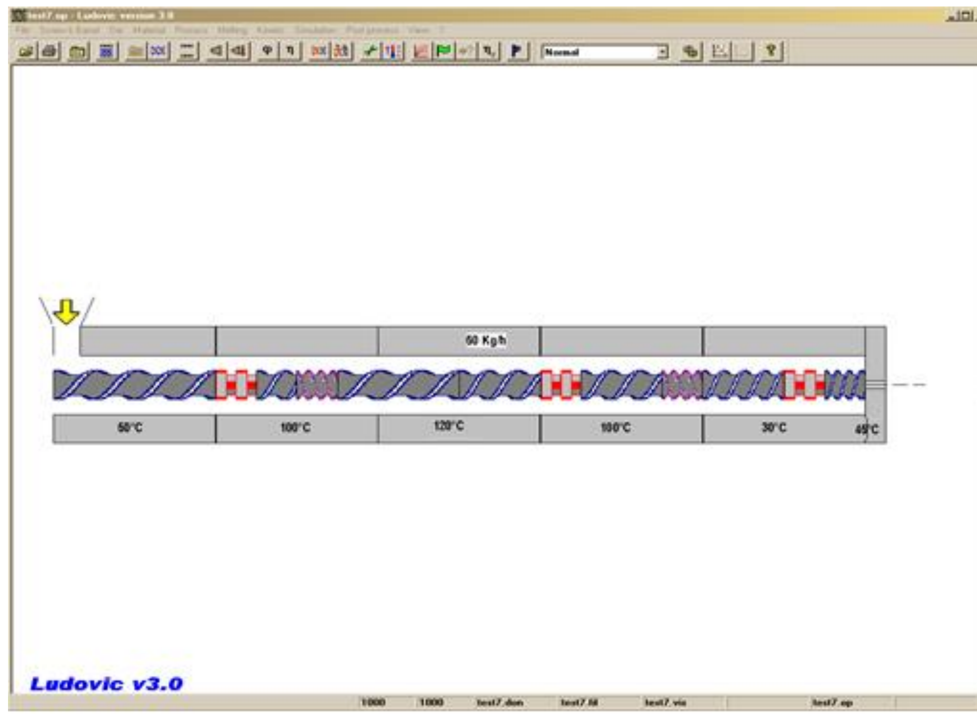
Nobelen, M. et al Engineering Science (2006), 61(16), 5334-5345.

Modélisation de l'écoulement

LUDOVIC

Logiciels de simulation de l'écoulement simulation de l'écoulement de la matière dans une extrudeuse bivis corotative

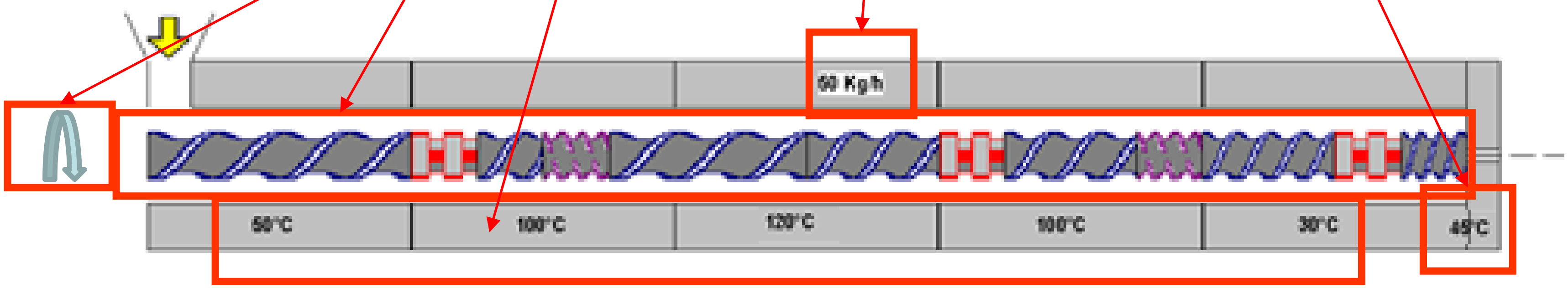
- Ludovic (CEMEF+INRA+S&CC (FRA))
- Sigma (Université de Paderborn (ALL))
- TXS (Polytech (USA))
- Akro-co-Twin-Screw (Université d'Akron (USA))



LUDOVIC Scale Up

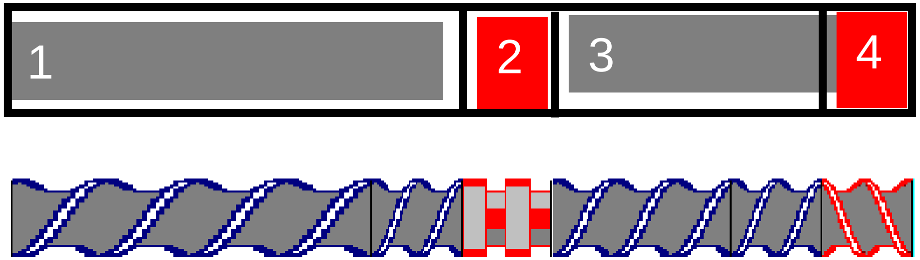
Les paramètres à optimiser sont :

1. Le profil de vis (suite ordonnée d'élt de vis)
2. Les températures des fourreaux
3. La température de la filière
4. La vitesse d rotation de la vis
5. Le débit



Extrusion réactive et passage d'échelle

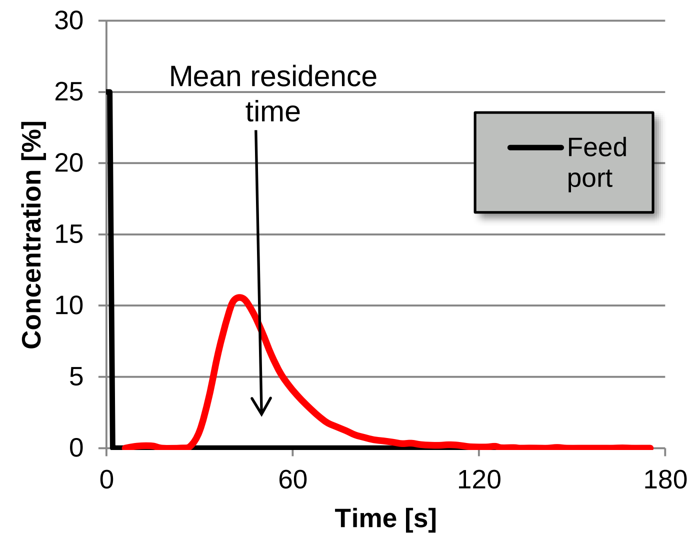
On suppose que les squelettes de la vis de laboratoire et de la vis industrielle sont identiques

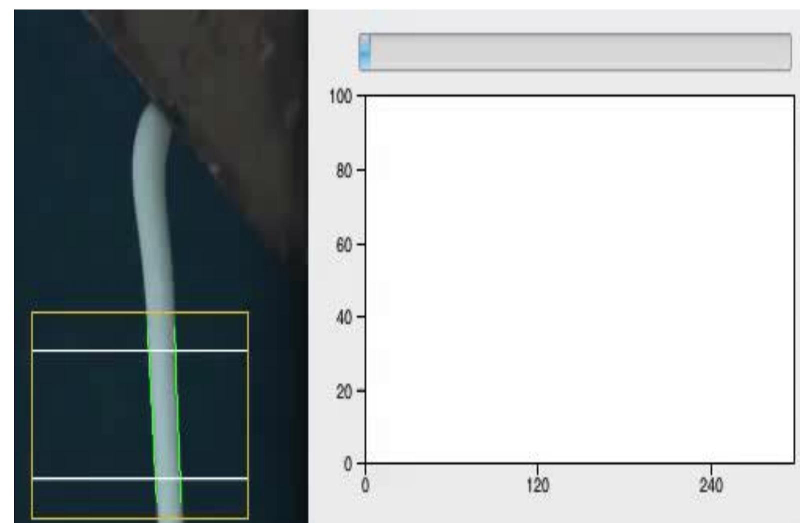


1. Zone de convoyage
2. Zone de malaxage
3. Zone de convoyage
4. Zone restrictive

Residence Time Measurement

- All known methods use tracers
  - At t_0 tracer added to feed port
  - Record tracer concentration at exit
  - Result: Residence time distribution
    - Mean residence time (calculated)
    - Width of distribution
  - Tracer selection criteria
    - Easy to detect
    - No influence on process
- Our approach:
  - Digital camera takes pictures (and records time),
  - Software detects strand and
  - calculates tracer color ratio (concentration)
  - Plots concentration vs. time





EMS -- L'énergie mécanique spécifique

$$SME\ (J/kg) = \frac{\omega(rpm)\ x\ T\ (N\ x\ m)\ x\ 60}{\varphi\left(\frac{kg}{h}\right)}$$

SME = Energie mécanique spécifique (kJ/kg)

ω = $vitesse\ de\ rotation(rpm)$

T = couple (N.m)

φ = débit massique (Kg/h)

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Université de Reims Champagne-Ardenne

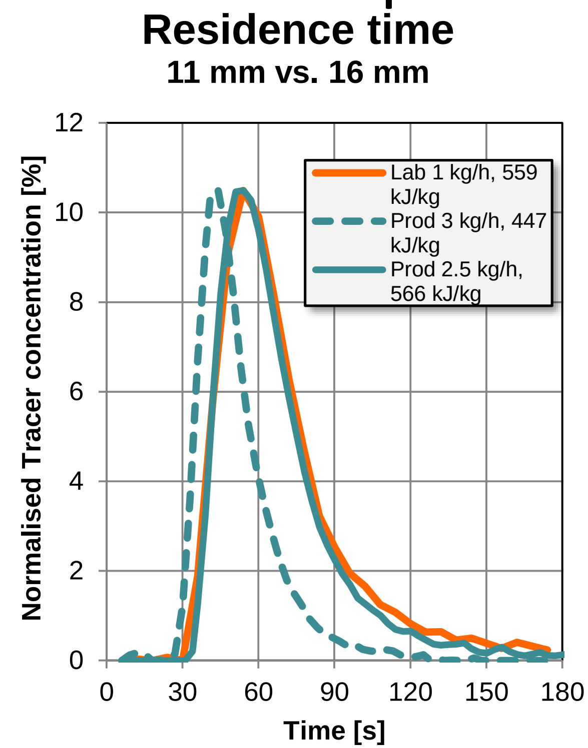
Process 11: Scale up Case Study

- Same process as production
- Portfolio wide constant geometry
- Trails on 11 mm compounder, save material and time
- Transfer knowledge to larger machine

Example (residence time)

- Same screw configuration
- Same screw speed
- Throughput transfer by:
- Adjust throughput until same specific energy obtained.

$$\dot{m}_P = \left(\frac{D_P}{D_L}\right)^3 \cdot \dot{m}_L$$



1. RT_m: 65.3 s
2. RT_m: 51.0 s
3. RT_m: 67.3 s

Almost perfect match within just 2 steps

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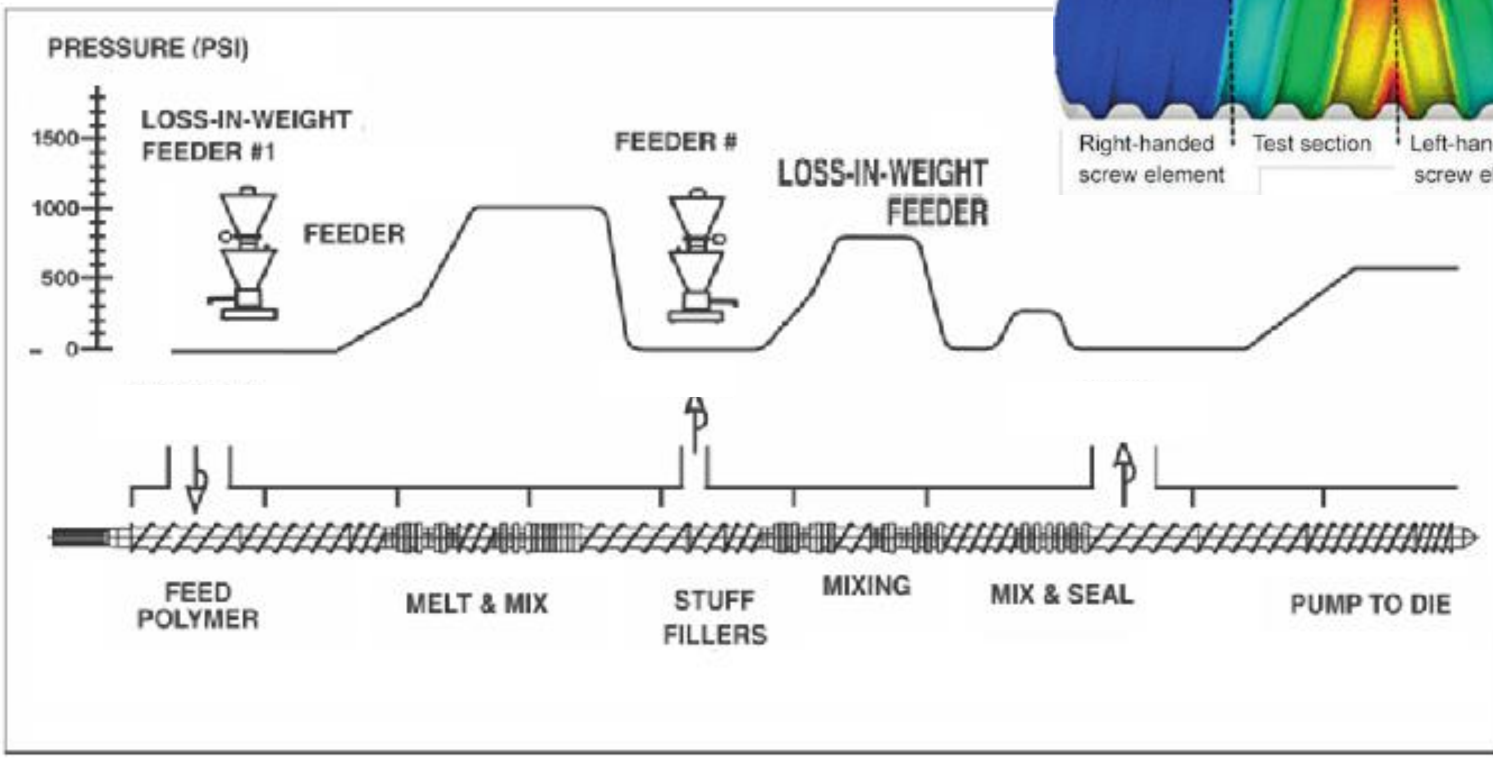
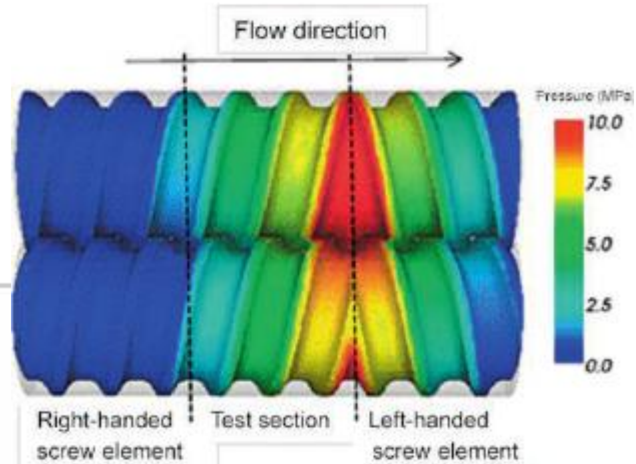
Addition séquentielle et profil de pression

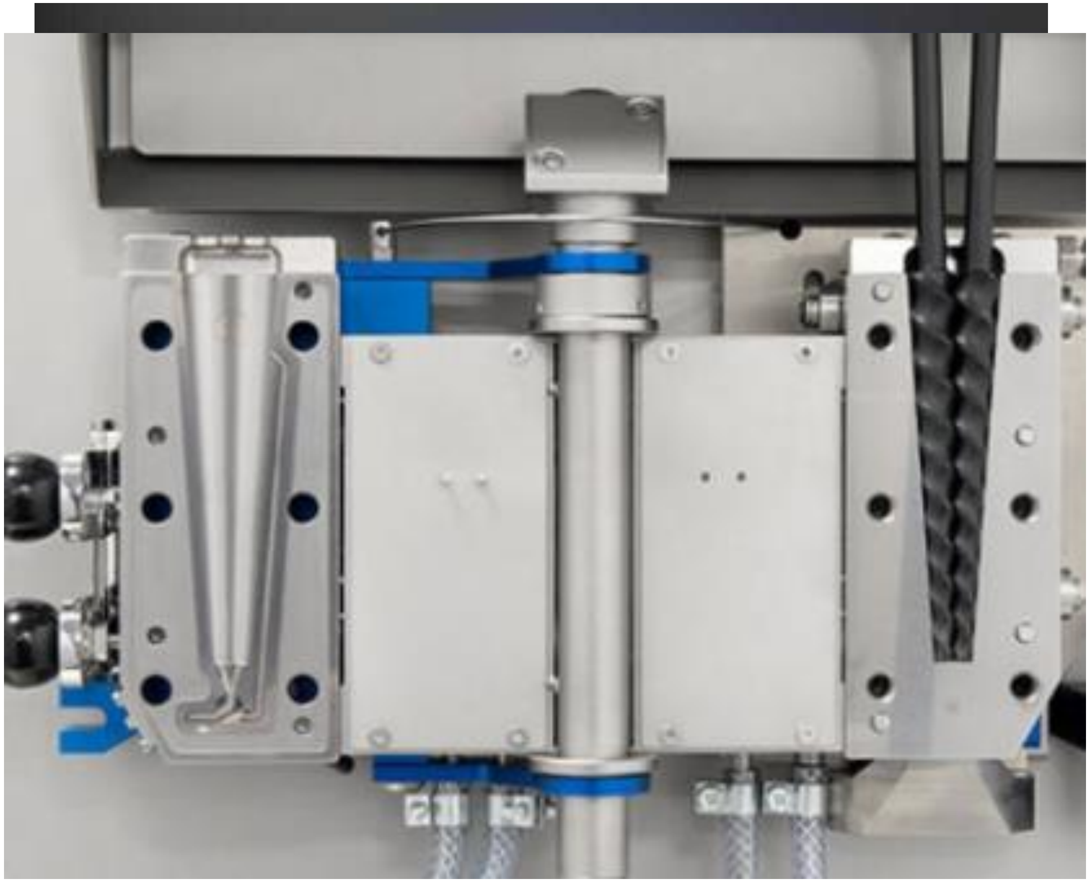




HAAKE MiniLab

Micro Rheology Compoun

1996 microcompoundeur



Conical twin-screw compounder:

co- and counter rotating option
automatic bypass operation for extrusion/recirculation
viscosity measurement integrated in backflow channel
pneumatic feeding, option continuous or manual feed
inert gas flush
High–Temperature up to 420°C
digital and graphic data display
manual and computer control

HAAKE MiniLab
Micro Rheology Compoun

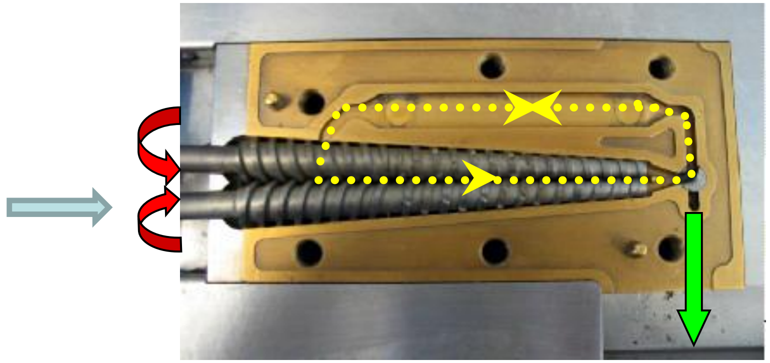
2000 microcompoundeur

Conical twin-screw compounder:

- co- and counter rotating option
- automatic bypass operation for extrusion/recirculation
- viscosity measurement integrated in backflow channel
- pneumatic feeding, option continuous or manual feed
- inert gas flush
- High–Temperature up to 420°C
- digital and graphic data display
- manual and computer control

Mini Extrudeuse 10g « De la Paillasse …

Bi- vis avec mode recirculation (cinétique) co- ou contra-rotative



Microextrudeur Bi-vis (10g)
Minilab rheomex (Thermo Process

Sample size	Approximately 4 to 5.5g
Maximum temperature	350°C
Screw diameter	5/14 mm (conical)
Screw length	109.5 mm
Screw speed	10-360 min^{-1}
Torque range	0-5 Nm
Number of heating/cooling zones	1
Cooling medium	Water

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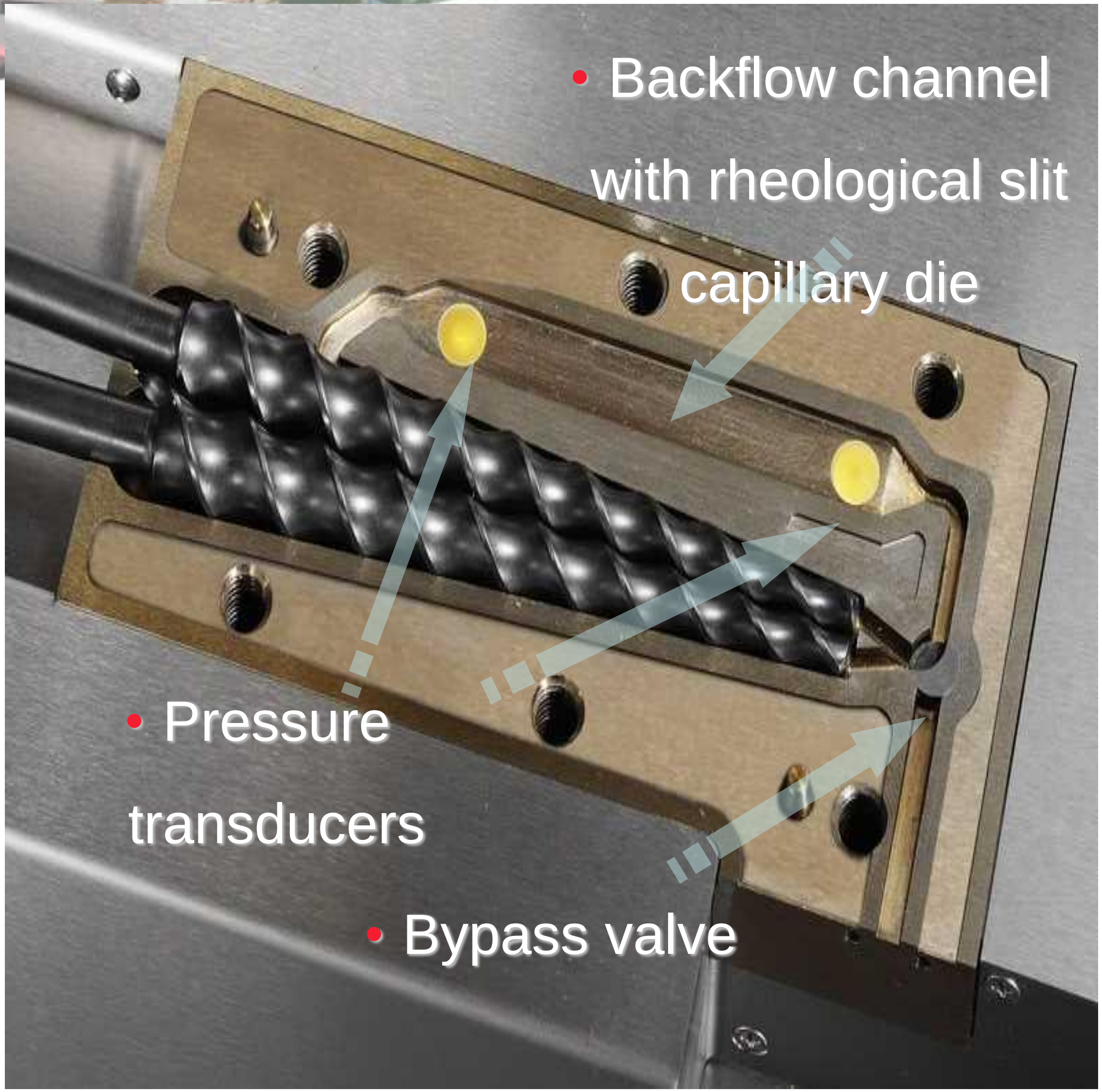
HAAKE MiniLab II – Typical Applications

Microextrudeur Bi-vis (10g)
Minilab rheomex (Thermo Process

Micro sample-amount (5 g)

- **Development of new polymers**
- **Testing of expensive materials**
- **Material studies at universities**
- **Reactive extrusion**
- **Compounding of nano materials**
- **Sample preparation (in combination with the HAAKE MiniJet injection moulder)**
- **Mini production e.g. “50 grams per hour”**
- **Hot Melt Extrusion (pharma)**
- **Additive formulation**
- **Quality Control**

HAAKE MiniLab
- Barrel Desig



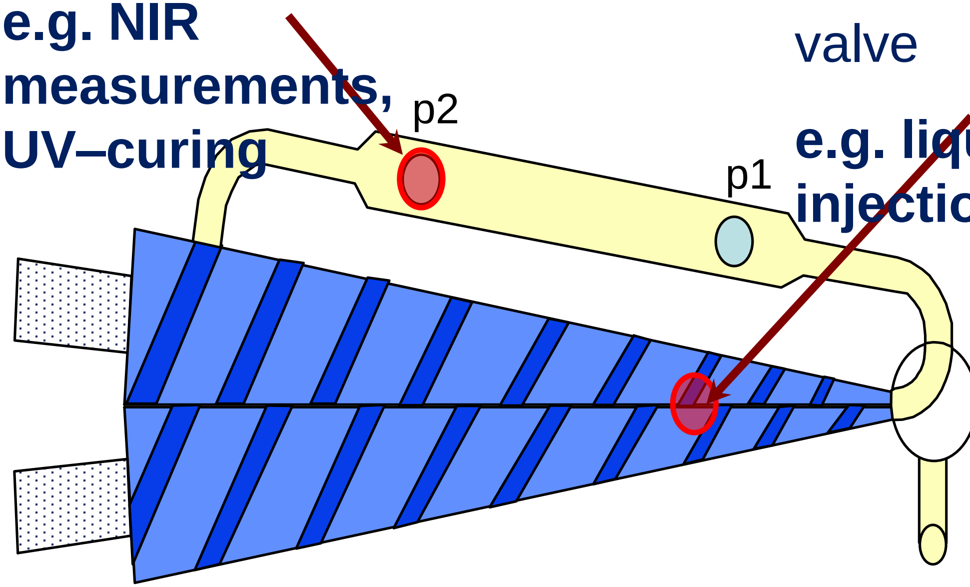
Optional sensor and feed ports 557-2197

½“ UNF port
opposite 2nd. pressure port (upper barrel half)

e.g. NIR measurements, UV–curing

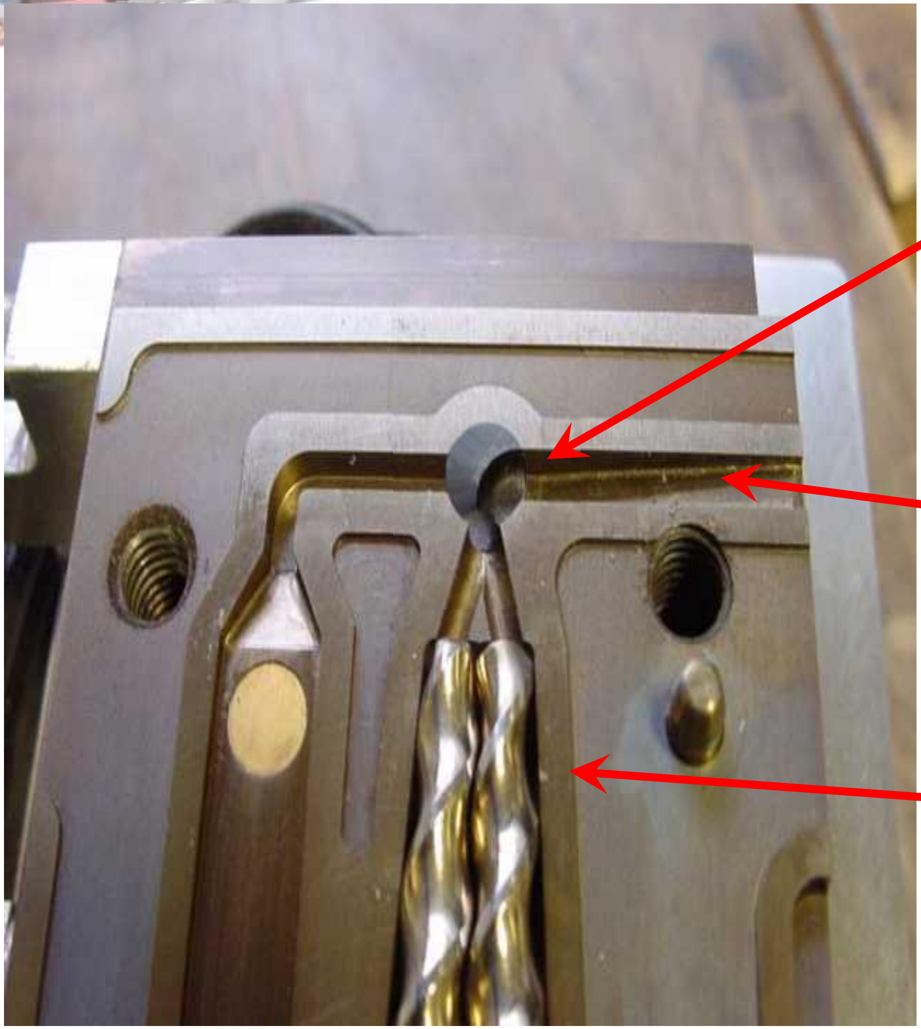
½“ UNF port
(upper barrel half) for non return valve

e.g. liquid, or gas injection



Factory installed only

HAAKE MiniLab II - Barrel Design



Easy cleaning of the outlet channel

Build in slit die

New rod die plates on request

Improved hardness, 58HRc, no TiN coating necessary

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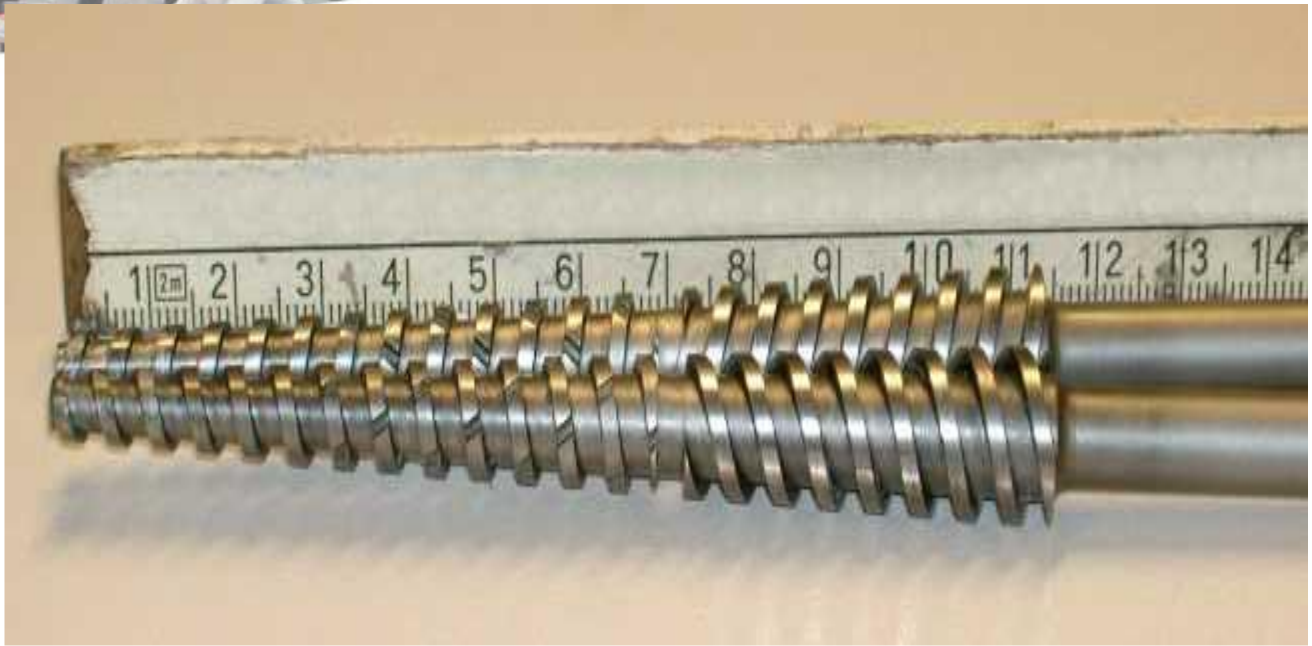
Characteristics of HAAKE MiniLab screw types

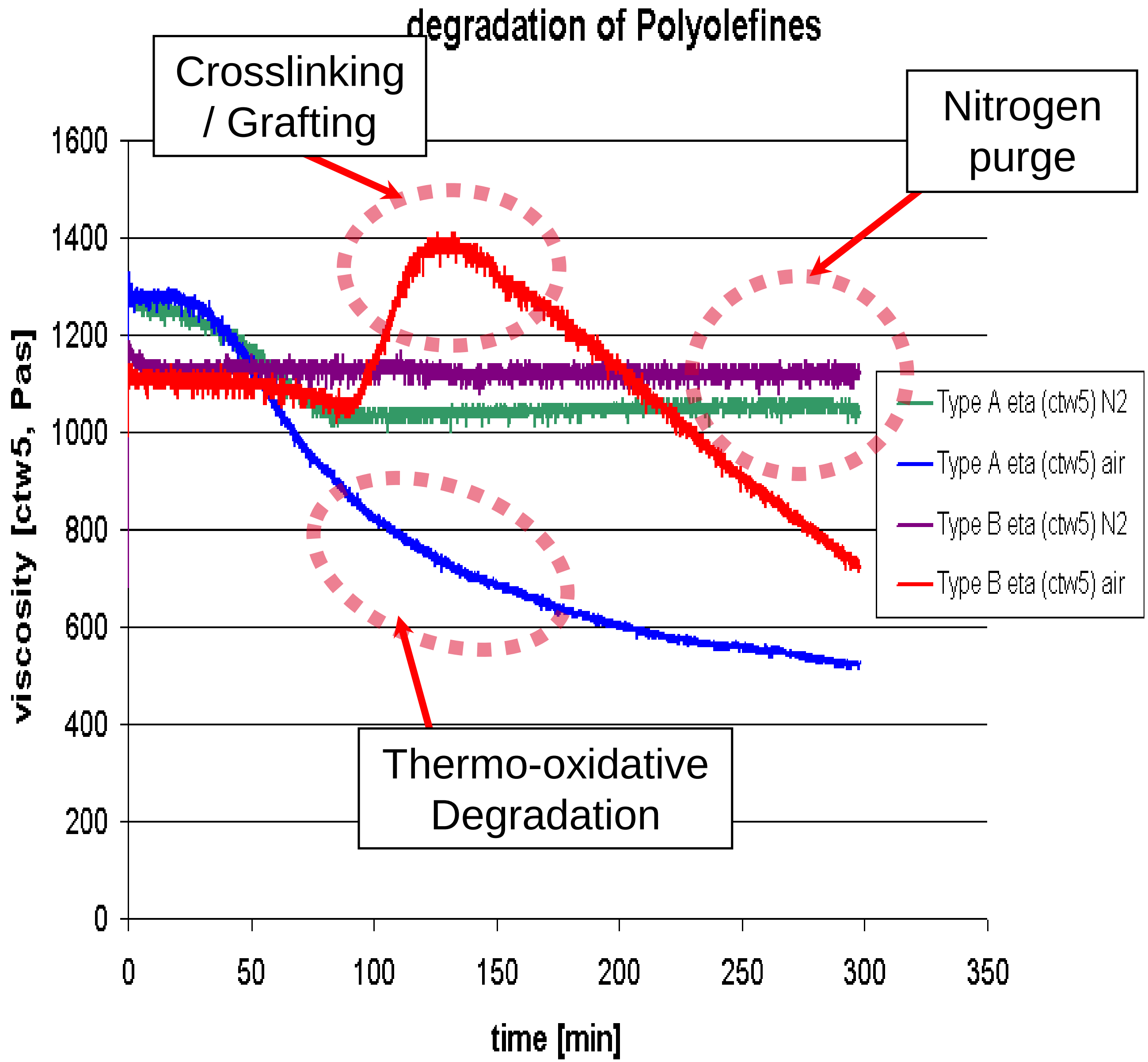
	Co-Rotating	Counter-Rotating
Residence time distribution	wide	narrow
Forced extrusion	-	+
Cleaning	+	-
Extruded amount	+	o
Mixing properties	++	o
Pressure built-up	o	++
Rheological measurements	o	++
Required duration of blending	++	o

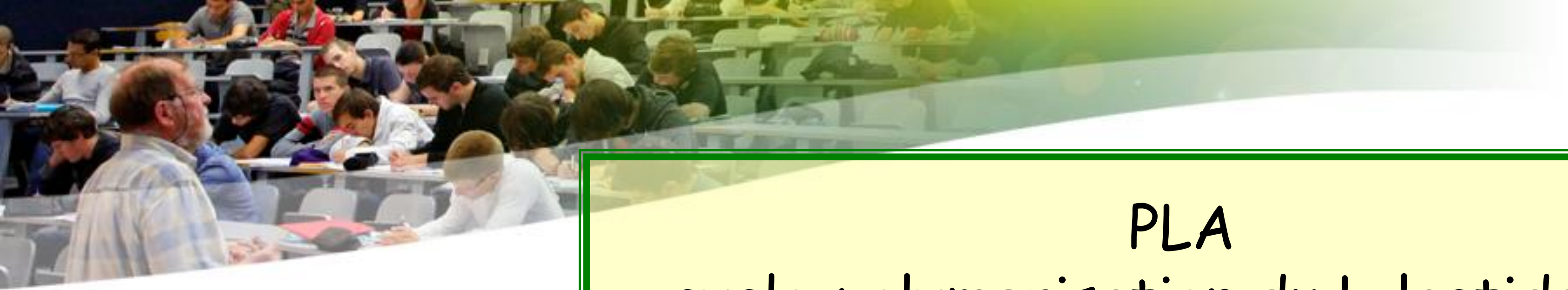
HAAKE MiniLab Counter Rotating Screws



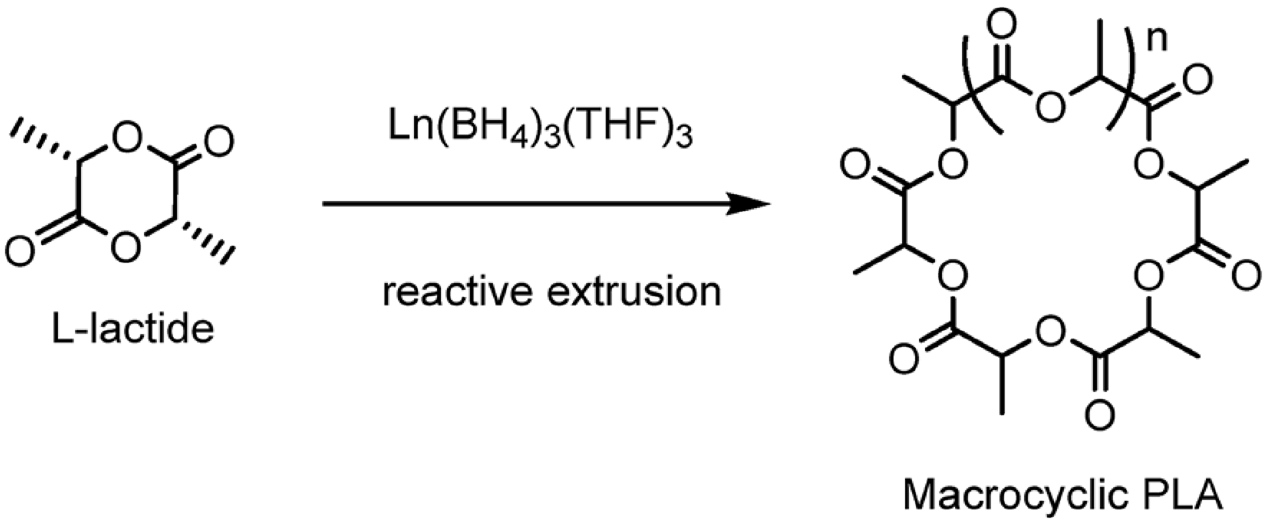
- Intermeshing counter rotating screws are most effective to improve results melt extrusion of multi wall carbon nanotube composites. Due to higher shear agglomerates are well distributed. Degradation of Stabilized PMMA and MWNT was not observed [1].

[1] R.E. Gorga, R.E. Cohan, (MIT), Toughness enhancements in PMMA by MWNT, Journal of Polymer Sci. ***42*** *2690-2702 (2004)*


degradation of Polyolefines
Crosslinking / Grafting
Nitrogen purge
Thermo-oxidative Degradation
viscosity [ctw5, Pas]
1600
1400
1200
1000
800
600
400
200
0
0
50
100
150
200
250
300
350
time [min]
Type A eta (ctw5) N2
Type A eta (ctw5) air
Type B eta (ctw5) N2
Type B eta (ctw5) air



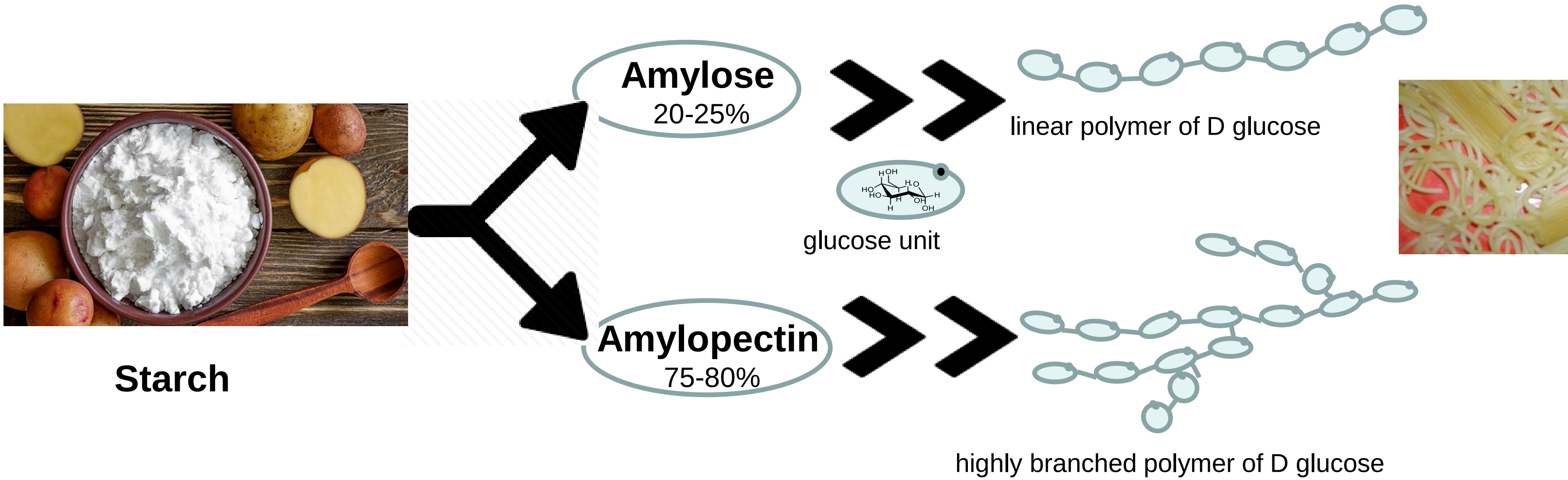
PLA
cyclo-polymerisation du L-lactide par Extrusion reactive



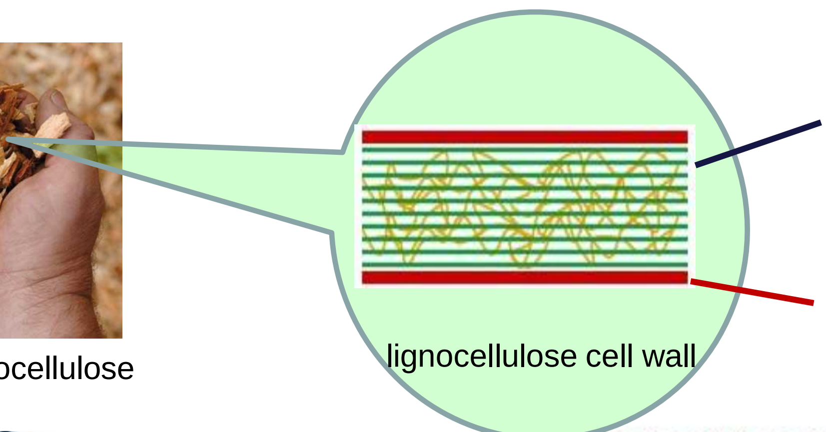
130°C ; 77% conversion; MW 30 000 g mol-1;
20 min ; poly-dispersité 1.23–1.79

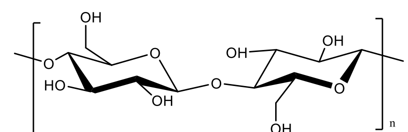
F. Bonnet ,F. Stoffelbach, G. Fontaine S. Bourbigot RSC Adv., 2015, 5, 31303

Extrusion réactive de polymères naturels

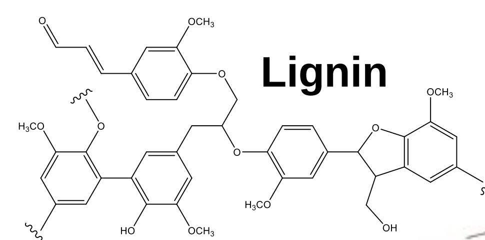


Wood = source of lignocellulose





Cellulose



Lignin

ICMR Institut de Chimie Moléculaire de Reims UMR CNRS 7312

Christophe Bliard

Université de Reims Champagne-Ardenne

Lignin

Chemical modification of starch by reactive extrusion.

3.1. Ring-opening of epoxides
3.1.1. Hydroxypropylation
3.1.2. Cationic starch.
3.1.3. Crosslinking with epichlorohydrin.
3.2. Ring-opening of lactones.
3.3. Esterification with anhydrides
3.4. Esterification with carboxylic acids and esters
3.5. Etherification with Alkyl Halides DS 0,1-0,3(1990-2000) DS 1 (2016)
3.6. Esterification with vinyl esters
3.7. Reaction with isocyanates or blocked isocyanates .

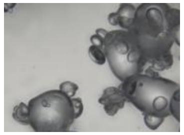
"*The advantages of REX processing are a flexible, lowcost infrastructure and, with the correct selection of chemistry, high throughput processing at high starch concentrations with high conversions and few by-products*"

Moad G., Progress in Polymer Science 36 (2011) 218–237

Extrusion et Photoréticulation

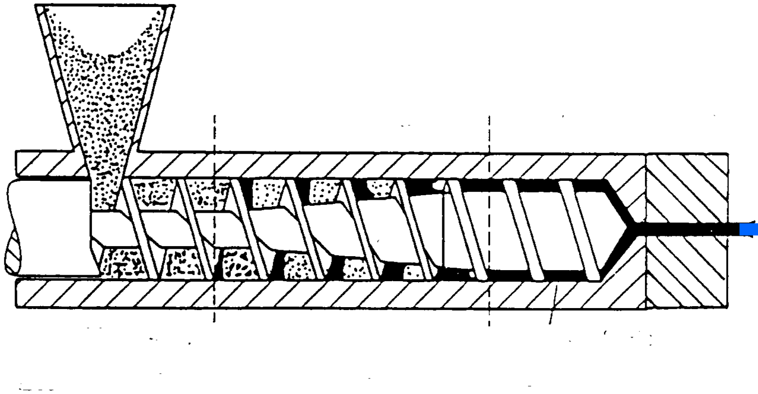
Premiers travaux

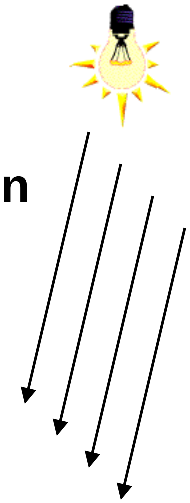
Amidon natif
+ Plastifiant
+ Photoactivateur

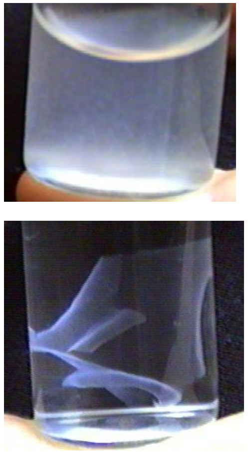


Extrusion

Photoréticulation



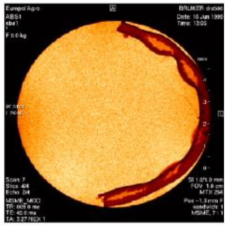




Insoluble & biodégradable

Amidon Photoréticulé

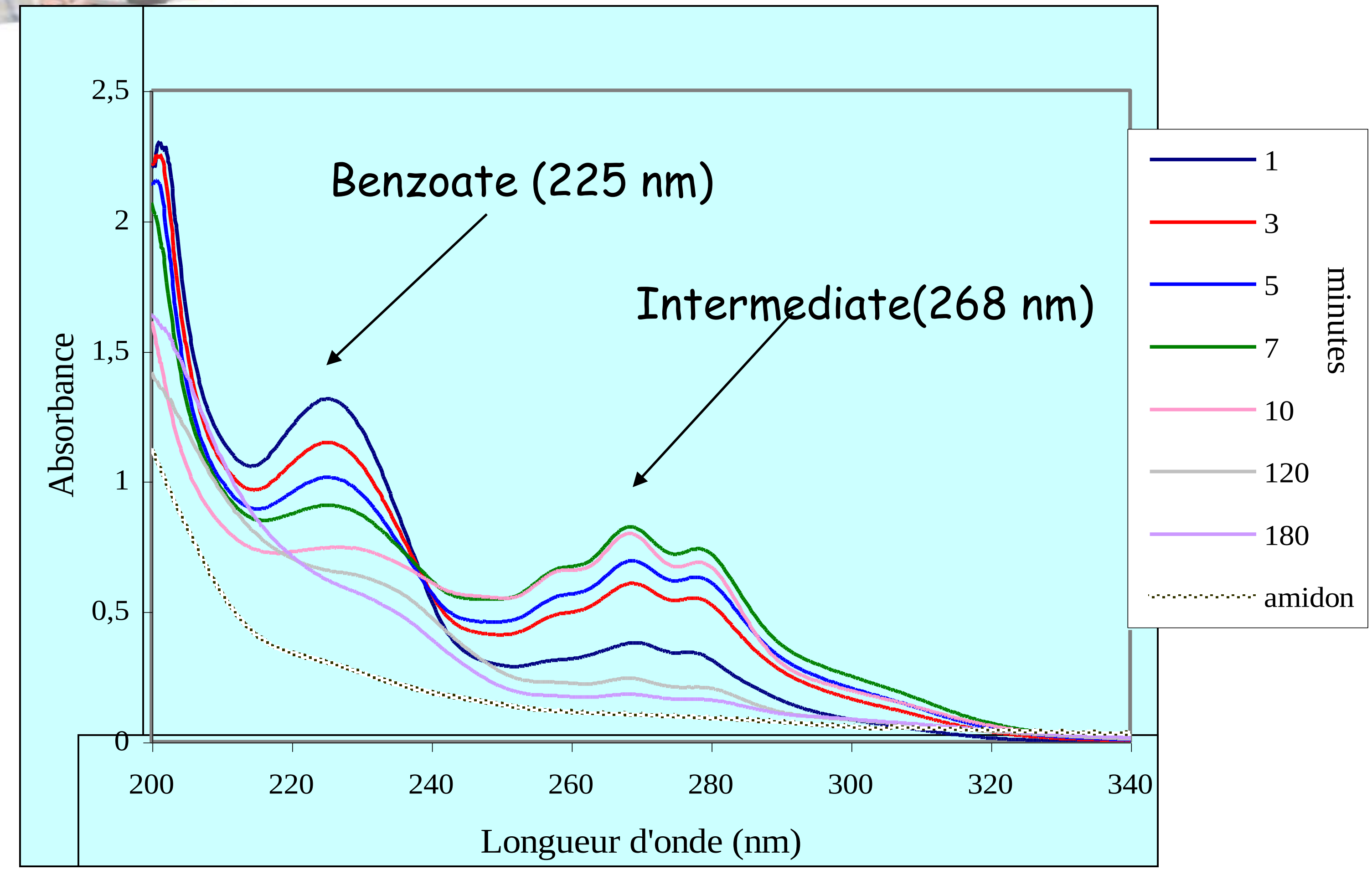
Irradiation



Mais Prop^{tés}. Mécaniques ↘

Brevet N° 0005652 du 03 mai 2000. J. Delville, C. Bliard, C. Joly, P. Dole. Pat. WO2001083610A1
Delville J.et al Carbohyd. Polym. 49 (2002)

[redacted]

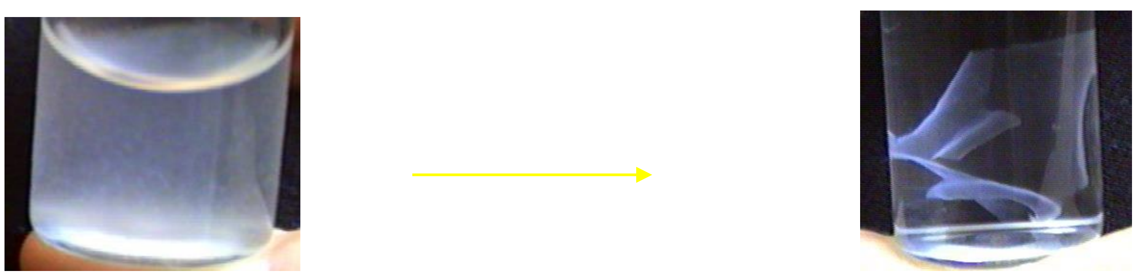


J. Delville, C. Joly, P. Dole, C. Bliard, Carbohyd. Polym., 49, 2002, 71-81.

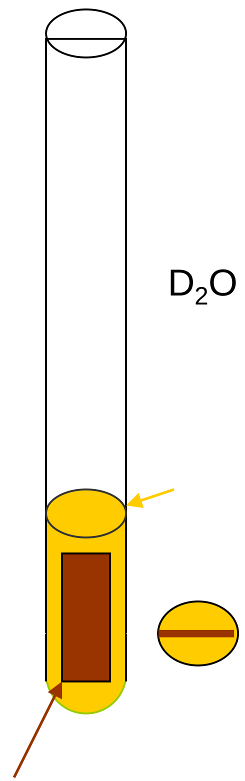
⇒ Optimal System

- 20% sorbitol/glycerol

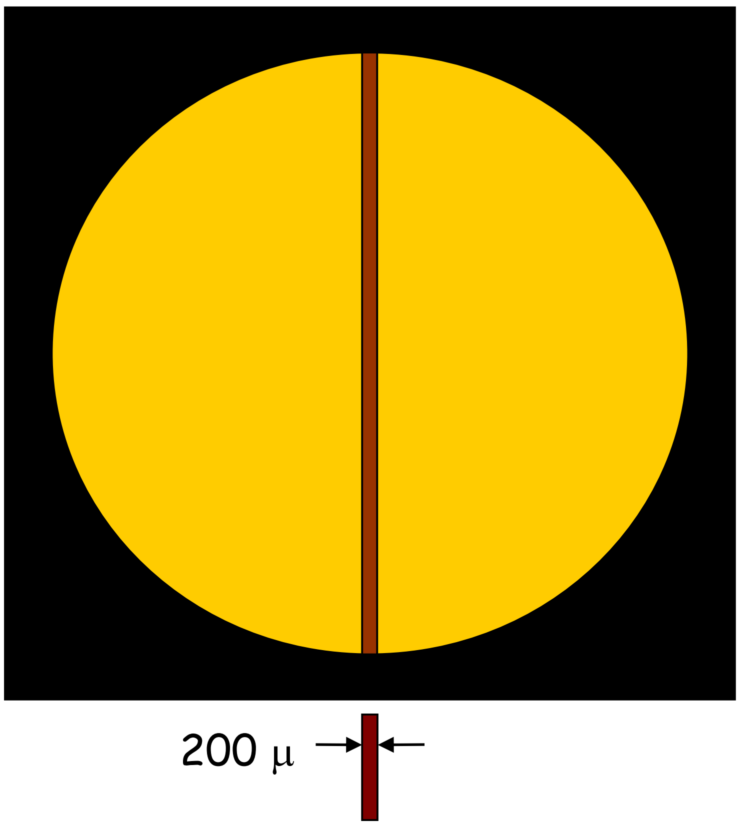
  3% Sodium benzoate
- 10 min. UV Curing
- Insolubles : 98%
- Swelling : 4



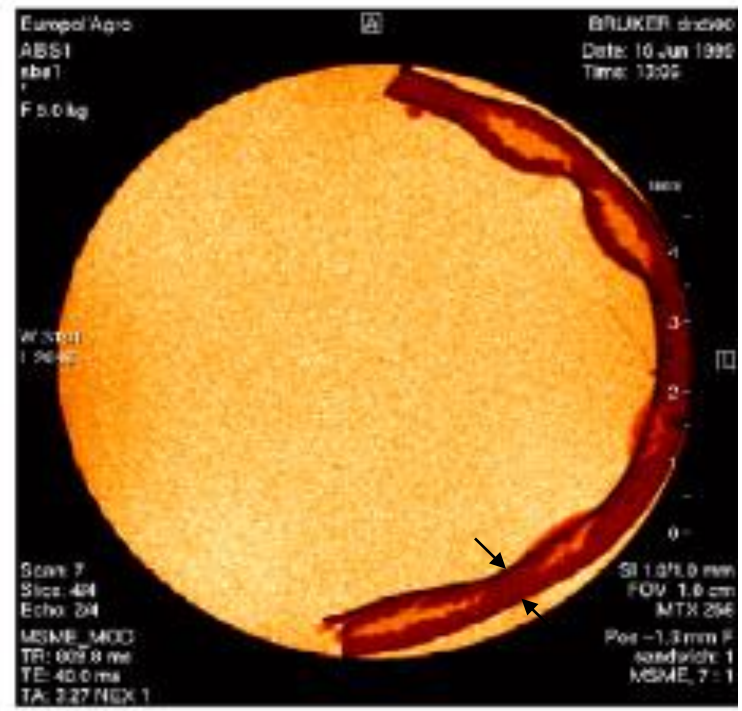
NMR imaging of a UV cured starch film in D_2O



before swelling

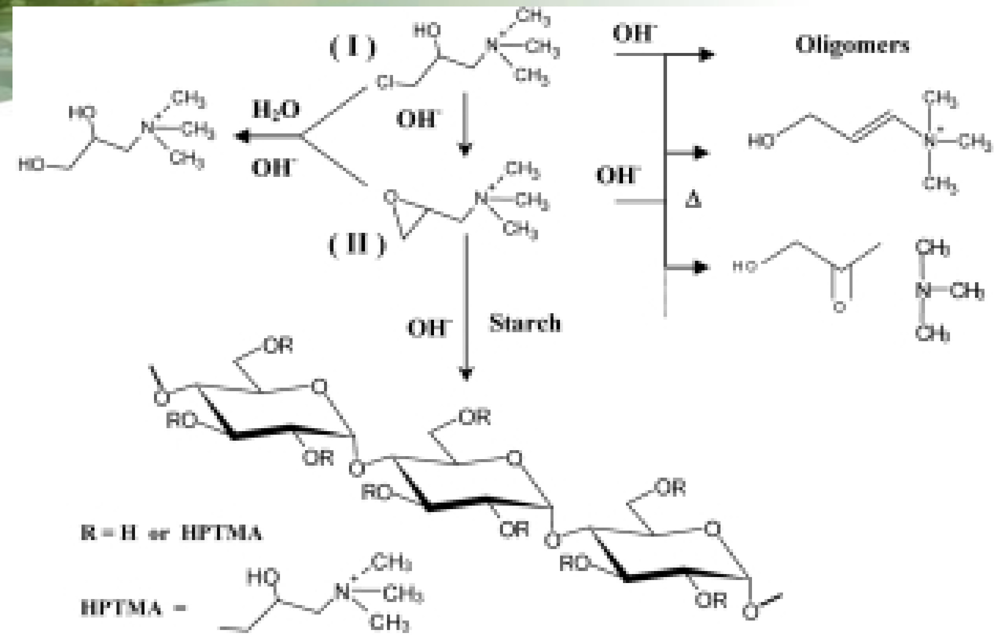


after swelling

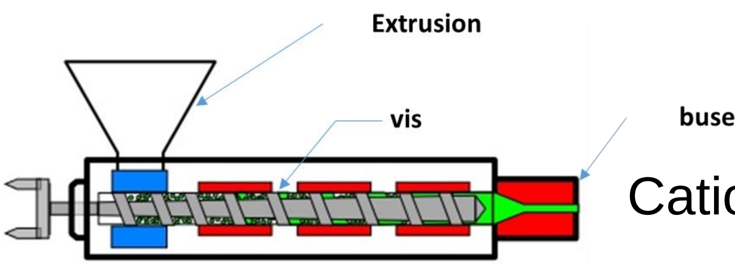


300 µ

The max depth of photo crosslinking is 100 µm



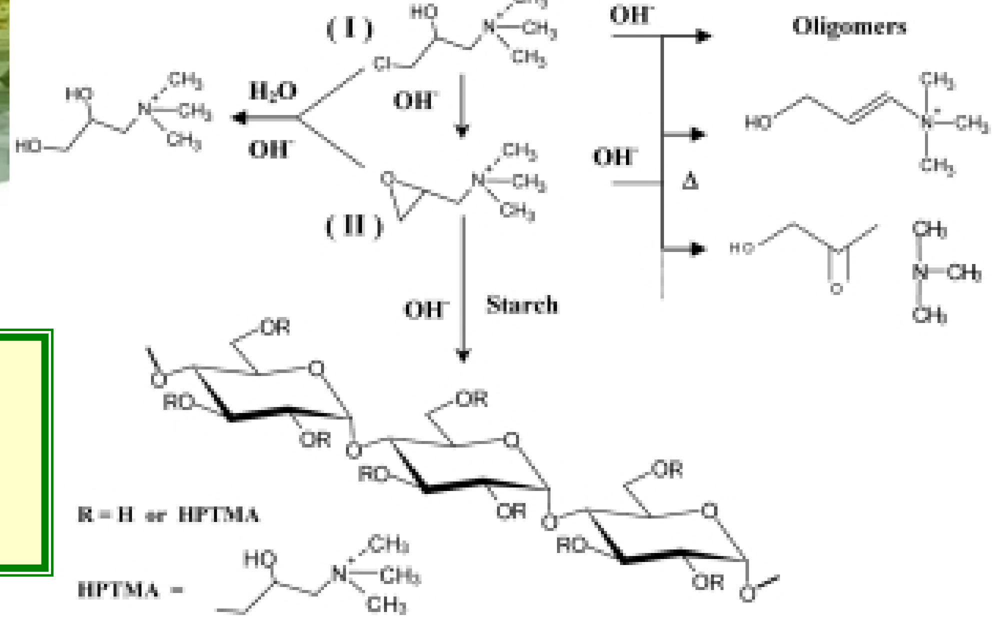
Starch + Gly + Quab



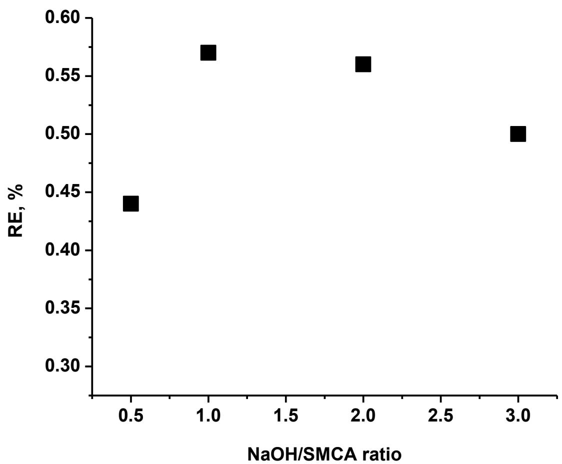
Cationic Starch

Modification chimique

Francoise Berzin, Lan Tighzert, Christophe Bliard, Ali Ayoub. Study of the Thermoplastic Wheat Starch Cationisation Reaction under Molten Condition. Starch/Stärke, 2004, 56 (11), pp.513-519. ⟨10.1002/star.200300272⟩. ⟨hal-02074504⟩



Cationisation de l'Amidon par Extrusion réactive



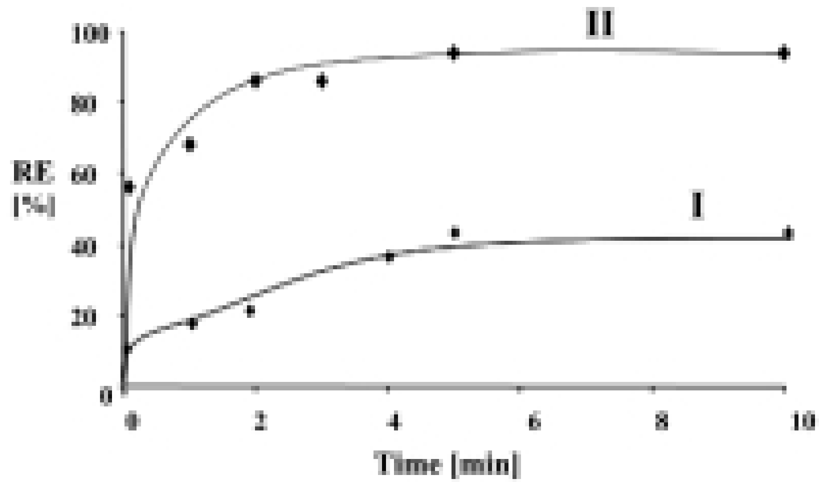
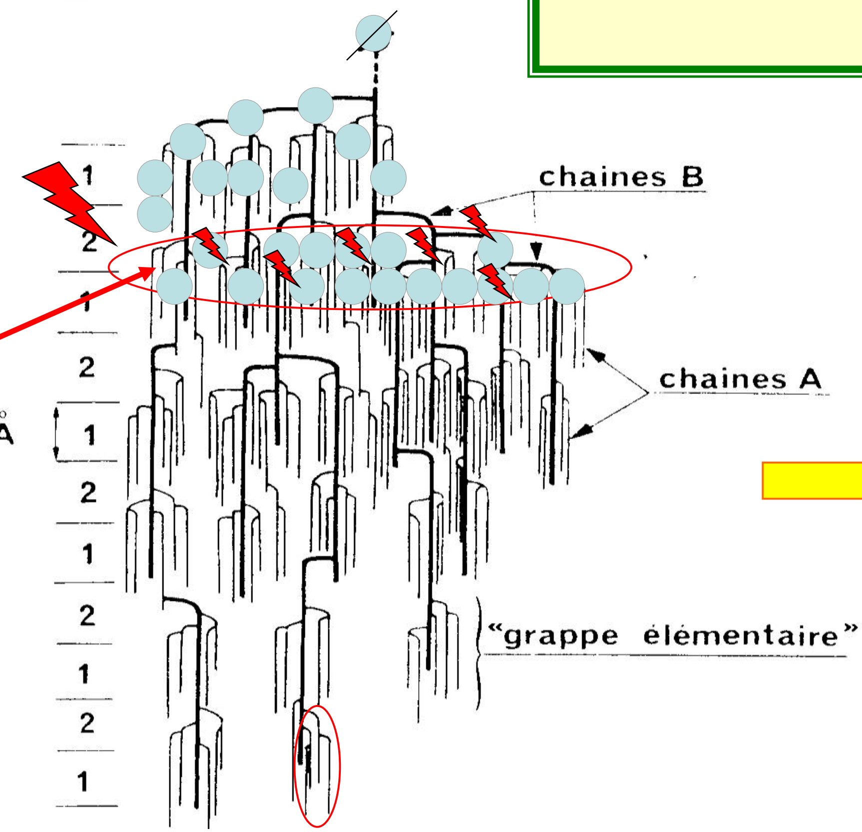


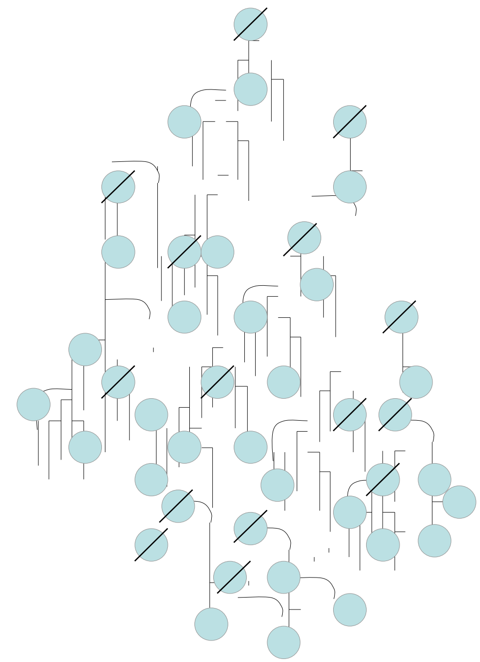
Figure 1 Influence of NaOH/SMCA ratio on the reaction efficiency

Ayoub A. Bliard C. ; Starch/Stärke 55 (2003) 297–303
Ibid. Starch/Stärke, 56 (2004) 513-519

Amylolyse enzymatique de l'Amidon par Extrusion réactive



Amylopectin



MIMOS : Malto – IsoMalto OligoSaccharides

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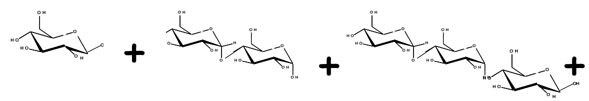
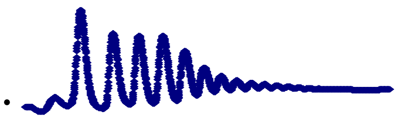
ICMR Institut de Chimie Moléculaire de Reims UMR CNRS 7312
Christophe Bliard

Amylose

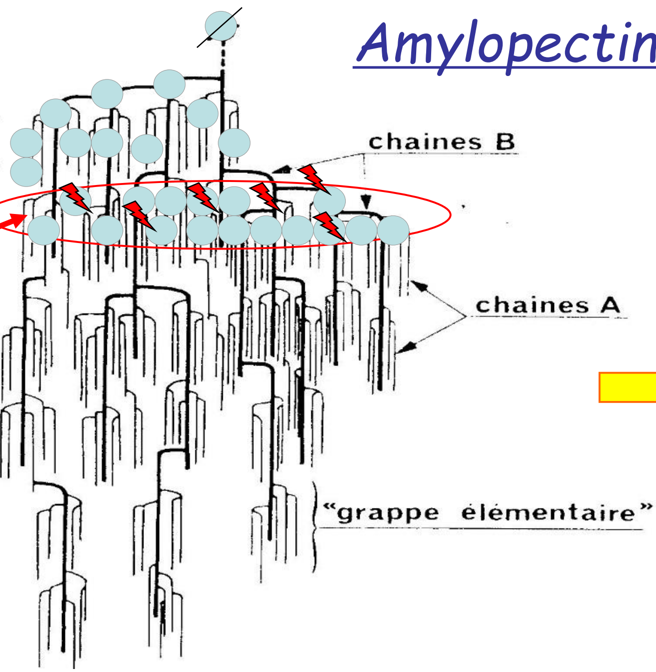
MOS



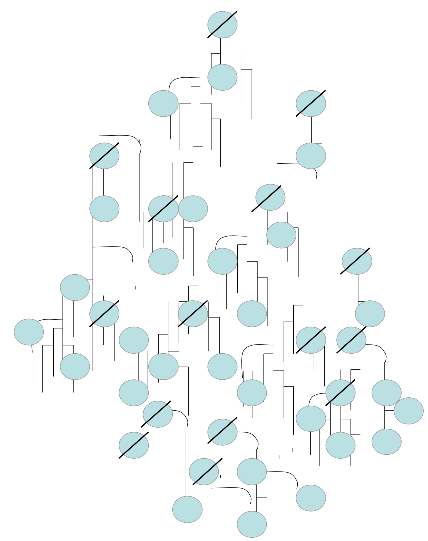
DP:1 2 3 4 5 6 7 8 9 ...



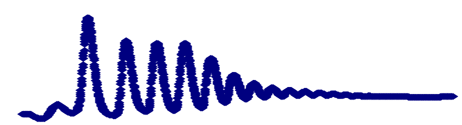
Amylopectin



MIMOS



DP:1 2 3 4 5 6 7 8 9 ...



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UMR CNRS 7312
Christophe Bliard
cnrs
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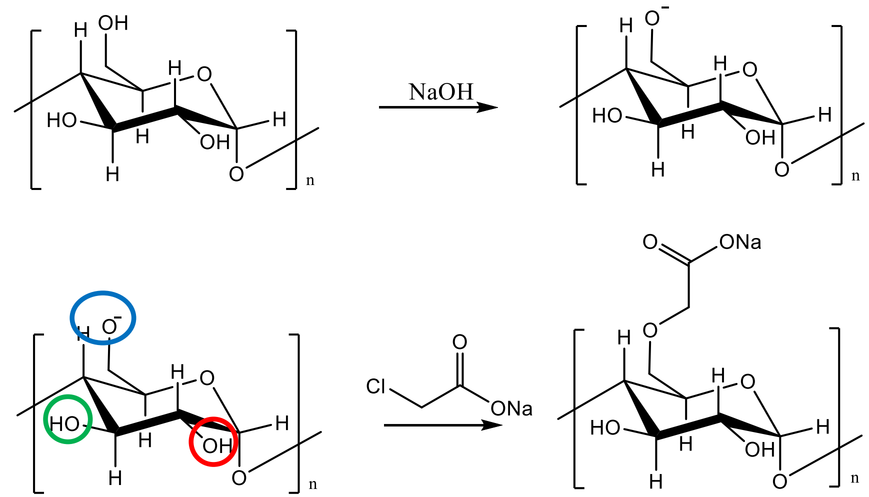
Carboxyméthyl Amidon Batch

Industrial large batch production of carboxymethylated starch (CMS) with sodium monochloroacetate (SMCA)



ClCH2COONa + ROH → ROCH2COONa

CMS

- substitution at the 3 OH positions of the AGU **C2, C3 and C6**
- maximum **theoretical DS** for starch is 3

- In practice, it is fairly difficult to achieve a high DS and **reaction efficiency (RE)** values without damaging the starch molecules

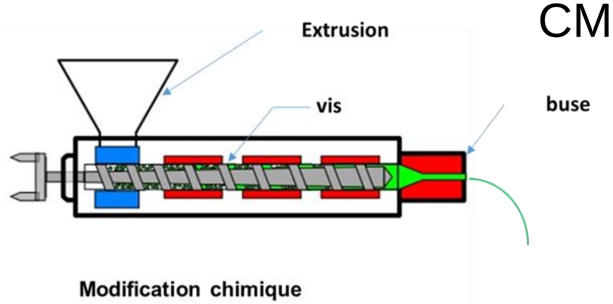
- ubiquitous equipment
- producing large amount of CMS
- quantity solvent & reagents used
- low RE & Poor reaction control
- high residence time
- slow heat transfer
- by-products

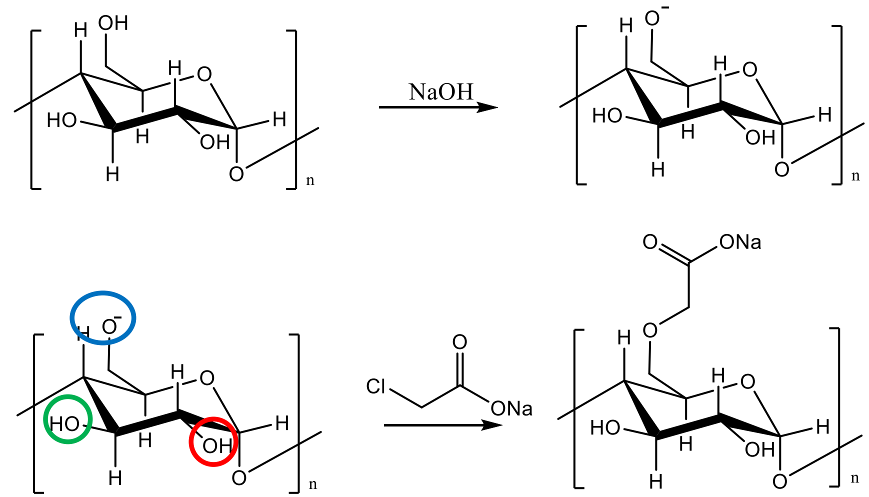
Carboxyméthyl Amidon par Extrusion réactive

Lab scale production of carboxymethyl starch (CMS) with sodium monochloroacetate (SMCA)

ClCH2COONa + ROH → ROCH2COONa

CMS





- substitution at the 3 OH positions of the AGU **C2, C3 and C6**
- maximum **theoretical DS** for starch is 3

- In practice, it is fairly difficult to achieve a high DS and **reaction efficiency (RE)** values without damaging the starch molecules

- Specific equipment
- producing large amount of CMS
- High RE & good reaction control
- Short residence time
- Fast heat transfer
- Few by-products

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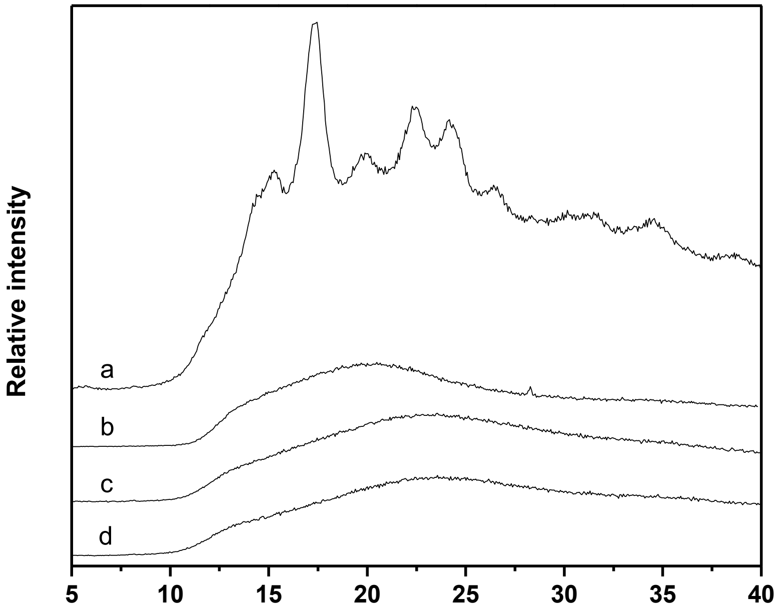
Université de Reims Champagne-Ardenne

Amorphisation de l'amidon après extrusion

Spectre RX



Amidon de départ semi cristallin (B)

Extrudé 1
Extrudé 2
Extrudé 3

XRD B patterns for native potato starch (a), CMS 30 min^{-1} (b),CMS 60 min^{-1} (c), CMS 180 min^{-1} (d).

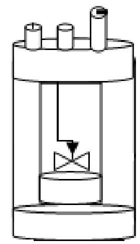
Carboxyméthyl Amidon par Extrusion réactive

Plasticized Starch (glycerol, dextrins)

+ Reagent (SMCA)

+ NaOH

Chemical modification of starch using REX



Ultrafiltration of product

Dry product

Experimental conditions:

- **different starch sources**
- **starch plasticized with 15-30% glycerol and dextrin**
- **T = 70-140°C, n = 60-180 min^{-1}**

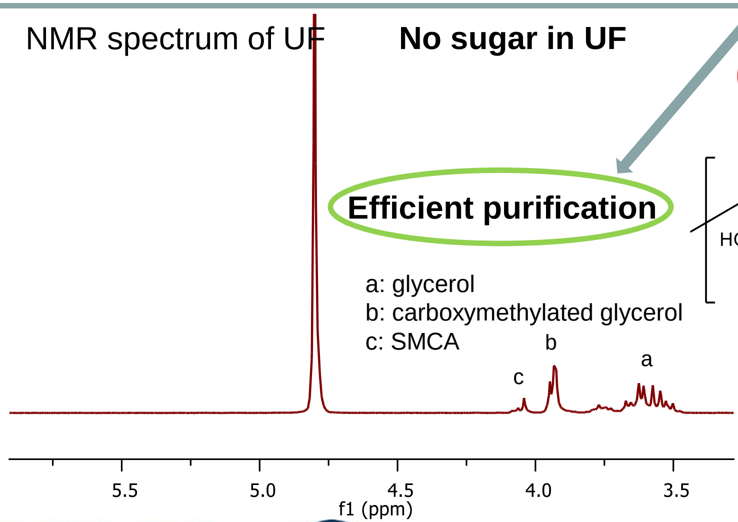
- **elimination of all by-products**
- **analysis of ultra-concentrate (UC) and ultra-filtrate (UF)**

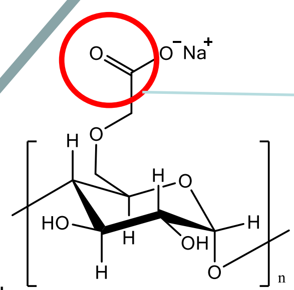
NMR spectrum of UF

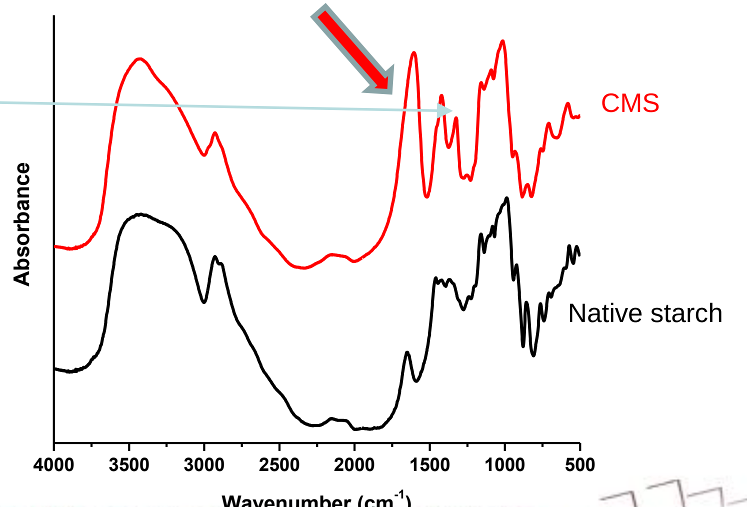
No sugar in UF

Efficient purification

a: glycerol
b: carboxymethylated glycerol
c: SMCA







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CNRS
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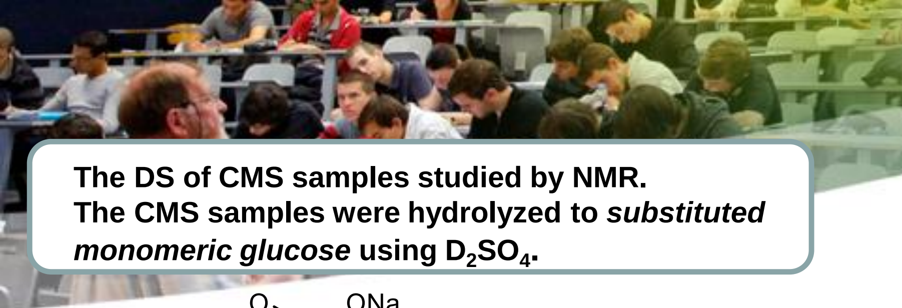
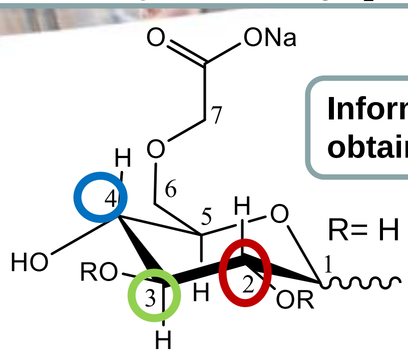


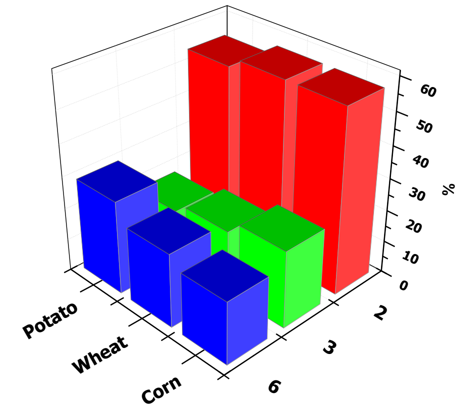
Mesures des DS & fonctions de distribution

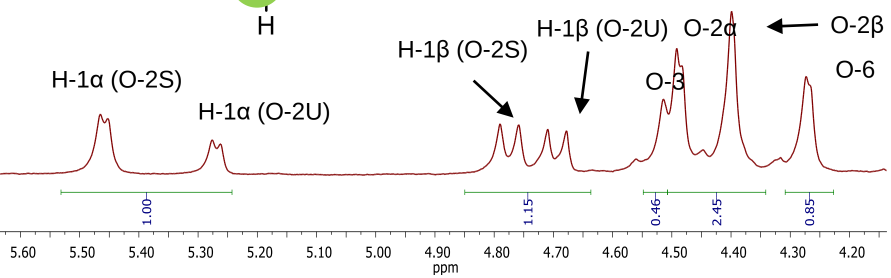
The DS of CMS samples studied by NMR.
The CMS samples were hydrolyzed to *substituted monomeric glucose* using D_2SO_4.



R= H or CH_2COONa

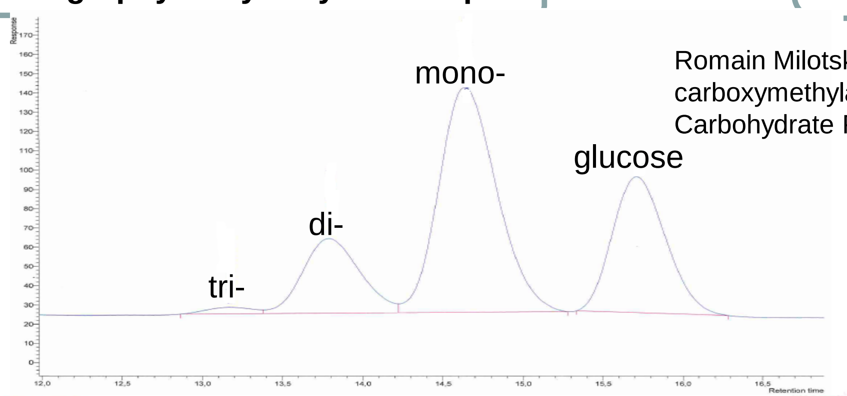
Information about average distribution of the substituents is obtained from the hydrolyzed CMS 250 MHz NMR spectrum.





The distribution of carboxymethyl groups was in the order 0-2>>O-6>O-3,except in the case of corn starch where O-3 > O-6.

HPLC chromatography of hydrolyzed samples



Romain Milotskyi, Christophe Bliard, Dominique Tusseau, Claude Benoit. Starch carboxymethylation by reactive extrusion: Reaction kinetics and structure analysis. Carbohydrate Polymers, Elsevier, 2018, 194, pp.193-199)

HPLC + NMR data
=
statistical approach

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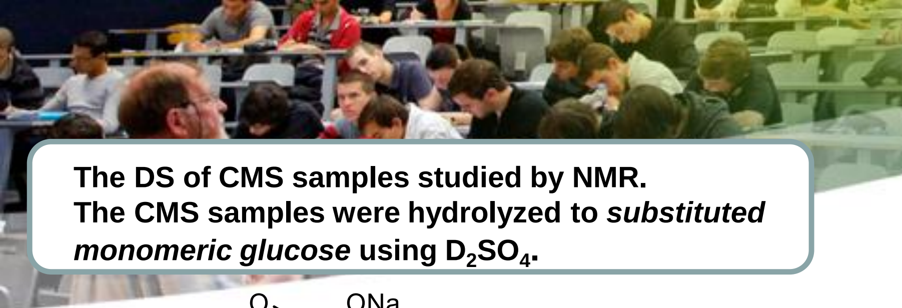
Mesures des DS & fonctions de distribution



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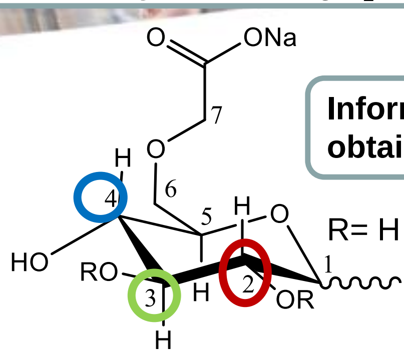

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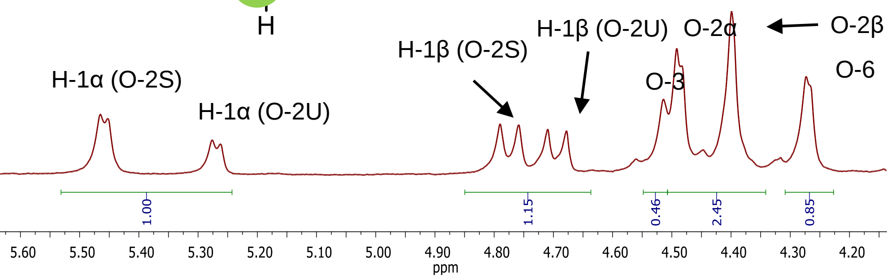

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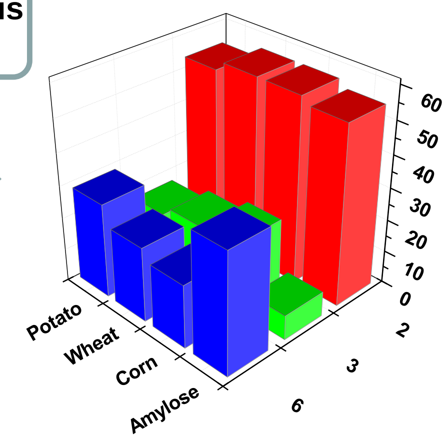

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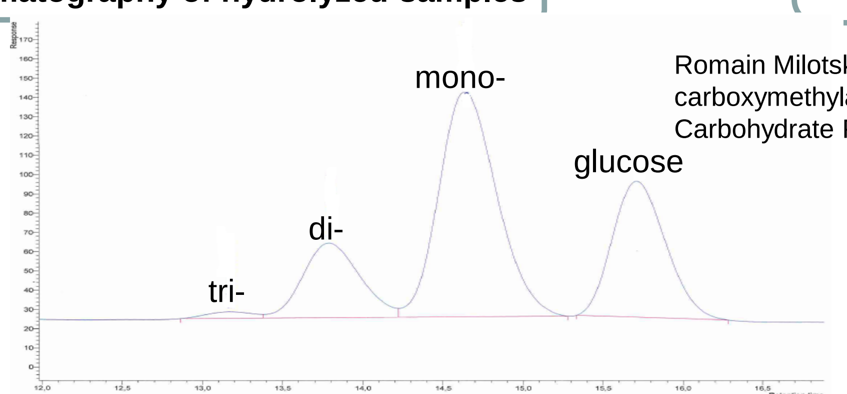

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HPLC + NMR data
=
statistical approach

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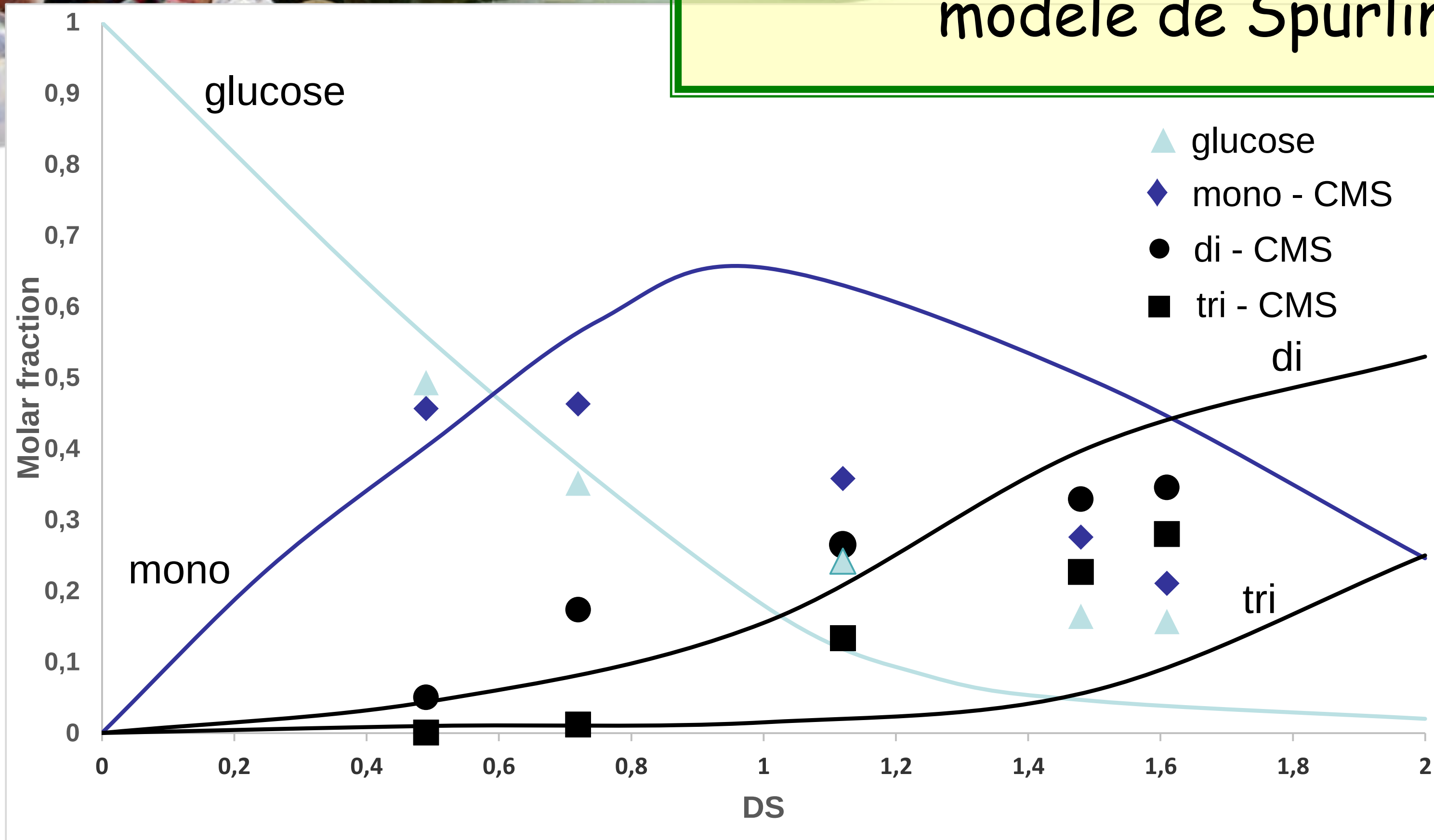
Université de Reims Champagne-Ardenne

Carboxyméthylation de Amidon modèle de Spurlin *

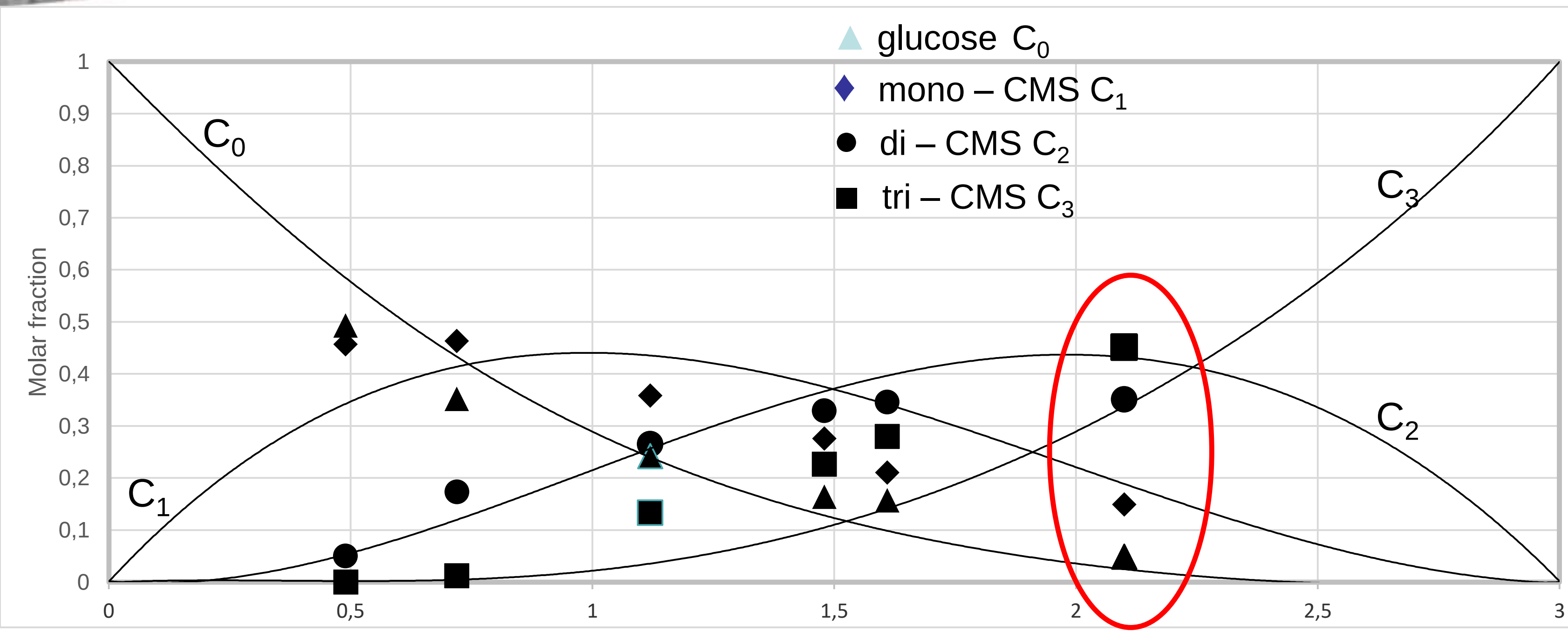


- **deviation from the statistics (heterogeneous substitution)**
- **tetra-O-carboxymethylated units are not included in this model**
- **new properties (solubilty, viscosity) ****

* *Spurlin, H.M.: Arrangement of substituents in cellulose derivatives. J. Am. Chem. Soc., 1939. 61. 2222-2227.*

** *Heinze Th., U. Erler, I. Nehls, and D. Klemm. Angew. Makromol. Chem., 215 (1994), 93–106.*

Carboxyméthylation de Amidon modèle de Spurlin *



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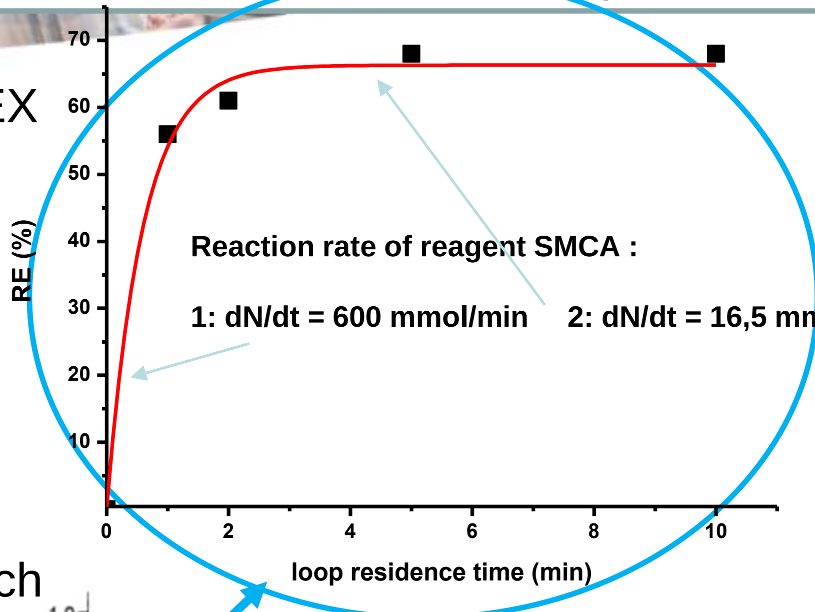
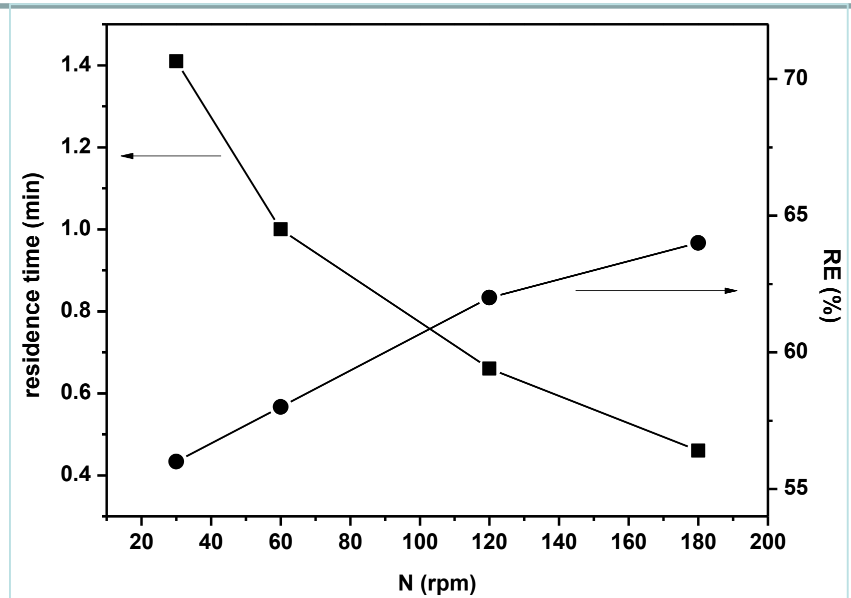
Carboxyméthyl Amidon par Extrusion réactive

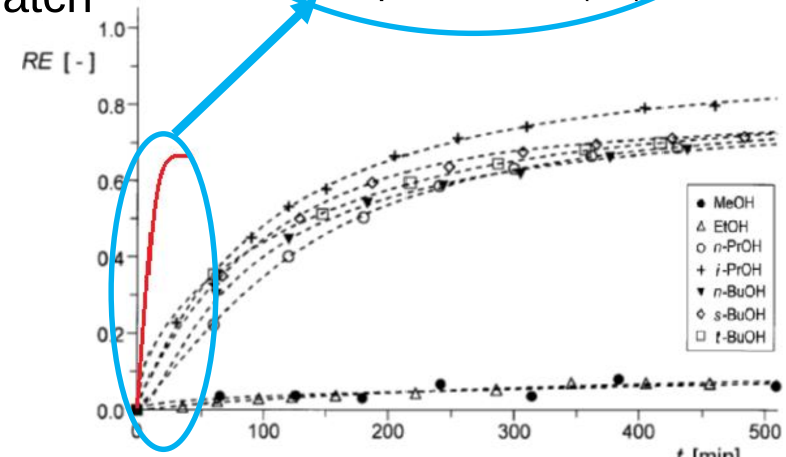
The reaction kinetics was studied using loop (recirculation) mode of extruder by varying the residence time of the melt. Different residence times of the CMS samples were studied: continuous direct extrusion, 2 min, 5 min and 10 min.

REX



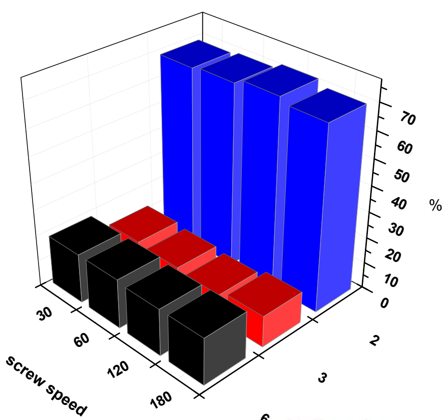


Batch



$$RE\ (\%) = \frac{DSexp}{DSt} \times 100\%,$$

No significant changes
in the distribution for different SME
(O-2>>O-6>O-3)



Tijsen, C. J., Kolk, H. J., Stamhuis, E. J., & Beenackers, A. A. C. M. (2001). . Carbohydrate Polymers, 45, 219-226.

CMS / REX
Effets des Plastifiants

Sample	DS	RE %	SME (kJ/kg)
CMS (glycerol 25%)	0.57	57	75
CMS (water 40%)	0.31	31	45
CMS (Glucor® 25%)	0.44	44	140
CMS (H-Maltor® 25%)	0.15	15	225
CMS (EP2 25%)	0.22	22	90

Glucor : dextrin rich in glucose

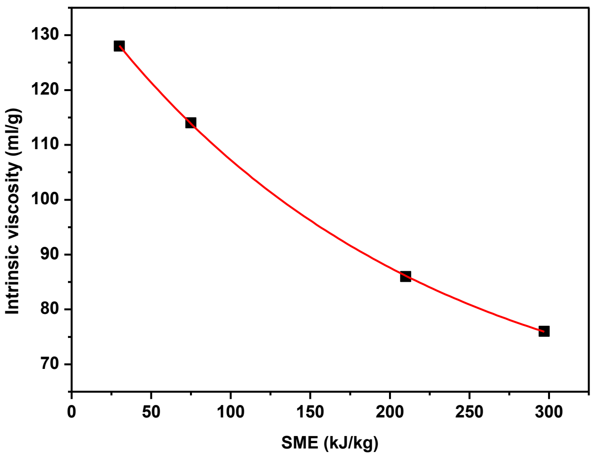
H-Maltor : dextrin rich in maltose

EP2: sugar syrup from sucrose refinery

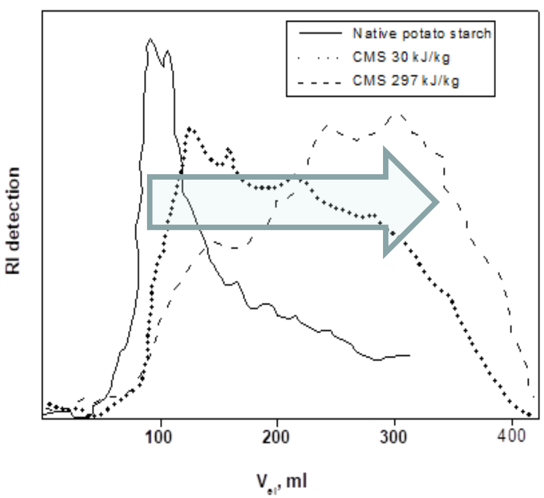
- **glycerol is one of the most efficient starch plasticizers**
- **reagent hydrolysis when water is used**
- **new cheap and eco-friendly plasticizers**

Influence de l'Extrusion réactive sur la masse moléculaire

Carboxyméthyl Amidons

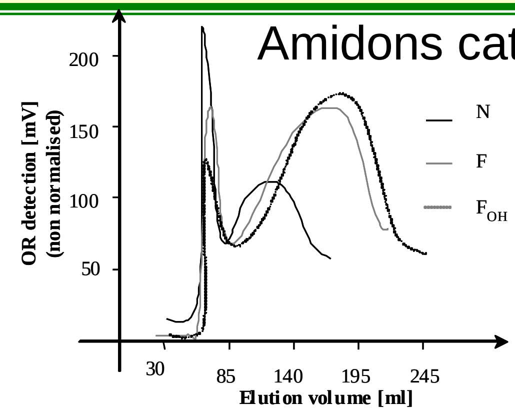


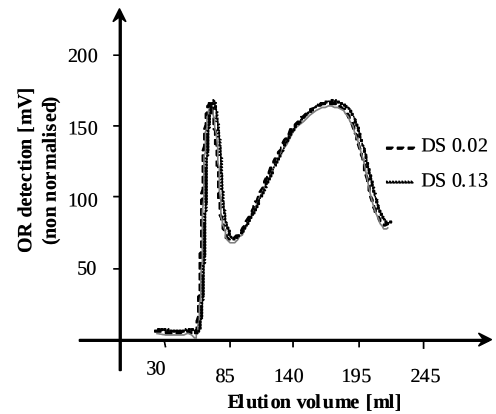
SME



SEC

Amidons cationiques



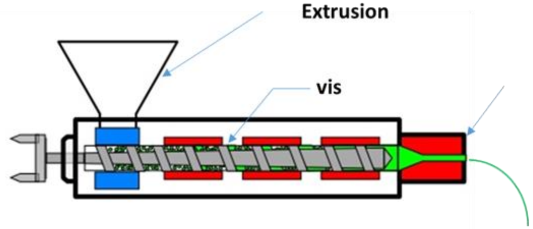


Esters de diacides de lignine par Extrusion réactive

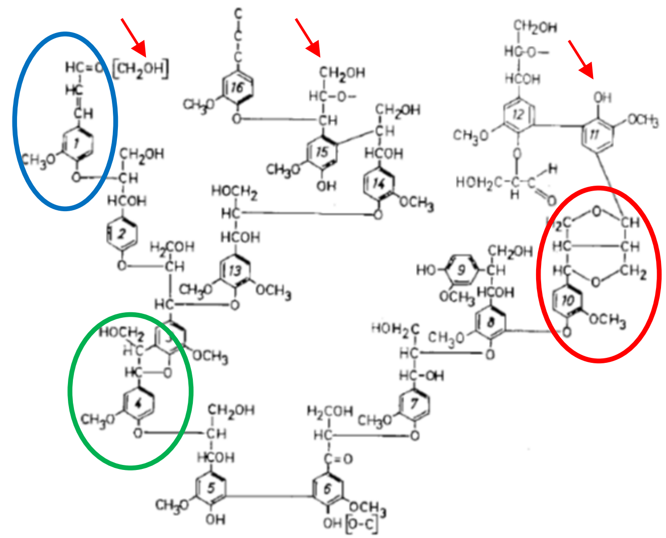
La lignine : biopolymère abondant :
Sous-prod. Papetterie
Unités phényl propane

Estérification des OH (phénolique / Aliphatiques)

(RCOO)2 + R'OH → RCOOR'



- L'esterification des OH libres de la lignine par des anhydrides maléique ou succinique conduit à l'introduction d'une function carboxylique sur le polymère.



Structure de la lignine d'épinette d'après Adler

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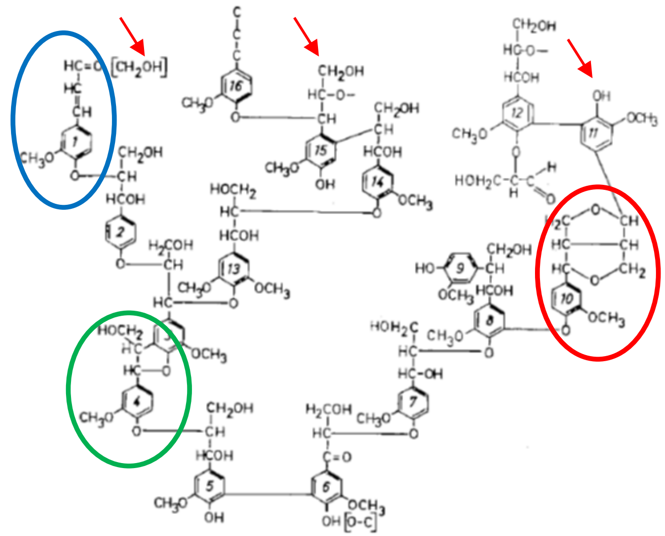
Université de Reims Champagne-Ardenne

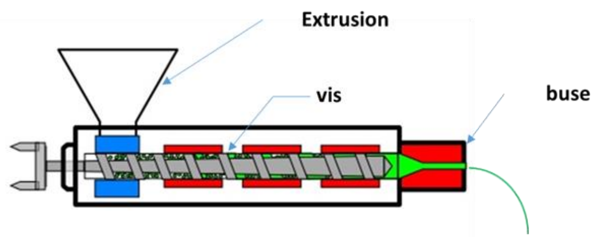
Esters de diacides de lignine par Extrusion réactive



Plastification de la lignine Kraft

DMSO
Glycol
Glycérol

(RCOO)2 + R'OH → RCOOR'



Modification chimique

- L'esterification des OH libres de la lignine par des anhydrides maléique ou succinique conduit à l'introduction d'une function carboxylique sur le polymère.

- producing large amount
- High RE & good reaction control
- Short residence time
- Fast heat transfer
- Few by-products
- Specific equipment

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Esters de diacides de lignine par Extrusion réactive

Plastification de la lignine Kraft

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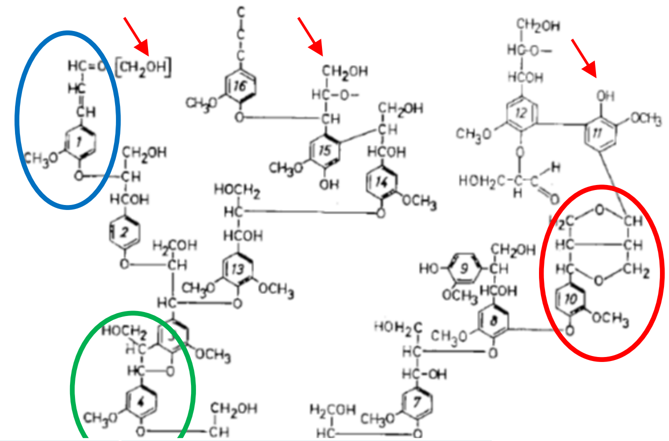
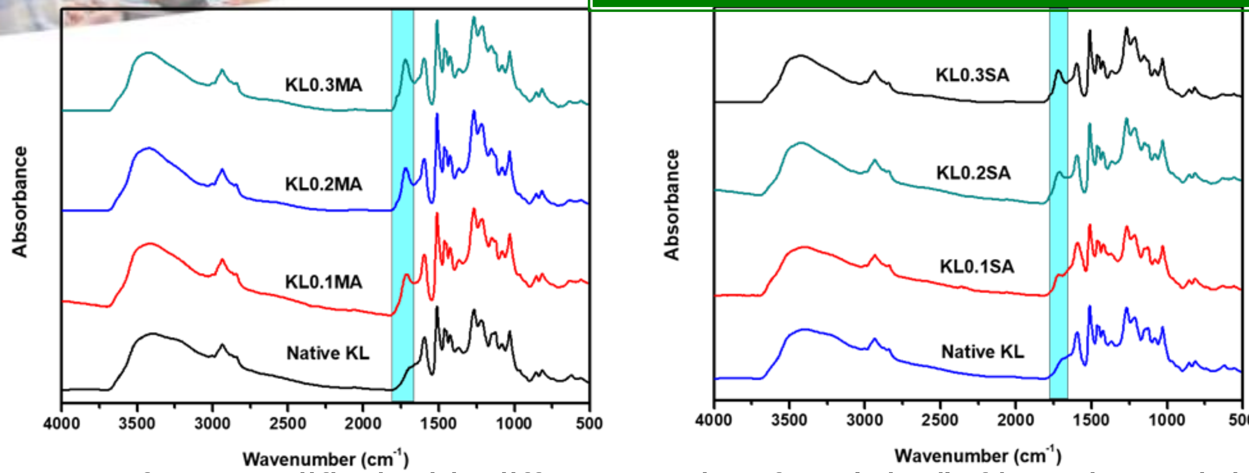


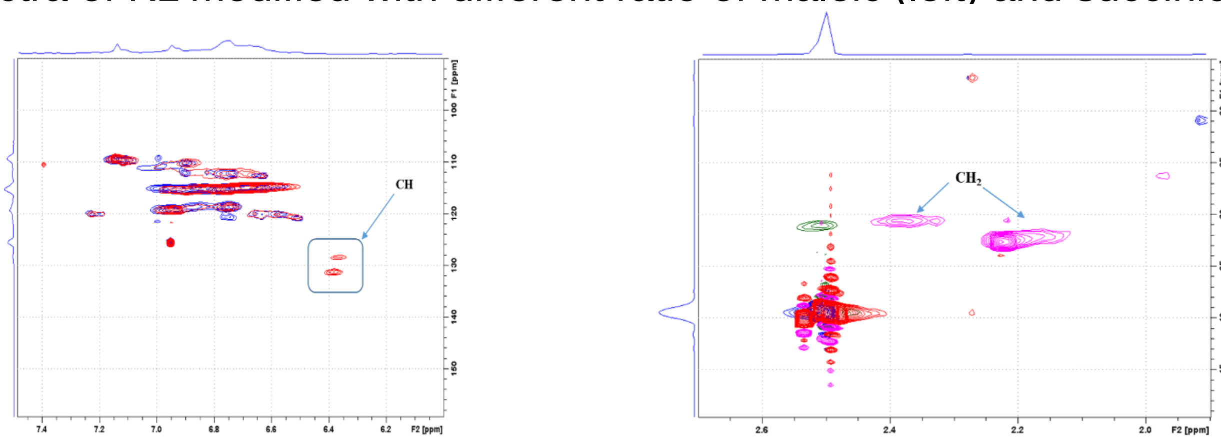
(RCOO)2 + R'OH → RCOOR'

Plastifiants	M (N×m)	EMS (kJ/kg)	Viscosité fondue (Pa.s)
KL 15 % DMSO	3.3	237	4.9×10^3
KL 20 % DMSO	2	144	1.2×10^3
KL 25 % DMSO	1.8	130	4×10^2
KLS 20% DMSO+H_2O	1.7	122	$8{,}96\times10^3$
KLS 20% Et Glycol	1.4	101	$2{,}5\times10^3$
KLS 20% Glycérol	1,5	108	$2{,}4\times10^3$

Esters de diacides de lignine par Extrusion réactive



FTIR spectra of KL modified with different ratio of maleic (left) and succinic (right) anhydrides



2D NMR spectra of KL modified with different ratio of maleic (left) and succinic (right) anhydrides

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cnrs
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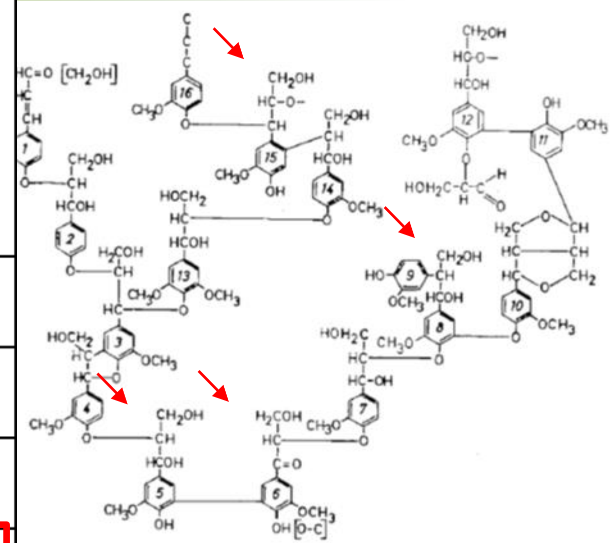
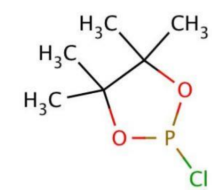
KL	COOH	G -OH	S -OH	H -OH	Total phenolic -OH	Total aliphatic -OH	Total hydroxyl
Native	0.22	1.43	0.23	0.15	1.81	1.54	3.35
0.1 MA	0.28	1.31	0.18	0.12	1.61	1.3	2.91
0.2 MA	0.34	1.25	0.14	0.1	1.49	1.15	2.64
0.3 MA	0.56	1.2	0.12	0.08	1.40	0.8	2.2
0.1 SA	0.27	1.32	0.2	0.1	1.62	1.25	2.87
0.2 SA	0.42	1.29	0.12	0.08	1.49	1.2	2.69



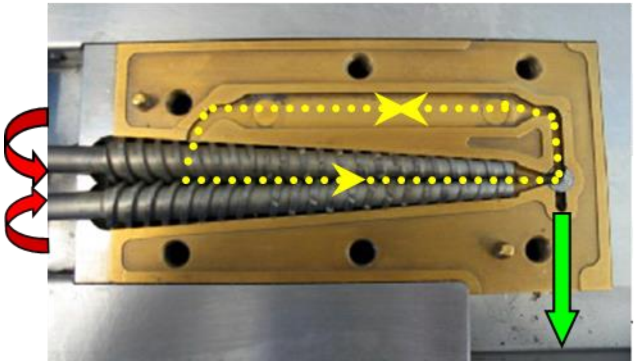


Phosphinylation with 2-chloro-4,4,5,5-tetramethyl-dioxaphospholane

$_{31}$P NMR spectra results of Phosphinylated KL modified with maleic and succinic anhydrides
Showing that the alyphatic OH are more reactive than phenolic OH

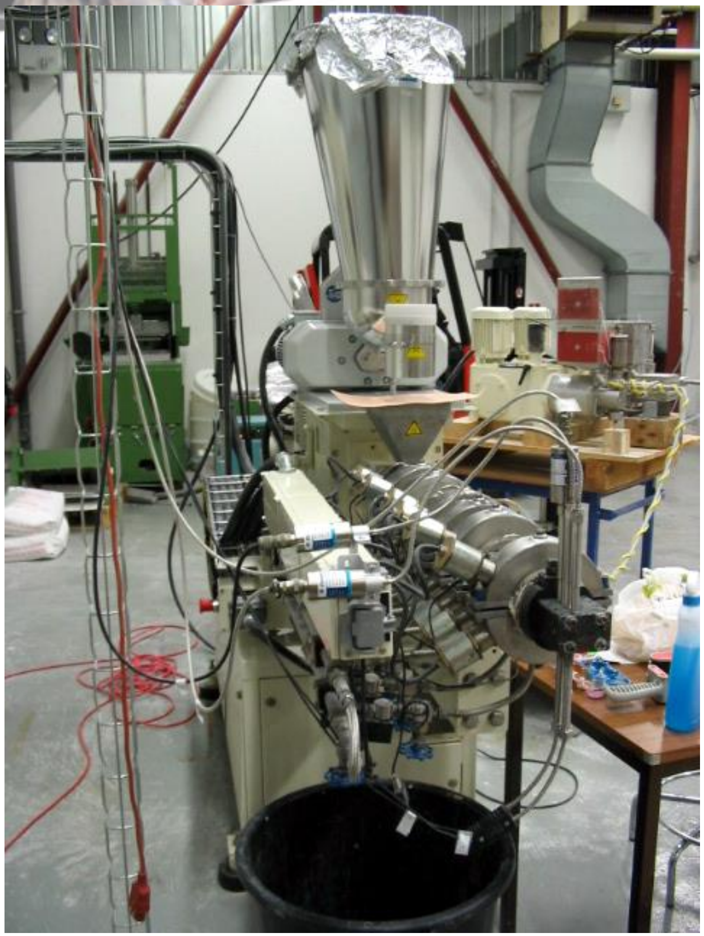
MILOTSKYI, R., Szabó, L., Takahashi, K., Bliard, C. Chemical Modification of Plasticized Lignins Using Reactive Extrusion
Frontiers in Chemistry, section Chemical and Process Engineering (in press)

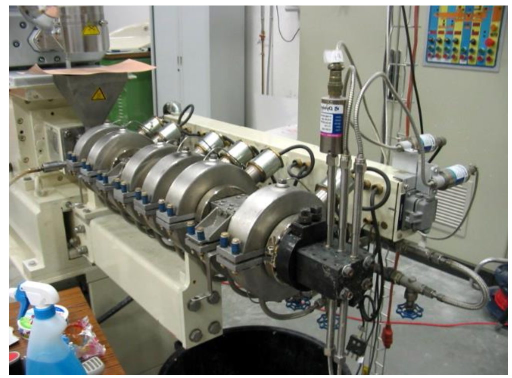
« de l'échelle laboratoire

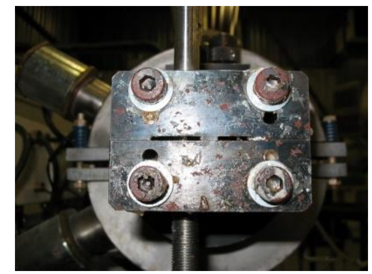


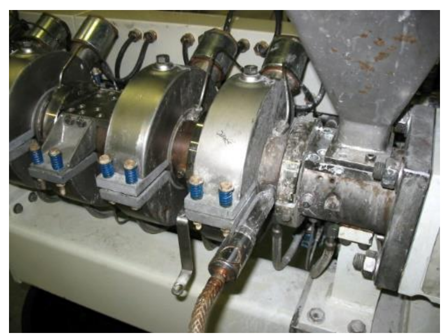
Follain et al. J. of Appl. Polym. Science, 97 (2005)1783-1794
Ibid Carbohydrate. Polymer 60 (2005)185-192.

… à la halle prépilote »









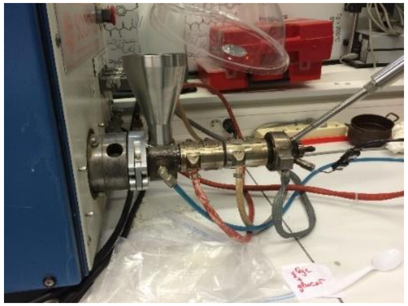
BC 21 Clextral 100 kg/h

Perspectives

Scale up

t/h

15 kg/h



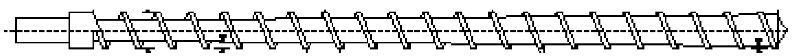
2 kg/h

100 g/h

Great challenge

Solution : using a process simulation

Extrusion réactive et intensification des réactions : Une alternative aux réactions industrielles en batch ?



Christophe Bliard

Université de Reims Champagne-Ardenne

Conclusions REX

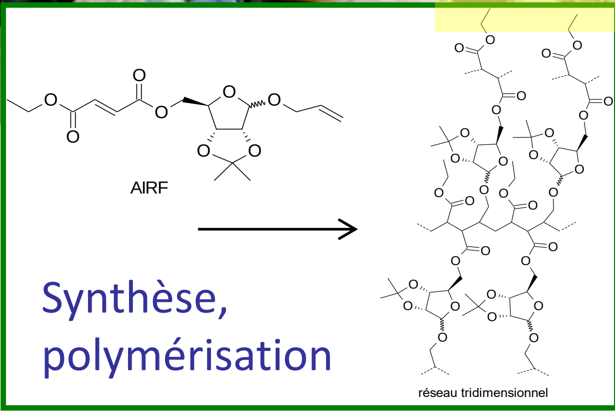
- Extrusion Réactive– un outil puissant pour l'intensification des réactions

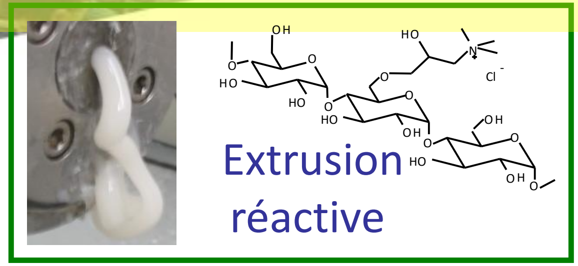
- Adaptation de la technologie aux paramètres réactionnels

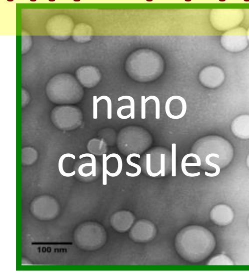
- Question : comment faciliter le transfer technologique à plus large echelle ?

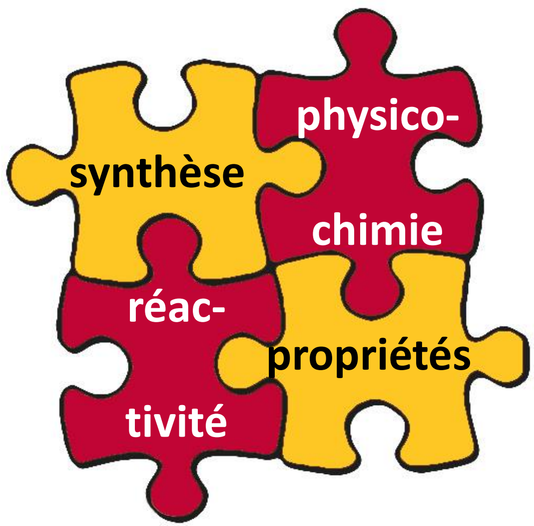
- Réponse : par la formation et la diffusion de l'information

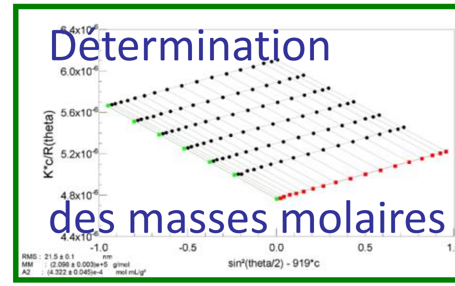
Groupe Polymères Fonctionnels et Réseaux ICMR - PFR

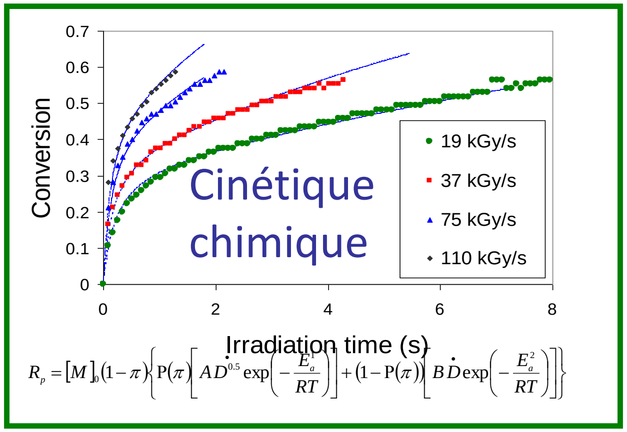




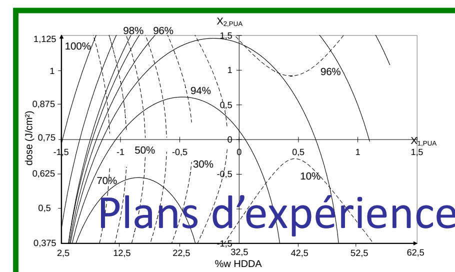








$$R_p = [M]_0 (1-\pi)\left\{ P(\pi)\left[A\dot{D}^{0.5}\exp\left(-\frac{E_a^1}{RT}\right)\right] + (1-P(\pi))\left[B\dot{D}\exp\left(-\frac{E_a^2}{RT}\right)\right]\right\}$$



→ 5 thèses en cours basées sur des réactions originales de polysaccharides et/ou de lignines fonctionnalisés

Procédés intensifs de modification chimique

Matériaux ablatifs, renforts d'élastomères, photolithographie

- Micro et nanoencapsulation pour applications diagnostiques et thérapeutiques

Polymères fonctionnels et réseaux

6 Ens.-chercheurs, 1 Chercheur CNRS, 1 IGR

Marie-Christine Andry	PR
Christophe Bliard	CR1-HDR
Maïté Callewaert	MCF
Xavier Coqueret	PR
Florence Edwards	MCF-HDR
Céline Guillermain	MCF
Christelle Kowandy	IGR
Barbara Rogé	MCF-HDR

Kamila Furtak	doctorante
Imane Hadef	doctorante
Patrycja Kozik	doctorante
Roman Milotskyi	doctorant
Siti Mohamad	doctorante
Hamze Karaky	doctorant
Ali Mhanna	post-doc
Gabriela Tataru	post-doc

Chimie macromoléculaire Pharmacotechnie Sucres et polysaccharides

→ Procédés propres de réticulation

- Encapsulation à visée cosmétique ou thérapeutique
- Monomères et polymères issus d'agro-ressources intensification des réactions
- Chimie sous rayonnement (polymérisation, réticulation, greffage)

UNIVERSITÉ DE REIMS CHAMPAGNE-ARDENNE

ICMR Institut de Chimie Moléculaire de Reims UMR CNRS 7312

Acknowledgement

cnrs dépasser les frontières

REGION CHAMPAGNE ARDENNE

Grand Est ALSACE CHAMPAGNE-ARDENNE LORRAINE

INRA SCIENCE & IMPACT

Conseil regional Champagne-Ardenne

Merci de votre attention