New high solid content cellulose nanofibrils production by twin screw extrusion optimization

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TAPPI NANO
Chiba-Tokyo, Japan

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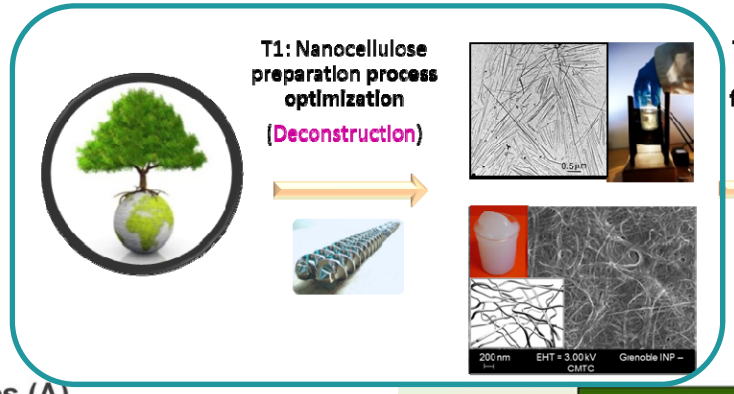
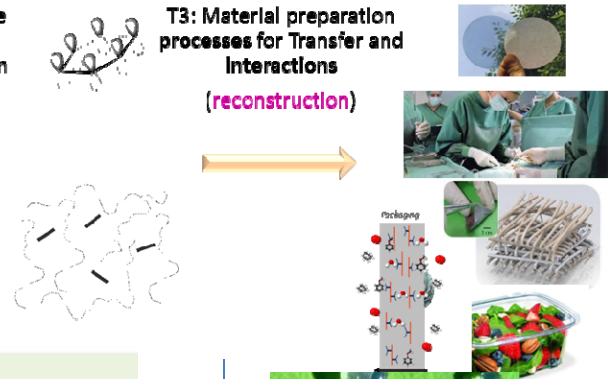
Nanocellulose – Futucell Project

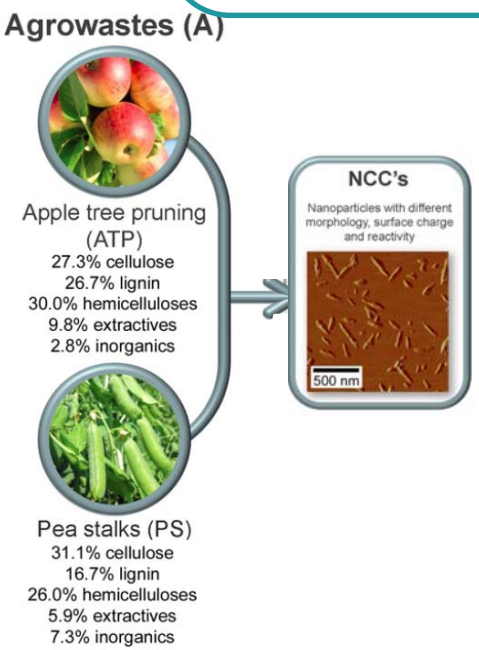
institut universitaire de France

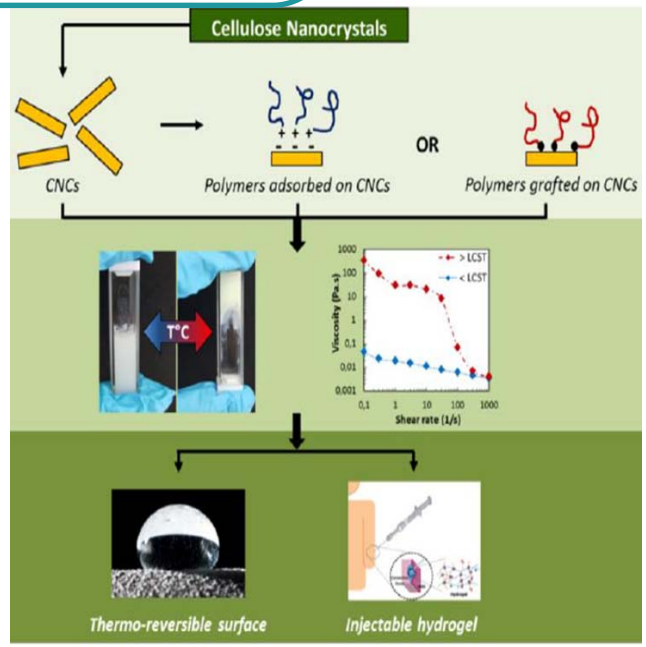
LGP2

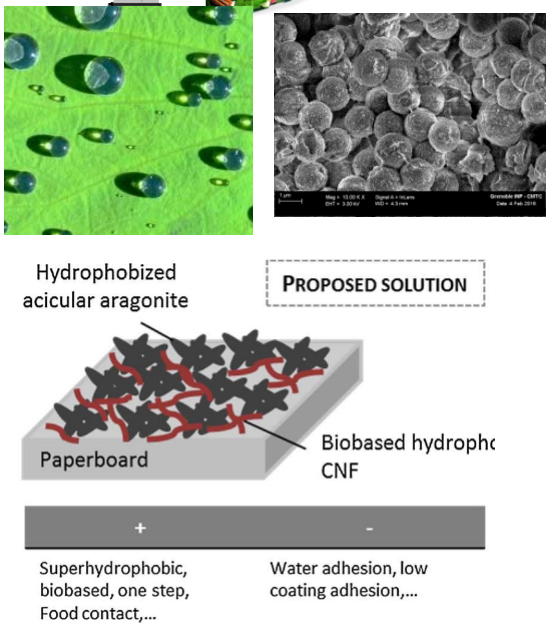
BIOMASS → **NANO-CELLULOSE** → **MATERIALS** → **APPLICATIONS**









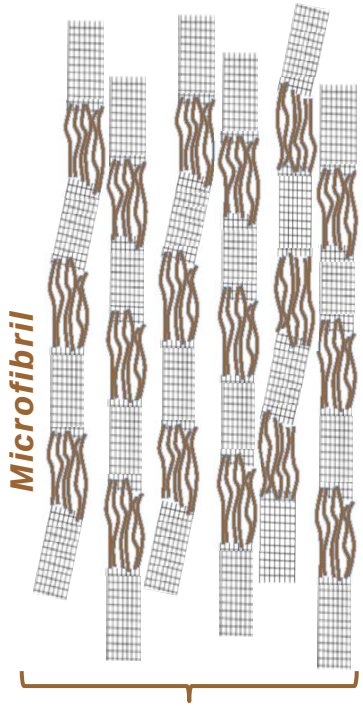


Garcia, A.; Labidi, J; Belgacem, M N; ***Bras, J*** *, The nanocellulose biorefinery: woody versus herbaceous agricultural wastes for NCC production, Cellulose (2017), 24(2), 693-704*

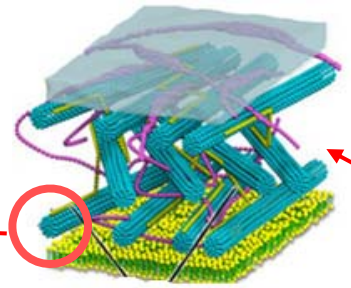
Gicquel, E; Martin, C; Heux, L; Jean, B; ***Bras, J*** *Adsorption versus grafting of poly(N-Isopropylacrylamide) in aqueous conditions on the surface of cellulose nanocrystals, Carbohydrate Polymers (2019), 210, 100-109*

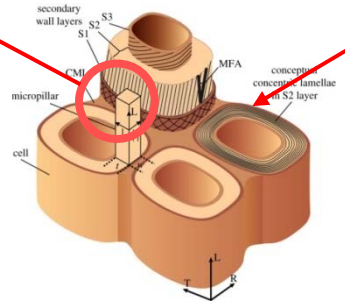
Reverdy, C; Belgacem, N; Moghaddam, M; Sundin, M; Swerin, A; ***Bras, J*** *Colloids and Surfaces, A: Physicochemical and Engineering Aspects (2018), 544, 152-158*

Cellulose



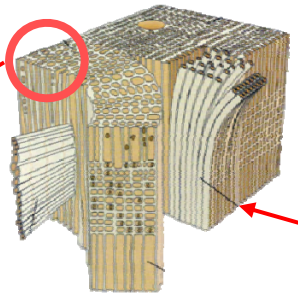
Cellulose microfibril in cell walls





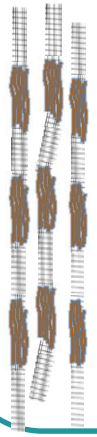
Cell wall layers

Wood cells

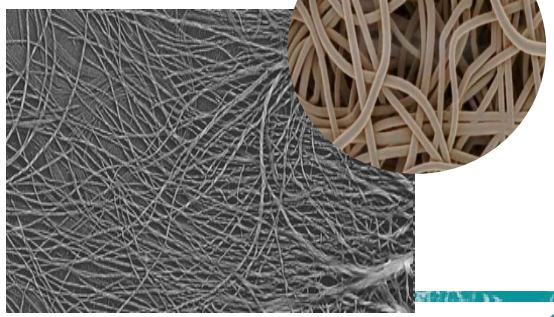


Forest product, biomass

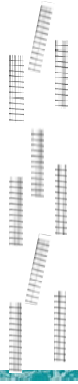
Microfibrillated cellulose (MFC)



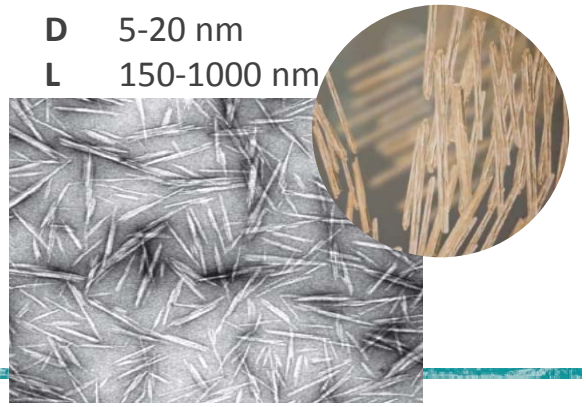
D >5-50 nm
L > 1000 nm



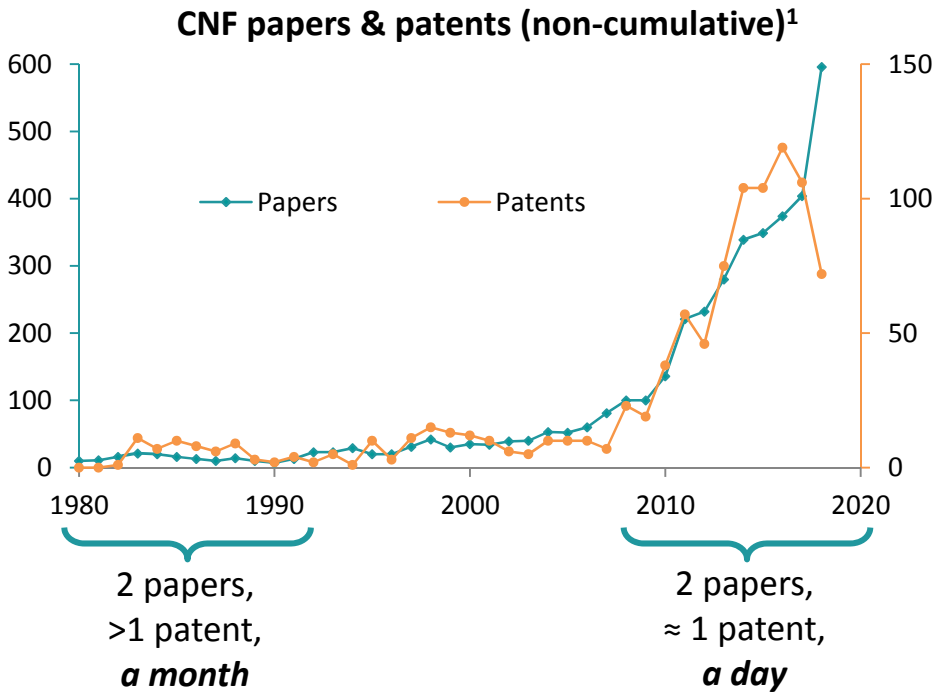
Cellulose Nanocrystals (CNC)



D 5-20 nm
L 150-1000 nm



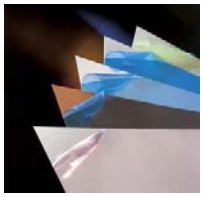
NanoCellulose



23 million tonne potential

(000 tonnes)

	Market Size	Potential Loading	Nano Cellulose Potential	Potential @ 5% Market Penetration	CNF Potential	CNC Potential	CNF	CNC
Paper and Paperboard	400,000	5.0%	20,000	1,000	95%	5%	950	10*
Paints and Coatings	40,000	2.0%	800	40	5%	95%	2	38
Composites	9,000	2.0%	180	9	5%	95%	0	9
Films and Barriers	9,670	2.0%	193	10		100%	0	10
Excipients	4,600	2.0%	92	5	10%	90%	0	4
Natural Textiles	34,500	2.0%	690	35		100%	0	35
Manufactured Textiles	56,300	2.0%	1,126	56		100%	0	56
Cement	15,000	0.5%	75	4	5%	95%	0	4
Oil and Gas	17,500	1.0%	175	9	10%	90%	1	8
Nonwovens	7,000	2.0%	140	7		100%	0	7
Adhesives	4,000	2.0%	80	4	5%	95%	0	4
TOTAL			**23,551**	**1,178**			954	184



=> Nanocellulose = 2nd **priority** of european Bioeconomy in 2016
=> Not only fashionable but also **sustainable**

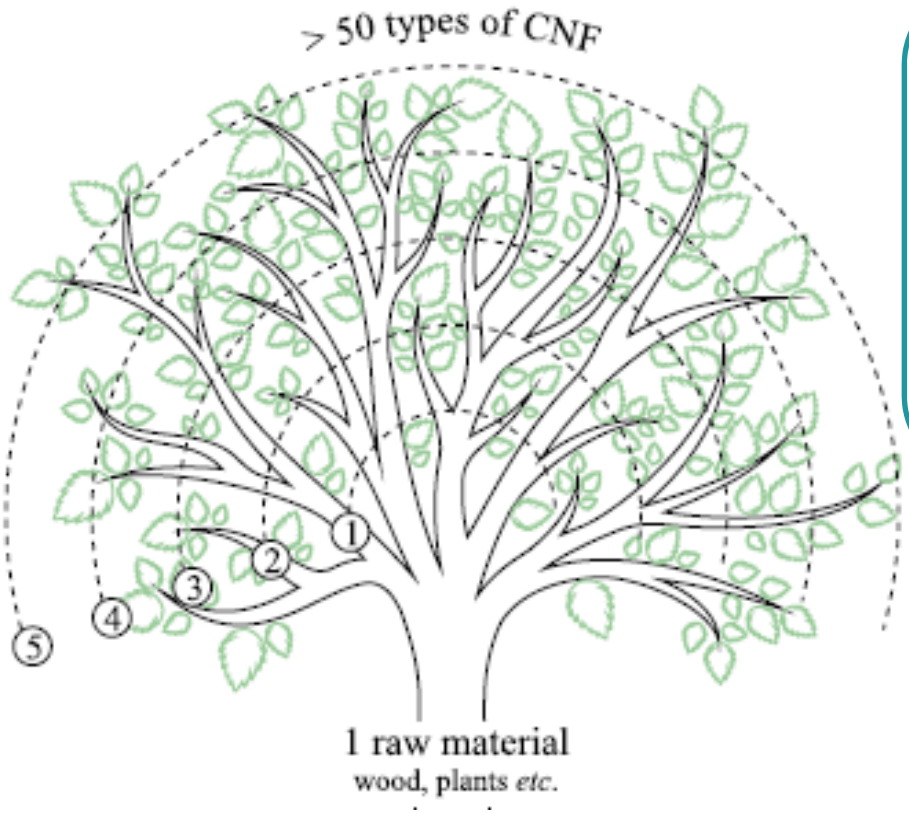
(1) Extracted from Scifinder (2019)
(2) Adapted from FutureMarket (2017)

CNF preparation

① Purification
cooking and bleaching

② Mechanical pretreatment
– blending;
– refining;
– grinding.

③ Biological/chemical pretreatment
– enzymatic hydrolysis;
– carboxylation;
– carboxymethylation;
– quaternization;
– sulfonation;
– solvent-assisted pretreatment.



④ Principal mechanical treatment
– homogenization;
– grinding;
– refining;
– extrusion;
– blending;
– ultrasonication;
– cryocrushing;
– steam explosion;
– ball milling;
– aqueous counter collision.

⑤ Post-treatment
– chemical modification;
– fractionation.

Nechyporchuk, Belgacem, Bras
Production of cellulose nanofibrils: a review of recent advances,
Ind crops (2016), 93, 2-25

OUTLINE

- Introduction to nanocellulose & production
- Nanocellulose production by TSE: proof of concept
- Optimization of TSE for CNF

OUTLINE

- Introduction to nanocellulose & production

- **Nanocellulose production by TSE: proof of concept**

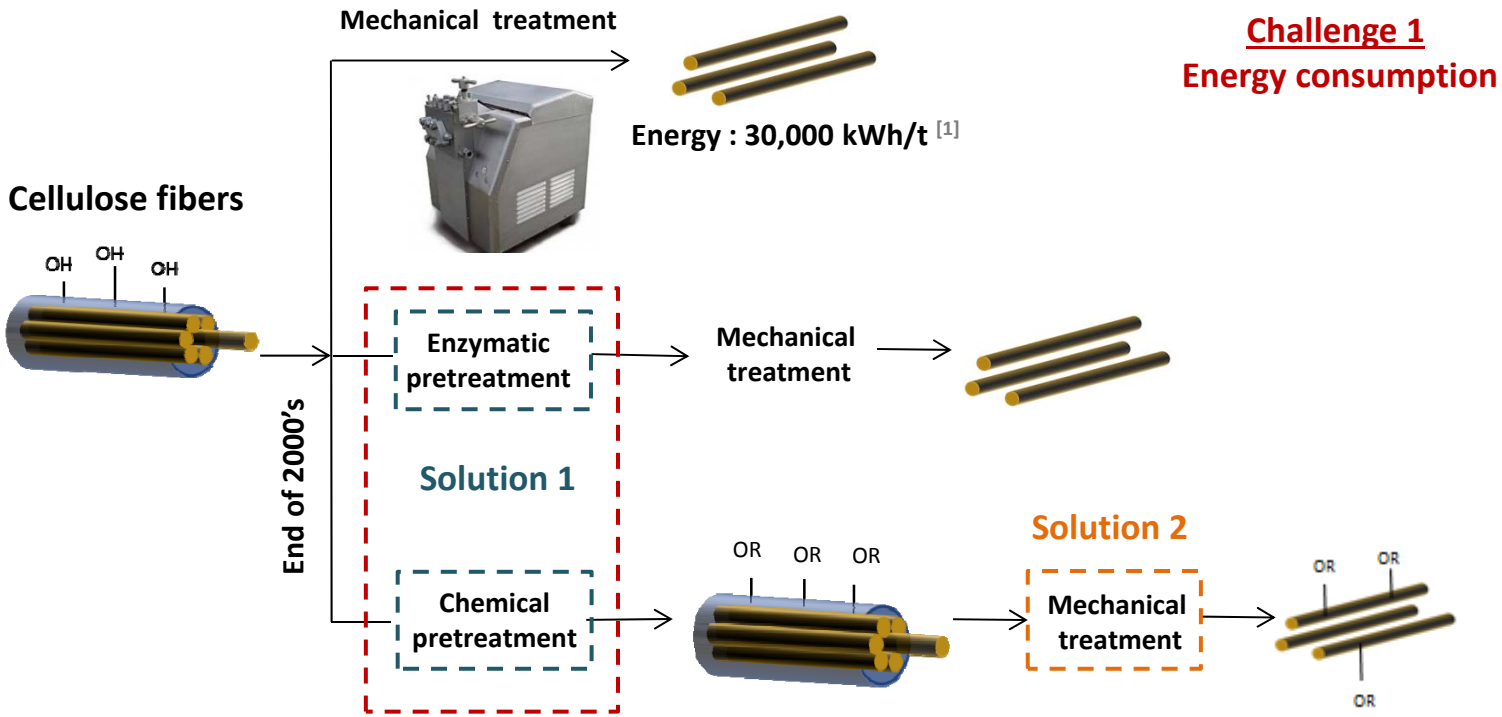
Adapted from:

*- F. Rol, B. Karakashov, O. Nechyporchuk, M. Terrien, V. Meyer, A. Dufresne, N. Belgacem, **J. Bras**. "Pilot-scale twin-screw extrusion and chemical pretreatment as an energy efficient method for the production of nanofibrillated cellulose at high solid content". ACS Sustainable Chemistry & Engineering, 2017, 5(8), 6524-6531*

*-F. Rol, N. Belgacem, A. Gandini, **J. Bras.** "Recent advances in surface-modified cellulose nanofibrils". Progress in Polymer Science, 2019, 88, 241-264*

- Optimization of TSE for CNF

Nanocellulose & pretreatments



[1] Spence et al. 2011. Cellulose

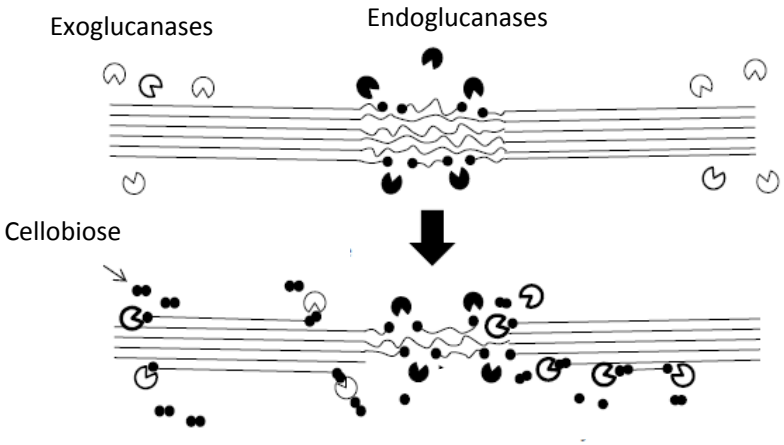
Nanocellulose & pretreatments

Solution 1: Weaken cellulose fibers

80% of the CNF production

Enzymatic pretreatment[1-2]

- Enzymes used: cellulases
- Efficient, high quality CNF
- Mostly used industrially

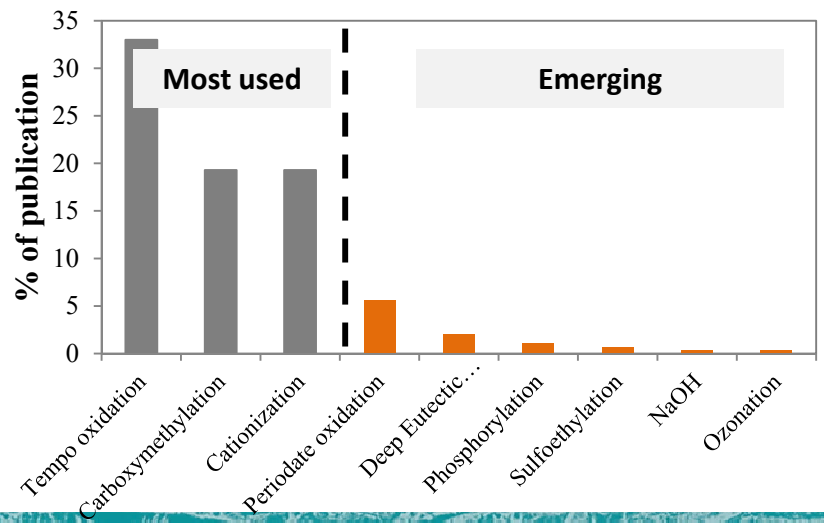


Extracted from [4]

20% of the CNF production

Chemical pretreatment

- Possible thanks to hydroxyl groups
- Decrease H-bonds & introduce charges on the fibers
- Around 15 different pretreatments [3]
- Functionalized CNF with additional properties



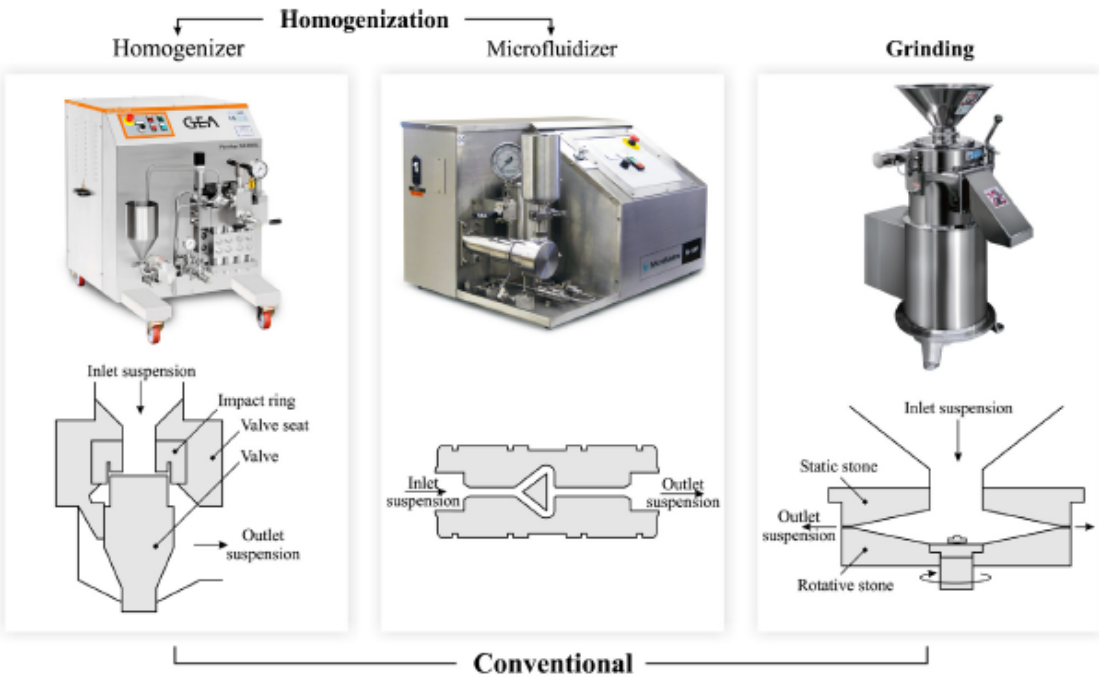
Extracted from [3]

[1] Pääkkö et al. 2007. Biomacro.
[2] Henriksson et al. 2007. Eur. Polym. J.
[3] Rol et al. 2018. Prog. Polym. Scien.
[4] Lavoine PhD thesis. 2013.

Nanocellulose & Mechanical treatments

Solution 2: Optimize mechanical process

Extracted from [1]



Mechanical processes for CNF production

Energy consumption

1,000 -30,000 kWh/t (dry) [2-4]

Cellulose solid content

2-5 wt%

X *Transport cost, storage, application*

Challenge 2

Increase solid content

Use of the Twin-Screw Extrusion

[1] Nechyporchuk et al. 2015. Ind. Crops. Prod. [2] Spence et al. 2011. Cellulose
[3] Siro et al. 2010. Cellulose [4] Tejado et al. 2012. Cellulose

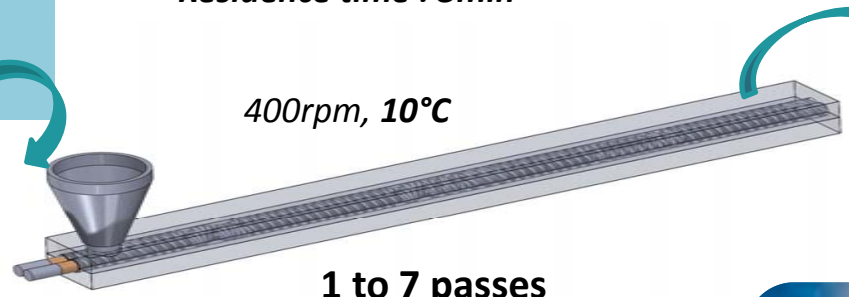
CERISE Project

CEllulose pRetreatment for a nanofibrillation by twIn-Screw Extrusion (CERISE)

Enzymatic cellulose pulp
Flow : 35 g/min
Dry matter content: 20%

Residence time : 3min

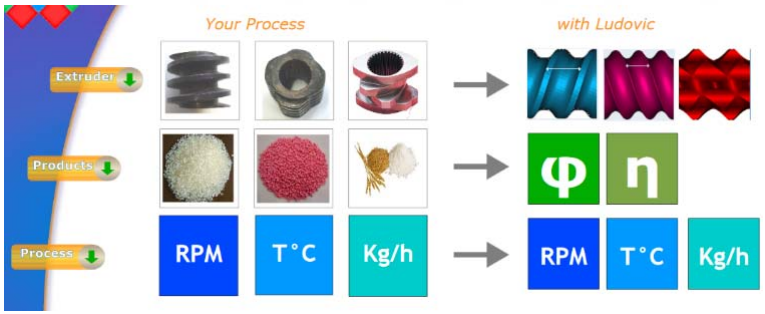
*400rpm, **10°C***



CNF

CNF at 20% dry matter content

1 to 7 passes



Dr Fleur ROL

Collab: CTP, LRP, LGP2 – Project 2015-2019

Nanocellulose & Mechanical treatments

LGP2

2011-2014

Several studies
(Nano)Fibrillation during compounding

[1] Yano et al. 2007. WO2005/003450

2015 VTT patent

CERISE project

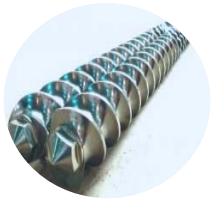
Pretreatment with enzymes
Nanofibrillation with high solid content mixer
10-60 wt%

[4] Hiltunen et al. 2015. WO2015/092146

Cellulose Nanofibrils

+

Twin-Screw Extrusion



2011 1st patent: production of CNF by extrusion

Extrusion can be used to produce CNF, with or without chemicals pretreatment, in situ or not

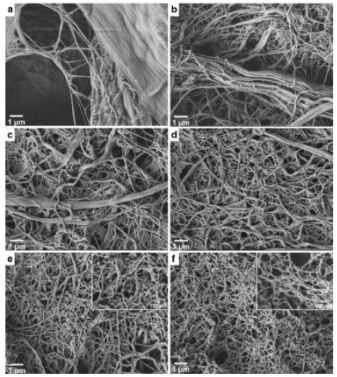
[2] Heiskanen et al. 2011. WO2011/051882

2016 University of Maine patent

Pretreatment with organic liquids
Extrusion can be used

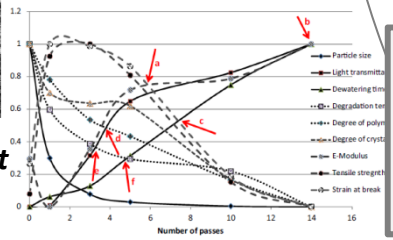
[5] Bilodeau et al. 2016. WO2016/172616

2014 1st study: CNF by TSE



Transmittance: 90%

Young's modulus: 6-8 GPa



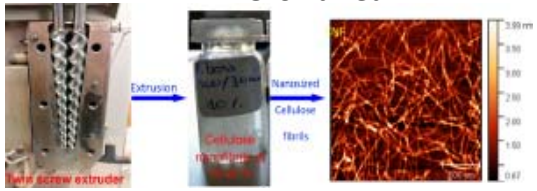
33-45 wt% solid content
1-14 passes

No pretreatment

No information regarding screw profile & energy

2017 CNF by micro-compounder

TEMPO-oxidized



10 wt% solid content
Recirculation ***30 min***

4,100 kWh/t

Baati et al. 2017. ACS Sus. Che. Eng.

√ Production of CNF (quality ?)
? TSE optimization & simulation
? Study of the « Black box » / Up-scaling

[3] Ho et al. 2014. Cellulose

CNF Pre-treatment with enzymes

Eucalyptus Fibria, Brazil
Kraft cooking, bleached

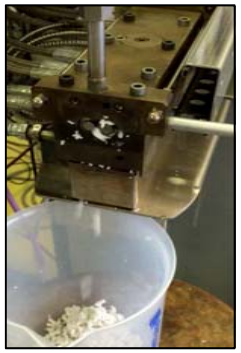
Refining step, 2 wt%
SR° 90

Enzymatic treatment

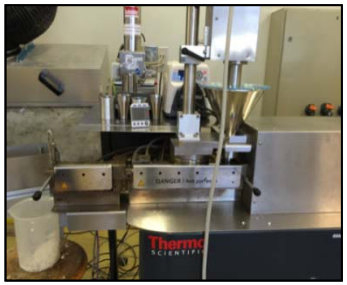
- FiberCare® Cellulase
- 2 wt%, 300 ECU/g of cellulose
- 50°C, pH 5, 2h

Twin-screw extruder

Solid content: 20 wt%

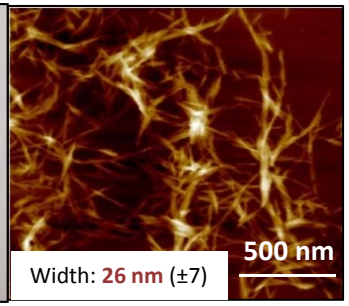


7 passes



d: 16 mm
L: 640 mm
400 rpm
10°C
3 kg/h (humid)
0.6 kg/h (dry)

4,700 kWh/t



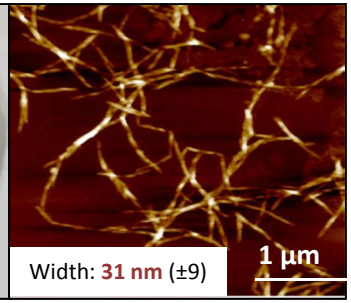
Ultra-fine grinder

1,500 rpm
2 kg/h (humid)
0.04 kg/h (dry)

40 passes

Solid content: 2 wt%

16,000 kWh/t



Rol F. et al, ACS Sustainable Chem. Eng. 2017, 5, 6524−6531

CNF Pre-treatment with enzymes

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Kraft cooking, bleached

Refining step, 2 wt%
SR° 90

Enzymatic treatment

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- 2 wt%, 300 ECU/g of cellulose
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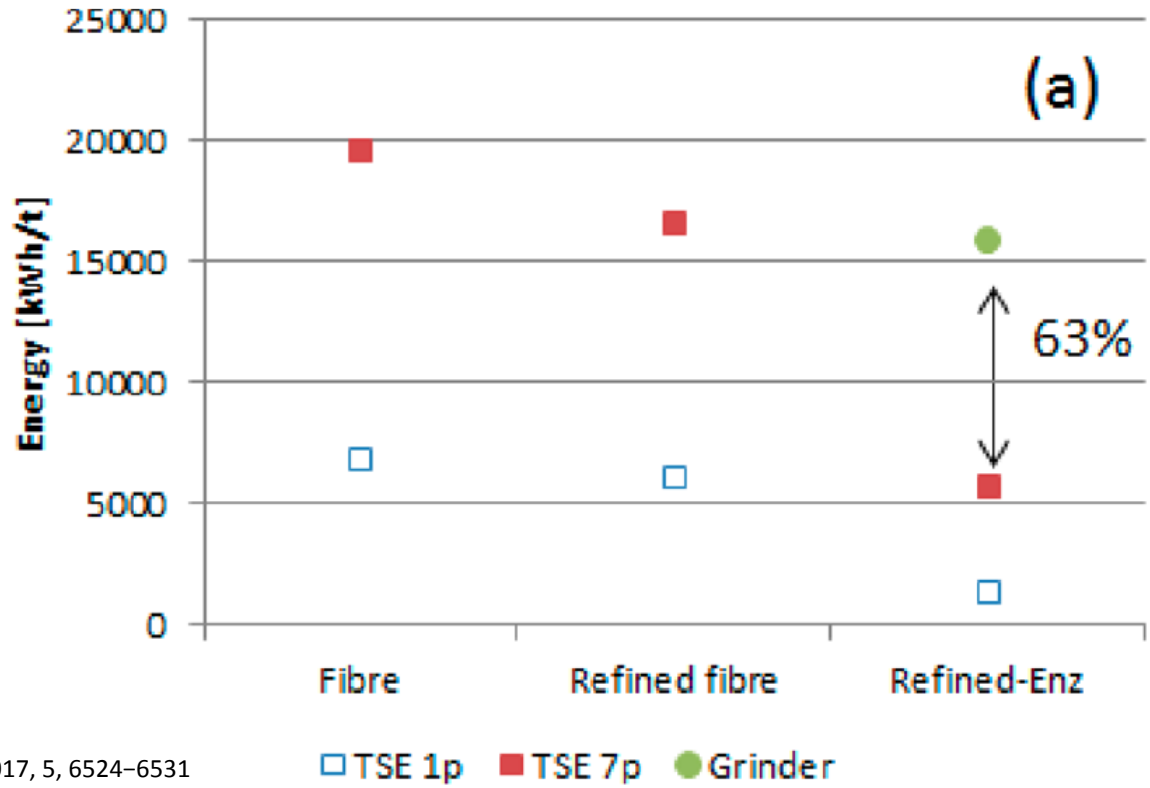
Twin-screw extruder

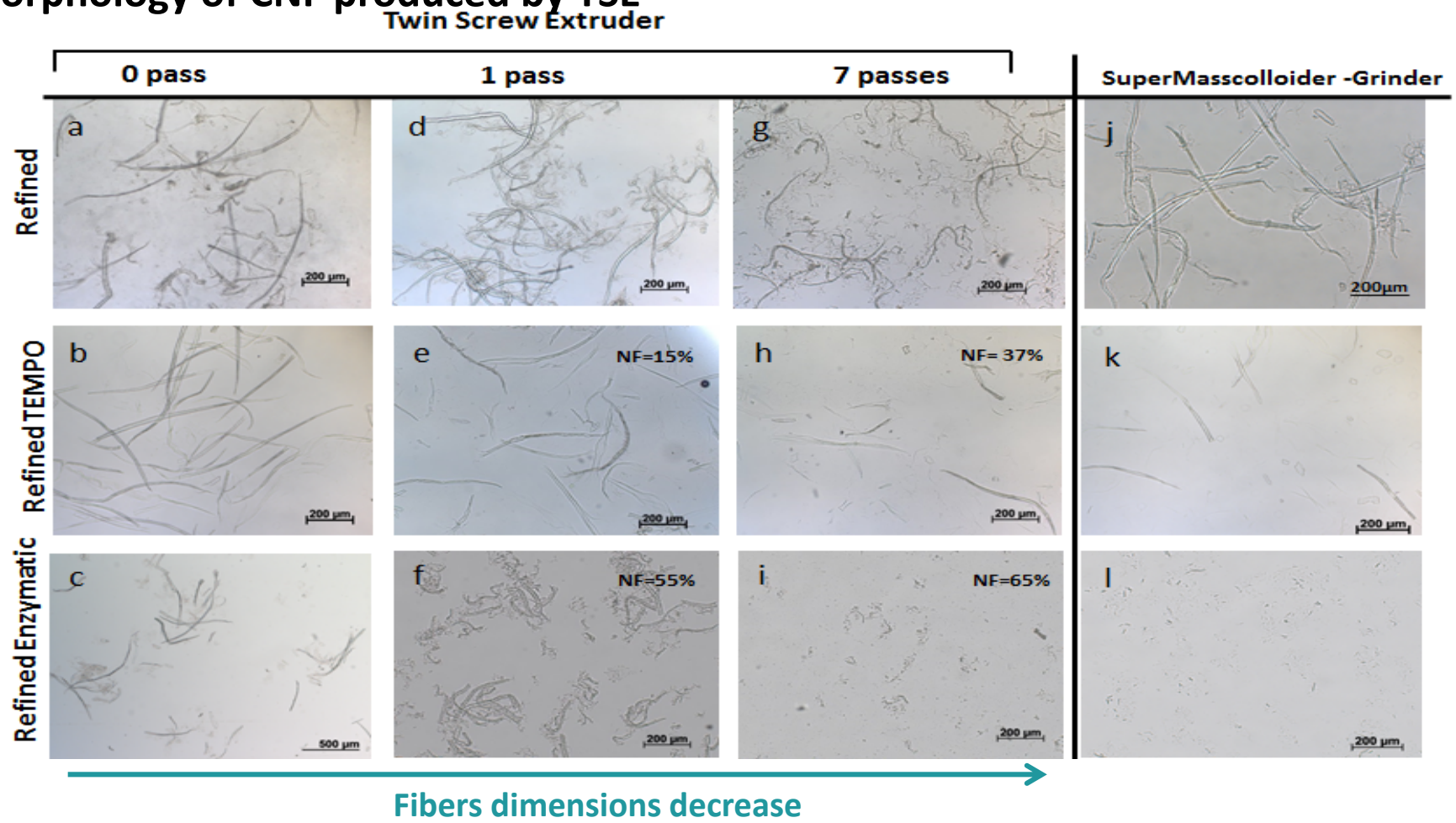
Ultra-fine grinder



Rol F. et al, ACS Sustainable Chem. Eng. 2017, 5, 6524−6531

CNF Pre-treatment with enzymes

Morphology of CNF produced by TSE



- TSE has a strong effect on fibrillation of cellulose fibers
- **Pretreatment** facilitates the nanofibrillation

Rol F. et al, ACS Sustainable Chem. Eng. 2017, 5, 6524−6531

CNF Pre-treatment with enzymes

CNF characterizations – Quality Index [1]

- Objectives: characterize easily CNF suspension and evaluate suspensions according to one data
- Two versions: 8 characteristic tests (QI) or 4 (simplified one QI*)

$$QI^* = 0.3\,x_1 - 0.03\,x_2 - 0.072x_3^2 + 2.54\,x_3 - 5.34\ln(x_4) + 58.62$$

x_1 Nanosized fraction [%]
x_2 Turbidity [NTU]
x_3 Young's modulus [GPa]
x_4 Macro size of residual fibers [µm²]

	20 wt%	2 wt%
	TSE – 7p	**Ultra-fine grinder**
Young's modulus [GPa]	11.6 ± 0.3	17.8 ± 0.2
Turbidity [NTU]	290 ± 13	413 ± 25
Nanosized fraction [%]	64.3 ± 9.9	73.2 ± 17.2
Macro size [µm²]	40.6 ± 11.5	27.3 ± 6.3
Simplified Quality Index (QI*) [2]	**69.5 ± 1.8**	**72.0 ± 1.2**

Proof of concept: promising results

BUT…

+

Same quality

Energy consumption reduction

High solid content

[1] Desmaisons et al. 2017. Carbohydrate Polymers (2017), 174, 318-329

OUTLINE

- ❑ Introduction to nanocellulose & production
- ❑ Nanocellulose production by TSE: proof of concept
- ❑ Optimization of TSE for CNF

Adapted from:

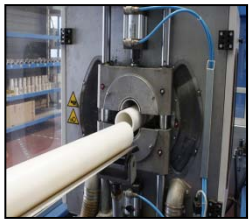
*- F. Rol, B. Vergnes, N. El Kissi**, J. Bras**. "Nanocellulose production by twin-screw extrusion: screw profile optimization by process modeling". Just Accepted at ACS Sustainable Chemistry & Engineering, (2019)*

CNF & TSE optimization

Literature review

√ Mainly used for polymer & composites

- Functionalization, compounding
- Coextrusion
- **Very low water content: < 10 wt%**



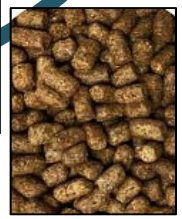
? Used for cellulose nanofibrillation

- Only 8 publications & 4 patents
- **No optimization & understanding**
- **« Black box »**
- **Water content: 80 - 90%**

Nanofibrillation:
a new use of the TSE

√ Used for Biomass at high solid content

- Fragmentation, molecules extraction [1]
- Pretreatment, cooking [2]
- Food application
- **Water content: 5 - 60%**



[1] Vandenbossche et al. 2016. Bioresour. Technol.
[2] Ralet et al. 1990. Journal of Cereal Sci.

CNF & TSE optimization

Methodology followed

Collab with B. Vergnes

Objectives

- Optimize TSE conditions and screw profile to produce **CNF** increasing the **productivity**
- Understand the « **Black box** »

Design of experiment

Screw speed
Feed rate
Solid content

Minitab 17

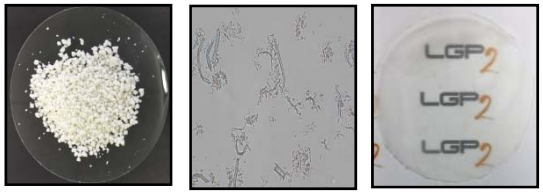
Different screw profiles

Conveying profile
Profile 1
Profile 2

Optimization using Ludovic

Ludovic®

Optimized screw profile

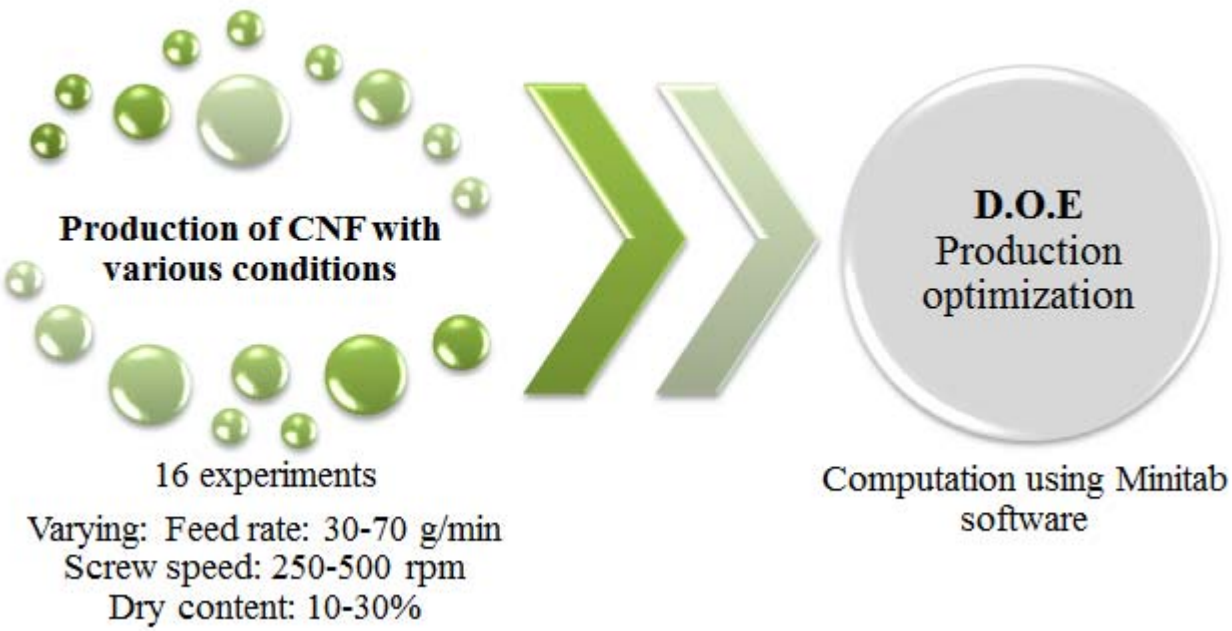


CNF & TSE optimization

Design of experiment results

Objectives

- Determine the influence of the TSE parameters on QI, Energy, Young's modulus,…
- Develop models for the different responses



Studied responses
- Young's modulus
- QI
- Energy consumption

Responses:

$$R_k = b_0 + \sum_{i=1}^{3} b_i * x_i + \sum_{\substack{i,j=1 \\ j \neq i}}^{3} b_{ij} * x_i * x_j + \sum_{\substack{i,j,k=1 \\ i \neq j \neq k}}^{3} b_{ijk} * x_i * x_j * x_k$$

bi: coefficients of the model
Bij * xi * xj : interactions

CNF & TSE optimization

Determination of the models

Energy consumption

$$y = 1.658\,x_1 + 4.847x_2 + 26.191\,x_3 - 0.05x_1 * x_2 - 257.737$$

X1: Flow rate
X2: Screw speed
X3: Solid content

$R^2 = 0.983$; $R^2_{adjust} = 0.961$; $R^2_{prev} = 0.943$

- Low solid content should be prefered
- High significance
- Excellent prediction

Simplified Quality Index

$$y = -0.35x_1 - 0.043\,x_2 - 2.541\,x_3 + 0.0352x_1 * x_3 + 0.0059 * x_2 * x_3 - 8.75 * 10^{(-5)}x_1 * x_2 * x_3 + 93.665$$

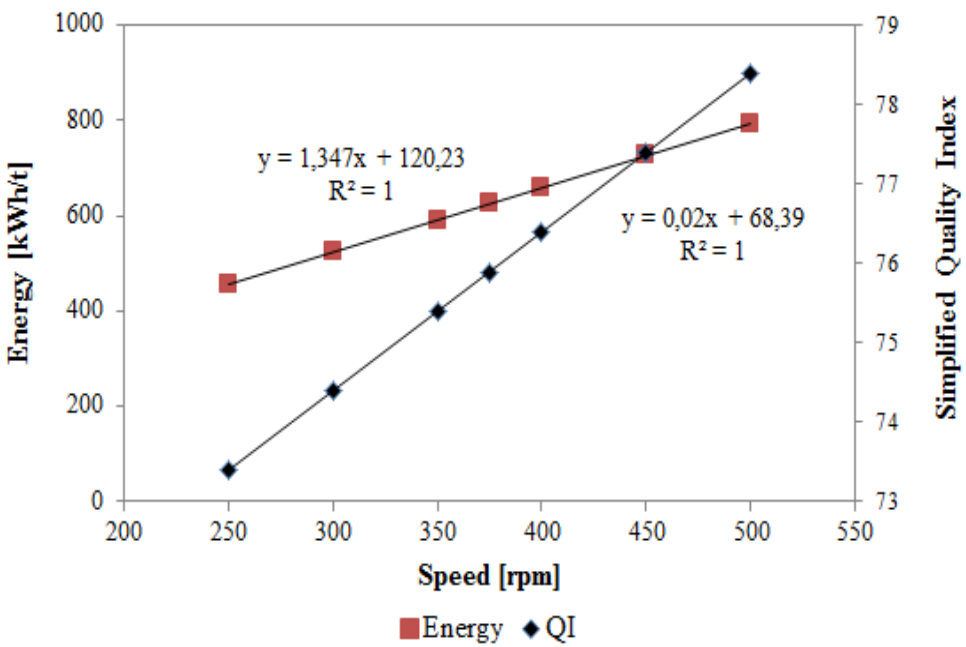
$R^2 = 0.995$; $R^2_{adjust} = 0.995$; $R^2_{prev} = 0.537$

- Significant model
- Cannot be used for prediction
- Most impacting parameter: screw speed
- High speed, high feed rate and low solid content should be used

CNF & TSE optimization

How to reduce energy consumption and increase QI*?

QI_{max} = 78.4			$Energy_{min}$ = 457 kWh/t		
Flow [g/min]	Screw speed [rpm]	Dry content [%]	Flow [g/min]	Screw speed [rpm]	Dry content [%]
70	500	10	70	250	10

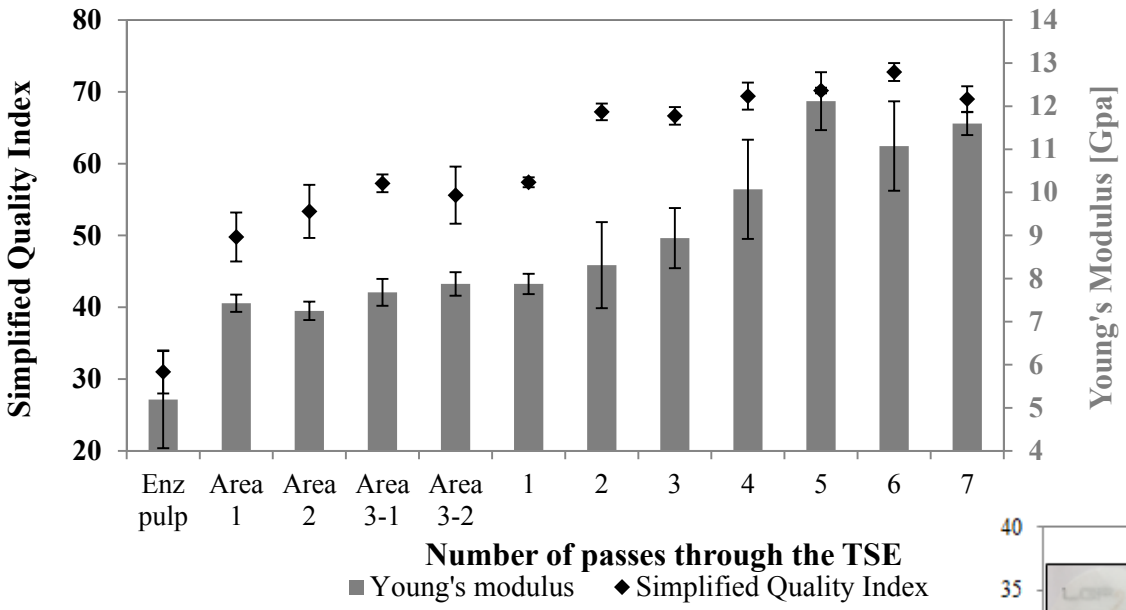


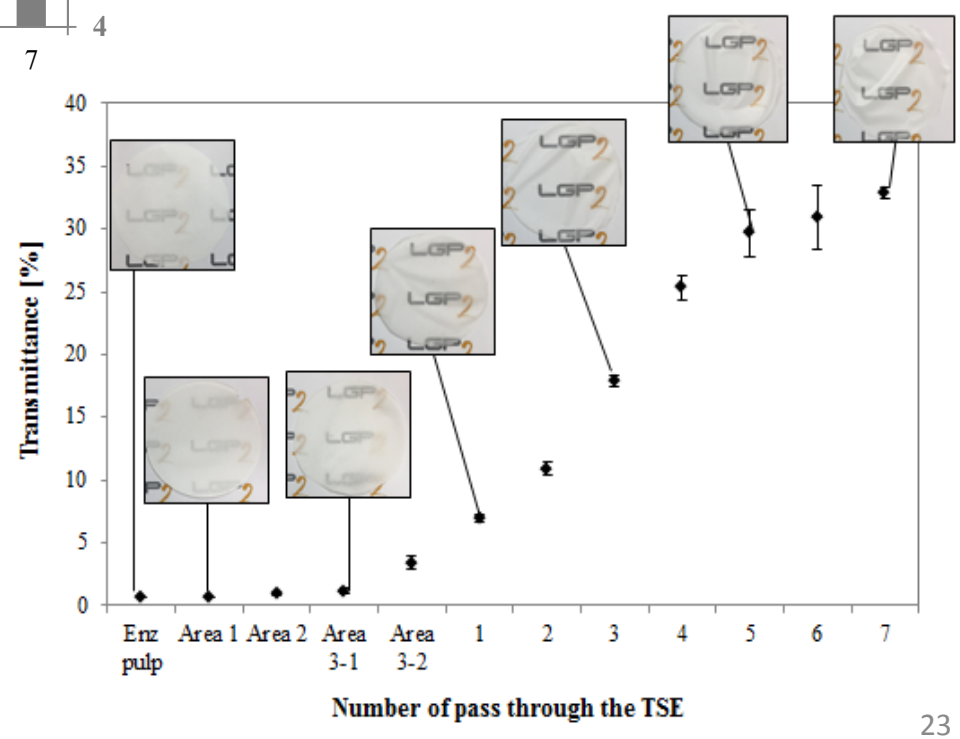
- **High flow rate**
- **Low dry content**
- **Compromises regarding screw speed**

An increase of 1 rpm increases the SME of 1.35 whereas the QI* is increased of only 0.02

CNF & TSE optimization

CNF quality with the number of passes through the profile 1





CNF & TSE optimization

Different screw profiles tested

Test of 3 profiles & characterizations of obtained CNF

Conveying Profile

Profile 1

10 Mixing elements at 30°
3 Mixing elements reverse at 30°

7 Mixing elements at 30°
4 Mixing elements at 60°
4 Mixing elements reverse at 60°

4 Mixing elements at 60°
12 Mixing elements at 90°
4 Mixing elements reverse at 60°

Profile 2

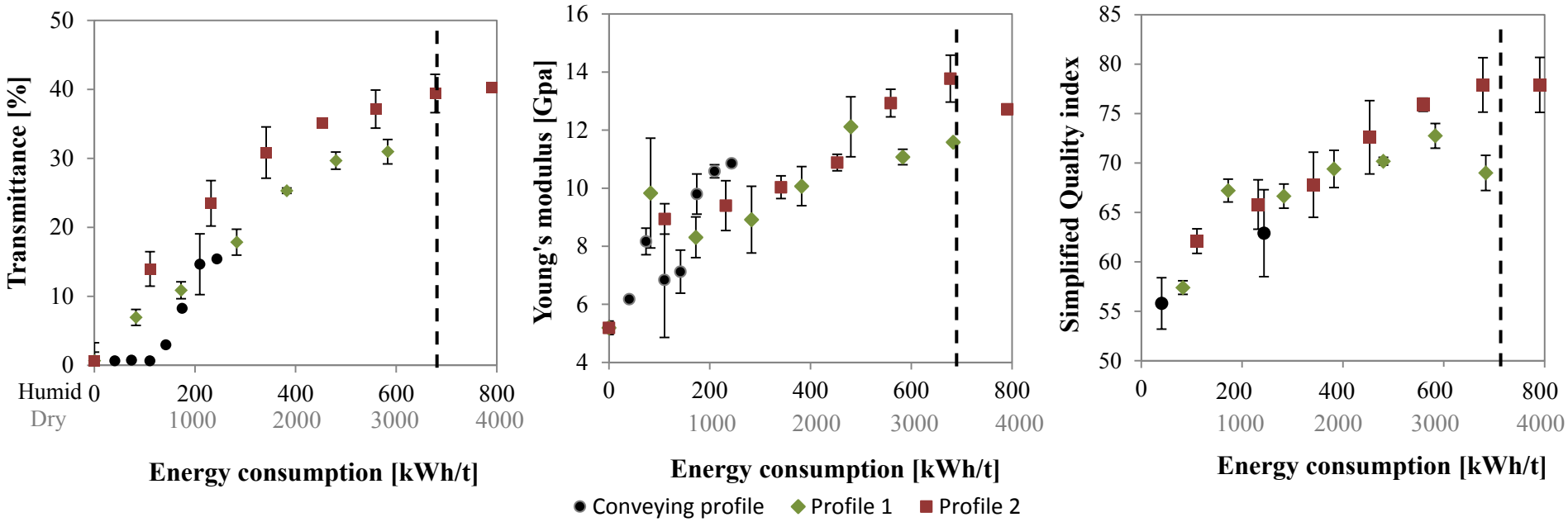
11 Mixing elements at 30°
5 Mixing elements at 60°

6 Mixing elements at 60°
6 Mixing elements at 90°
3 Mixing elements reverse at 60°

8 Mixing elements at 90°
3 Mixing elements reverse at 30°
8Mixing elements at 90°

CNF & TSE optimization

Different screw profiles tested



- Increased **QI*** with energy & Stabilization of the properties around **3,000 kWh/t (dry) or 700 kWh/t (humid•)**

- Screw profile optimization to obtain 3,000 kWh/t (dry) in **1 pass ?**
  -> limitation of the energy consumption
  -> increase in the productivity

• *Humid = 20 wt% solid content*

CNF & TSE optimization

Optimization of the screw profile using Ludovic software

Input Data

- Screw profile
- TSE conditions (feed rate, speed, T°C)
- Materials properties
  - Thermal conductivity
  - Heat capacity
  - Density

Calculated according to classical mixture law

- Viscosity of **20 wt% solid** content materials

Ludovic®

Cemef
CENTRE DE MISE EN FORME DES MATERIAUX

B. Vergnes

Output Data

$$\mathrm{SME}\left[\frac{\mathrm{kWh}}{\mathrm{t}}\right] = \frac{N * C * P_{max}}{N_{max} * C_{max} * Q}$$

Specific Mechanical Energy
Can be calculated without the use of a software

N: screw speed [rpm], N_{max}: 1,100 rpm
C: torque [N.m], C_{max}: 130 N.m
P_{max}: maximal power 7 kW
Q: dry flow rate [t/h]

$$\text{Shear rate } \dot{\gamma} = \frac{\omega * r}{H}$$

Can be calculated using Ludovic®
ω: angular speed [rad/s]
r: radius [m]
H: screw depth [m]

$$\text{Cumulated Strain} = \sum_i \dot{\gamma}_i \; t_i$$

Can be calculated using Ludovic®
γ_i: shearing rate [s^{-1}]
t: time [s]

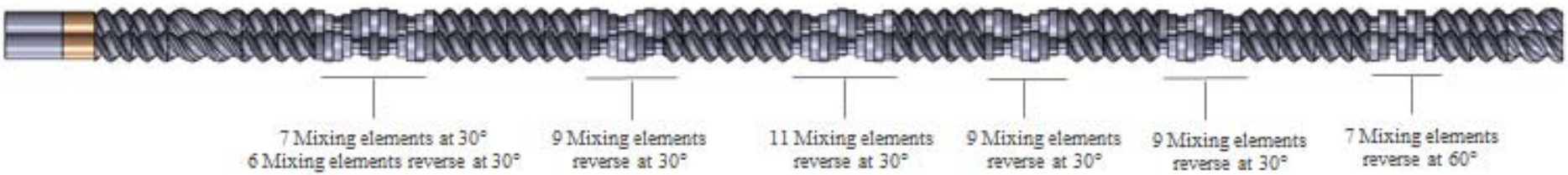
[1] Vergnes et al. 1998. Polym. Eng. Sci.

Extracted from [1]

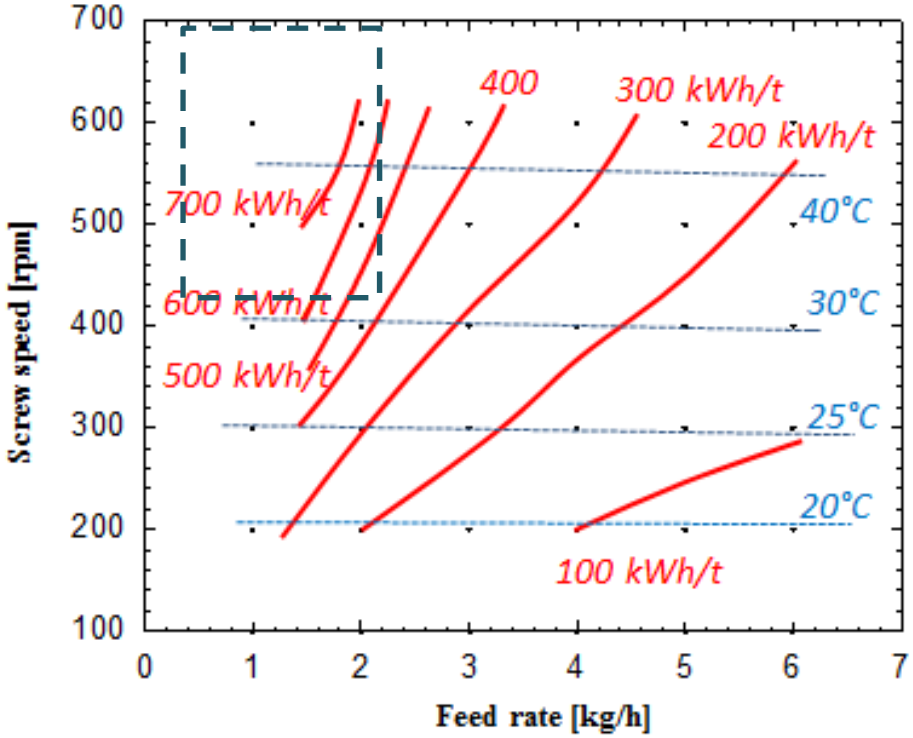
CNF & TSE optimization

Proposition of a new screw profile

Collab with B. Vergnes



Conditions to obtain 700 kWh/t (humid) or 3,000 kWh/t (dry)



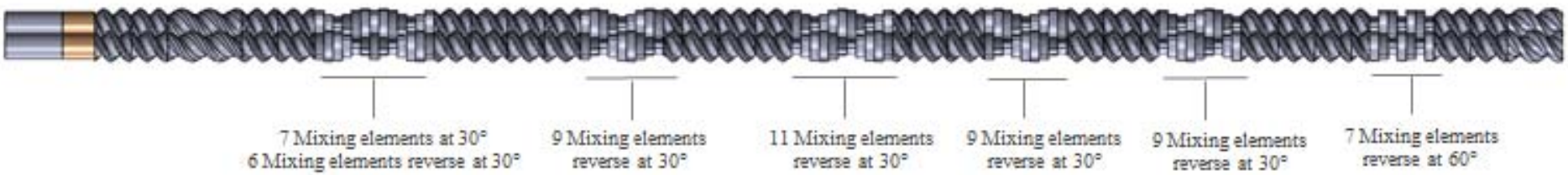
- Flow rate: **1-2 kg/h**
- Screw speed: **500 rpm**

CNF & TSE optimization

Proposition of a new screw profile

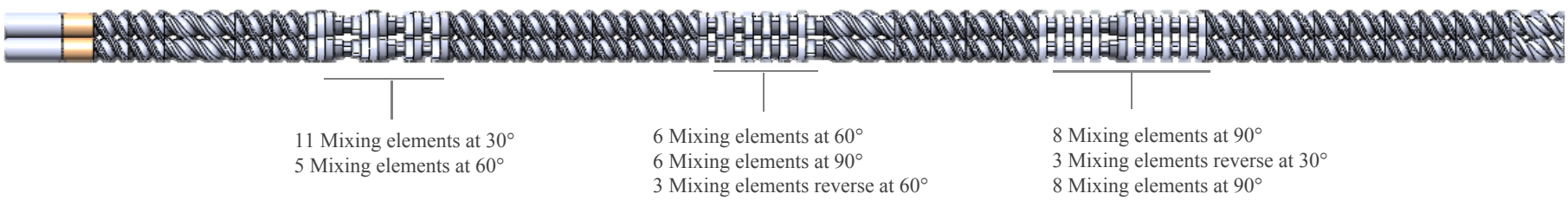
Collab. B. Vergnes

New profile



VS

Profile 2

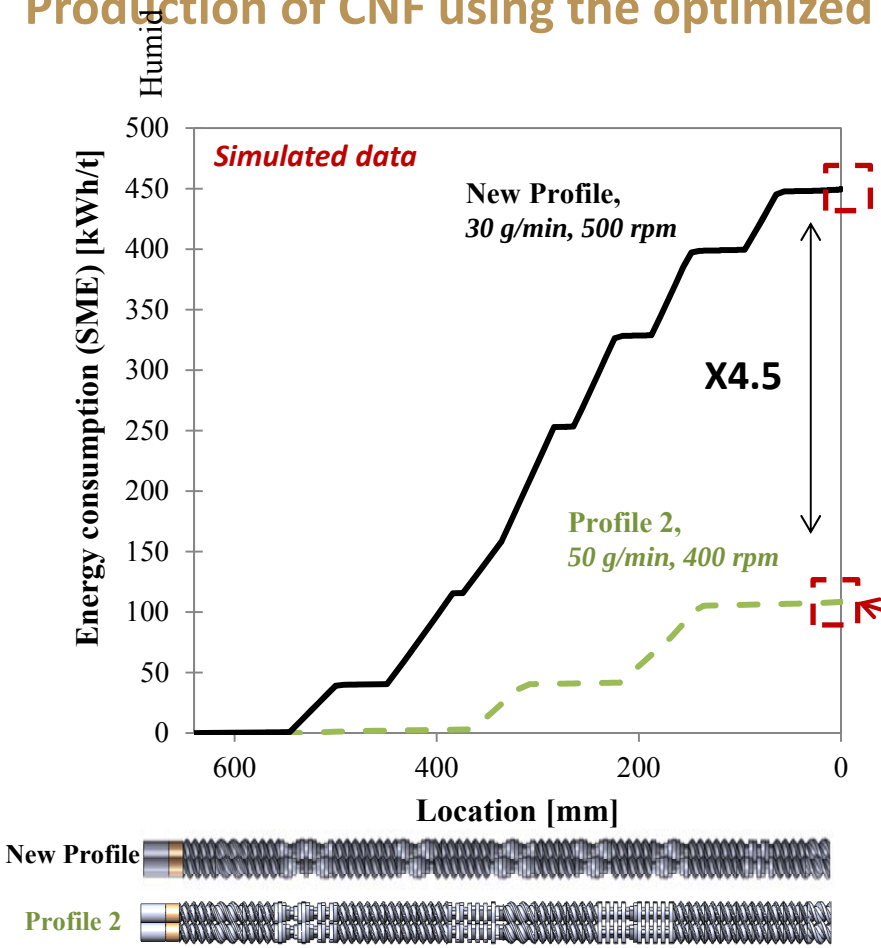


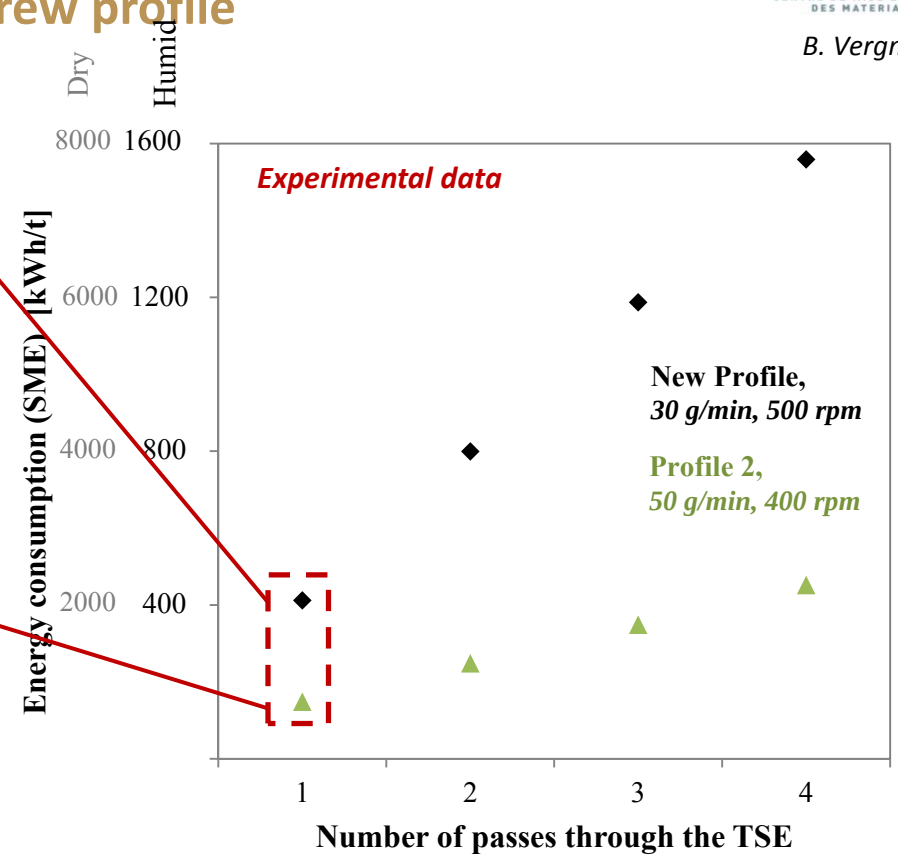
Screw profile used for preliminary studies

CNF & TSE optimization

Production of CNF using the optimized screw profile

B. Vergnes





$$\mathrm{SME}\left[\frac{\mathrm{kWh}}{\mathrm{t}}\right] = \frac{\mathrm{N} * \mathrm{C} * \mathrm{P}_{max}}{N_{max} * C_{max} * Q}$$

- Increase of cumulated strain due to higher **residence time**

New profile: **128 sec**

Profile 2: **58 sec**

- **Accordance** between experiments and simulation

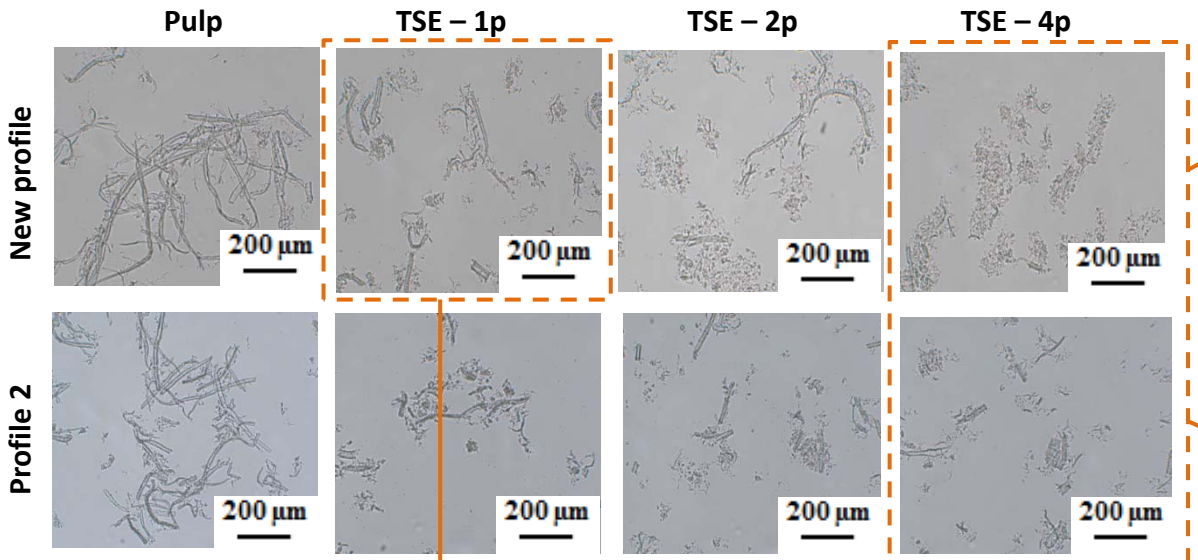
Datas obtained with Ludovic® software for 1 pass through the TSE equipped with each profile

CNF & TSE optimization

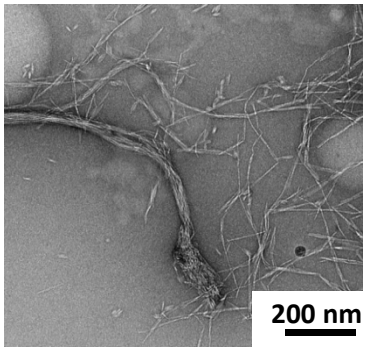
CNF obtained with the optimized screw profile

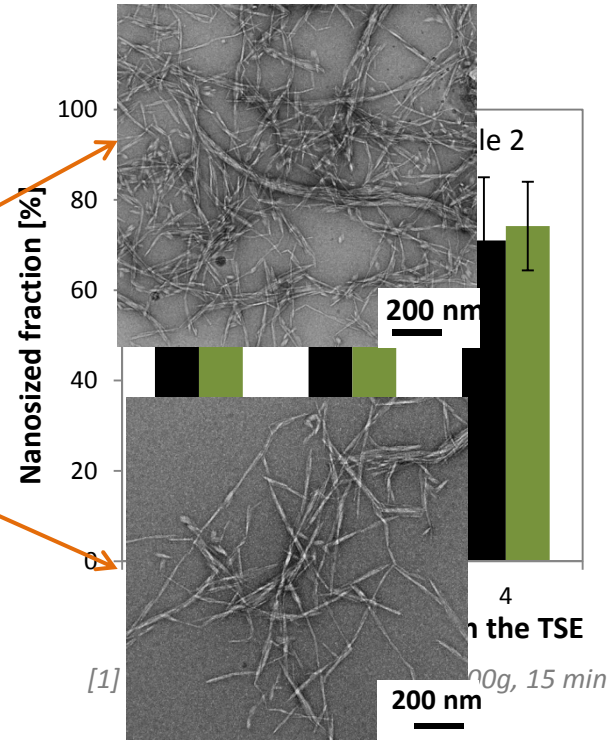
Objective: Produce CNF in 1 pass or at least decrease the number of passes required to obtain 3,000 kWh/t (dry) or 700 kWh/t (humid)

CNF pulp morphologies



Optical microscopy, 0.5 wt%



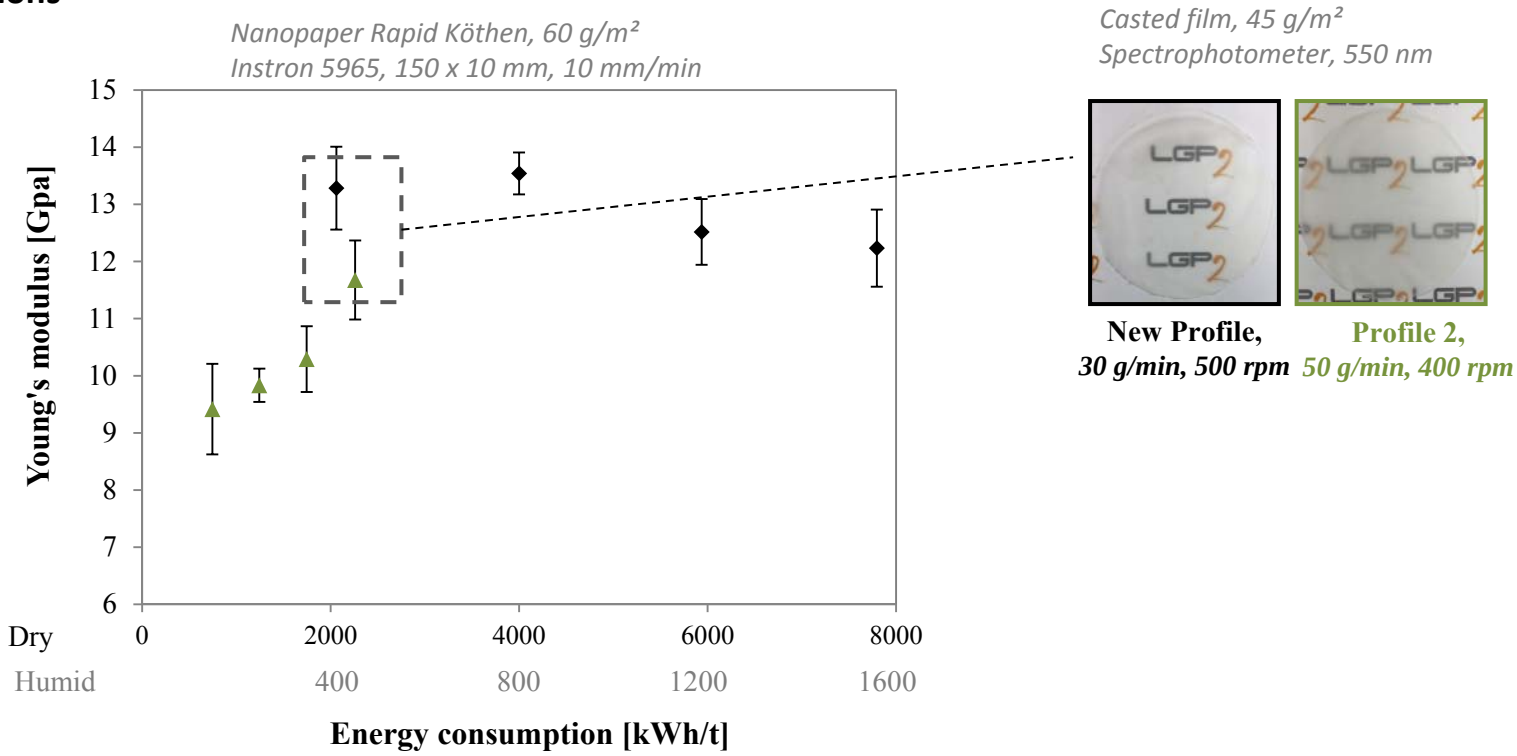


[1] *00g, 15 min*

[1] Naderi et al. 2015. Cellulose.

CNF & TSE optimization

Films characterizations

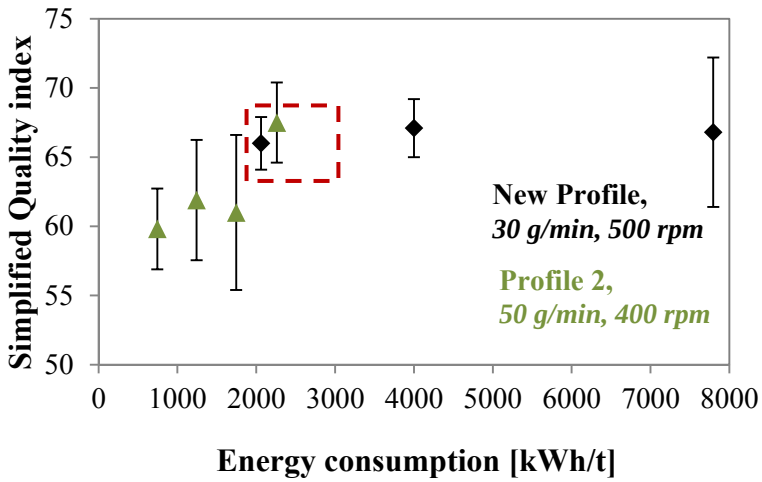


New profile

- High Young's modulus reached in **1 pass**
- No evolution of the Young's modulus with the number of passes
- At fixed energy, higher Young's modulus and **reduction of the number of passes**
- High transparency reached in one pass

CNF & TSE optimization

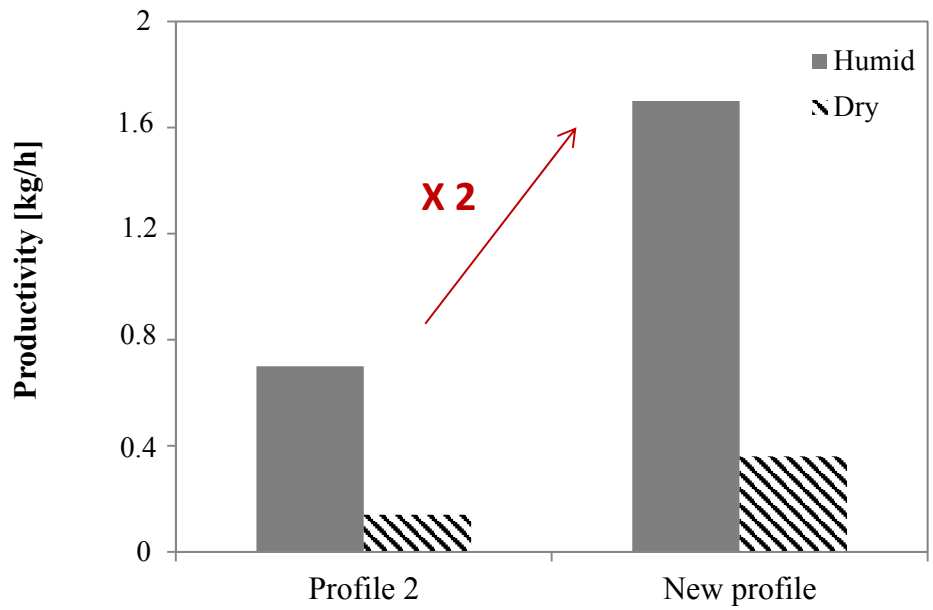
CNF obtained with the optimized screw profile



- Same quality for same energy consumption but **1 pass instead of 4**
- Final QI* of **68,** in the range of commercial CNF

$$\text{Productivity} = \frac{Q}{N} * \left(\frac{60}{60+t}\right)$$

Q: flow rate [kg/h] (dry or humid)
N: number of passes through the TSE
t: latency time [min]



Can we produce CNF at larger scale for same QI*?

CNF & TSE optimization

A. Rouilly

Enzymatic hydrolyzed pulp

Pilot-scale TSE

ThermoFisher PTW 16

Diameter: 16 mm

Length: 64 cm

L/d: 40

Maximum speed: 1,100 rpm

Maximal torque: 130 N.m

Flow rate (humid) used: 3 kg/h

Speed: 400 rpm

Solid content: 18 wt%

Semi-Industrial scale TSE

Clextral BC45

Distance between center of the screw: 45 mm

Length: 1,4 m

Maximum speed: 600 rpm

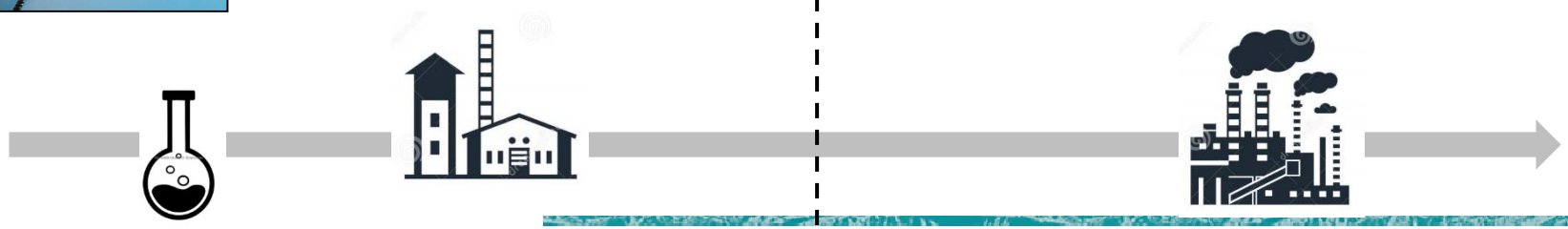
Maximum tension: 460 W

Flow rate (humid) used: 19 kg/h

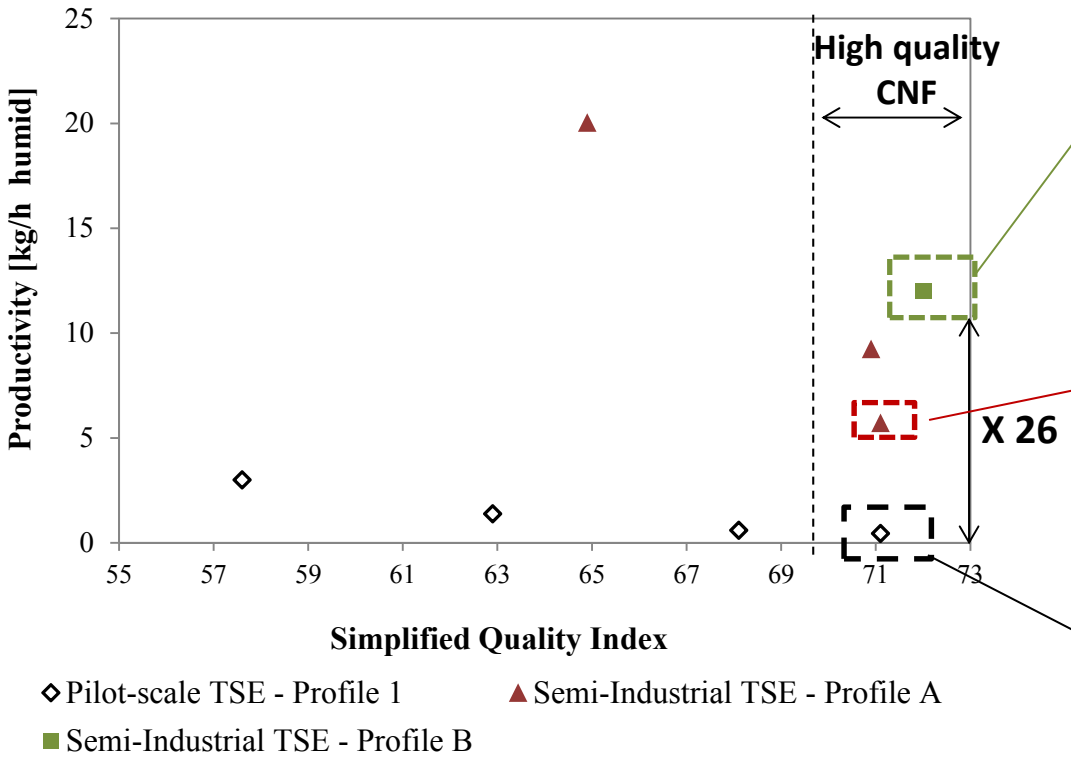
Speed: 300 – 400 rpm

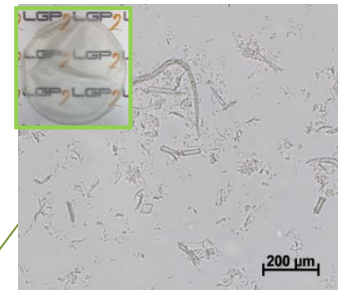
2 different screw profiles

Solid content: 18 wt%

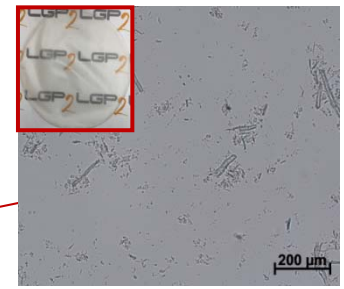


CNF & TSE optimization

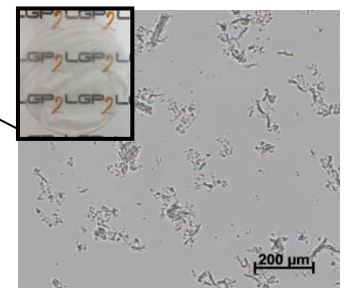




SME: 1,570 kWh/t
Nanosized fraction: **79.4%**
Young's modulus: **11.0 GPa**



SME: 2,040 kWh/t
Nanosized fraction: **74.1%**
Young's modulus: **10.0 GPa**



SME: 2,200 kWh/t
Nanosized fraction: **72%**
Young's modulus: **12.1 GPa**

OUTLINE

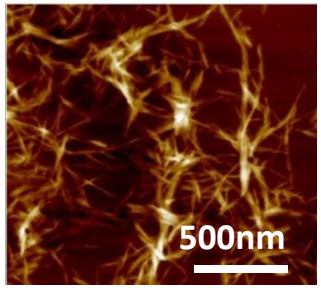
- ❑ Introduction to nanocellulose & production
- ❑ Nanocellulose production by TSE: proof of concept
- ❑ Optimization of TSE for CNF

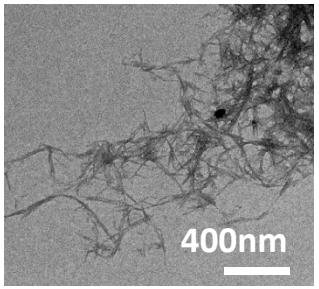
CONCLUSIONS

CNF & TSE optimization

CNF production by TSE

- **Solid content** multiplied by **10**
- **Energy consumption** divided by more **than 2**
- CNF of high quality: **QI* = 70 ± 5**





Optimization of the process

- **Design** of an **optimized screw profile using Ludovic®**
- Increase of the **productivity by more than 2**
- Production of **high quality CNF in one pass**
- **Production at large scale is confirmed**
- Production of **100 t/y (humid)** with only **1** semi-industrial **TSE**

High quantity of CNF can be produced: Applications?

Perspectives

Objectives

- **New applications** for high solid content CNF
- Production of **high content CNF objects**

=> NACECO Project in progress (2018-2020)

Formulations

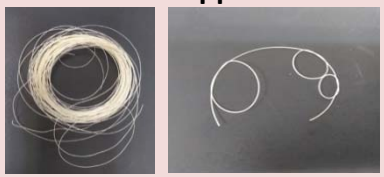
Starch/ CNF composites

Collaboration with USP – Brazil
A. J. F. De Carvalho

Use in 3D printing

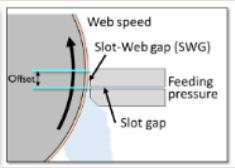
C. Thibaud PhD thesis, LGP2

Use in fibre spinning for biomedical application



Collaboration with R. Abouzeid, National Research Center of Egypt

Slot Die coating

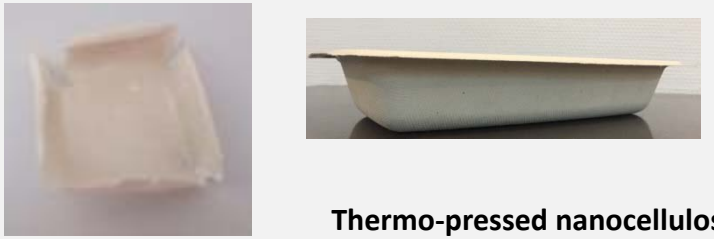


Collaboration with Åbo University –Finland
M. Toivakka

High solid content CNF

All nanocellulose objects

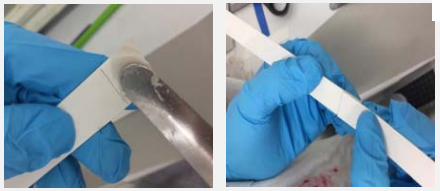
Molded nanocellulose



Thermo-pressed nanocellulose

Freeze dried nanocellulose

Glue



Collaboration with A. Rouilly

Thank you

PRESENTED BY

Julien BRAS

Ass. Professor

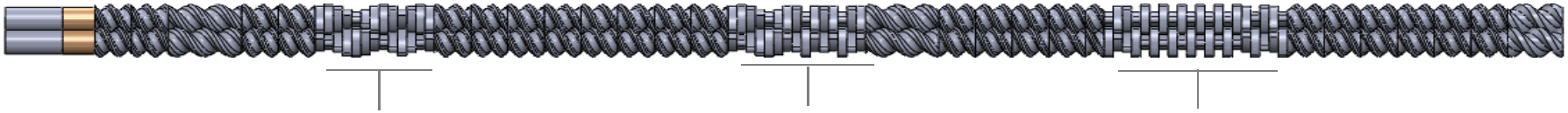
Univ. Grenoble Alpes, CNRS, Grenoble INP, LGP2

Julien.bras@grenoble-inp.fr

Screw profiles

Conveying Profile

Profile 1



10 Mixing elements at 30°
3 Mixing elements reverse at 30°

7 Mixing elements at 30°
4 Mixing elements at 60°
4 Mixing elements reverse at 60°

4 Mixing elements at 60°
12 Mixing elements at 90°
4 Mixing elements reverse at 60°

Profile 2

11 Mixing elements at 30°
5 Mixing elements at 60°

6 Mixing elements at 60°
6 Mixing elements at 90°
3 Mixing elements reverse at 60°

8 Mixing elements at 90°
3 Mixing elements reverse at 30°
8Mixing elements at 90°

New profile

7 Mixing elements at 30°
6 Mixing elements reverse at 30°

9 Mixing elements reverse at 30°

11 Mixing elements reverse at 30°

9 Mixing elements reverse at 30°

9 Mixing elements reverse at 30°

7 Mixing elements reverse at 60°

Characteristics of the TSE

- Diameter: 16 mm
- Length: 640 mm
- L/d: 40
- Maximum speed: 1,100 rpm
- Maximal torque: 130 N.m
- **Flow rate used: 3 kg/h**
- **Speed: 400 rpm**
- **Force Feeder**

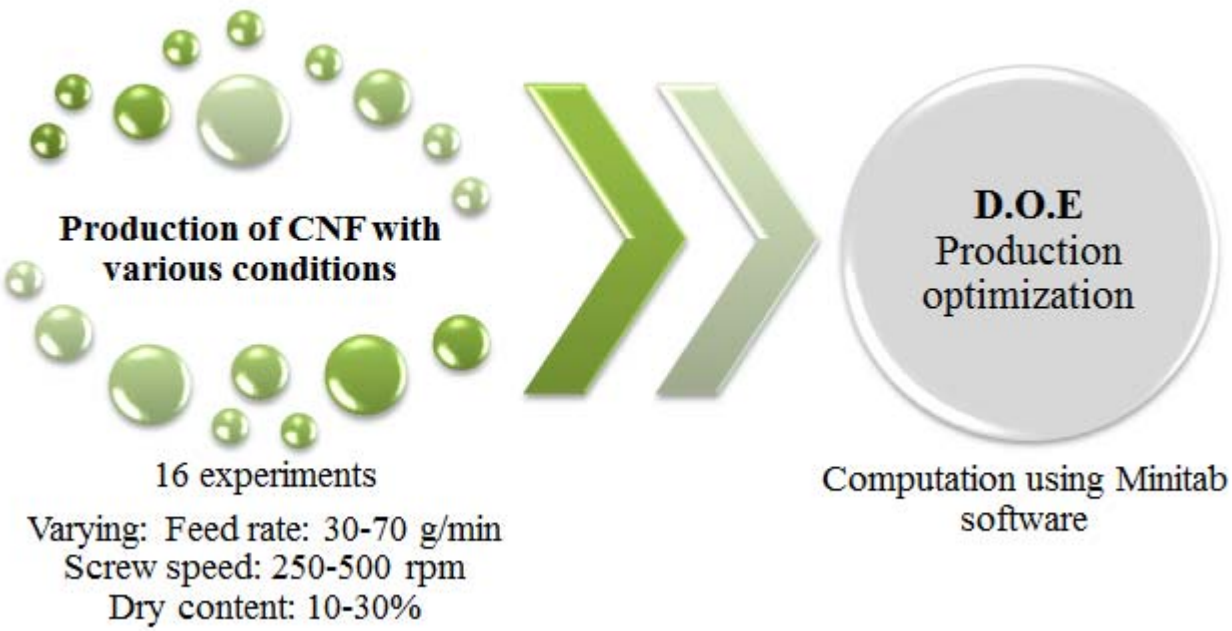
Use of TSE for biomass application

Cellulose type	Process	Extruder (Clextral model)	T[°C]	Dry content [%]	EMS [Wh/kg]	Reference
Sugar beet pulp	Destructuring Coumpounding	BC 45	98-115	89.9	213-745	Rouilly et al.[185]
Wheat Straw	Destructuration	BC 45	120	89	380-500	Vandenbossche et al.[175]
Sunflower oilcake	Melting Destructuring	BC 45	80-100	92.8	78.5-104.1	Evon et al.[186,187]
Sweet corn	Destructuration using chemicals	Evolum 53	22-100	27.2	88	Vandenbossche et al. [177]
Sugar can bagasse	Destructuration using chemicals	Evolum 53	25-75	38	408	Vandenbossche et al. [177]
Eucalyptus	Destructuration using chemicals	Evolum 53	25-75	40.1	445	Vandenbossche et al. [177]
Vineyard pruning	Destructuration using chemicals	Evolum 53	25-75	34.1	207	Vandenbossche et al. [177]
Blue agave bagasse	Destructuration using chemicals	Evolum 53	22-75	32.7	288	Vandenbossche et al. [177]
Pea hulls	Extrusion cooking	BC 45	100	40-70	115-363	Ralet et al.
Wheat Bran	Extrusion cooking	BC 45	100	82-94	230-380	Ralet et al.
Sugar beet	Extrusion cooking	BC 45	100	70-80	155-287	Ralet et al.

Design of experiment results

Objectives

- Determine the influence of the TSE parameters on QI, Energy, Young's modulus,…
- Develop models for the different responses



Studied responses
- Young's modulus
- QI
- Energy consumption

Responses:

$$R_k = b_0 + \sum_{i=1}^{3} b_i * x_i + \sum_{\substack{i,j=1 \\ j \neq i}}^{3} b_{ij} * x_i * x_j + \sum_{\substack{i,j,k=1 \\ i \neq j \neq k}}^{3} b_{ijk} * x_i * x_j * x_k$$

bi: coefficients of the model
Bij * xi * xj : interactions

Design of experiment results

Matrix of experiments

Complete factorial design

	Trials #	P_1 : Flow	P_2 : Speed	P_3 : Dry content	Energy [kWh/t]	Young's modulus [GPa]	Quality index
Complete factorial Design	1	-1	-1	-1	845	15.6	72.9
	2	+1	-1	-1	483	14.3	72.7
	3	-1	+1	-1	1688	15	76.8
	4	+1	+1	-1	820	14.8	77.8
	5	-1	-1	+1	1453	6.7	57.5
	6	+1	-1	+1	940	10.4	68.9
	7	-1	+1	+1	2277	12.1	78.8
	8	+1	+1	+1	1261	11.4	73
Face center	9	-1	0	0	1487	12	69.2
	10	+1	0	0	863	11	73.9
	11	0	-1	0	1055	9.2	68.5
	12	0	+1	0	1398	12.3	72
	13	0	0	-1	837	13.8	73.3
	14	0	0	+1	1478	13	63.5
Center	15	0	0	0	1026	9.6	67.9
	16	0	0	0	1269	12.7	69.1

Variables were reduced centering to compare each parameter in the same variation field

Model determination

- Minitab proposes an equation containing all the parameters and their interactions

- The significance of each parameters were evaluated using Student factor T

If T< 2.28 (95% confidence interval), the parameters or the interactions is removed from the equation

=> Equation corresponding to each responses are hence obtained

Validity of the model

- Comparison of **regression coefficients**

- **R^2**: the deviation of the model.

R^2 increases with the addition of new parameters

If $R^2 < 0.7$: rejection of the model

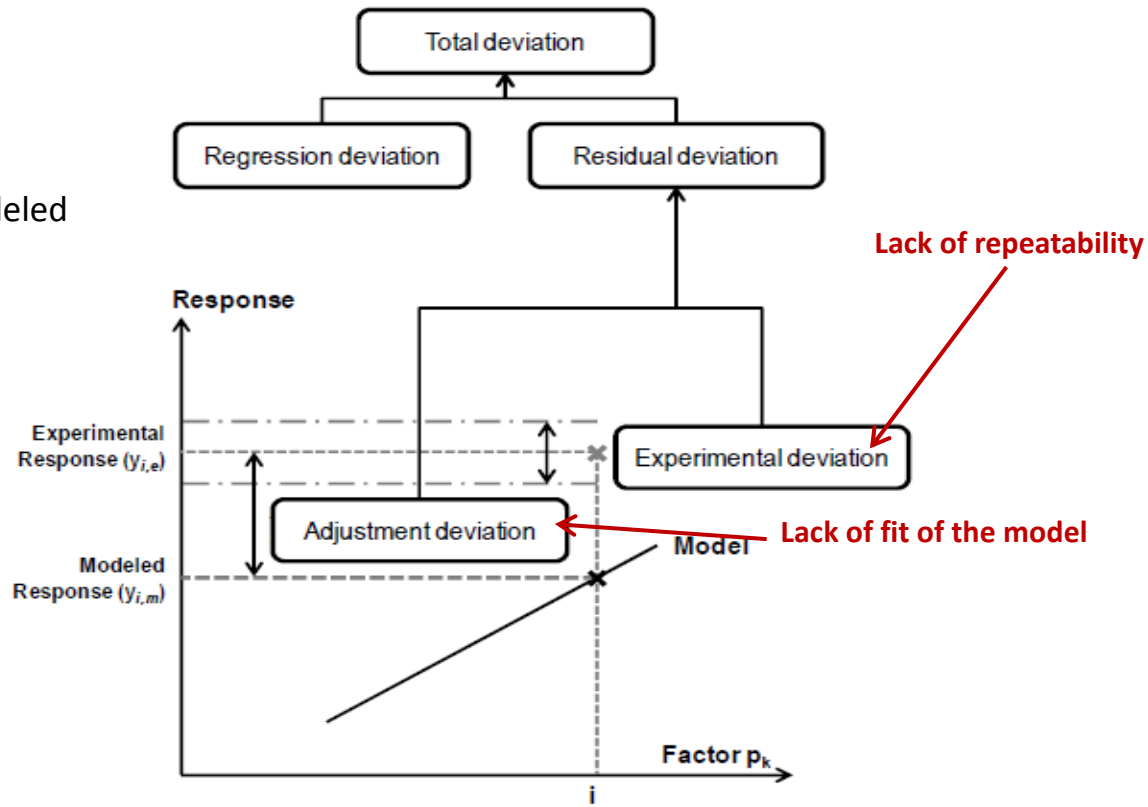
- **R^2_{adjust}** takes into account the number of parameters used to design the model

- **R^2_{prev}** determines the capacity of the model to predict answer

$R^2_{prev} > 0.7$ indicates an excellent predictive power and ideally $R^2 - R^2_{prev} < 0.2$

Variance analysis

- Total deviation of the model can be due to :
  - The regression deviation of the model
  - The residual deviation which cannot be modeled



- **Model is significant if**

Regression deviation > residual deviation

Experimental deviation > adjustment deviation

- Can also be evaluated using Fisher Test

$$F1 = \frac{V_{reg}}{V_{res}} \qquad F2 = \frac{V_{adj}}{V_{exp}}$$

If $F_1 \leq F_\alpha$: the model cannot explain for the total variance with a probability α.

If $F_1 > F_\alpha$: the model can explain the total variance and the model is considered significant.

If $F_2 < F_\alpha$: the lack of fit of the model is negligible compared to the experimental production.

F_α determined with a table for a probability of 0,05

Variance analysis

	Sum of squares	Degrees of liberty	Variance	Test
Total Deviation	$SS_{tot} = \sum_{i=1}^{n}(\eta_i - \bar{Y}_i)^2$	$v_{tot} = n+n_0-1$	$V_{Tot} = \frac{SS_{Tot}}{v_{Tot}}$	
Residual Deviation	$SS_{Res} = \sum_{i=1}^{n}(\eta_i - y_i)^2 = \sum_{i=1}^{n} e_i$	$v_{Res} = n+n_0-r$	$V_{Res} = \frac{SS_{Res}}{v_{Res}}$	F_1
Regression Deviation	$SS_{Reg} = SS_{tot} - SS_{Res}$	$v_{Reg} = v_{Tot} - v_{Res} = r-1$	$V_{Reg} = \frac{SS_{Reg}}{v_{Reg}}$	
Experimental Deviation	$SS_{Exp} = \sum_{i=1}^{n}\left(y_i^0 - \overline{y^0}\right)^2$	$v_{Exp} = n_0-1$	$V_{Exp} = \frac{SS_{Exp}}{v_{Exp}}$	F_2
Adjustment deviation	$SS_{Adj} = SS_{Res} - SS_{Exp}$	$v_{Adj} = v_{Res} - v_{Exp} = n-r+1$	$V_{Adj} = \frac{SS_{Adj}}{v_{Adj}}$	

η_i: model predicted response; Y_i: experiments' mean response; e_i: error; y_0: response for replicate experiments
n: Total number of experiments, n_0: number of replicate, r: number of coefficient in the model

Determination of the models

Energy consumption

$$y = 1.658\, x_1 + 4.847 x_2 + 26.191\, x_3 - 0.05 x_1 * x_2 - 257.737$$

X1: Flow rate
X2: Screw speed
X3: Solid content

$R^2 = 0.983$; $R^2_{adjust} = 0.961$; $R^2_{prev} = 0.943$

- Low solid content should be prefered
- High significance
- Excellent prediction

Simplified Quality Index

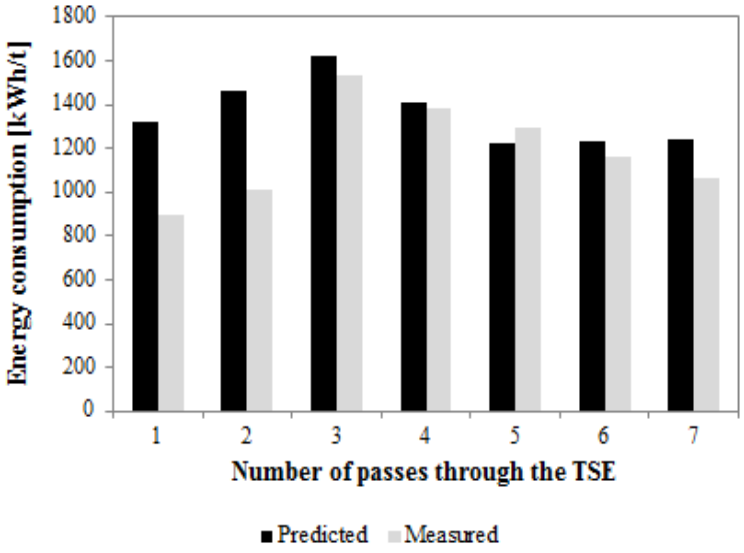
$$y = -0.35 x_1 - 0.043\, x_2 - 2.541\, x_3 + 0.0352 x_1 * x_3 + 0.0059 * x_2 * x_3 - 8.75 * 10^{(-5)} x_1 * x_2 * x_3 + 93.665$$

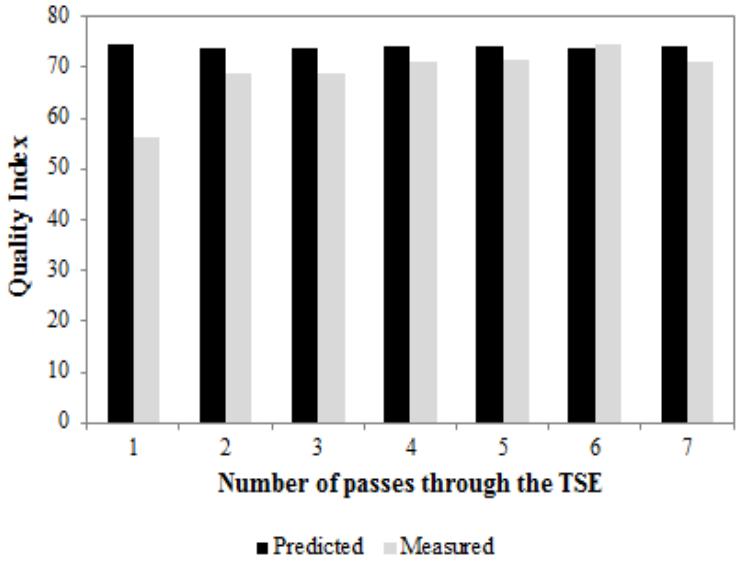
$R^2 = 0.995$; $R^2_{adjust} = 0.995$; $R^2_{prev} = 0.537$

- Significant model
- Cannot be used for prediction
- Most impacting parameter: screw speed
- High speed, high feed rate and low solid content should be used

Model examination

Using a new batch of enzymatic cellulosic pulp





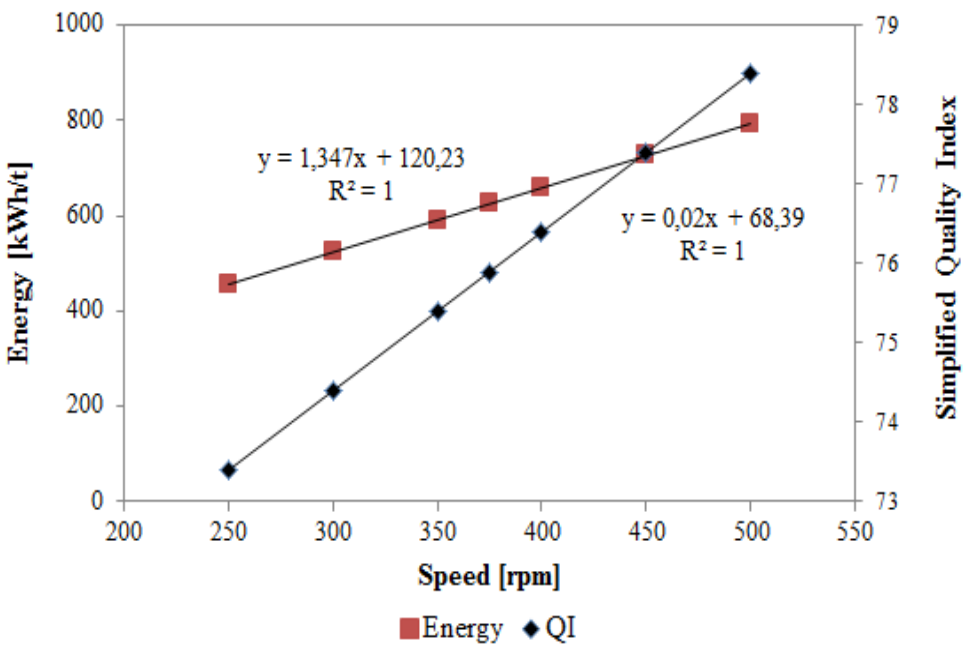
- Concordance is not evident
  Due to block effect

- The difference are less visible with the number of passes because cellulose are nanofibrillated and finally reached a same morphology

Design of experiment results

How to reduce energy consumption and increase QI*?

QI_{max} = 78.4			$Energy_{min}$ = 457 kWh/t		
Flow [g/min]	Screw speed [rpm]	Dry content [%]	Flow [g/min]	Screw speed [rpm]	Dry content [%]
70	500	10	70	250	10



- High flow rate
- Low dry content
- Compromises regarding screw speed

An increase of 1 rpm increases the SME of 1.35 whereas the QI* is increased of only 0.02

Optimization of the screw profile using Ludovic software

Bruno Vergnes

- Developed by Science computers consultants, 30 years ago
- Simulate the global flow of the TSE & predict material behavior
- Calculate the main flow thermomechanical parameters such as: shear rate, residence time, SME, pressure
- Based on a global modelization of the flow using a 1D approach
- <u>Materials properties</u>

- Viscosity
- Thermal conductivity
- Density
- Heat capacity
- Heat exchanges: represented by the Nusselt number in the software, Nu=11 in our case

- Viscosity law should be defined

Choosen parameters

Obtained with classical mixture law: 80% water, 20% cellulose

Parameter	Water	Cellulose	Value Used
Thermal conductivity [W/(m.K)]	0.607	0.035-0.041	0.49
Heat capacity [kJ/(kg.K)]	4.18	1.9	3.6
Density [g/cm³]	1	1.5	1.1

[1] Vergnes et al. 1998. Polym. Eng. Sci.

Extracted from [1]

Ludovic software

- The flow is modelized in each screw elements from the end to the beginning of the TSE
- Connection of all modelization leads to the global model

1- The user define a final temperature according the experiments

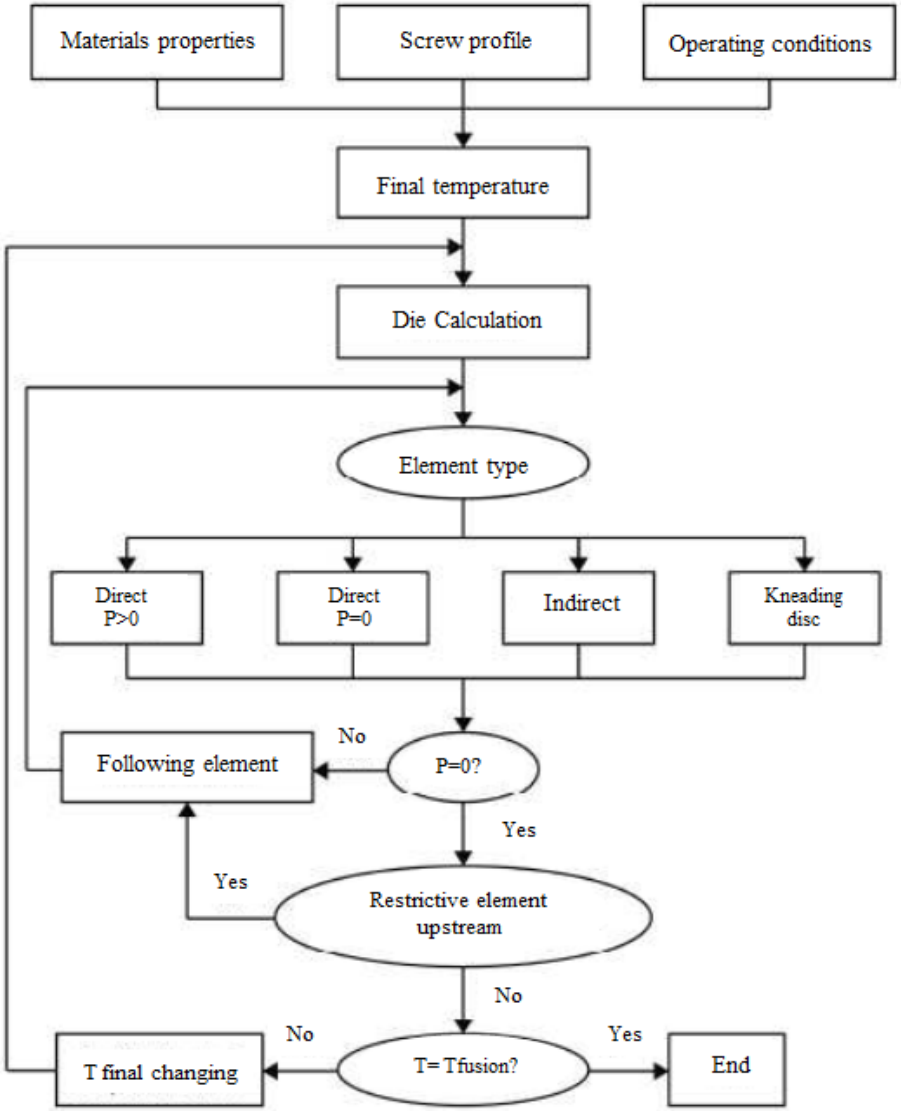
2- Pressure and temperature are determined along the screw until a P=0

At P=0, T should be equal to Tfusion

3- If P=0, the software checks if there is a restrictive element upstream, If no the simulation is finished

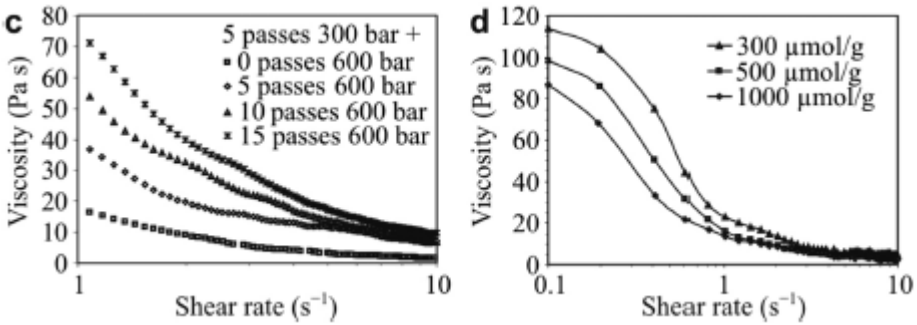
4- The temperature at this point is compared to the temperature given at the begining.

If it does not correspond, the user needs to give an other temperature and simulation restart.



Rheological measurement of CNF

Current progress in rheology of cellulose nanofibril suspensions, Nechyporchuk et al. Biomacromolecules



Rheological behavior of CNF…

- CNF possess **agglomerates** structure
- Water release can occurs – **phase separation**
- Very **heterogeneous** suspension
- CNF morphologies are really different depending on the production process
- The strain can disrupt and rearrange the materials structure
- Network strength depends on the type of pretreatment and on the extent of fibrillation
- Due to the heterogeneity and the size of the gap, **the measurement can correspond to residual fibers instead of nanofiber network**
- CNF can **slip on the geometry** due to the existence of lubricating layers on the boundary of the geometry surfaces
- Presence of hemicelluloses also influence the rheological behavior
- **Preshear** protocol is very important

Rheological measurement of CNF at 20 wt%

- Samples are stored in the fridge

- Parallel plate geometry of 25 mm, gap 2mm

Roughened surface

Pelletier cooled plate to 15°C

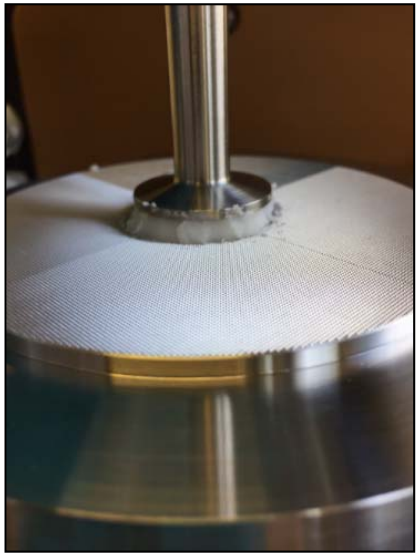
- **Protocol used**

- Ball of 1g, presheared by hand and excess removed
- Oscillatory measurement were perfomed to determine the linear domain

Strain sweep experiments at angular frequency of 10 rad/s were performed and the optimal strain was found at 0.02%

- Measurement were then performed from 0.1 to 100 rad/s at a fixed strain of 0.02%

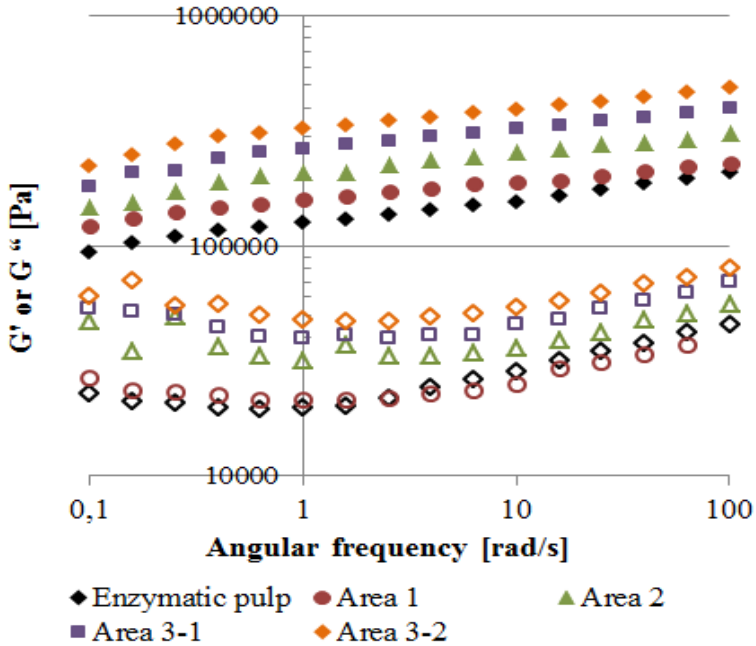
ARG2 (TA instruments)

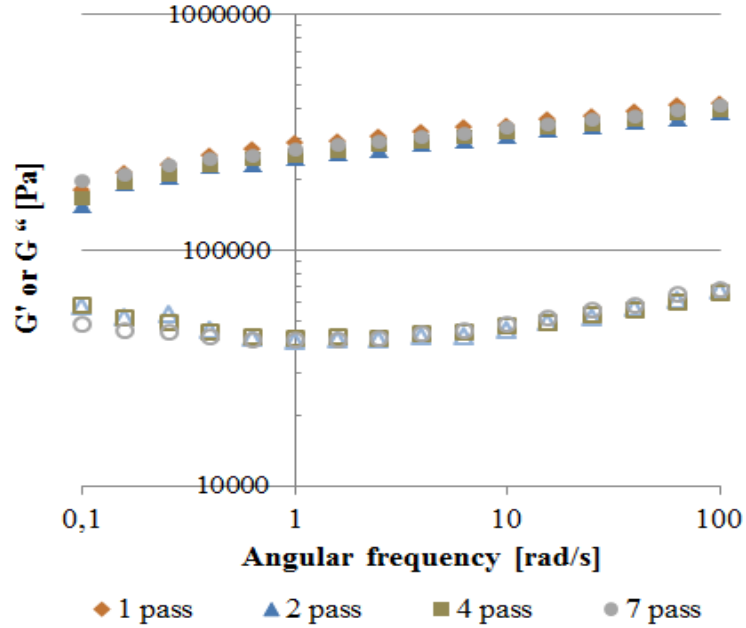


Rheological measurement of CNF at 20 wt%

Linear domain, strain 0.02%

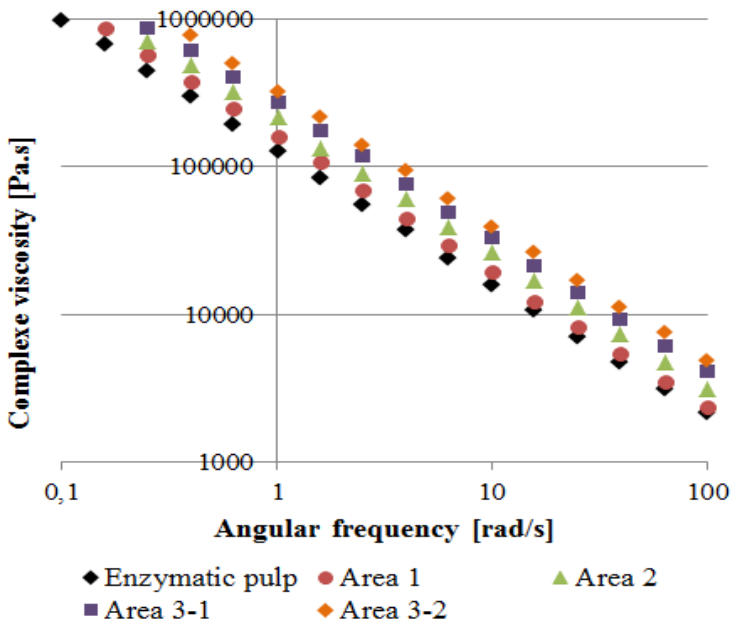
G'>G'' : solid-like behavior

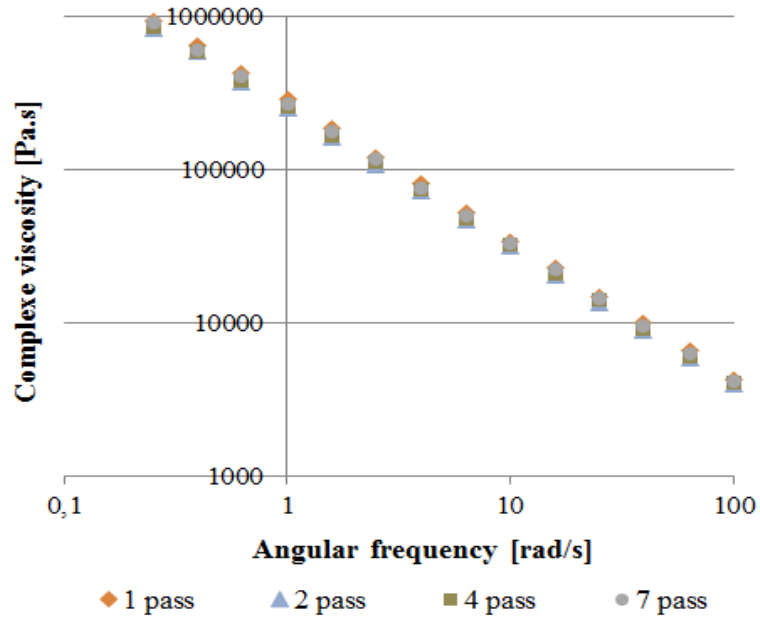




- CNF structured **as 3D interconnected network** which create a solid-like structure
- When **quality increases**, specific surface area increase, higher entanglement leading to **stronger network**
- Effect are visible just during the **first pass**
  -> Probably due to limit of the technic used here
- **G' and G''** are higher than the one reported in the literature due to **higher dry content**

Rheological measurement of CNF at 20 wt%





- **Shear thinning** and thixotropic behavior
- No evolution with the number of passes
- Data should be treated with caution

Rheological measurement of CNF at 20 wt%

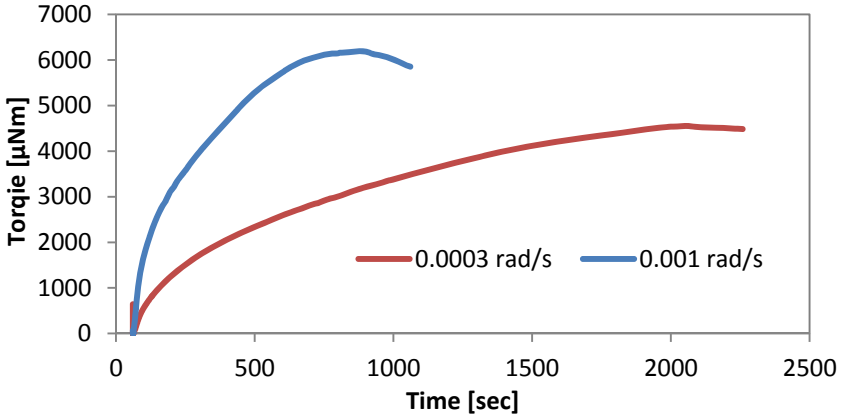
Flow threshold?

1- Scissometry analysis

- Speed between 0.0001 and 0.01 are imposed

- Torque and maximal strain are measured

=> If for two differents speeds, the maximal strain is the same, we are the flow threshold
Indeed, at the threshorld, strain does not depend on speed



Strain at the flow threshold = torque/ K

Speed [rad/s]	Maximal Torque [µNm]	Contrainte seuil [Pa]	Contrainte Réelle [Pa]
0,001	6206	2495	3647
0,0003	4553	1831	3478

Strain around 3500 Pa

Rheological measurement of CNF at 20 wt%

Flow threshold?

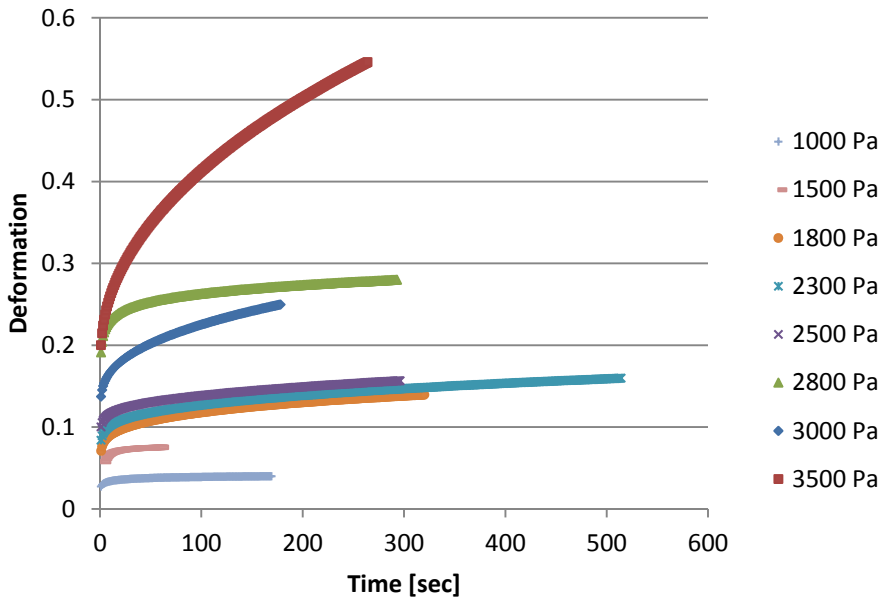
2- Creep experiments

- Parallel plate, rough
- Gap : 2 mm
- Normal force around 1 N

Try different samples obtained with different speed, feed rate and solid content on the TSE

Sample 3

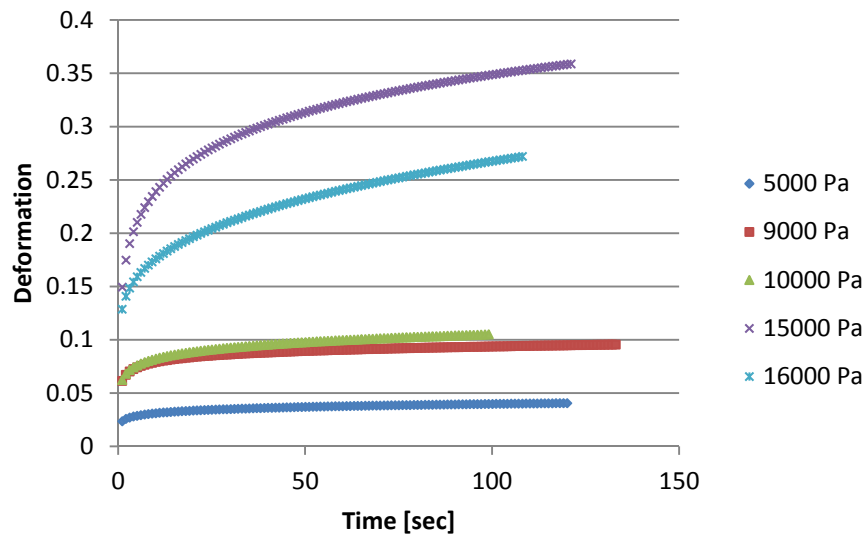
10%, 30g/min, 500 rpm



Threshold strain: **2,800-3,000 Pa**

Sample 5

30%, 30g/min, 250 rpm

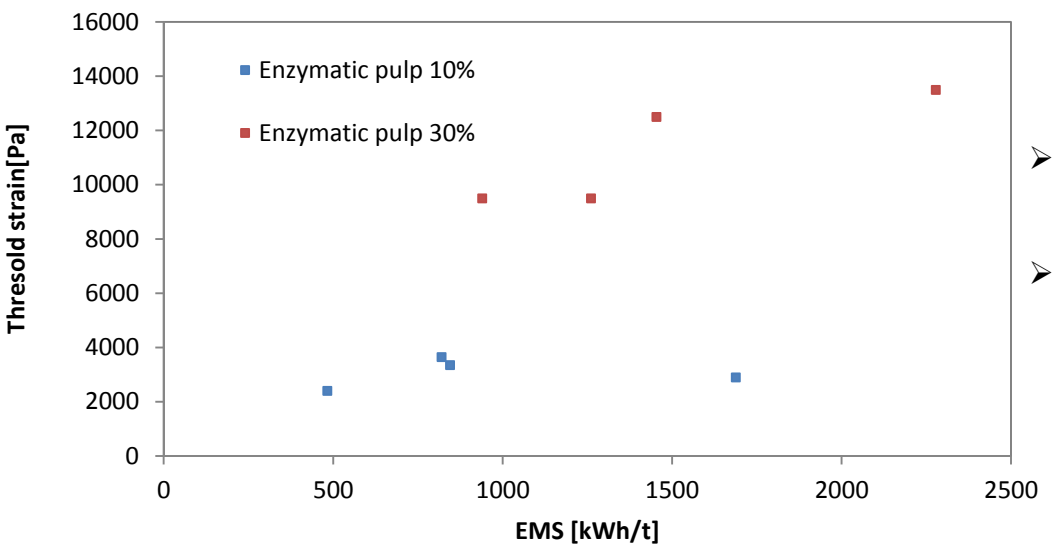


Threshold strain: **10,00-15,000 Pa**

Rheological measurement of CNF at 20 wt%

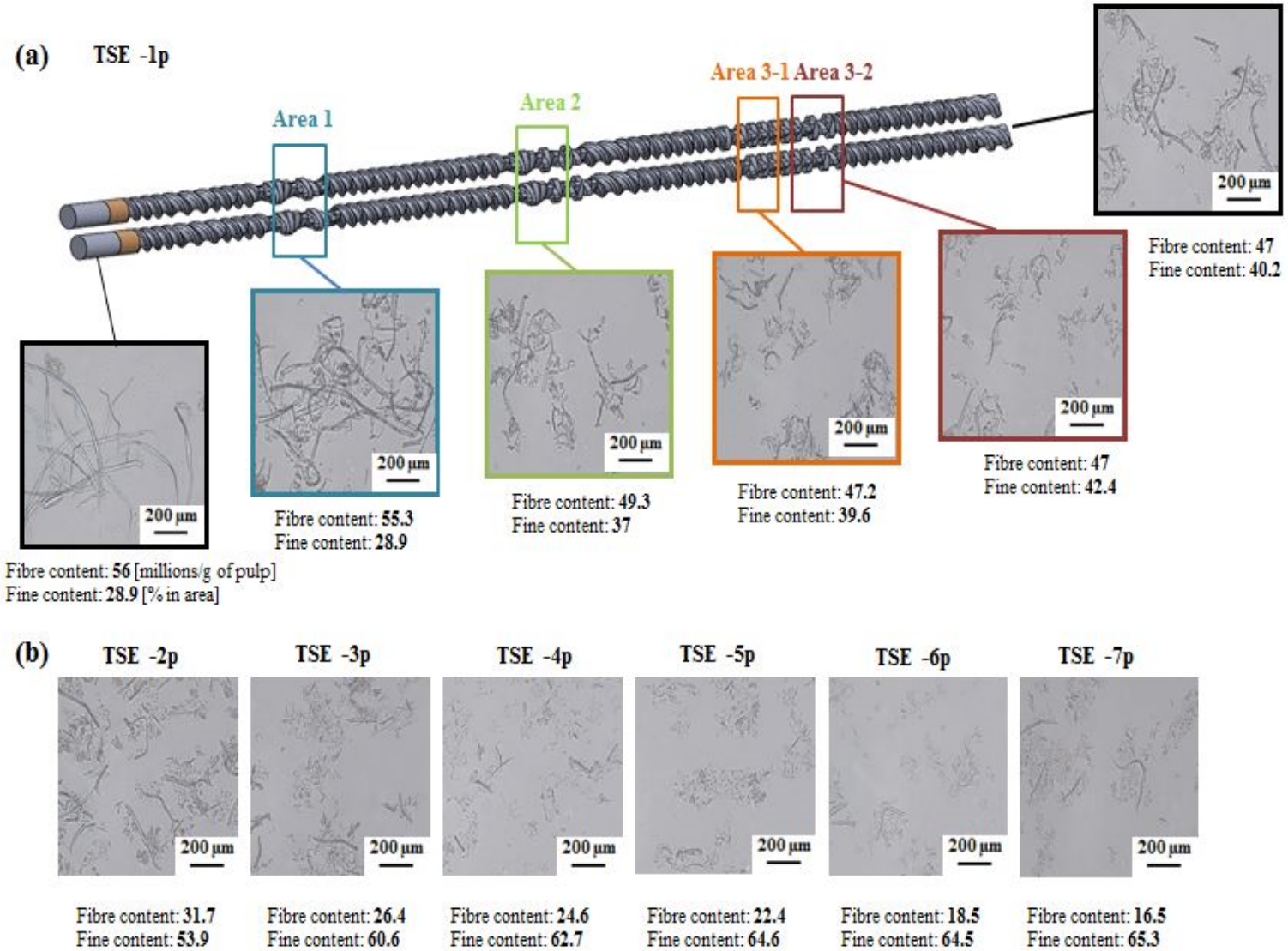
Flow threshold?

Sample	Dryness content [%]	Seuil max [Pa]	Seuil min [Pa]	Average	EMS [kWh/t]
2	10	2500	2300	2400	483
4	10	3800	3500	3650	820
1	10	3500	3200	3350	845
3	10	3000	2800	2900	1688
6	30	10000	9000	9500	940
8	30	10000	9000	9500	1261
5	30	15000	10000	12500	1454
7	30	15000	12000	13500	2278

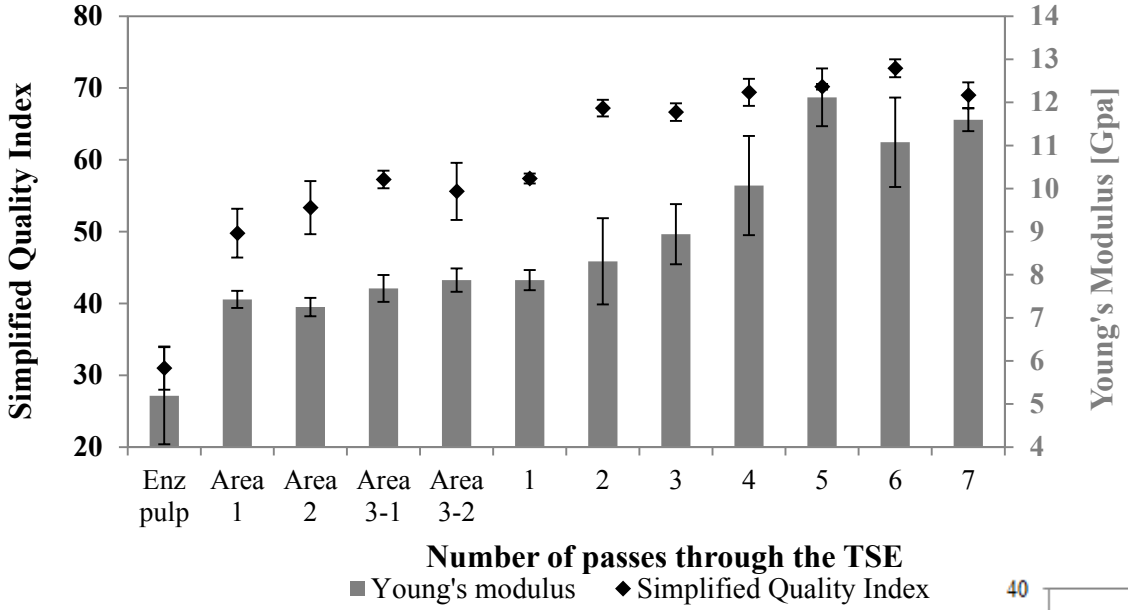


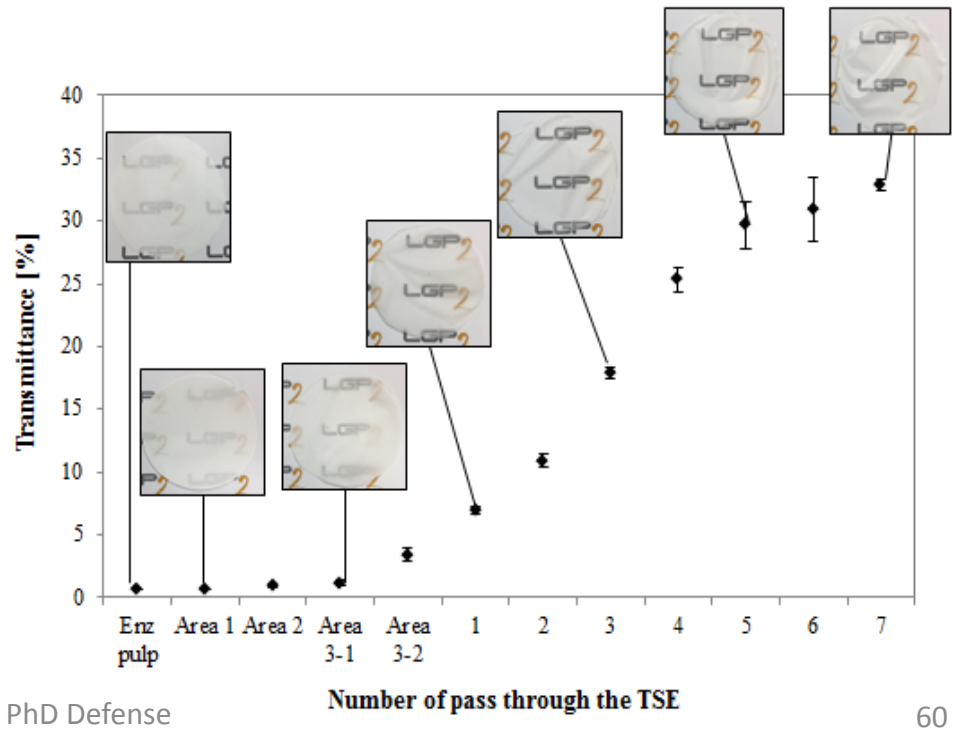
- Pulp at 10 wt% present a lower thresold and the deformation during the second passes in the TSE will be easier
- In the TSE, higher strain should be created to modify the pulp

CNF quality with the number of passes through the profile 1



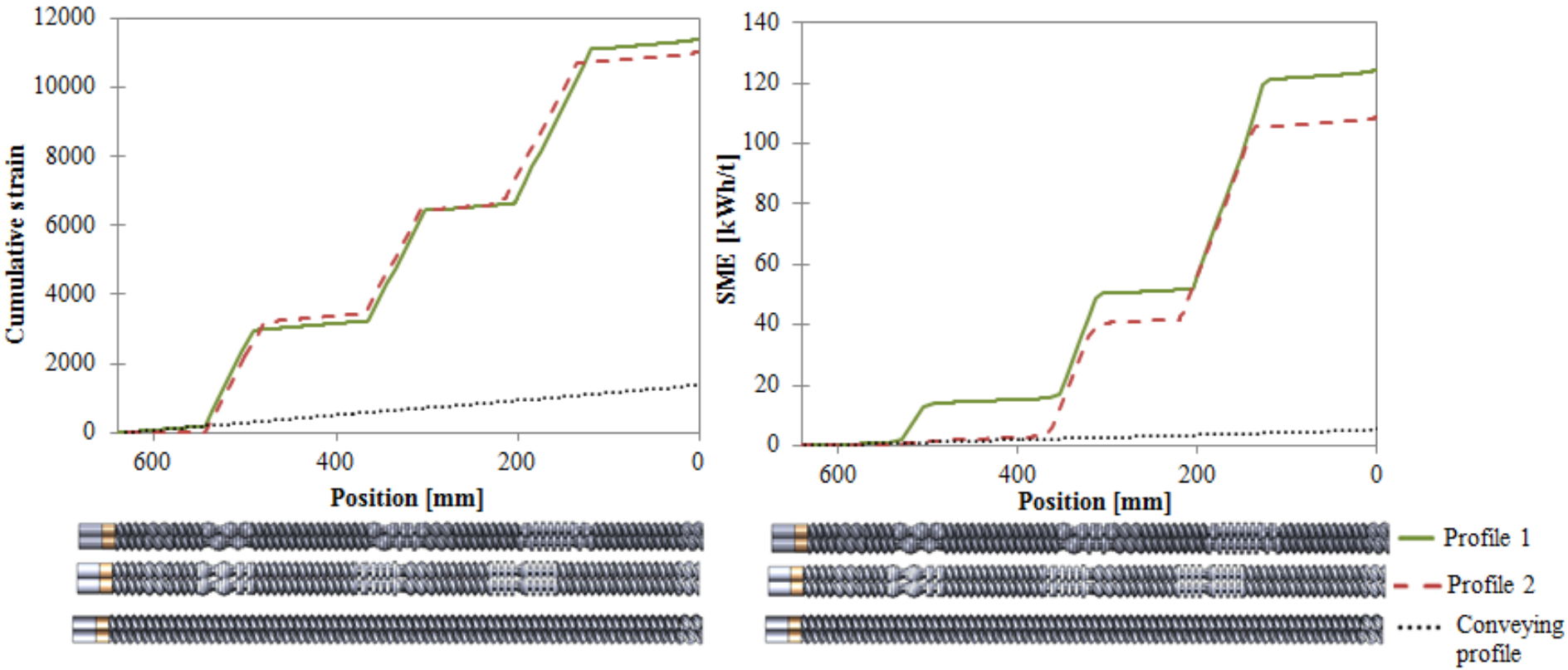
CNF quality with the number of passes through the profile 1





CNF production according to different screw profiles

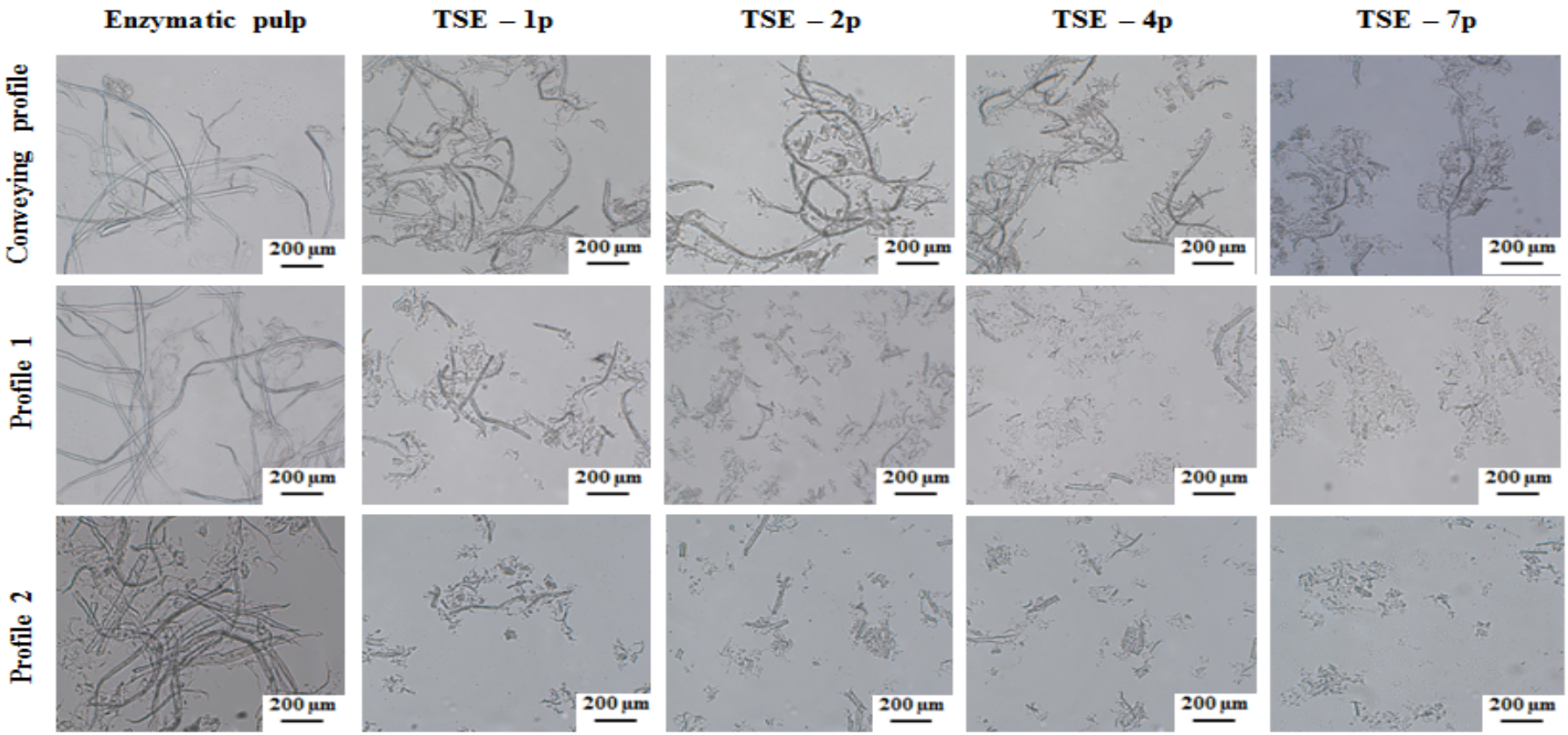
Analysis of the three screw profiles with Ludovic® software



- Same shear rate for profiles 1 and 2 : 100-220 s^{-1} (400 rpm, 3 kg/h)
- Left handed staggering at the end of the shearing zone increase enerdy dissipation without increasing the cumulated strain

CNF production according to different screw profiles

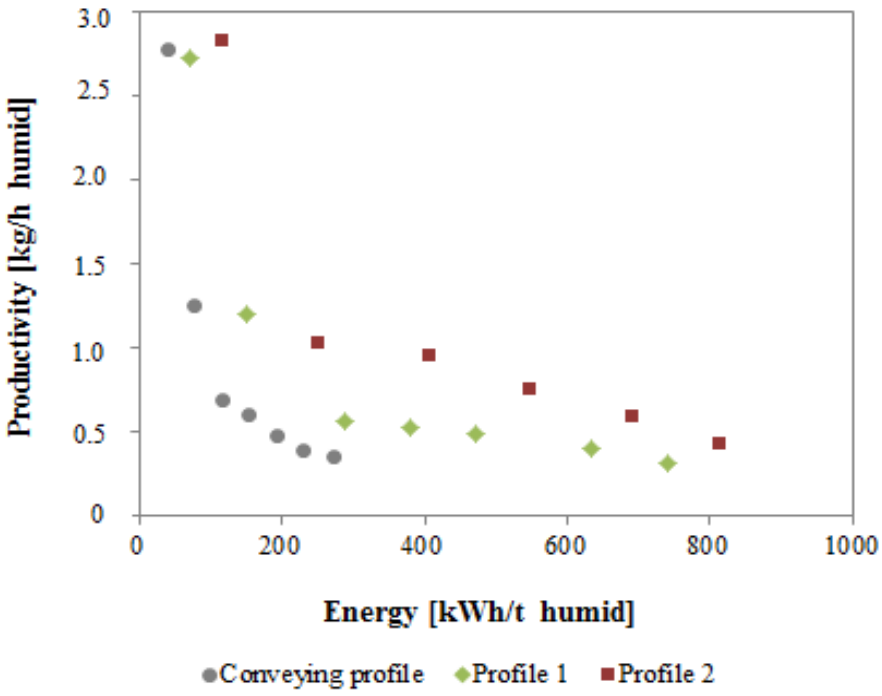
Morphology of the CNF produced with the 3 profiles

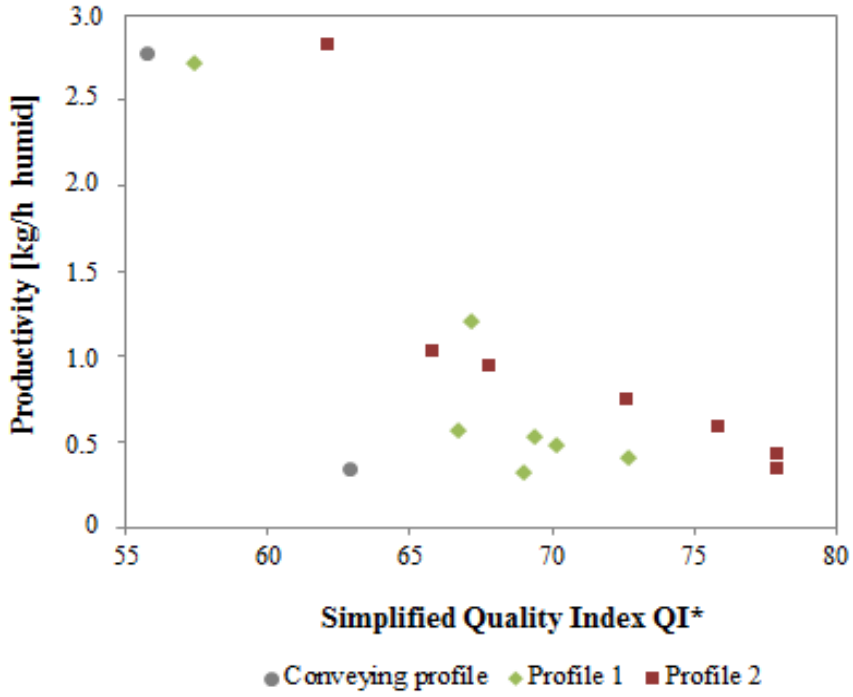


- Conveying profile does not produce CNF
- Stabilization after 3,000 -3,500 kWh/t (dry)

CNF production according to different screw profiles

Productivity of the 3 profiles





New profile vs Profile 2

Details of the QI calculation

Screw profiles	Number of passes through the TSE	Energy consumption (dry)[kWh/t]	Young's modulus [GPa]	Nanosized fraction [%]	Macro length [µm²]	Turbidity [NTU]
New profile	1	2061	13.4 ± 0.8	69.4 ± 8.1	70 ± 12	397 ± 23
	2	4000	13.7 ± 0.4	70.2 ± 8.0	59 ± 11	407 ± 9
	3	5937	12.5 ± 0.6	-	-	386 ± 11
	4	7796	12.2 ± 0.7	71.0 ± 14.0	62 ± 8	380 ± 16
Profile 2	1	745	9.4 ± 0.8	59.8 ± 5.2	63 ± 6.5	403 ± 7
	2	1243	9.9 ± 0.3	70.7 ± 14.6	75 ± 7	432 ± 46
	3	1746	10.2 ± 0.6	66.7 ± 21.3	63 ± 4	422 ± 48
	4	2261	11.7 ± 0.7	74.2 ± 9.8	60 ± 14	384 ± 9