IIBCC 2024
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Nanocellulose, a promising raw material: Towards scalability and industrial production

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Content

1. Introduction
2. TEMPO-mediated oxidation (TMO)
3. Steps to move from lab to pilot-plant scale
   3.1. TMO optimization (of reaction conditions)
   3.2. Reactor Configurations
4. Conclusions

THE ROLE OF NANOCELLULOSE IN SUSTAINABLE FUTURE MATERIALS

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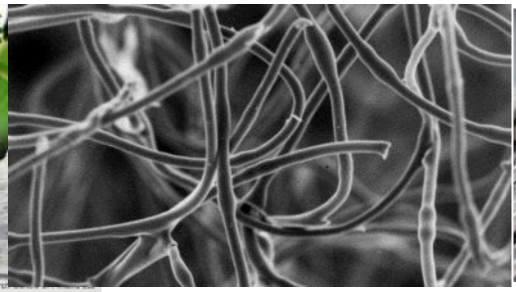


Incentives for Manufacturing Industry

- New source of raw material with wide, largely unexplored range of applications
  - New products

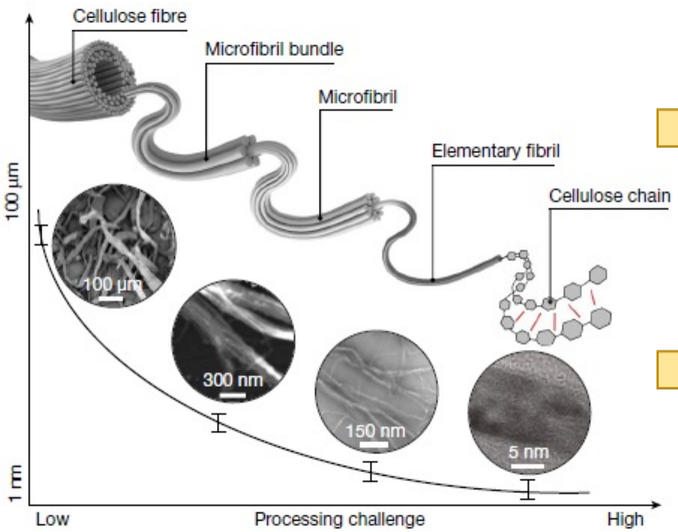
Nature-based
Huge applications

1. Introduction

High Availability

CELLULOSE

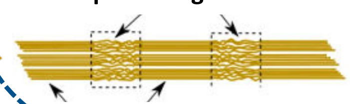
- Renewable
- Biodegradable
- Lightweight
- High chemical reactivity
- Barrier properties



NANOMATERIALS

- Diameter < 100 nm
- Higher surface area
- Higher mechanical strength
- Higher water absorption
- Free defect material

Cellulose Nanofibrils (CNFs)



Acid hydrolysis

Only crystalline regions
↓ L/D

Cellulose Nanocrystals (CNCs)

Bacterial Cellulose

1. Introduction: CNF Applications

PAPER / PACKAGING

FIBER-CEMENT

NANOCOMPOSITES

MEDICINE

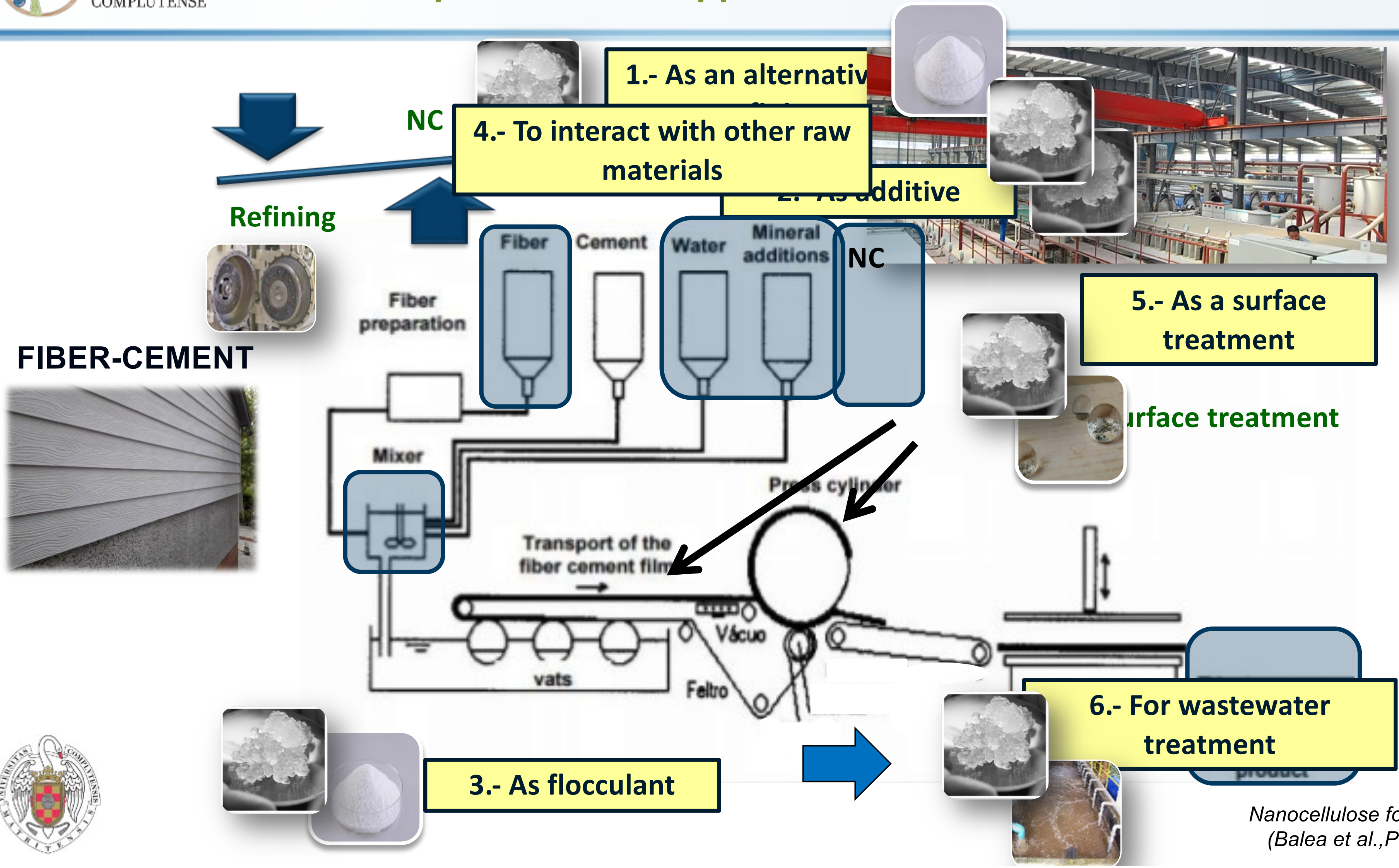
PAINTS & RESINS

FOOD INDUSTRY

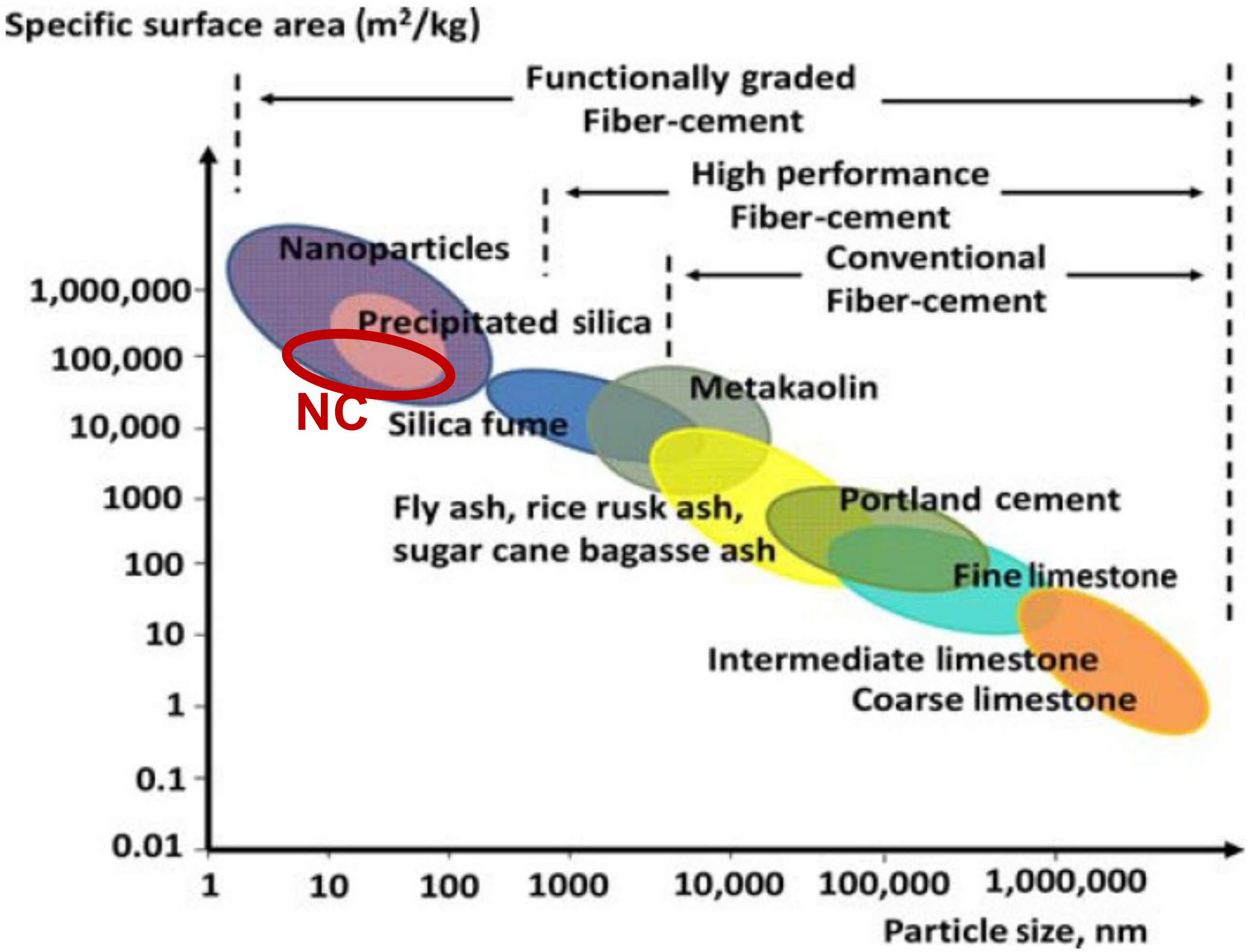
ABSORBENTS

WATER TREATMENT

1. Example: Potential applications of NC in the fiber cement industry



Nanocellulose for fiber cement (Balea et al.,Polymers, 2019)


Specific surface area (m²/kg)
Functionally graded Fiber-cement
High performance Fiber-cement
Conventional Fiber-cement
Nanoparticles
Precipitated silica
NC
Silica fume
Metakaolin
Fly ash, rice rusk ash, sugar cane bagasse ash
Portland cement
Fine limestone
Intermediate limestone
Coarse limestone
1,000,000
100,000
10,000
1000
100
10
1
0.1
0.01
1
10
100
1000
10,000
100,000
1,000,000
Particle size, nm

1. Introduction: Production

Cellulose

TEMPO-mediated Oxidation

Mechanical pretreatments | **Enzymatic pretreatments** | **Chemical pretreatments**

Mechanical Treatments

- Homogenization
- Microfluidization
- Grinding
- Twin-screw extruder
- Milling

Cellulose Nanofibrils

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3. Steps to move from lab to pilot-plant scale
   - 3.1. TMO optimization (of reaction conditions)
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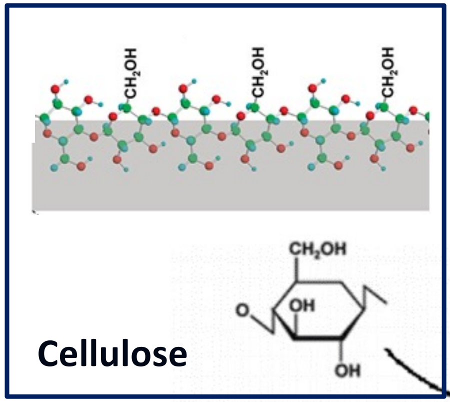
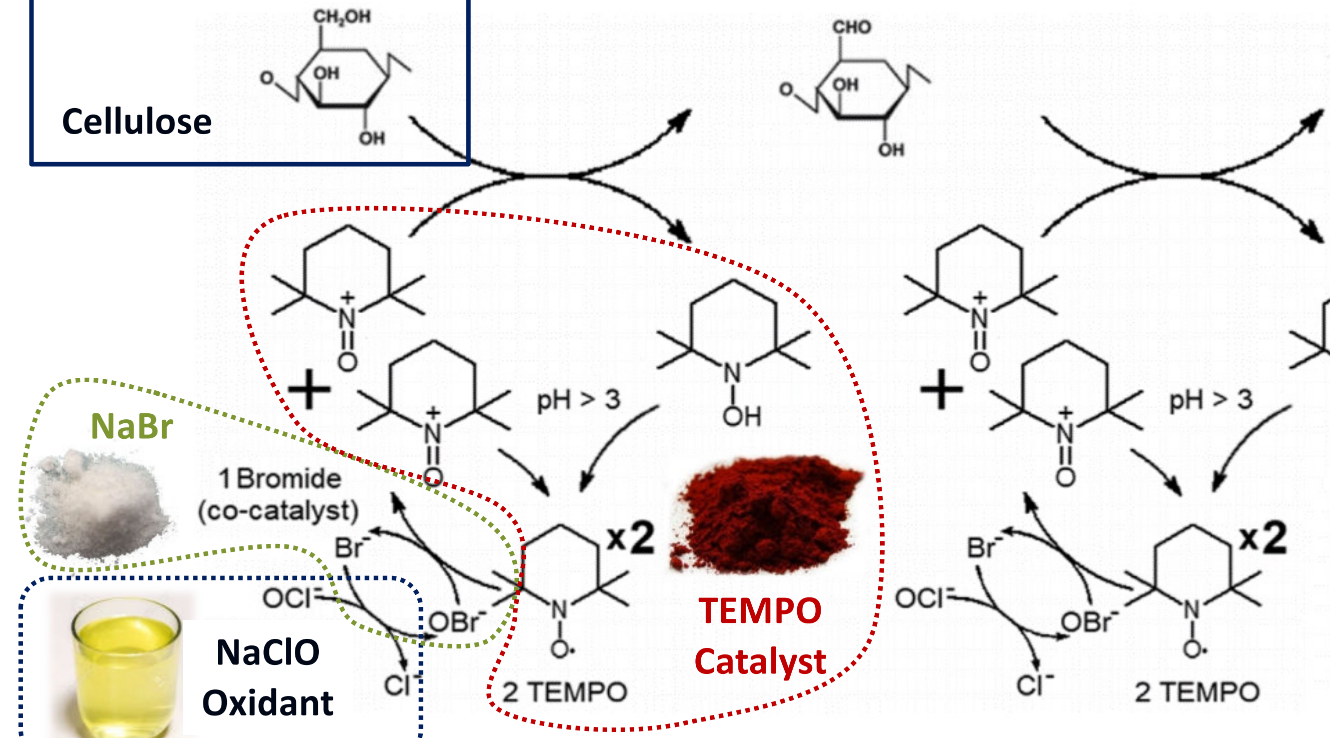
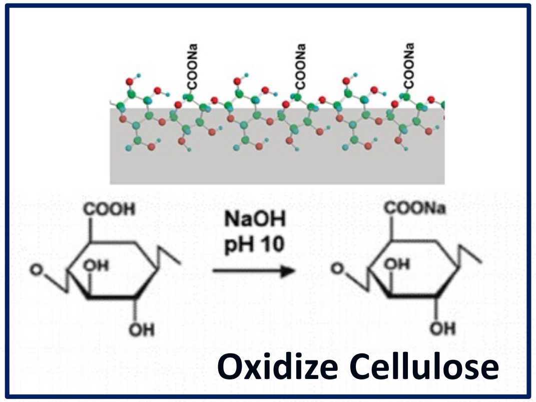
2. TEMPO-mediated oxidation (TMO)

The most common pretreatment to obtain Highly Fibrillated CNFs







2,2,6,6-Tetramethyl-1-piperidiny6-1-oxyl

Parallel Reactions:

$$3\ ClO^- \xrightarrow{BrO^-} ClO_3^- + 3H^+ + 2Cl^-$$

$$2\ ClO^- + HBrO^- \rightarrow BrO_3^- + 3H^+ + 2Cl^-$$

C2/C3 ketones in Cellulose

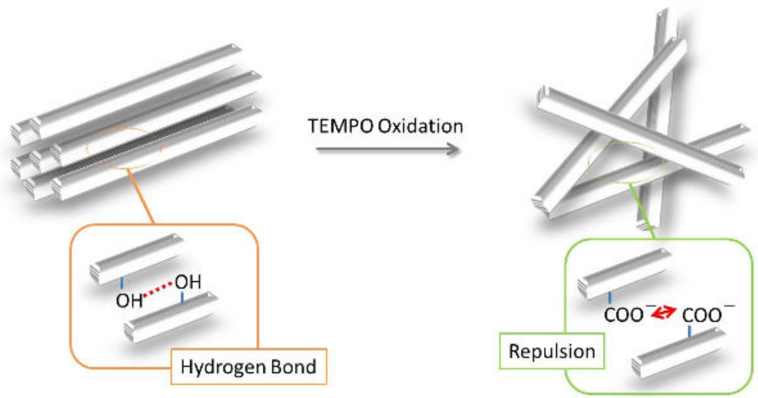
TEMPO-mediated oxidation (Saito and Isogai, 2007; Isogai et al., 2011)

2. TEMPO-mediated oxidation (TMO)

Benefits and Drawbacks

- ✓ Very high fibrillation
- ✓ Good homogeneity of fibrils after high-pressure homogenization (HPH)
- ✓ ↑ Carboxyl groups

- ➢ Long oxidation time (> 2h)
- ➢ Low pulp concentration (10 g/L)
- ➢ Catalysts are not recovered (↑ Cost)
- ➢ Sodium hypochlorite consumption
- ➢ Generation of basic residues
- ➢ Salts formation
- ➢ Side reactions
- ➢ Challenges to upscaling

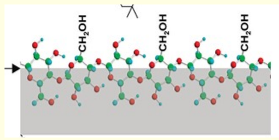


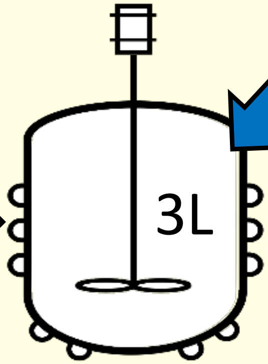
2. TEMPO-mediated oxidation (TMO)

Traditional TMO conditions:

NaClO
5-10
mmol /
g pulp

Cellulose 10 g/L





NaOH to maintain pH ~ 10

2h reaction

Stirred reactor

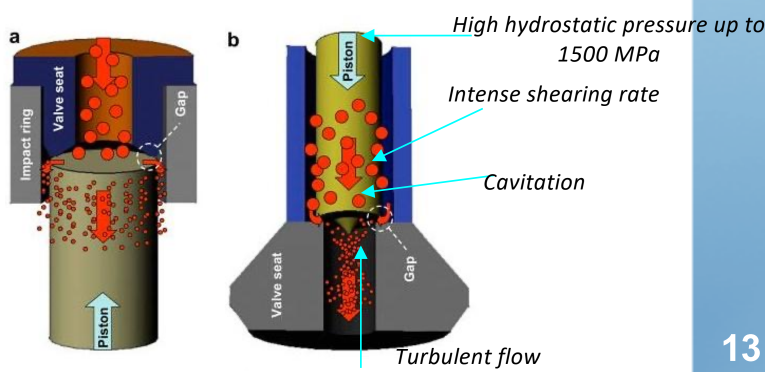
Catalysts

TEMPO 0.1 mmol/g pulp

NaBr 1 mmol /g pulp

Filtration

HPH



Conditions of Saito et al. 2007

Content

Equipment sizing

CNF suspensions in HPH
10-30 g cellulose/L:

100-300 kg/h dry CNFs

TMO oxidation

Stirred reactor

L → m^3

OPTIMIZED TMO CONDITIONS:
BEFORE UPSCALING

Filtration

Mechanical treatment

HPH

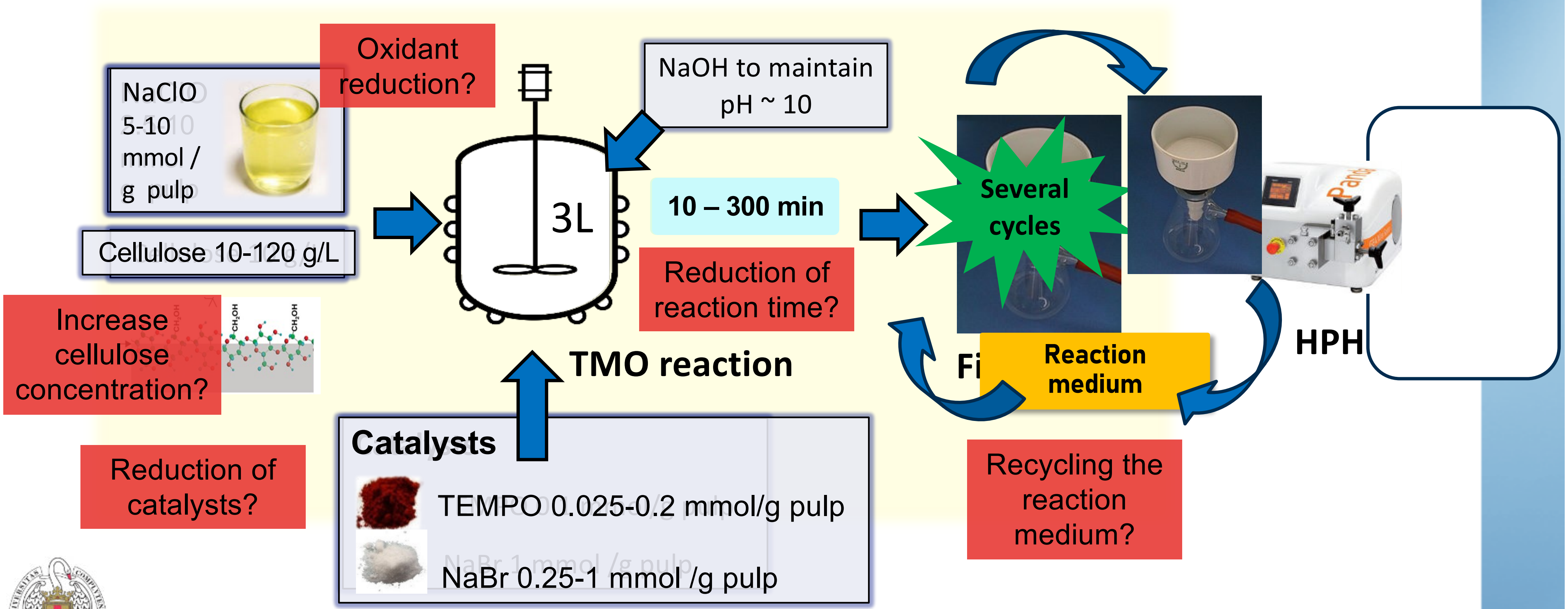
19-100 L/h

Max 6200 bar

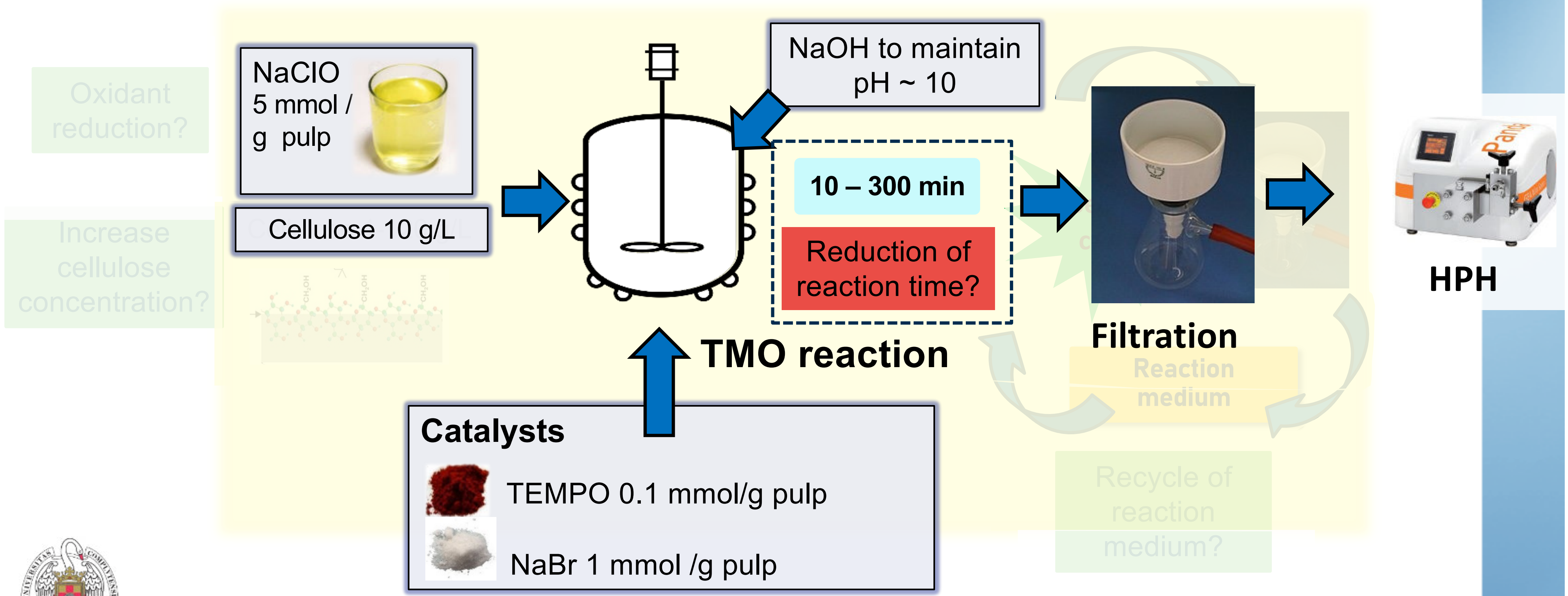
(Use: 600 bar)

Content

Optimizations in stirring reactor



3.1. TMO optimization: Time monitoring



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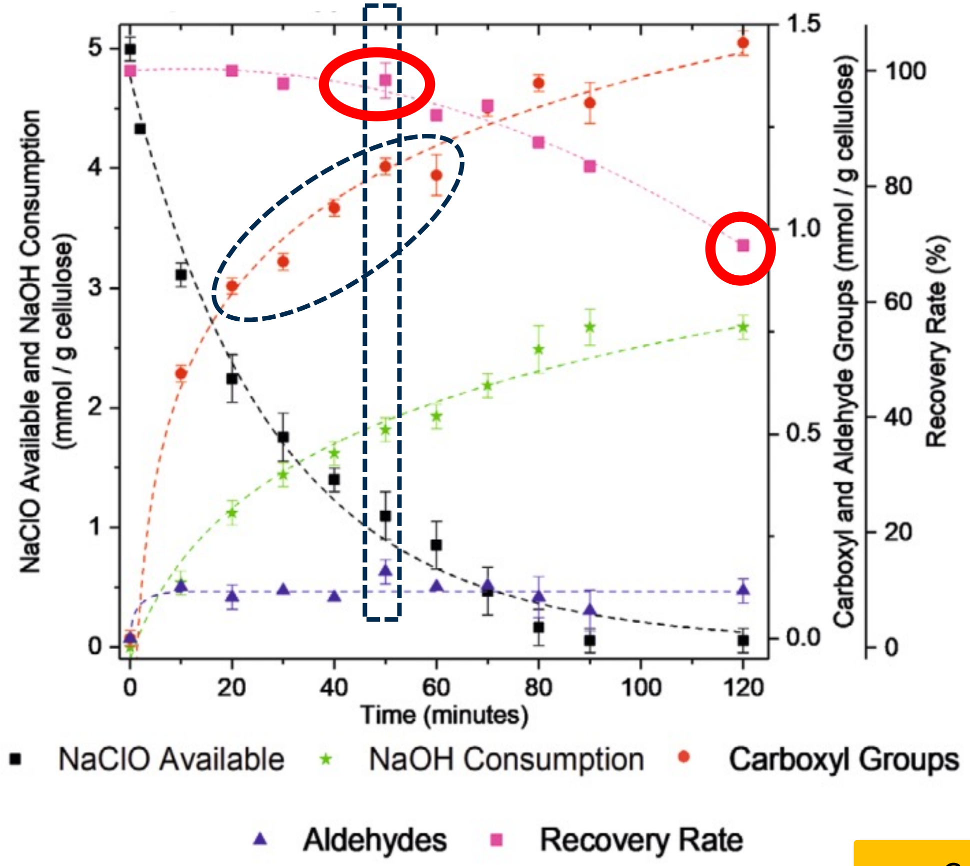
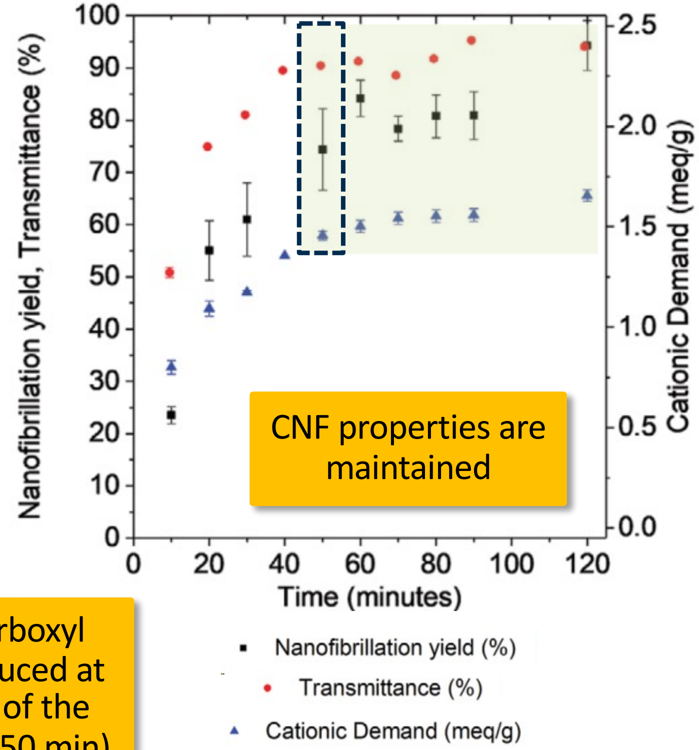


CNFs



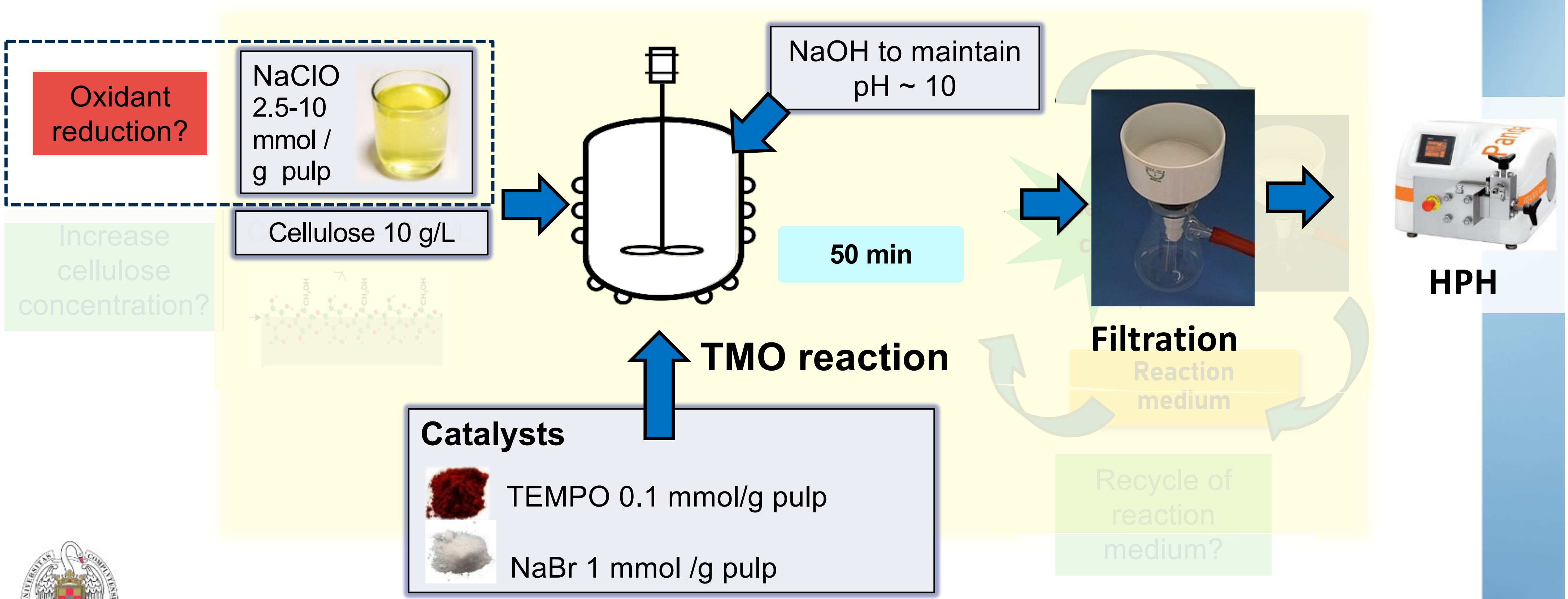
CNF properties are maintained

Oxidation (Carboxyl groups) is produced at the beginning of the reaction (2h → 50 min)

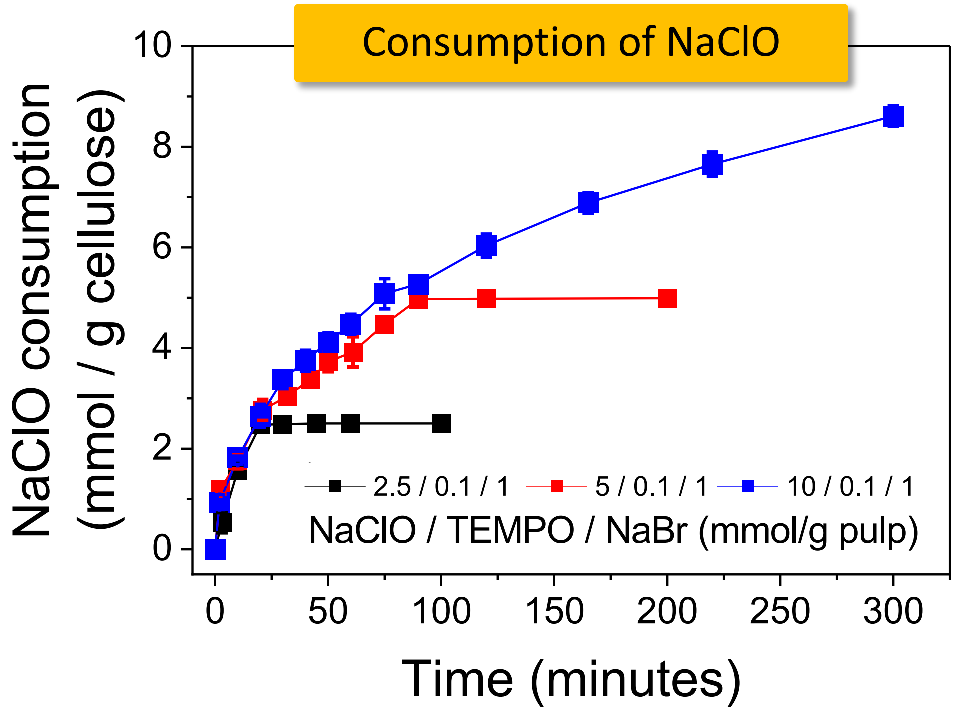
Cellulose recovery increases from 70 to 90%

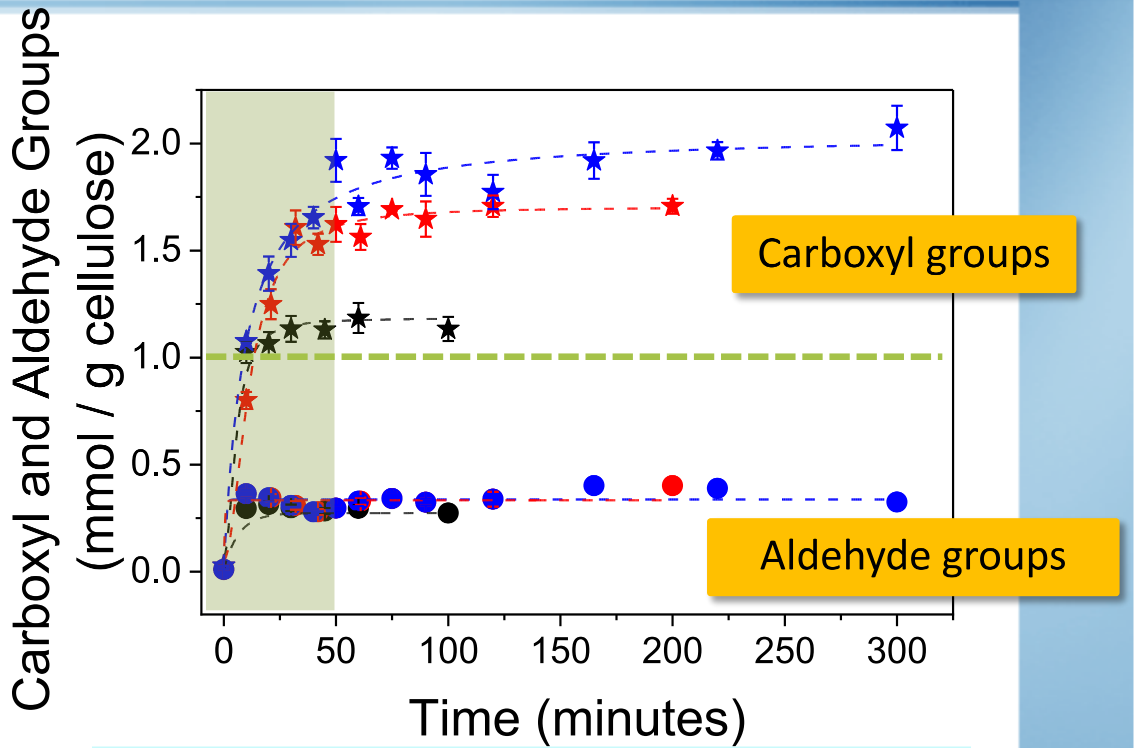
Sanchez-Salvador et al. 2021, Advanced Sustainable Systems, 5(4), 2000277

3.1. TMO optimization: Oxidant reduction



3.1. TMO optimization: Oxidant reduction





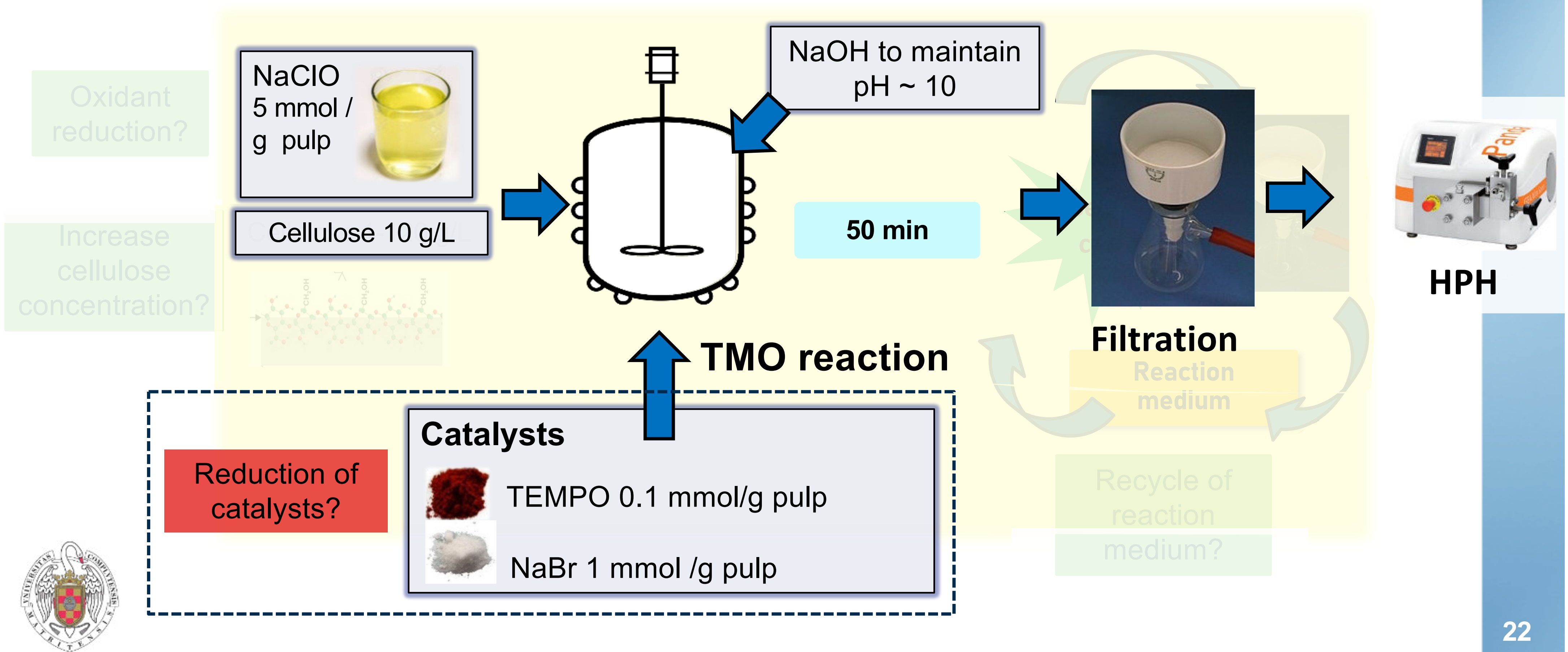
- Reaction rate is not afected by the NaClO
- It is a zero order reaction respect NaClO

5 mmol NaClO/g pulp produce the same carboxyl groups than large NaClO doses

Even 2.5 mmol NaClO/g pulp is sufficient: Oxidized pulps with 1 mmol/g carboxyls produce highly fibrillated CNFs

Xu et al. 2022, Cellulose, 29(12), 6611-6627

3.1. TMO optimization: Reduction of catalysts



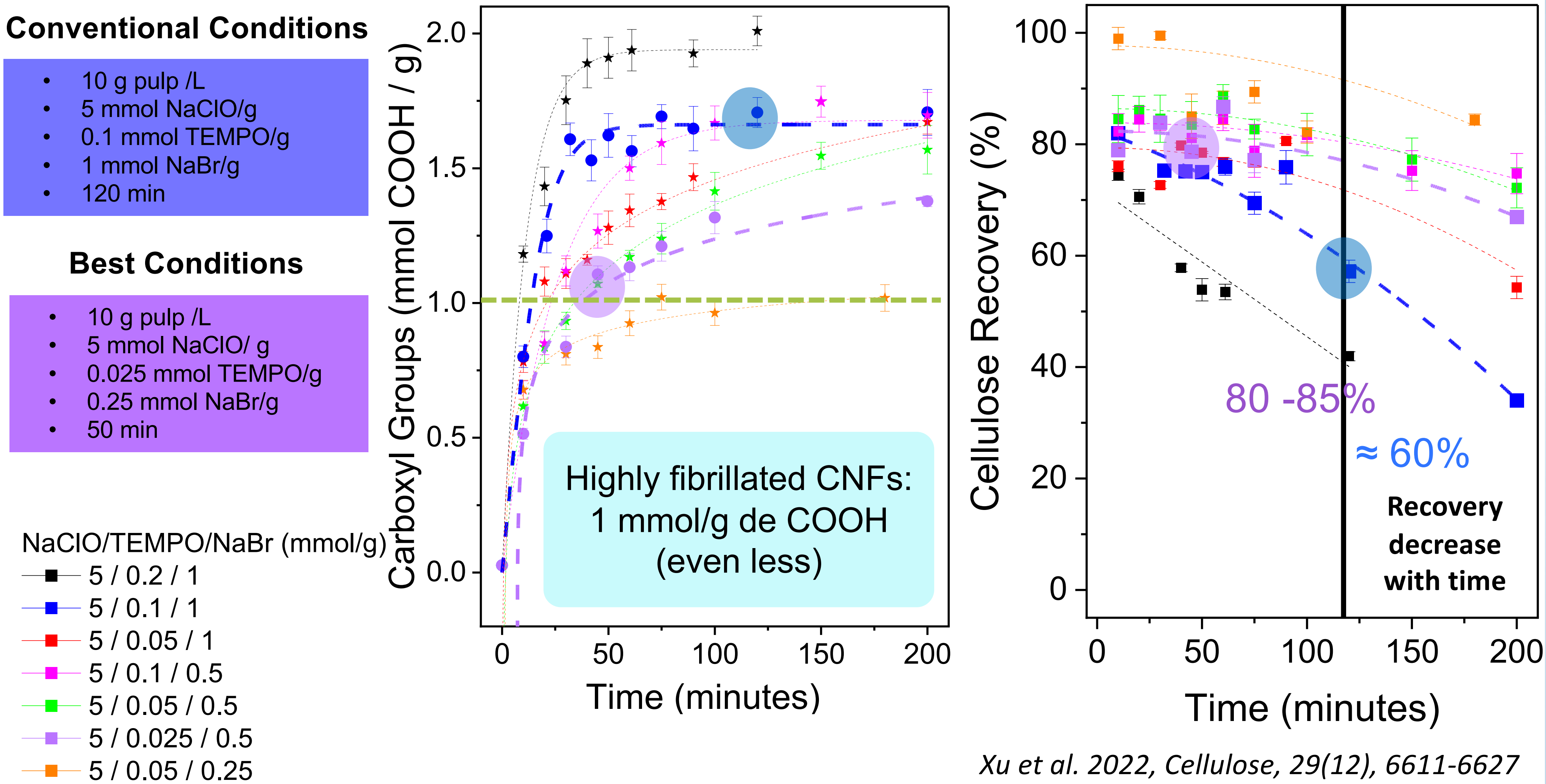
3.1. TMO optimization: Reduction of catalysts

Conventional Conditions

- 10 g pulp /L
- 5 mmol NaClO/g
- 0.1 mmol TEMPO/g
- 1 mmol NaBr/g
- 120 min

Best Conditions

- 10 g pulp /L
- 5 mmol NaClO/ g
- 0.025 mmol TEMPO/g
- 0.25 mmol NaBr/g
- 50 min

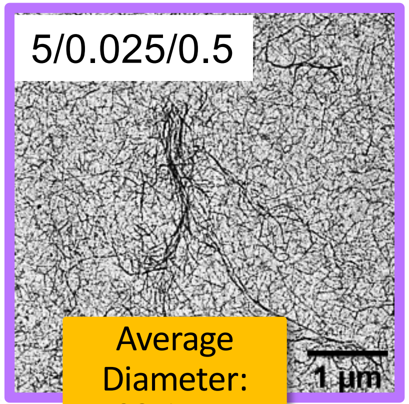


Xu et al. 2022, Cellulose, 29(12), 6611-6627

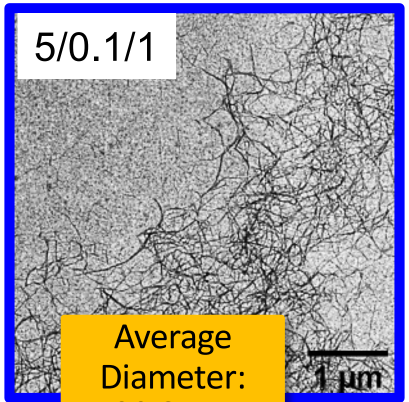
Economic Impact

-80% Catalyst Cost compared to Traditional Conditions

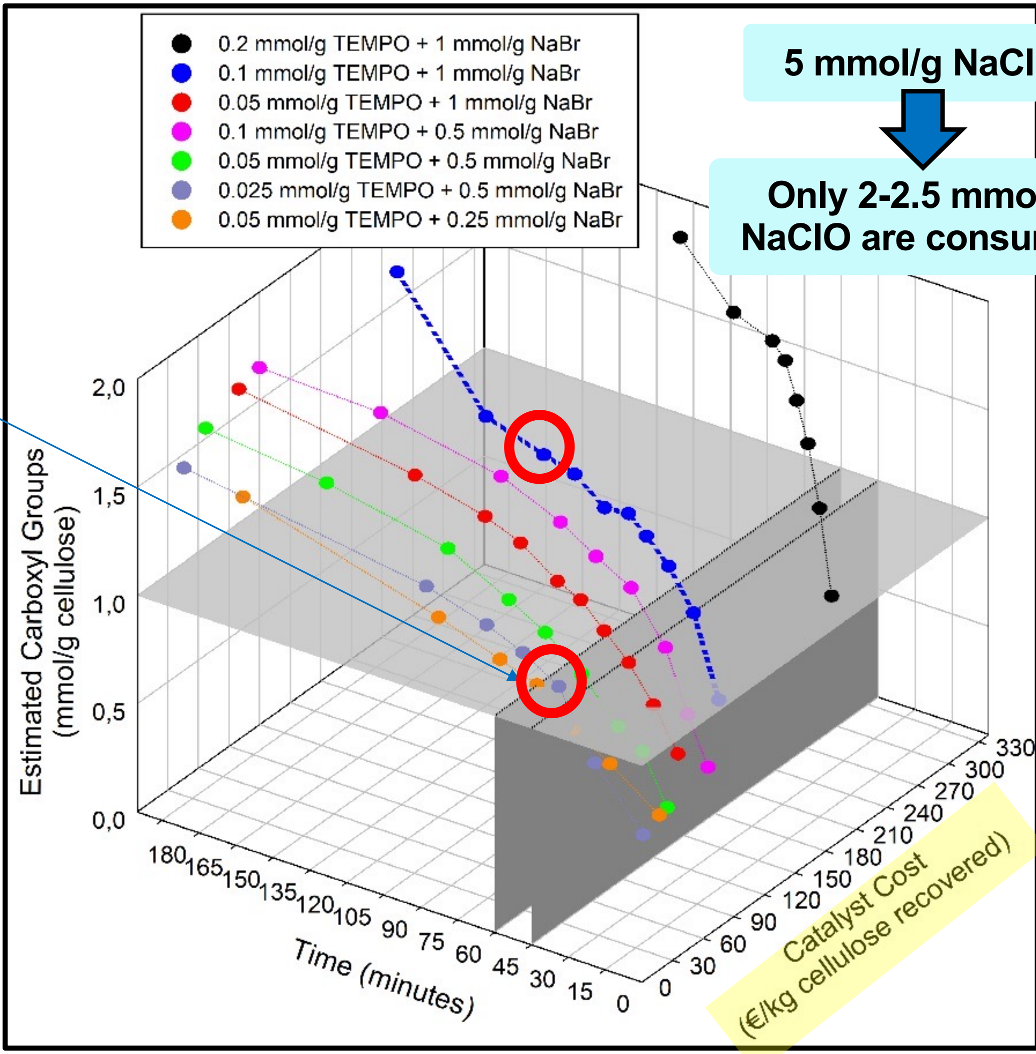
0.025 mmol/g TEMPO (-75%)
0.5 mmol/g NaBr (-50%)



Average Diameter: 23.1 nm



Average Diameter: 20.8 nm

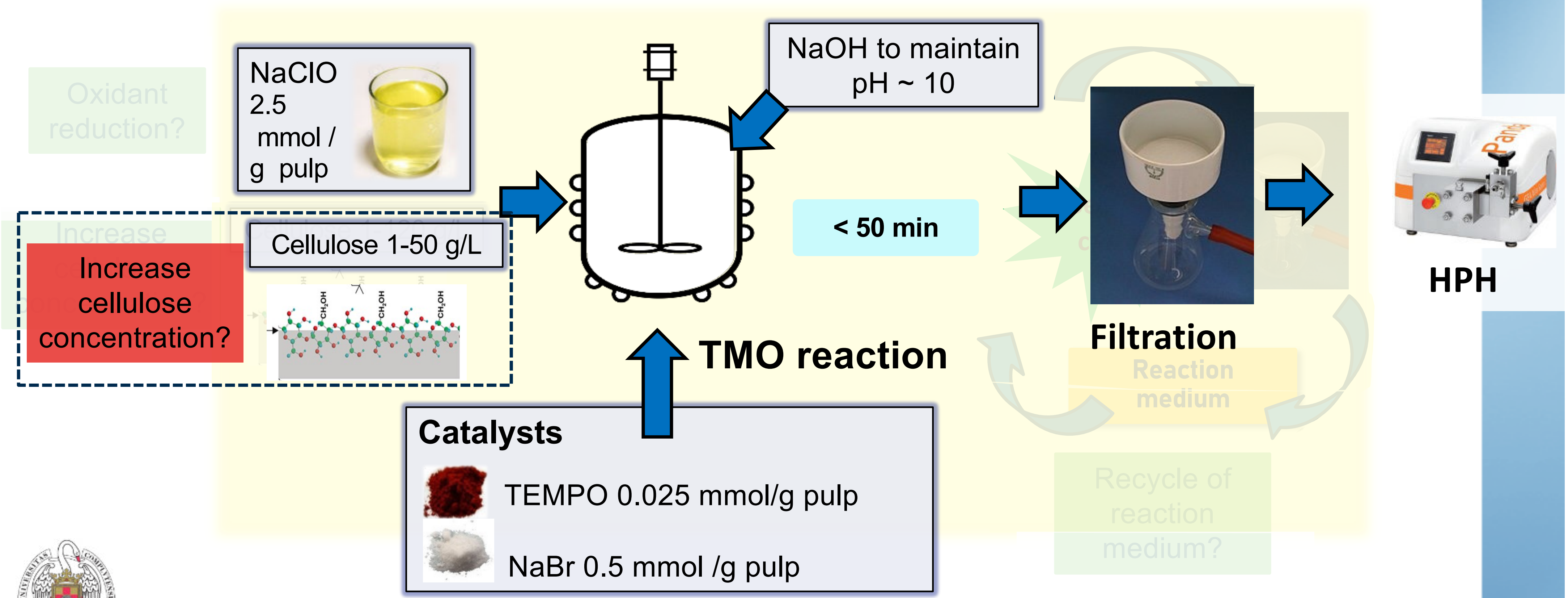


5 mmol/g NaClO

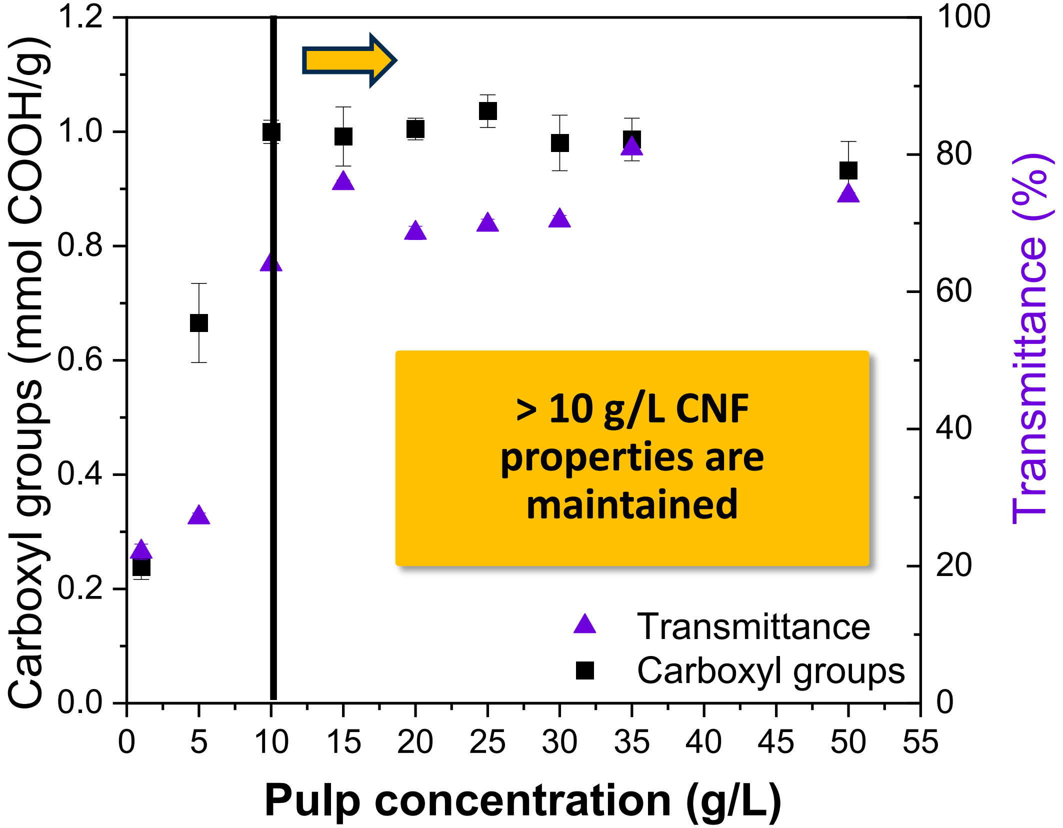
Only 2-2.5 mmol/g NaClO are consumed

Xu et al. 2022, Cellulose, 29(12), 6611-6627

3.1. TMO optimization: Effect of pulp concentration



3.1. TMO optimization: Effect of pulp concentration

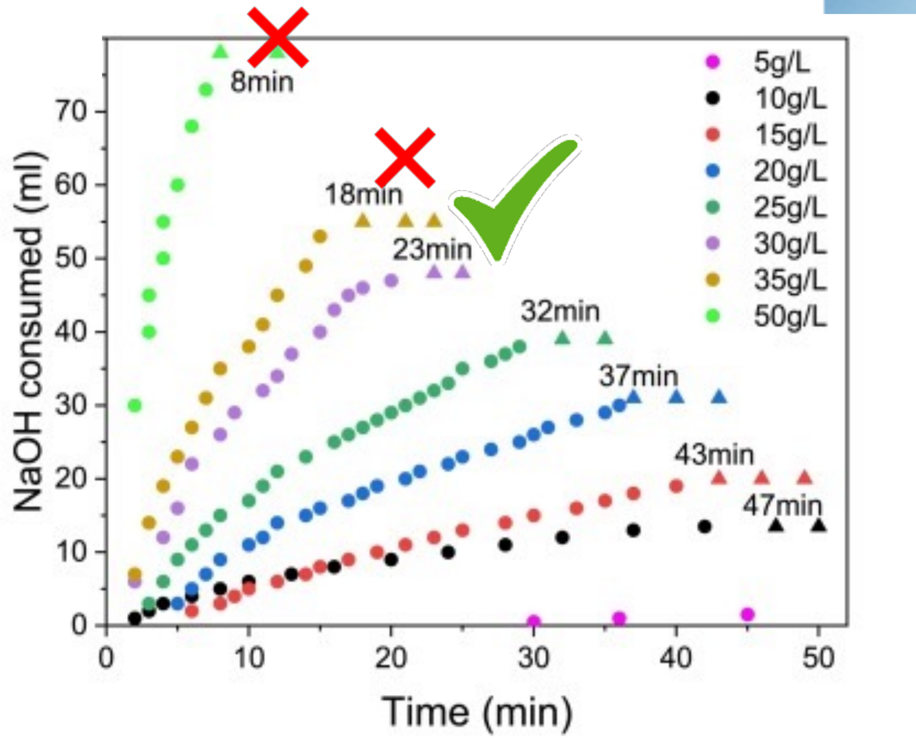


> 10 g/L CNF properties are maintained

Less basic residues due to high concentration

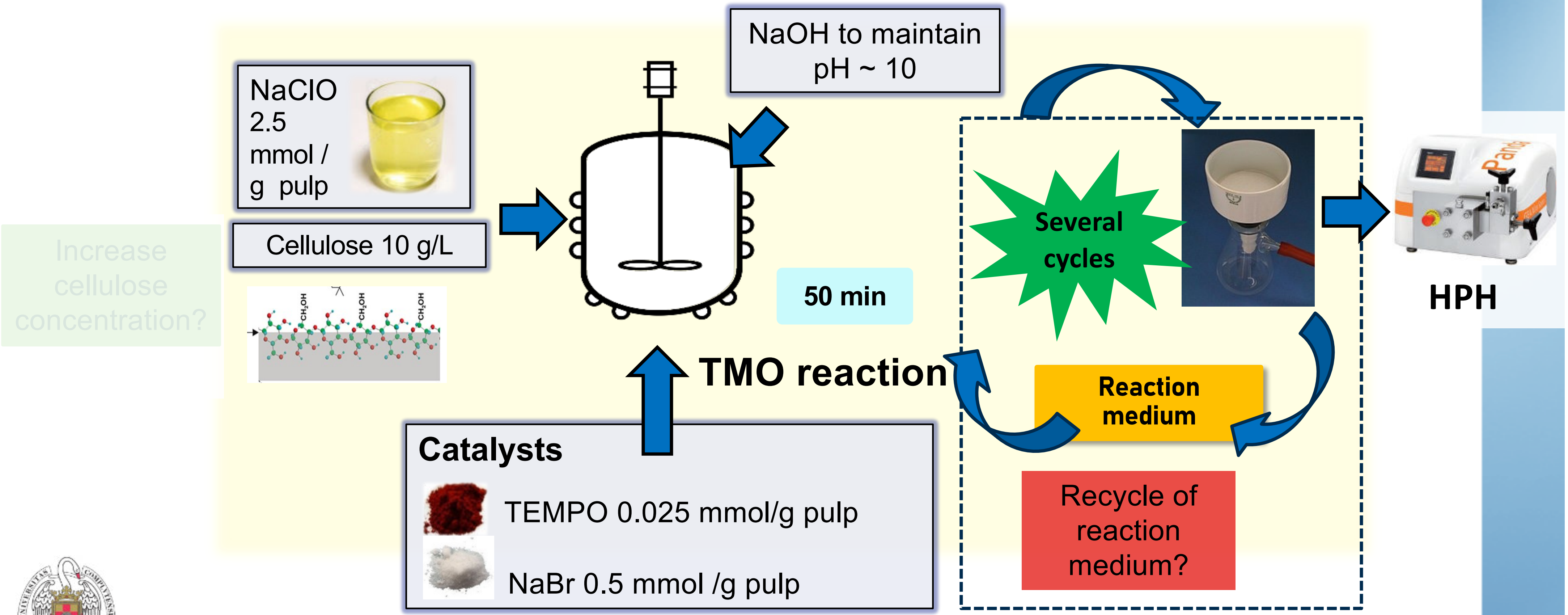
Xu et al. 2023, Carbohydrate Polymers, 319, 121168.

mmol/g: 2.5 NaClO – 0.025 TEMPO – 0.5 NaBr



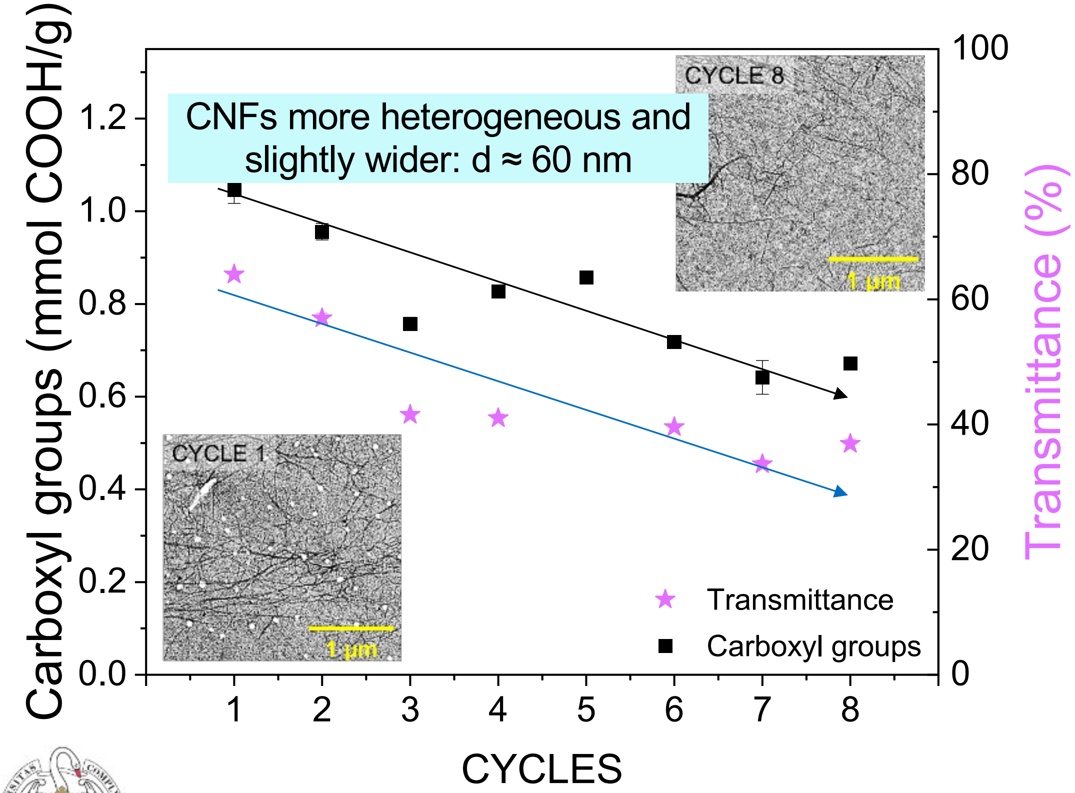
> 30 g/L CNF agitation problems in the reactor

3.1. TMO optimization: Recycle of reaction medium

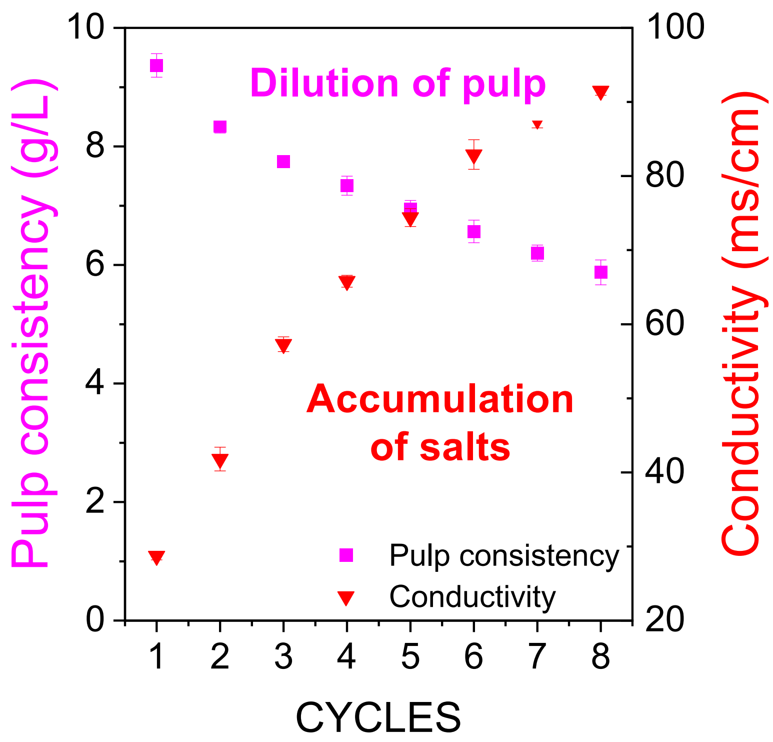


3.1. TMO optimization: Recycle of reaction medium

Oxidized pulp and CNF characterization



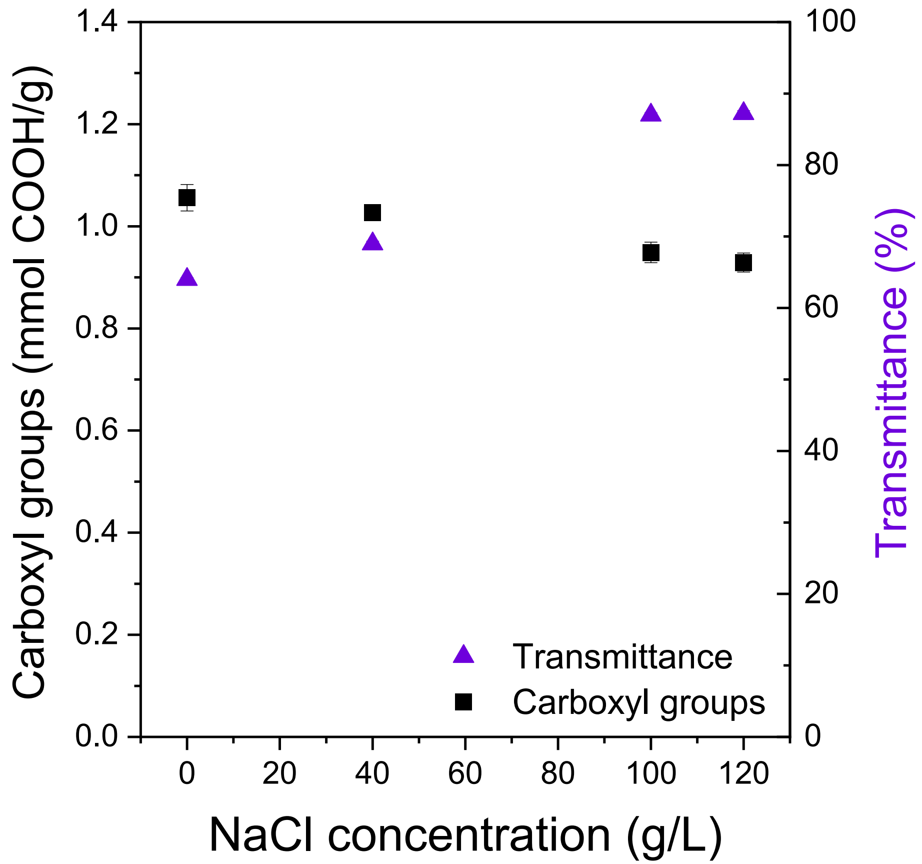
Reaction monitoring



Without addition of fresh medium

Xu et al. 2023, Carbohydrate Polymers, 319, 121168.

3.1. TMO optimization: Recycle of reaction medium

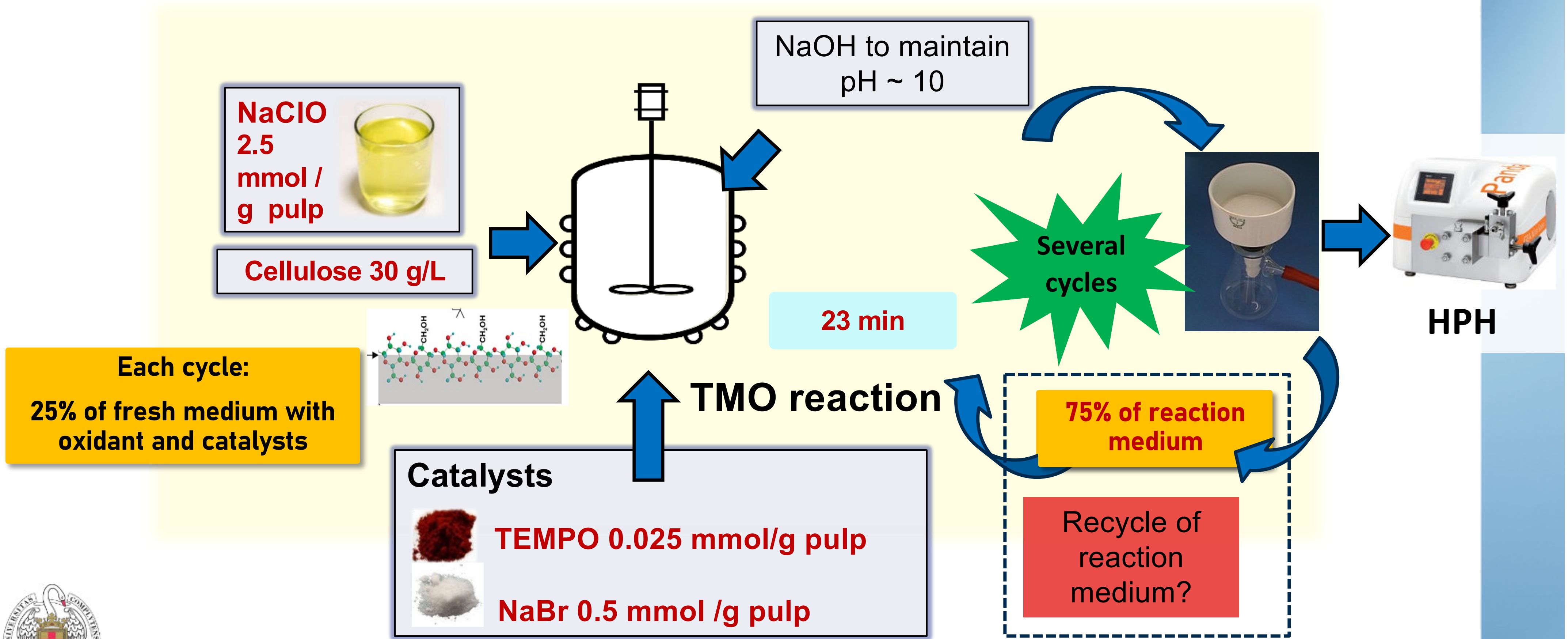


Salt accumulation?

Accumulation of salts is NOT key parameter in carboxylation
Network swelling: counterion Na^+

Xu et al. 2023, Carbohydrate Polymers, 319, 121168.

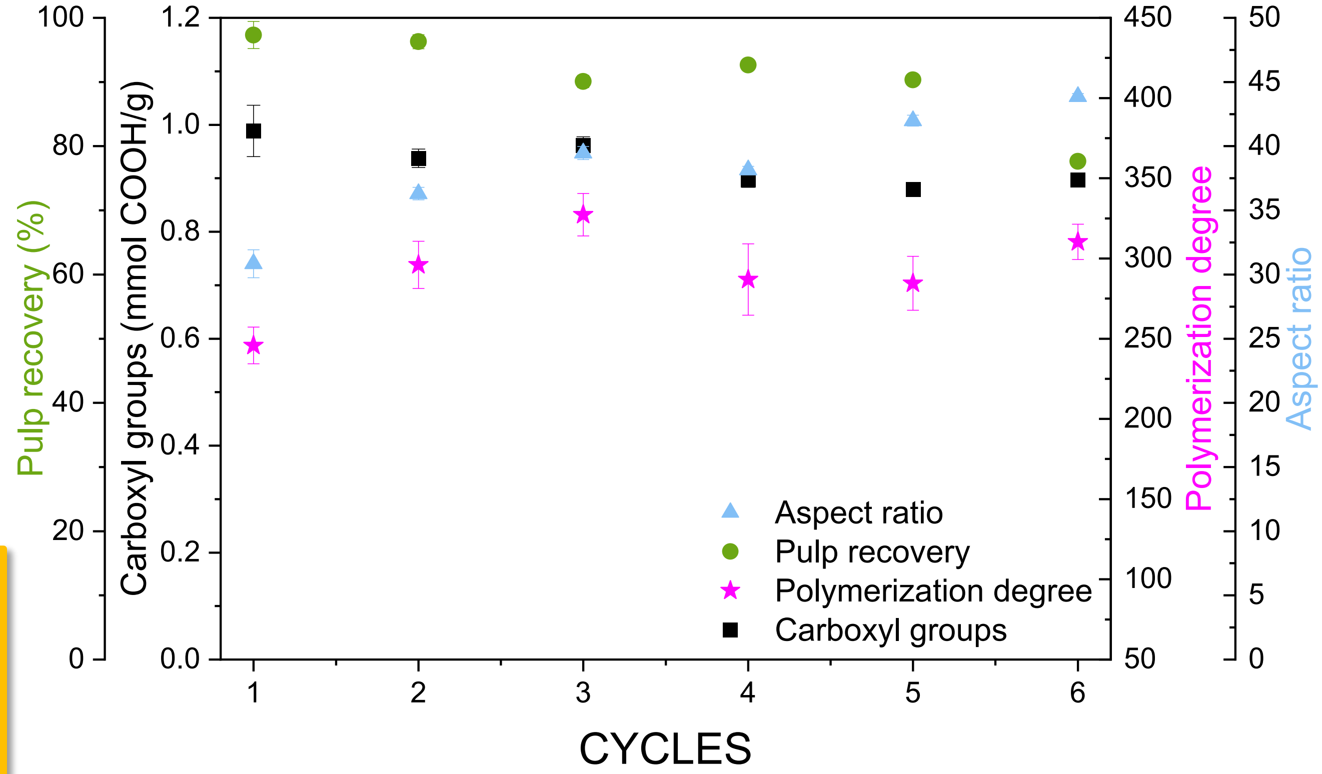
3.1. TMO optimization: Best Configuration (Stirred Reactor)



Recycling reaction medium with 30 g/L pulp concentration

Reaction conditions:

- 2.5 mmol NaClO/g
- 0.025 mmol TEMPO/g
- 0.5 mmol NaBr/g
- **30 g pulp/L**
- **23 minutes**

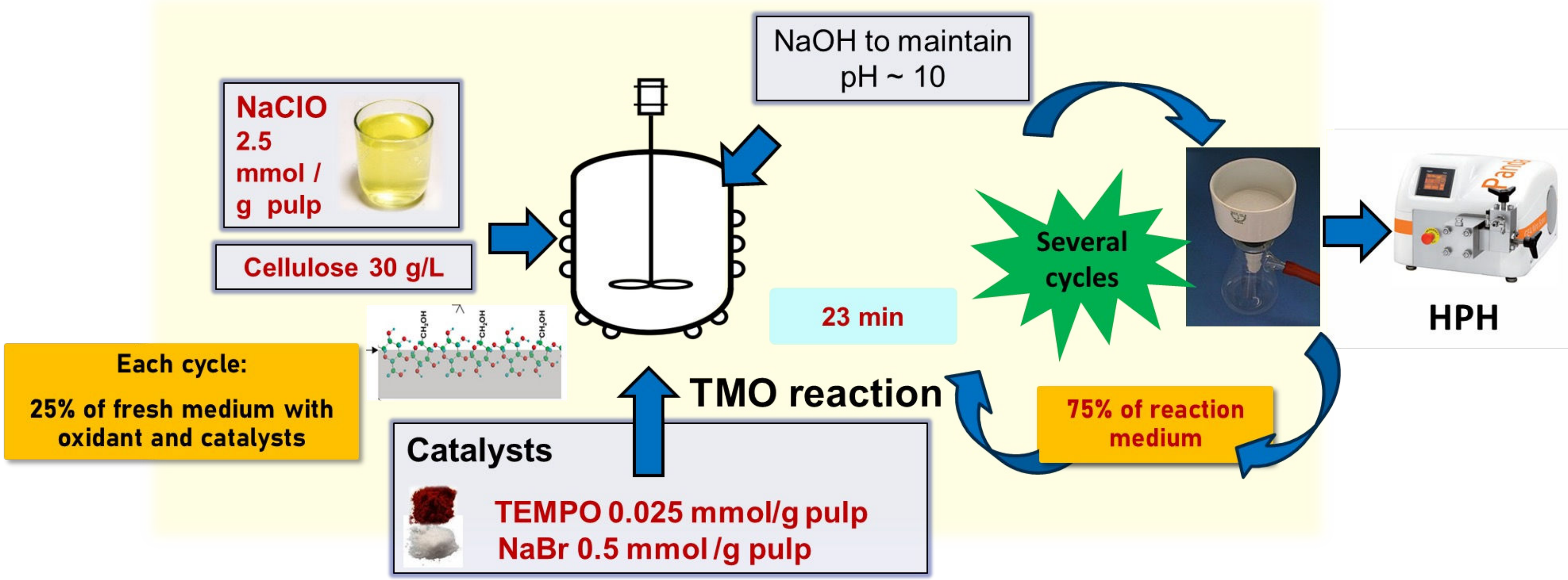


Properties are maintained

after several cycles (> 12 cycles)

Xu et al. 2023, Carbohydrate Polymers, 319, 121168.

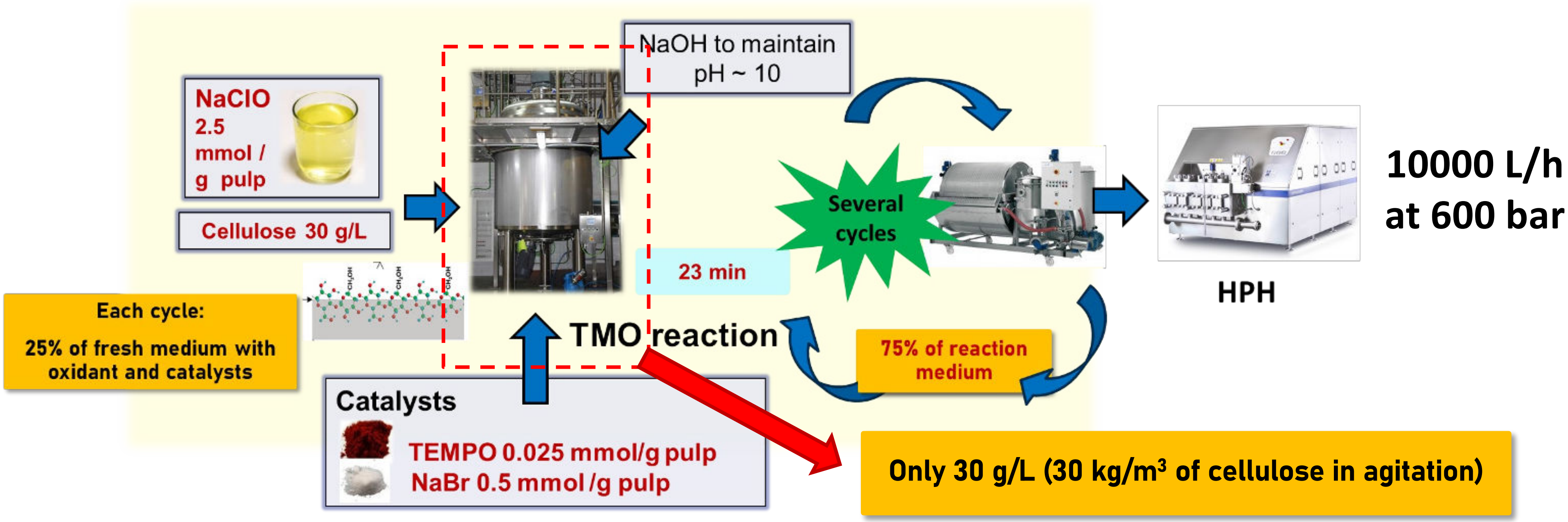
3.1. TMO optimization: Best Configuration (Stirred Reactor)



	Pulp	Recovery	Time	Production	NaClO	TEMPO	NaBr
Recycle	30 g/L	90%	23’	128 g/h*	2.5	0.00625	0.125
Initial	10 g/L	70%	120’	9.3 g/h*	5-10	0.1	1
				+1276%	-50/75%	-94%	-87.5%

*Including a downtime of 15 min per batch

3.1. TMO optimization: Best Configuration (Stirred Reactor)



	Pulp	Recovery	Time	Production	NaClO	TEMPO	NaBr
Recycle	30 g/L	90%	23’	kg/h	2.5	0.00625	0.125
Initial	10 g/L	70%	120’		5-10	0.1	1
				+↑↑%	-50/75%	-94%	-87.5%

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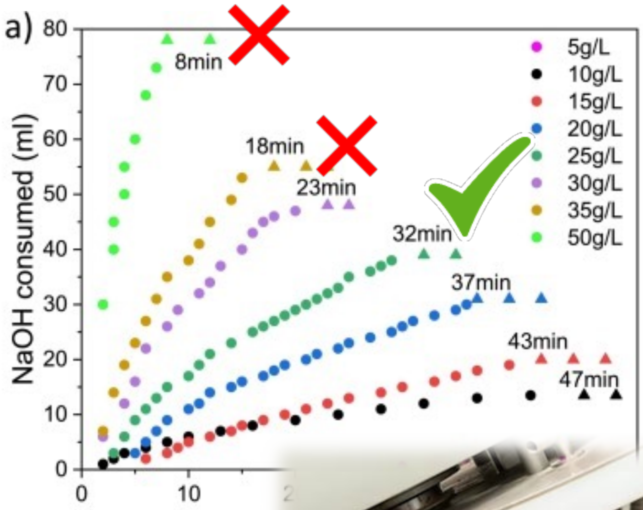
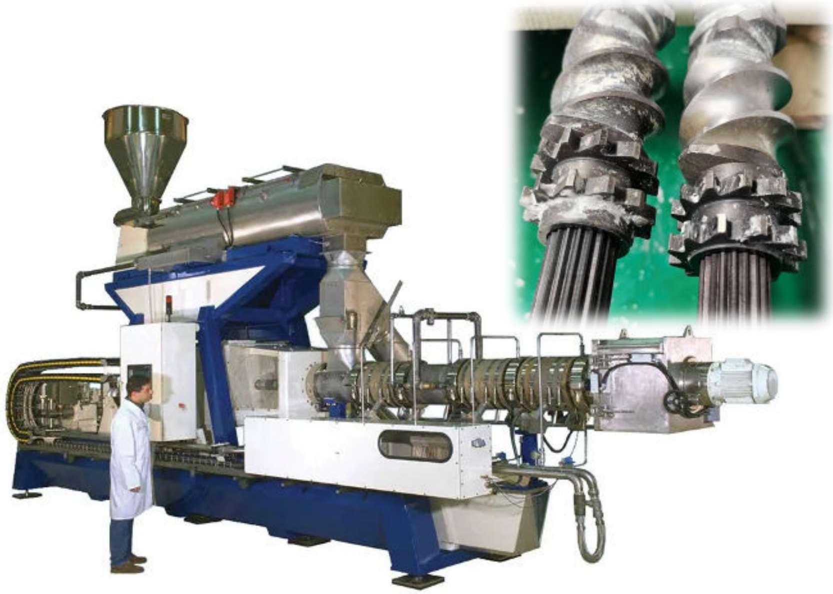
3.2. Steps to move from lab to pilot-plant scale: Reactor Configuration



> 30 g/L CNF agitation problems in the stirring reactor

Other reactor configurations?

KNEADERS



TWIN-SCREW EXTRUDER

3.2. Reactor Configuration: Kneading

How to increase pulp concentration?

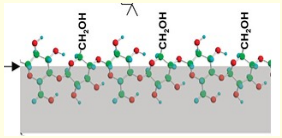
Proof of concept: Kneading

NaClO 2.5 mmol / g pulp

pH maintenaince?

Cellulose 120-140 g/L

Increase cellulose concentration?



Short time

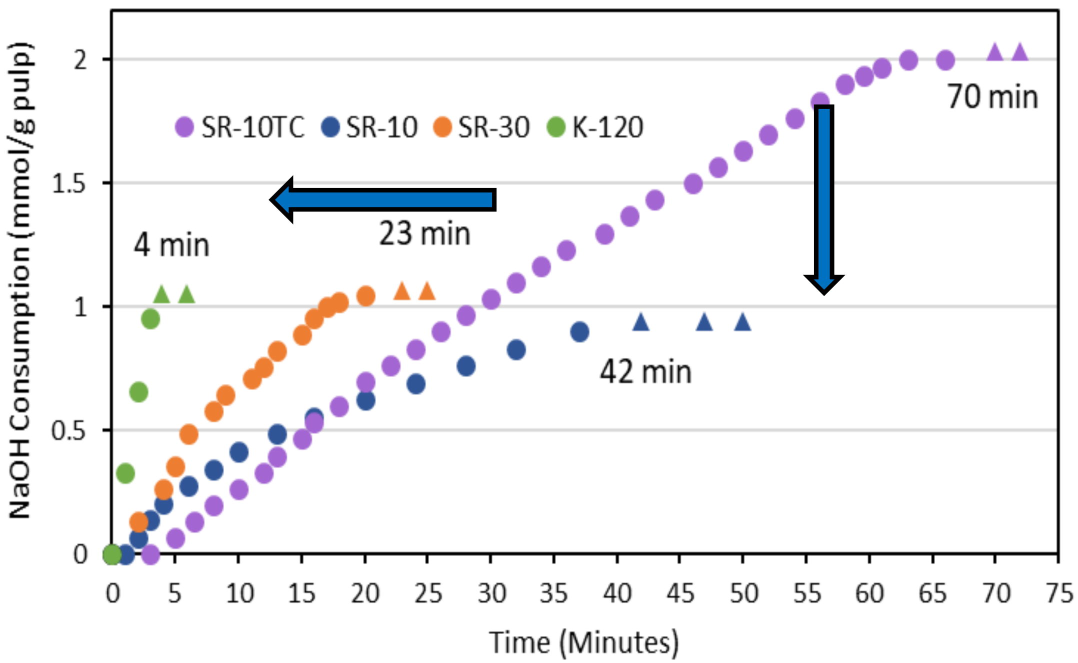
TMO reaction

Catalysts

TEMPO 0.025 mmol/g pulp

NaBr 0.5 mmol /g pulp

3.2. Reactor Configuration: Kneading



- SR-10TC: Reactor 10 g/L (5/0.1/1 mmol/g)
- SR-10: Reactor 10 g/L (2.5/0.025/0.5 mmol/g)
- SR-30: Reactor 30 g/L (2.5/0.025/0.5 mmol/g)
- K-120: Kneading 120 g/L (2.5/0.025/0.5 mmol/g)

Proof of concept: Kneading

Cellulose: 120 g/L
4-5 min oxidation
0.84 mmol COOH/g
Pulp recovery = 94%

Buffer to maintain pH ~ 10
Properties are maintained

0.90 mmol COOH/g
Pulp recovery = 98%

Objective: kneader (↑ kg mixture)

Sanchez-Salvador et al. (2024) International Journal of Biological Macromolecules, 261, 129612.

3.2. Reactor Configuration: Kneader

Reaction conditions:

- 2.5 mmol NaClO/g
- 0.025 mmol TEMPO/g
- 0.5 mmol NaBr/g
- Buffer to maintain pH

- **100 g pulp/L**
- **Mixing Paddle**
- **250 g dry pulp/batch**
  (more quantity could be used)

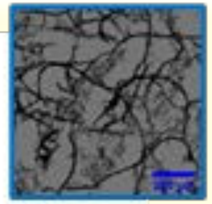
Upscaling: Pilot-plant scale

Oxidation time: 10 minutes (to ensure total oxidation)
Carboxyl groups: 1.00±0.05 mmol/g
Cellulose Recovery: 93%

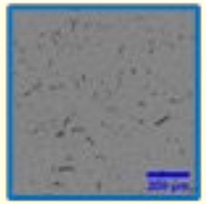
3.2. Reactor Configuration: Pilot-plant twin-screw extruder (TSE)

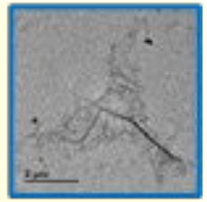
Oxidation and soft fibrillation at the same time

125-150 g/L



HPH: 4 pases 600 bares





CNFs

mmol/g (total): 2 NaClO – 0.08 TEMPO – 0.8 NaBr
Buffer to control pH without NaOH
(Catalysts and oxidant dose: Require optimization)

Carboxyl groups
0.75 mmol/g

1, 2 and 4 passes in TSE
2 min/pass

Content

4. Conclusions

Sustainable CNF production using TMO has been improved in stirring reactor by:

- **Monitoring reaction time**
- **Reducing oxidant dose**
- **Reducing catalyst dose (TEMPO and NaBr)**
- **Increasing pulp concentration (From 10 to 30 g/L)**
- **Recycling part of reaction medium (75%)**

TMO reaction in kneaders and pilot-plant twin-screw extruder (TSE) is feasible and allows for further upscaling TMO reaction process:

- **Higher production of OPs and CNFs**
- **The increase of pulp concentration reduce oxidation time (Up to 100-150 g/L)**
- **TSE produce a soft fibrillation during oxidation**
- **Require the use of carbonate buffers to control pH**
- **Increase pulp recovery**

Nanocellulose, a promising raw material: Towards scalability and industrial production

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