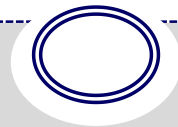


Evaluation of Different Cellulose Nanofibrils (CNFs) as a Replacement for Xanthan Gum (XGD) in Water Based Drilling Fluids (WBM) to be Used in Shale Formations

By: Dra Yurany Villada



7º CONGRESO **iAPG**
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I N T E C



INSTITUTO ARGENTINO
DEL PETRÓLEO Y DEL GAS

5 – 8 de Noviembre 2019
Mar del Plata, Argentina

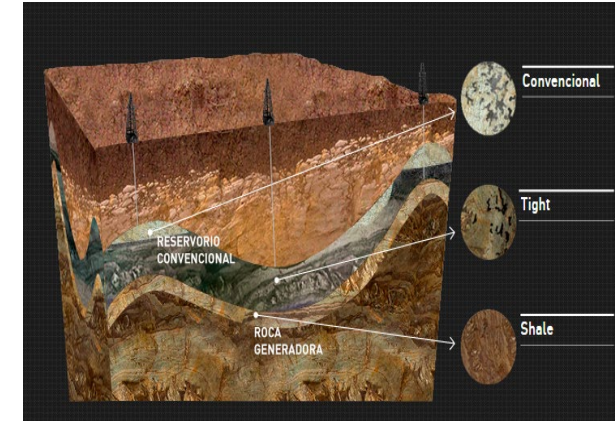
Outline

- ❖ Introduction
- ❖ Objectives
- ❖ Experimental and theoretical work
- ❖ Conclusions

Hydrocarbon Exploitation

- Conventional Reservoirs

- Unconventional reservoirs



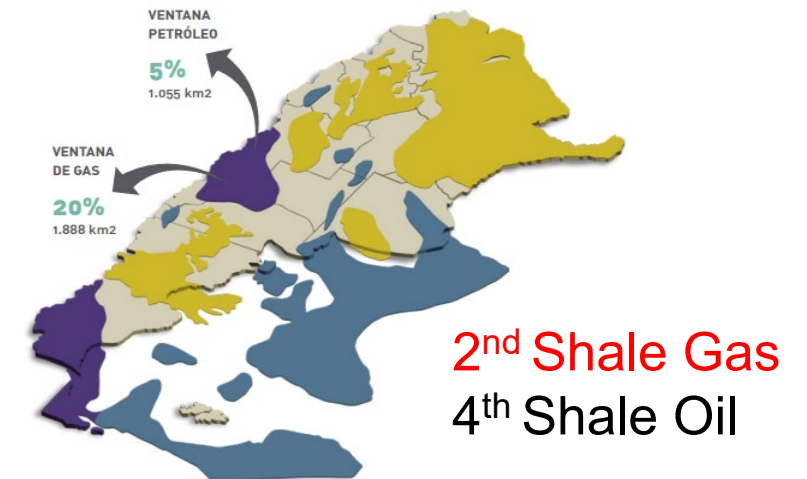
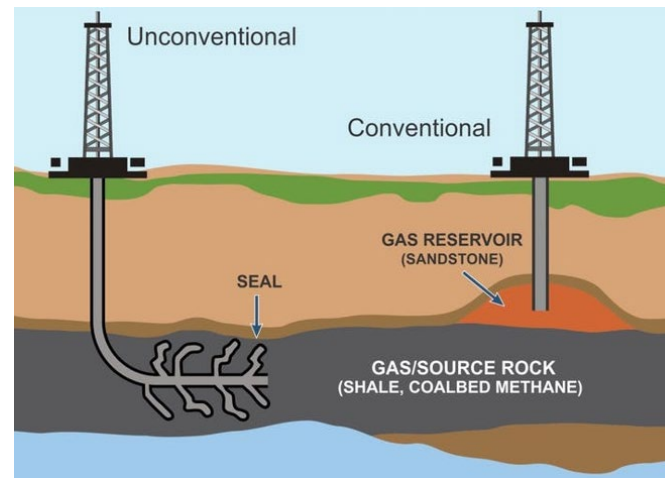
✓ Low permeability

✓ The hydrocarbons are trapped within the formation

Energy Deficit

High consumption:

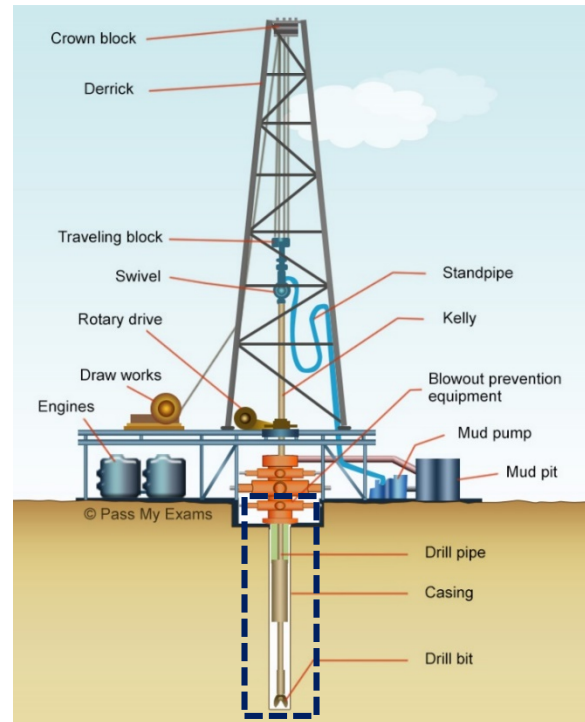
- ✓ Energy
- ✓ Materials derives from petroleum



- Exploration
- **Drilling**
- Termination
- Production

Drilling Fluids

- ✓ Transport the cuttings to surface
- ✓ Control pressures
- ✓ Preserve wellbore stability
- ✓ Cool and lubricate tools
- ✓ Transmit hydraulic energy



Physical properties of fluids

▪ Rheological

Shear thinning

Viscosity range (40-50mPa.s)

Viscoelastic behavior

▪ Filtration

Filtrate volume (<10 mL)

Low permeability

Thickness of filter cake (< 6 mm)

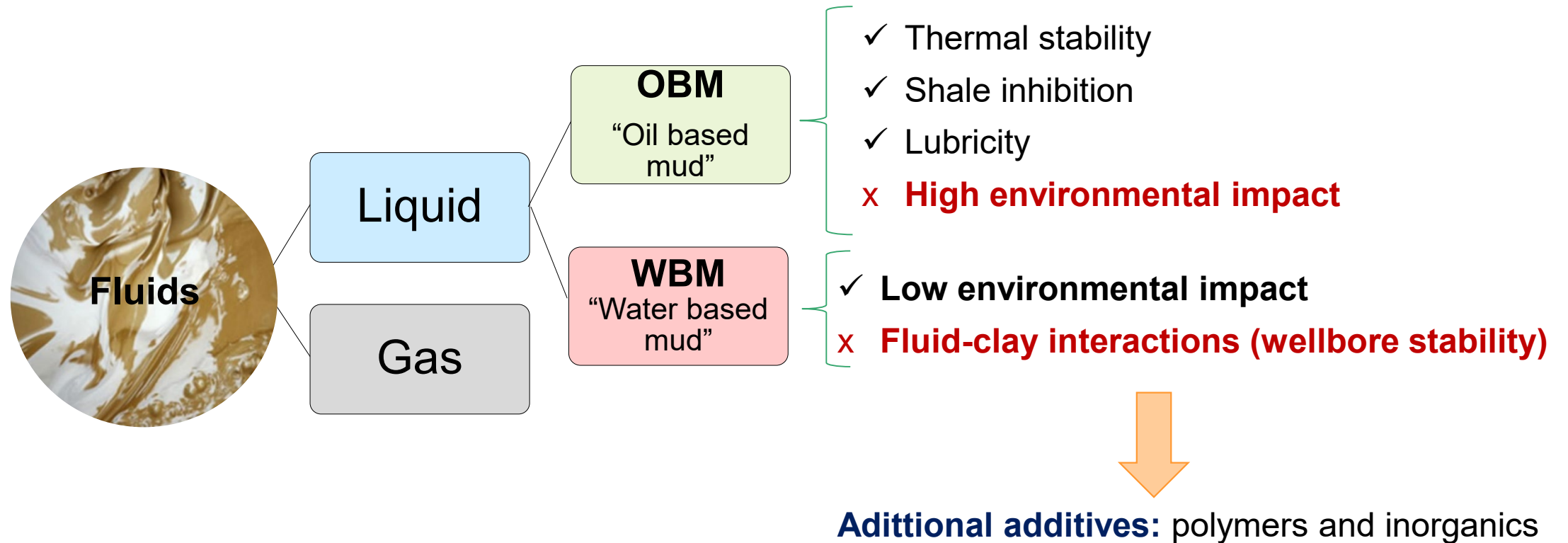
▪ Thermal

Thermal stability

▪ Others..

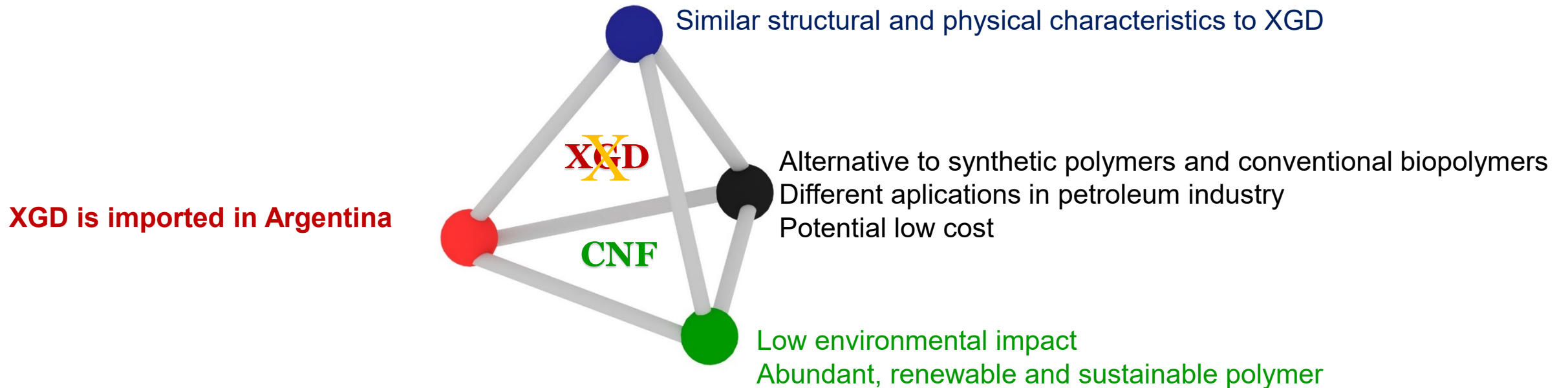
Density

Environmental behavior



Objectives

- To design WBMs with rheological properties similar to the OBMs used in shale formations of Argentina.
- To study the use of different cellulose nanofibrils (CNFs) as a replacement of xanthan gum (XGD) in WBM.
- To evaluate the effect of CNFs on the main functional properties of WBM (rheological, filtration, thermal and structural properties).



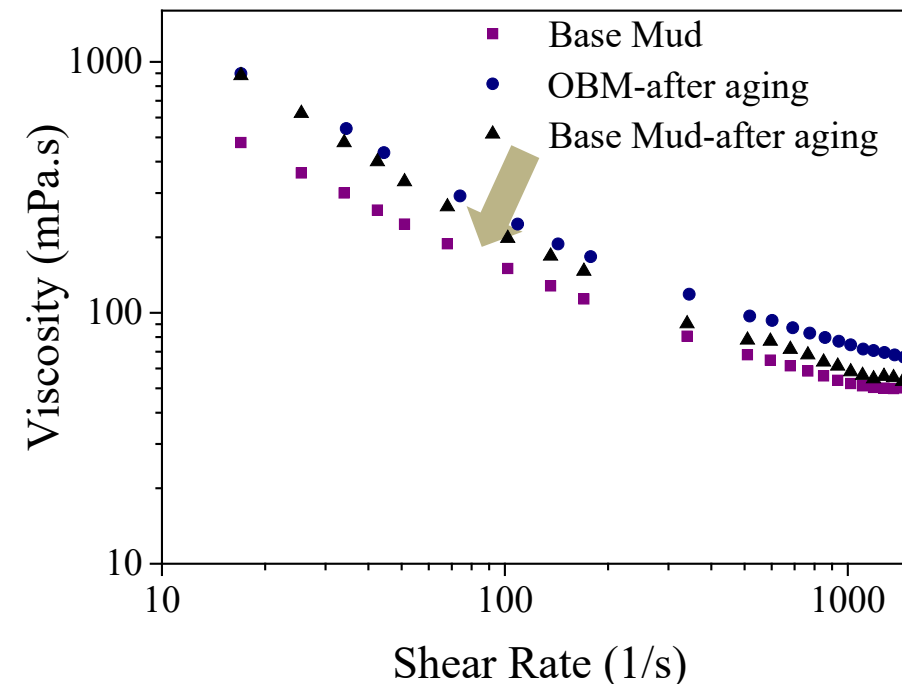
Base mud composition

Order of Addition	Component	Dosage	Function
1	Na-Bentonite A		Base Viscosifier and filtration control agent
2	Polyanionic cellulose (PAC)	8.00 g/L	Filtration control agent
	Xanthan gum (XGD)	1.50 g/L	Viscosifier
	B		Encapsulator
	C		Inhibitor
3	D		Lubricant
4	E		Filtration control agent
	F		Filtration control agent
	G		Densifier
5	H		pH control
6	I		Cuttings



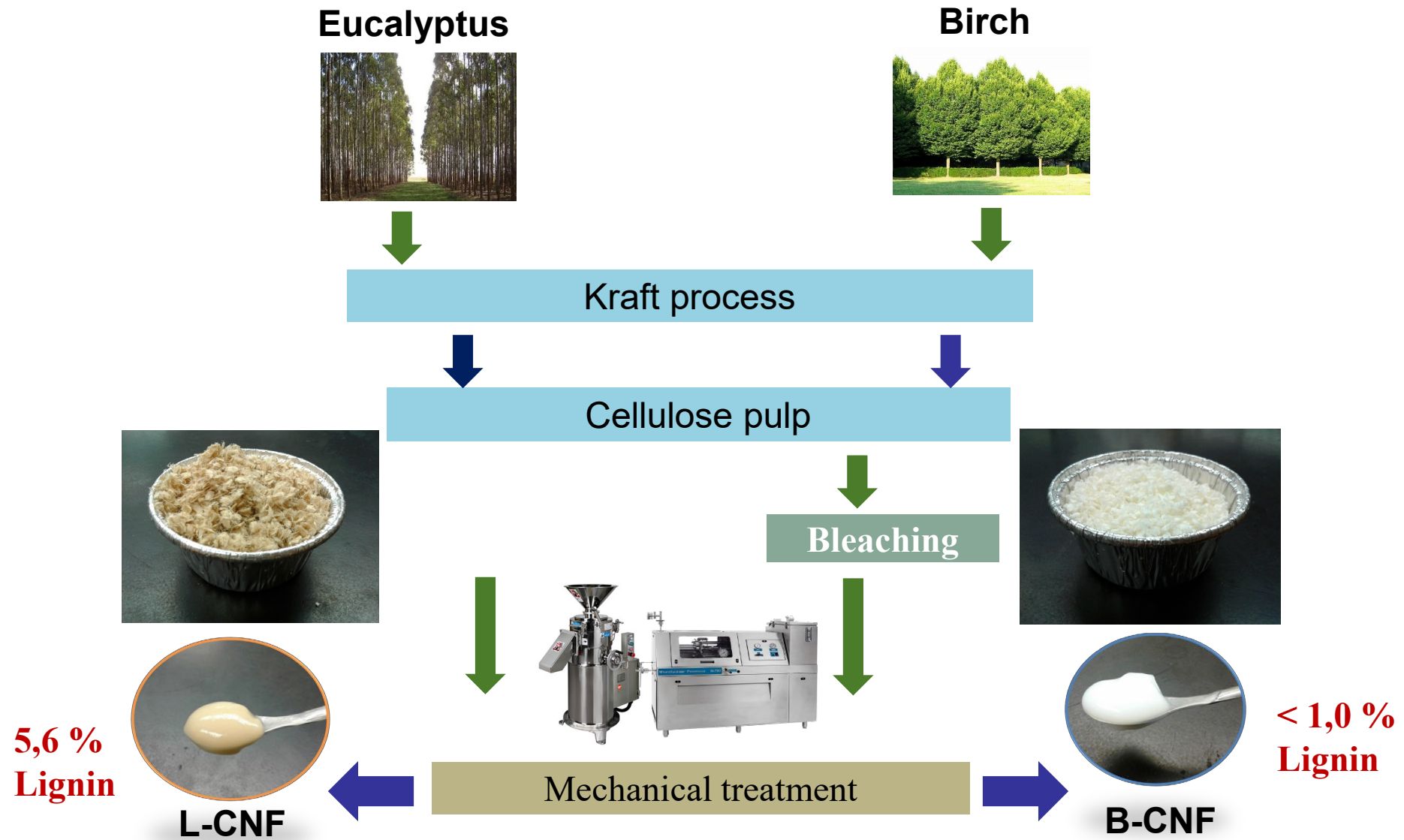
XRD Characterization of Shale (Vaca Muerta)

Polymer	$\overline{M}_n$ (g/mol)	$\overline{M}_w$ (g/mol)
PAC	692.000	1.146.000
XGD	881.000	1.622.000

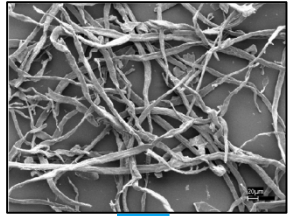


✓ WBM with similar rheological properties to OBM

L-CNF and B-CNF Isolation



R-CNF Isolation



Organic acid
hidrolysis



Centrifuge



Dialysis

Acid
Sugars

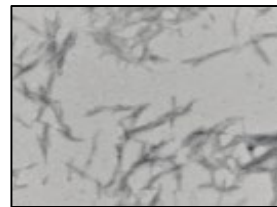
Crystallization

Sugars

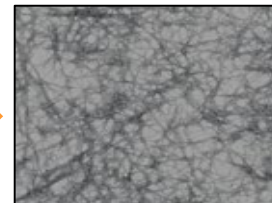
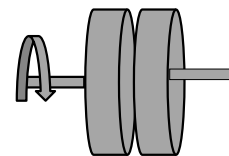
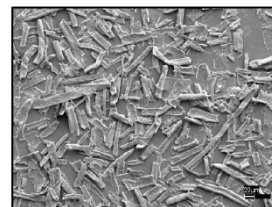
Solid Acid



Centrifuge



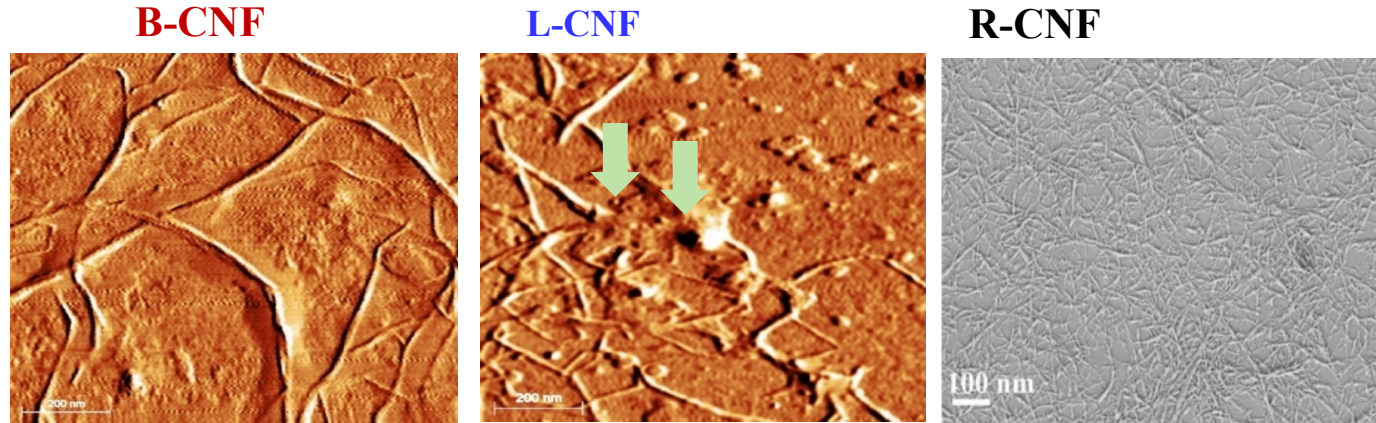
Cellulose Nanocrystals (CNC)



**Carboxilated cellulose nanofibrils
(R-CNF)**

CNFs Characterization

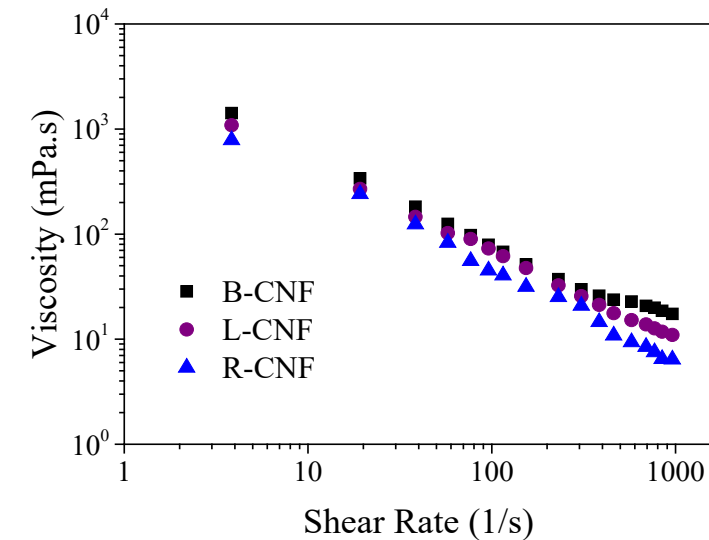
❑ Morphological Characterization



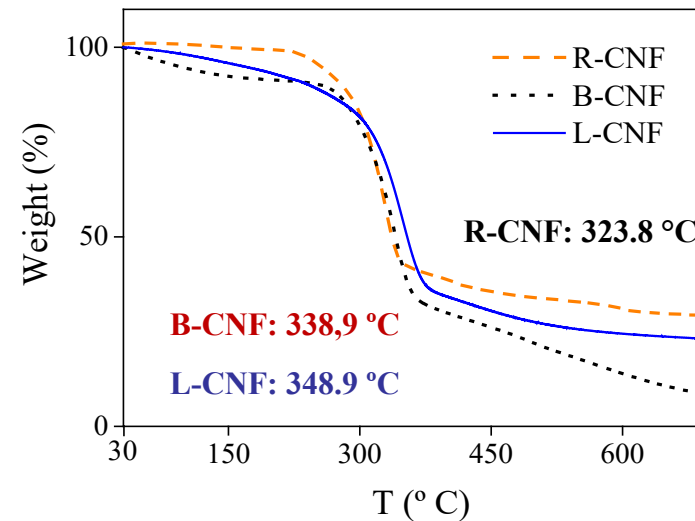
❑ Surface Characterization

Sample	Charge density ($\mu\text{eq/g}$)	ζ Potential (mV)
B-CNF	-50.11 ± 0.51	-24.70 ± 0.70
L-CNF	-58.00 ± 0.85	-34.70 ± 2.40
R-CNF	-101.00 ± 0.35	-36.21 ± 1.40

❑ Rheological Characterization



❑ Thermal Characterization



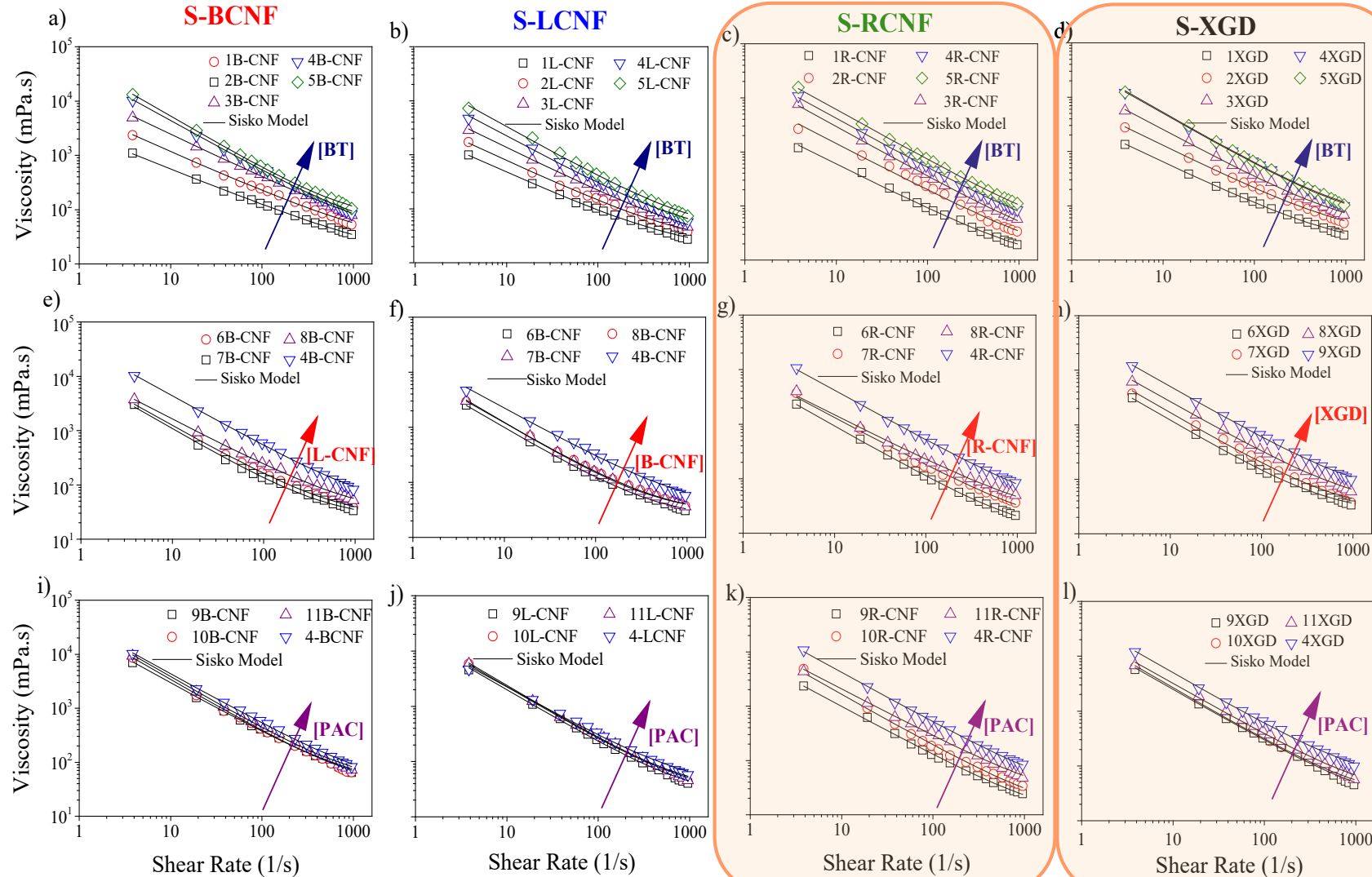
- ✓ Lower aspect ratio for R-CNF
- ✓ Higher charge density for R-CNF
- ✓ Higher thermal stability for L-CNF

Preparation of Systems: BT/CNFs/PAC/H₂O – BT/XGD/PAC/H₂O

System S-BCNF: BT/B-CNF/PAC/H ₂ O				System S-LCNF: BT/L-CNF/PAC/H ₂ O			
Fluid	BT (% m/m)	B-CNF (% m/m)	PAC (% m/m)	Fluid	BT (% m/m)	L-CNF (% m/m)	PAC (% m/m)
1B-CNF	0.00	0.50	0.50	1L-CNF	0.00	0.50	0.50
2B-CNF	1.00	0.50	0.50	2L-CNF	1.00	0.50	0.50
3B-CNF	3.00	0.50	0.50	3L-CNF	3.00	0.50	0.50
4B-CNF	4.50	0.50	0.50	4L-CNF	4.50	0.50	0.50
5B-CNF	6.00	0.50	0.50	5L-CNF	6.00	0.50	0.50
6B-CNF	4.50	0.00	0.50	6L-CNF	4.50	0.00	0.50
7B-CNF	4.50	0.10	0.50	7L-CNF	4.50	0.10	0.50
8B-CNF	4.50	0.25	0.50	8L-CNF	4.50	0.25	0.50
9B-CNF	4.50	0.50	0.00	9L-CNF	4.50	0.50	0.00
10B-CNF	4.50	0.50	0.10	10L-CNF	4.50	0.50	0.10
11B-CNF	4.50	0.50	0.25	11L-CNF	4.50	0.50	0.25
System S-RCNF: BT/R-CNF/PAC/H ₂ O				System S-XGD: BT/XGD/PAC/H ₂ O			
Fluid	BT (% m/m)	R-CNF (% m/m)	PAC (% m/m)	Fluid	BT (% m/m)	XGD (% m/m)	PAC (% m/m)
1R-CNF	0.00	0.50	0.50	1XGD	0.00	0.50	0.50
2R-CNF	1.00	0.50	0.50	2XGD	1.00	0.50	0.50
3R-CNF	3.00	0.50	0.50	3XGD	3.00	0.50	0.50
4R-CNF	4.50	0.50	0.50	4XGD	4.50	0.50	0.50
5R-CNF	6.00	0.50	0.50	5XGD	6.00	0.50	0.50
6R-CNF	4.50	0.00	0.50	6XGD	4.50	0.00	0.50
7R-CNF	4.50	0.10	0.50	7XGD	4.50	0.10	0.50
8R-CNF	4.50	0.25	0.50	8XGD	4.50	0.25	0.50
9R-CNF	4.50	0.50	0.00	9XGD	4.50	0.50	0.00
10R-CNF	4.50	0.50	0.10	10XGD	4.50	0.50	0.10
11R-CNF	4.50	0.50	0.25	11XGD	4.50	0.50	0.25



Rheological Properties

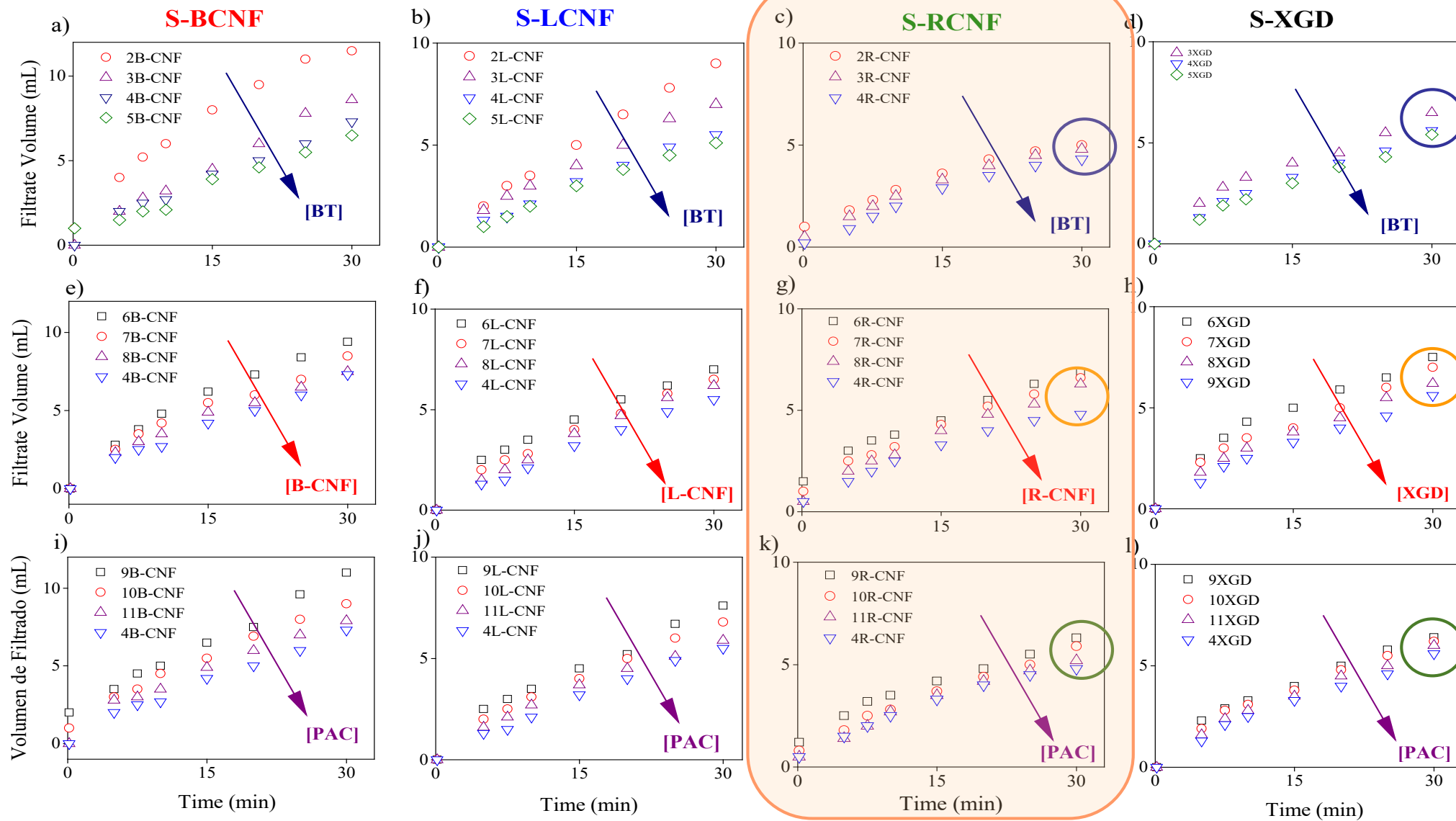


- ✓ A higher viscosifier effect of **R-CNF**
- ✓ Similar rheological behavior for **SR-CNF** and **S-XGD** systems

Sisko Model

$$\eta = \eta_{\infty} + k\dot{\gamma}^{n-1}$$

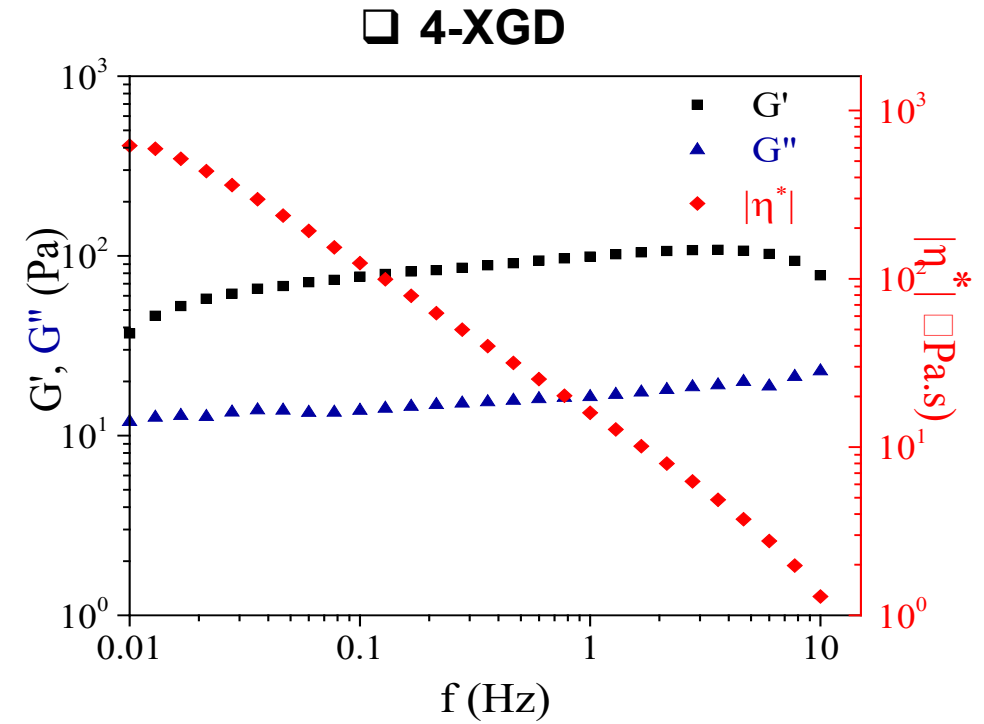
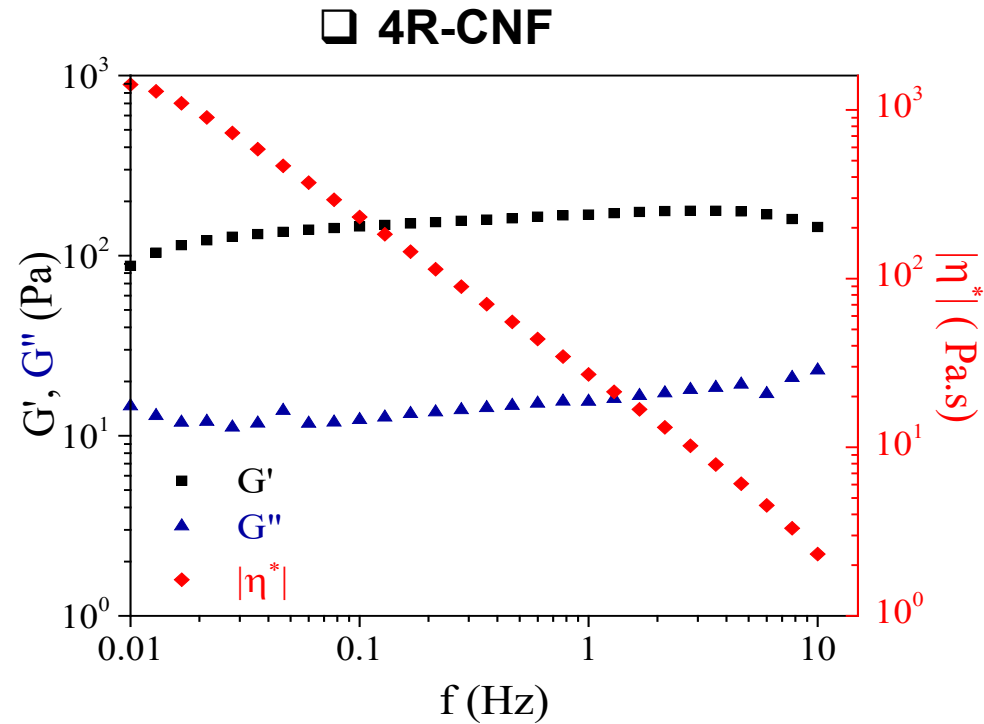
Filtration Properties



✓ Lower filtrate volume for **S-RCNF**

Viscoelastic Behavior

□ Oscillatory-shear rheological properties

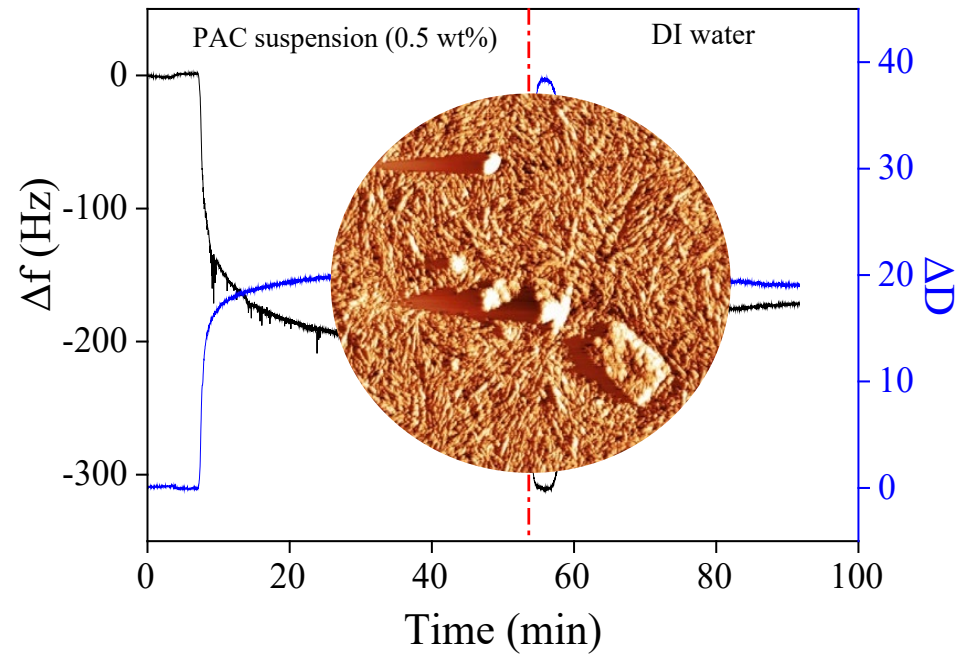


- ✓ $G' > G''$ more noticeable for **4R-CNF**
- ✓ Stable structures
- ✓ Viscoelastic behavior
- ✓ Shear-thinning behavior

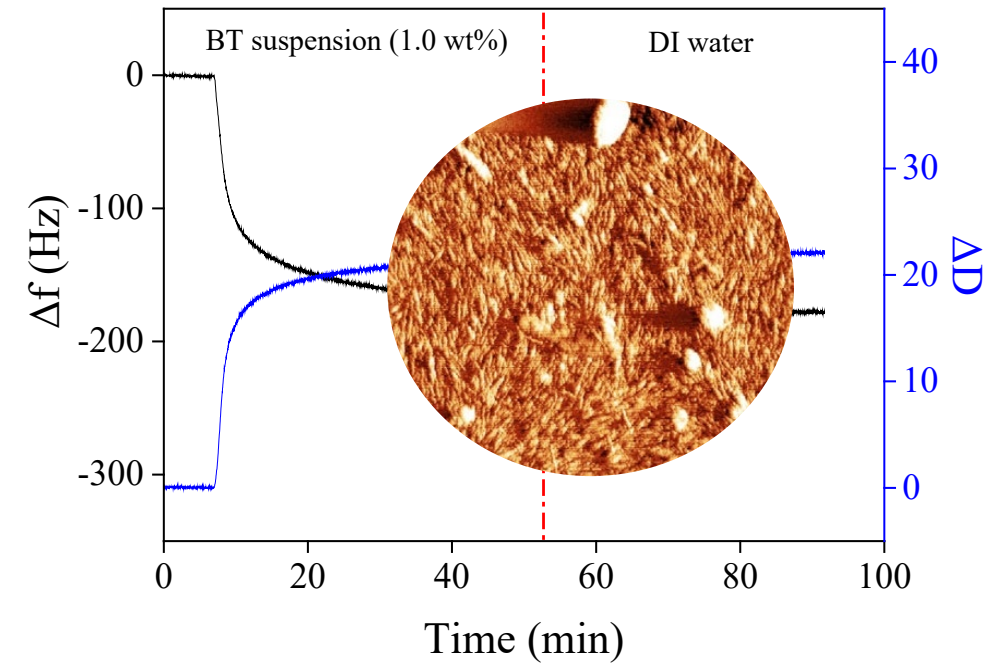
Surface Interactions

□ QCM-D analyses

□ PAC/R-CNF



□ BT/R-CNF

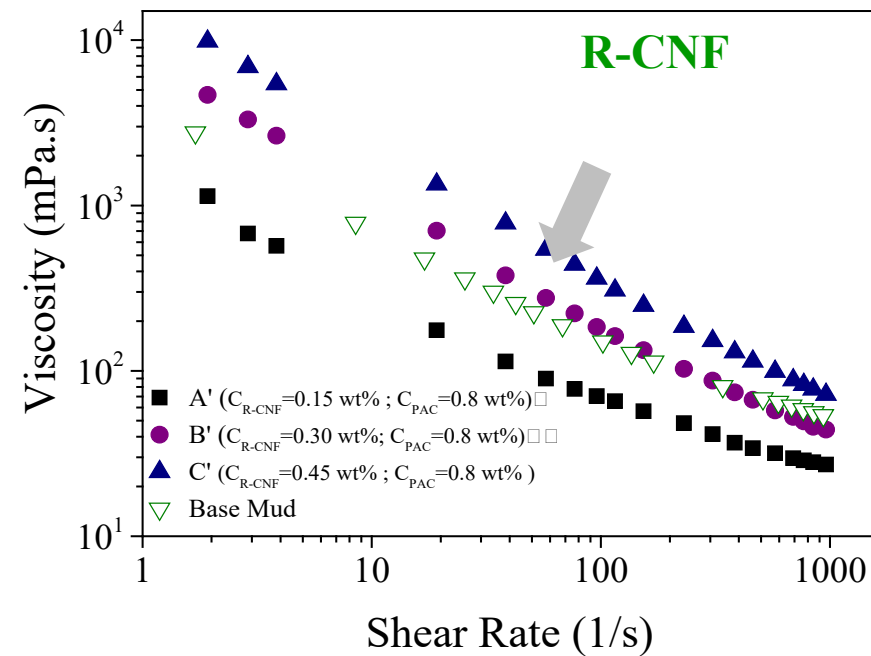
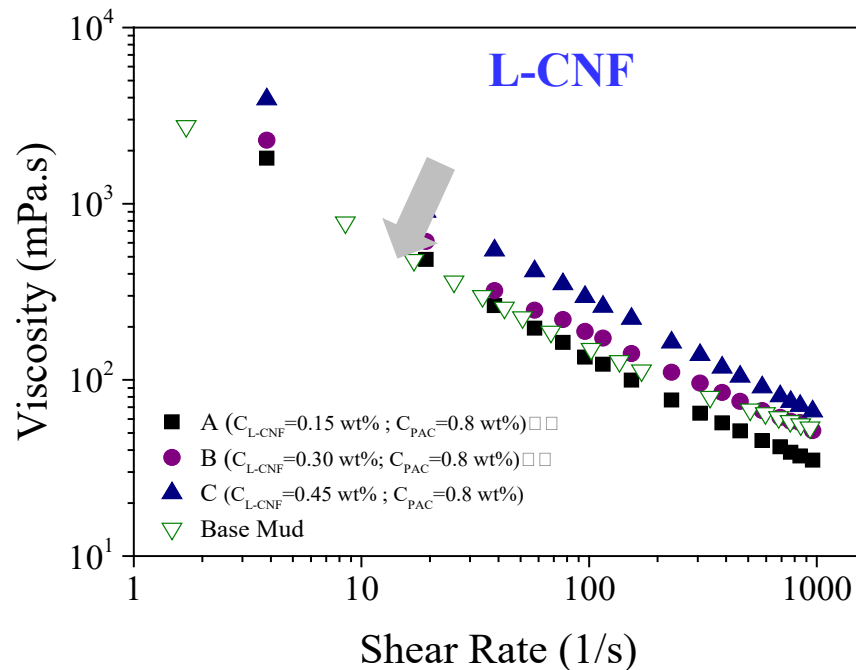


- ✓ Higher interaction with PAC
- ✓ Viscoelastic films ($\Delta D/\Delta f > 5\%$)

Replacement of XGD by R-CNF/L-CNF in WBM for Argentina Shale

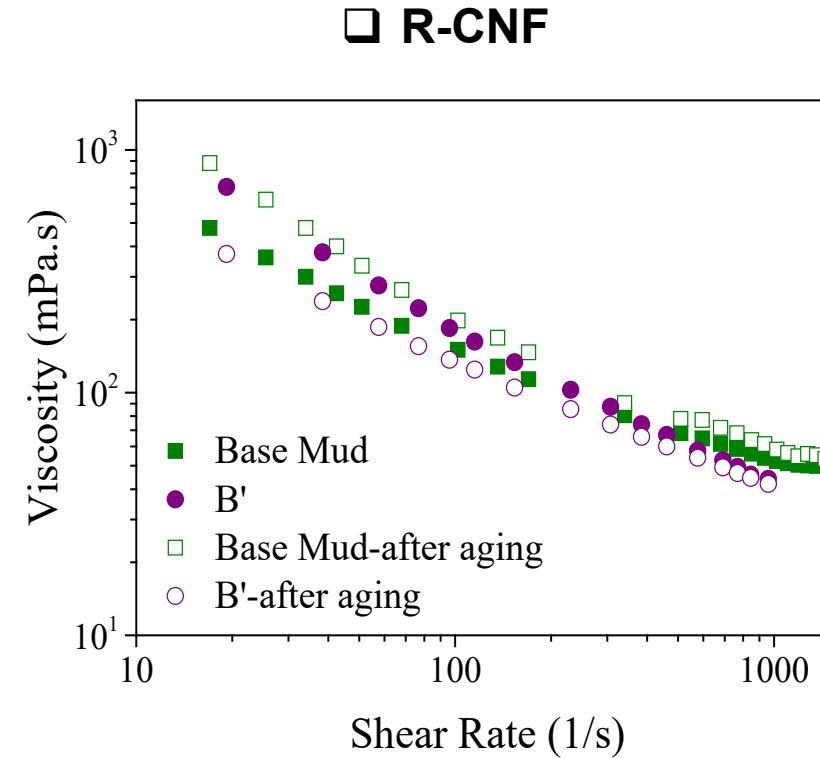
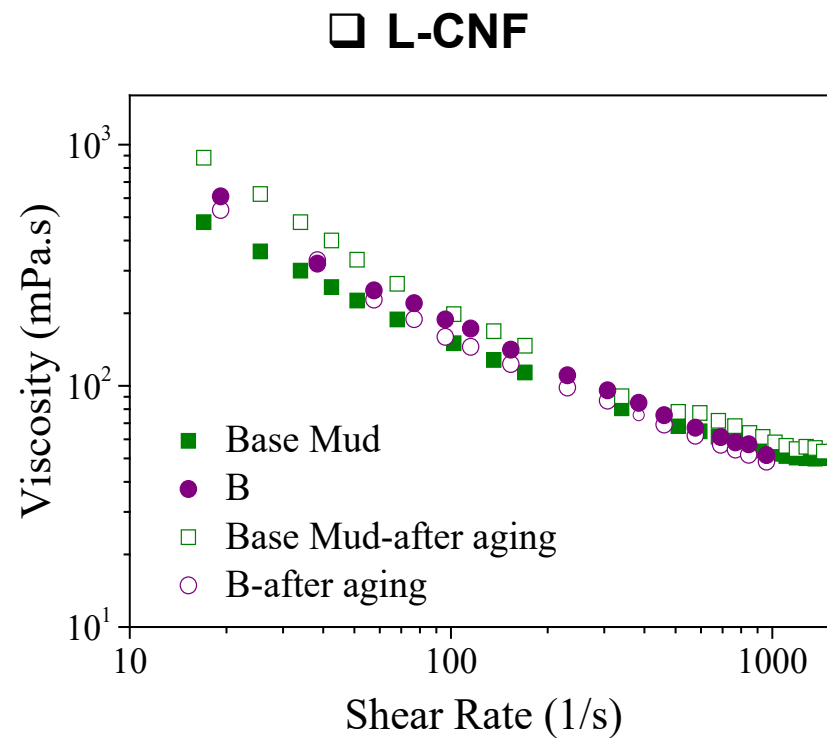
□ Steady-shear rheological properties

Fluid	C_{XGD} (wt%)	C_{PAC} (wt%)	$C_{L-CNF \text{ or } R-CNF}$ (wt%)
Base Mud	0.15	0.80	—
A – A'	—	0.80	0.15
B – B'	—	0.80	0.30
C – C'	—	0.80	0.45



✓ Fluid with $C_{L-CNF/R-CNF} = 2 C_{XGD}$ (**Base Mud**) exhibited a similar rheological behavior

□ Dynamic aging test



✓ Fluids with **L-CNF** and **R-CNF** (B and B') exhibited better thermal stability

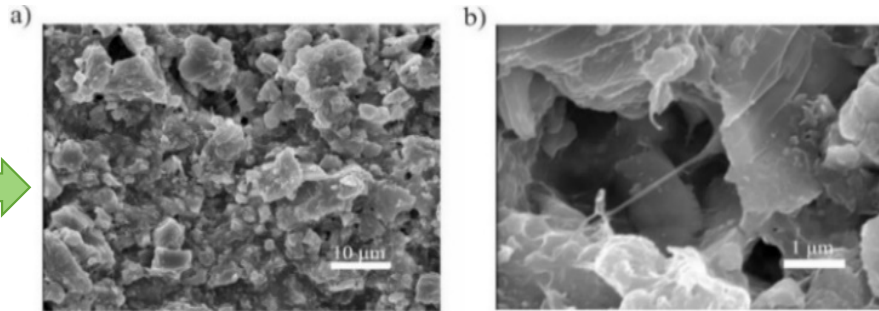
Structural Characteristics

□ SEM

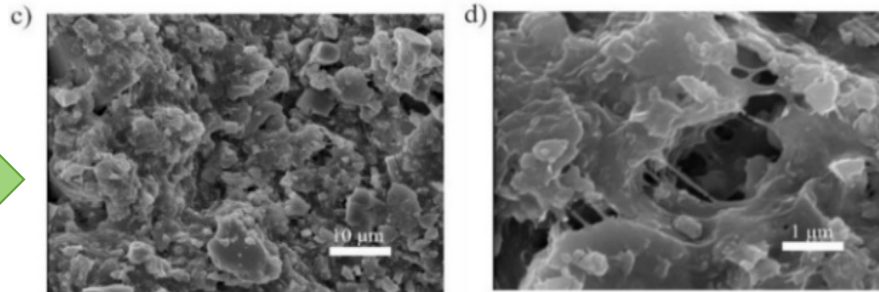
WBMs with **L-CNF**

WBMs with **R-CNF**

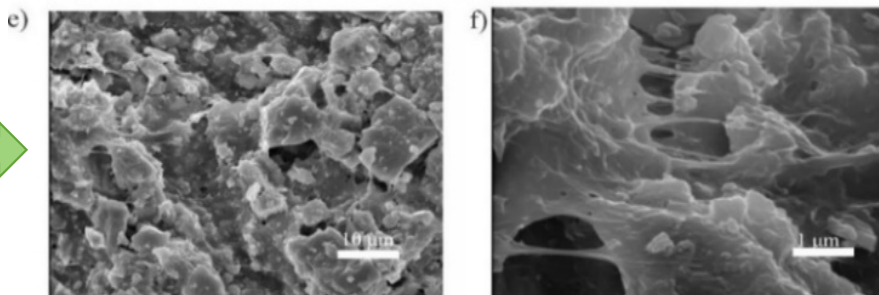
Fluid A →



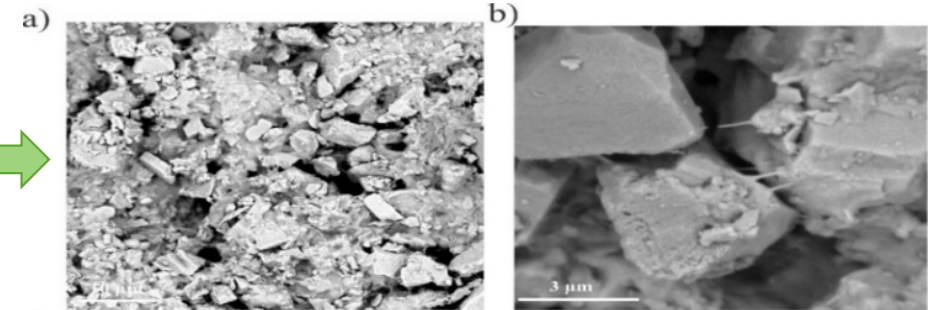
Fluid B →



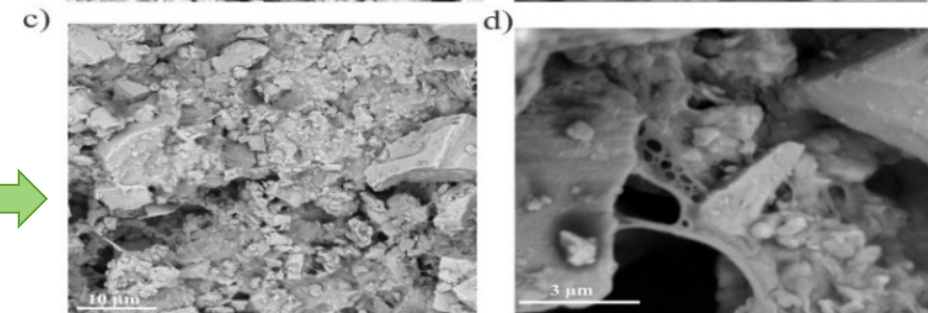
Fluid C →



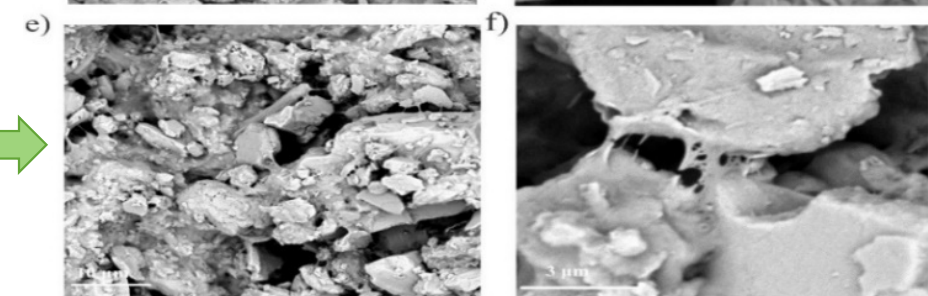
Fluid A' →



Fluid B' →



Fluid C' →



C_{R-CNF}



- ✓ Film formation
- ✓ Particles agglomeration

Conclusions

❑ The differences in surface characteristics, particle sizes, structures, lignin contents and functionalization of the CNFs significantly affected the functional properties of the WBM.

❑ **For simple WBMs**

- i) Pseudoplastic behavior and similar viscosities.
- ii) Lower filtrate volumes for WBMs containing R-CNF
- iii) Similar thicknesses of the filter cakes.
- iv) Lower filtration rates and permeabilities for WBMs containing R-CNF.

❑ The results obtained by QCM-D indicated higher interaction between PAC and R-CNF.

❑ The fluids studied followed the rheological model of Sisko.

Conclusions

- ❑ For **specific WBM**s:

- i) Rheological behavior very similar respect to the traditional fluid containing XGD with the double concentration of L-CNF and R-CNF.
- ii) Higher thermal stability for WBMs containing R-CNF and L-CNF.
- iii) Film formation and higher particle agglomeration with increasing concentration of L-CNF and R-CNF.
- iv) Lower filtrate volumes for the fluid with R-CNF

- ❑ The use of CNFs as additives in WBMs is a promising alternative for the efficient design of WBMs for shale formations of Vaca Muerta.

- ❑ The L-CNF and the R-CNF presented advantages related to the performance of fluids and the potential economic and environmental benefits.

Acknowledgements

Thanks to:

- ✓ Dra Diana Estenoz and Dra Natalia Casis (INTEC)
- ✓ Dra Soledad Peresin-School of Forestry and Wildlife Sciences, Auburn University (USA).
- ✓ Celeste Iglesias, PhD Student.

¡THANK YOU FOR YOUR ATTENTION!



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Cellulose

<https://doi.org/10.1007/s10570-018-2081-z>



ORIGINAL PAPER

Cellulose nanofibrils as a replacement for xanthan gum (XGD) in water based muds (WBMs) to be used in shale formations

Yurany Villada · María Celeste Iglesias · Natalia Casis · Eleonora Erdmann ·
María Soledad Peresin · Diana Estenoz

Applied Clay Science 149 (2017) 59–66



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Research paper

Functional characterization on colloidal suspensions containing xanthan gum (XGD) and polyanionic cellulose (PAC) used in drilling fluids for a shale formation



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