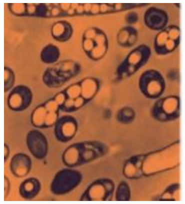
NOVEL POLYMERIC MATERIALS AND SUSTAINABLE TECHNOLOGIES BASED ON THE USE OF RENEWABLE RESOURCES FROM THE CENTRAL REGION OF ARGENTINA

Diana A. Estenoz

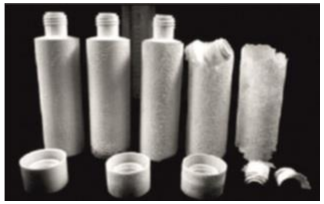
Grupo de Polímeros y Reactores de Polimerización

Instituto de Desarrollo Tecnológico para la Industria Química

UNL CONICET INTEC



BioPOLI 2018
III WORKSHOP POLÍMEROS BIODEGRADABLES y BIOCOMPUESTOS



Outline

1. Introduction and main objectives
2. Work in progress
3. Nanocelullose as additive in drilling fluids

   3.1 Introduction

   3.2 Objectives

   3.2 Experimental and theoretical work

   3.3 Conclusions

1.

Introduction

Polymeric Materials

Challenges

- ✓Expand industrial activity
- ✓Respond to market demand (quality, cost)
- ✓Environmental regulation

Strategies

Use of Renewable Sources

- **Byproducts**
  - Proteins
  - Glycerol
- **Raw Materials**
  - Vegetable Oils
  - Proteins
  - Nanocelulosa
- **Industrial waste**
  - Whey
  - Furfural
  - Lignins

General objective:

✓ To develop innovative strategies for the synthesis of polymeric materials that increase the industrial/commercial value of renewable resources from economic activities in the Central Region.

Specific objectives:

- ✓ Chemical modification and characterization of the renewable resources.
- ✓ Synthesis of the materials and post-processing.
- ✓ Structural characterization of monomers, prepolymers and polymers.
- ✓ Characterization of application properties.
- ✓ Evaluation of the environmental impact and biodegradation.
- ✓ Economical analysis

3.

Work in progress

Work in progress

Polyurethanes from vegetable oils

Charact. – Chem. Mod. → Synthesis → Characterization → Environmental impact → Economical analysis

- Charact. – Chem. Mod.: → Characterization and chemical modification of castor oil
- Synthesis: → TPUs → Foams
- Characterization: → Mechanical properties, FTIR, SEM, NMR, SEC
- Environmental impact: → Biodegradation by different microorganisms

Lignins in phenolic resins: Production of laminates

Charact. – Chem. Mod. → Synthesis → Characterization → Environmental impact → Economical analysis

- Charact. – Chem. Mod.: → Activation of lignins
- Synthesis: → Base resin and production of laminates
- Characterization: → Mechanical properties, FTIR, SEM, water absorption
- Environmental impact: → Replacement of phenol

Lignins in agriculture area: Controlled release applications

Charact. – Chem. Mod. → Synthesis → Characterization → Environmental impact → Economical analysis

- Charact. – Chem. Mod.: → Lignin characterization
- Synthesis: → Microparticles
- Characterization: → Size, morphology, encapsulation efficiency, release behavior
- Environmental impact: → Leaching experiments in soil

Work in progress

Synthesis of PLA from whey

Charact. – Chem. Mod. → Synthesis → Characterization → Environmental impact → Economical analysis

- Charact. – Chem. Mod.: → Fermentation, extraction, purification and characterization of lactic acid from whey
- Synthesis: → Poly(lactic acid)
- Characterization: → SEC, NMR, GC

Hybrid Latexes for coatings and adhesives

Charact. – Chem. Mod. → Synthesis → Characterization → Environmental impact → Economical analysis

- Charact. – Chem. Mod.: → Characterization and chemical modification of proteins
- Synthesis: → Obtention of the latexes by emulsion and miniemulsion
- Characterization: → Morphol., thermal, mechanical, and optical characterization of latexes and films
- Environmental impact: → Degradation under composting conditions

Hyaluronic acid microgels for enzymatic-triggered release of hydrophobic drugs

Charact. – Chem. Mod. → Synthesis → Characterization → Environmental impact → Economical analysis

- Charact. – Chem. Mod.: → Methacrylation and characterization of hyaluronic acid
- Synthesis: → Microgels
- Characterization: → Size, morphology, encapsulation efficiency, release behavior
- Environmental impact: → Enzymatic degradation

Work in progress

Drug release systems based on regional proteins

Charact. – Chem. Mod. → Synthesis → Characterization → Environmental impact → Economical analysis

- **Charact. – Chem. Mod.:** → Characterization and chemical modification of casein and collagene
- **Synthesis:** → Obtention of the films and nanoformulation for medical treatments
- **Characterization:** → Morphol., thermal, mechanical, and surface charact. Load and release behavior
- **Environmental impact:** → Degradation under composting conditions
- **Economical analysis**

Nanocelullose as additive in drilling fluids

Charact. – Chem. Mod. → Synthesis → Characterization → Environmental impact → Economical analysis

- **Charact. – Chem. Mod.:** → Manufacturing process for production of nanocelullose
- **Synthesis:** → Preparation of water-based drilling fluids
- **Characterization:** → Rheometric, filtration, thermal and structural assays
- **Environmental impact:** → Additives from renewable and biodregadable source
- **Economical analysis:** → Additives with low cost of production

3.

Nanocelullose as additive in drilling fluids

Hydrocarbon Exploitation

Conventional Reserves

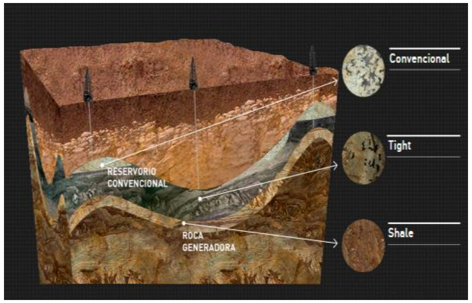
Unconventional Reserves

Energy Deficit

High consumption:

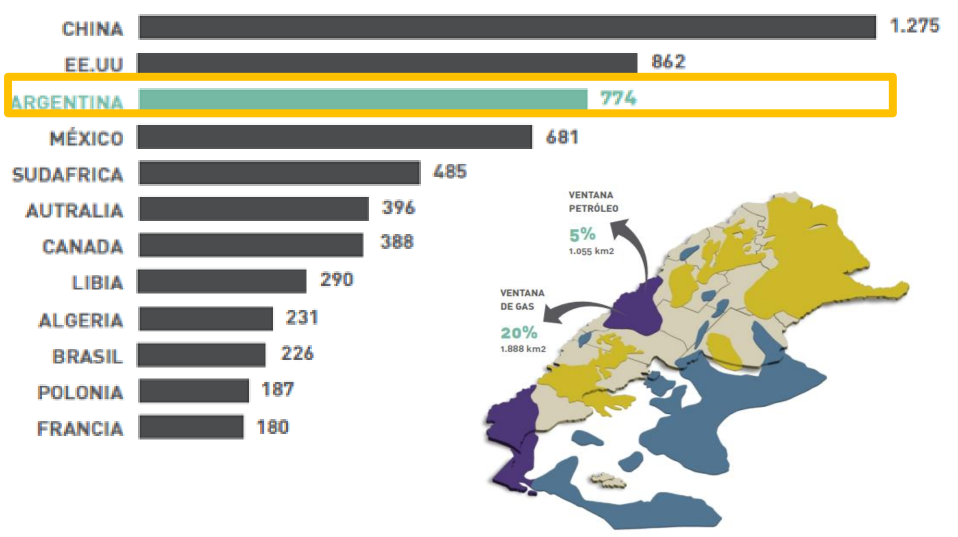
- ✓ **Energy**
- ✓ **Materials derived from petroleum**

SHALE



The hydrocarbons are trapped within the formation

Shale resources are globally abundant

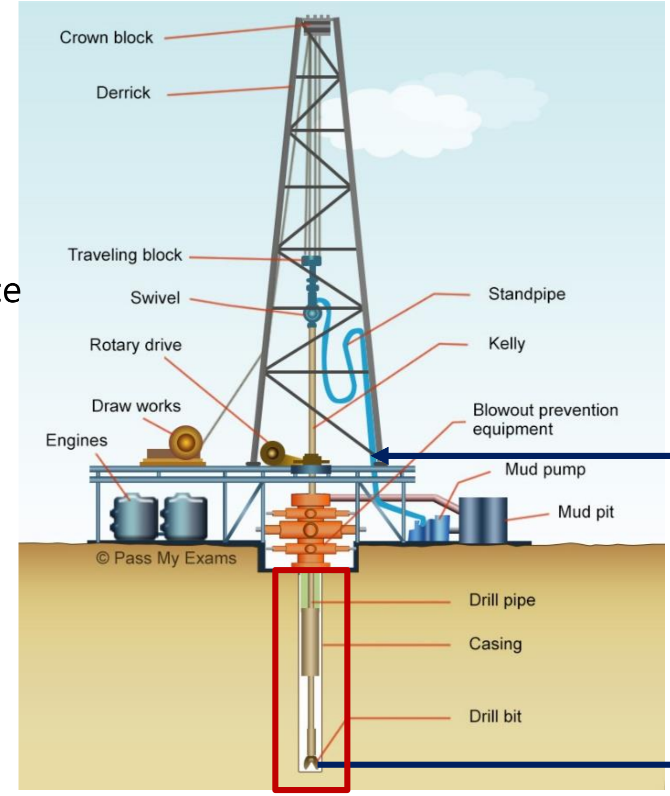


Operation – Stages – Drilling Fluids

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

Drilling Fluids

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



Input: Drill string

Output: Drill bit

Physical properties of fluids

- **Rheological**
  Shear thinning
  Viscosity range (40-50mPa.s)
- **Filtration**
  Filtrate volume
  Permeability
  Thickness of filter cake
- **Others..**
  Density
  Environmental behavior

Drilling Fluids - Types

Drilling Fluids

OBM
Oil based mud

Continuous phase: oil

- **Shale inhibition**
- **Thermal stability**
- **Lubricity**

χ **High environmental impact**

WBM
Water based mud

Continuous phase: water

- **Low environmental impact**

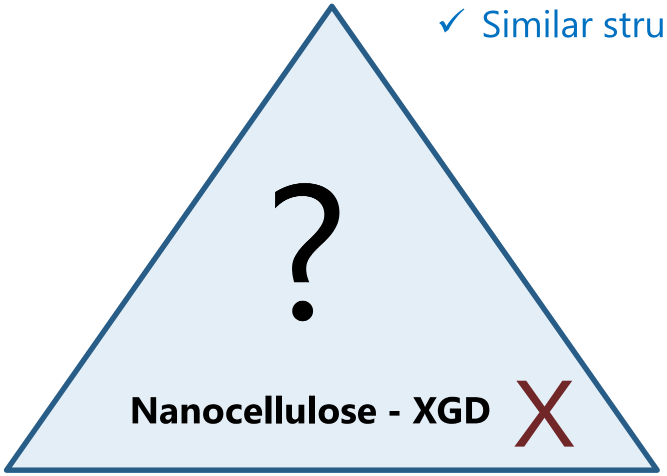
χ **Fluid-Clay interaction (wellbore instability)**

Additional additives: **polymers (PAC, XGD)** and inorganics

To propose a more sustainable alternative for the design of WBMs for a shale formation with environmental and economic advantages.

To study the use of cellulose nanofibrils (CNF) from eucalyptus and birch pulps as replacement of xanthan gum (XGD) in WBMs.

- ✓ Low environmental impact
- ✓ Similar structural and physical characteristics to XGD



- ✓ Cost of XGD

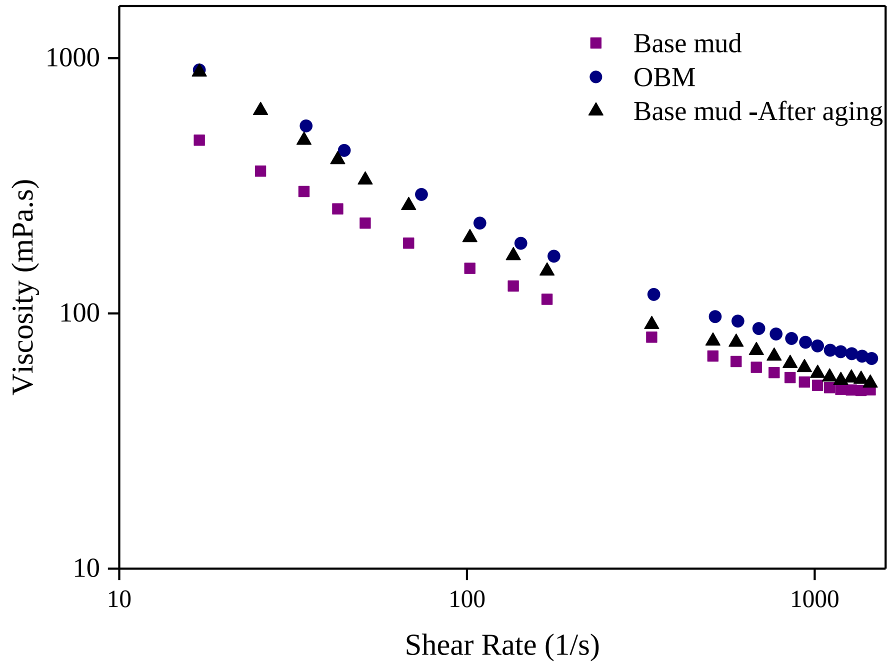
Preparation of Fluid - Base Mud Design

Base mud composition

Order of Addition	Component	Dosage	Function
1	Na-Bentonite		Base
	A		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)

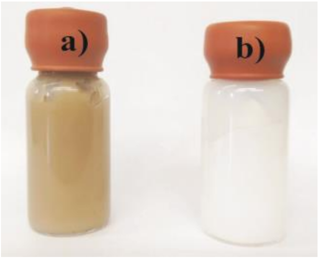
Polymer	$\overline{M_n}$(g/mol)	$\overline{M_w}$(g/mol)
PAC	692.000	1.146.000
XGD	881.000	1.622.000



✓ **WBM with similar rheological properties to OBM**

CNFs Characterization

CNF2: Unbleached pulps (5.6% Lignin)



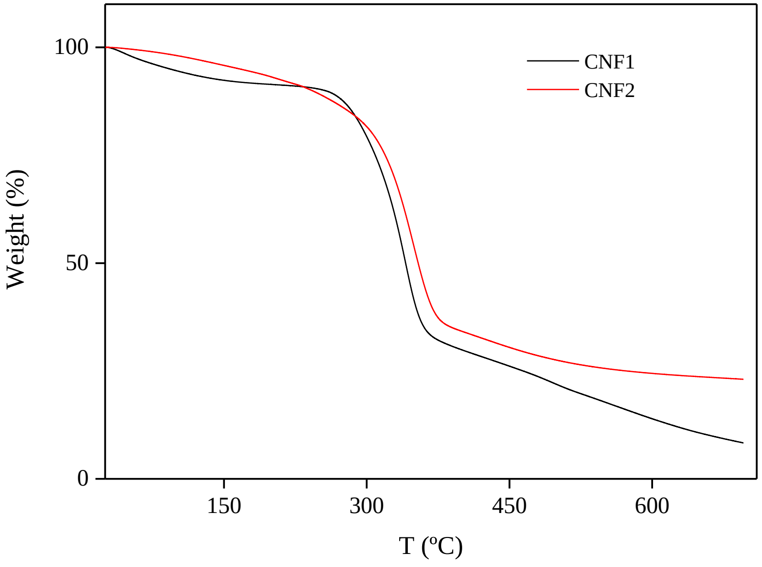
CNF1: Fully bleached pulps (0% Lignin)

➢ **Surface characterization**

Sample	ζ Potential (mV)
CNF1 (pH:7.0)	-24.7
CNF2 (pH:7.0)	-34.7

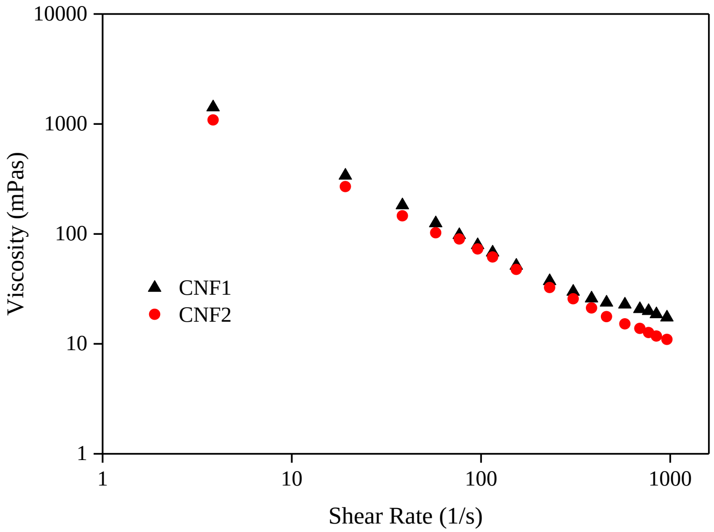
✓ Surface charge: washing treatment (sodium form)

➢ **Thermal Characterization**



✓ Higher thermal stability of CNF2

➢ **Rheological Characterization**



✓ CNF2: more stabilized suspension

✓ CNF2: more shear-thinning behavior

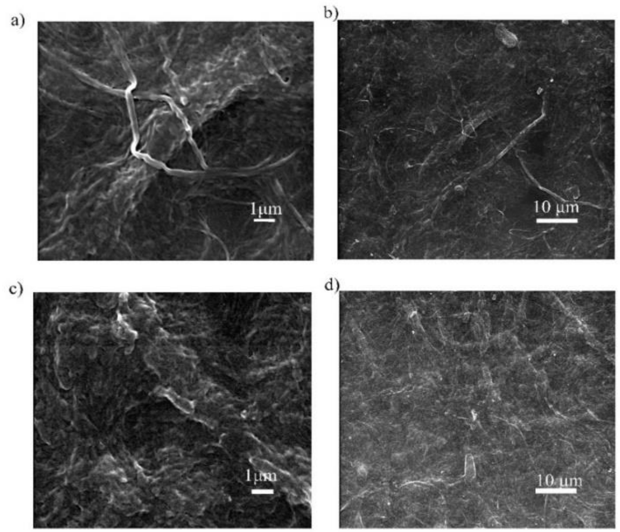
CNFs Characterization

- **Morphological Characterization**

  - SEM

CNF1

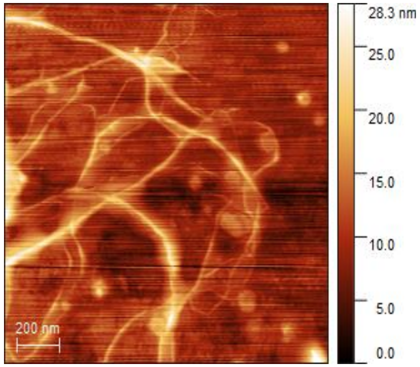
CNF2



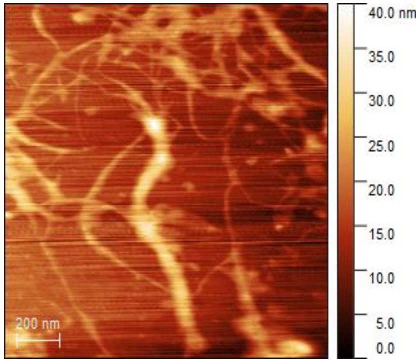
✓ Higher degree of fibrillation in the structure for CNF2

  - AFM

CNF1



CNF2



✓ Smaller fibril width, coarser fibrils and smaller roughness for CNF2

Preparation of Systems: BT/CNFs/PAC/H_2O – BT/XGD/PAC/H_2O

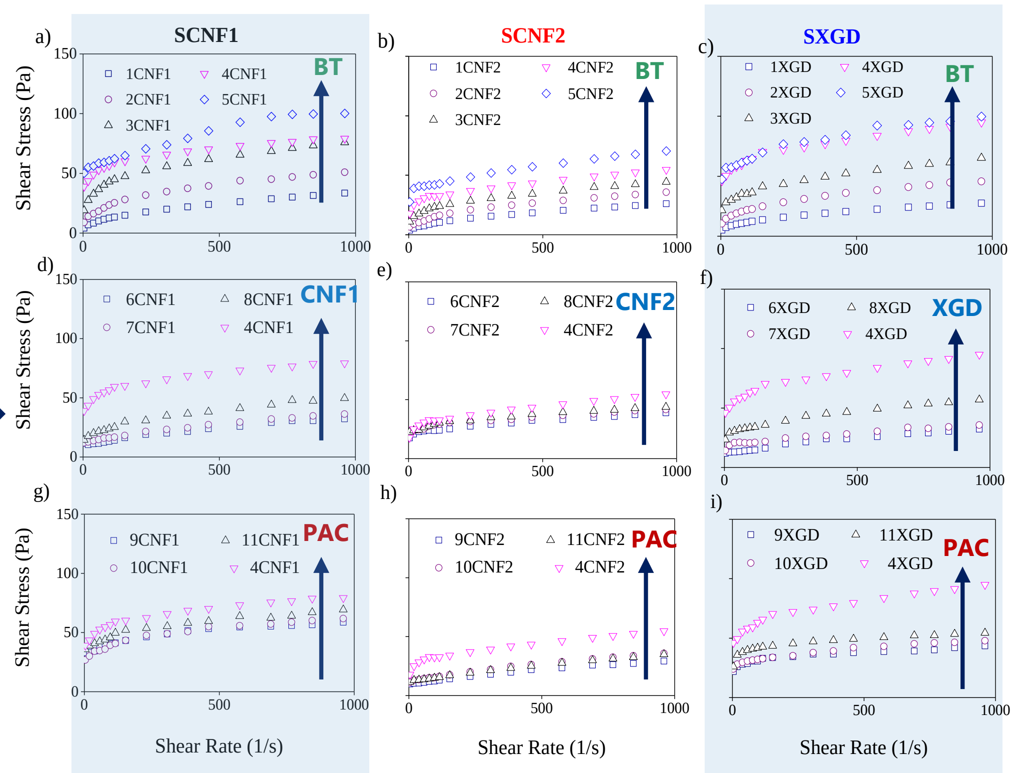
System: SCNF1(BT/CNF1/PAC/H_2O)				System: SCNF2(BT/CNF2/PAC/H2O)				System: SXGD(BT/XGD/PAC/H2O)			
Fluid	BT(%wt)	**CNF1**(%wt)	PAC(%wt)	**Fluid**	BT(%wt)	**CNF2**(%wt)	PAC(%wt)	**Fluid**	BT(%wt)	**XGD**(%wt)	PAC(%wt)
1CNF1	0.00	0.50	0.50	**1CNF2**	0.00	0.50	0.50	**1XGD**	0.00	0.50	0.50
2CNF1	1.00	0.50	0.50	**2CNF2**	1.00	0.50	0.50	**2XGD**	1.00	0.50	0.50
3CNF1	3.00	0.50	0.50	**3CNF2**	3.00	0.50	0.50	**3XGD**	3.00	0.50	0.50
4CNF1	4.50	0.50	0.50	**4CNF2**	4.50	0.50	0.50	**4XGD**	4.50	0.50	0.50
5CNF1	6.00	0.50	0.50	**5CNF2**	6.00	0.50	0.50	**5XGD**	6.00	0.50	0.50
6CNF1	4.50	0.00	0.50	**6CNF2**	4.50	0.00	0.50	**6XGD**	4.50	0.00	0.50
7CNF1	4.50	0.10	0.50	**7CNF2**	4.50	0.10	0.50	**7XGD**	4.50	0.10	0.50
8CNF1	4.50	0.25	0.50	**8CNF2**	4.50	0.25	0.50	**8XGD**	4.50	0.25	0.50
9CNF1	4.50	0.50	0.00	**9CNF2**	4.50	0.50	0.00	**9XGD**	4.50	0.50	0.00
10CNF1	4.50	0.50	0.10	**10CNF2**	4.50	0.50	0.10	**10XGD**	4.5	0.50	0.10
11CNF1	4.50	0.50	0.25	**11CNF2**	4.50	0.50	0.25	**11XGD**	4.50	0.50	0.25

Rheological Properties

Bentonite variation

CNF1, CNF2 or XGD variation

PAC variation

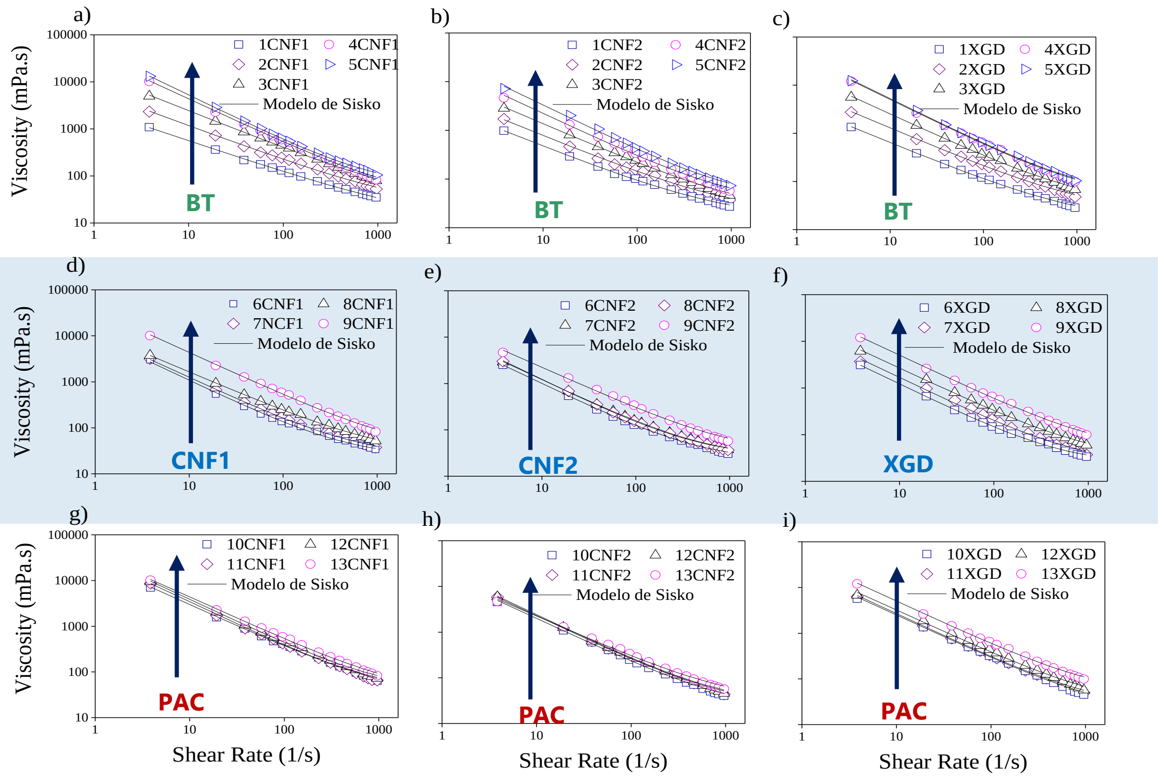


- ✓ Shear thinning behavior
- ✓ Increase of yield stress and viscosity with composition (more noticeable for **SCNF1** and **SXGD)**

Bentonite variation

CNF1, CNF2 or XGD variation

PAC variation



- **Sisko Model**

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

- ✓ Lower viscosity and yield stress for **SNCF2**
- ✓ A higher viscosifier effect of **XGD**
- ✓ No significant effect of **PAC**

- ✓ Very good predictions of Sisko Model

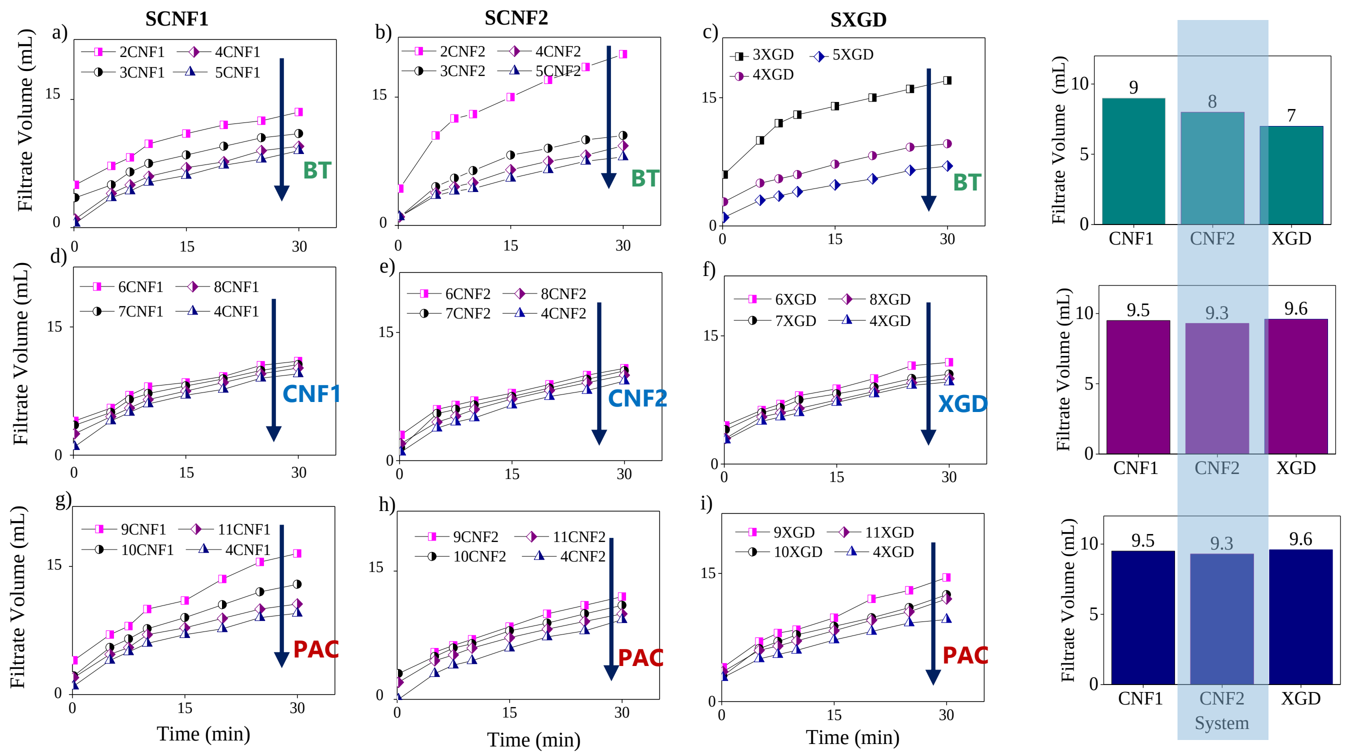
Filtration Properties

- **API Filtration**

Bentonite variation

CNF1, CNF2 or XGD variation

PAC variation



✓ Higher BT and PAC effect on filtering properties

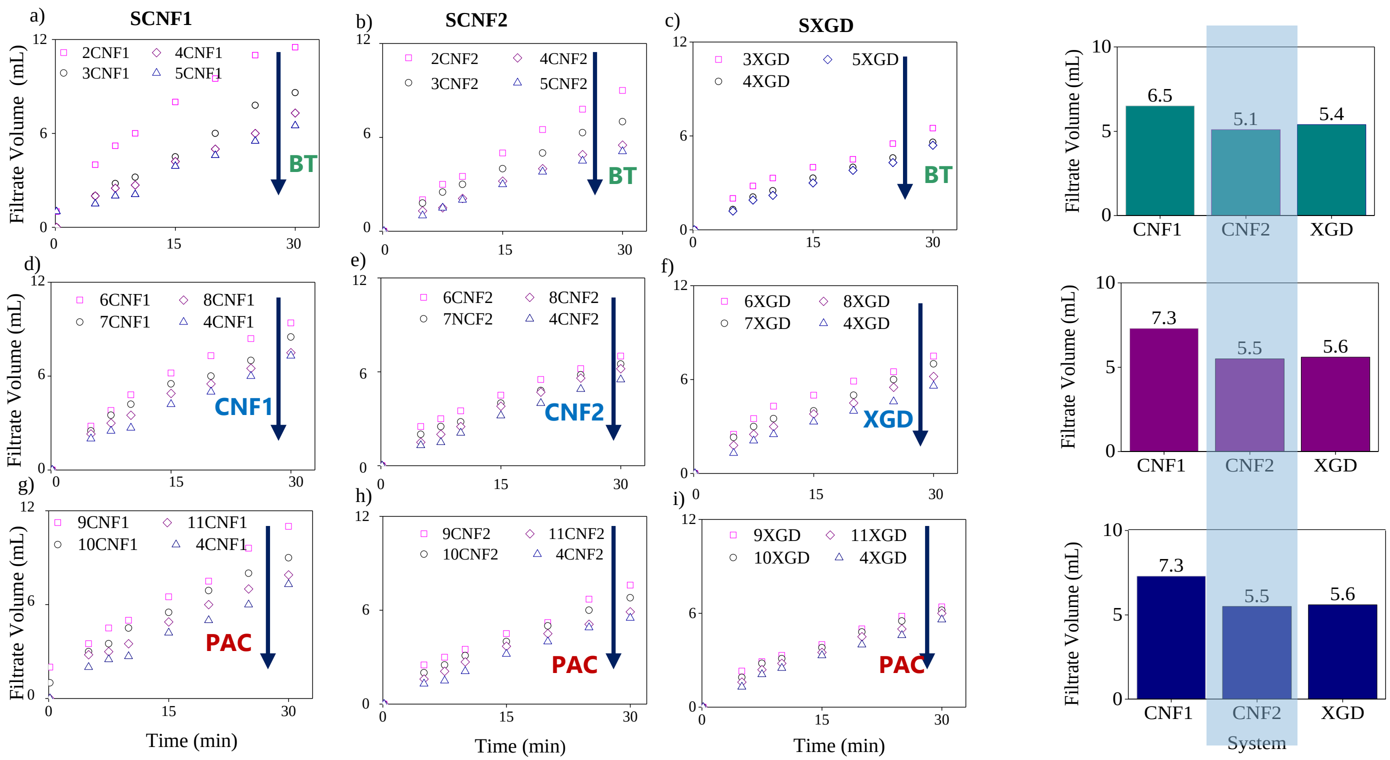
✓ Better filtering properties for **SCNF2**

- **Filter Cake**

Bentonite variation

CNF1, CNF2 or XGD variation

PAC variation



✓ Smaller fluid loss for cakes with **CNF2**

✓ Important effect of lignin (sealing the filter cake)

- **Filter Cakes**

System	Tc (cm)	q x 10 $^{-3}$ (cm^3/s)	Kc x10 $^{-3}$ (mD)
SCNF1	0.08 - 0.11	3.25 - 4.93	1.27 - 1.92
SCNF2	0.09 - 0.14	3.08 - 4.91	1.07 - 1.47
SXGD	0.09 - 1.13	3.09 - 3.73	0.91 - 1.13

✓ Increase of thickness and decrease of filtration rate with composition

✓ Similar properties for **SCNF2** and **SXGD**

a) **SCNF2**

b) **SXGD**

c)

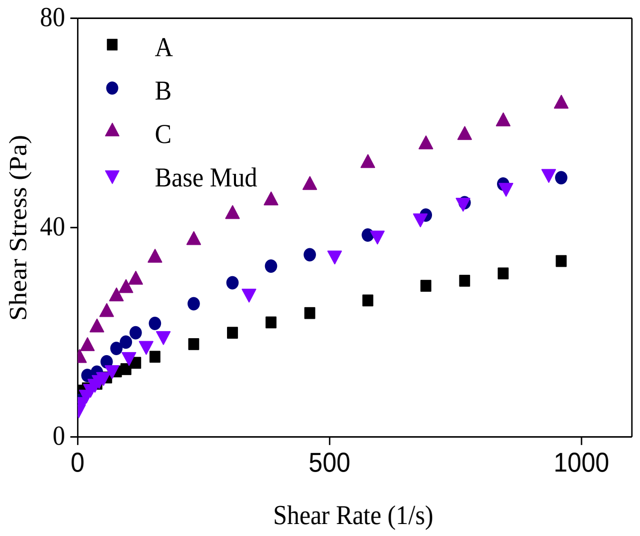
SCNF1

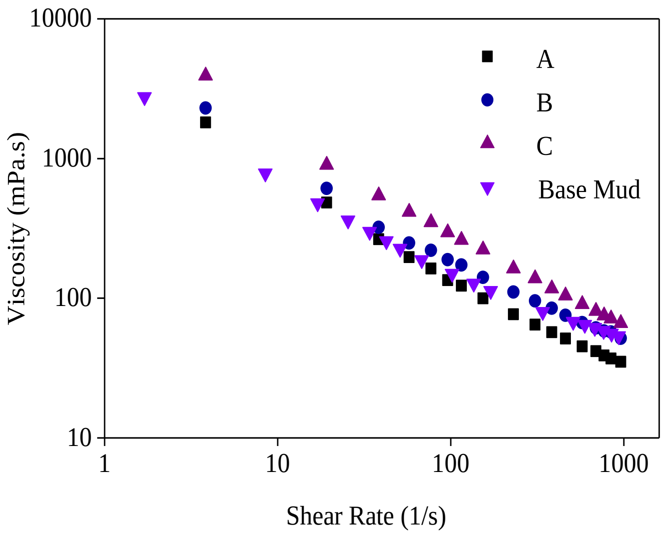
✓ Filter cakes: more compact in **SCNF2**

Replacement of XGD by CNF2 in WBMs for Argentina Shale

- **Rheological Properties**

Fluid	C_{XGD} (%wt)	C_{PAC} (%wt)	C_{CNF2} (%wt)
Base Mud	0.15	0.80	----
A	-----	0.80	0.15
B	-----	0.80	0.30
C	-----	0.80	0.45



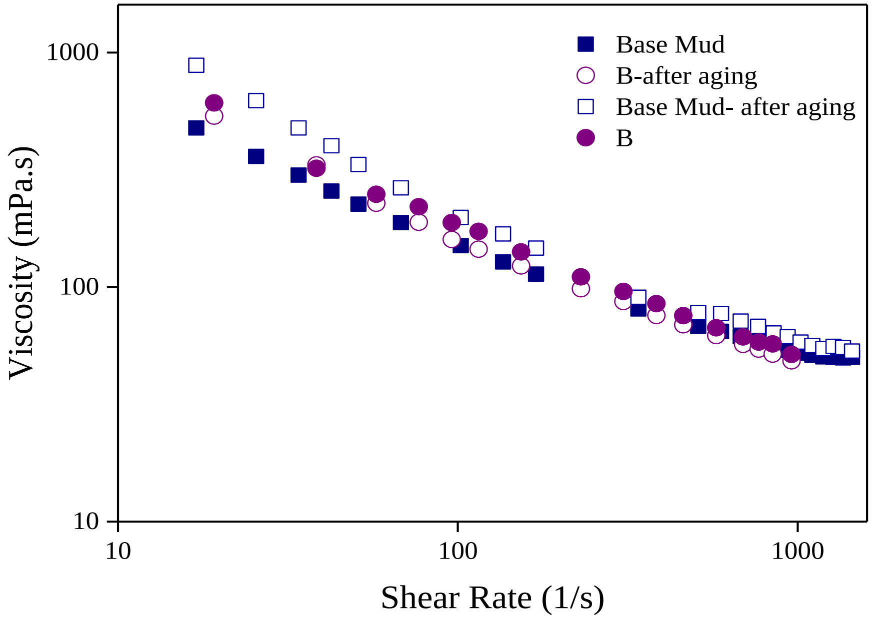


✓ Fluid with **C_{CNF2}** = **2** **C_{XGD}** (Base Mud) exhibits a similar rheological behavior

Thermal Properties

- **Dynamic aging test**

Roller oven, OFITE, 91°C , 960 min



✓ Fluid with **CNF2** (B) showed better thermal stability

- ✓ The system with CNF2 (BT/CNF2/PAC/H_2O) has both rheological and filtering properties similar to the XGD system (BT/XGD/PAC).
- ✓ Suspensions containing CNF1 exhibited more viscosifier characteristics in WBMs, and suspensions containing CNF2 improved filtration properties.
- ✓ Rheological parameters were obtained by following the Sisko model. The adjusted model can be used to obtain a better optimization of the drilling fluid composition.
- ✓ Rheological properties very similar to the base mud were obtained by duplicating the composition of CNF2 in WBMs for Argentina shale. In addition, the WBMs for Argentina shale with CNF2 presented a better thermal stability.
- ✓ CNF2 seems to be a viable additive in WBMs for Argentina shale.
- ✓ The structural differences in dimension, shape, surfaces characteristics, rheological behavior and lignin content, between CNF1 and CNF2 produced different effects on the rheological and filtration properties of the studied fluids.

¡ Thank you very much for your attention !