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NI-FUNCTIONALIZED CARBON NANO-FILAMENTS AS BIODIESEL STEAM REFORMING CATALYST

Nicolas Abatzoglou and Carmina Reyes Plascencia



Outline



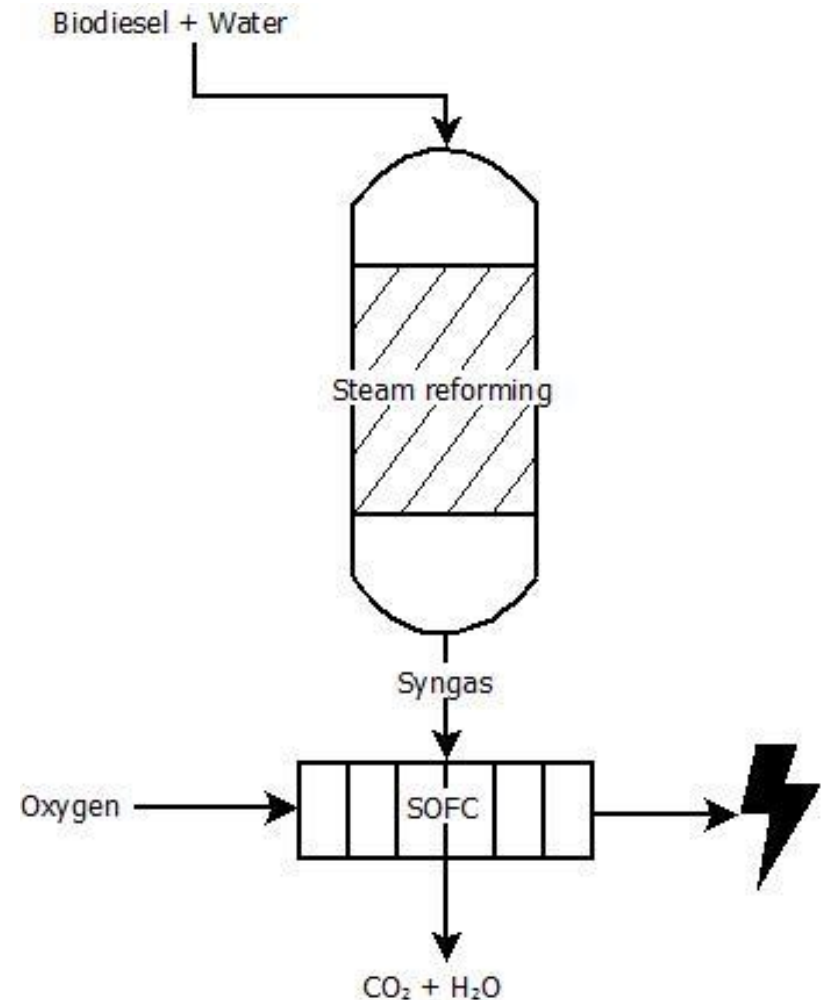
- Rational
- Objectives
- Carbon-nanofilaments production
- Carbon-nanofilaments functionalization
- Biodiesel Steam Reforming
- Conclusions
- Future Work

Rational

- Cover the energy demand

Why used the Biodiesel?

- High H_2 density
- Safe and easy transport and storage
- Could be free of CO_2 production
- **Biodiesel must be reformed to syngas to use it in SOFC**



Objectives

□ **Main objective**

- Hydrogen production by steam reforming reaction of biodiesel over CNF-supported Ni.

□ **Specific Objectives**

- Deposition of nickel in CNF by impregnation of $\text{Ni}(\text{NO}_3)_2$
- Steam Reforming over Ni/CNF

□ **Why use CNF?**

- Controlled CO_2 sequestration to form the CNF
- High external surface area + less sintering expected

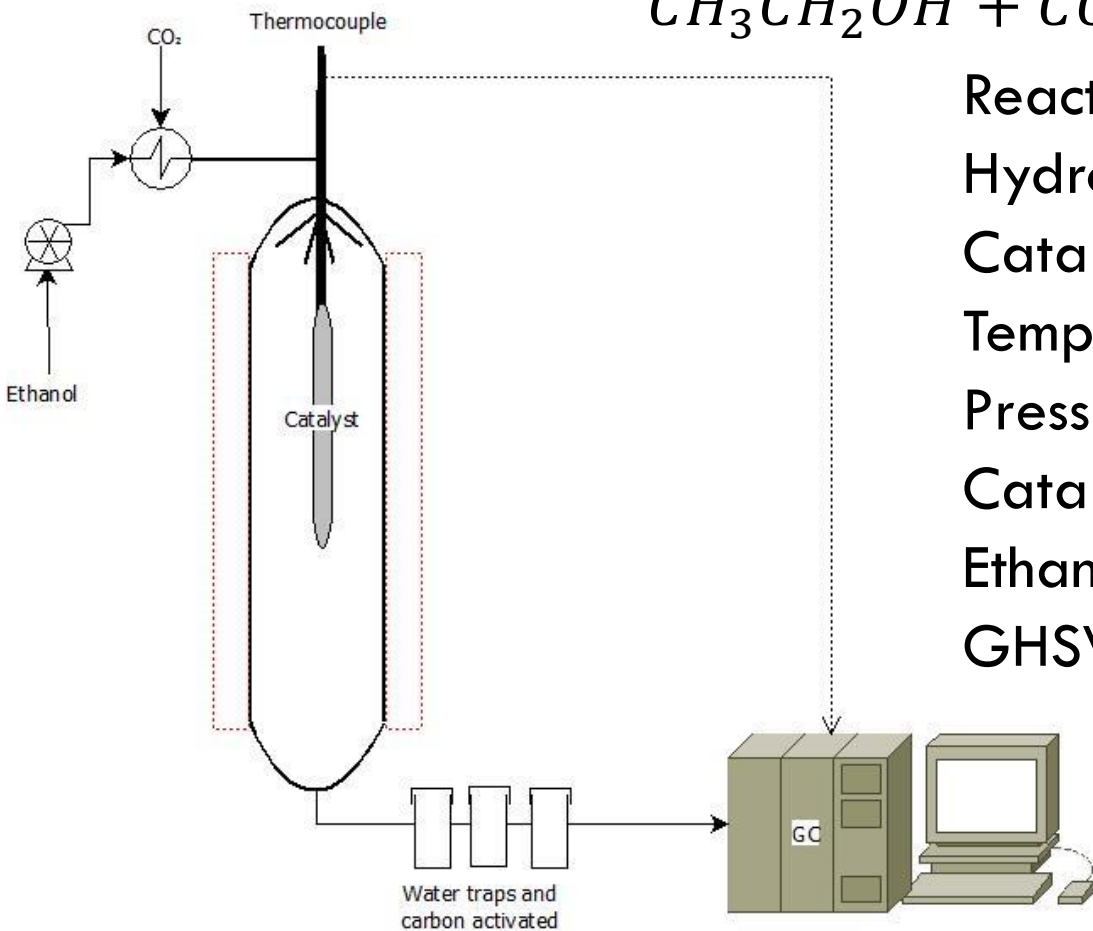
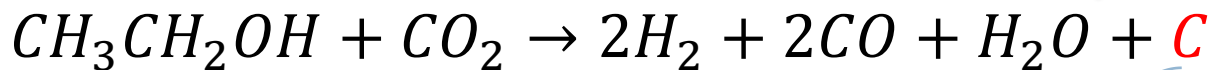
CNF's production

Acid treatment

Ni impregnation by $\text{Ni}(\text{NO}_3)_2$

Calcination & Reduction

Steam reforming reaction



Reaction conditions

Hydrocarbon

Ethanol

Catalyst

Stainless steel

Temperature

550°C

Pressure

1 atm

Catalyst mass

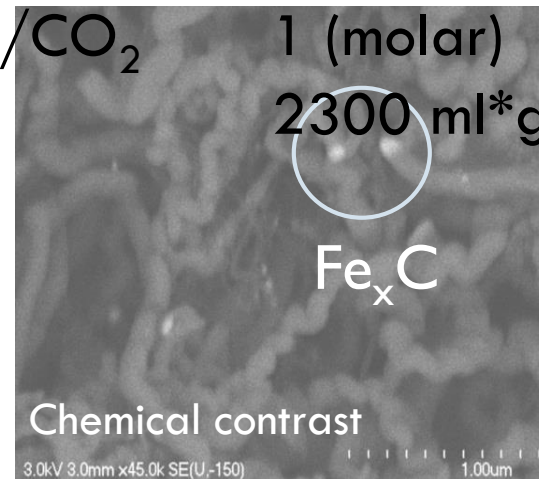
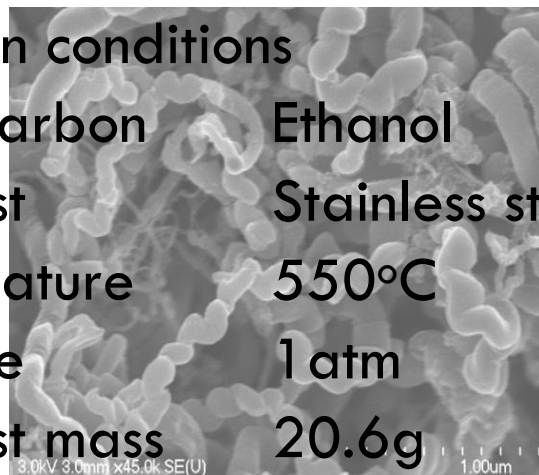
20.6g

Ethanol/ CO_2

1 (molar)

GHSV

2300 $\text{ml} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$



CNF's
production

**Acid
treatment**

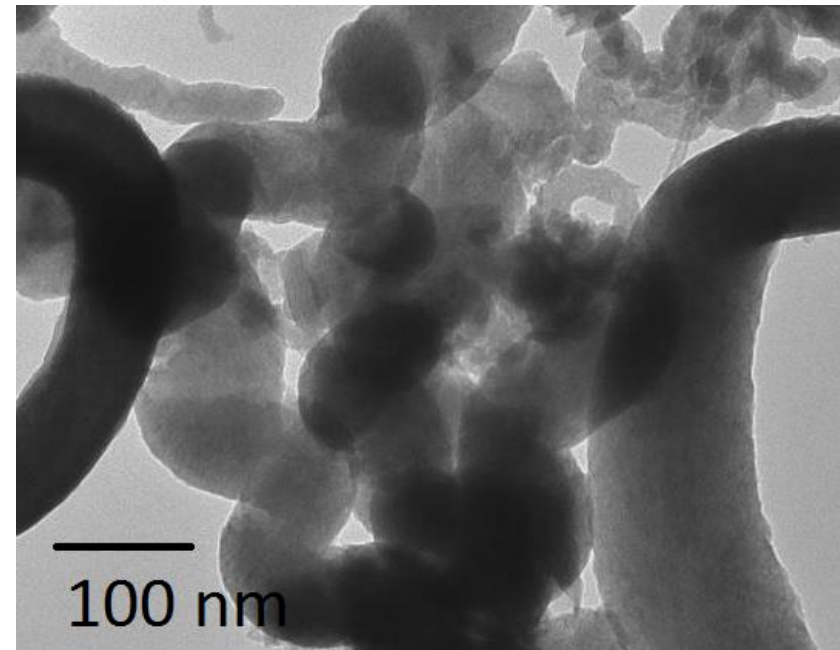
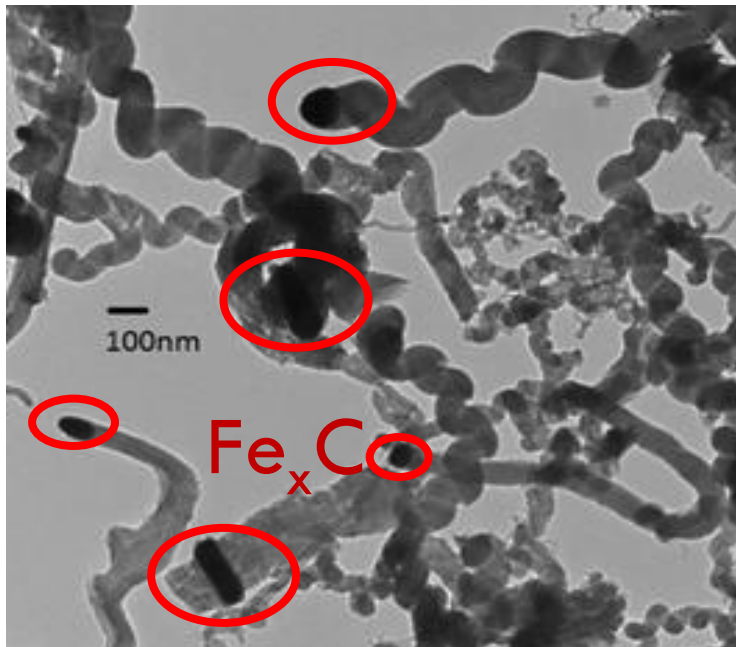
Ni impregnation
by $\text{Ni}(\text{NO}_3)_2$

Calcination
&
Reduction

Steam
reforming
reaction

Nickel impregnation
by $\text{Ni}(\text{NO}_3)_2$ at $\text{pH} = 5.5$
Without acid treatment

Nickel not found



CNF's
production

**Acid
treatment**

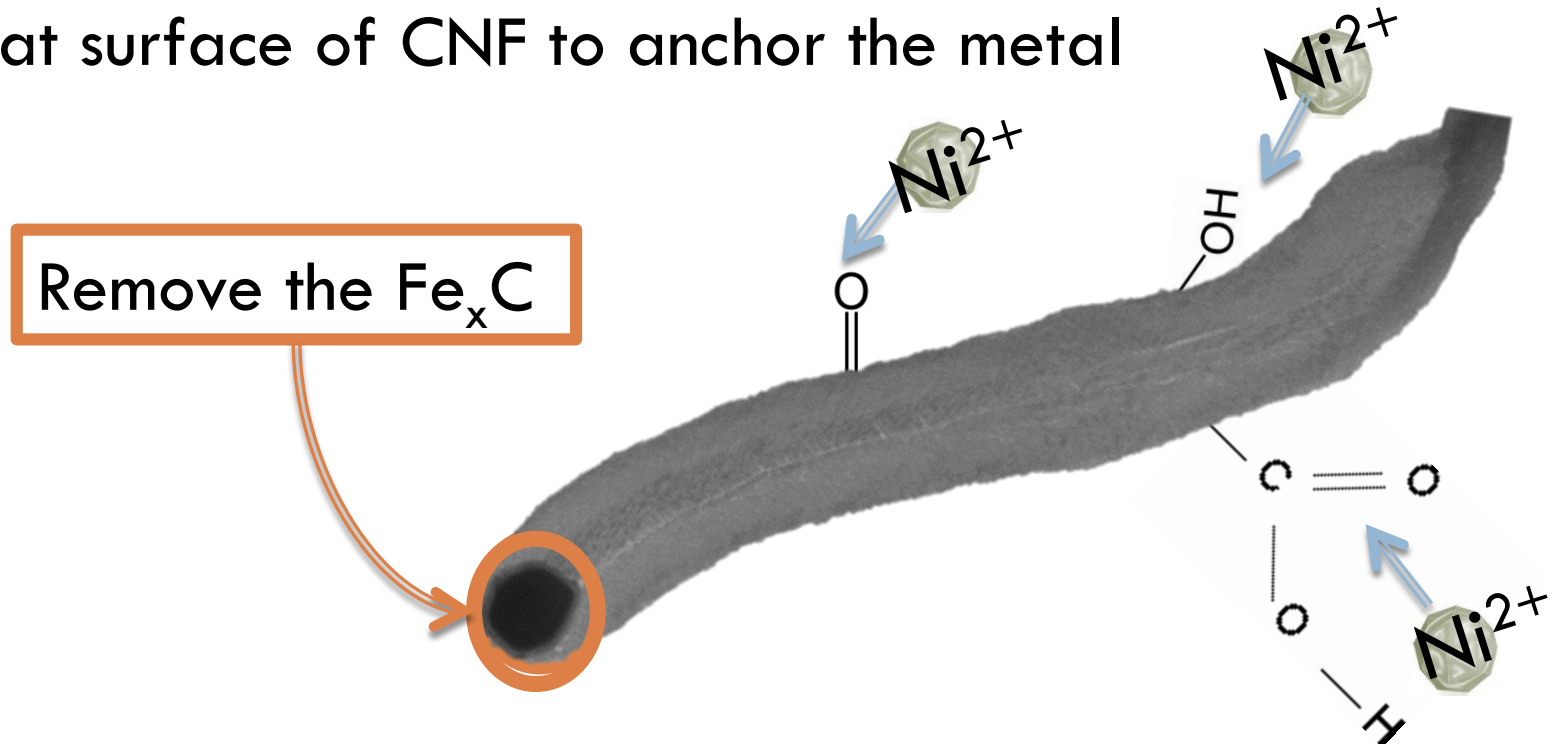
Ni impregnation
by $\text{Ni}(\text{NO}_3)_2$

Calcination
&
Reduction

Steam
reforming
reaction

Acid treatment objectives

- Remove the Fe_xC particles of CNF
- Introduce oxygenated groups and imperfections at surface of CNF to anchor the metal



CNF's
production

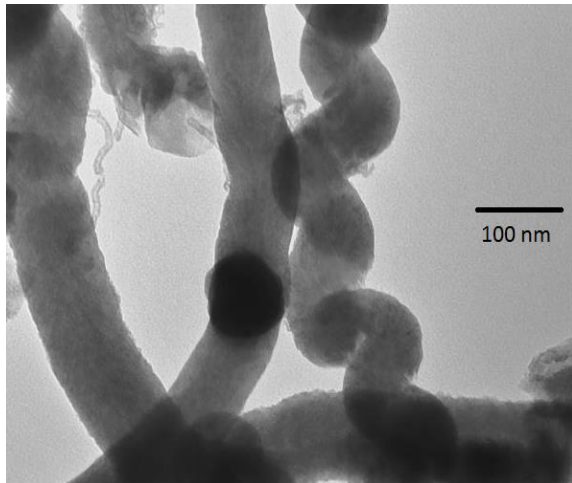
**Acid
treatment**

Ni impregnation
by $\text{Ni}(\text{NO}_3)_2$

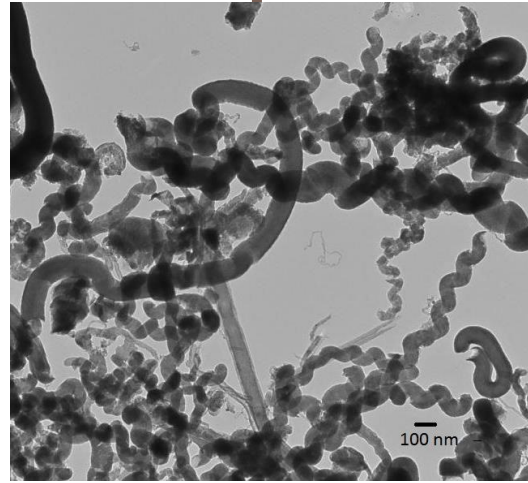
Calcination
&
Reduction

Steam
reforming
reaction

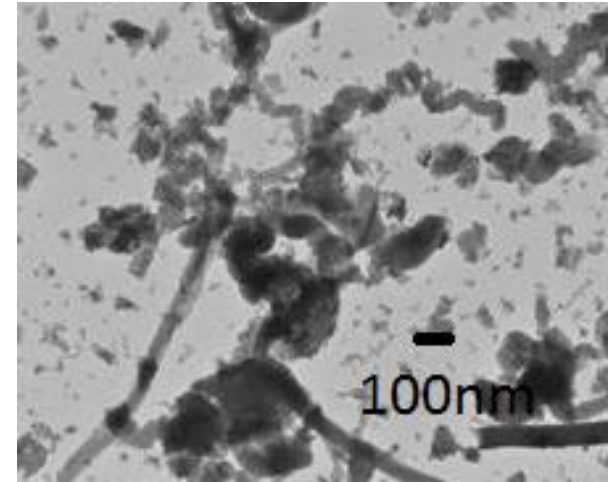
Acid treatment optimization



4 M
Temperature 110°C
(reflux)
Contact time 1 h



4 M
Temperature 110°C
(reflux)
Contact time 3 h



4 M
Temperature 110°C
(reflux)
Contact time 6 h

Optimal

CNF's
production

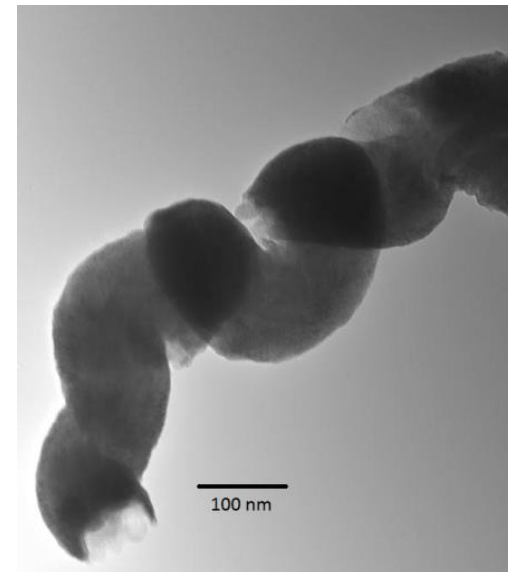
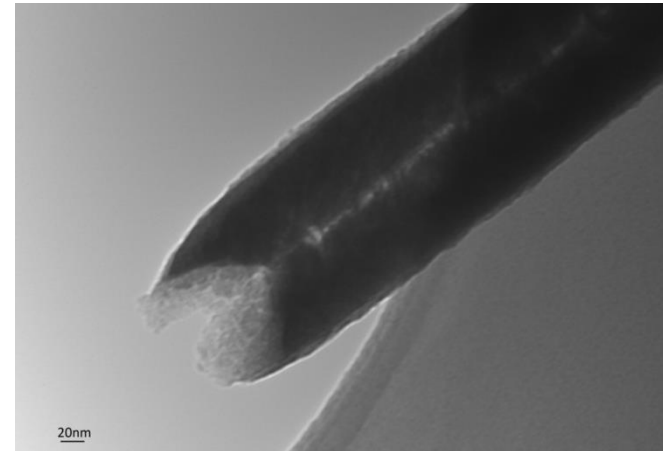
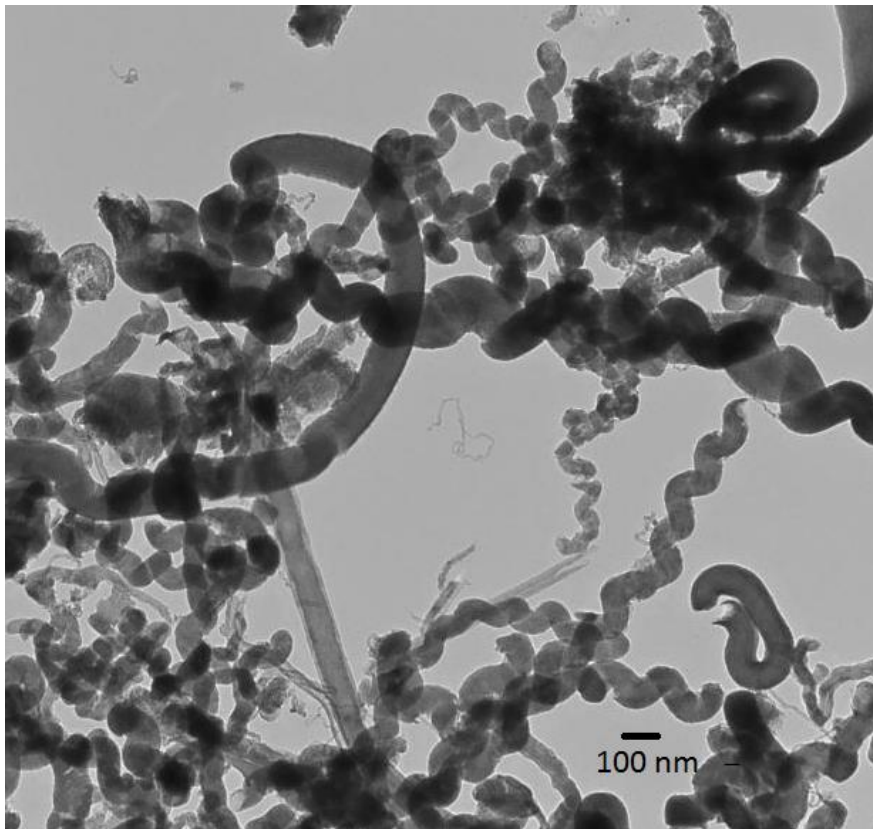
**Acid
treatment**

Ni impregnation
by $\text{Ni}(\text{NO}_3)_2$

Calcination
&
Reduction

Steam
reforming
reaction

4 M of HNO_3
Temperature 110°C
(reflux)
Contact time 3 h



CNF's
production

Acid
treatment

Ni
impregnation
by $\text{Ni}(\text{NO}_3)_2$

Calcination
&
Reduction

Steam
reforming
reaction

Wet impregnation

- Using $\text{Ni}(\text{NO}_3)_2$
- Agitation in the solution for 1h

Calcination

- At 290°C over Ar
- For 8h

Reduction

- At 450°C over H_2
- For 1h

CNF's production

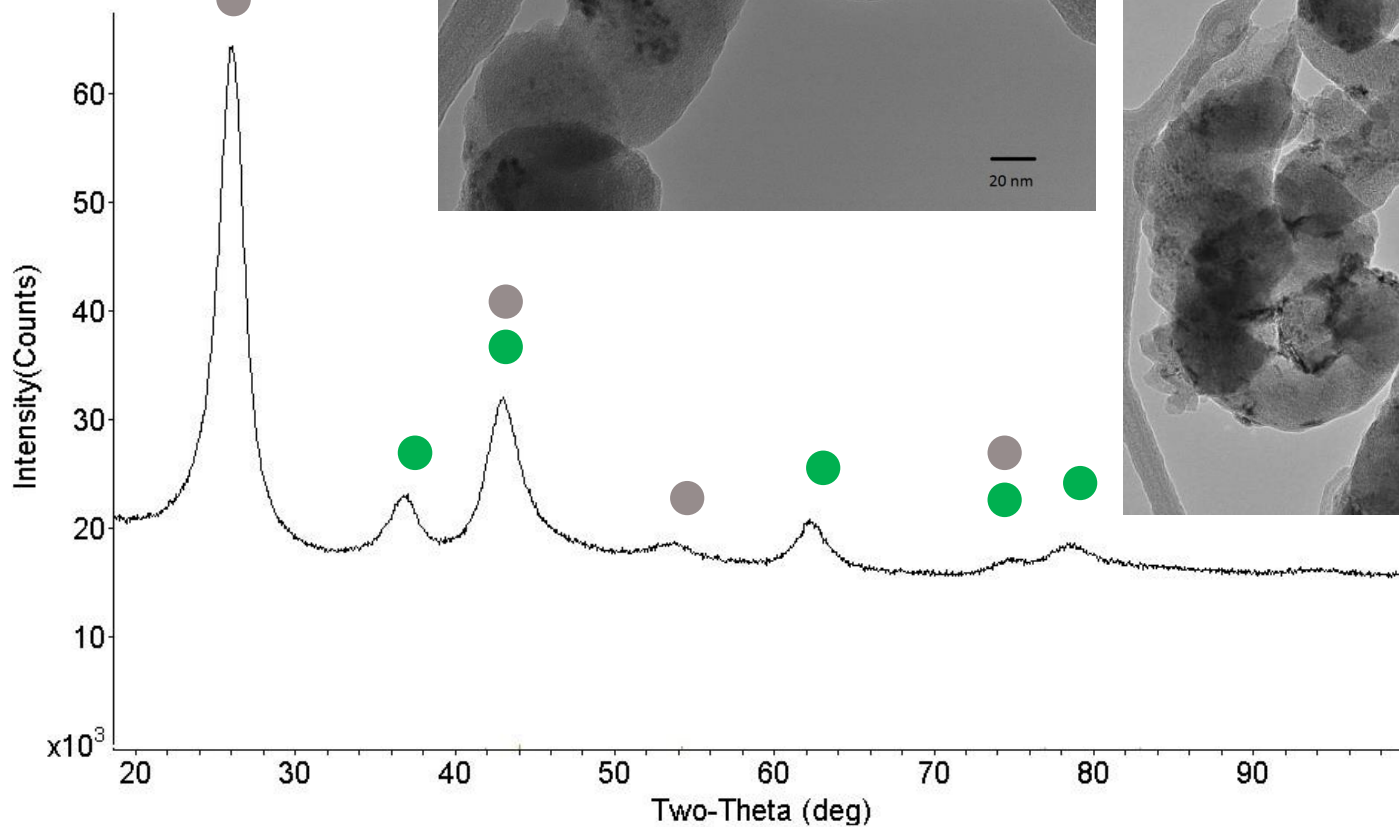
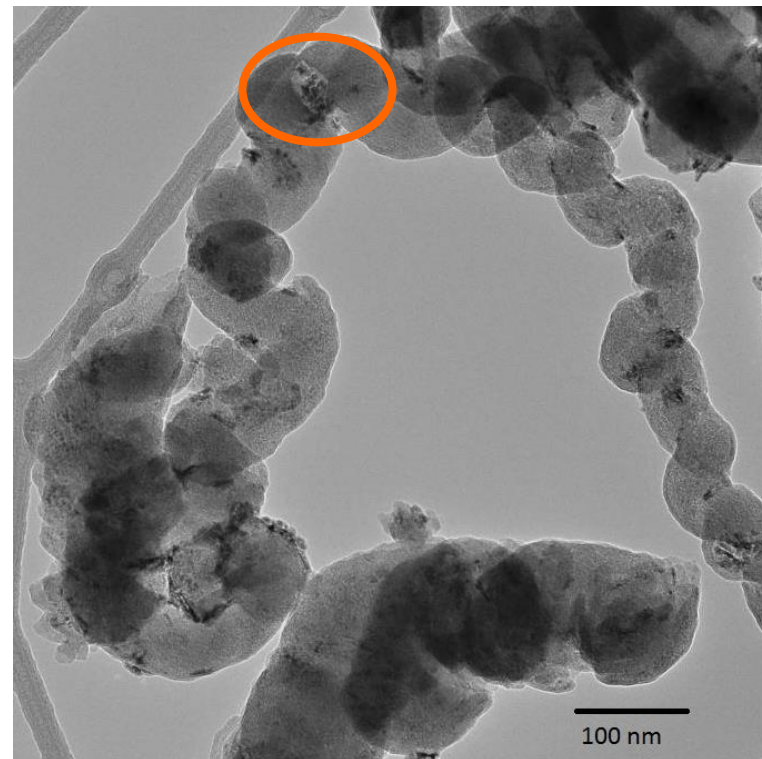
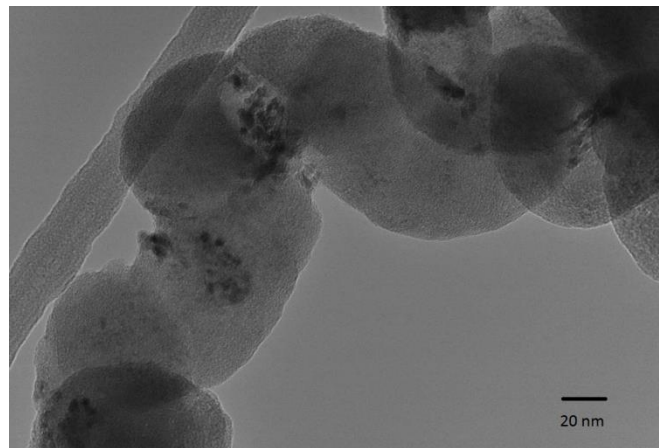
Acid treatment

**Ni impregnation
by $\text{Ni}(\text{NO}_3)_2$**

**Calcination
&
Reduction**

Steam reforming reaction

● Graphite
● NiO



CNF's
production

Acid
treatment

Ni
impregnation
by $\text{Ni}(\text{NO}_3)_2$

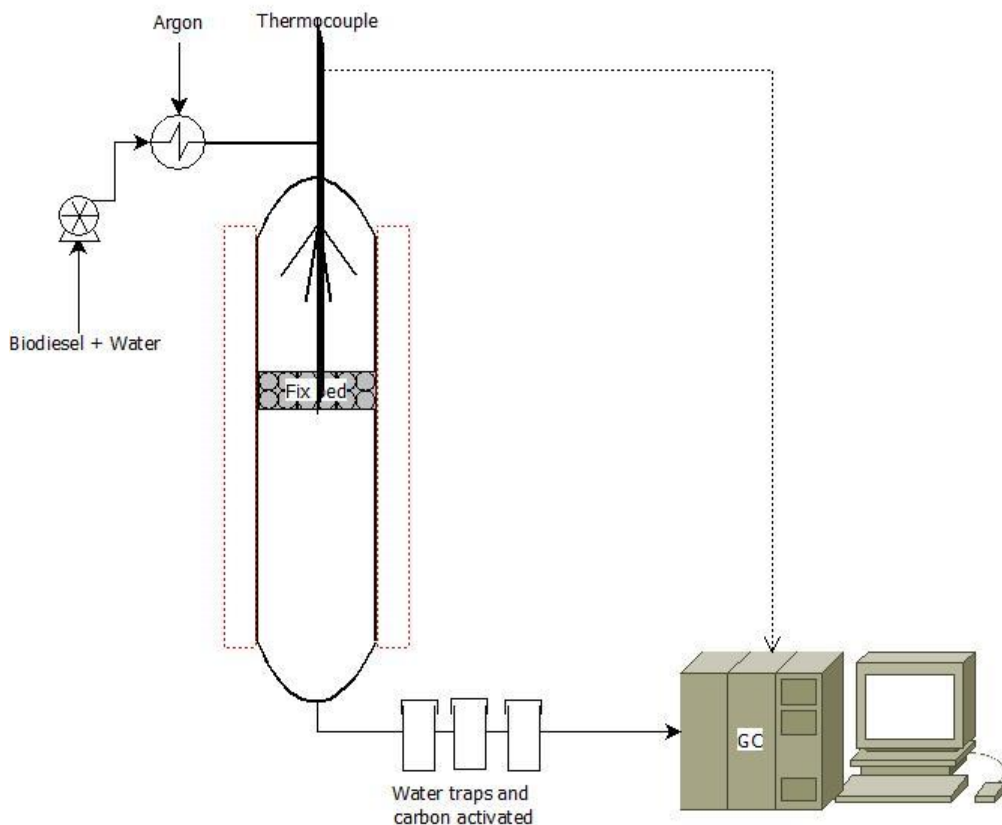
Calcination
&
Reduction

Steam
reforming
reaction

Reforming methodology

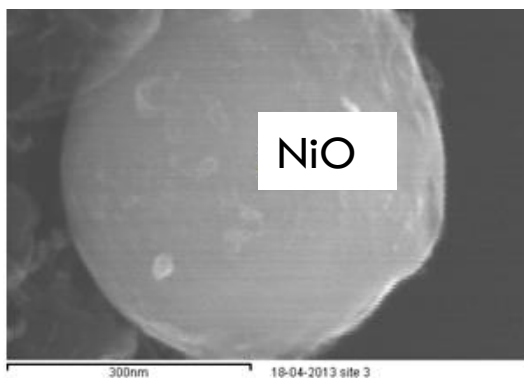
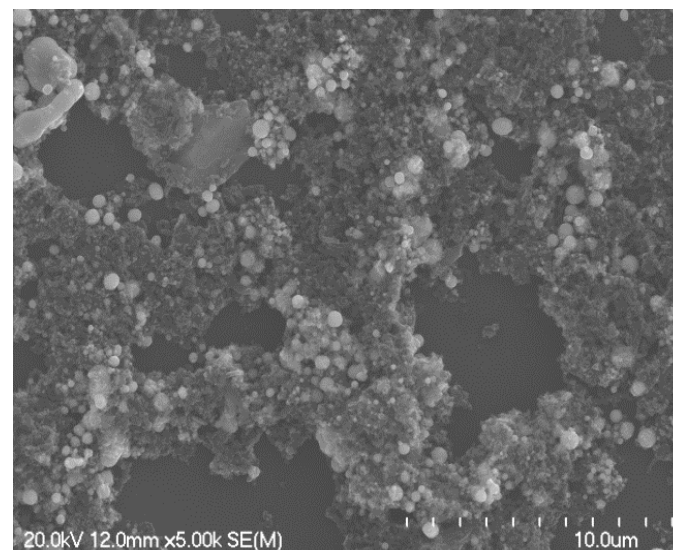
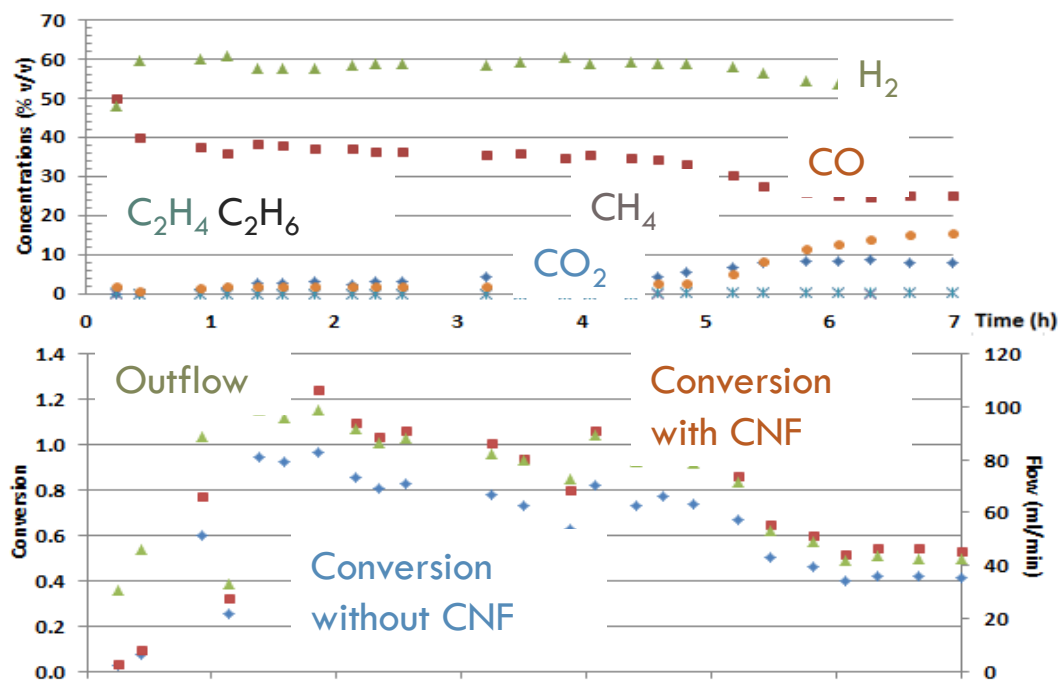
Reaction conditions

Hydrocarbon	Biodiesel
Catalyst	Ni/CNF
Reduction T	450°C over
Temperature	10% H ₂
Pressure	Variable
Catalyst mass	1 atm
H ₂ O/C ratio	3g
MHSV	1.95
	46 g*g ⁻¹ *h ⁻¹



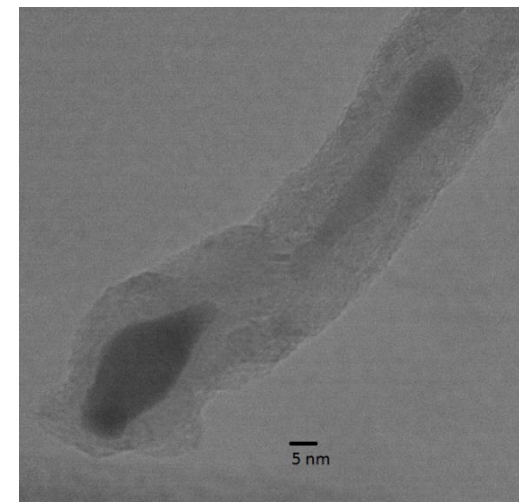
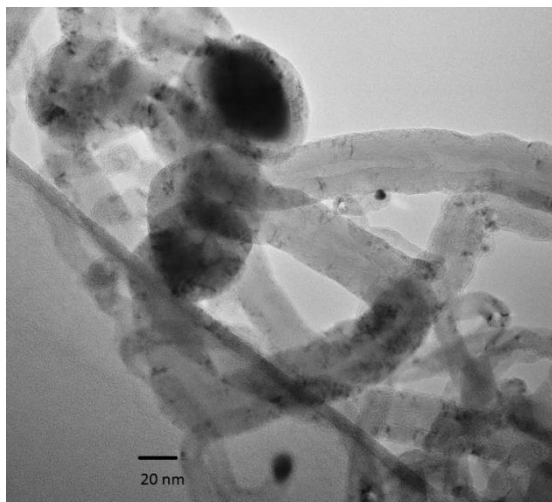
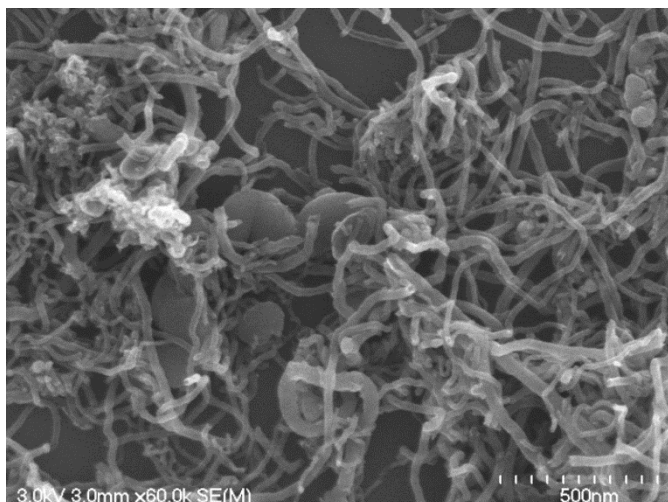
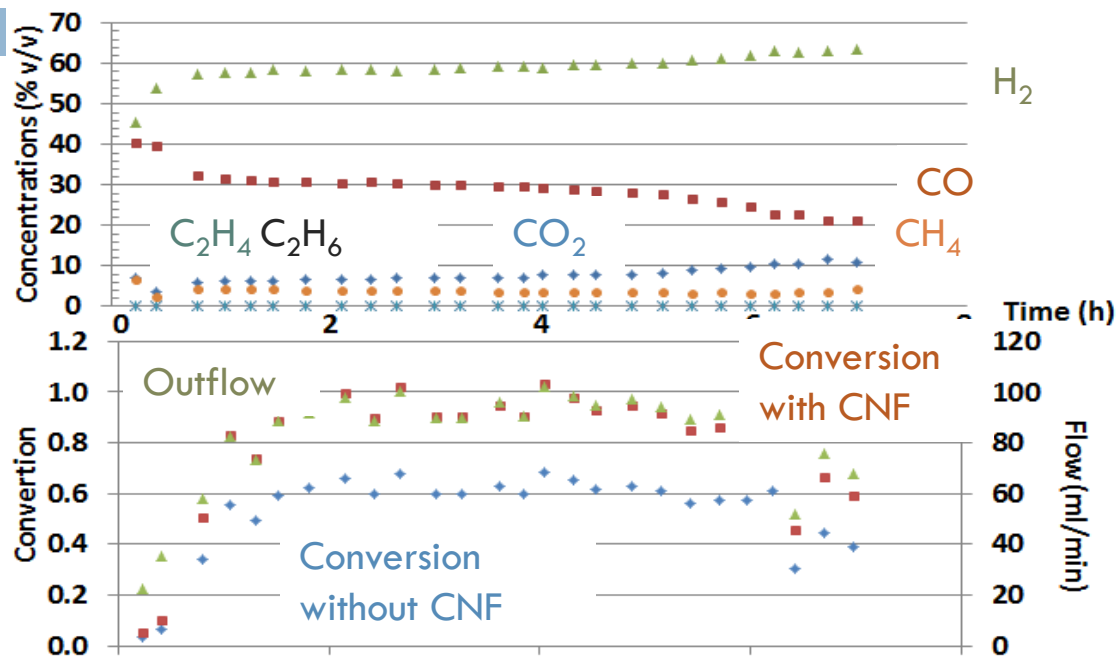
Reaction to 800°C

Conversion 93.9%



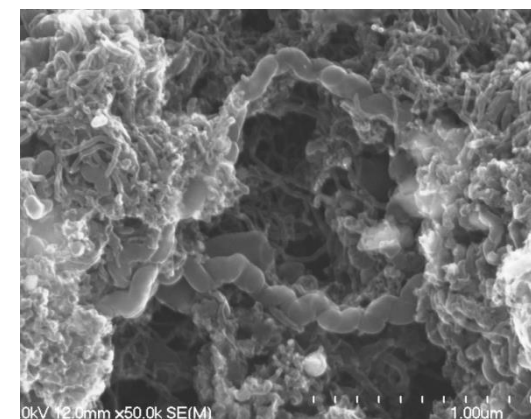
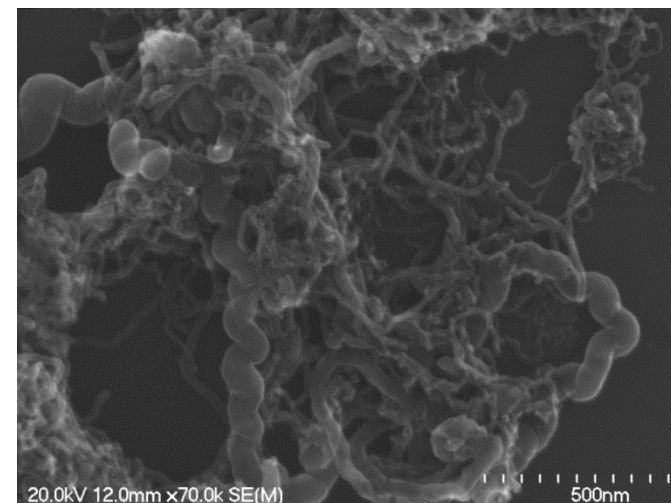
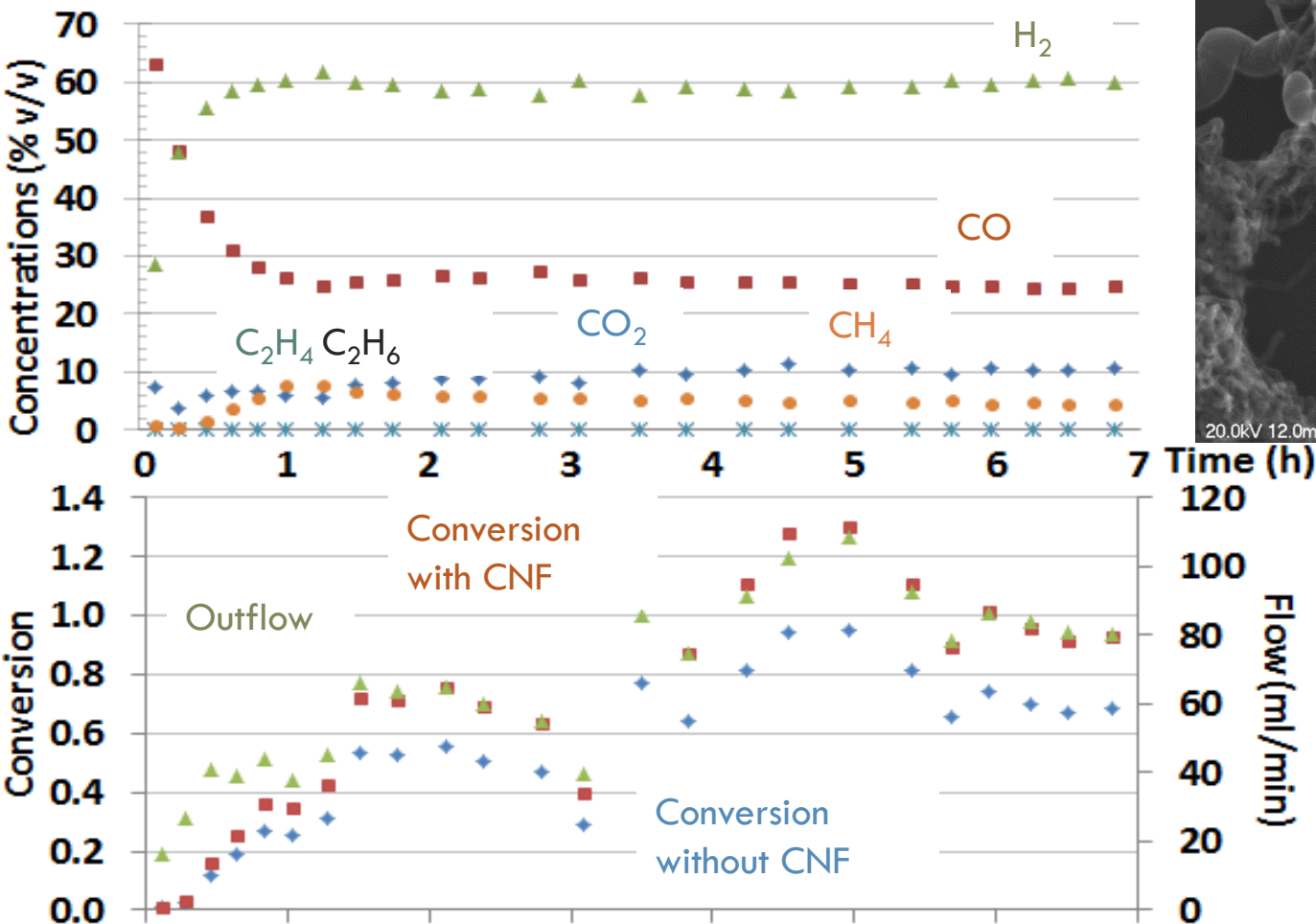
Reaction to 700°C

Conversion 99%

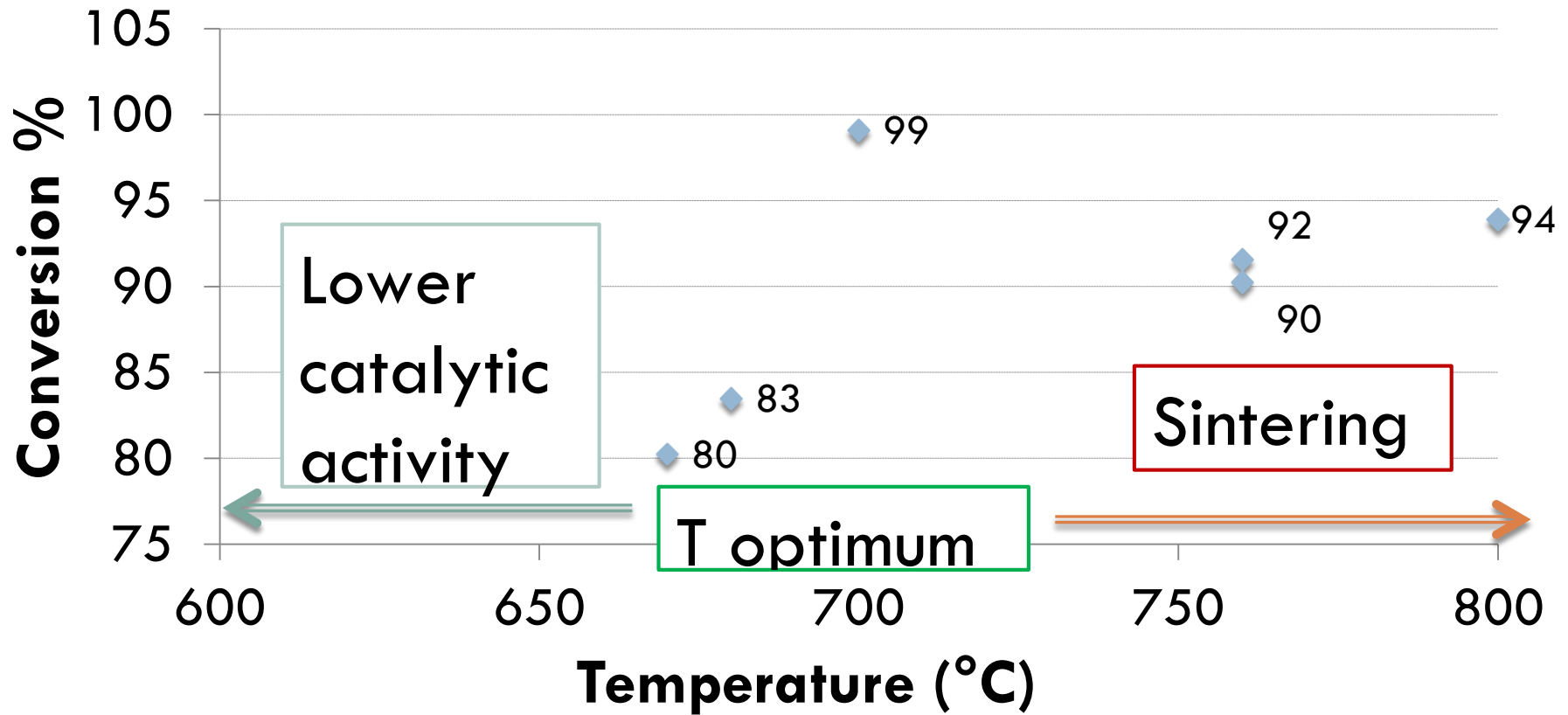


Reaction to 670°C

Conversion 80.2%



Conversion as function of T



Mass balance

Temperature	°C	800	760	760	700	680	670
MHSV	$\text{g}^*\text{g}^{-1}*\text{h}^{-1}$	50.0	47.6	46.6	45	43.7	44.1
Δ mass	g	-0.73	-0.37	-0.97	-0.77	-1.40	0.01
Error %	%	-2.8	-1.57	-2.07	-2.37	-4.41	0.02
Conversion	%	93.9	91.56	90.24	99.11	83.47	80.23
Reaction time	h	7	5.5	12	7	7.38	6.8

Conclusion

- The acid treatment is necessary for the impregnation of Ni over CNF's
- The Ni-NFC's show catalytic activity for the steam reforming of Biodiesel
- The optimum reaction temperature is 700°C
 - ▣ Sintering of Ni at highest temperature
 - ▣ Lower catalytic activity at lower temperature
- The CNF shows damage structure after the steam reforming reaction

Future work

- Confirm conversion at 700°C
- Thermal treatment after acid treatment in order to remove CNF of low quality
- Functionalize CNF with nickel spinel (NiAl_2O_4) instead of metallic nickel

Acknowledgements

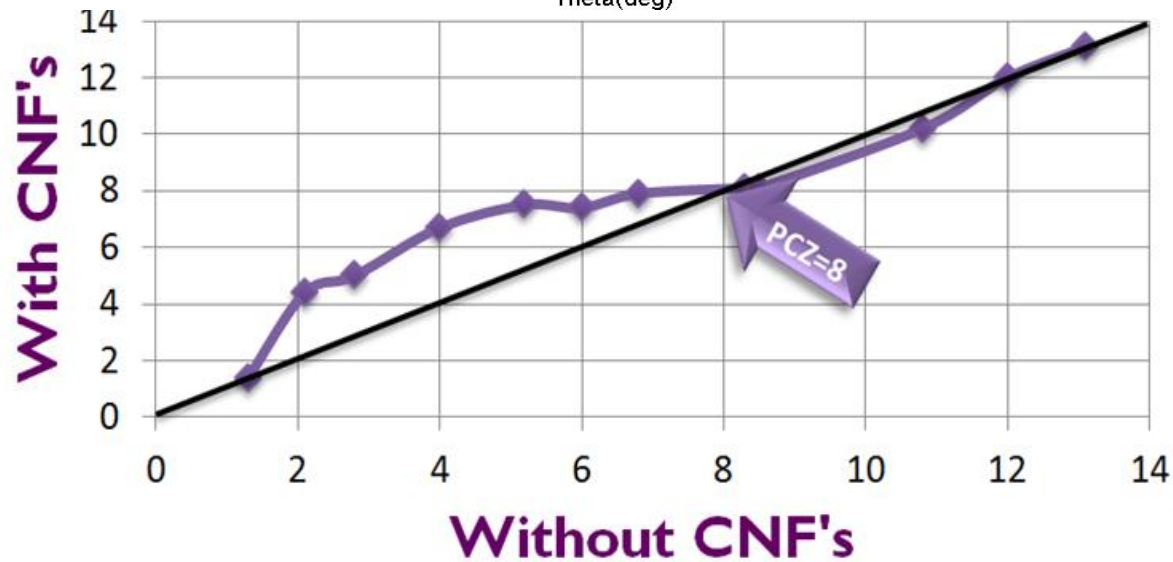
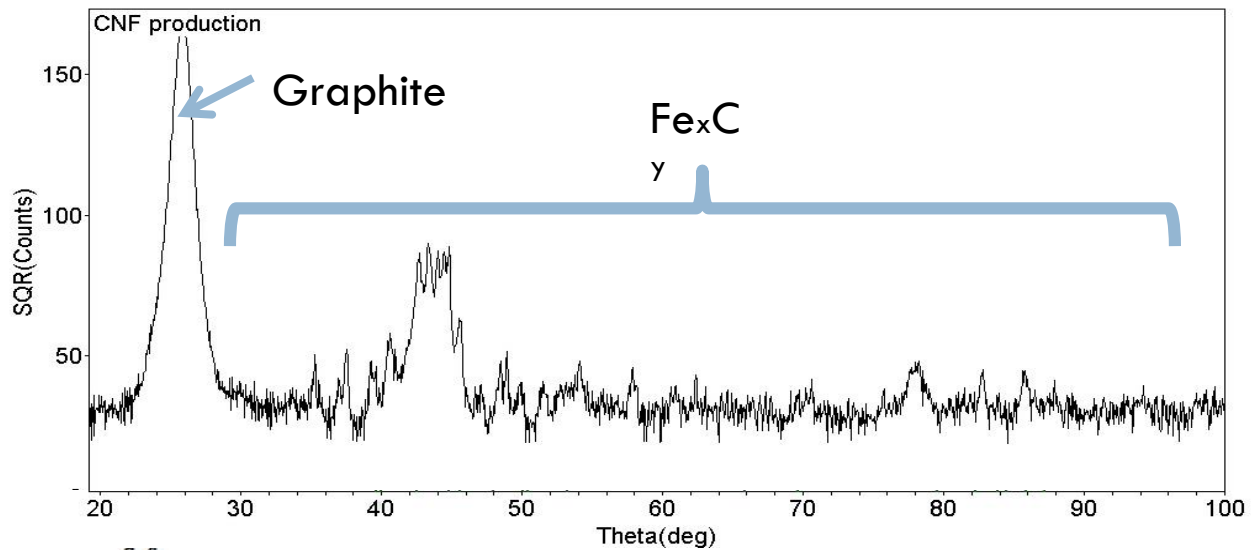
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Questions



Thank you

Characterization des NFC



Replicated 760°C

