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Ni-functionalized carbon nano-filaments as biodiesel steam reforming catalyst

Nicolas Abatzoglou
Universite de Sherbrooke

Camrina Reyes Plascencia
Universite de Sherbrooke

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

Nicolas Abatzoglou and Carmina Reyes Plascencia

UNIVERSITÉ DE SHERBROOKE

Outline

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

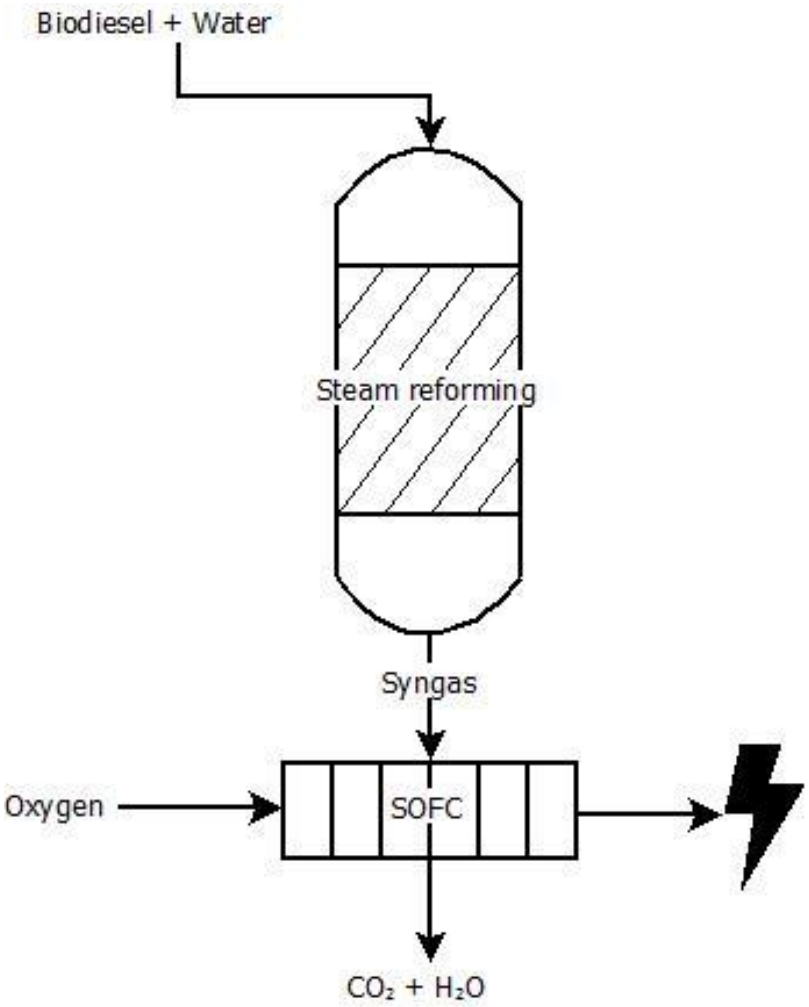
Rational

- 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**

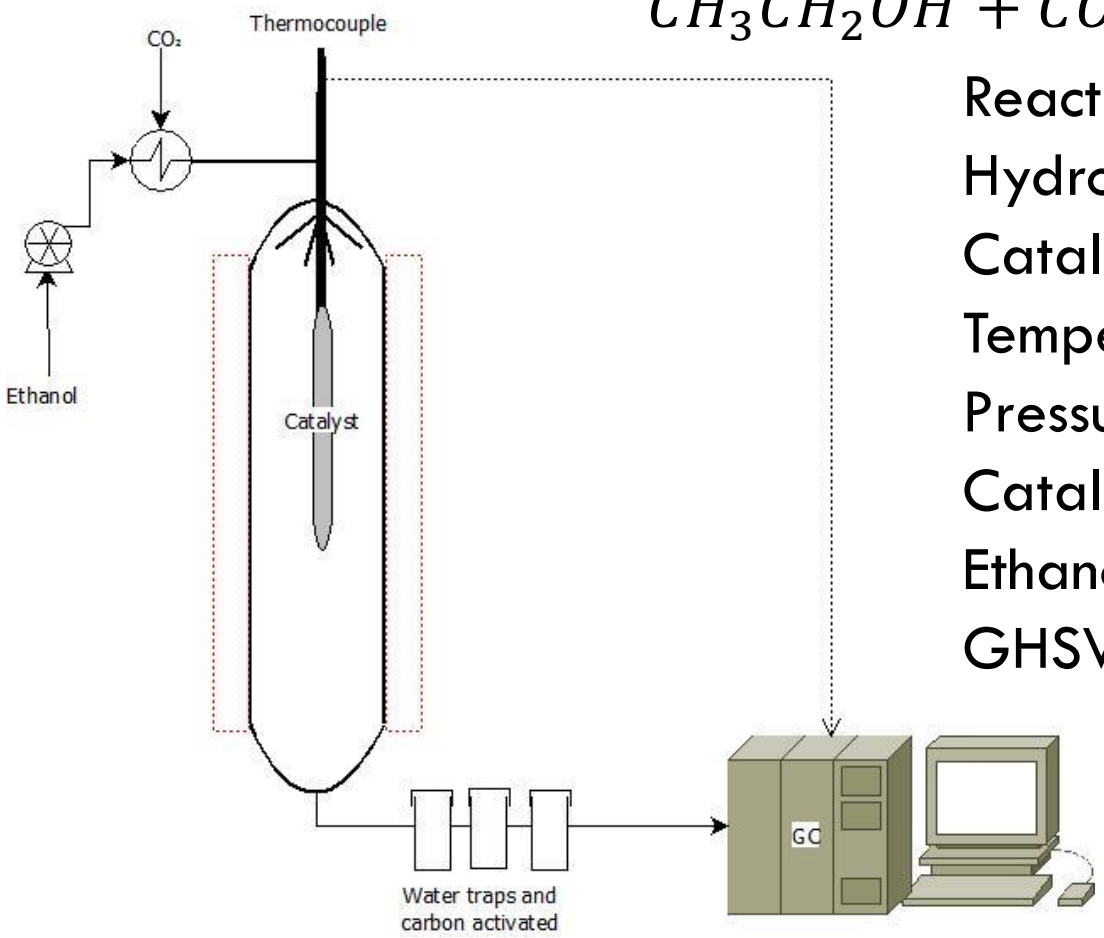


Objectives

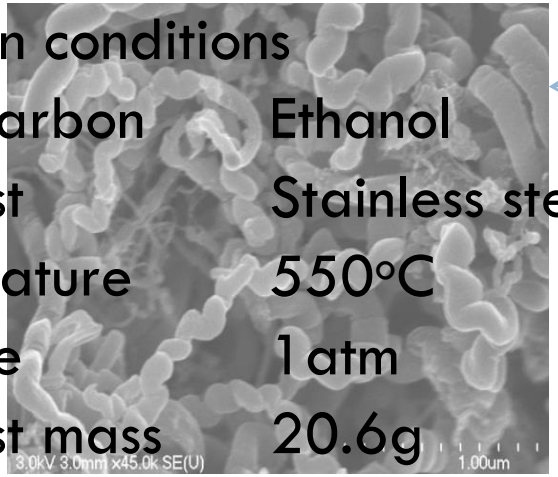
- **Main objective**
  - Hydrogen production by steam reforming reaction of biodiesel over CNF-supported Ni.
- **Specific Objectives**
  - Deposition of nickel in CNF by impregnation of $Ni(NO_3)_2$
  - Steam Reforming over Ni/CNF
- **Why use CNF?**
  - Controlled CO_2 sequestration to form the CNF
  - High external surface area + less sintering expected

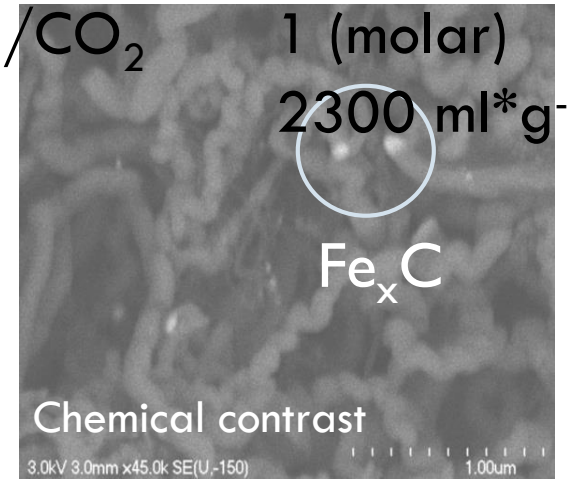
CNF's production | Acid treatment | Ni impregnation by $Ni(NO_3)_2$ | Calcination & Reduction | Steam reforming reaction

$$CH_3CH_2OH + CO_2 \rightarrow 2H_2 + 2CO + H_2O + C$$



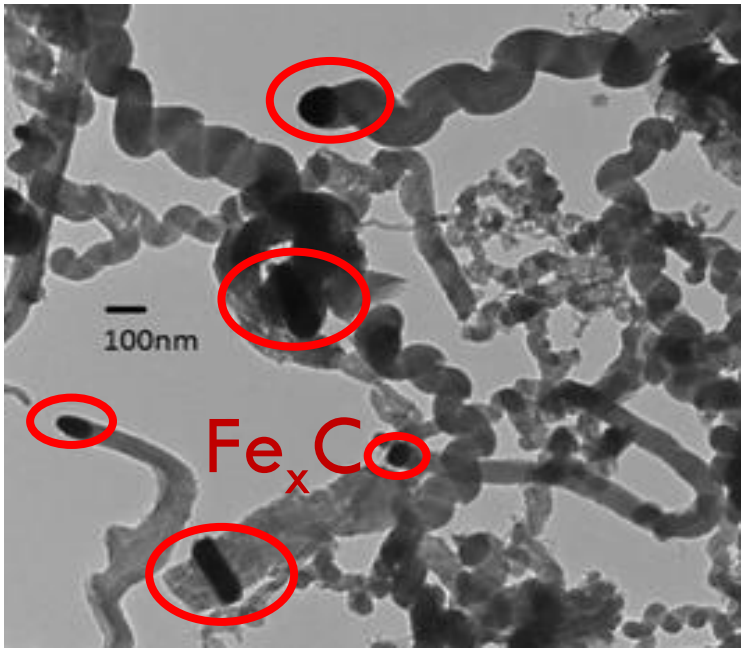
Reaction conditions	
Hydrocarbon	Ethanol
Catalyst	Stainless steel
Temperature	550°C
Pressure	1atm
Catalyst mass	20.6g
Ethanol/CO_2	1 (molar)
GHSV	2300 $ml*g^{-1}*h^{-1}$

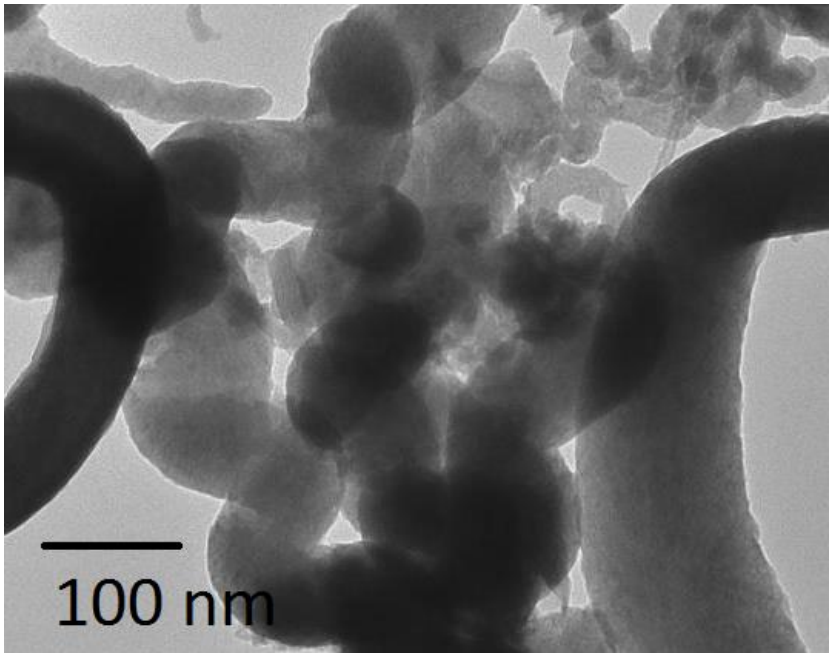




Nickel impregnation by $Ni(NO_3)_2$ at pH= 5.5
Without acid treatment

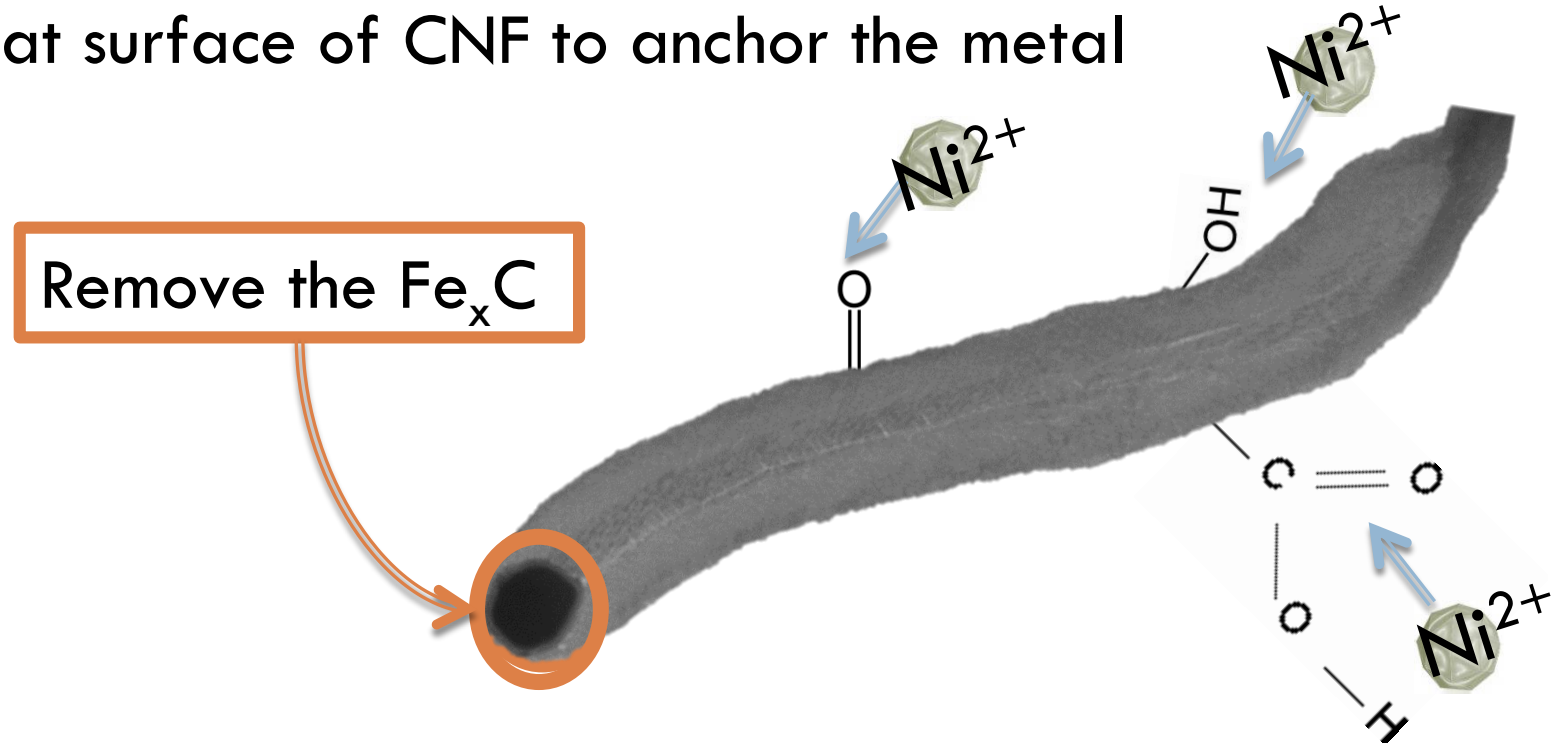
Nickel not found



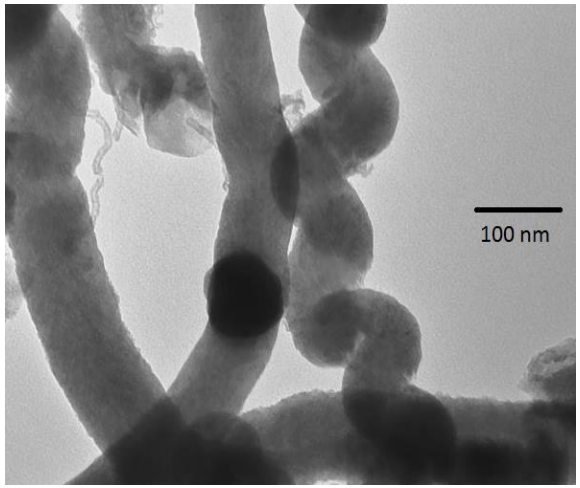


Acid treatment objectives

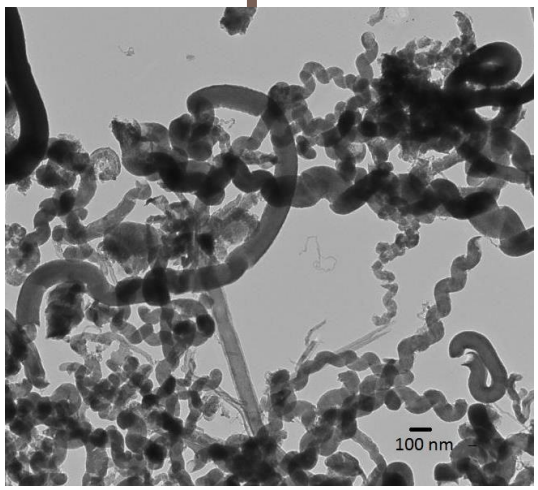
- Remove the Fe_xC particles of CNF
- Introduce oxygenated groups and imperfections at surface of CNF to anchor the metal



Acid treatment optimization

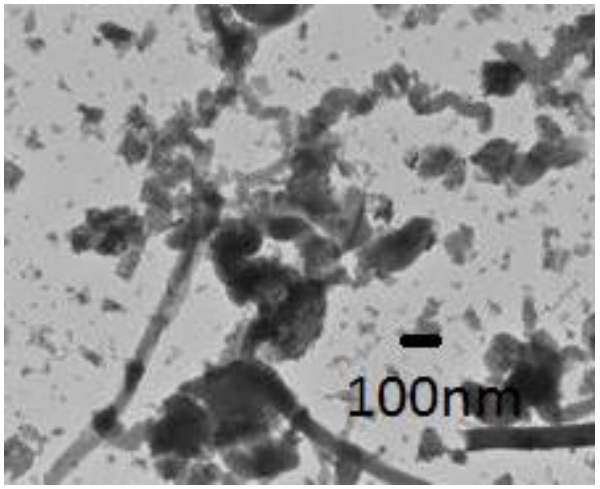


4 M
Temperature 110°C (reflux)
Contact time 1 h



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

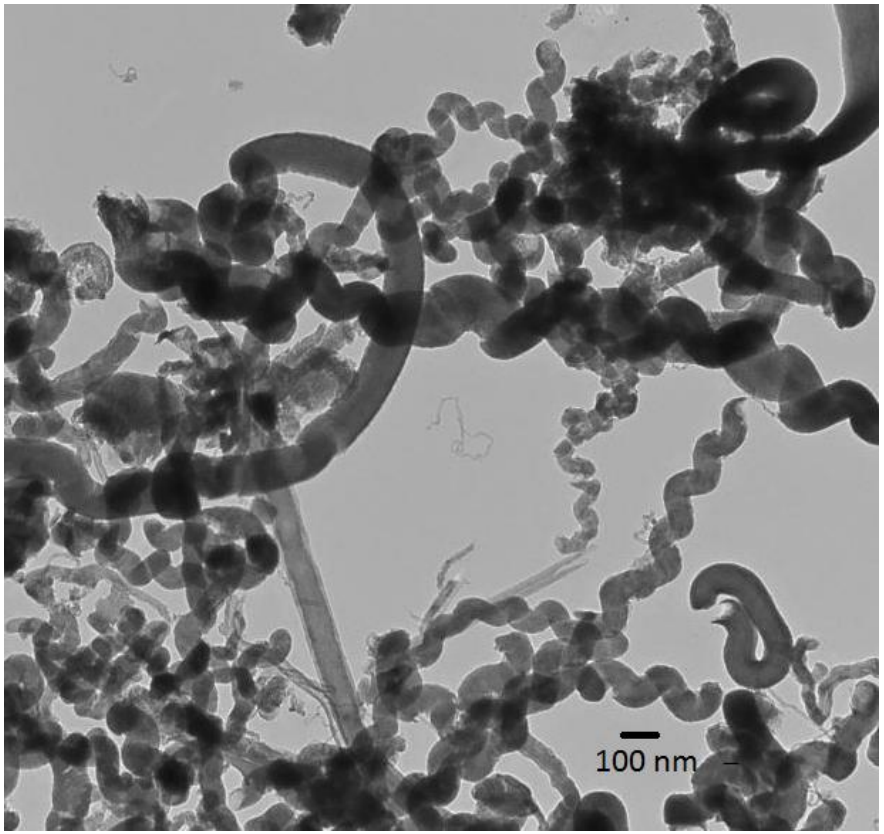
Optimal

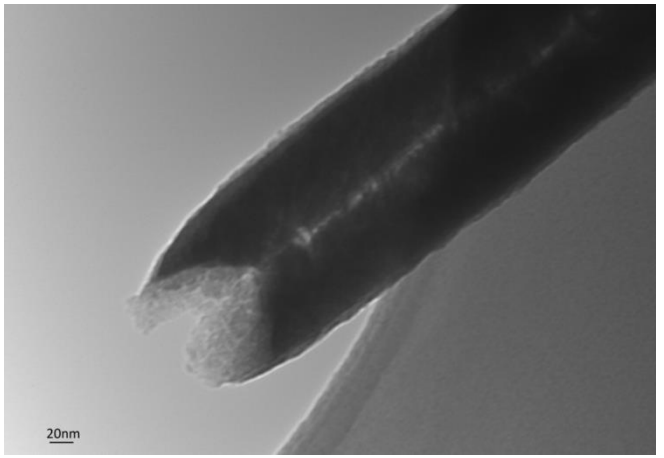


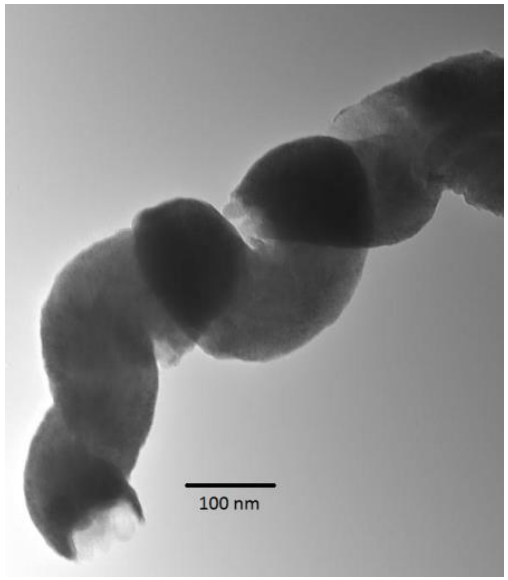
4 M
Temperature 110°C (reflux)
Contact time 6 h

CNF's production | **Acid treatment** | Ni impregnation by $Ni(NO_3)_2$ | Calcination & Reduction | Steam reforming reaction

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







Wet impregnation

- Using Ni $(NO_3)_2$
- Agitation in the solution for 1h

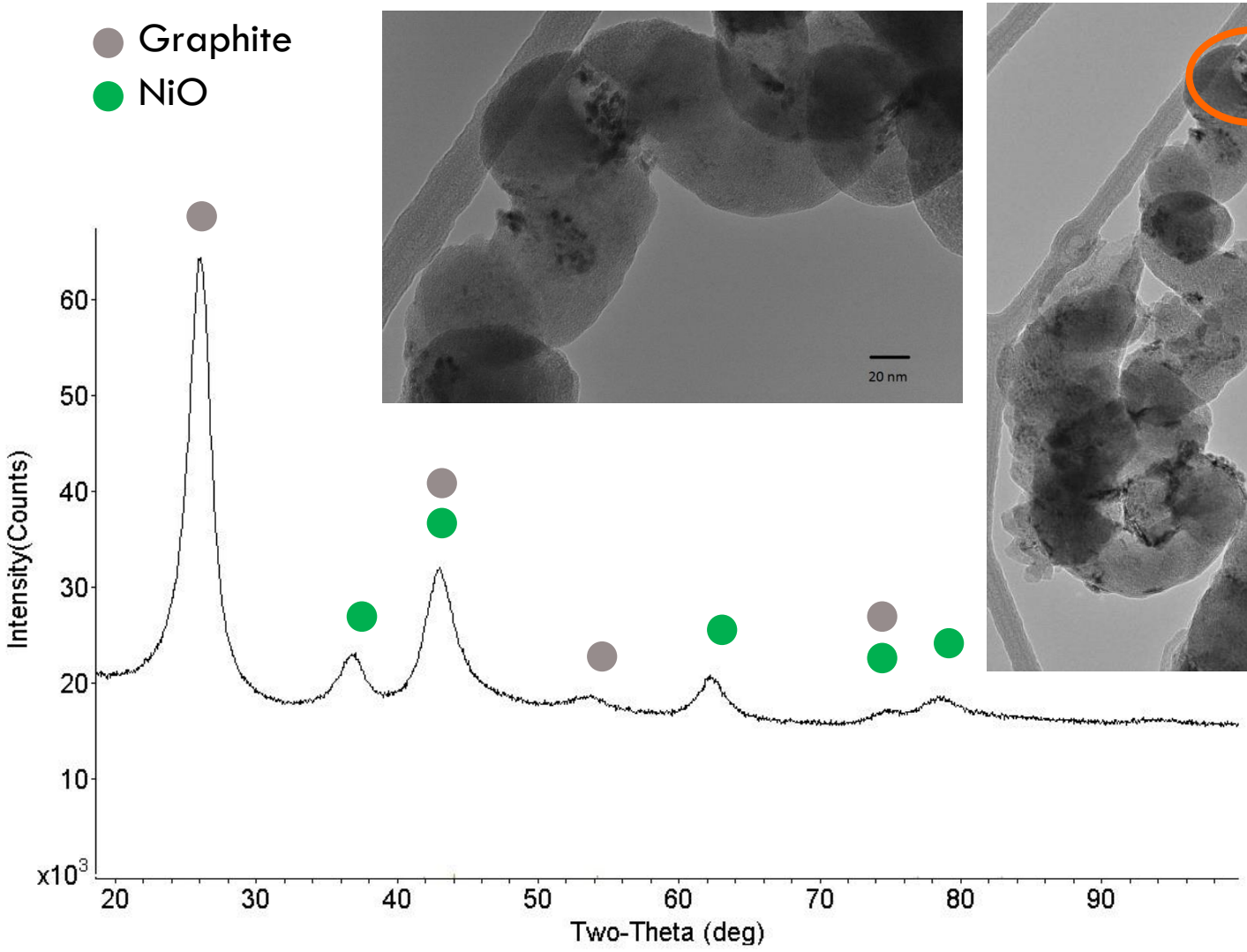
Calcination

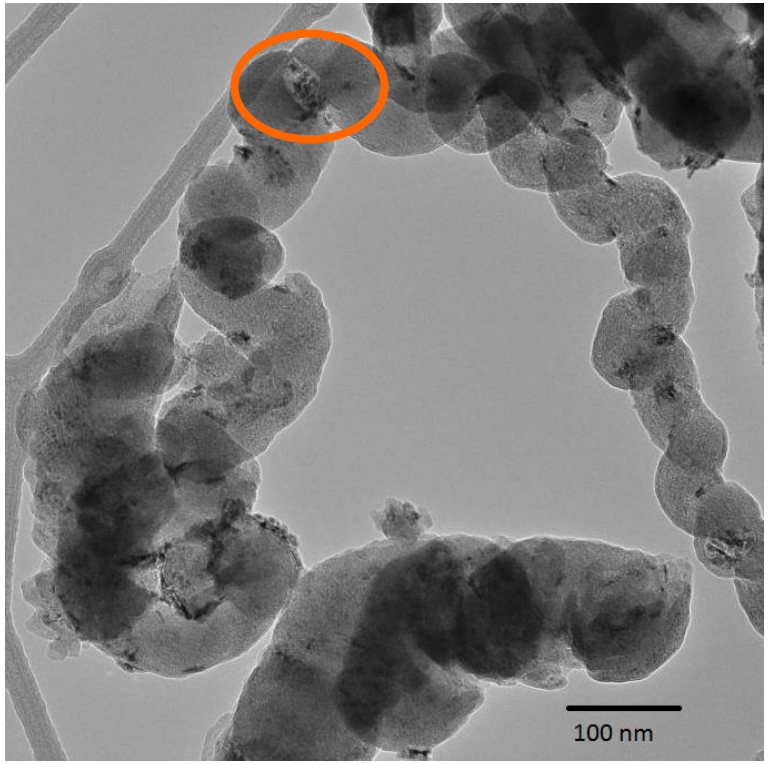
- At 290°C over Ar
- For 8h

Reduction

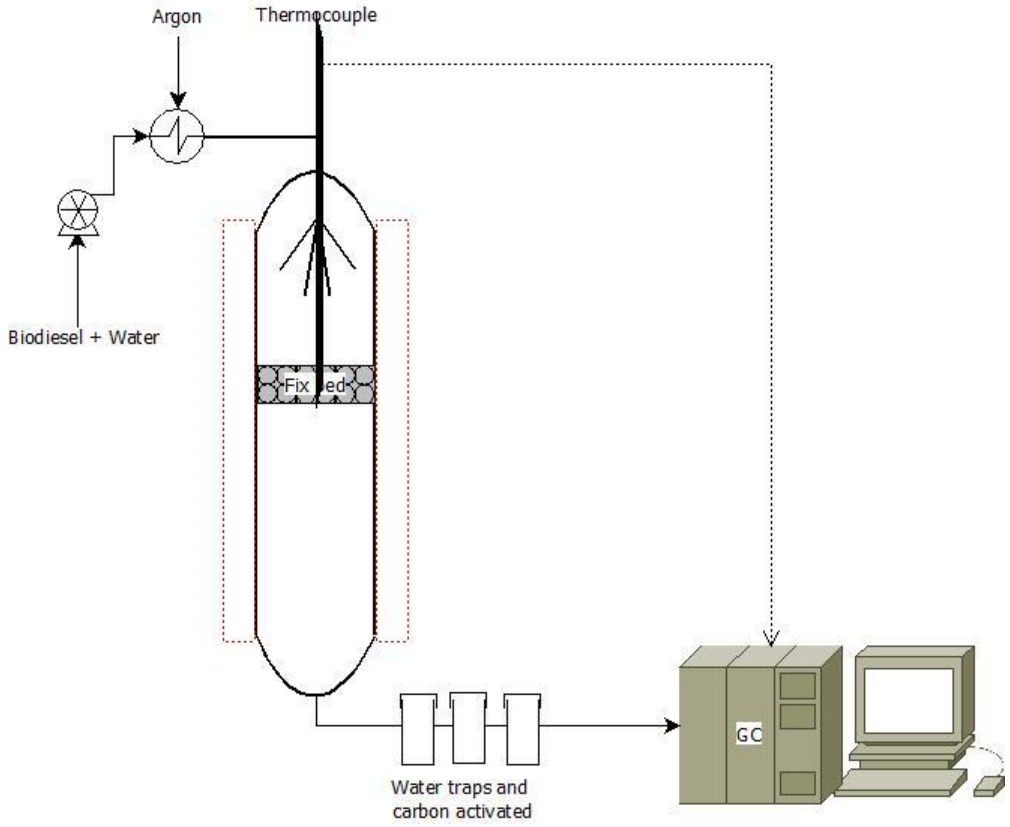
- At 450°C over H_2
- For 1h

CNF's production | Acid treatment | **Ni impregnation by $Ni(NO_3)_2$** | **Calcination & Reduction** | Steam reforming reaction





Reforming methodology

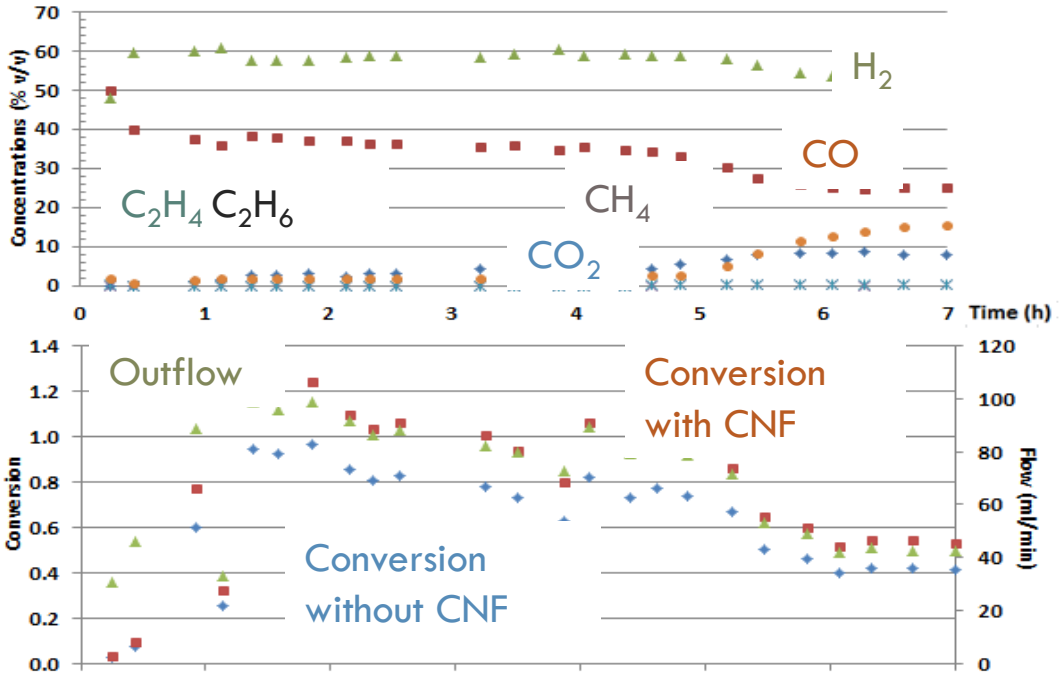


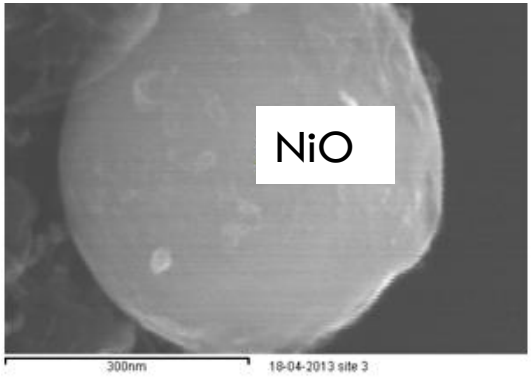
Reaction conditions

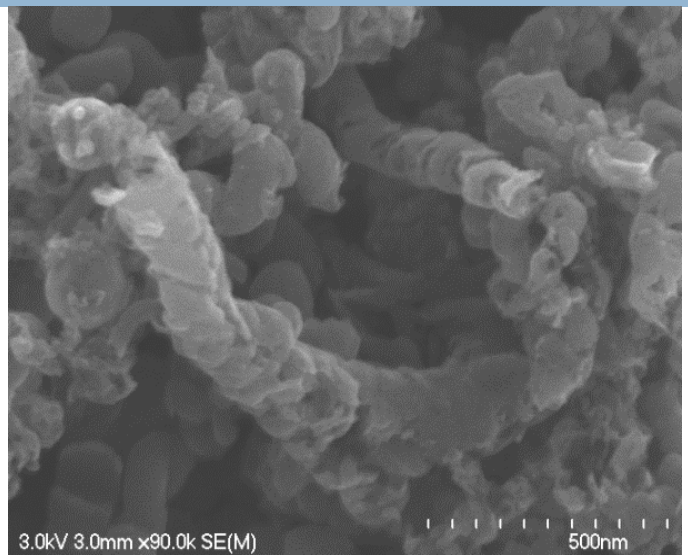
Hydrocarbon	Biodiesel
Catalyst	Ni/CNF
Reduction T	450°C over 10% H_2
Temperature	Variable
Pressure	1atm
Catalyst mass	3g
H_2O/C ratio	1.95
MHSV	46 $g*g^{-1}*h^{-1}$

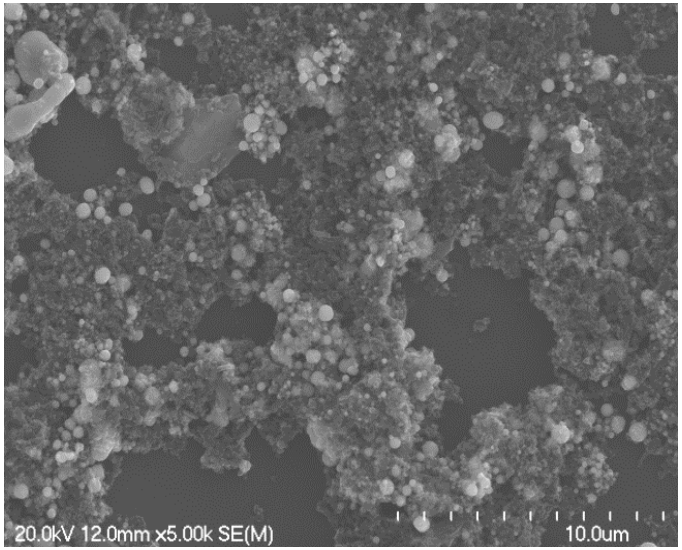
Reaction to 800°C

Conversion 93.9%



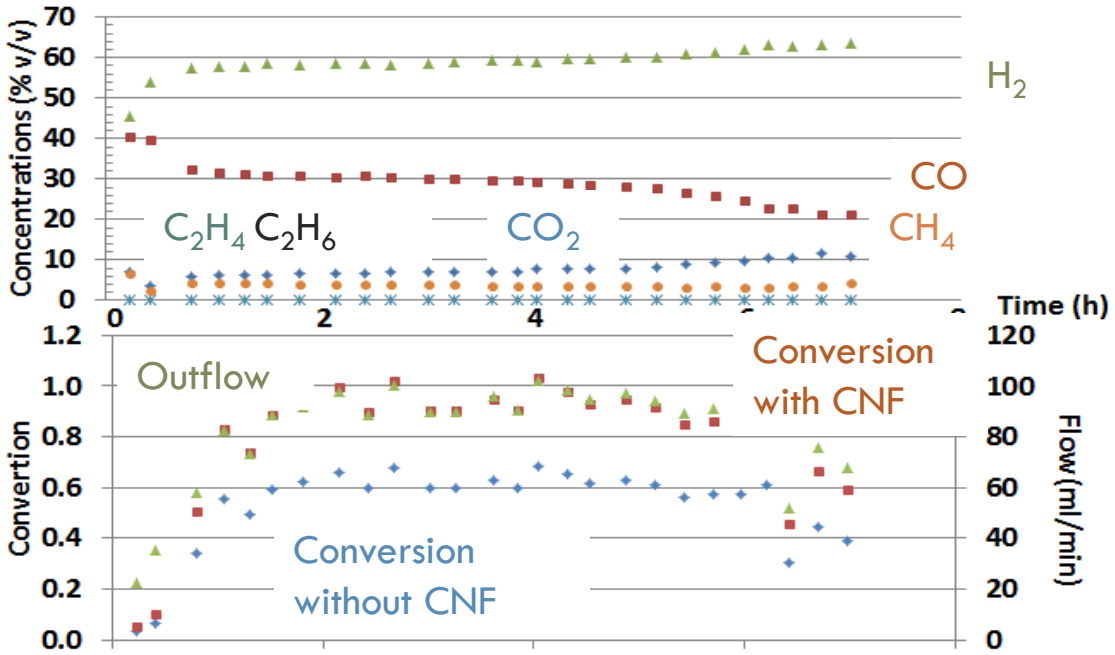


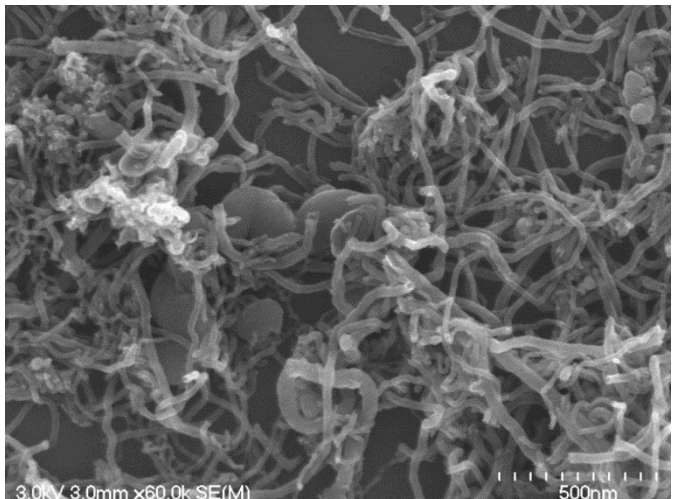


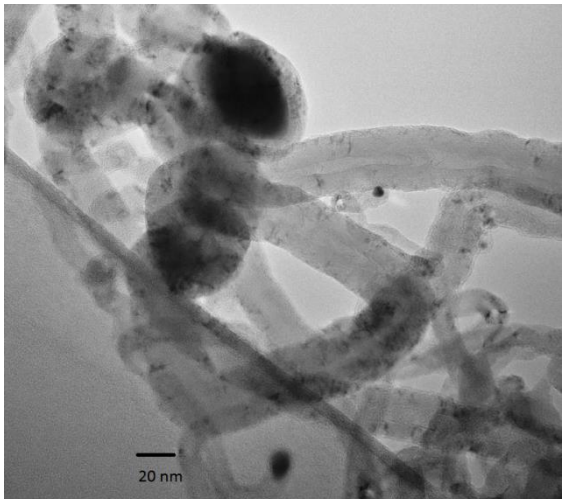


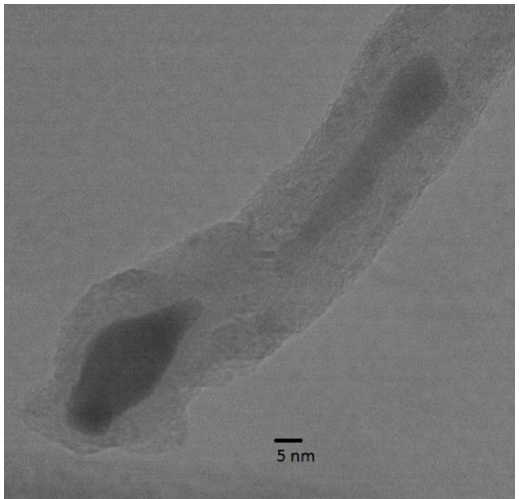
Reaction to 700°C

Conversion 99%



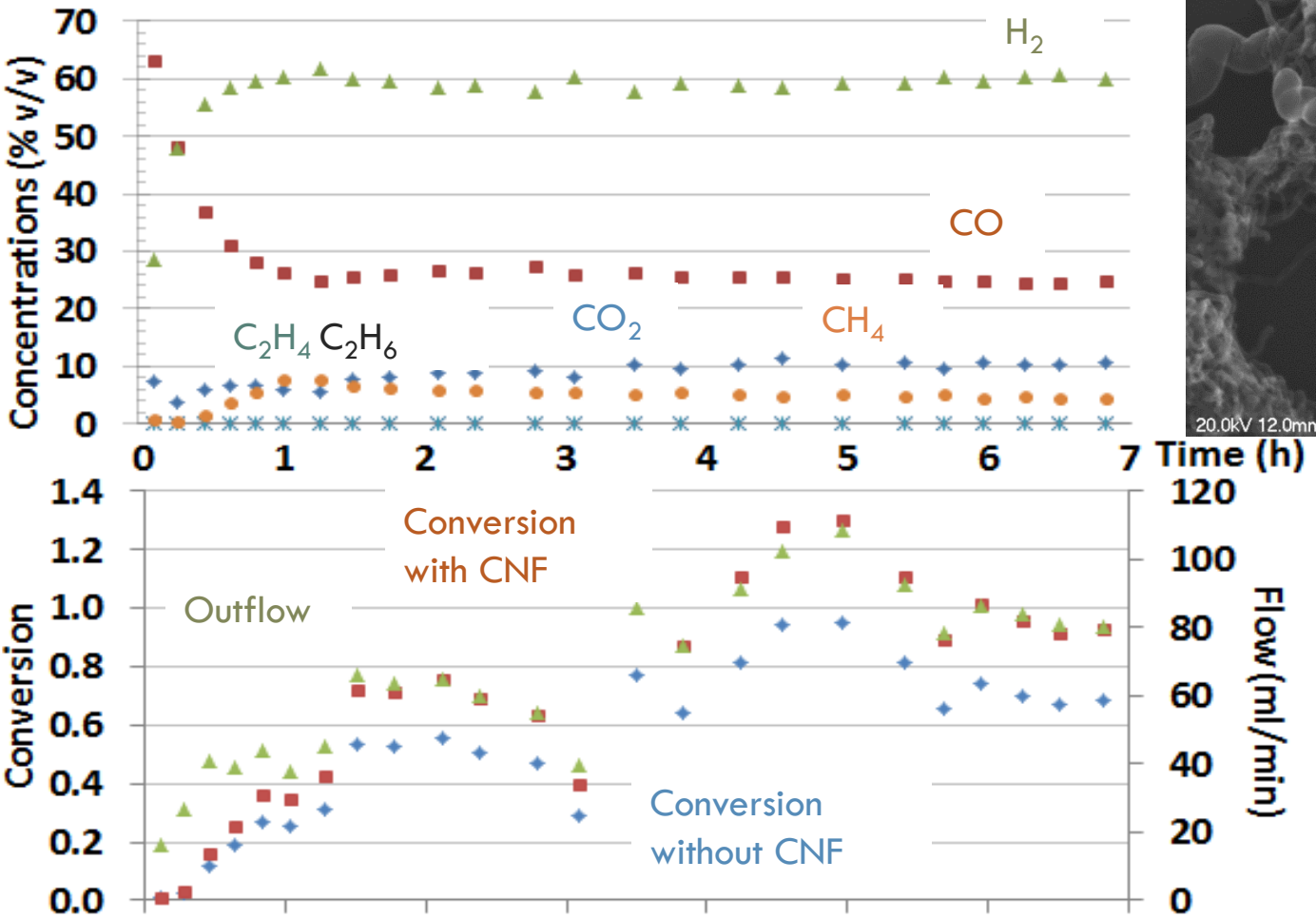


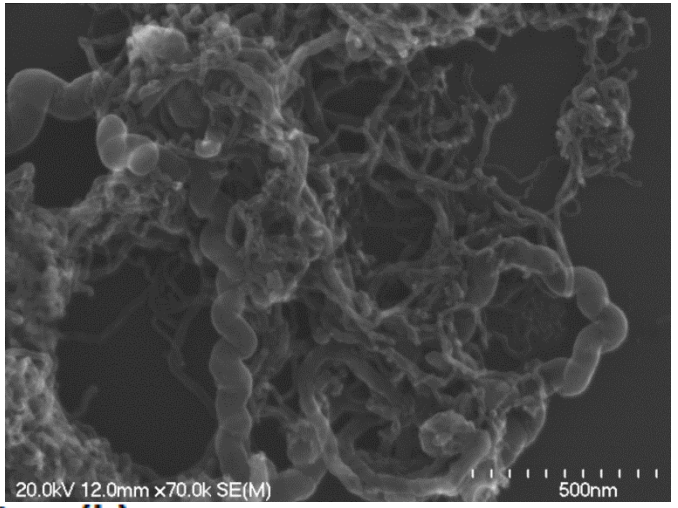


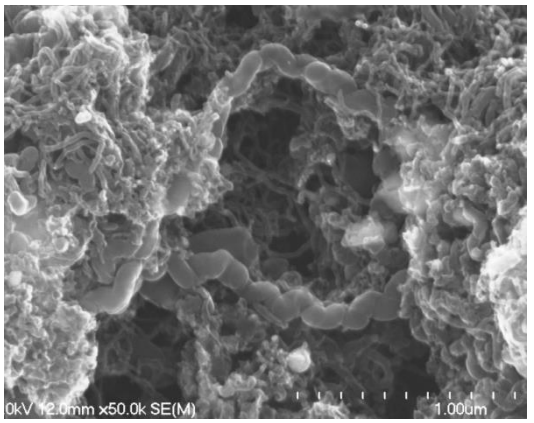


Reaction to 670°C

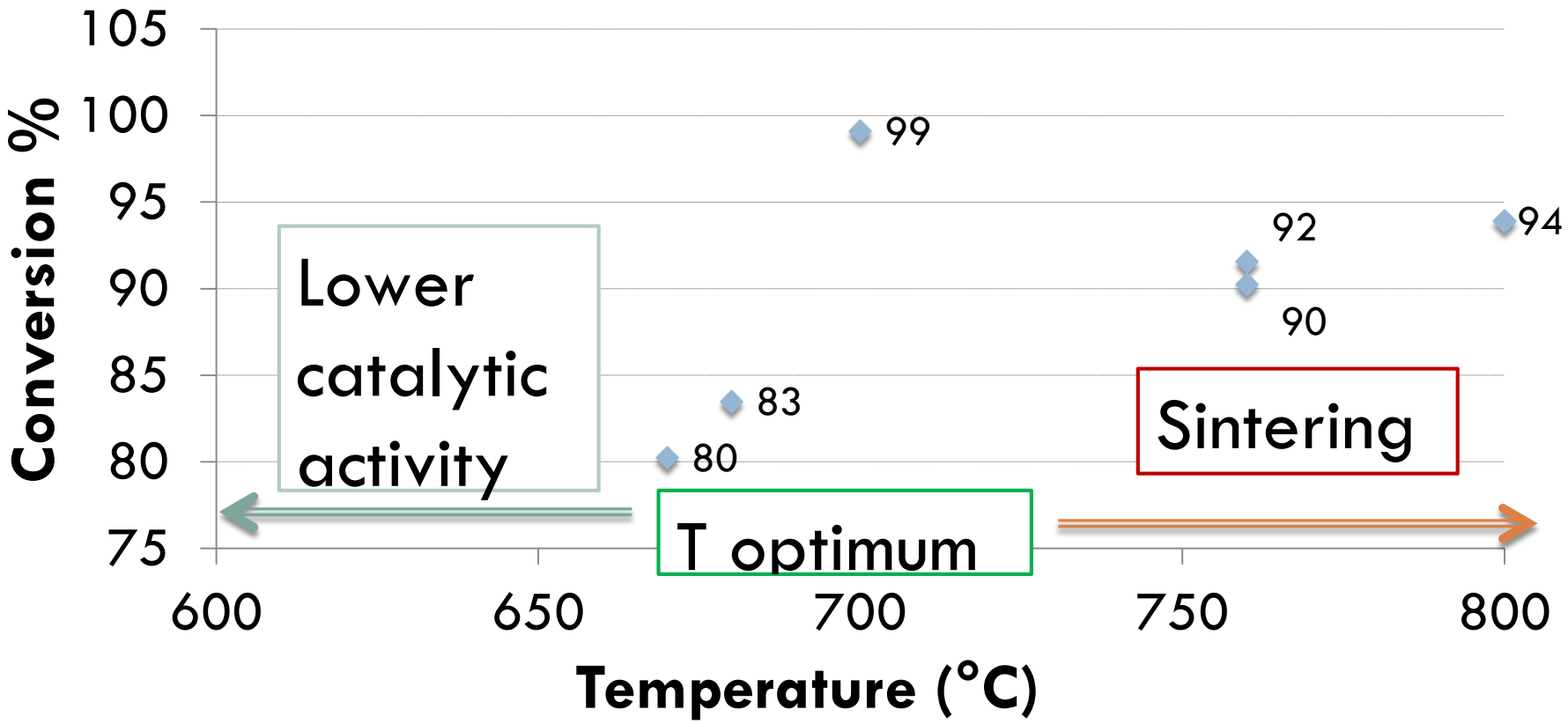
Conversion 80.2%







Conversion as function of T



Mass balance

Temperature	°C	800	760	760	700	680	670
MHSV	$g*g^{-1}*h^{-1}$	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

- Prof. Nadi Braidy
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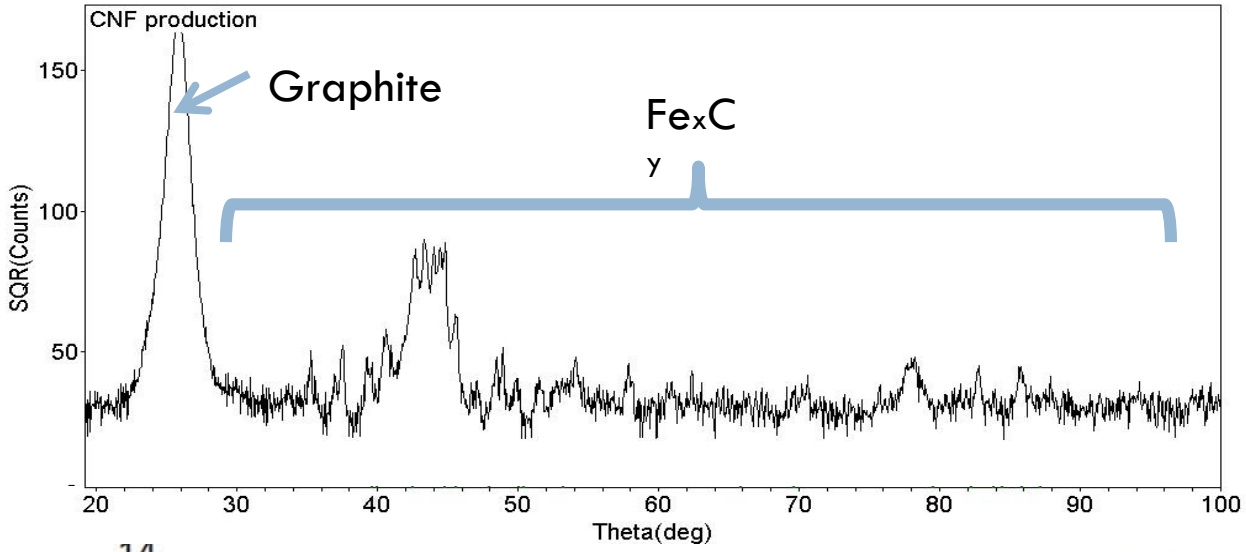
  - NCE BioFuelNet

Questions

Thank you

Characterization des NFC



Replicated 760°C