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Activated biochar-based metal catalysts for steam reforming of pyrolysis bio-oil model compound

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GreenCarbon framework

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Pyrolysis Conversion Routes for Dry Feedstocks

Refining of Biochars and Advanced Applications

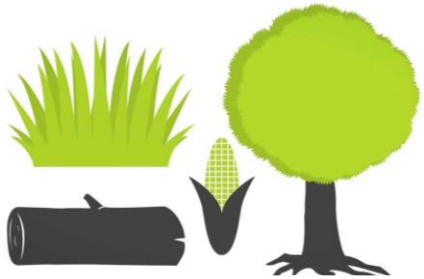
Hydrothermal Carbonization (HTC) Conversion Routes for Wet Feedstocks

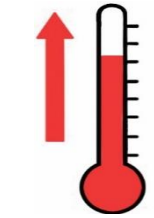
Sequential Biochar Systems

Outline

- Introduction
- Objective
- Methodology
- Results
- Conclusions and future work

Introduction

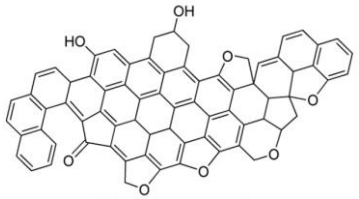




N_2

or

$N_2 + CO_2$



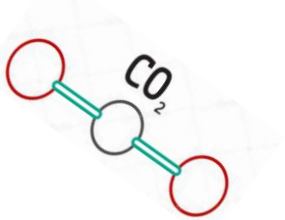
PYROLYSIS VAPORS

H_2,CH_4, CO, CO_2,C_2H_x,C_3H_y

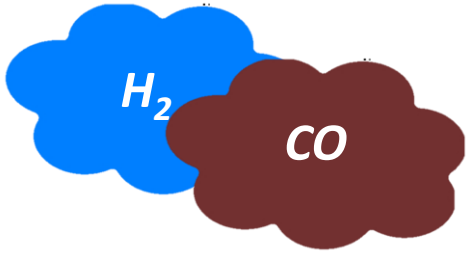
+ H_2O

+ Organic condensable fraction

Pollutant removal



Catalyst/Catalyst support



Soil amendment

Introduction

Organic condensable fraction (i.e. Bio-oil)

- ✗ The high water content lowers the heating value of the products
- ✗ Heterogeneous composition depending on the feedstock
- ✗ Systems breakdown caused by the condensation in pipes and heat exchangers

- The solution could be represented by the steam reforming of the liquid products
  - ✓ Less condensation extent
  - ✓ No external water is needed
  - ✓ More valuable permanent gases

Organic condensable fraction (i.e. Bio-oil)

Composition of bio-oil from slow pyrolysis of eastern redcedar woods[a] (SW/HW450/550 = sapwood/heartwood pyrolyzed at 450/500 °C).

Chemicals	Group	SW450	HW450	SW500	HW500
Cellulose/hemicellulose derived compounds (area%)					
Acetic acid	Acid	18.18 ± 1.45	11.25 ± 1.52	18.15 ± 0.16	9.75 ± 1.84
Propionic acid	Acid	2.42 ± 3.17	2.42 ± 0.36	3.42 ± 0.62	2.32 ± 0.85
1-Hydroxy-2-butanone	Ketone[b]	2.54 ± 0.31	1.49 ± 0.28	2.09 ± 0.66	1.21 ± 0.26
Cylcopentanone	Ketone	2.92 ± 0.28	1.79	3.58	1.54 ± 0.13
2-Cyclopenten-1-one, 2-methyl-	Ketone	4.42 ± 0.46	1.56 ± 0.56	2.58 ± 0.91	1.51 ± 0.25
Furfural	Furan	22.69 ± 0.40	26.20 ± 2.16	20.10 ± 3.39	21.80 ± 3.23
2-Furanmethanol	Furan	3.61 ± 1.54	–	1.47 ± 0.26	–
Ethanone, 1-(2-furanyl)-	Furan	0.99 ± 0.15	–	–	–
2-Furancarboxaldehyde, 5-methyl-	Furan	3.16 ± 0.57	4.46 ± 0.97	2.94 ± 0.21	4.43 ± 0.38
Lignin derived compounds (area%)					
Toluene	Aromatic	1.97 ± 1.02	–	–	–
p-Xylene	Aromatic	1.90 ± 0.14	1.65 ± 0.59	1.54 ± 0.51	1.77 ± 0.67
Phenol	Phenol	4.27 ± 2.08	3.04 ± 0.12	3.25 ± 1.24	3.55 ± 1.30
Phenol, 2-methyl-	Phenol	2.43 ± 0.79	2.54 ± 0.19	1.83 ± 0.39	2.71 ± 2.07
p-Cresol	Phenol	1.31 ± 0.68	1.67 ± 0.63	–	–
Phenol, 2-methoxy-	Guaiacol	10.34 ± 1.63	7.98 ± 0.67	10.13 ± 1.82	5.22 ± 0.03
Creosol	Guaiacol	4.28 ± 0.02	5.71 ± 0.33	4.24 ± 0.14	4.34 ± 0.61
Cedar oil compounds (area%)					
(−)-alpha-cedrene	Olefin	8.39 ± 1.12	12.97 ± 1.08	8.65 ± 1.46	18.15 ± 0.74
(+)-beta-cedrene	Olefin	2.27 ± 0.32	1.93 ± 0.93	1.81 ± 0.10	2.89 ± 0.34

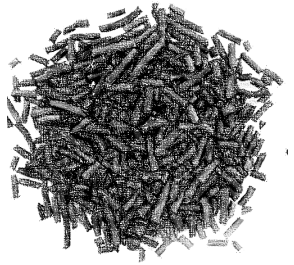
[a] "–"means the relative peak area percentage of the detected compound is less than 0.5%.
[b] Values listed above are means ± standard deviation of two subsamples.

Due to the numerous compounds present in a real bio-oil, model compounds such as acetic acid (AcOH), ethanol, benzene, toluene and eugenol, are usually employed to study the reaction system

*Z. Yang, A. Kumar, R. L. Huhnke, M. Buser, and S. Capareda, "Pyrolysis of eastern redcedar: Distribution and characteristics of fast and slow pyrolysis products," *Fuel*, vol. 166, pp. 157–165, 2016.

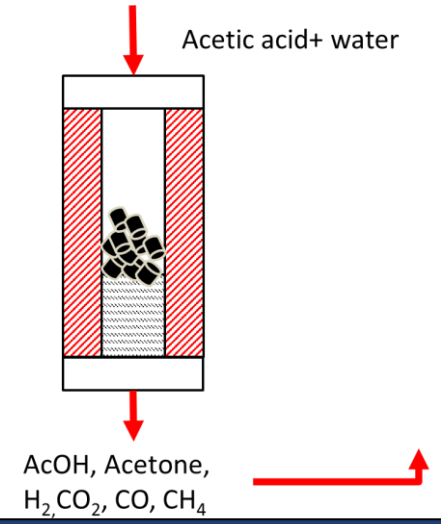
Aim of the work

1. Production of physically activated biochar with proper specific textural properties to be employed as catalyst support



2. Production of mono and bimetallic biochar-supported catalysts

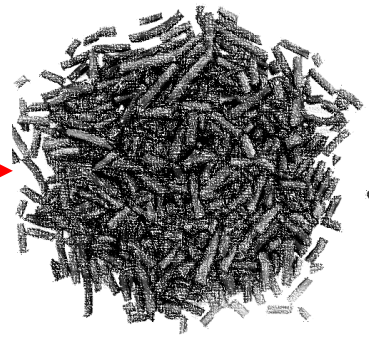
3. Test of the produced catalysts for the steam reforming of acetic acid (AcOH) as bio-oil model compound



Biochar Activation (i.e. Catalysts Support Production)

$$CO_2 + C \rightleftarrows 2\,CO$$

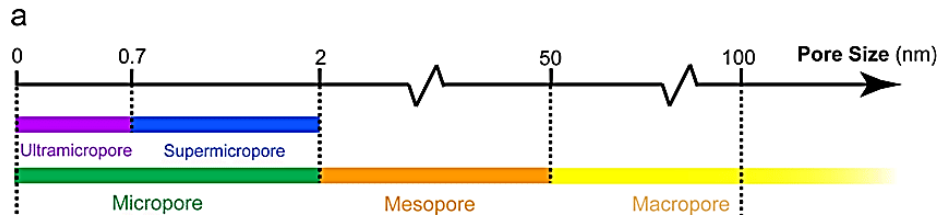
T=700°C; P= 1.0 MPa; CO_2 = 100 vol.%; t= 2.5 h



Material	*Apparent specific surface area ($m^2\ g^{-1}$)*		*Specific pore volume ($cm^3\ g^{-1}$)*			
	S_{BET}[a]	S_{BET}[b]	V_t	V_{mic}	V_{mes}	V_{ultra}
BC	1.68	72.4	ND	ND	ND	0.023
ActBC	743	414	0.333	0.301	0.032	0.226

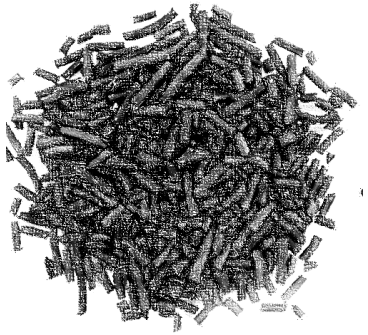
[a] Determined from N_2 adsorption data a –196 °C.

[b] Determined from CO_2 adsorption data a 0 °C.



***BC=wheat straw biochar produced at 500°C and 0.1 MPa**

Catalyst synthesis



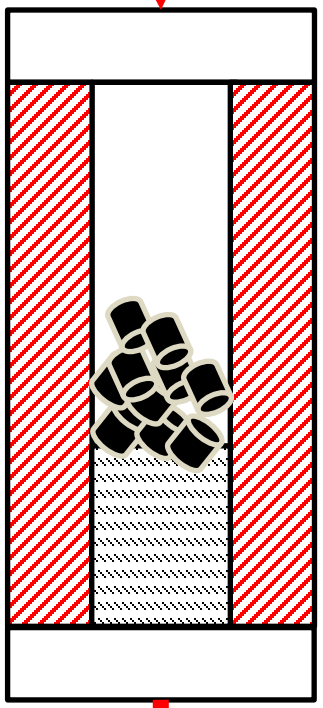
- $Fe(NO_3)_3 \cdot 9H_2O$
- $Ni(NO_3)_2 \cdot 6H_2O$
- $Co(NO_3)_2 \cdot 6H_2O$
- $Ce(NO_3)_3 \cdot 6H_2O$
- KNO_3

Wet impregnation
&
Calcination at 600°C in N_2

Monometallic		
Sample	**Active phase**	**Load (wt. %)**
BC	/	/
BCFe	Fe	7
BCCo	Co	7
BCCe	Ce	7
BCK	K	7
BCNi7	Ni	7
BCNi4	Ni	4
BCNi10	Ni	10
Bimetallic		
Sample	**Active phase**	**Load (wt. %)**
BCFeNi	Fe/Ni	7/10
BCCoNi	Co/Ni	7/10
BCCeNi	Ce/Ni	7/10
BCKNi	K/Ni	7/10

Steam reforming of AcOH

Acetic acid+ water



T= 400 - 600°C

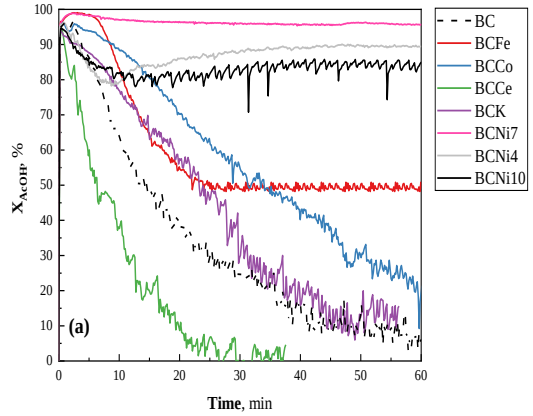
P= 0.1 MPa

t_r=135 ms

molH_2O/molAcOH = 4

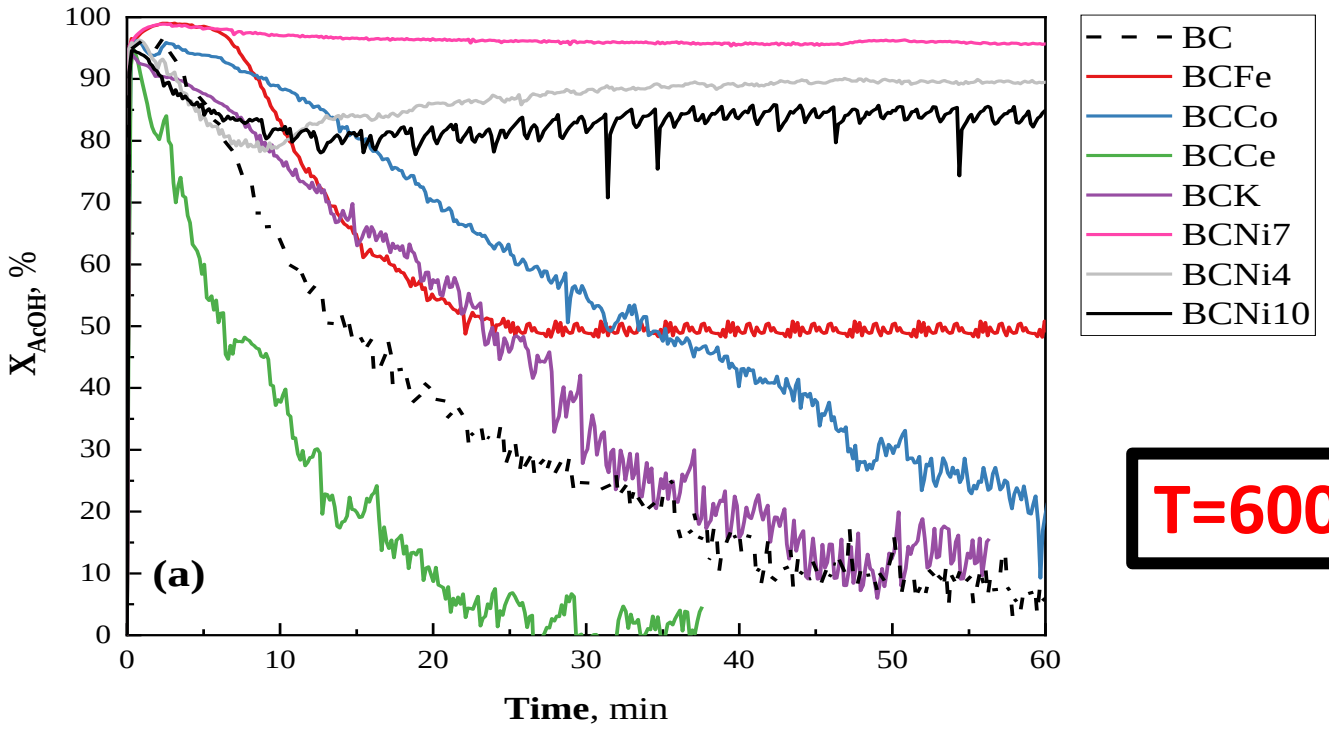
- $\mathbf{X_{AcOH}} = (F_{AcOH,\,in} - F_{AcOH,\,out})\, F_{AcOH,\,in}^{-1}\, 100$
- $\mathbf{Y_{H2}} = F_{H2,\,out}\, (4\, F_{AcOH,\,in})^{-1}\, 100$
- $\mathbf{Y_{Ac}} = 2\, F_{Ac,\,out}\, F_{AcOH,\,in}^{-1}\, 100$

Quadrupole mass spectrometer analyzer

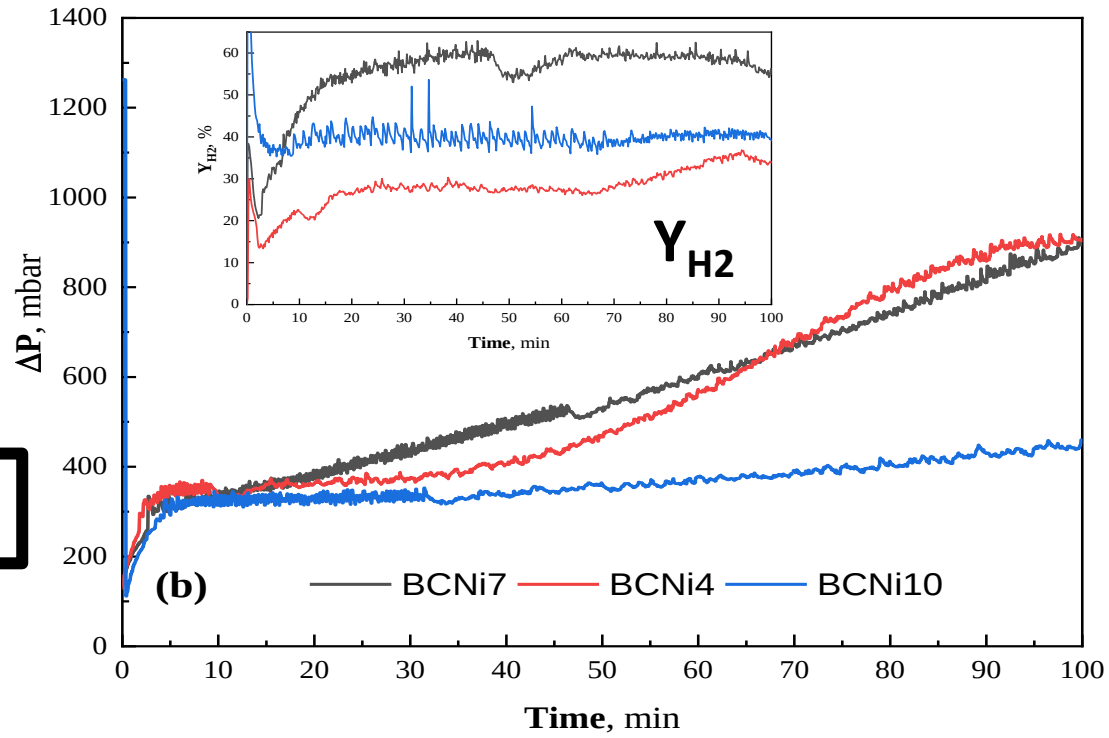


AcOH, Acetone,
H_2,CO_2, CO, CH_4

Monometallic catalysts



T=600°C



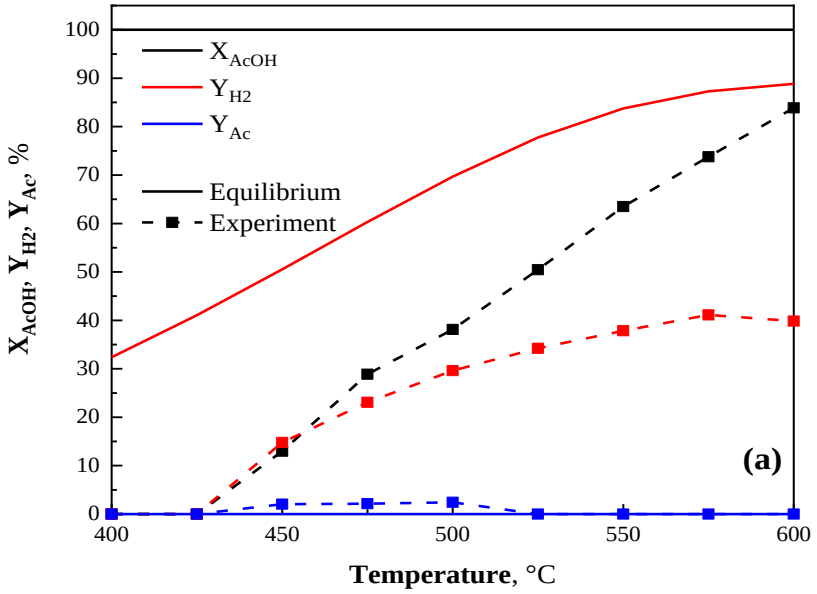
Best performances with the Ni-based catalysts (no deactivation)

10% Ni loading represented the best tradeoff between conversion and stability (less coke deposition)

Bimetallic catalysts

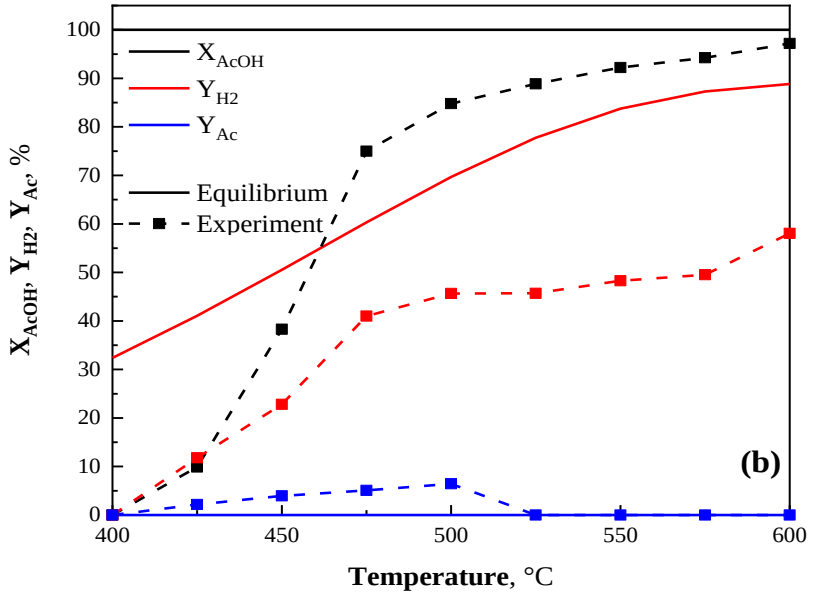
BCKNi was very unstable. Therefore the results are not reported.

BCFeNi



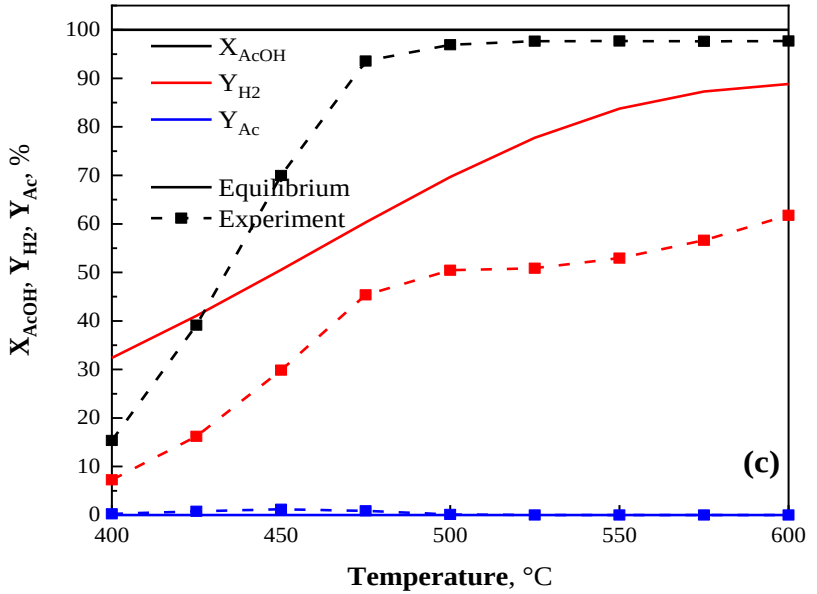
- Low conversions and hydrogen yields, even at high temperature

BCCeNi



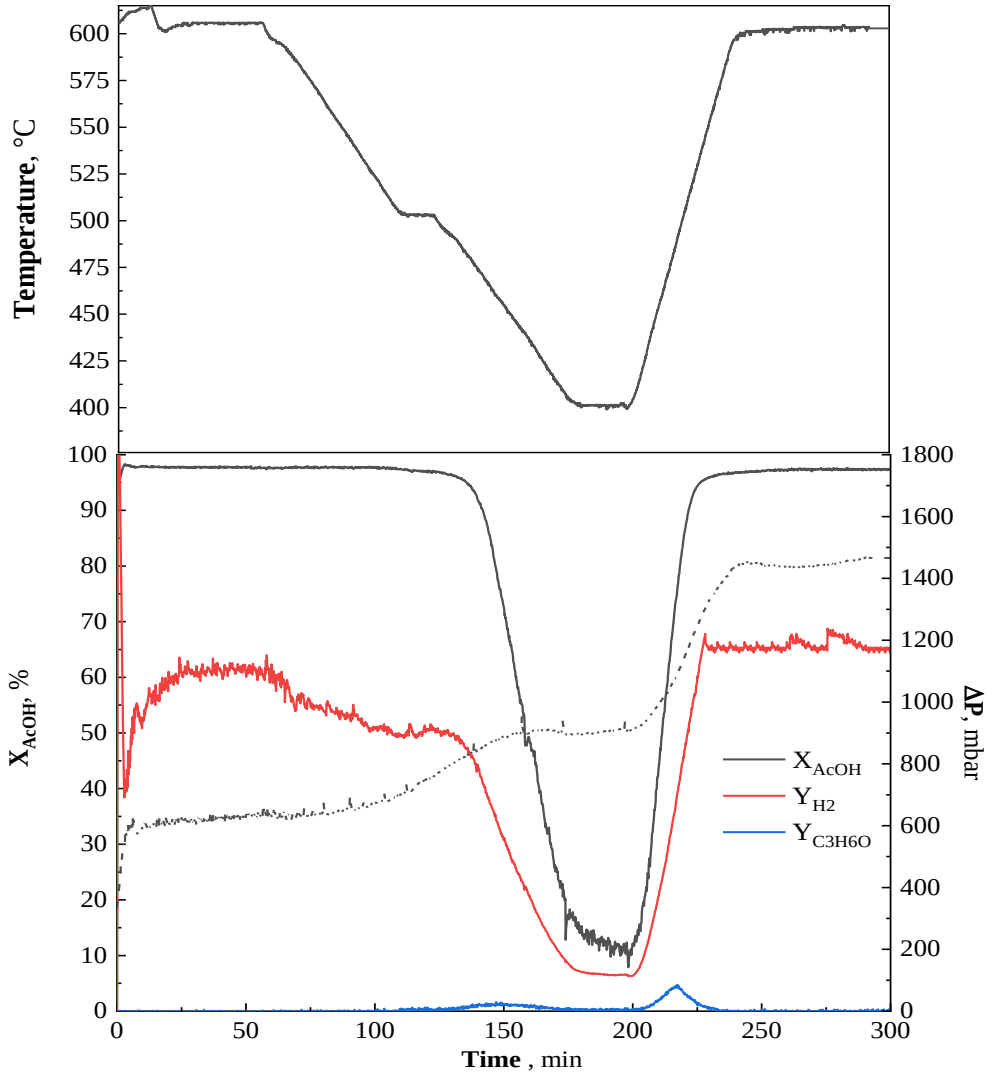
- High conversions from 550 to 600°C.
- Acetone yield not negligible.

BCCoNi



- Highest conversions, close to the equilibrium, even at 475°C.
- No acetone production.

Cycling stability test of BCCoNi



- Constant AcOH conversion and pressure drop value from 600 to 475 °C.
- When the reactor was heated up again, the pressure drop increased again until the set temperature was reached.
- The final conversion was the same that that measured for the fresh catalyst, indicating negligible deactivation extent.

Conclusions and future work

- The physically activated biochar showed an excellent potential to be employed as support for metal active phases.

- Most of the tested metal catalysts showed rapid deactivation degree probably due to high coke deposition and/or sintering of the active phases.

- Among the monometallic catalysts, the Ni-based showed negligible deactivation rates. In particular a loading of 10 wt. % guaranteed a good tradeoff between performances and coke deposition.

- The Co-Ni bimetallic catalyst showed the best results obtained in this study, with high conversions even at low temperatures and almost no coke production.

Conclusions and future work

- Deep catalysts characterization (FT-IR, Raman, SEM, XRD).

- Add more model compounds to better simulate a real bio-oil composition.

Thank you for your attention

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