“Reformado en fase acuosa de la fracción ligera del bio-aceite obtenido por pirólisis de biomasa residual para la recuperación de energía y/o hidrógeno”

“Aqueous-phase reforming of light fraction of bio-oil obtained by waste biomass pyrolysis for energy and/or hydrogen recovery”

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__Workshop 2020__: Innovative technologies for sustainable management of urban and industrial waste streams

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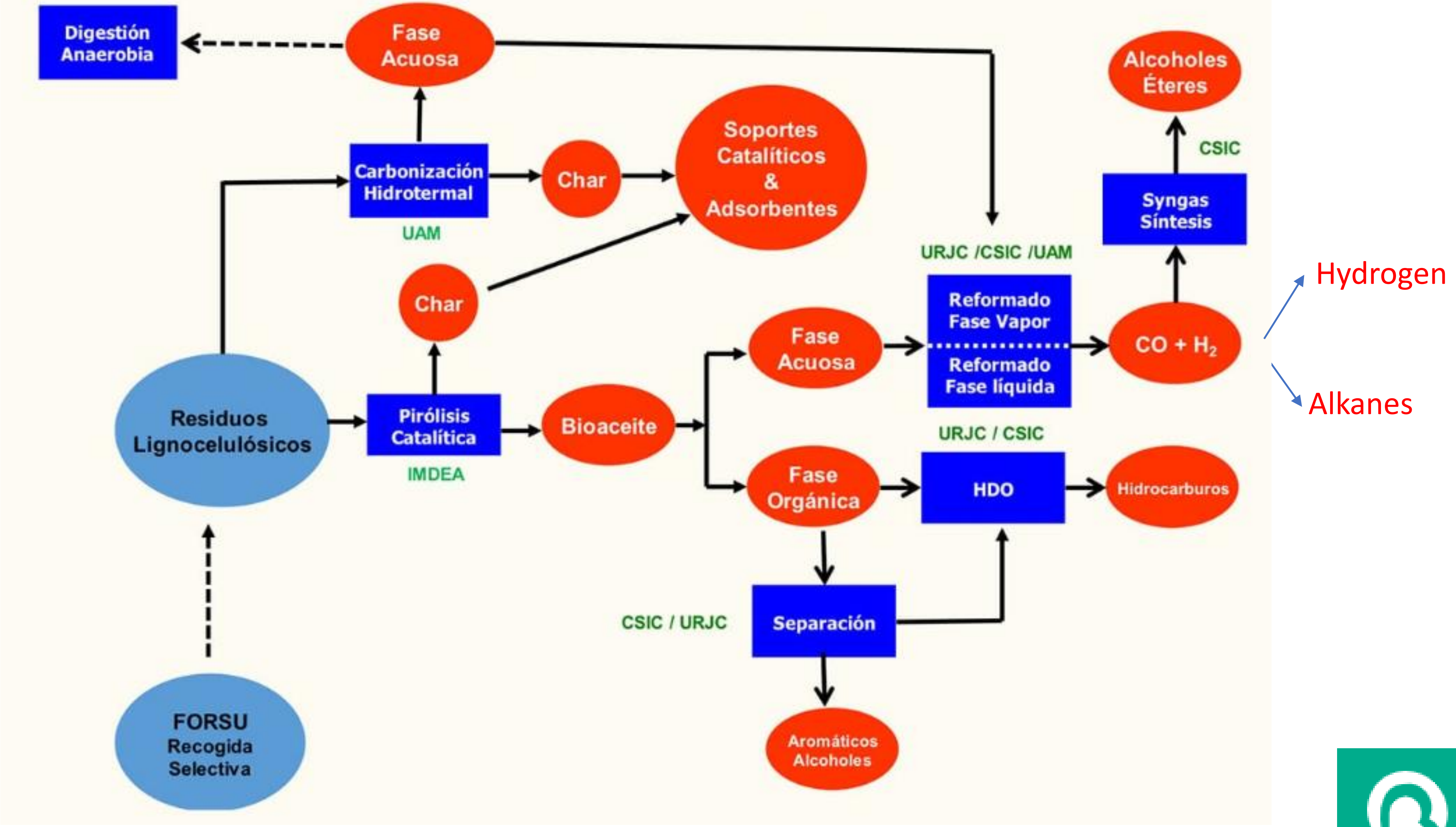
BIO3

OBJECTIVE 4.2: ***AQUEOUS PHASE REFORMING OF PYROLYSIS OILS AND OTHER RESIDUAL CURRENTS***



AQUEOUS-PHASE REFORMING

$$C_nH_{2n+2}O_n + nH_2O \leftrightarrow nCO + (2n+1)H_2 \quad \Delta H > 0 \qquad (1)$$
Reforming reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H < 0 \qquad (2)$$
Water-gas shift reaction

Main Reactions

- Catalytic system
- Pressure
- Temperature

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H < 0 \qquad (3)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H < 0 \qquad (4)$$

Methanation

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \quad \Delta H < 0 \qquad (5)$$

$$(2n)H_2 + nCO \rightarrow C_nH_{2n} + nH_2O \quad \Delta H < 0 \qquad (6)$$

Fischer-Tropsch

$$C_nH_{2n+2}O_n + H_2 \leftrightarrow \frac{carbohydrate}{alkane} + H_2O \quad \Delta H < 0 \qquad (7)$$

$$C_nH_{2n+2}O_n + H_2 \leftrightarrow carbohydrates \quad \Delta H < 0 \qquad (8)$$

Dehydration/hydrogenation

Secondary reactions

AQUEOUS PHASE REFORMING: *Operating Conditions*

- More studied feeds: sugar alcohols in aqueous solution
- Pre-evaporation of reactor inlet is not neccesary
- Temperature: 210-280^{o}C ; Pressure: 15-50 bar
- The operating pressure allows the separation of the H_2 by simple processes
- Catalyst: Best results with **Pt**, followed by **Ni, Ru, Rh, Pd e Ir**

AQUEOUS PHASE REFORMING: *Operating Conditions*

- Substrates with C:O atomic ratio C:O close to 1:1 give higher H_2 yields
- Feed concentration: less than 3% in mass of the substrate
- Most common reactors: batch and fix bed (much better results in batch).
- Higher yields of both H_2 and alkanes can't be reached (two different alternatives for process conduction)
- Higher acidity of the catalyst provoques higher extent of secondary reactions
- Longer residence time in the reactor, higher selectivity to alkanes

GENERAL OBJECTIVE: to use the aqueous fraction of the bio-oil from pyrolysis of waste biomass as a feed to an APR process, with the aim to reduce or eliminate their polluting potential while a valuable gas stream is obtained (because of either H_2 or energy content)

1. Literature-based definition of a model composition of the aqueous fraction of pyrolysis bi-oil (AFB)
2. Tune-up of characterization and analysis procedures
3. Delimitation of APR process operation windows using model compounds and mixtures of them as substrate
4. Validation of previous studies and process optimization using AFB obtained by biomass pyrolysis
5. Technical-economic evaluation of APR process upon Aspen HYSYS simulation

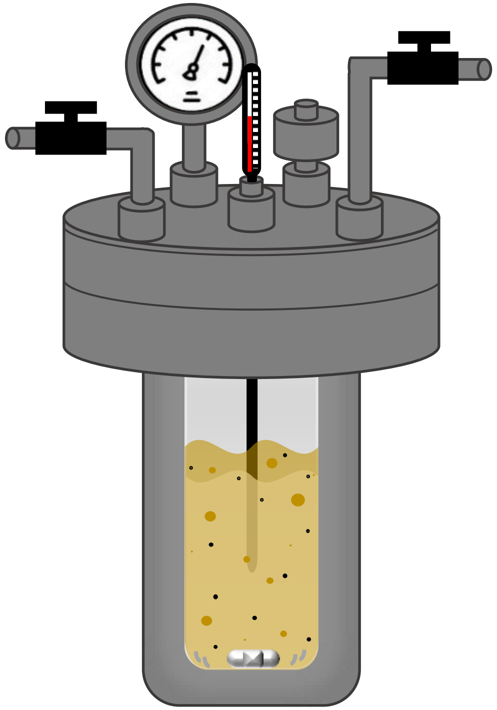
BATCH REACTOR

Catalyst: 0.15 g

V reaction: 15 mL

$P_{initial}$ Argon: 5 bar

T: 220ºC ; 4 h

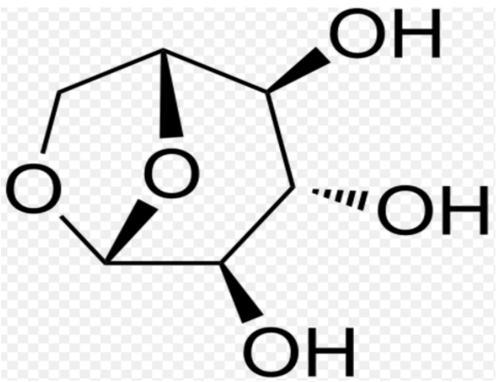


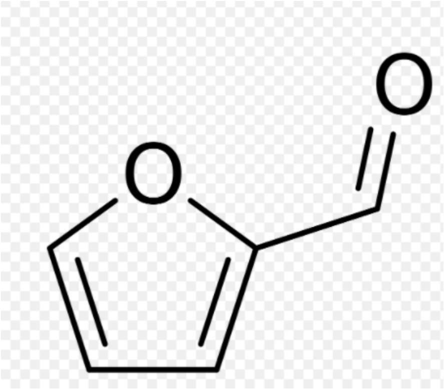
Pt/ENS

Pt-Re/ENS
Pt-Mn/ENS
Pt-Ni/ENS
Pt-Fe/ENS
Pt-Pd/ENS

✓ Qualitative model composition aqueous phase of bio-oil (dry base)

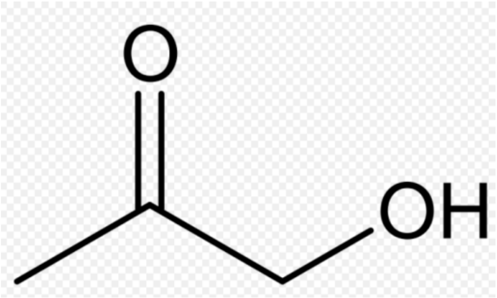
Levoglucosan
$C_6H_{10}O_5$

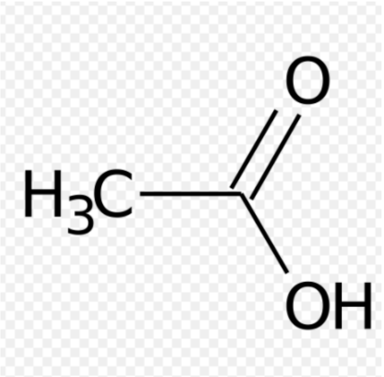




Furfural
$C_5H_4O_2$

Hydroxyacetone
$C_3H_6O_2$

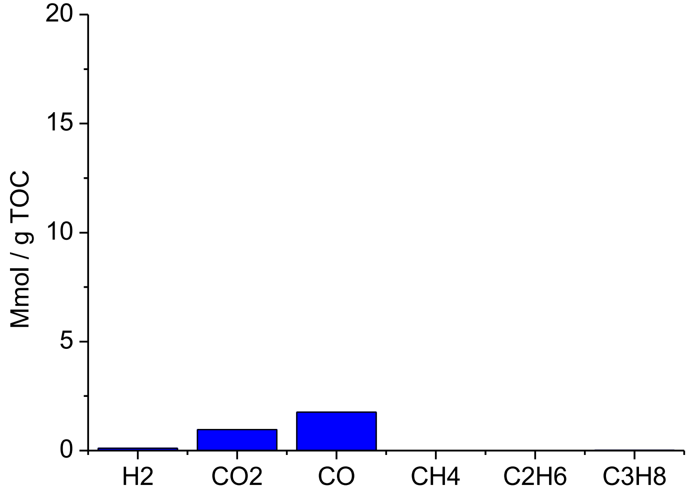


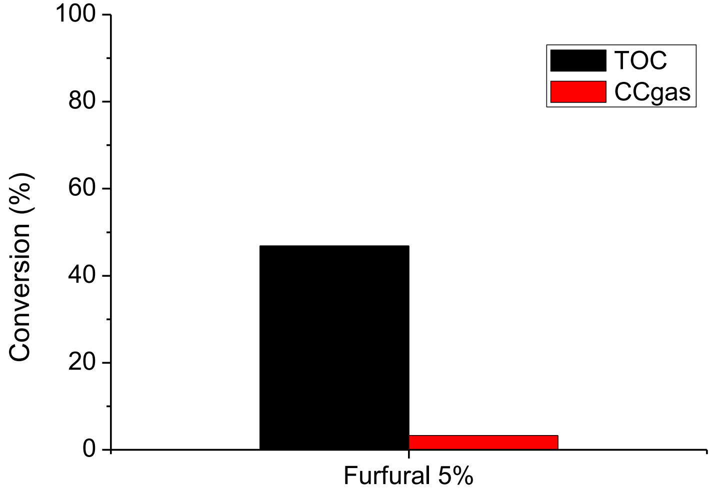


Acetic acid
$C_2H_4O_{2g}$

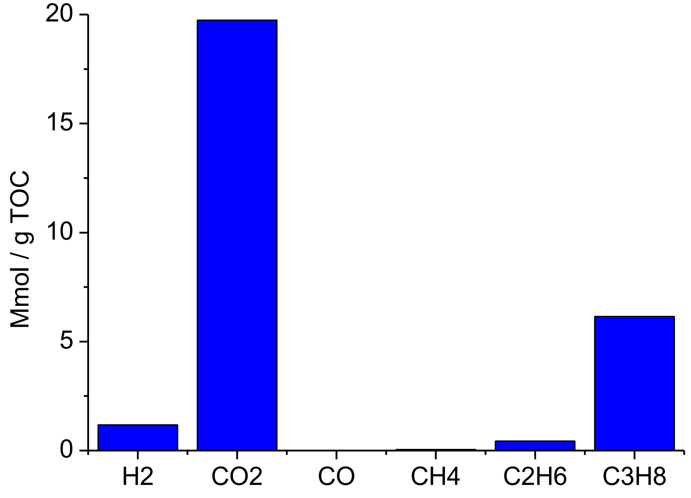
✓ Influence of feed concentration

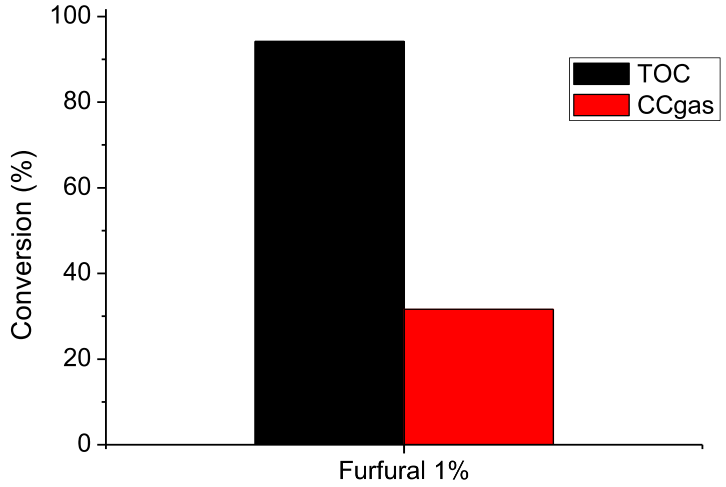
5% wt Furfural





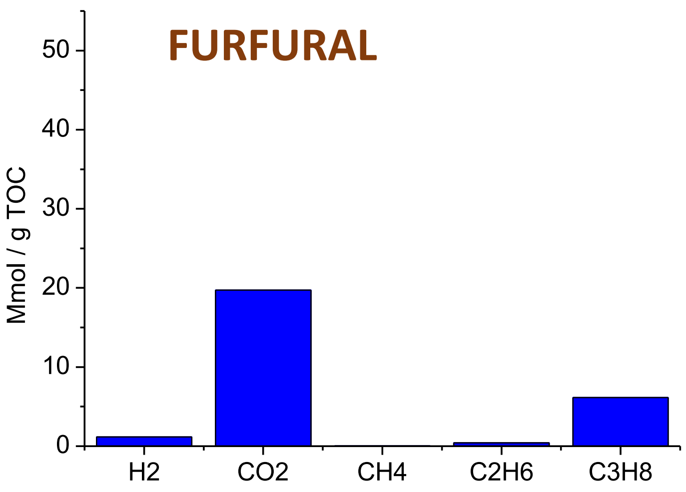
1% wt Furfural

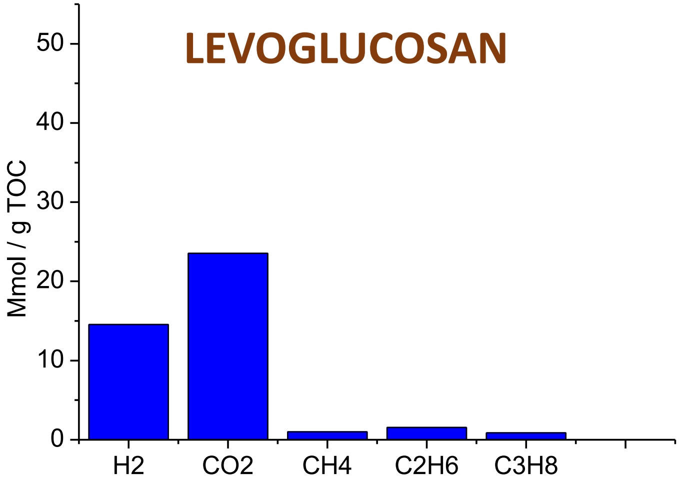




✓ Individual main compounds at low concentration (1% wt)

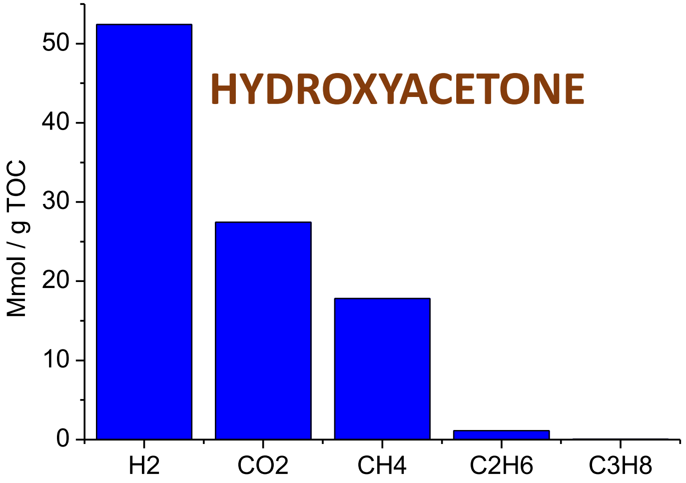
X TOC (%)	94,2
CC gases (%)	31,6

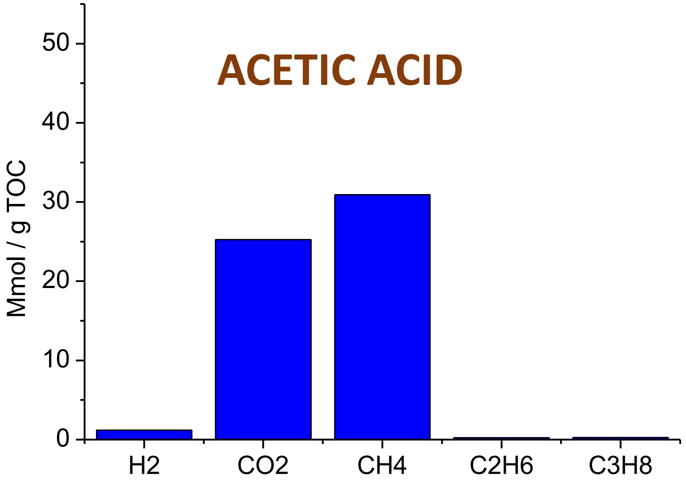




X TOC (%)	89,8
CC gases (%)	35,4

X TOC (%)	78,6
CC gases (%)	55,8

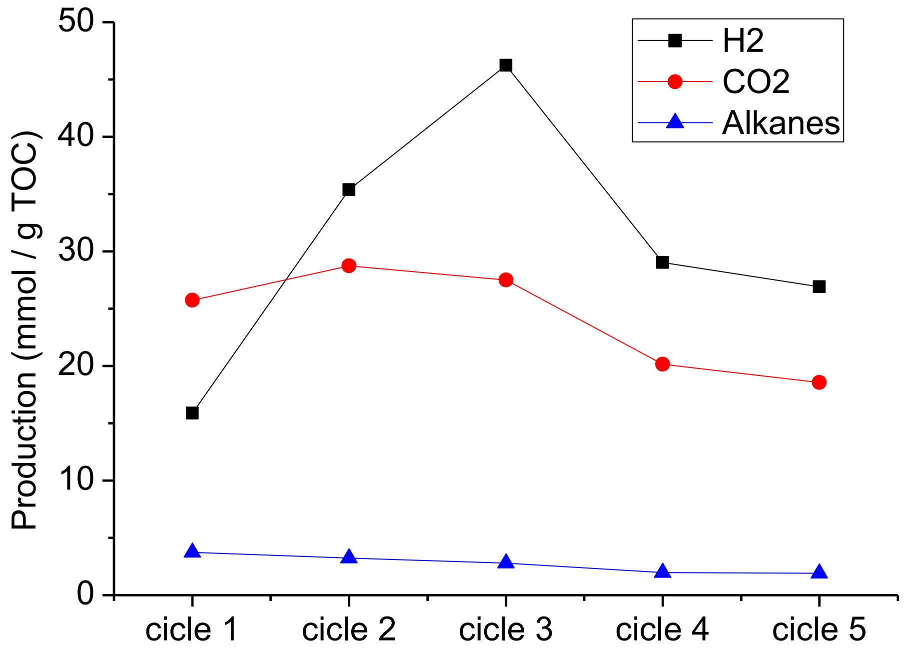


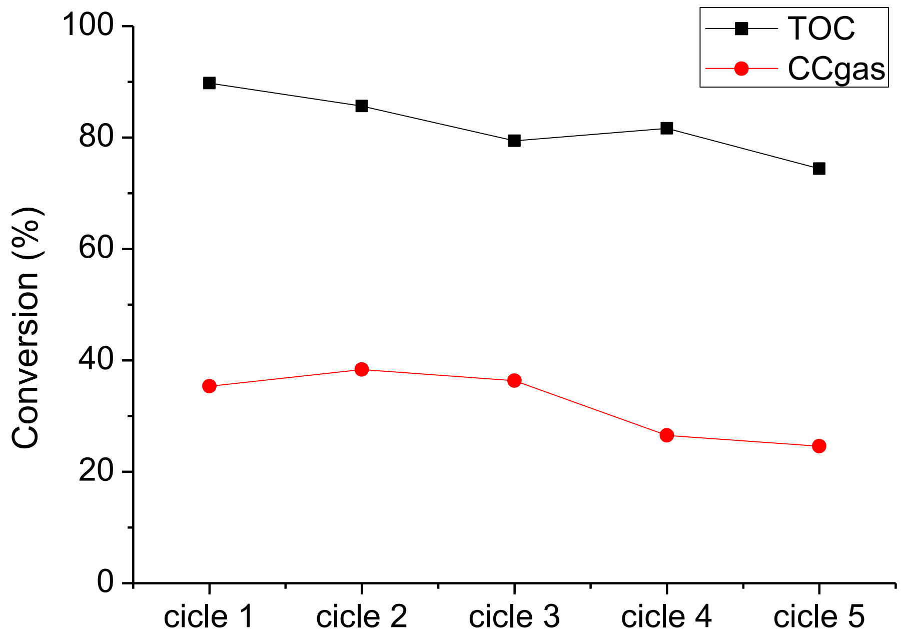


X TOC (%)	62,7
CC gases (%)	68,0

✓ Stability in several reaction cicles

- **Levoglucosan:** Very good results ⟶ Up to 5 cicles (20 hours of operation)





- **Furfural:** ↑ X TOC Ɇ CCgas

- **Hydroxyacetone, acetic acid:** Don't allow reuse

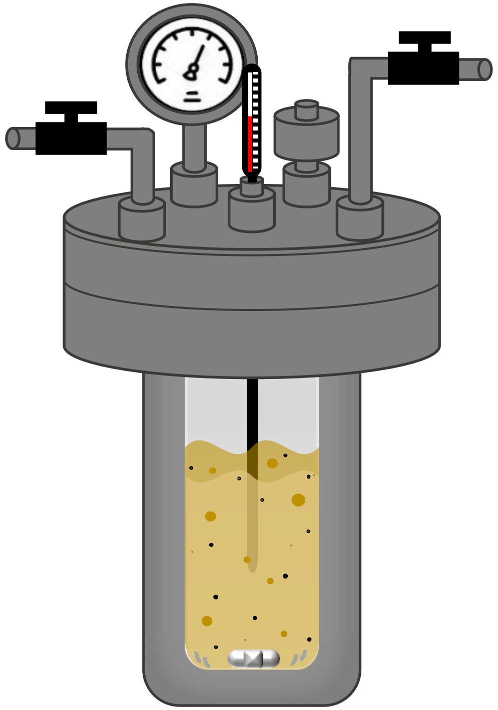
✓ Bimetallic catalyst → *Master Thesis in course*

Pt/ENS

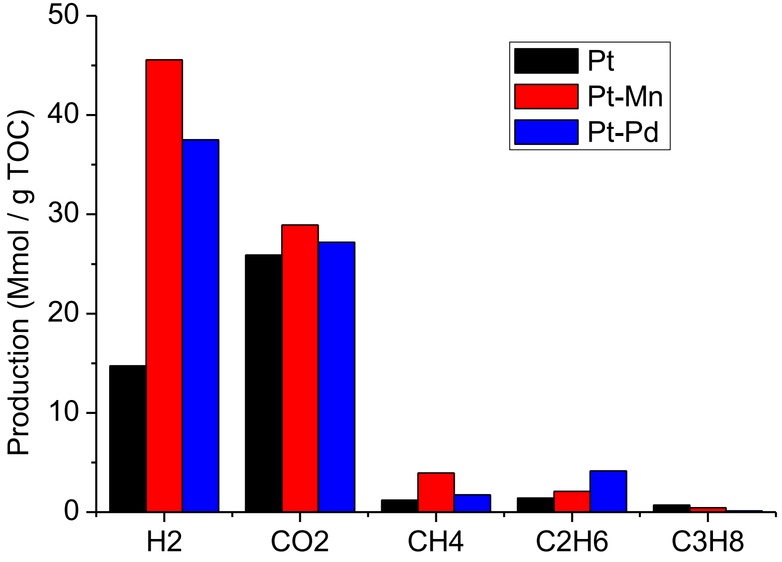
Pt-Re/ENS
Pt-Ni/ENS
Pt-Fe/ENS
Pt-Mn/ENS
Pt-Pd/ENS

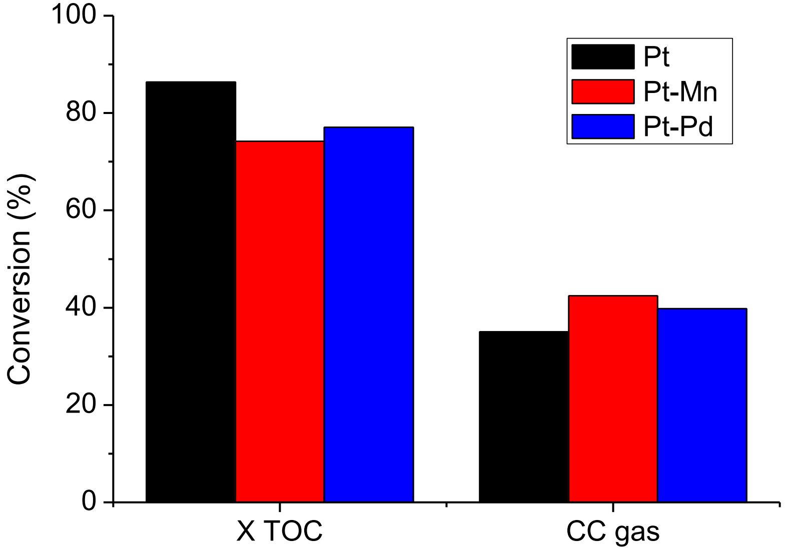
- Sequential incipient wetness impregnation
- Drying: 60ºC
- Calcination: 250ºC, 2 h
- Reduction: 300ºC, 2 h (Pt-Ni 350ºC)

Pt-Re, Pt-Ni, Pt-Fe:
Worse results than Pt's monometallic

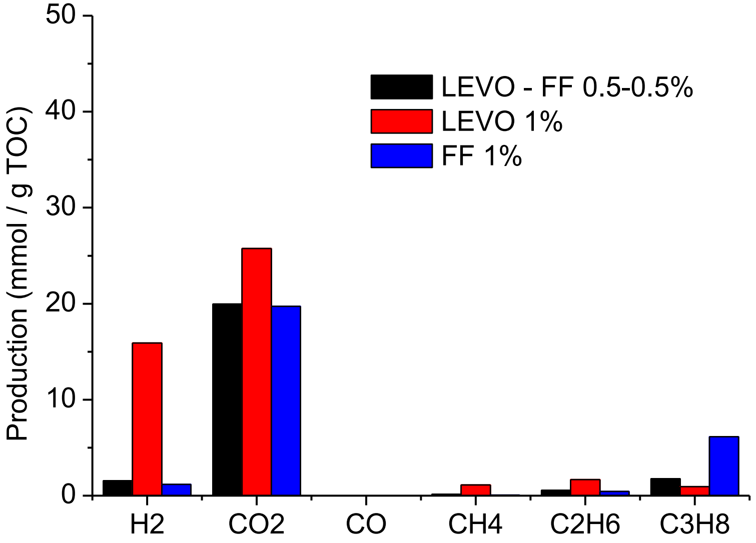


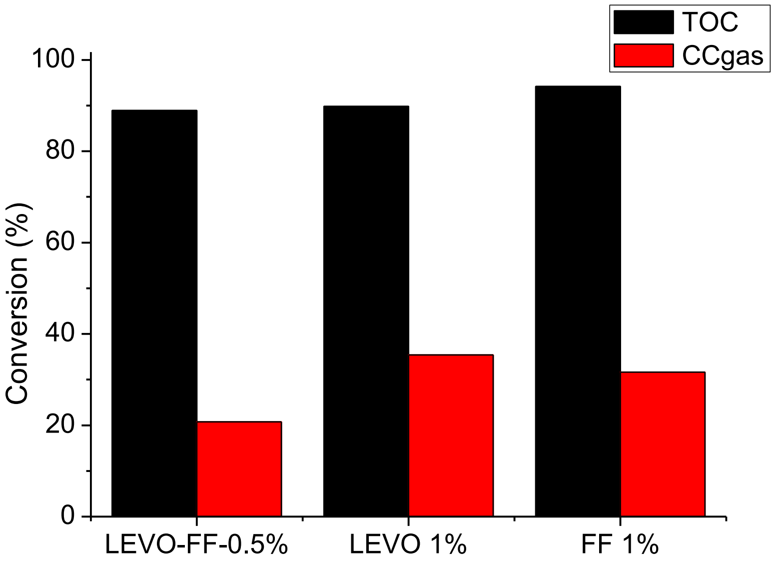
Batch tests, levoglucosan 1% wt





✓ Binary Mixtures 0,5-0,5% wt *(In progress)*





✓ **Furfural reduces the H_2 yield observed for the other model compounds**

Their presence should be minimized before treating

To continue…

- **Possible removing of furfural (distillation?)**
- **Relation between raw biomass and bio-oil composition (AFB)**
- **Whole AFB (both synthetic and real)….**

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