Aqueous phase reforming of the waste-water derived from lignin hydrothermal liquefaction

From the simplicity of model compounds to the complexity of real streams

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Aqueous phase reforming

$$C_nH_{2y}O_n + nH_2O \leftrightarrow nCO_2 + (y+n)H_2$$

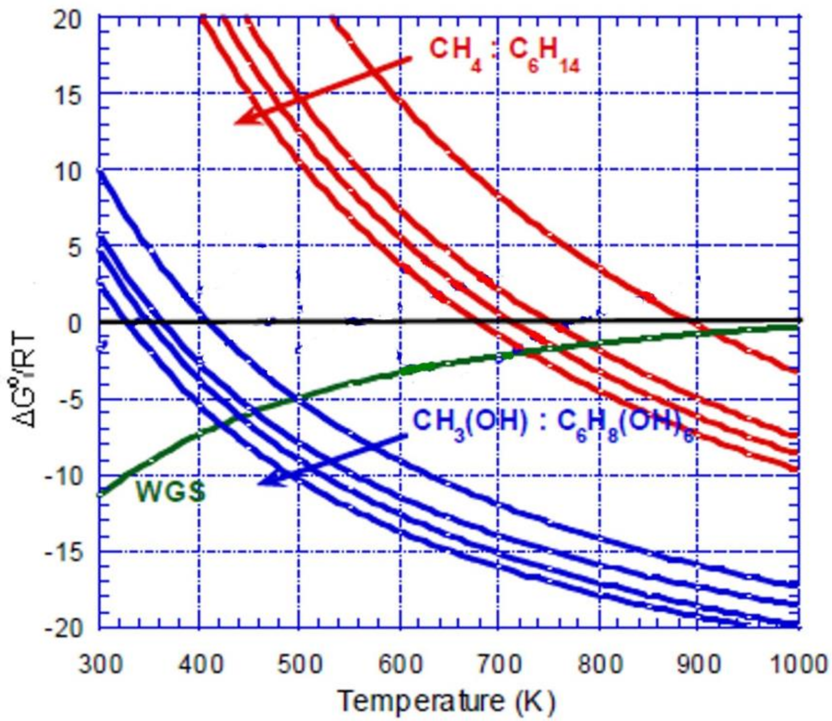
Most investigated compounds

Methanol

Ethylene glycol

Glycerol

Sorbitol



Production of H_2 from oxygenated hydrocarbons more thermodynamically favorable

Water gas shift reaction carried out in the same reactor

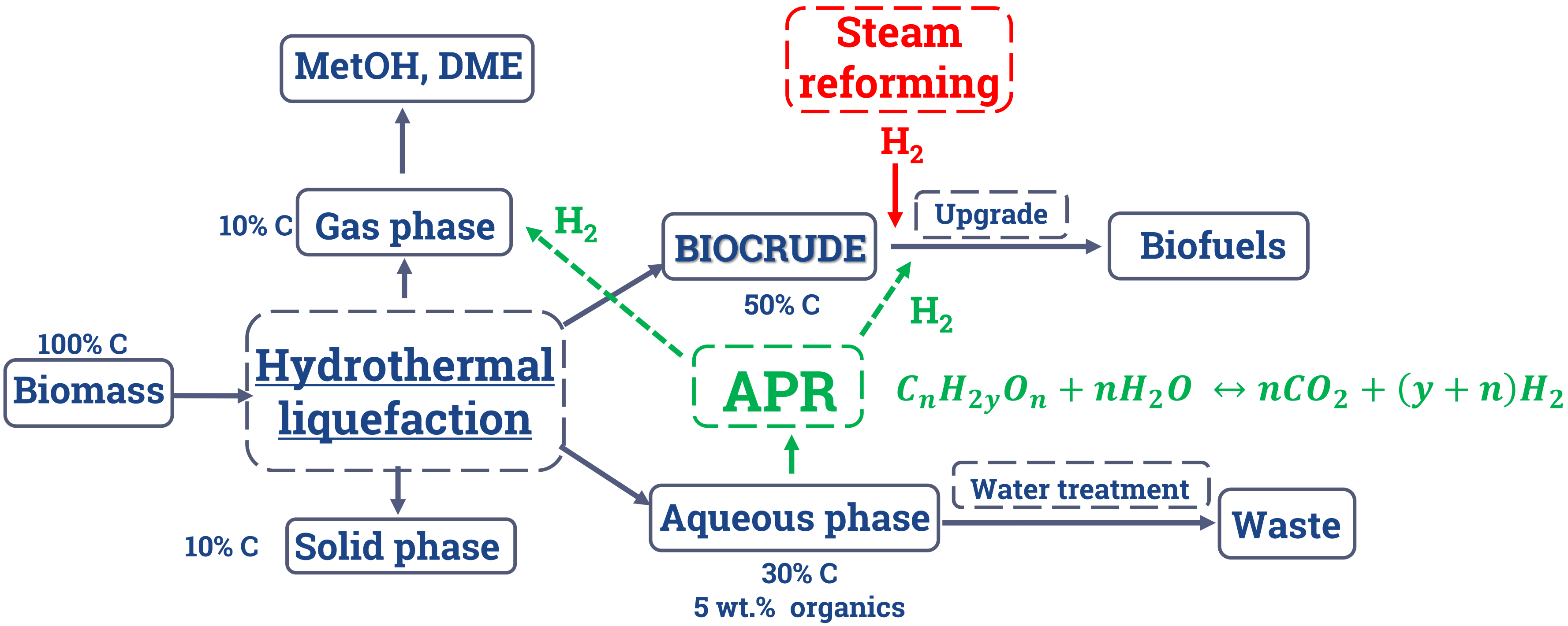
Energetic efficiency due to the prevention of water vaporization

Field of investigation

Aquatic biomass **Hydrothermal processes** **Bioethanol/biodiesel production**

R.R. Davda et al., A review of catalytic issues and process conditions for renewable hydrogen and alkanes by aqueous-phase reforming of oxygenated hydrocarbons over supported metal catalysts, 2005

Hydrothermal liquefaction

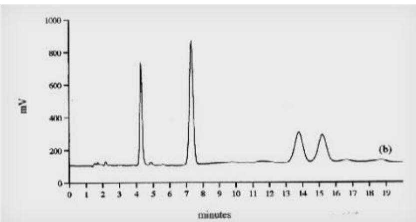


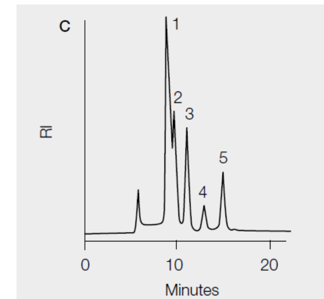
An important fraction of C is lost in the aqueous phase

The organics are present in a diluted solution

Experimental activity: methods

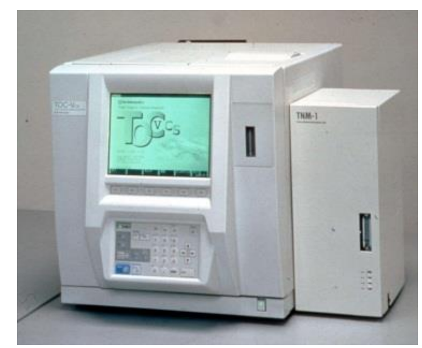
Liquid phase composition



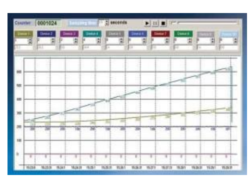


Gas phase composition

TOC of liquid phase



Catalyst Recovery and C content determination with TGA;
Catalyst analysis: BET, TGA, XRD, FT-IR

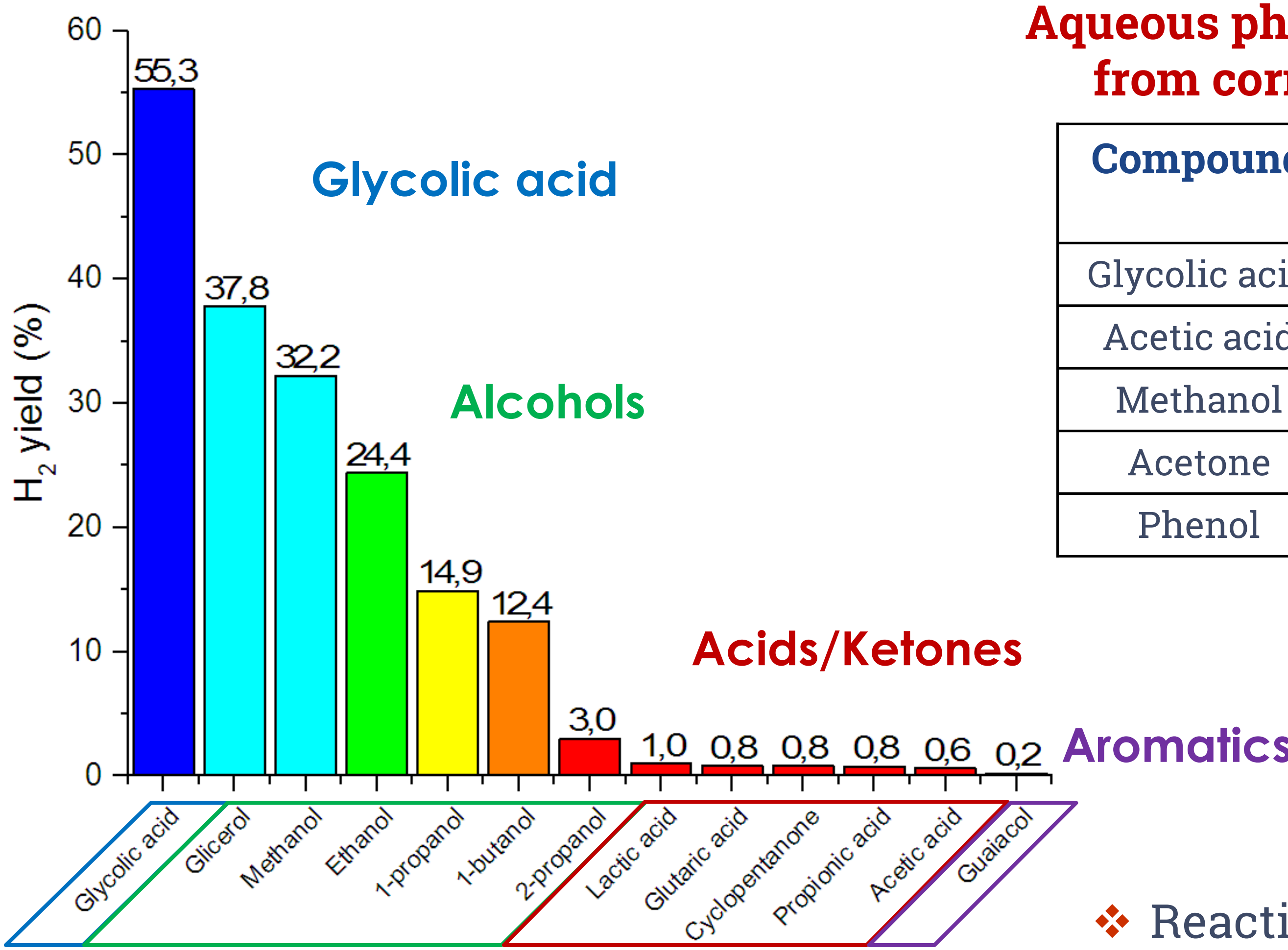


T, P real-time Monitoring

Experimental activity: APR with Pt/C

- Reaction volume: 75 ml
- Substrate concentration: 0.3 and **0.9 wt.% C** (≈ 1 and 3 wt.% of organics)
- Catalyst: **5wt% Pt/Carbon**; 0,375 g, i.e. 5 g/l or 0,5 wt.%
- Reaction time: 0h-8h
- Reaction temperature: 230-250-**270°C**
- APR Performance parameters: $C_nH_{2y}O_n + nH_2O \leftrightarrow nCO_2 + (y+n)H_2$
  - **Carbon to Gas conversion (%):** $100 * \frac{C_{gas}}{C_{feed}}$
  - **H_2 yield APR (%):** $100 * \frac{(H_2)_{gas}}{(y+n) * \text{substrate molarity}_{feed}}$
  - H_2 gas distribution selectivity (%): $100 * \frac{(H_2)_{gas}}{(H_2 + 2*CH_4 + 3*C_2H_6 + 4*C_3H_8)_{gas}}$
  - H_2 selectivity APR (%): $100 * \frac{(H_2/CO_2)_{gas}}{((y+n)/n)_{APR}}$

Results: APR with Pt/C with model compounds



Aqueous phase composition from corn stover HTL[1]

Compound	Concentration (wt.%)
Glycolic acid	1.7-1.8
Acetic acid	0.8-0.9
Methanol	0.4-0.6
Acetone	0.07-0.1
Phenol	0.03-0.05

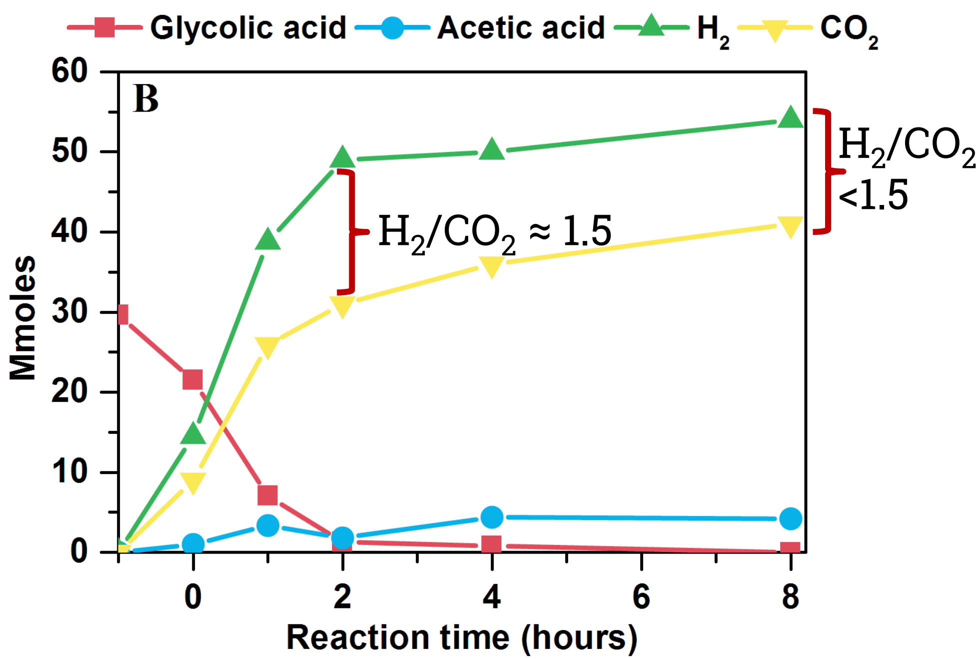
- Reaction conditions: 0.9 wt.%, 2h, 270°C

1. E. Panisko et al, Biomass and Bioenergy. 74 (2015)

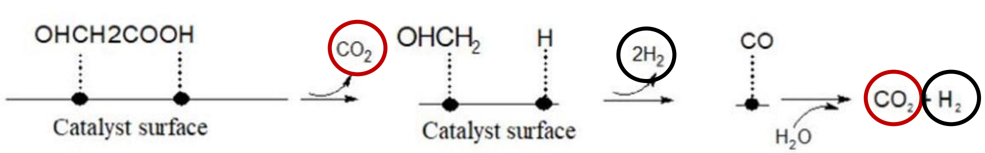
Results: APR with Pt/C with model compounds

Influence of time ❖ Reaction conditions: 0.9 wt.%, 270°C, single compounds

APR of Glycolic acid

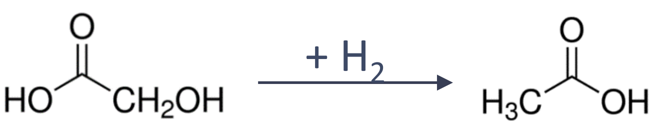


APR



Glycolic acid

Secondary reaction



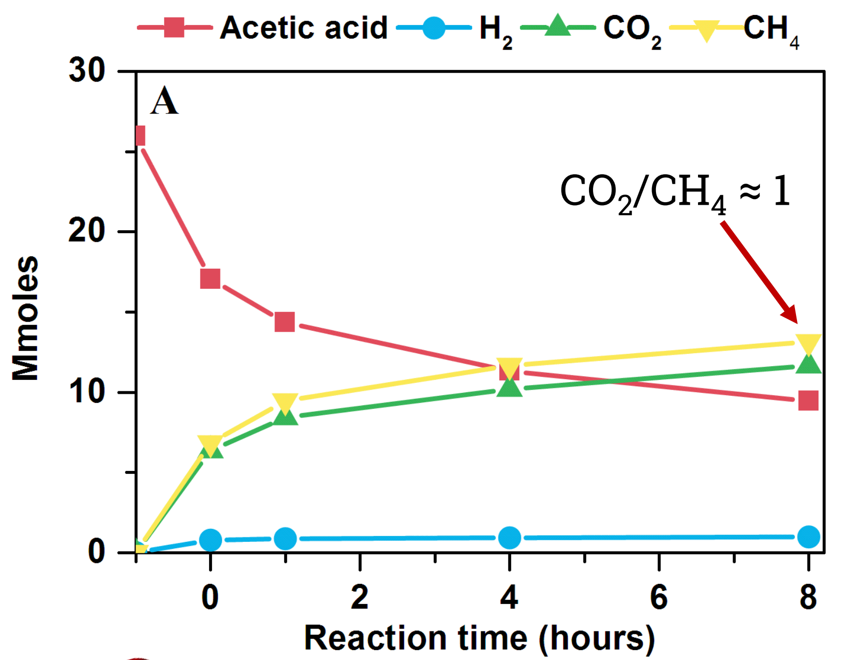
Glycolic acid **Acetic acid**

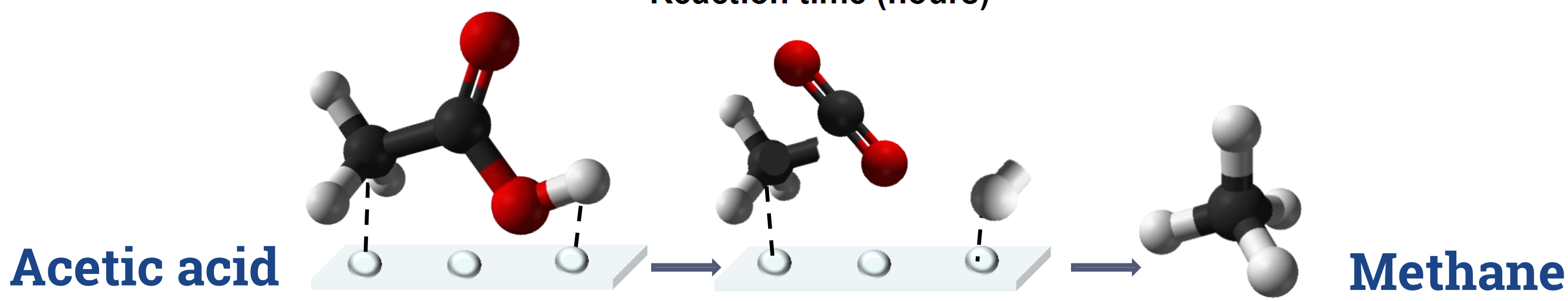
Results: APR with Pt/C with model compounds

Influence of time

- Reaction conditions: 0.9 wt.%, 270°C, single compounds

APR of Acetic acid

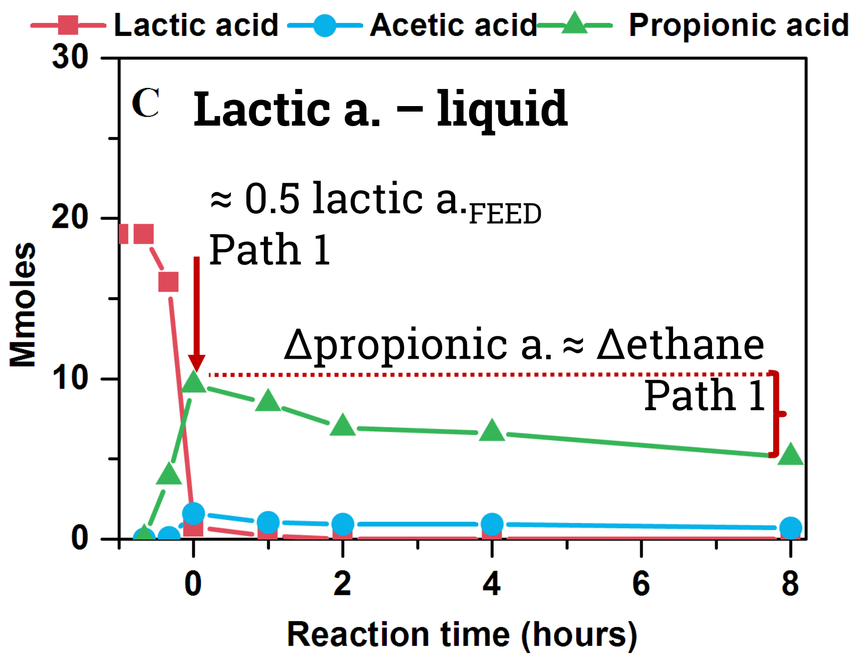


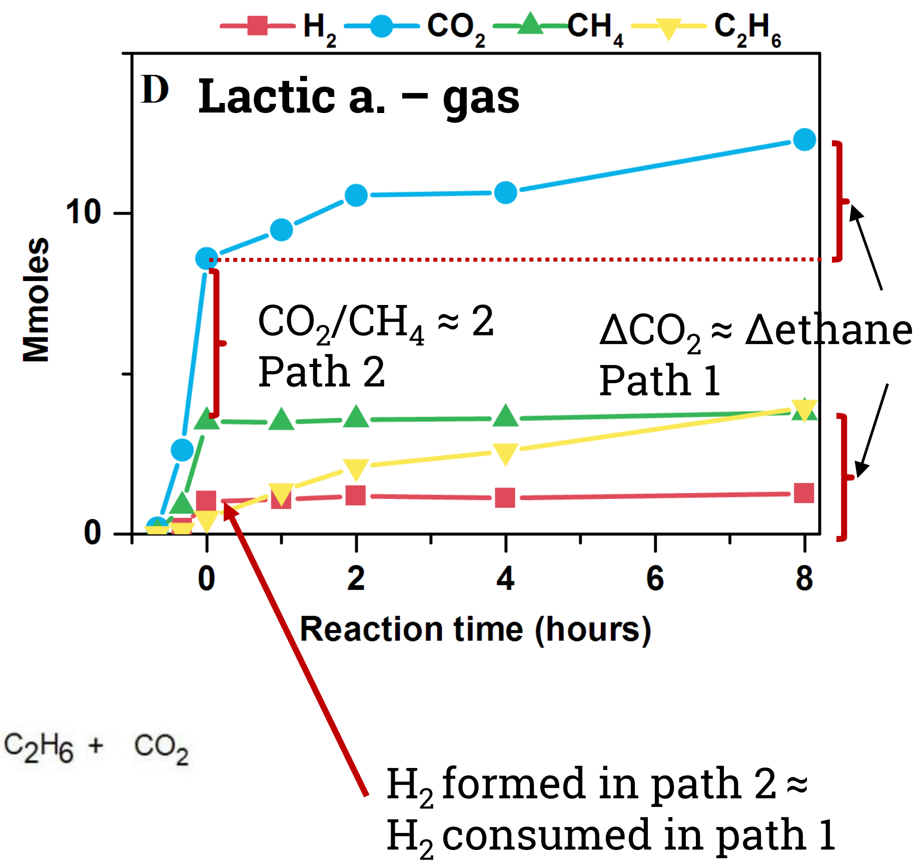


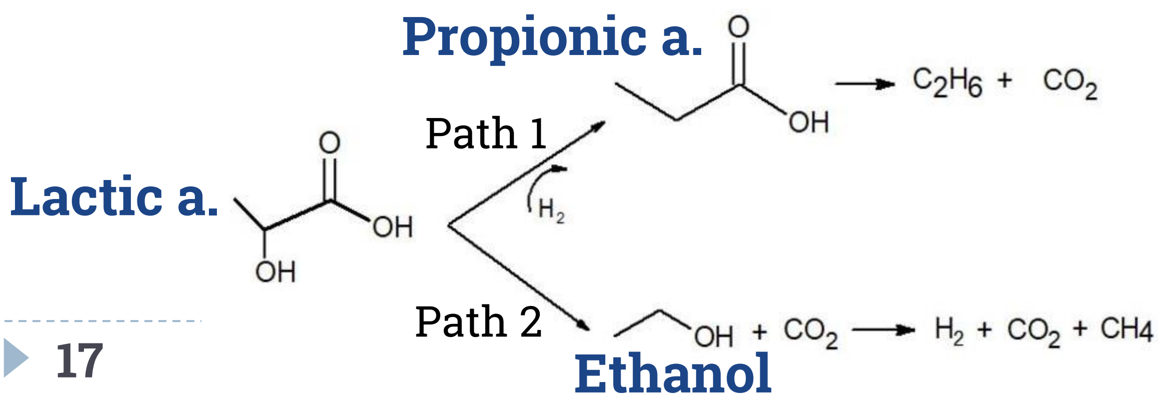
Results: APR with Pt/C with model compounds

Influence of time

❖ Reaction conditions: 0.9 wt.%, 270°C, single compounds





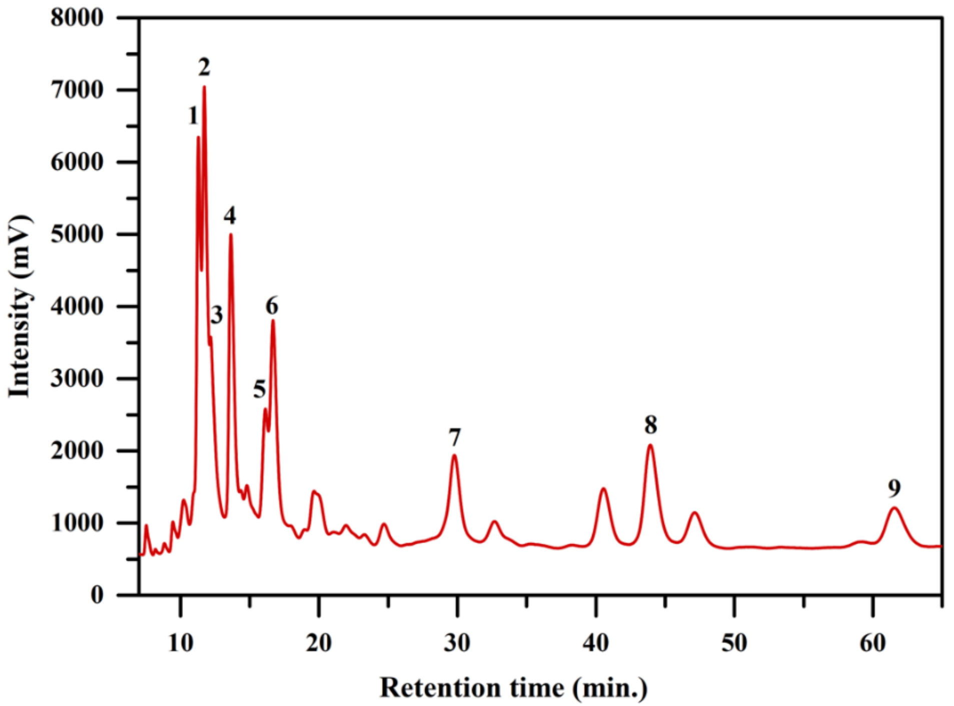


Results: APR with Pt/C with lignin-HTL waste waters

Characterization

HPLC chromatograms of the **HTL-AP**:
1: glycolic acid, 2: lactic acid, 3: glycerol, 4: acetic acid, 5: acetaldehyde, 6: methanol, 7: catechol, 8: phenol, 9: guaiacol.

Sample obtained with HTL at: 350°C, autogenous pressure, residence time of 10 min, dry lignin-rich coproduct to water ratio of 10% by weight

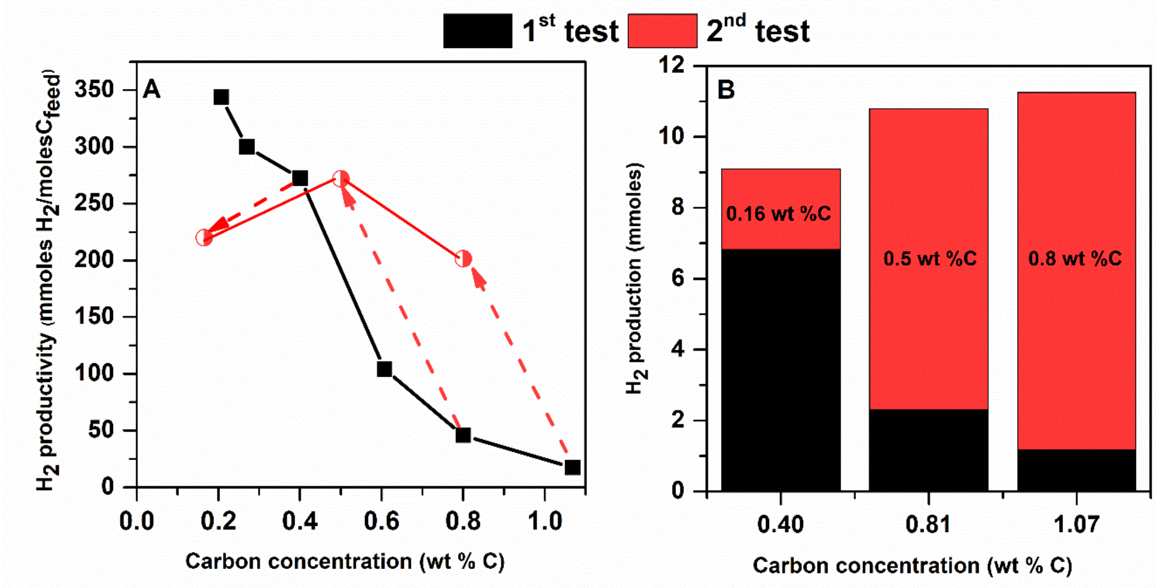


	Carbon weight concentration (wt % C)						Inorganic species (ppm)					
Sample	Glycolic	Lactic	Acetic	Methanol	Glycerol	Phenolic compounds	Na	K	Ca	S	P	TOC (mgC/L)
HTL-AP	0.047	0.112	0.083	0.138	0.029	0.116	518	281	13	116	11	11558

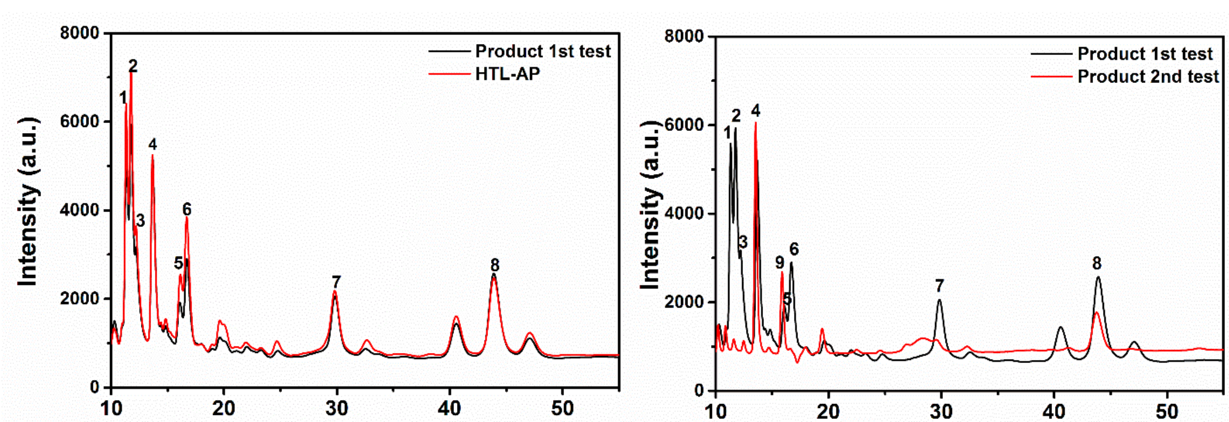
Results: APR with Pt/C with lignin-HTL waste waters

Influence of concentration

❖ Reaction conditions: 2h, 270°C,~1wt.% C, **HTL-AP**



1^{st} test with decreasing H_2 production *vs* initial concentration (not only yield!)



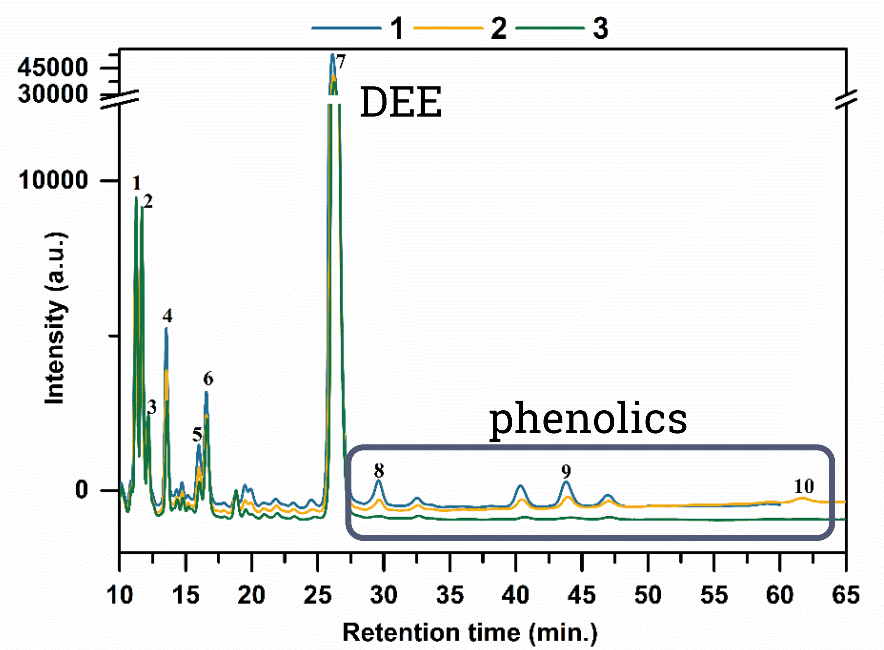
2^{nd} test with the same residual aqueous feedstock but a fresh catalyst

Results: APR with Pt/C with lignin-HTL waste waters

Characterization

HPLC chromatograms of the **HTL-AP**:
1: glycolic acid, 2: lactic acid, 3: glycerol, 4: acetic acid, 5: acetaldehyde, 6: methanol, 8: catechol, 9: phenol, 10: guaiacol.

Treated HTL-AP 1-2-3: selective removal of phenolic compounds with DEE (7).
* TOC includes residual DEE



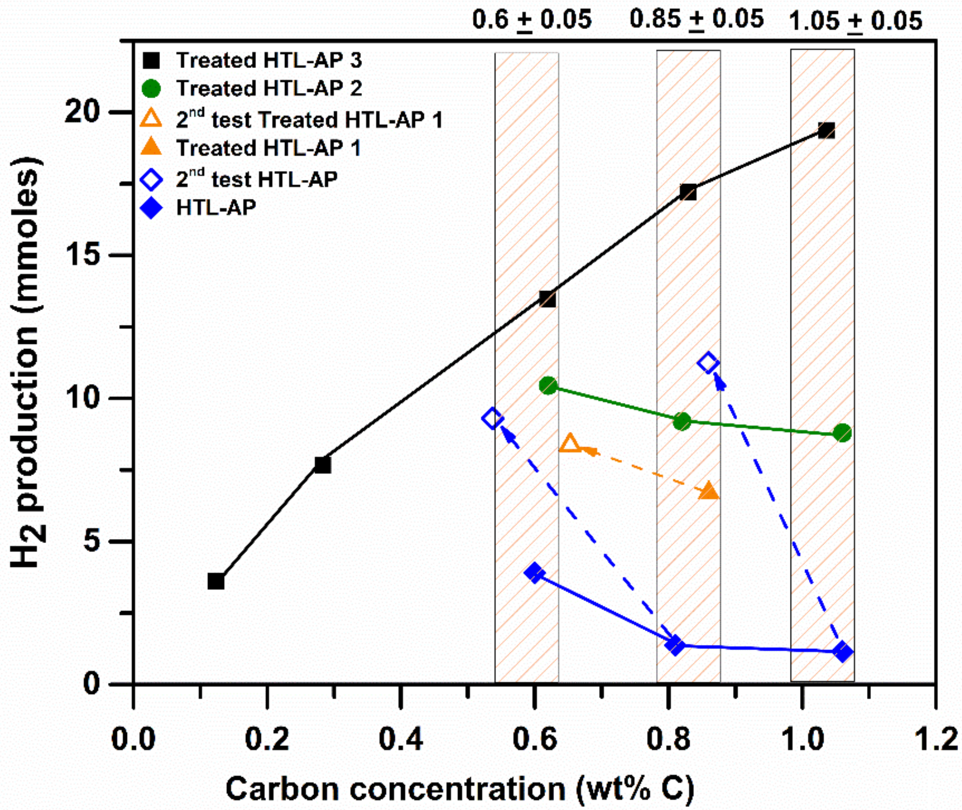
Sample	Carbon weight concentration (wt % C)						Inorganic species (ppm)					TOC (mgC/L)
	Glycolic	Lactic	Acetic	Methanol	Glycerol	Phenolic compounds	Na	K	Ca	S	P	
HTL-AP	0.047	0.112	0.083	0.138	0.029	0.116	518	281	13	116	11	11558
Treated HTL-AP 1	0.049	0.102	0.078	0.124	0.022	0.056	190	140	15	19	1	10810*
Treated HTL-AP 2	0.051	0.109	0.051	0.099	0.020	0.017	n.a.	n.a.	n.a.	n.a.	n.a.	10540*
Treated HTL-AP 3	0.050	0.099	0.044	0.096	0.020	≈ 0	350	233	0	**53**	43	10358*

Mainly under the form of SO_4^{2-} from the step of cellulose acid hydrolysis

Results: APR with Pt/C with lignin-HTL waste waters

Influence of concentration and of phenolic compounds

❖ Reaction conditions: 2h, 270°C,0.9wt.% C, **HTL-AP and Treated HTL-AP 1-2-3**



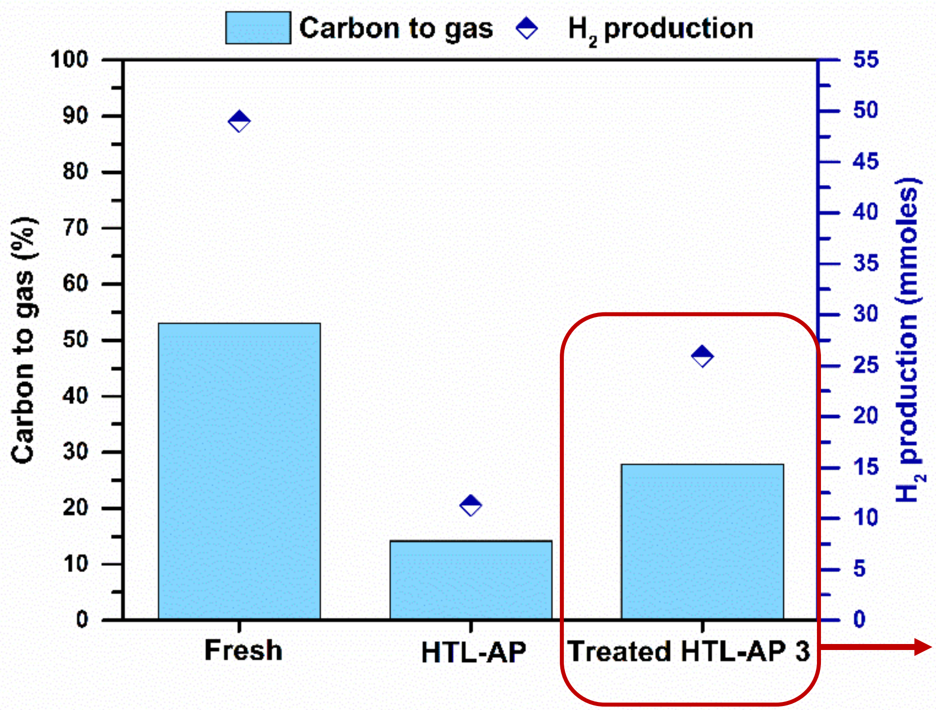
Positive effect towards H_2 production coming from the removal of phenolic compounds

Test	Hydrogen (mmoles)	Carbon dioxide (mmoles)	Methane (mmoles)
Synthetic mixture	19.5	16.1	2.0
Synthetic mixture + DEE	20.6	16.5	2.2

*** Checked negligible APR activity of DEE**

Results: APR with Pt/C with lignin-HTL waste waters

Catalyst stability ❖ Reaction conditions: 2h, 270°C, 0.9wt.% C, **glycolic acid**



Test with exhaust catalysts after a test with HTL-AP and HTL-AP3 (without phenolic compounds)

Pore plugging and Pt inaccessibility not fully prevented by DEE.

In addition, other deactivation mechanisms could be present (i.e. S)

Sample	BET surface area (m^2/g)	Pore Volume (cm^3/g)	Average pore size (nm)
Fresh	923	0.632	5.1
HTL-AP 0.8% C	195	0.344	5.7
HTL-AP 1.1% C	216	0.361	5.6
HTL-AP 1.1% 2nd test	430	0.480	5.2
Treated HTL-AP 3 0.8% C	410	0.471	5.3

Concluding remarks

- New classes of compounds were challenged against APR, with Pt/Alumina and Pt/C catalysts
- Mixtures of compounds behaved differently than the single compounds tests
- Real waste waters from lignin HTL were investigated, evidencing strong deactivation phenomena
- The removal of the phenolic compounds seemed to reduce the fouling associated to these feedstock.

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Thank you all for your attention

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