

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

Samir Bensaid

This project has received funding from European Union's Horizon 2020 research and innovation programme under grant agreement n° 764675

Aqueous phase reforming

$C_n H_{2y} O_n + n H_2 O \leftrightarrow n C O_2 + (y+n) H_2$

Most investigated compounds

Methanol Ethylene glycol Glycerol Sorbitol



Field of investigation

Production of H₂ 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

Aquatic biomass

Hydrothermal processes

Bioethanol/biodiesel production

Hydrothermal liquefaction



An important fraction of C is lost in the aqueous phase

The organics are present in a diluted solution

3



Results: APR with Pt/C with model compounds



Heat

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, 2 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



Retention	time	(min.)
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	Carb	on we	eight o	concent	ration (wt % C)	Ino	rgani	ic spe	cies (ppm)	
Sample	Glyc olic	La cti c	Ace tic	Meth anol	Glyc erol	Phenol ic compo unds	Na	K	Ca	S	Ρ	TOC (mgC/ L)
HTL-AP	0.04 7	0.11 2	0.0 83	0.138	0.029	0.116	518	281	13	116	11	11558



6

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

Influence of concentration

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





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



	Carbon weight concentration (wt % C)				Inorganic species (ppm))			
Sample	Glycolic	Lactic	Acetic	Methanol	Glycerol	Phenolic compounds	Na	K	Ca	S	Р	TOC (mgC/L)
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*



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 H₂ 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% 2 nd test	430	0.480	5.2
Treated HTL-AP 3 0.8% C	410	0.471	5.3



Results: continuous APR of lignin-HTL waste waters

Continuous reactor testing



- Substrate concentration: 1 wt.% (≈ 0.3 wt.% C)
- Catalyst: 5wt% Pt/Carbon; 1 g_{cat}
- Reaction time: 0h-10h
- Reaction temperature & pressure: 270°C, 60 bar
- $\tau_{reactor} \approx 3.7 \min$
- WHSV = 0.36 $g_{substrate}/g_{cat}$ ·h
- Composition: Synthetic mixture and lignin-HTL waste waters

Effect of DEE-treatment and sulfur content ($\approx 40 \text{ ppm SO}_4^{-2-}$)

Results: continuous APR of lignin-HTL waste waters

Effect of initial SO₄²⁻ contents



Synthetic mixture:

Compound	Wt.%
Glycolic a.	0.16
Lactic a.	0.19
Glycerol	0.05
Acetic a.	0.19
Methanol	0.42

Reported conversion of glycolic a., being representative of the deactivation phenomena

WHSV = 0.36 $g_{substrate}$ / g_{cat} ·h



12

Results: continuous APR of lignin-HTL waste waters

Synthetic vs real mixtures (untreated and DEE-treated)





13

Results: continuous APR of lignin-HTL waste waters

Treated real mixture for phenols and sulfur removal



Effect of sulfur removal



With the almost complete removal of sulfates, the remaining unreactive molecules partially saturate the active sites, yet not irreversibly, thus reducing the activity but also allowing to have a constant conversion.

WHSV = 0.1 $g_{substrate}/g_{cat}$ ·h



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
- Acid biomass hydrolysis leaves some sulfates in the HTL waste-waters, though highly deactivating the APR catalyst → strategies for SO42- removal must be implemented to reach stable operation (i.e. amberlite pre-adsorption bed).

THANK YOU

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FARRIKA

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Güssing Energy Technologie

Special thanks to phD

Pipitone (POLITO)

students G. Zoppi and G.

and to RE-CORD for the



ΚΗΙΜΠΠ