

Electrooxidation of the pyrolysis aqueous phase on boron-doped diamond electrodes

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AGENDA

- 1 Thermo-catalytic reforming technology – formation of the aqueous phase
- 2 Quantity and composition of the aqueous phase from sewage sludge
- 3 Wastewater parameters
- 4 Theory of electrooxidation
- 5 Electrooxidation results
- 6 Summary & Conclusion
- 7 Outlook

Thermo-catalytic reforming (TCR[®])

Formation of the aqueous phase

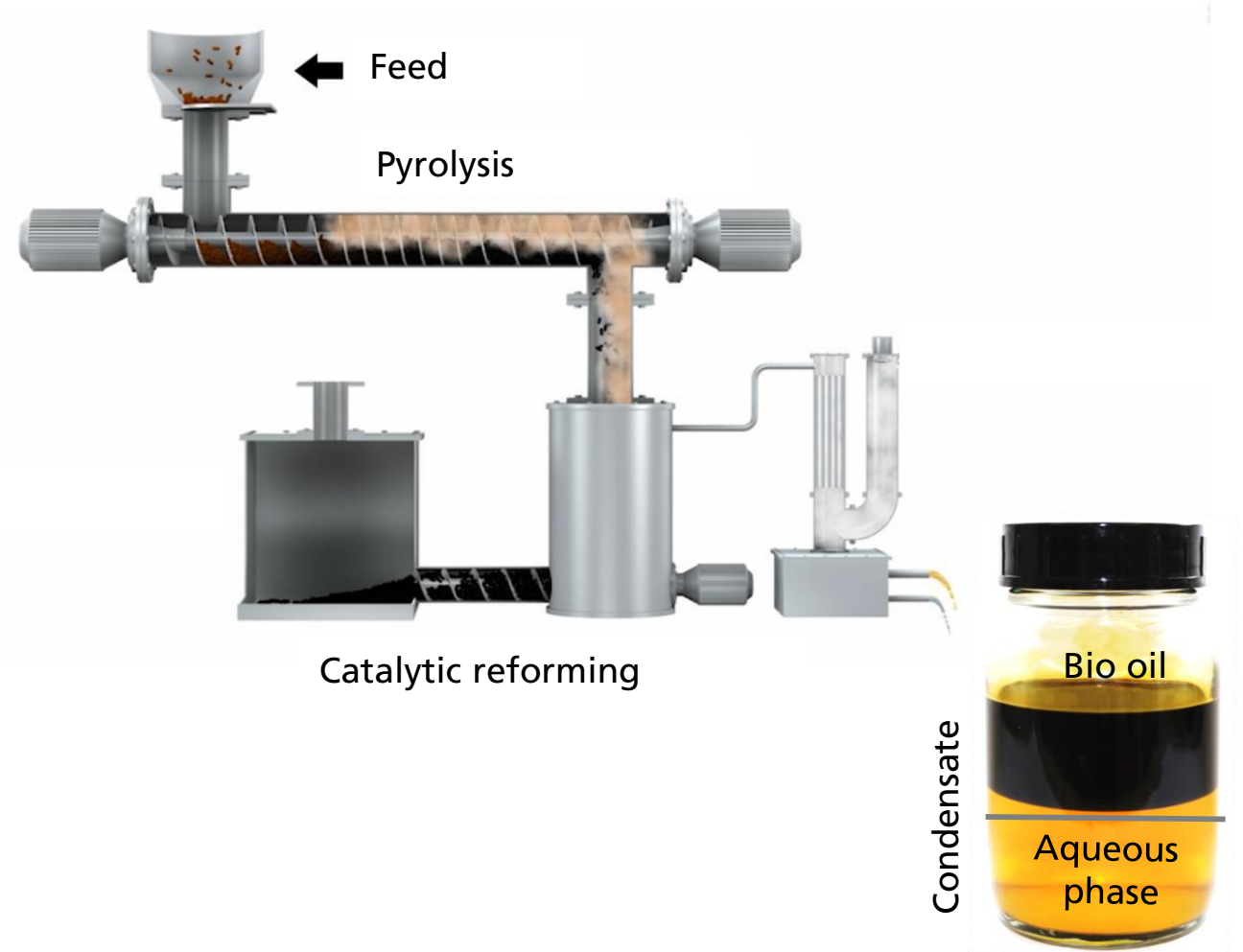
Formation due to:

- Initial moisture of feedstock
- Chemical reactions during conversion

Composition and quantity depend on:

- Initial moisture of feedstock
- Chemical composition of feedstock

For this study: Feedstock sewage sludge



Aqueous phase from sewage sludge

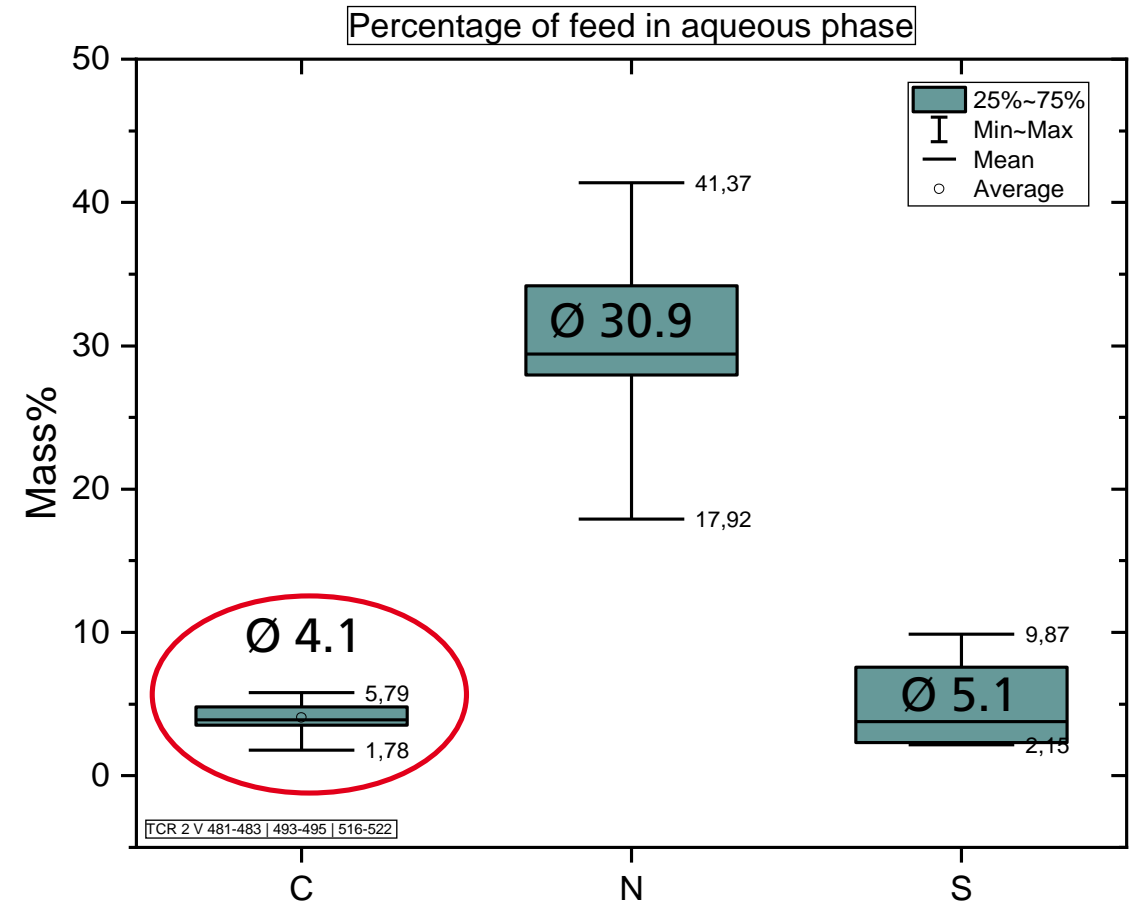
Composition and quantity

Elemental analysis of TCR[®] aqueous phase

| | C in m% | H in m% | N in m% | O in m% | S in m% | H ₂ O in m% |
|--------------------|---------|---------|---------|---------|---------|------------------------|
| Average | 6.41 | 2.55 | 8.55 | 9.73 | 0.23 | 72.54 |
| Median | 5.87 | 2.51 | 8.18 | 8.95 | 0.14 | 73.68 |
| Standard deviation | 1.30 | 0.51 | 1.46 | 2.15 | 0.12 | 4.08 |

Further characteristics of the aqueous phase

- Quantity: ~20 – 30 m% of feedstock
- Lower heating value: < 0.2 MJ/kg



Aqueous phase from sewage sludge

Wastewater parameters and carbon distribution

Wastewater parameter:

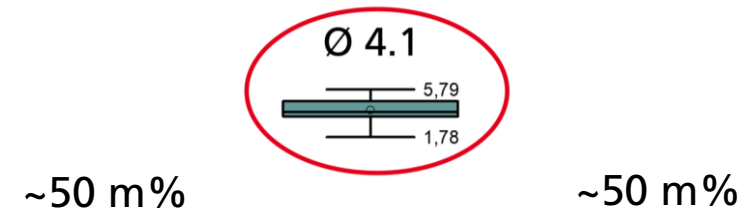
- Total organic carbon (TOC)
- Chemical oxygen demand (COD)

Typical organic compounds found in the aqueous phase:

| Chemical group | Typical representative |
|-------------------|------------------------|
| Carboxylic acids: | Acetic acid |
| Nitriles: | Acetonitrile |
| Azines: | Pyridine, Pyrazine |
| Azoles: | Pyrrole |
| Phenols | Phenol |

→ No solemn biological treatment possible

Total Carbon (TC)



Inorganic
Carbon (TIC)

Total Organic Carbon
(TOC)

→ 2 m% of aqueous phase as TOC
≙ 80.000 mg/l COD

~80x municipal wastewater

Electrooxidation

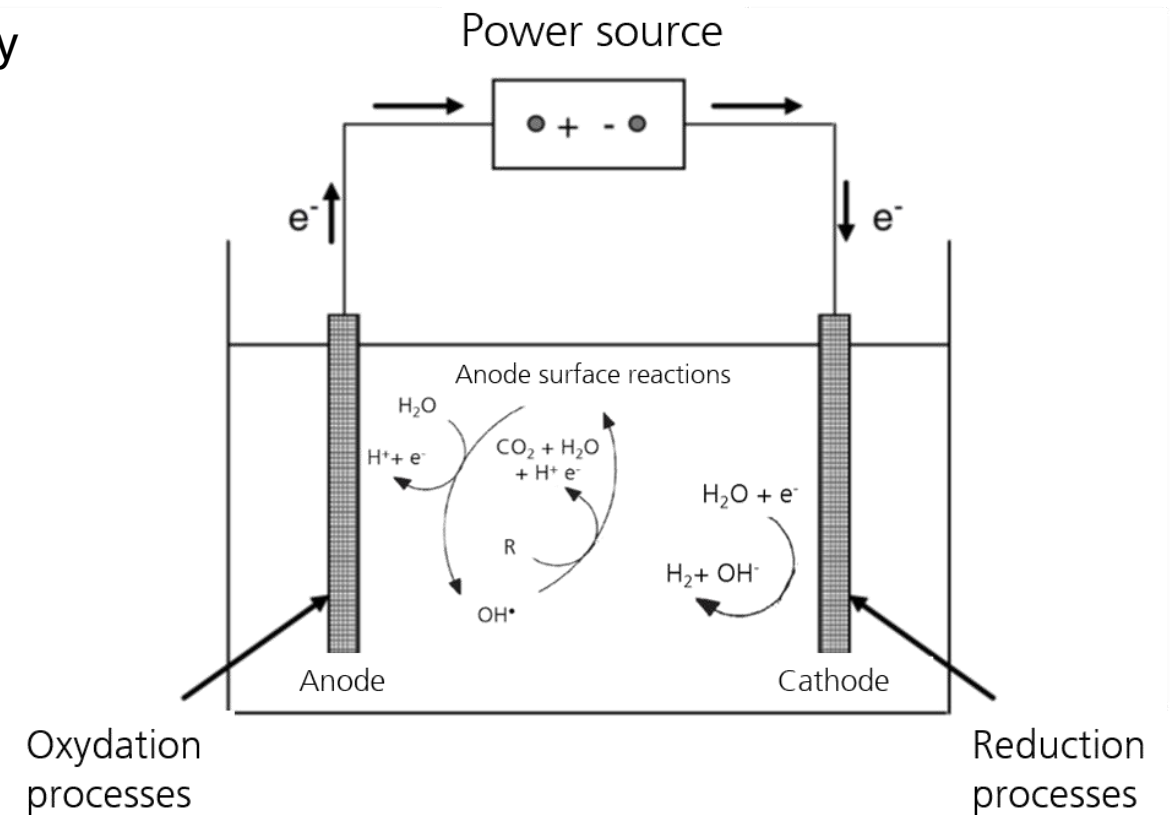
Theory and advantages

Theory

- Electrooxidation class of advanced oxidation processes (AOP's)
- In-situ production of oxidants through electricity
- Non selective in regards to organics

Advantages of boron-doped diamond electrodes:

- Chemical stable
- Highest overpotential towards oxygen
- Highest production yield of hydroxyl radicals



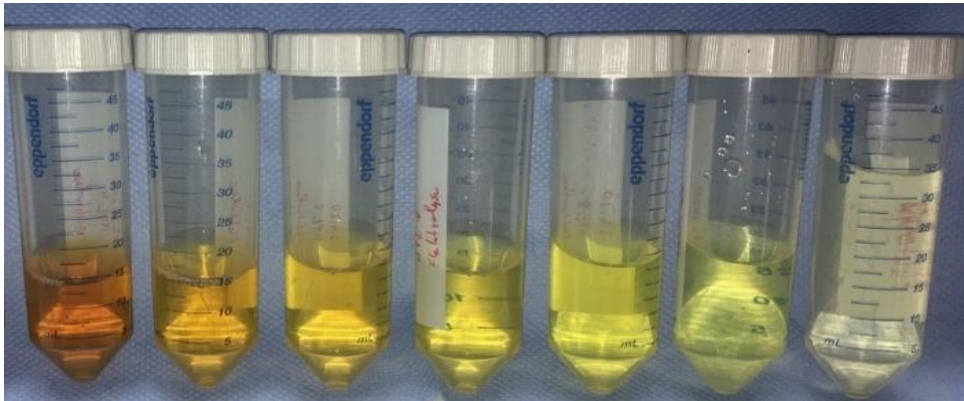
Electrooxidation

Model TCR[®] aqueous phase and COD results

Model TCR[®] aqueous phase

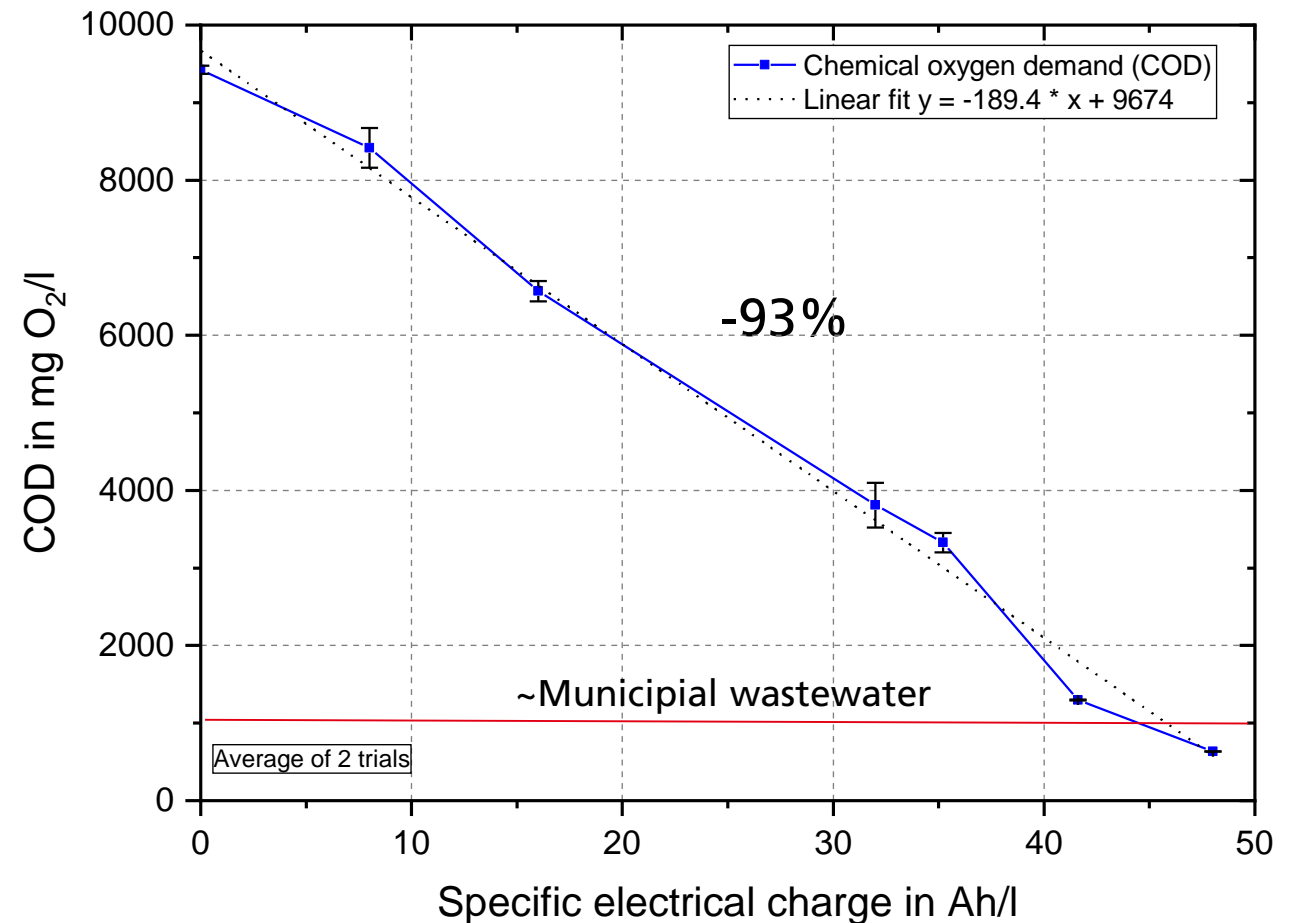
| | |
|-------------------------|--|
| COD | 10.000 mg/l |
| Added organic compounds | Acetonitrile, Acetic acid, Pyrrole, Pyridine, Phenol |

Colour reduction



Treatment duration →

COD reduction of aqueous phase due to electrooxidation



Electrooxidation

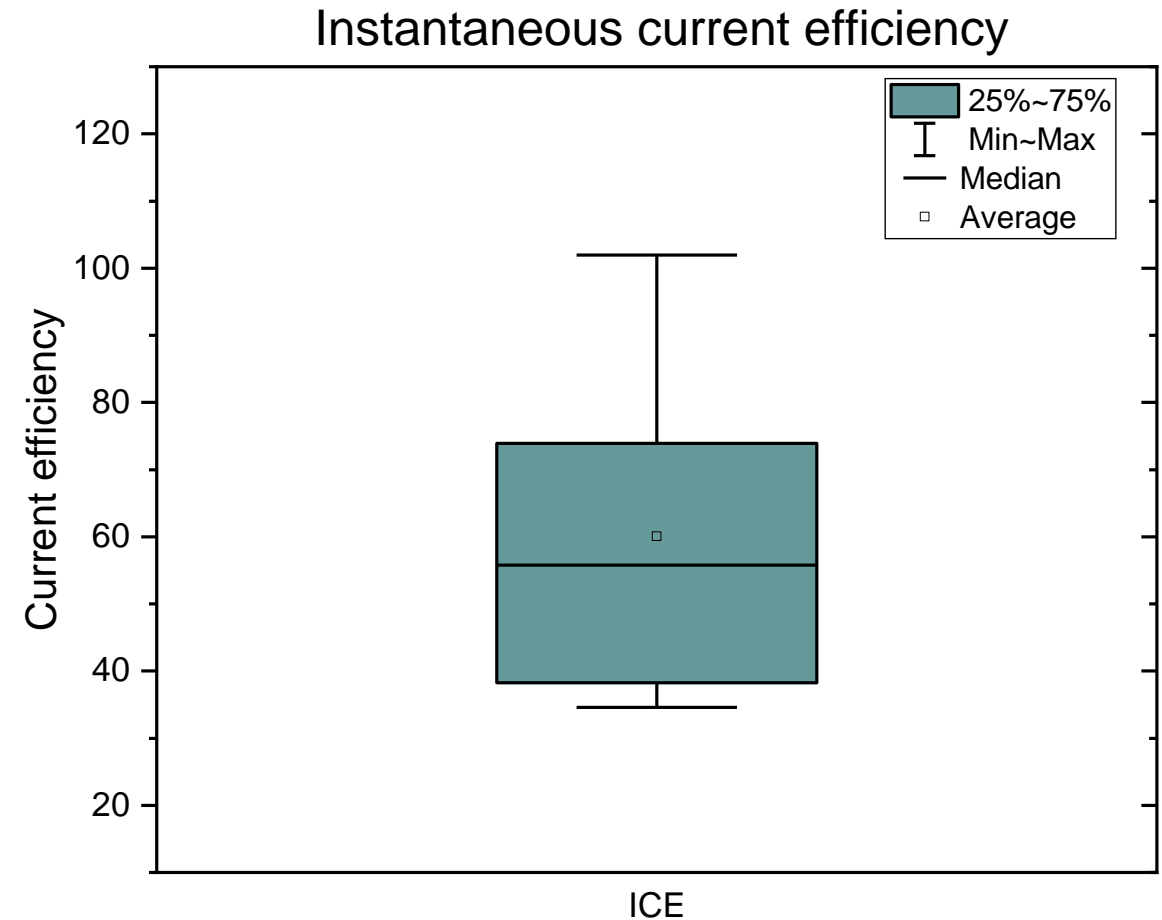
Energy efficiency in regards to the COD

Instantaneous current efficiency (ICE)

$$ICE_{COD} = \frac{FV}{8I} \frac{[(COD)_t - (COD)_{t+\Delta t}]}{\Delta t}$$

| Symbols and constants | |
|-----------------------|-----|
| Faraday constant | F |
| Volume of electrolyte | V |
| Applied Current | I |

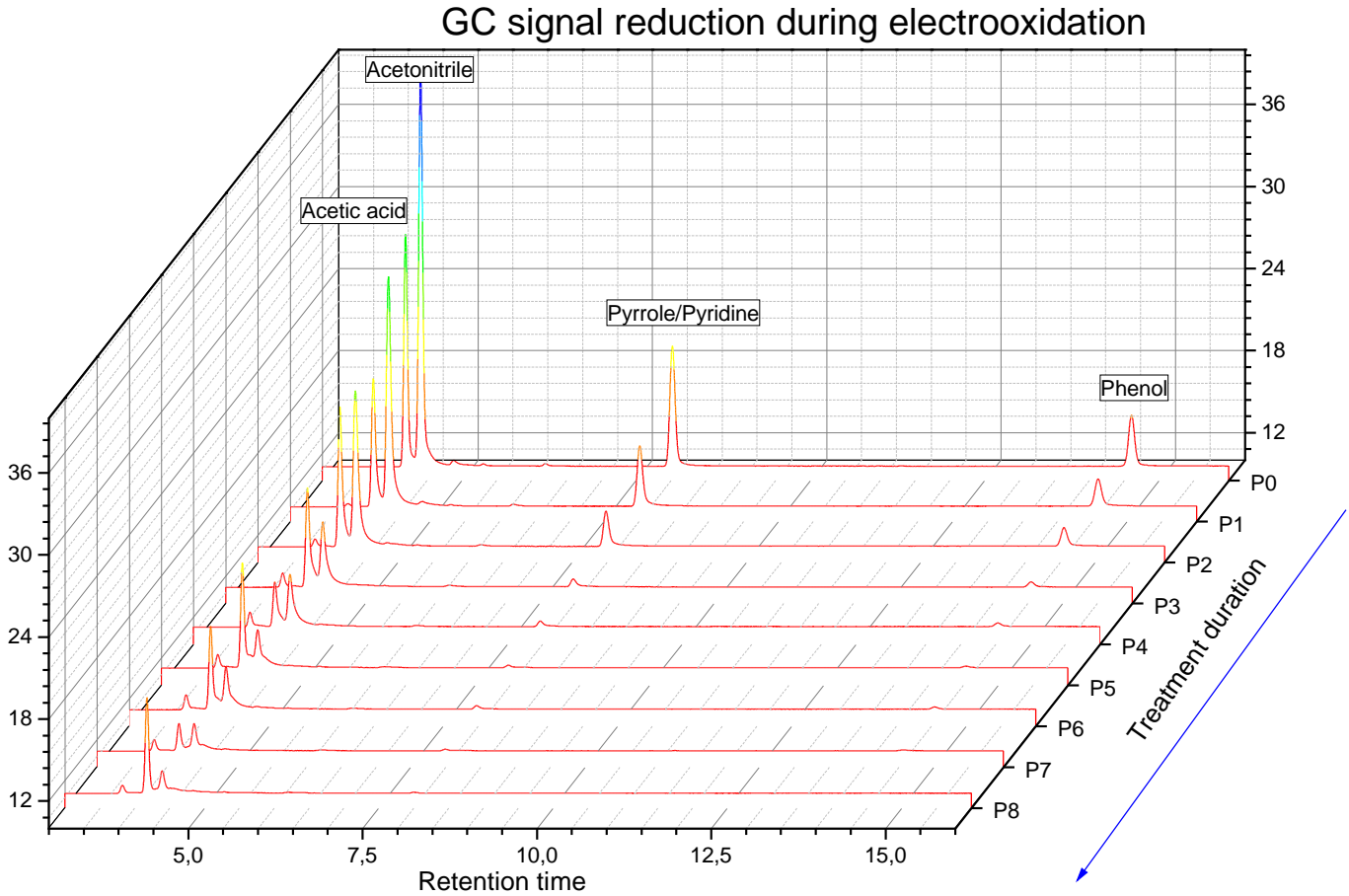
| COD results | |
|---|----------------------------|
| Theoretical maximum spec. COD reduction | 0.298 g _{COD} /Ah |
| Ø Specific COD reduction | 0.18 g _{COD} /Ah |
| Ø ICE | 60 % |



Electrooxidation

Gas chromatography results

| Compound | Achieved area reduction |
|------------------|-------------------------|
| Acetic acid | 84% |
| Acetonitrile | 88% |
| Pyrrole/Pyridine | >98% |
| Phenol | >96% |



Summary and Conclusion

- Thermo-catalytical reforming of biomass produces an aqueous phase
- In case of sewage sludge it has a low energy content and consists out of ~72 m% H₂O, 6.4 m% C
- About 50 % of this carbon is of organic nature consisting of various organic compounds
- The persistence of some of those compounds make a solemn biological treatment not possible
- Electrooxidation is suitable for reduction of those organic compounds (COD -93%, non-selective)
- The current efficiency for the model aqueous phase was ~ 0.18 g_{COD}/Ah equally to an ICE of 60%

Outlook

Whats next

- Testing of a real TCR[®] aqueous phase from sewage sludge
- Parameter variation in order to further increase the current efficiency
- Separation tests for evolving hydrogen

