# Characterization, purification and resource recovery of process water from Hydrothermal Carbonization

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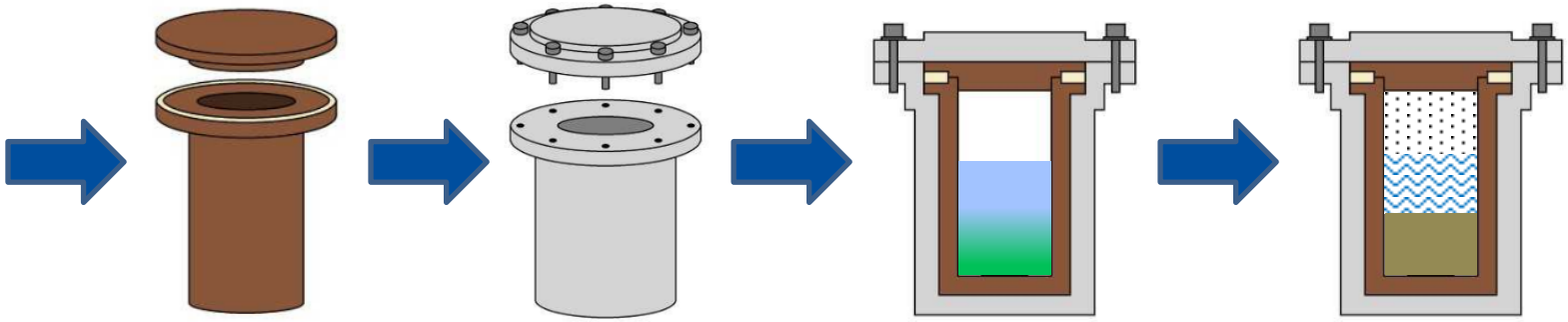
Technical Chemistry 1 - Photocatalysis & Sustainable Feedstock Utilization
19. July 2019

# Basics of Hydrothermal Carbonization (HTC)

water
+
biomass



hydrochar

process water

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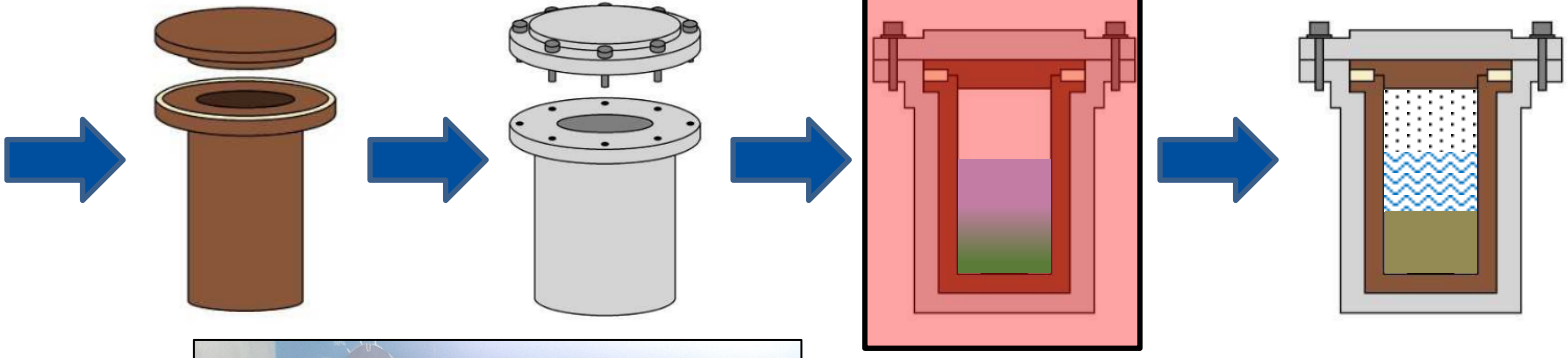
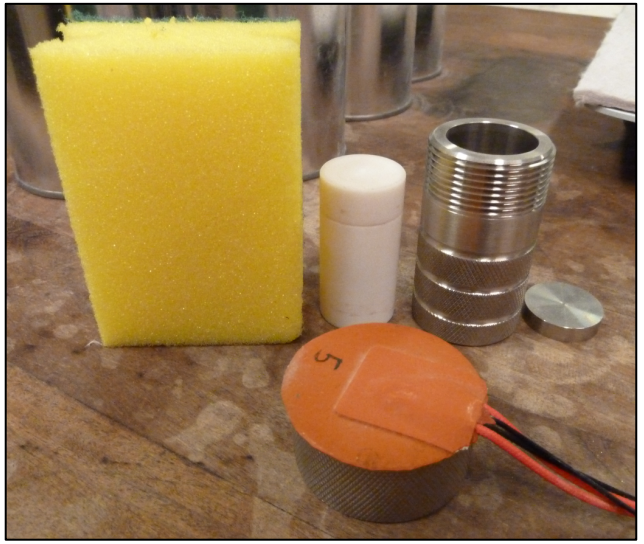



4–24 h
180–230 °C
20–50 bar



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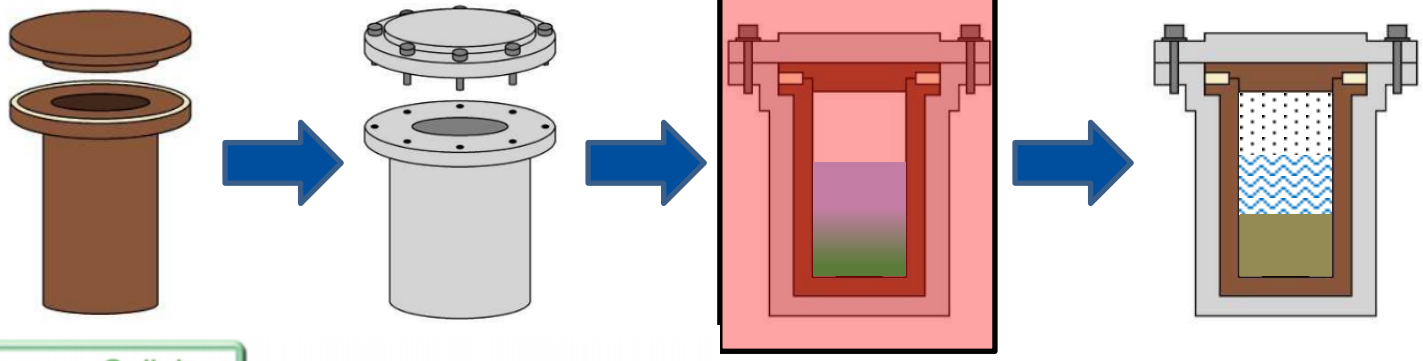
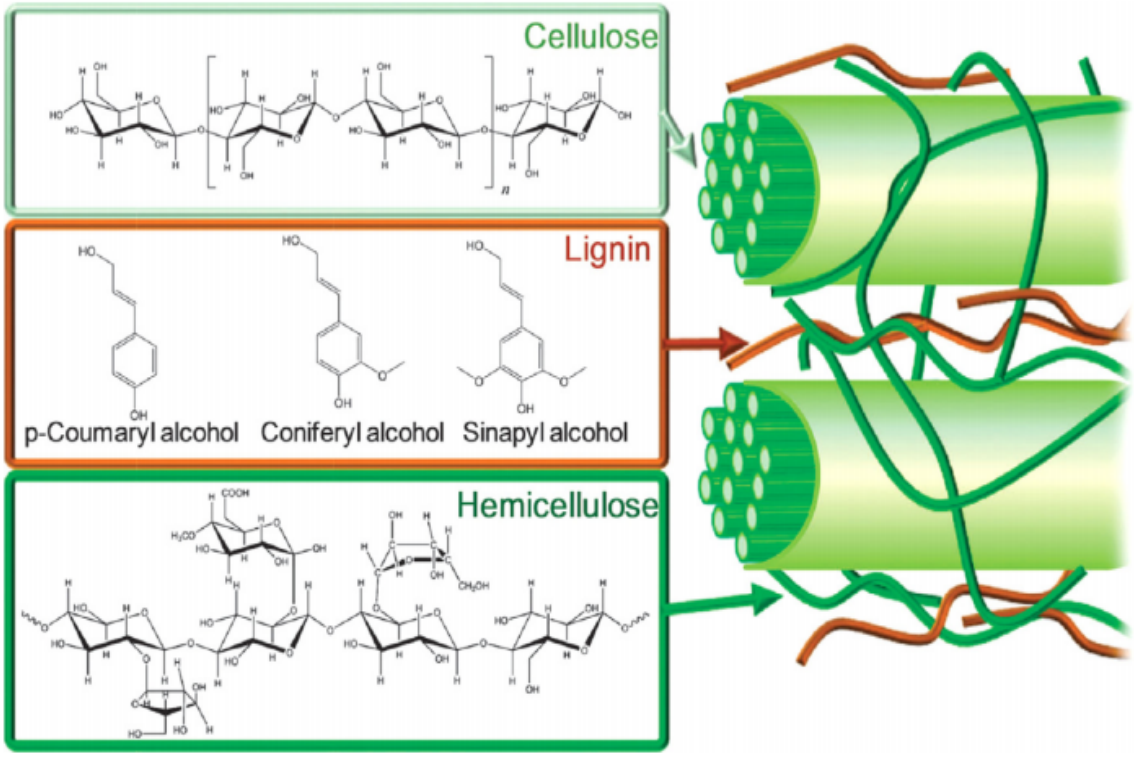





4–24 h
180–230 °C
20–50 bar

→ physical breaking of the structure due to high pressure

→ dissolving of the organic material with follow up reactions

Picture taken from: H. S. Kambo, A. Dutta, *Renewable and Sustainable Energy Reviews* **2015**, *45*, 359.

# Basics of Hydrothermal Carbonization (HTC)

polymerized hydrocarbons

value product

energetic use?

at best: neutral power efficiency

material utilization?

high potential, especially with post treatment

**main aims:**

**process water analysis**

**production of HMF**

**TOC degradation**

sugar derivatives; organic acids; phenols….

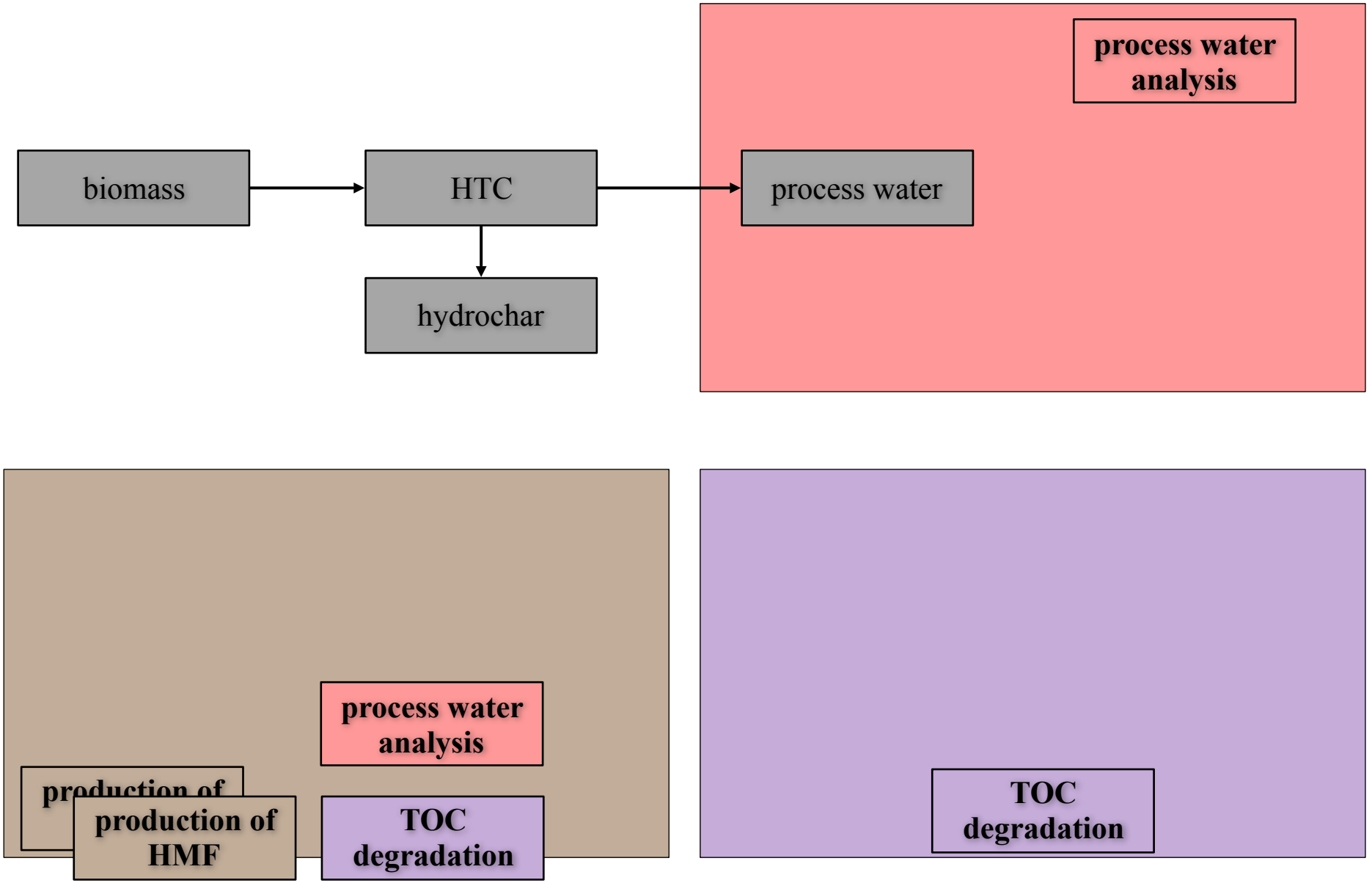
contaminated water

HTC-Water ca. 10.000 mg/l

algae cultivation ca. 1.000 mg/l

carp pond ca. 10 mg/l

# Overview


process water analysis
biomass
HTC
process water
hydrochar
process water analysis
production of HMF
TOC degradation
TOC degradation

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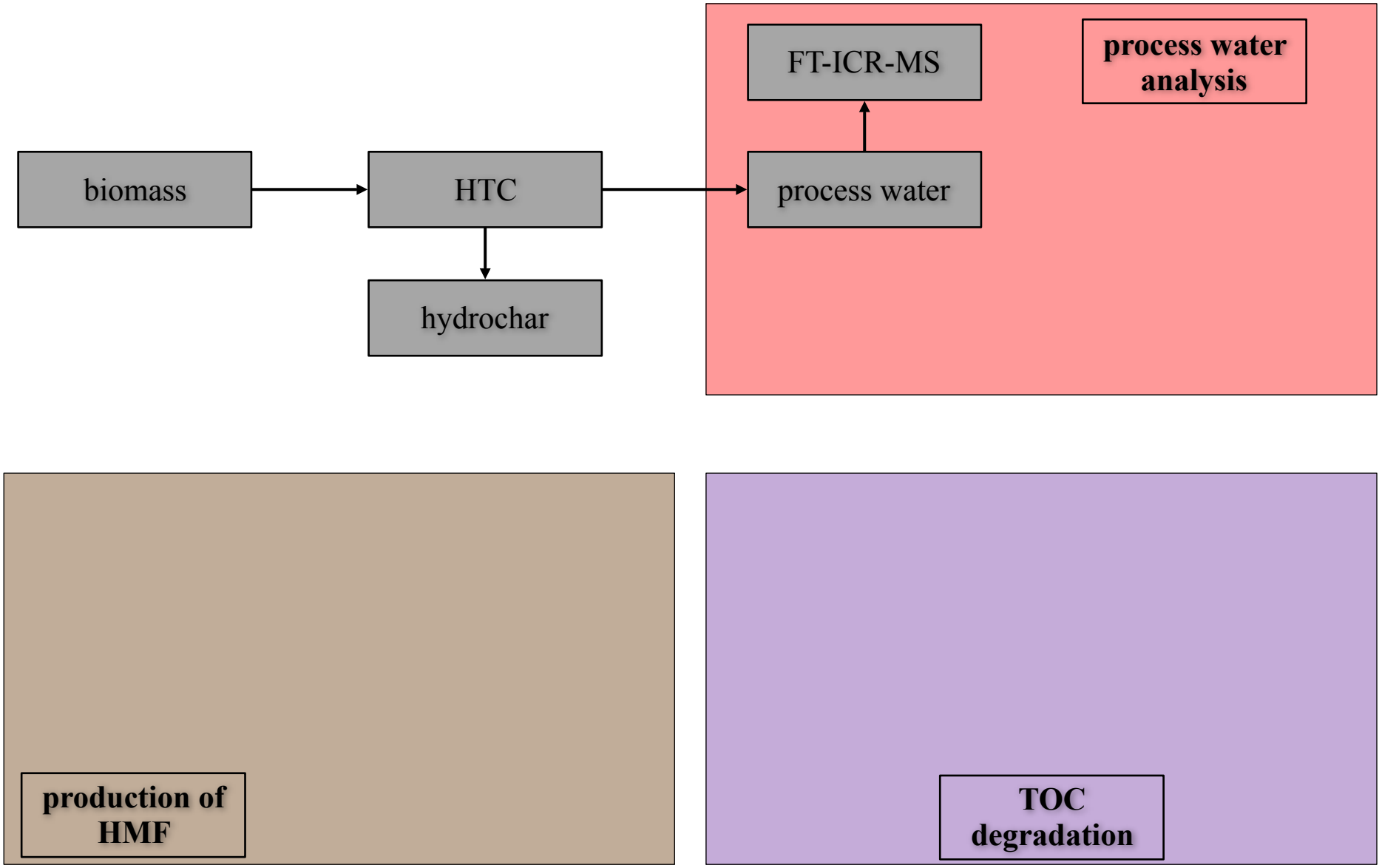
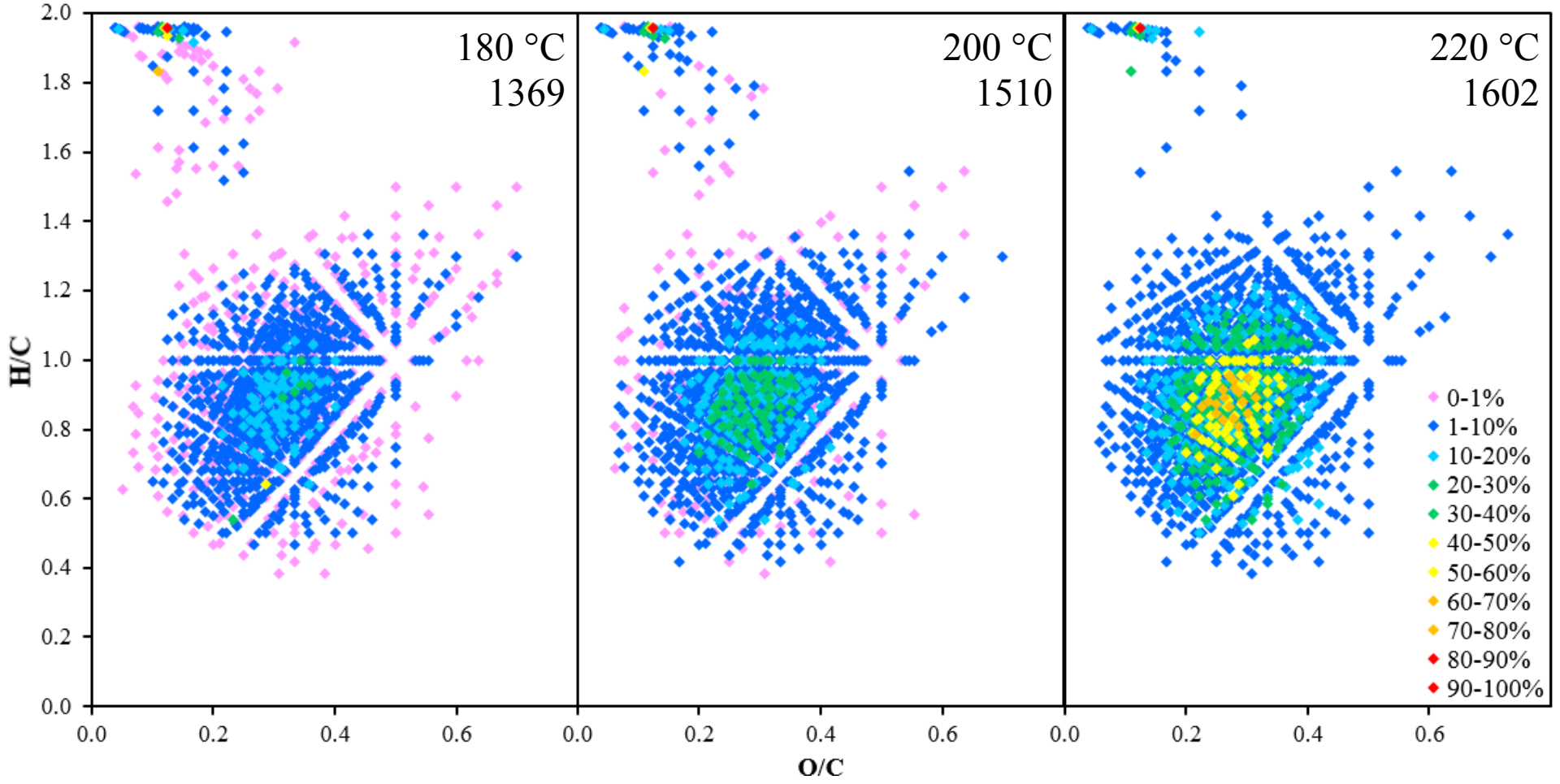
# Overview



# FT-ICR-MS: Van-Krevelen Diagram 3D

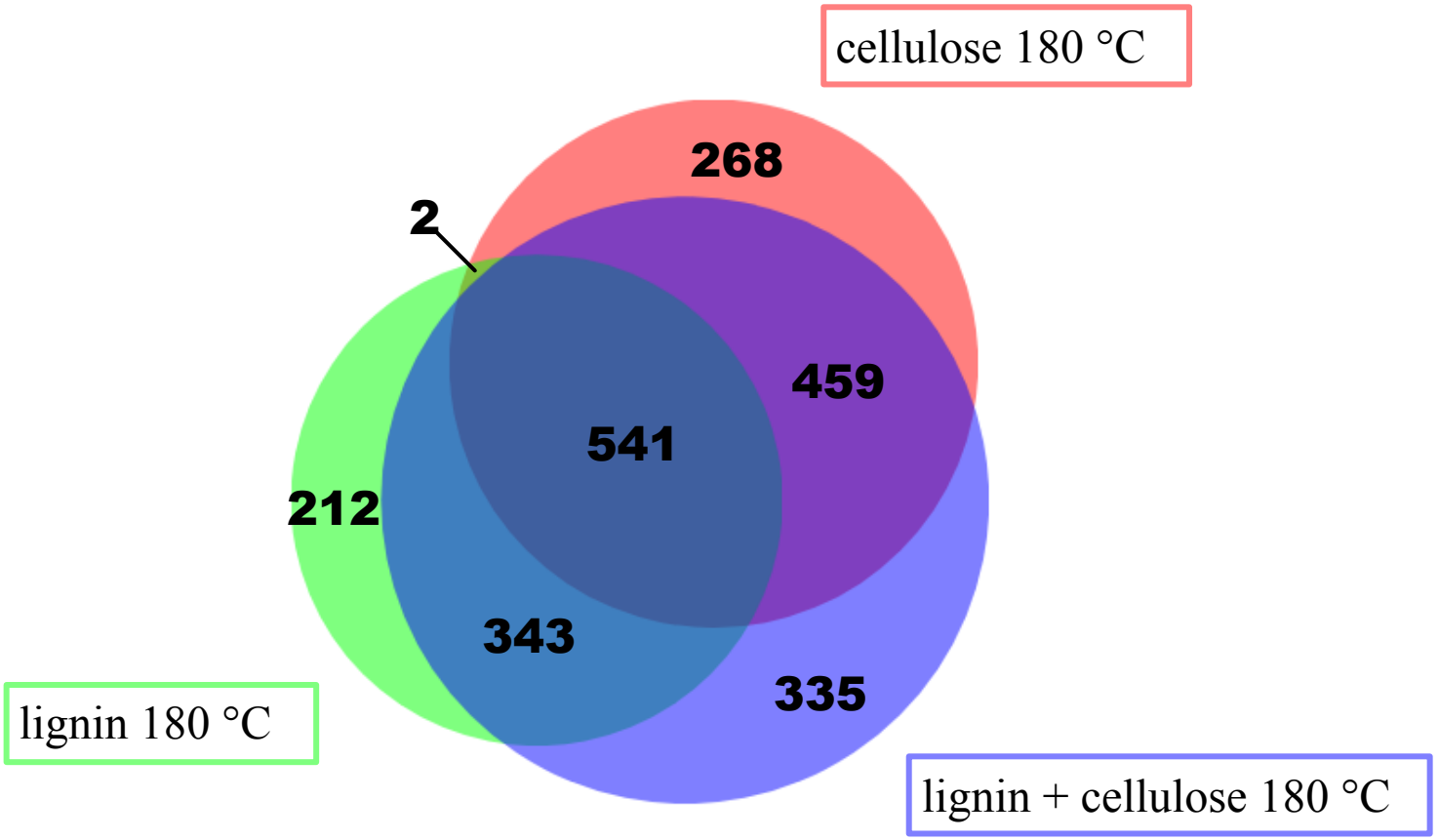
coconut shell powder 12 h, $O_xN_0S_0$




→ With higher temperature the number of compounds increases.

→ The distribution pattern of the signal intensities is concentrated towards the center.

# FT-ICR-MS: Interactions of lignin and cellulose




→ Interaction of lignin and cellulose compounds in two ways confirmed!

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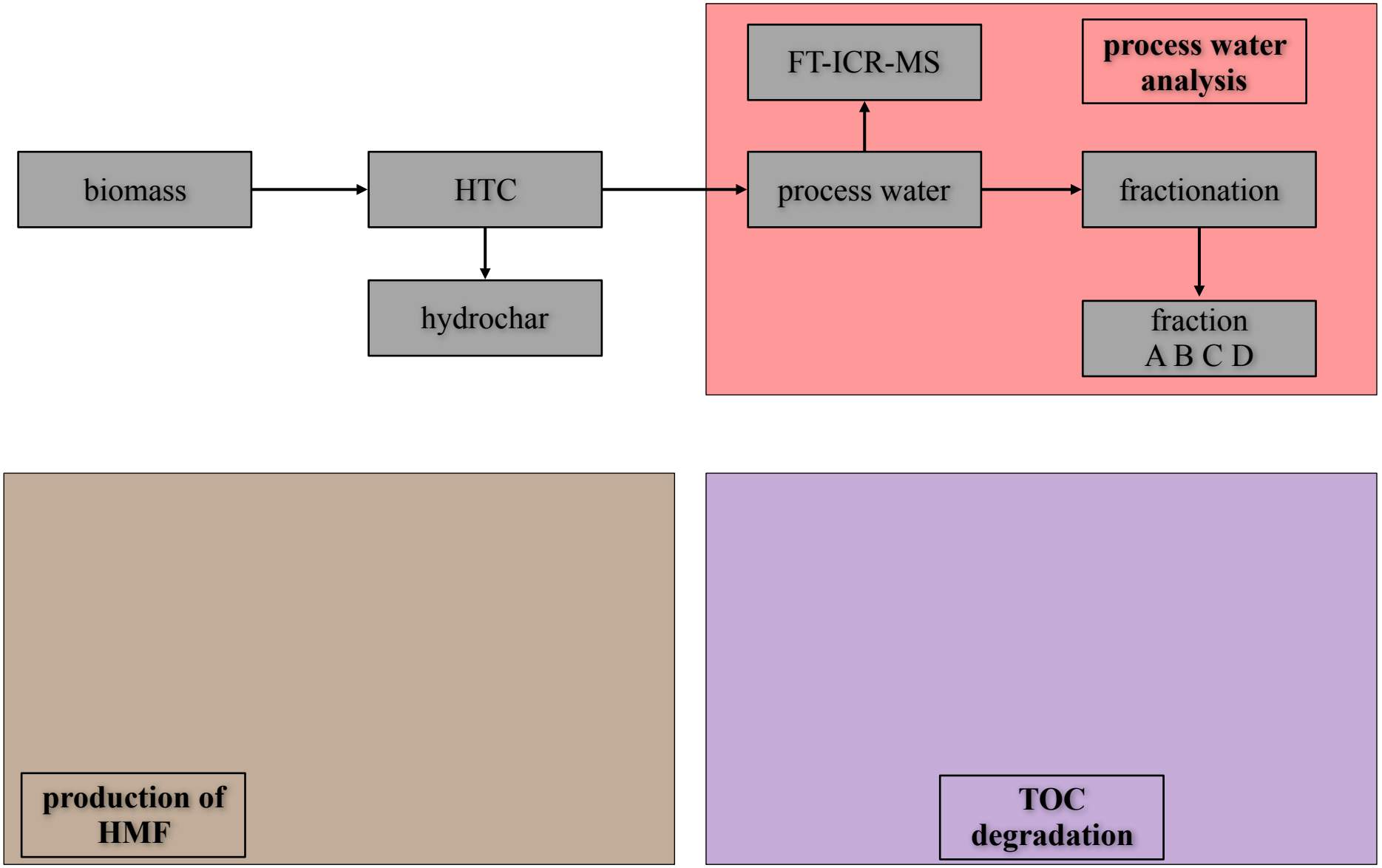
# Overview

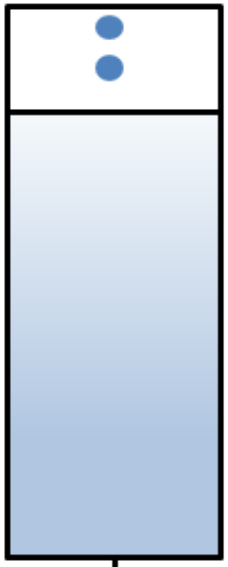


# Fractionation

40 ml hexane

60 ml hexane with 10 vol. % DCM

80 ml DCM with 10 vol. % MeOH

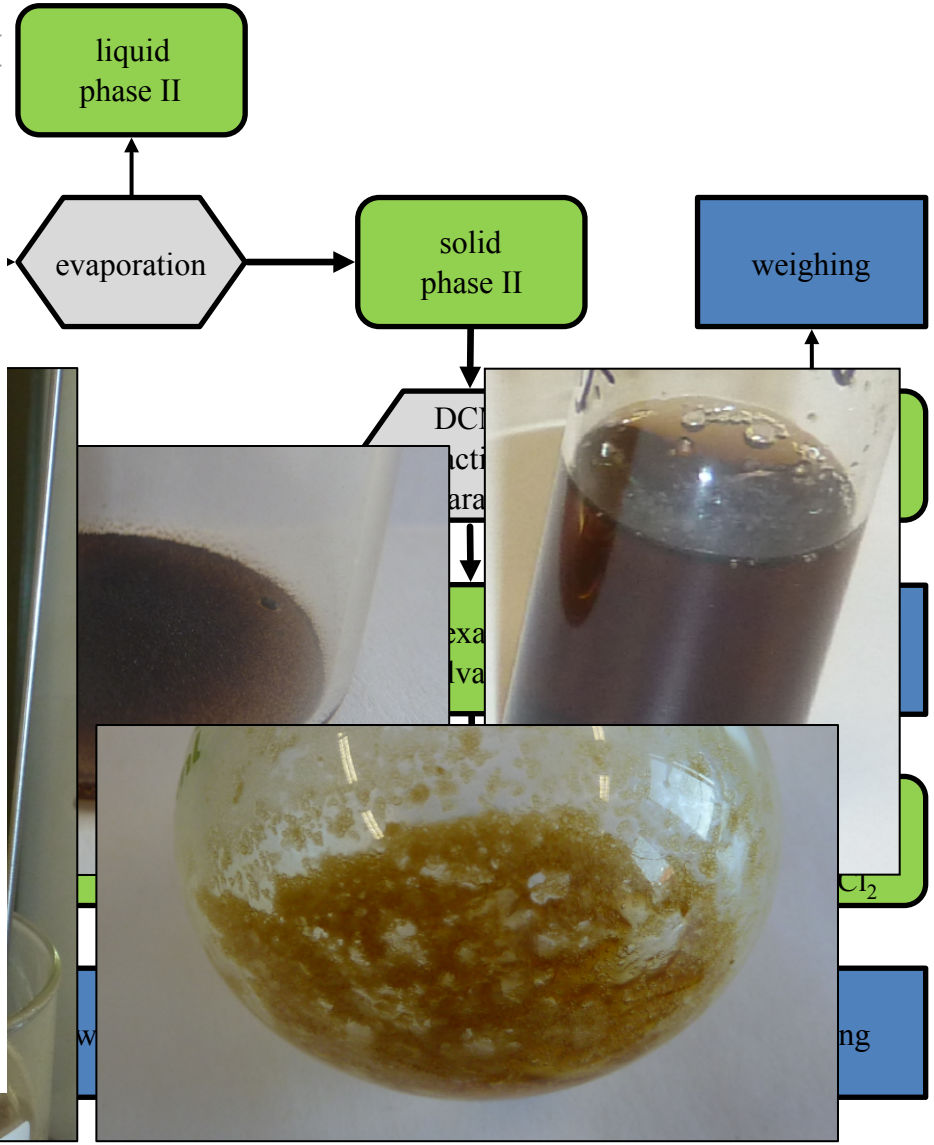


silica gel

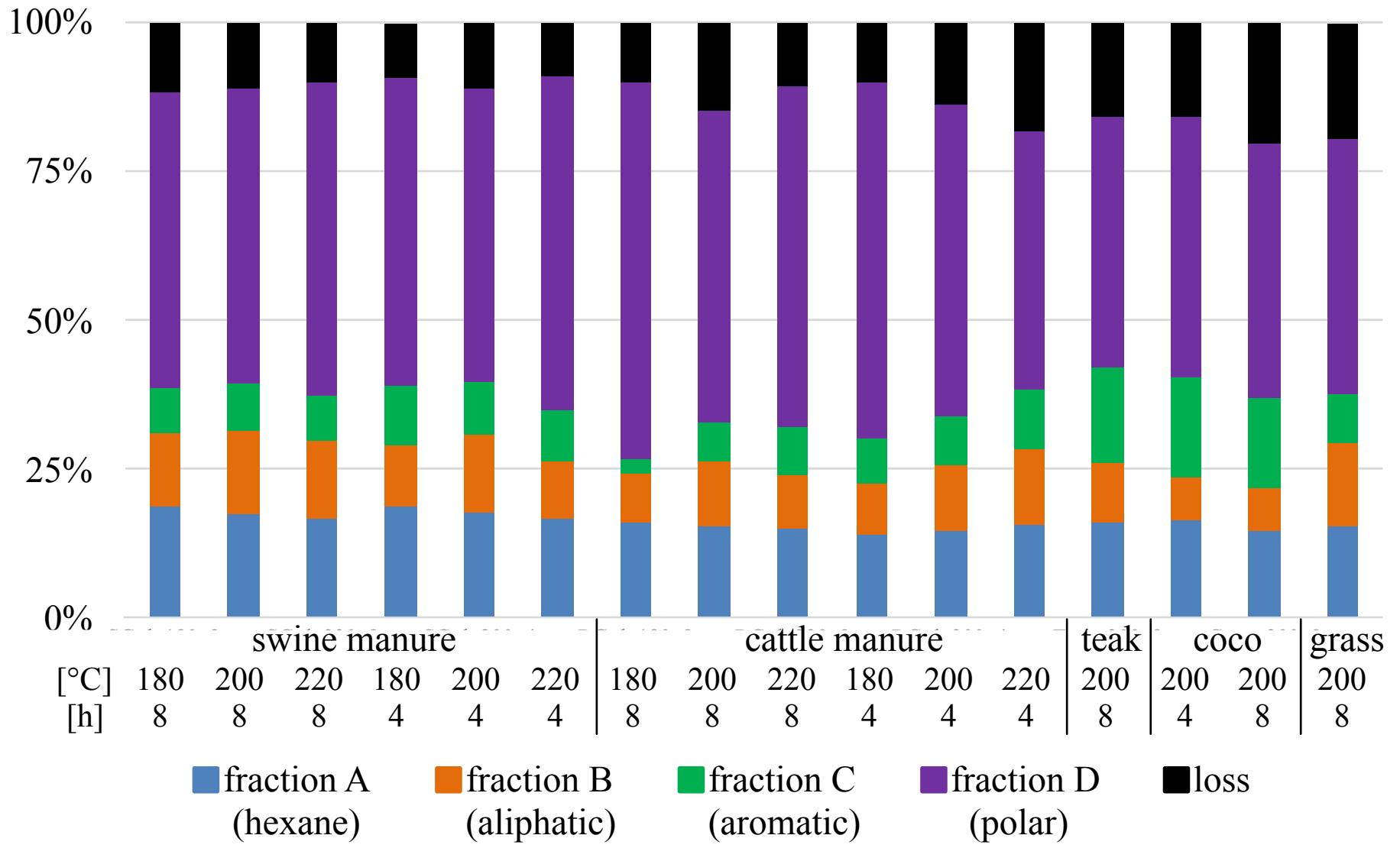
frac. B → aliphatic hydrocarbons

frac. C → aromatic hydrocarbons

frac. D → NSO-fraction

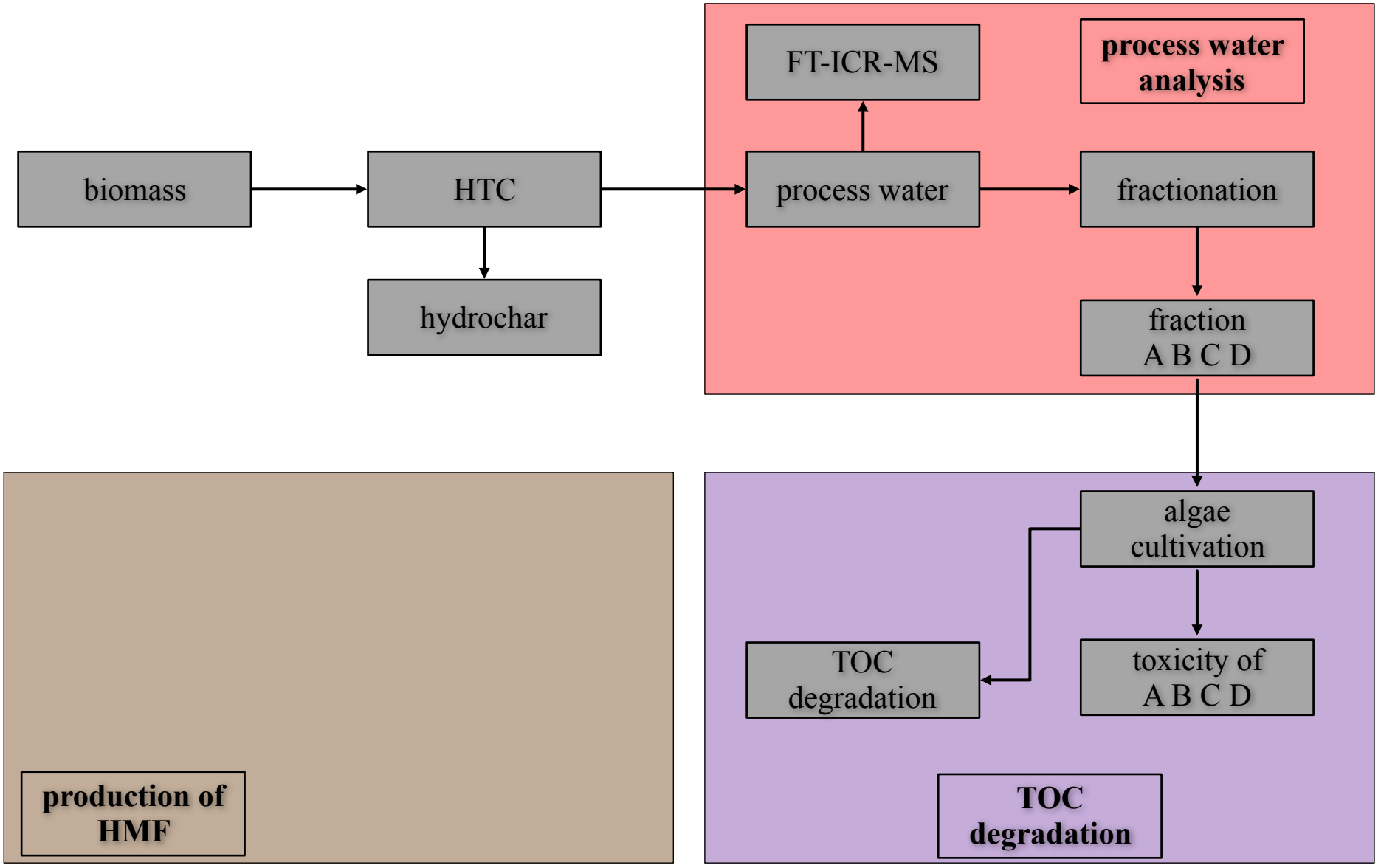


# Fractionation: Summary of results




→ The polar fraction D is dominant in every process water sample.

# Overview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A B C D
algae
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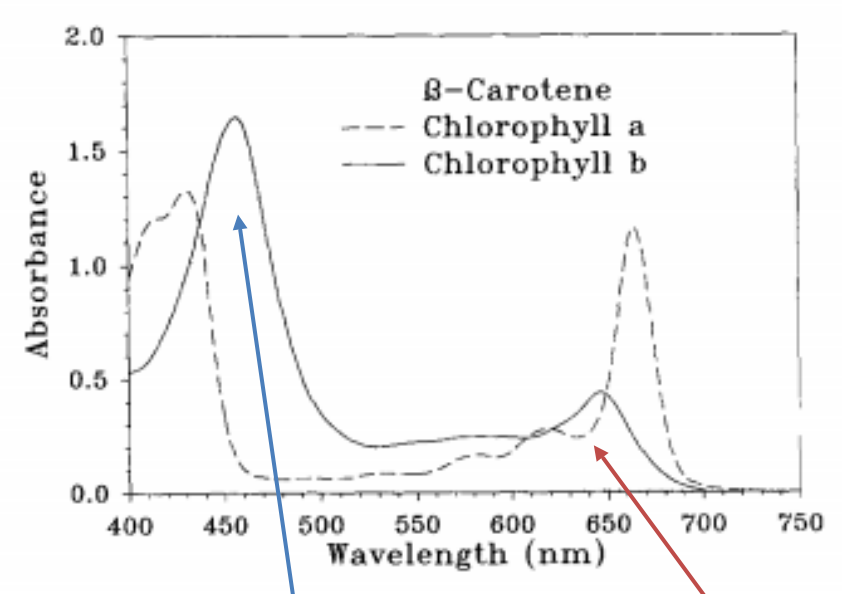
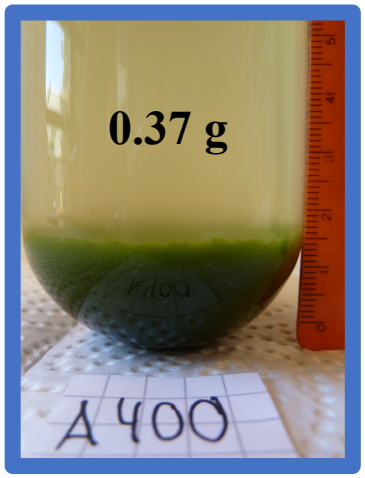
degradation
toxicity of
A B C D
production of
HMF
TOC
degradation

# Algae cultivation: Experimental setup




| LED | blue | green | red |
|---|---|---|---|
| λ [nm] | 467-470 | 570-575 | 620-625 |
| status | max | off | max |

# The cultivation of microalgae: A selection of results







A – hexane unsolvable
B – aliphatic
C – aromatic
D – polar "NSO"
only water and algae

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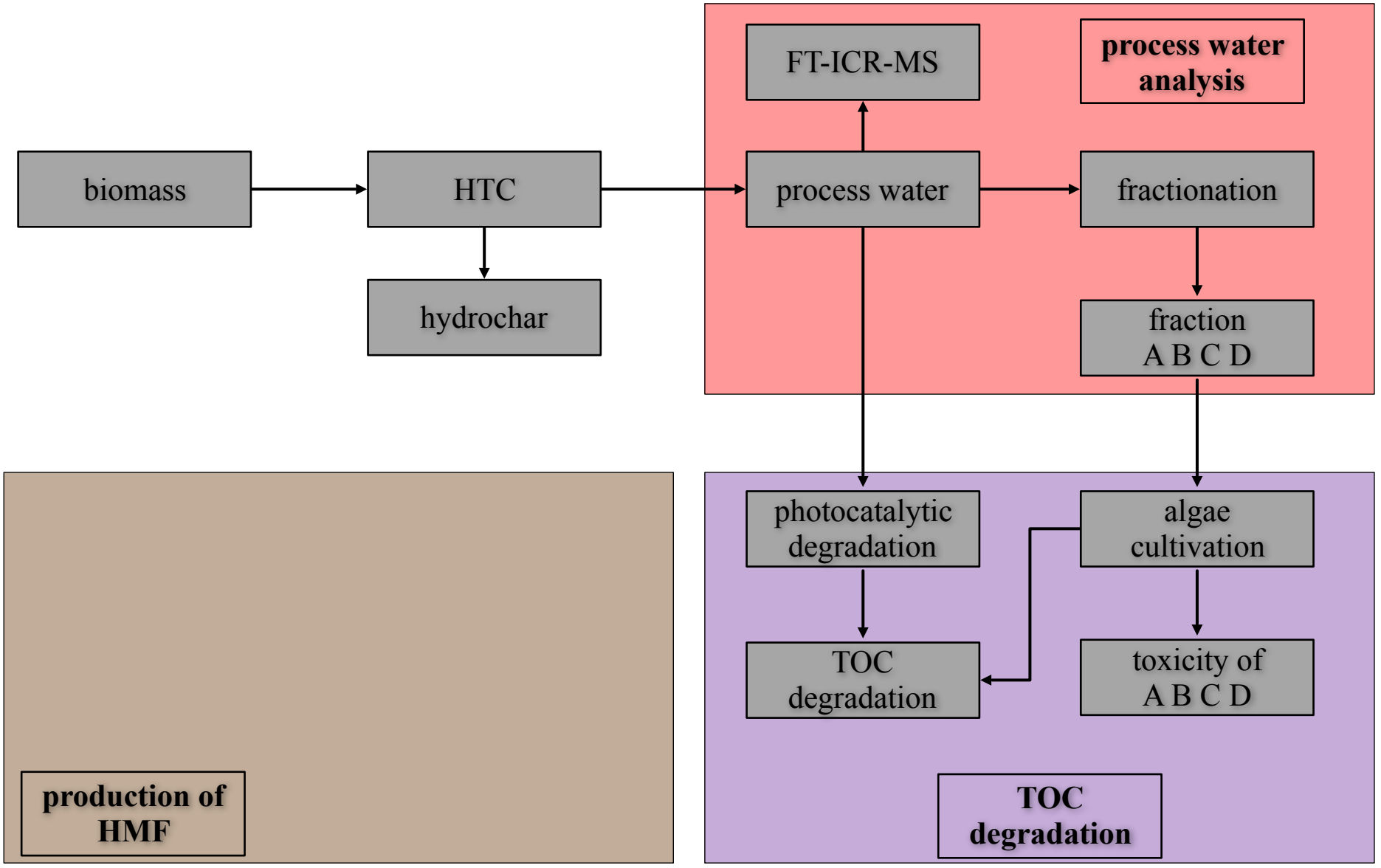
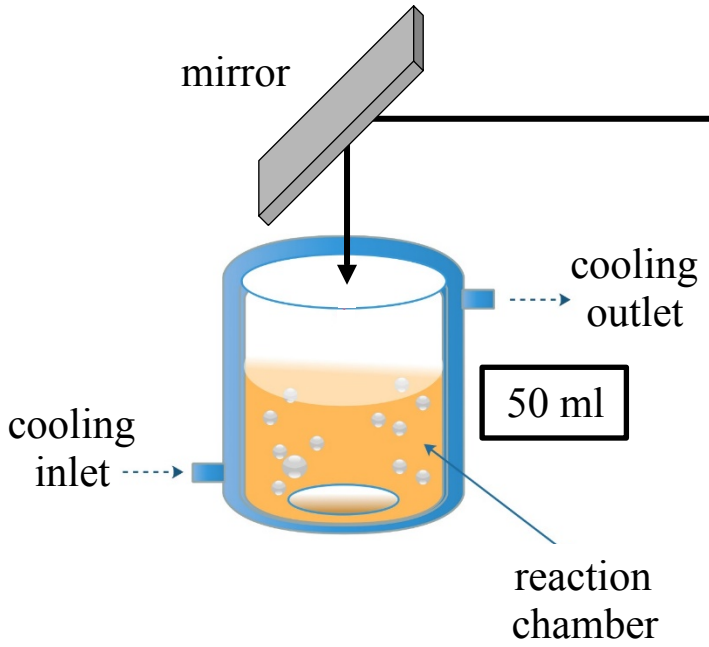


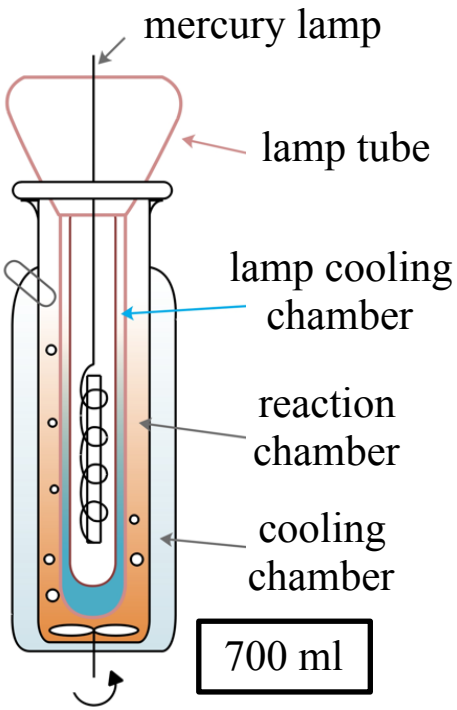
# Photo-Fenton degradation: Experimental setup and results

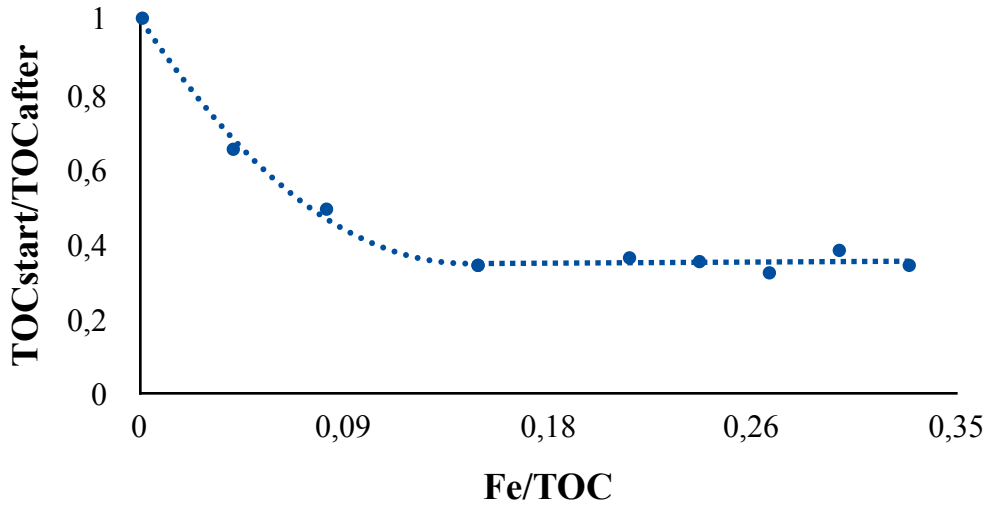
small setup




reacting agents:
- process water
- Fe(II)-salt
- $H_2O_2$

large setup




→ TOC-reduction up to 84 % within 60 minutes

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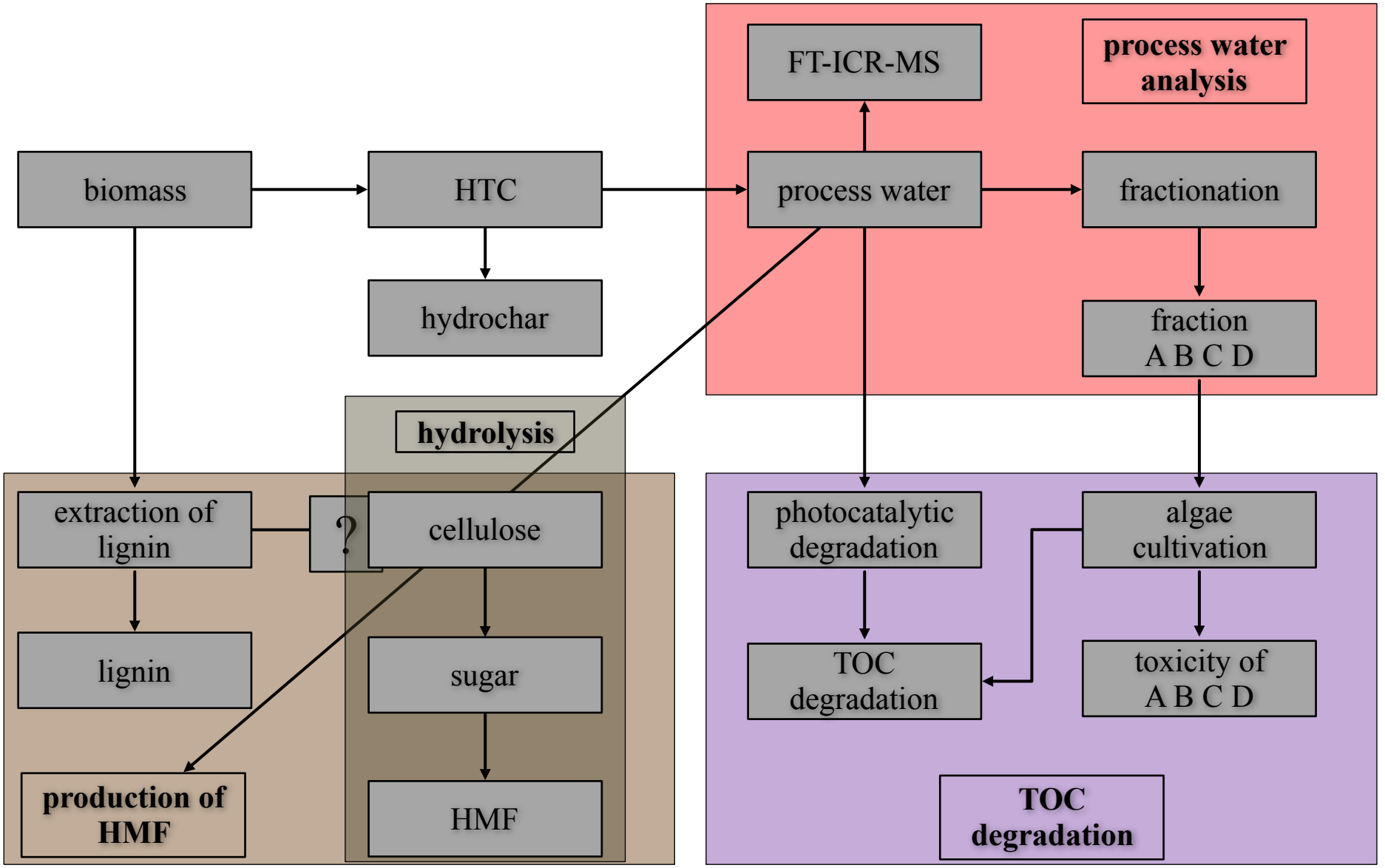


# Separation of lignin and cellulose: Experimental setup

teak wood
lignin content*
37.3 %

formic/acetic acid
(7:3 ratio)
2 h, 115 °C

filtration

2nd time

1st time

heat up
to 105 °C

add $H_2O$
6:1 ratio

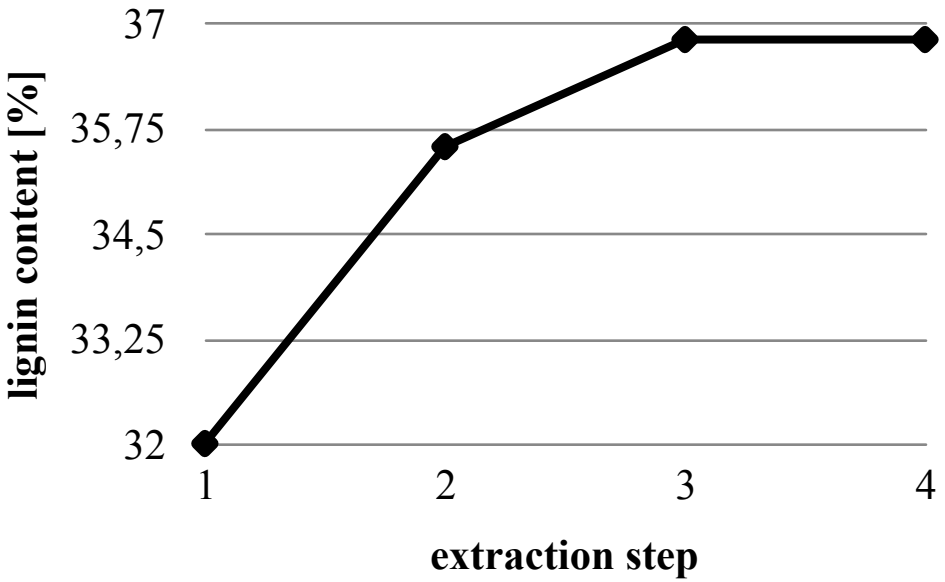

+ $H_2O_2$ aq.
2 h, 80 °C

cellulose

A. Lourenço, D. Neiva, J. Gominho, A. V. Marques, H. Pereira, *Wood Science and Technology* **2014**, *49*, 159.

# Separation of lignin and cellulose: A selection of results

| | lignin content |
|---|---|
| **teak*** | **37.30 %** |




| extraction 1 | extraction 2 | extraction 3 |
|---|---|---|
| 36.52 % | 37.54 % | 36.38 % |

**36.81 % ± 0.51 %**

→ reproducible extraction

* A. Lourenço, D. Neiva, J. Gominho, A. V. Marques, H. Pereira, *Wood Science and Technology* **2014**, *49*, 159.

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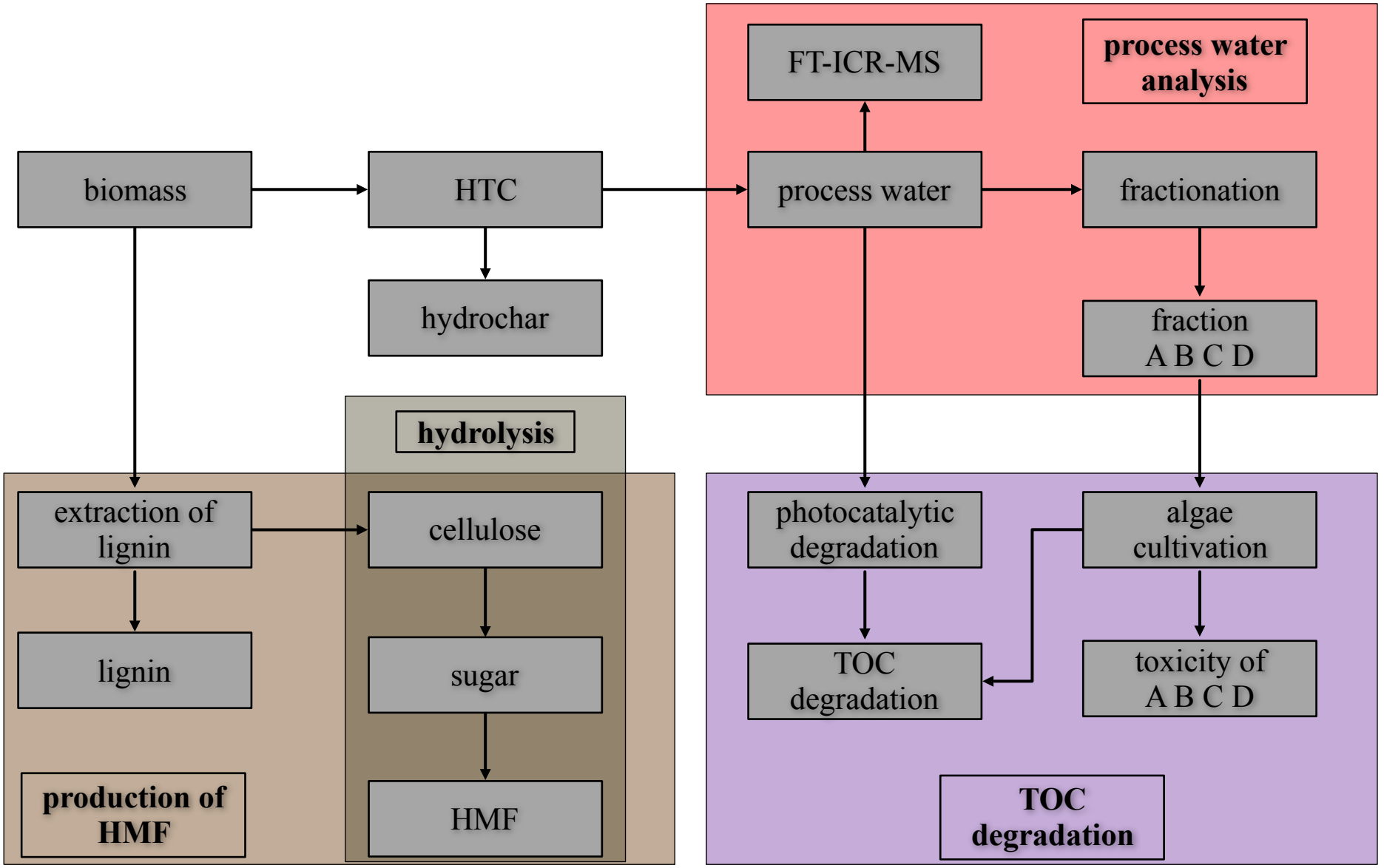
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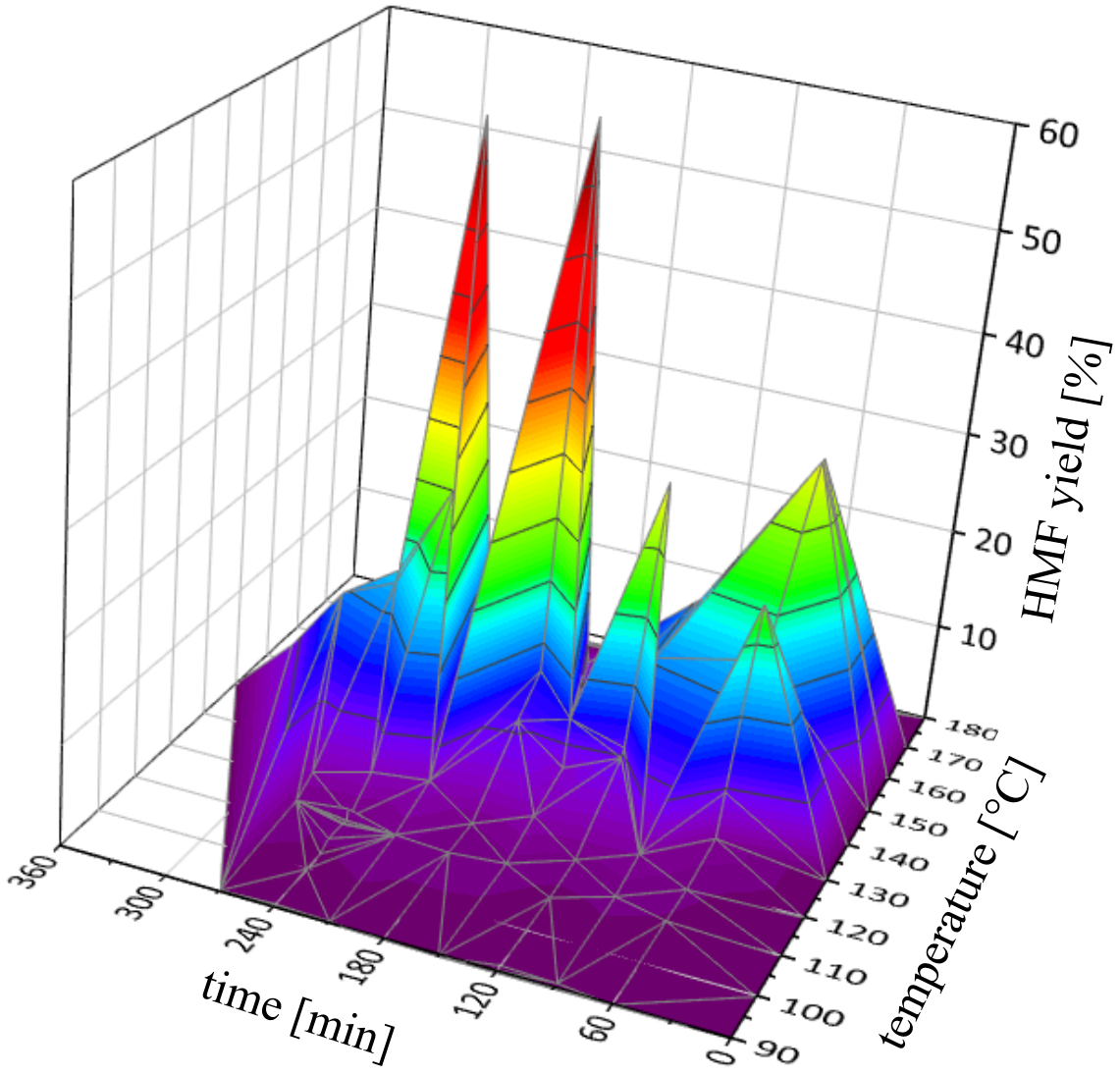
toxicity of A B C D
production of HMF
HMF
TOC degradation

# Parameter screening for maximum HMF yield




parameter screening glucose

→ two processes compete against teach other:

1) formation of HMF
2) follow up reactions

→ optimum at 143 °C and 3 h

# Hydrolysis: A selection of results

| substrate | temp. [°C] | time | water/biomass | HMF yield |
|---|---|---|---|---|
| cellulose (commercial) | 144.8 | 5 h 21 min | ~200:1 | 7.6 % |
| cellulose (self-extracted) | 143.9 | 5 h 21 min | ~200:1 | 7.4 % |
| glucose | 143.0 | 3 h 02 min | ~6:1 | 61.4 % |
| fructose | 105.7 | 4 h 03 min | ~12:1 | 73.6 % |
| fig (48.5 % fruct.) | 110.8 | 4 h 03 min | ~12:1 | 62.9 % |
| pineapple (64.5 % fruct.) | 112.1 | 4 h 03 min | ~19:1 | 75.4 % |
| raisin (65.0 % fruct.) | 102.3 | 4 h 03 min | ~18:1 | 82.6 % |

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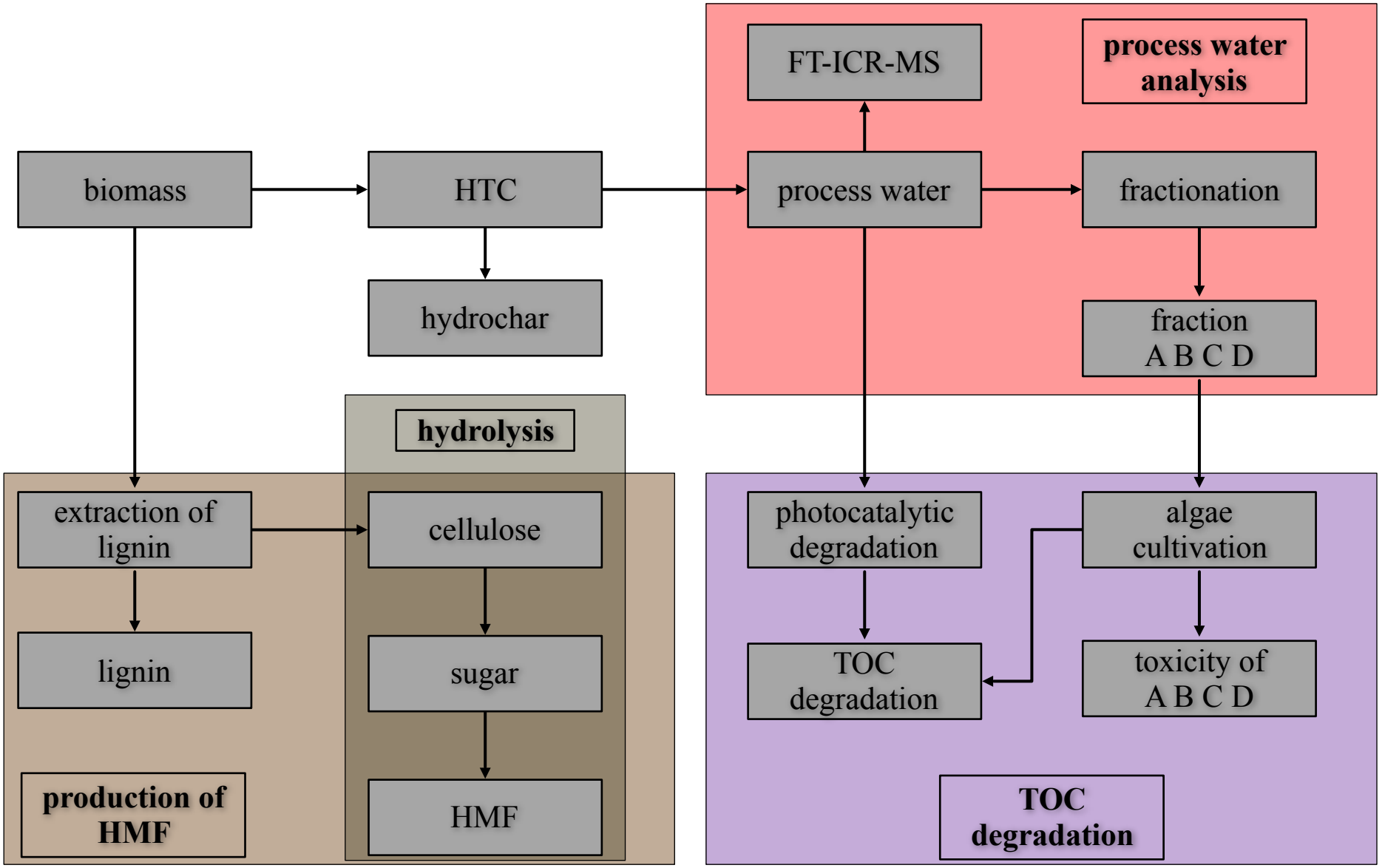
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