Process Water Recirculation During Hydrothermal Carbonization as a Promising Process Step Towards the Production of N-doped Carbonaceous Materials

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Research Article

Keywords: ioeconomy, Biorefinery, Hydrothermal Carbonization, process water recirculation, Maillard reaction, N-doped carbonaceous materials.

Posted Date: February 24th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-232186/v1

Abstract

Hydrothermal Carbonization (HTC) refers to the conversion of biogenic wastes into char-like solids with promising perspectives for application, but a process water (PW) results which is difficult to dispose untreated. Thus, a biorefinery approach including one or two recirculation steps with the additional objective of improving the physico-chemical characteristics of the solid was performed. During HTC, constitutive biomass molecules decompose into hundreds of organic compounds, following complex reactions. To get deeper insights a combination of proximate, ultimate and structural analysis for solid products as well as liquid chromatography for liquid products were the choice. The main reactions could be identified by key compounds of low and high molecular weight resulting from hydrolysis, dehydration, decarboxylation, deamination as well as amide formation and condensation reactions. Their intensity was influenced by the feedwater pH and reaction temperature. Reactions of Maillard character result in N-containing heterocycles incorporated into the hydrochar (HC), which promises the fabrication of high added-value materials, i.e. N-doped carbonaceous materials.

Full Text

Due to technical limitations, full-text HTML conversion of this manuscript could not be completed. However, the latest manuscript can be downloaded and accessed as a PDF.

Figures

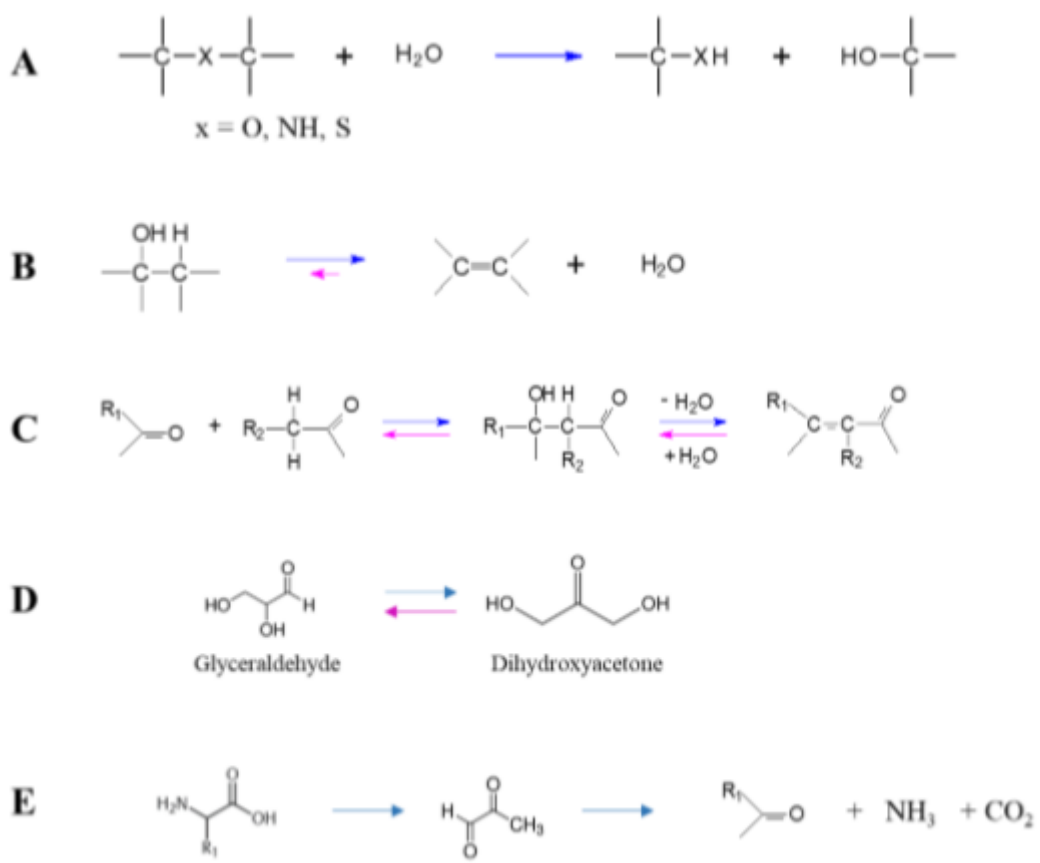

Figure 1

he most important reaction steps occuring during hydrothermal conversion of bio-based compounds. A: Hydroylsis of ethers, amines etc., B: Water elimination, C: Aldol addition and aldol condensation and their reverse reactions, D: Keto-Entol Tautomerisation (example), E: Strecker degradation

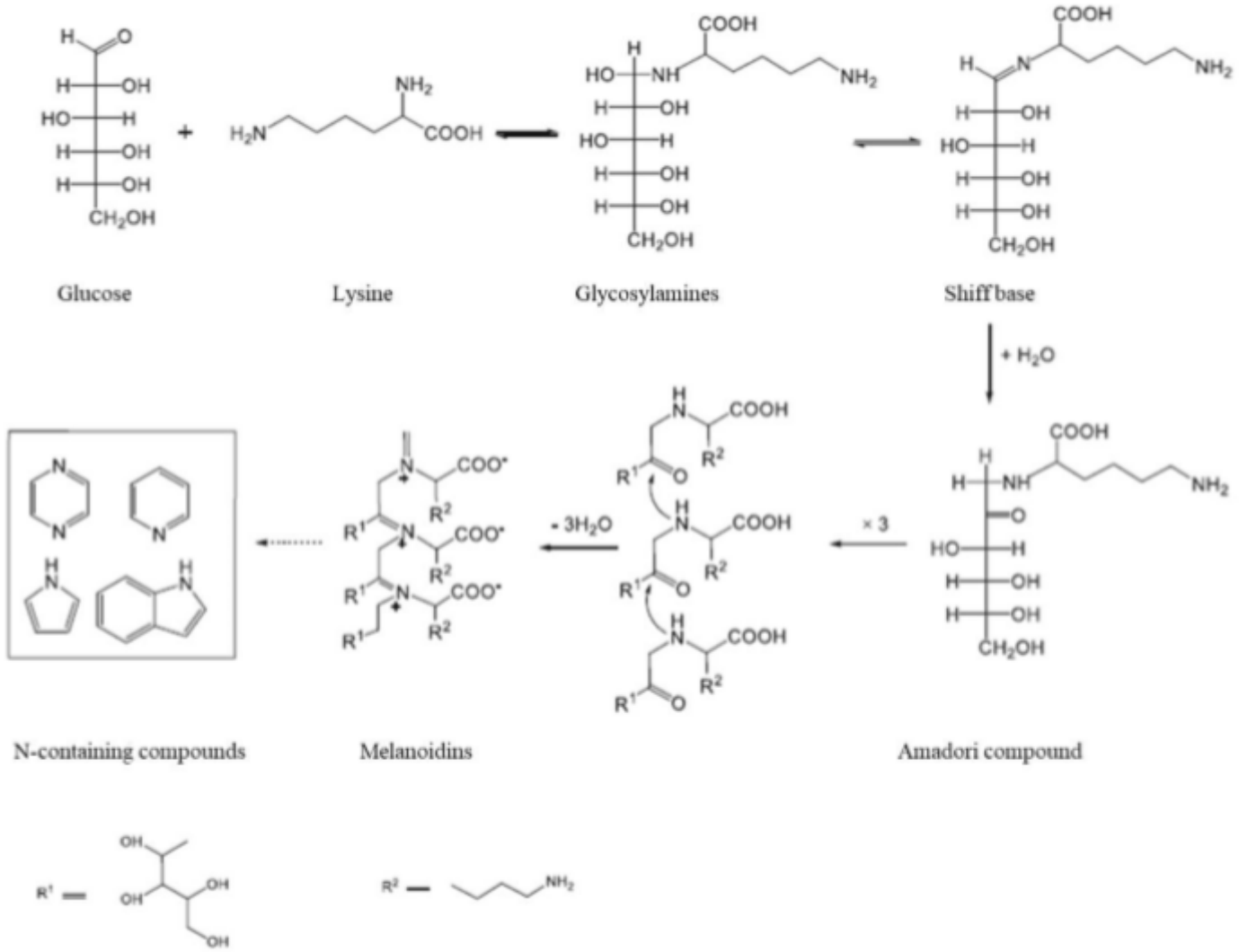

Figure 2

Proposed mechanisms of Maillard reaction pathways during HTC, reprinted with kind permission of [26]

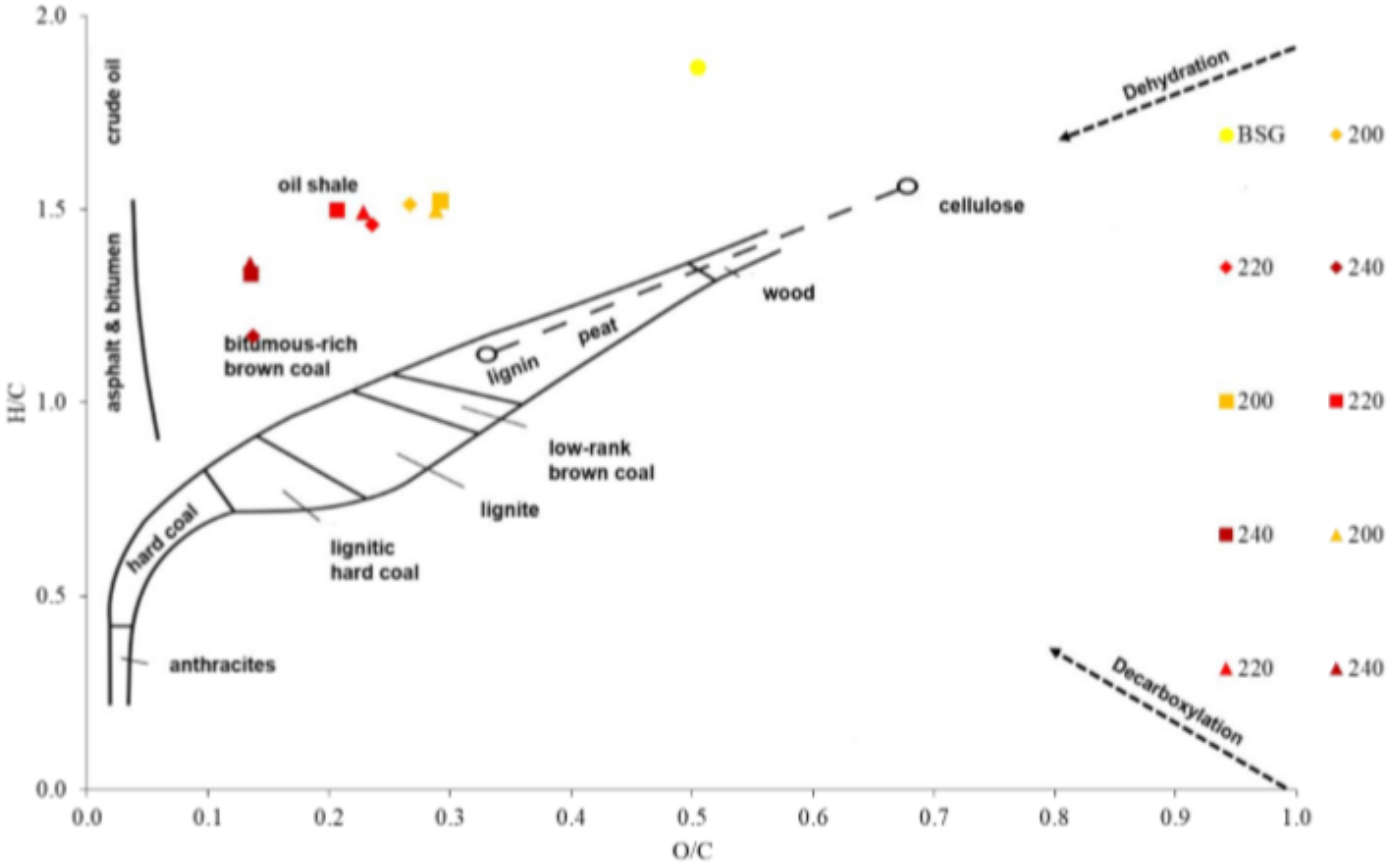

Figure 3

Coalification degree of hydrochars obtained from hydrothermal carbonization of brewer's spent grains with water and after recirculation of its process water in two further steps at 200, 220, 240 °C for 2 hours (e.g. 2nd 220) illustrated in the van Krevelen diagram by plotting H/C atomic ratios versus O/C atomic ratios. Whereas the rhombus-shaped data points stand for the initial HTC-run, the triangle-shaped and the square-shaped data points stand for the HTC-run after the 1st and the 2nd recirculation. BSG = Brewer's Spent Grains

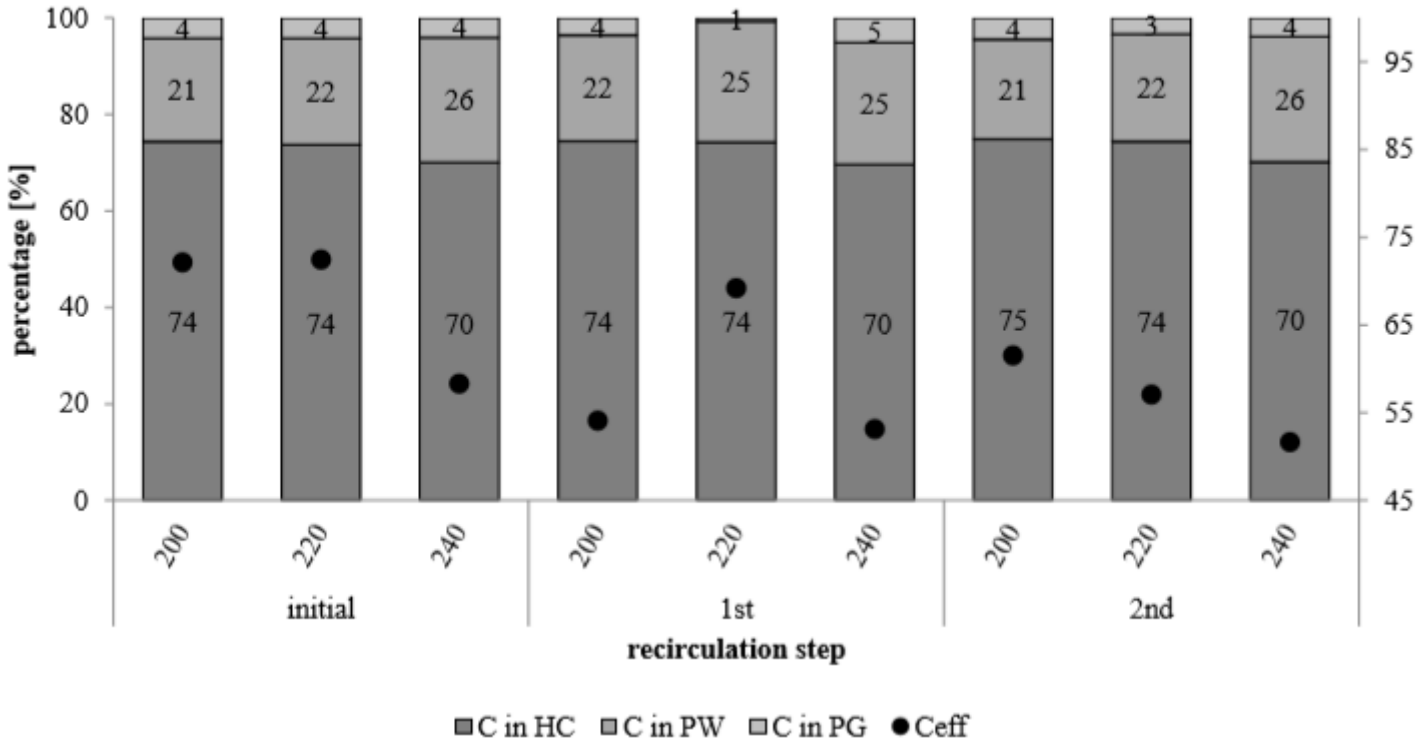

Figure 4

Carbon distribution (primary or left y-axis) and efficiencies (secondary or right y-axis) related to the product phases after Hydrothermal Carbonization of brewer's spent grains with water and two further recirculation steps of its process water. The process gas is assumed as 100% CO2. HC=hydrochar; PW= process water; PG = process gas; Cfix = fixed Carbon

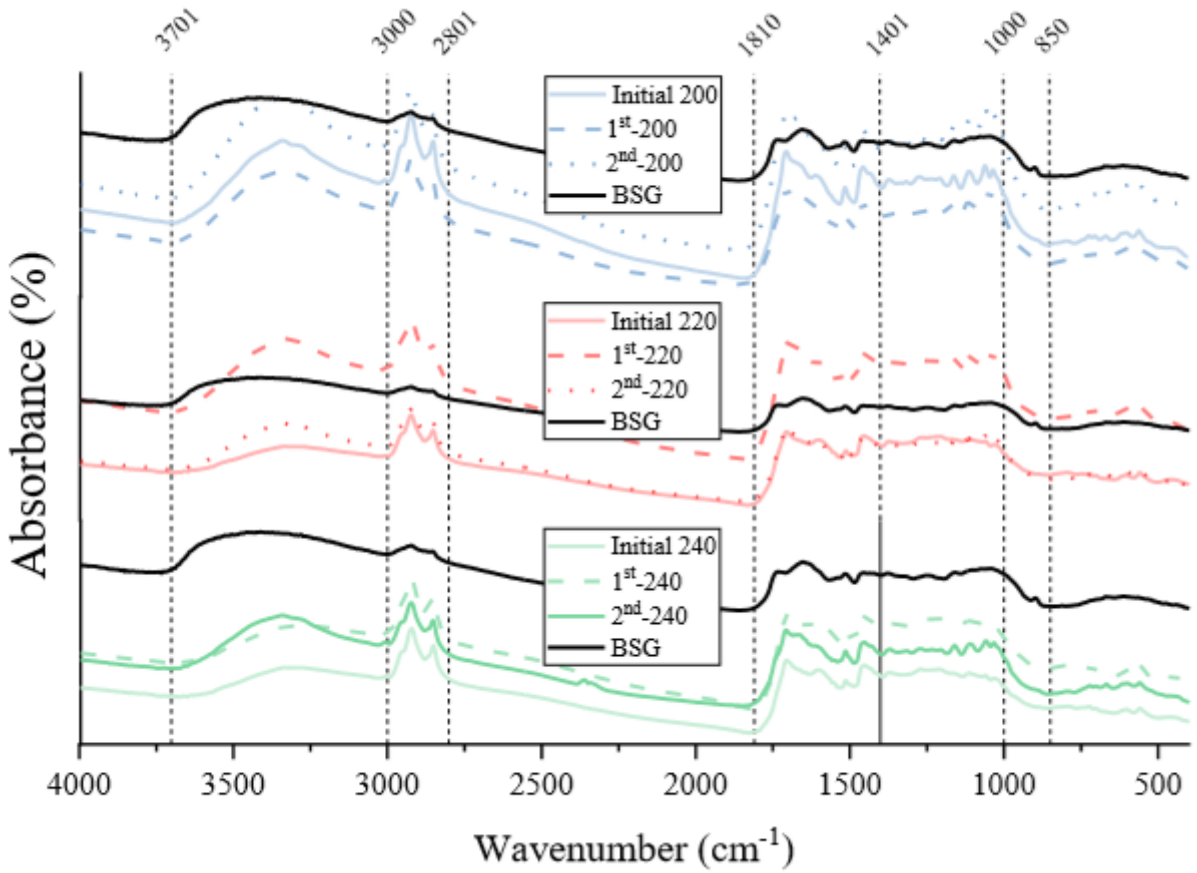

Figure 5

FT-IR of Brewer's Spent Grains (BSG) and its hydrochars produced at 200, 220 and 240 °C with water (initial) and after two recirculation steps of process water (1st, 2nd)

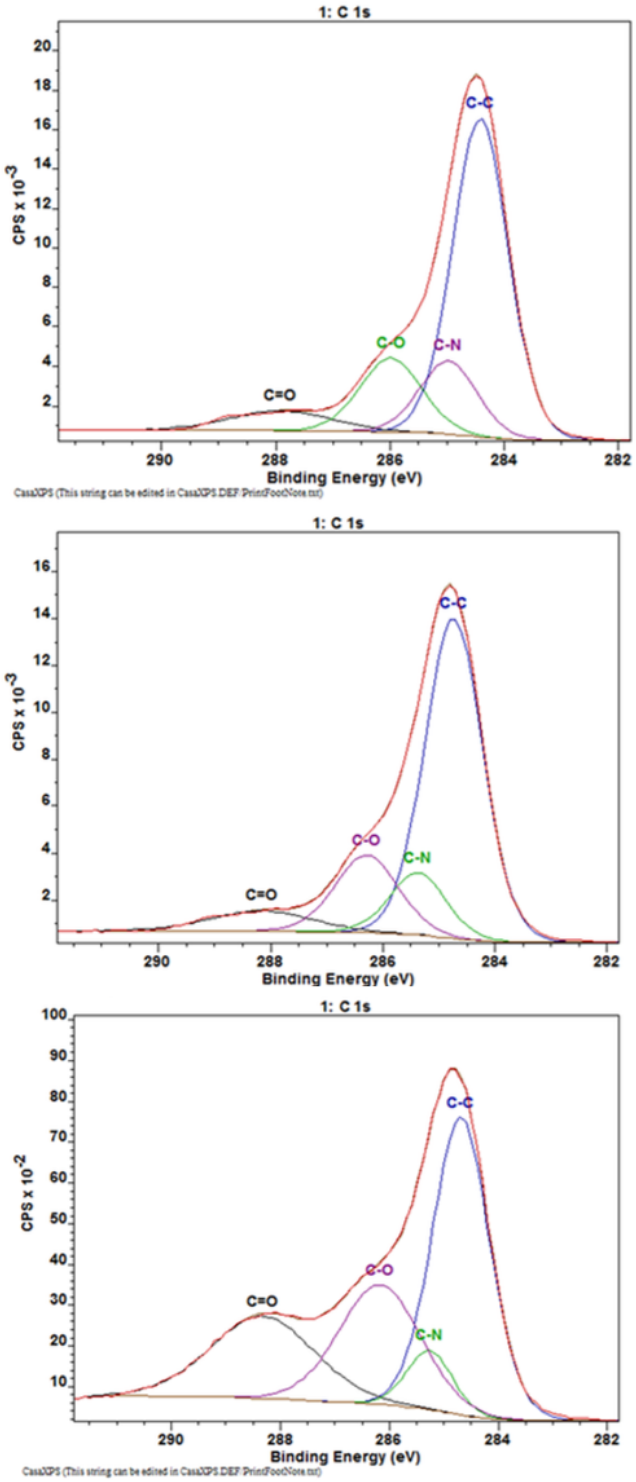

Figure 6

X-ray photoelectron spectroscopy of hydrochars produced from Brewer's spent grains at 220 with water (top – initial 220), after the 1st (middle – 1st 220) and 2nd recirculation of process water (bottom – 2nd 220). Only the range of the C-N and C-O bonds are shown

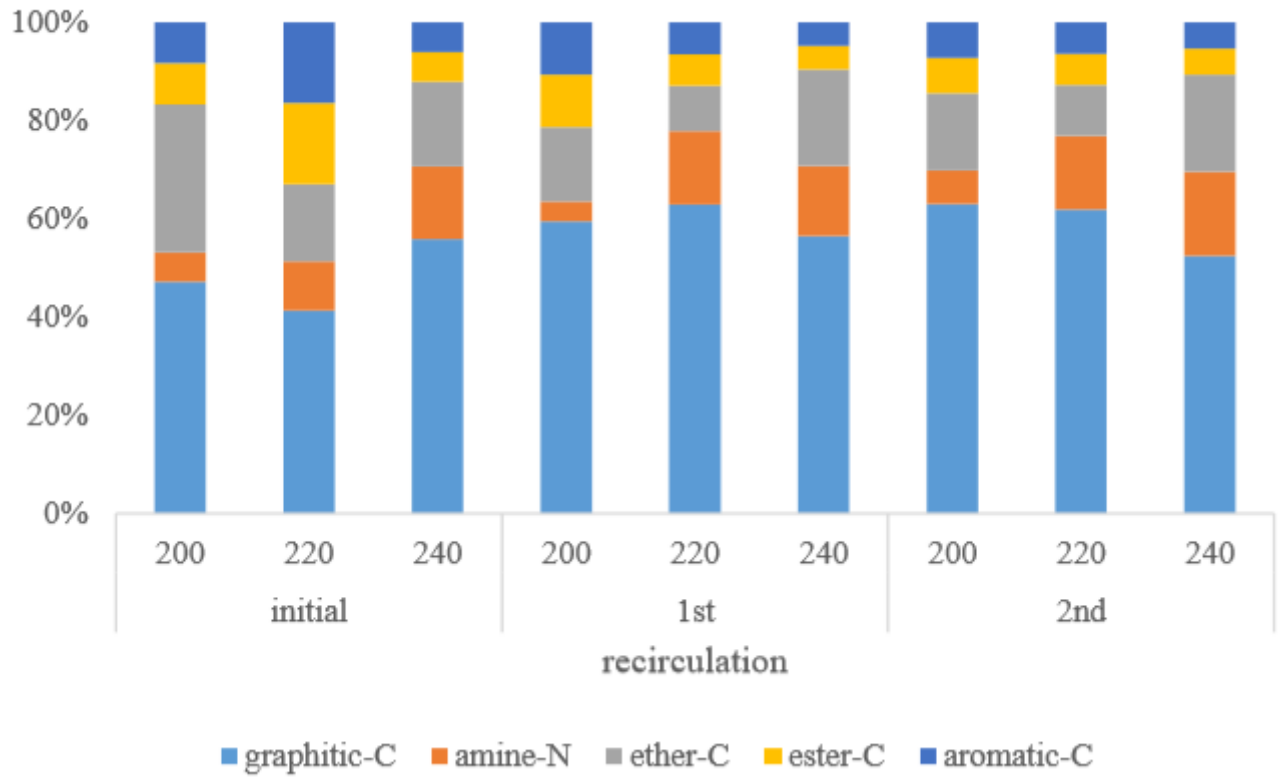

Figure 7

X-ray photoelectron spectroscopy of hydrochars produced from Brewer's spent grains at 200, 220 and 240 °C with water and after one or two recirculation steps of process water focussing on Carbon structures

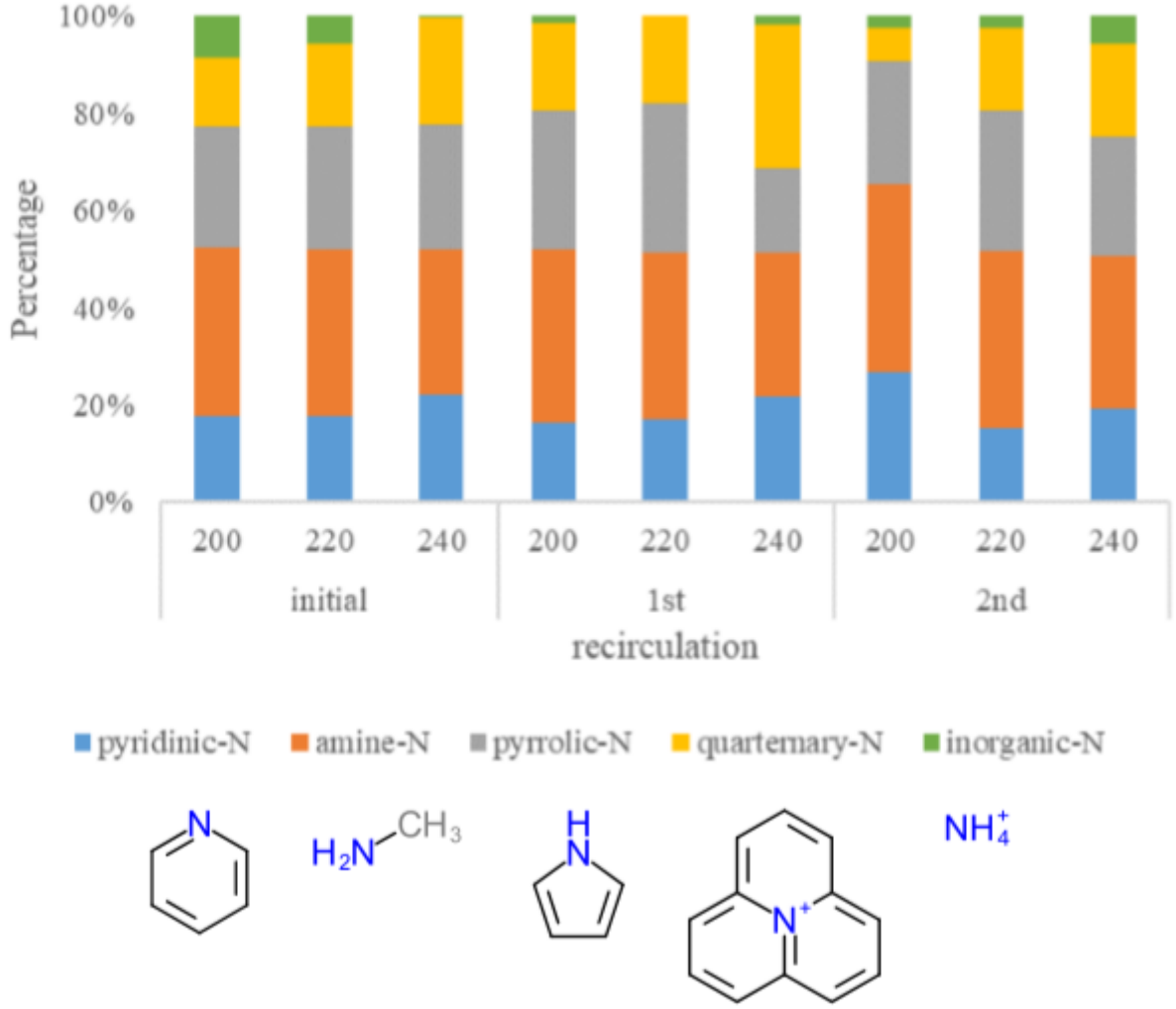

Figure 8

X-ray photoelectron spectroscopy of hydrochars produced from Brewer's spent grains at 200, 220 and 240 °C with water and after two recirculation steps of process water regarding N-containing structures. Examples for the different N-species are also presented

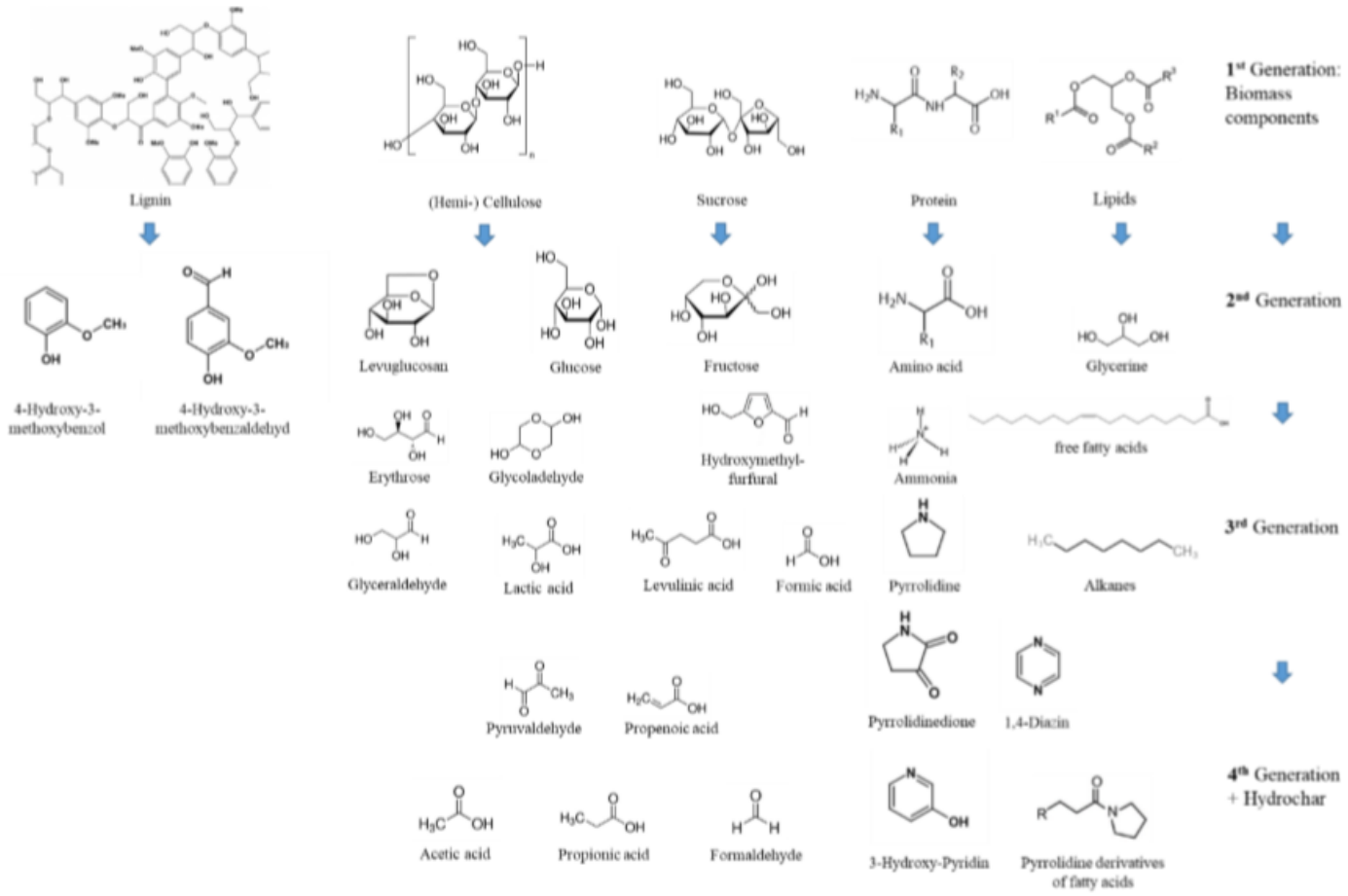

Figure 9

Scheme of reaction products detected in the process water after hydrothermal carbonization of lignocellulosic biomass classified into 4 gnerations depending on their accumulation

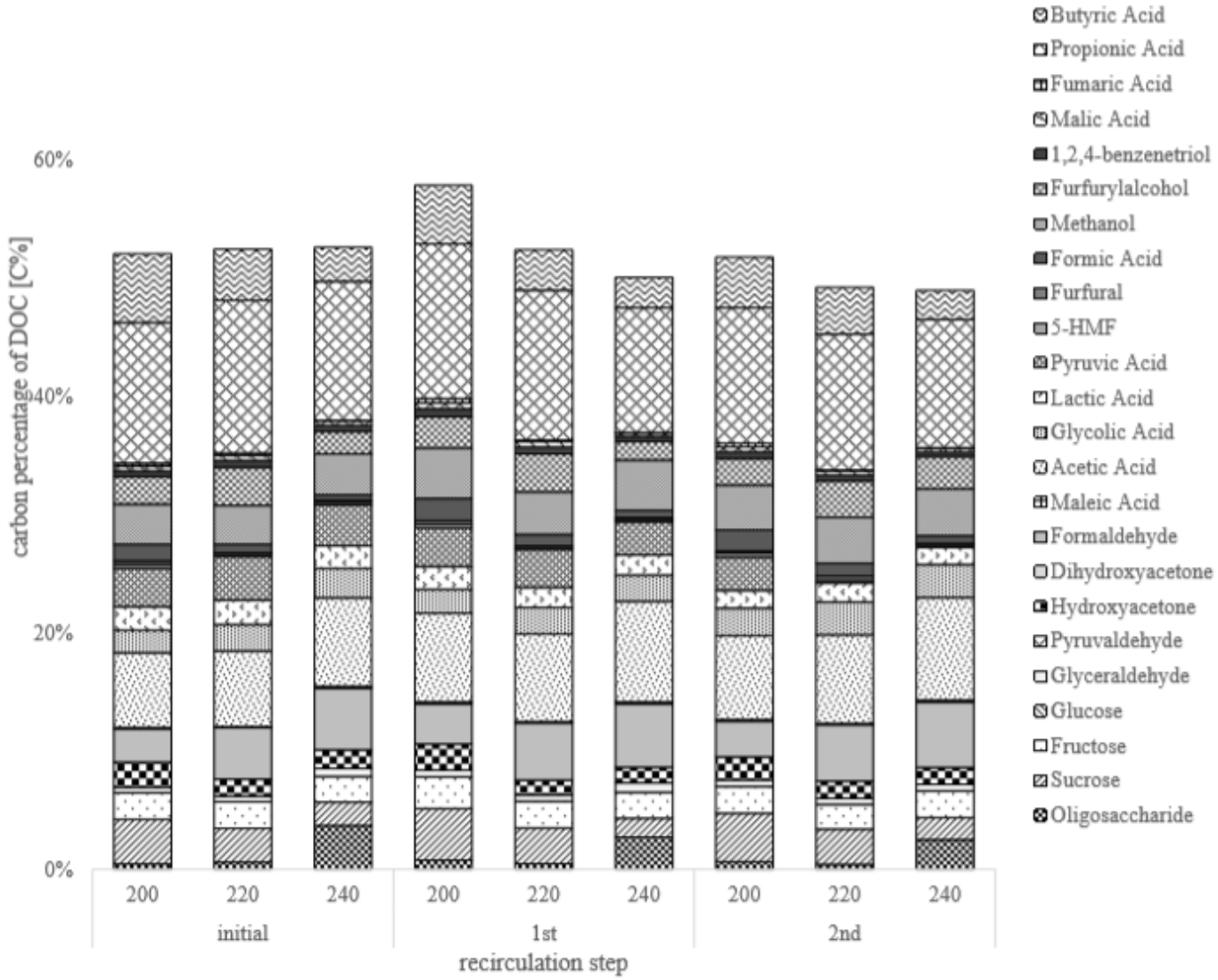

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Figure 10

Carbon percentages of detected carbohydrate-based reaction products in the process waters from hydrothermal carbonization experiments with brewer's spent grains in distilled water (initial) as well as recirculated processs water (1st, 2nd recirculatgion step) related to the dissolved organic carbon (DOC)

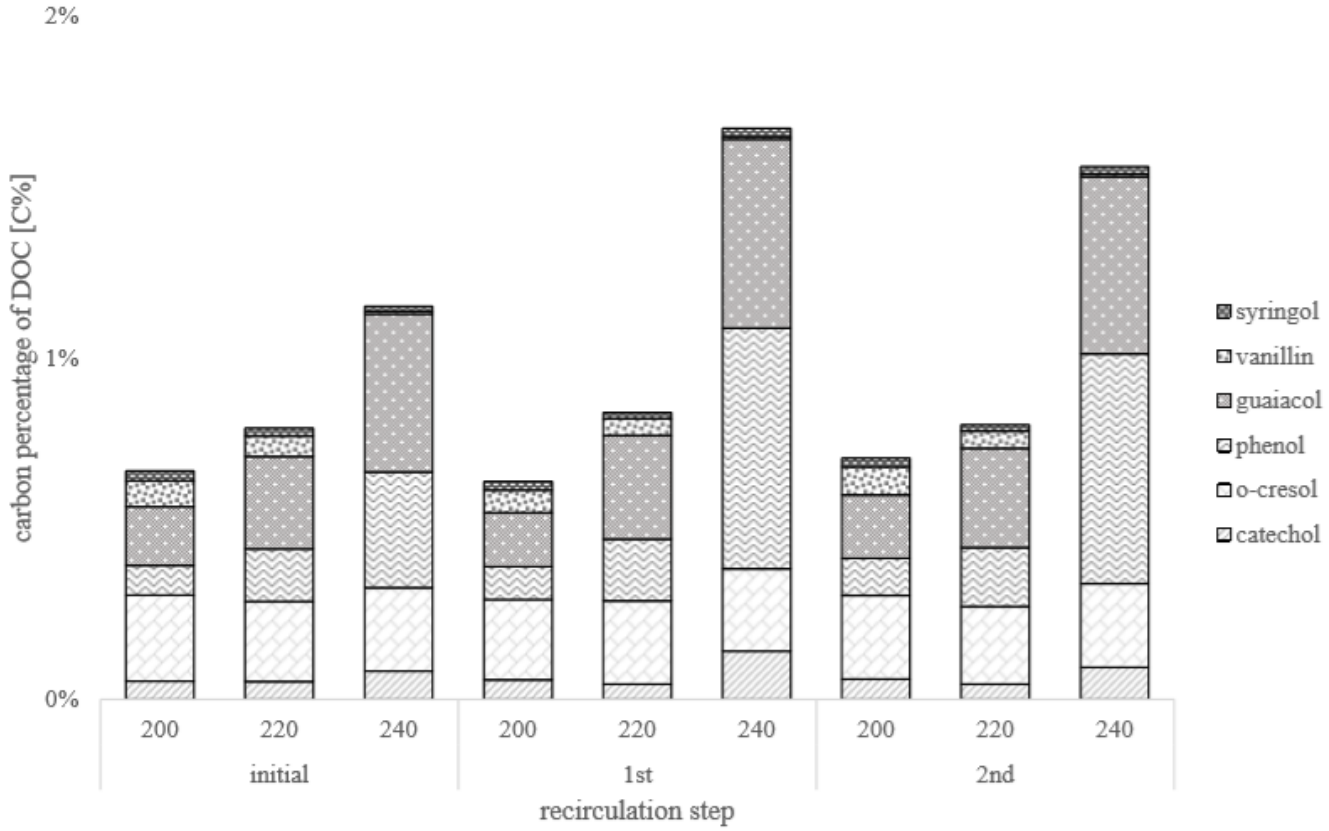

Figure 11

Carbon percentages of detected lignin related reaction products in the process waters from hydrothermal carbonization experiments with brewer's spent grains in water (initial) as well as recirculated processs water (1st + 2nd recirculation step) related to the dissolved organic carbon (DOC). Syringol = 2,6-dimethoxyphenol, 4-Hydroxy-3-methoxybenzaldehyd = vanilin, 2-methoxy-phenol = guaiacol, 2-methyl-phenol = o-cresol, 1,2-dihydroxybenzene = catechol

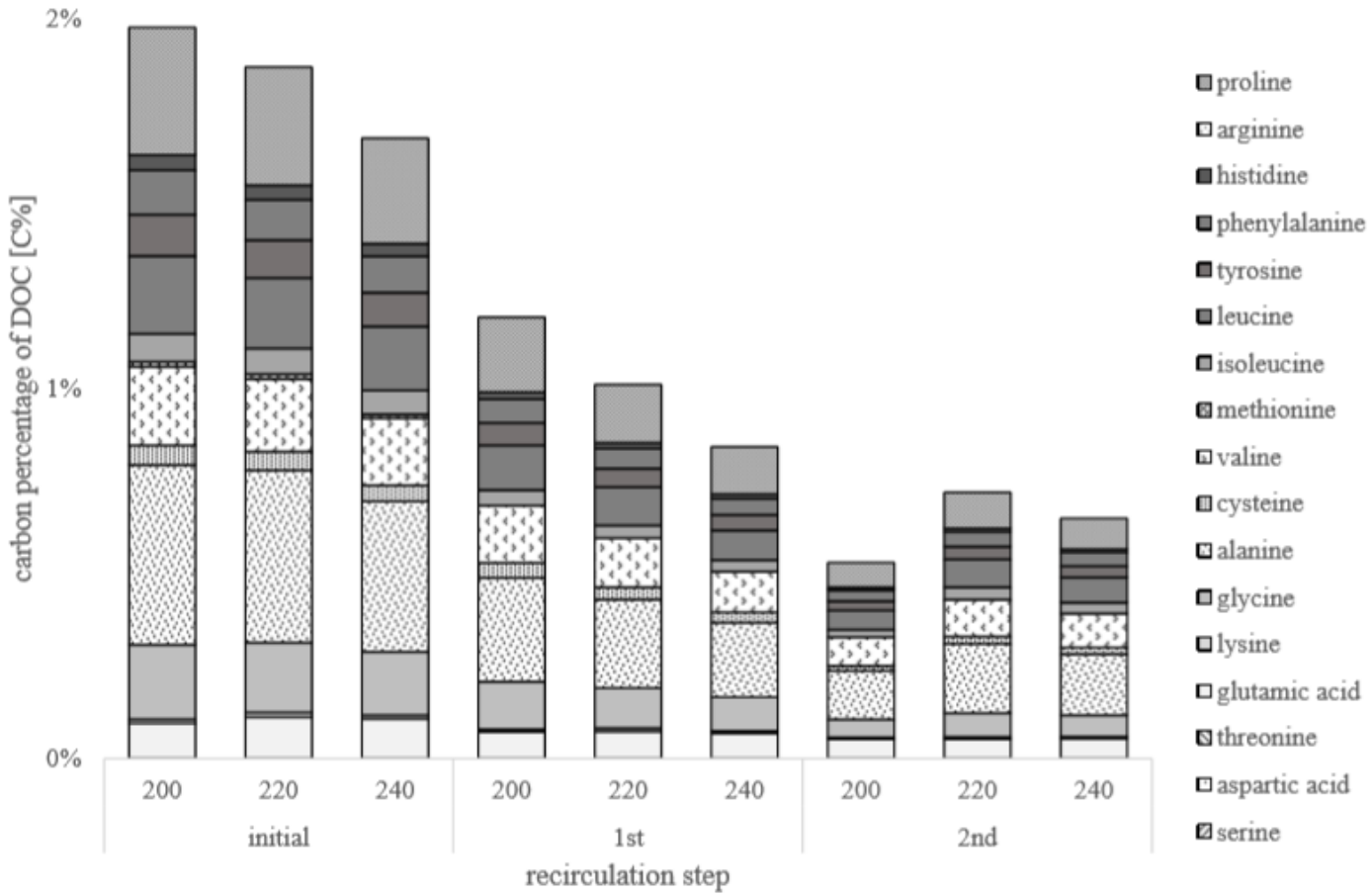

Figure 12

Carbon percentages of detected protein-related reaction products in the process waters from hydrothermal carbonization experiments with brewer's spent grains in water (initial) as well as recirculated processs water (1st and 2nd recirculatgion) related to the dissolved organic carbon (DOC)

Supplementary Files

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