SUPPLEMENTARY DATA

Hydrothermal carbonisation of paper sludge: effect of process conditions on hydrochar fuel characteristics and energy recycling efficiency

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Section A: Reactor Design, construction and costs

A 1: Schematic view of the reactor prototype

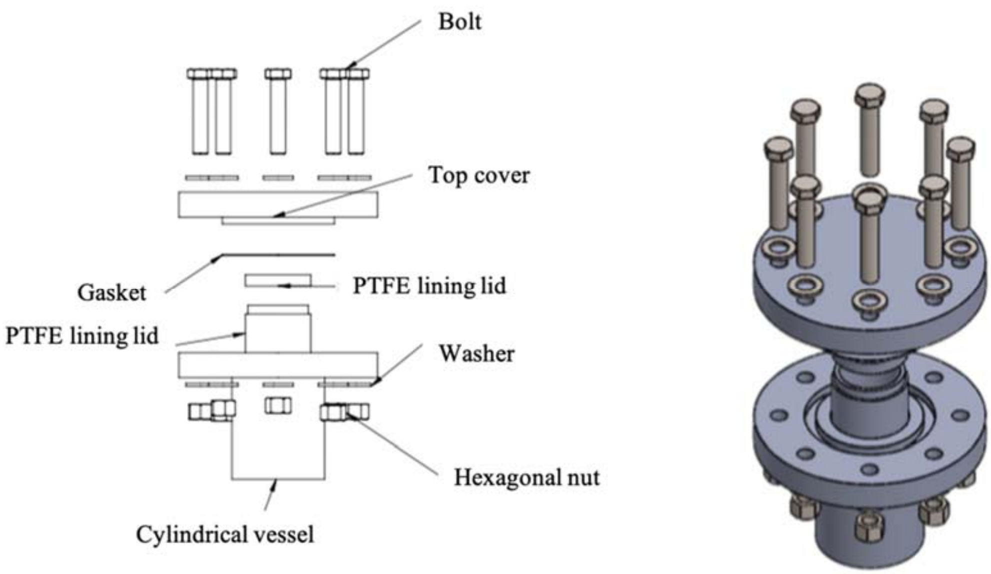

Figure A 1: Schematic view of the reactor prototype.

A 2: Stress Analysis

Before reactor fabrication, stress analysis was conducted to ensure the reactor sustains the design HTC pressure of 1-3 MPa. The designed cylindrical vessel is considered thick-walled because the ratio of the radius and the wall thickness is smaller than 10 (Fryer and Harvey, 1998). During HTC, the pressurised vessel experiences stress across the thickness of the wall. Yielding initially occurs at the internal pressurised space and spreads through the wall thickness from the inside to the non-pressurised outer wall as pressure rises. Thus, when the entire wall thickness reaches yield, failure occurs. A thick-walled cylindrical pressure vessel experiences longitudinal or axial stress, circumferential or hoop stress, and radial stress (Mott, 2008); the three forces combined is designated uniaxial force. The stress distribution across the steel vessel is illustrated in **Figure A 2**.

For the reactor vessel, parameters such as yield pressure and internal stress limit were calculated considering the vessel internal radius of 27.5 mm, the external radius of 37.5 mm, EN19 steel material yield strength of 415 MPa, and allowing a design stress factor of 1.5.

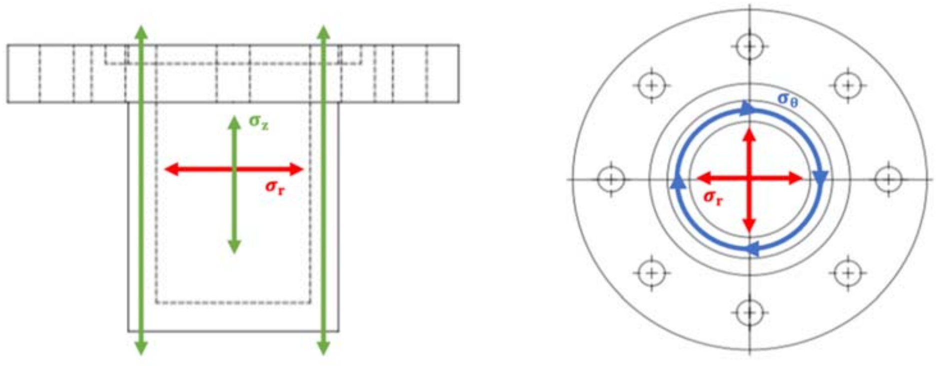

Figure A 2. Stress across the cylindrical vessel.

Since pressure is internal, the first yield occurs at the internal part of the vessel in the radial direction; the following assumptions were made for radial stress (σ_{ri}) determination:

- σ_{ri} at internal diameter $(27.5) = -P$
- σ_{r0} at external diameter $(37.5) = 0P$, as the vessel is subjected to internal pressure (P) only.

Considering that the stress across the sectional area of a material is given by equation A.1.

$$\sigma = \frac{F}{A_x} \tag{A.1}$$

Equation A.1 can be written as:

$$\sigma = \frac{P \times \frac{\pi {r_i}^2}{2}}{\frac{\pi {r_o}^2}{2} - \frac{\pi {r_i}^2}{2}} \tag{A.2}$$

Which, after simplification, becomes:

$$\sigma = \frac{{r_i}^2}{{r_o}^2 - {r_i}^2} P \tag{A.3}$$

Thus, radial stress at internal diameter (σ_r) for the first yield was determined according to equation A.4.

$$\sigma_r = \left(A - \frac{B}{r^2}\right) P \tag{A.4}$$

Variable A was determined according to equation 4.5.

$$A = \frac{r_i^2}{r_O^2 - r_i^2} \quad (A.5)$$

Variable B was determined according to equation A.6.

$$B = \frac{r_i^2 \times r_O^2}{r_O^2 - r_i^2} \quad (A.6)$$

The circumferential stress at the internal radius (σ_θ) for the first yield was calculated using equation A.7.

$$\sigma_\theta = \left(A + \frac{B}{r^2}\right) P \quad (A.7)$$

The axial stress (σ_z) at internal diameter for the first yield was calculated according to equation A.8.

$$\sigma_z = 0.5(\sigma_r + \sigma_\theta) \quad (A.8)$$

The uniaxial stress at internal diameter for the first yield is given by equation A.9.

$$P_y = \frac{\sigma_y}{\sigma_{max}} \quad (A.9)$$

Where P_y represents the uniaxial or internal pressure for first yield, σ_y represents the stress yield, and σ_{max} is the uniaxial stress calculated according to Tresca or Von Mises method (Fryer and Harvey, 1998).

The pressure at the limit was calculated according to equation A.10.

$$\sigma = \sigma_y \ln r + C \quad (A.10)$$

Where C is a constant and it was calculated for σ_r, σ_θ and σ_z based on the outer radius and the assumption that the external pressure (OP) equals 0.

Tresca method

For the Tresca method, the uniaxial stress at first yield is given by equation A.11.

$$\sigma_{max} = \sigma_\theta - \sigma_r \quad (A.11)$$

Limit occurs when all values of radius reach yield; thus, assuming uniform stress across the wall of the vessel, stress limit was given by equation A.12.

$$\sigma_\theta - \sigma_r = \sigma_y \qquad \text{(A.12)}$$

Von Mises method

For the Von Mises method, the uniaxial stress at first yield is given by equation A.13.

$$2\sigma_{max}^2 = (\sigma_r - \sigma_\theta)^2 + (\sigma_\theta - \sigma_z)^2 + (\sigma_z - \sigma_r)^2 \qquad \text{(A.13)}$$

Limit occurs when all values of radius reach yield, thus assuming uniform stress across the wall of the vessel; stress limit was given by equation 4.14.

$$\sigma_\theta - \sigma_r = \frac{2}{\sqrt{3}}\sigma_{max} \qquad \text{(A.14)}$$

Where σ_{max} equals yield stress (σ_y).

The stress analysis parameters for the PTFE lining were determined following the steps described above, but considering the lining internal radius of 21.5 mm, external radius of 26.5 mm, typical PTFE tensile yield strength of 28.68 MPa, and allowing a design stress factor of 1.5.

Table A 1: Stress analysis parameters

Parameter	EN19 Vessel		PTFE Lining	
	Tresca	Von Mises	Tresca	Von Mises
P_y (MPa)	64.04	73.97	3.26	3.76
C_r	908.42	1048.85	69.42	80.16
C_θ	1185.07	1368.42	88.54	102.24
C_z	1046.75	1208.69	78.98	91.2
σ_{ri} (MPa)	- 85.81	- 99.09	- 4	- 4.62
σ_θ (MPa)	276.67	319.45	19.12	22.08
σ_z (MPa)	138.33	159.74	9.56	11.03

The stress analysis, constants and pressure limits for the vessel and the lining are presented in **Table A 1**. For the vessel, the uniaxial pressure required for the first yield at the internal diameter is 64.04 and 73.97 MPa for the Tresca and Von Mises method, respectively, based on radial stress. The internal stress limit for the design is 85.81 and 99.09 MPa for the Tresca and Von Mises method, respectively.

For the lining, the uniaxial pressure required for the first yield at the internal diameter is 3.26 and 3.76 MPa for the Tresca and Von Mises method, respectively, based on radial stress. The internal stress limit for the design is 4 and 4.62 MPa for the Tresca and Von Mises method, respectively. These values are higher than the maximal operating HTC pressure of 1-3 MPa, which suggest that the designed reactor is safe to sustain typical HTC reaction pressures at subcritical water condition. Thus, since PTFE lining has the lowest stress limit, which was 3.26 MPa according to Tresca theory, the pressure of 3 MPa will be set as the maximal pressure for the reactor unit, to give a margin of approximately 8 %.

Table A 2: Summary of the reactor design.

Reactor Specification	
Material	EN19 and PTFE
Type	Batch
Capacity	125 mL
Maximum operating temperature	260 °C
Maximum operating pressure	3 MPa

Based on the design specification and material stress analyses, the summary of the assembled reactor is presented in **Table A 2**. The reactor material consists of EN19 steel and PTFE lining, and it is designed for batch mode operation with a maximum volume of 125 mL. The maximum operating temperature and pressure is 260 °C and 3 MPa, respectively.

A 3: Reactor size, dimensions, and cost estimations

The technical drawing of the reactor was done in SolidWorks software. The 2D, 3D views and dimensions are illustrated in **Figure A 3**. The list of the different parts is presented in **Table A 3**.

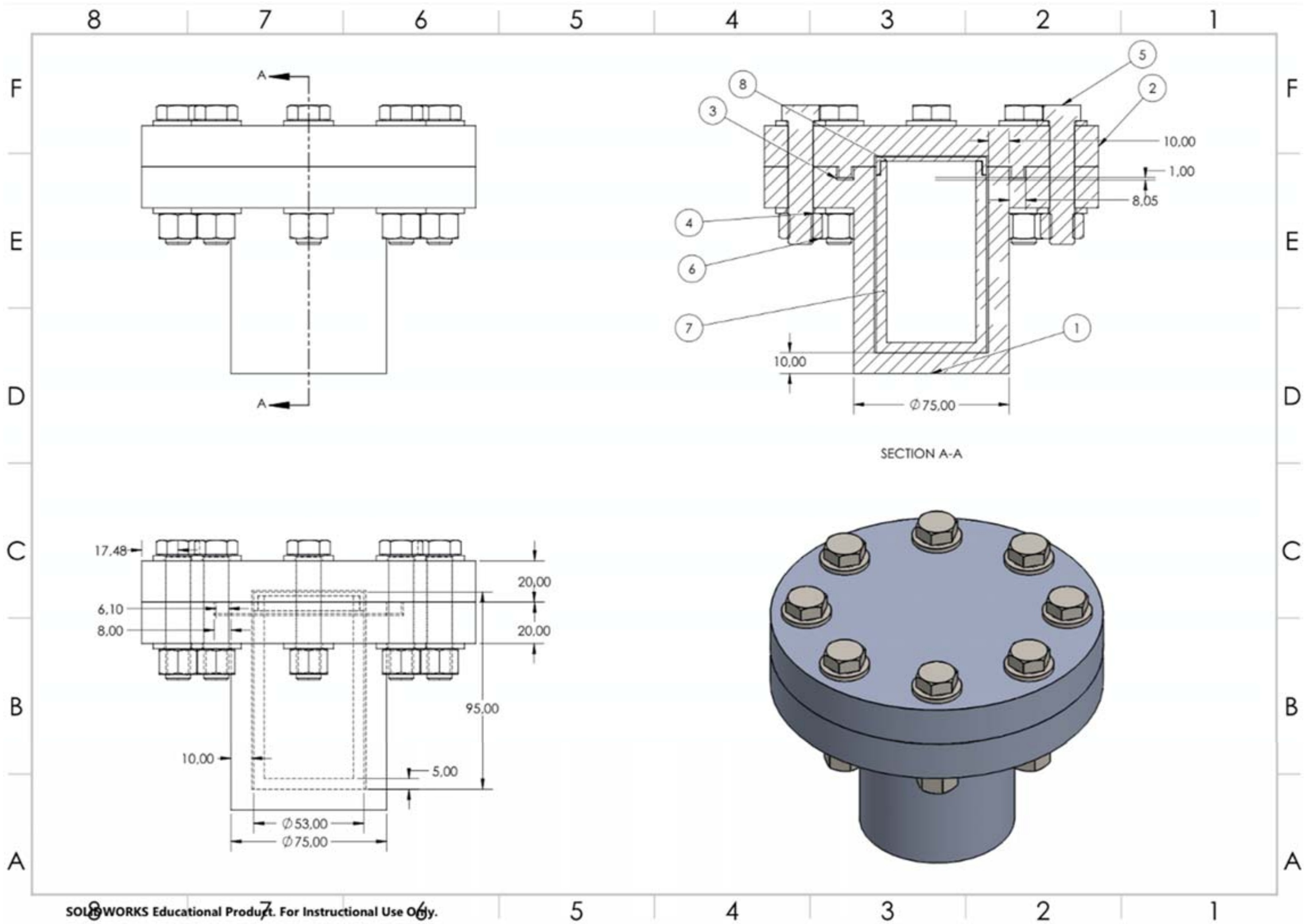

Figure A 3. Technical drawing of the reactor

Table A 3

Different parts of the reactor.

Item	Designation	Quantity
1	Cylindrical vessel	1
2	Vessel Lid	1
3	Gasket	1
4	Washer	16
5	Hexagonal screw	8
6	Hexagonal nuts	8
7	PTFE lining	1
8	PTFE lining lid	1

Reactor Construction and Costs

The reactor was constructed at Specialist Mechanical Engineers Pty Ltd (Pretoria, South Africa), and the PTFE was manufactured by Rui Jorge Pty Ltd (Johannesburg, South Africa), according to the design specifications. The assembled reactor is shown in **Figure A 4**, and the overall costs to fabric one reactor unit are summarised in **Table A 4**.

Table A 4: Costs of the reactor fabrication.

Item	Cost ($)
EN19 round steel bar (250 mm OD x 250 mm L)	214.77
PTFE lining and lid fabrication	82.48
Cylindrical vessel fabrication	400.34
Others (includes bolts, nuts and washers)	33.56
Total	**731.15**

Figure A 4. Visualization of a) alloy steel vessel; b) vessel with the PTFE lining; c) top view of the assembled reactor; d) view of the reactor after running the first HTC test.

Prior to HTC experiments, an aluminium foil adhesive type was placed on the surface of the vessel flange and on the lid to reinforce proper sealing. Since the vessel material has a very low concentration of chromium (Cr) and lacks elements such as copper (Cu), Nickel (Ni) and Vanadium (V) which are corrosion, oxidation and wear-resistant (Black and Kohser, 2017), the vessel corroded as a result of the exposure to moisture and heat for a prolonged period of time.

Section B: Effect of process parameters on the mass yield, calorific value and visual aspects of the hydrochar.

Table B 1: Effect of HTC reaction temperature and residence time on hydrochar yield and calorific values.

Temperature (h)	Time (min)	SF	HY * (%)	HHV (MJ/ kg)	Process wastewater pH
220	60	5.31	93.60	15.83	6.22
	120	5.79	74.44	17.90	4.00
	300	6.01	65.43	19.22	4.19
240	60	5.90	84.54	16.63	4.77
	120	6.38	50.25	21.27	3.83

	300	6.60	39.93	22.18	3.46
	60	6.49	73.86	17.75	4.49
260	120	6.97	34.93	21.59	3.40
	300	7.19	32.86	21.95	3.51

*HY: hydrochar yield.

To evaluate the impact of the mutual effect of HTC temperature and residence time in the conversion of feedstock, the reaction severity factor (SF)was given by equation B 1 and B 2, based on the Arrhenius equation (Heidari et al., 2019, Wang et al., 2018).

$$R_O = t \times e^{[(T-100)/14.75]} \quad (B.1)$$

$$SF = \log R_O \quad (B.2)$$

Where R_O represents the reaction ordinate (min), t is the residence time (min), T is the HTC reaction temperature (°C), and SF is the severity factor or the logarithm of the reaction ordinate. The evaluation of the severity factors determined at different reaction conditions for the preliminary and optimisation experiments are presented in Tables A 1 and A 2, respectively.

Table B 2: Severity factors for optimisation experiments conducted at varying reaction temperatures and residence times.

Temperature (°C)	Time (min)	SF
210	30	4.72
	105	5.26
	180	5.49
230	30	5.30
	105	5.85
	180	6.08
250	30	5.89
	105	6.44
	180	6.67

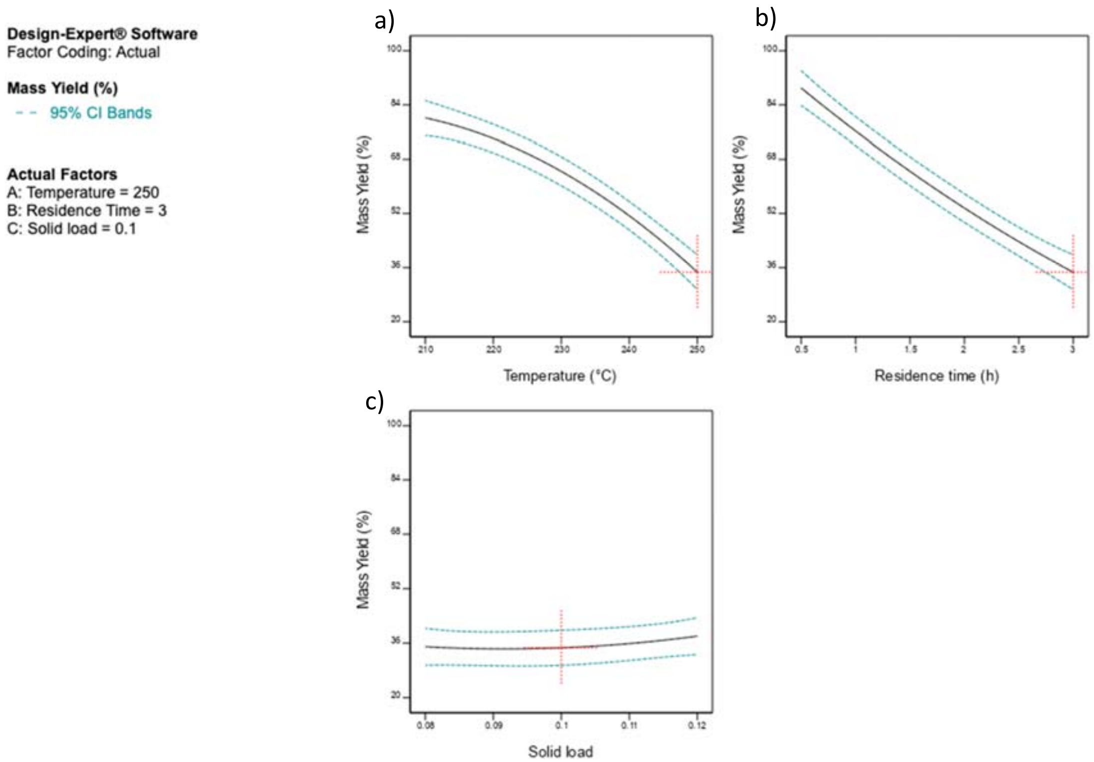

Figure B 1: Effect of a) temperature, residence time, and c) solid load on hydrochar yield at maximum reaction severity.

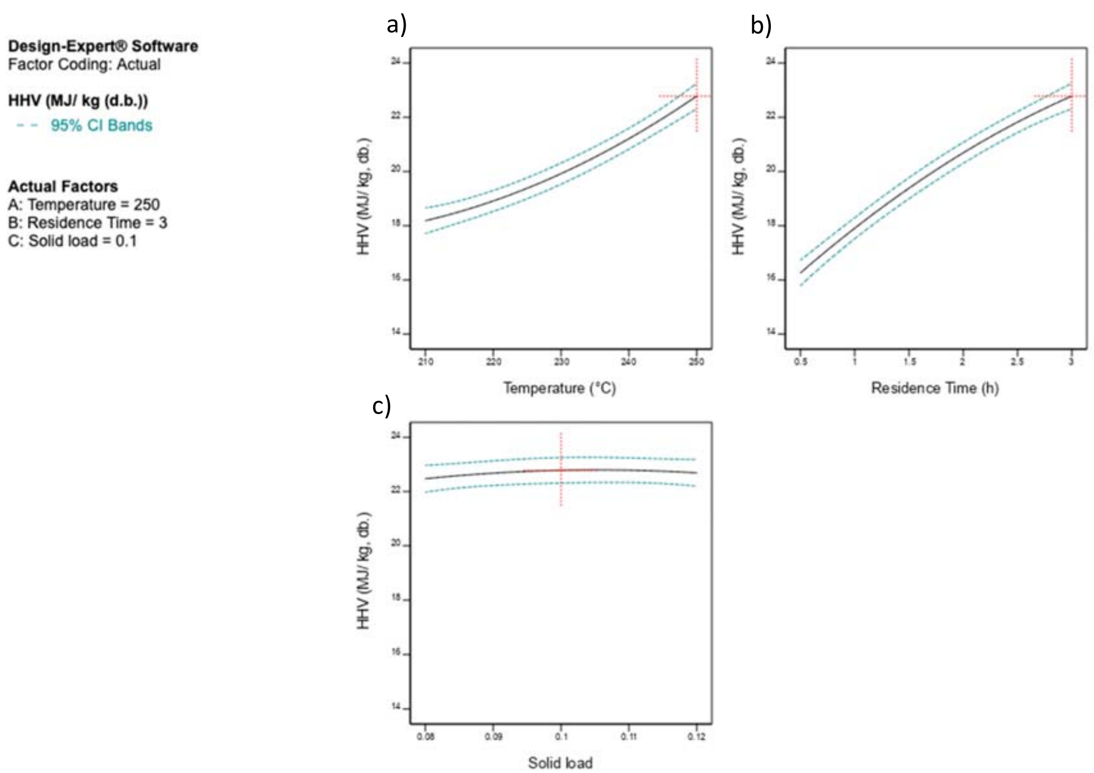

Figure B 2: Effect of a) temperature, b) residence time, and c) solid load on calorific value at maximum reaction severity.

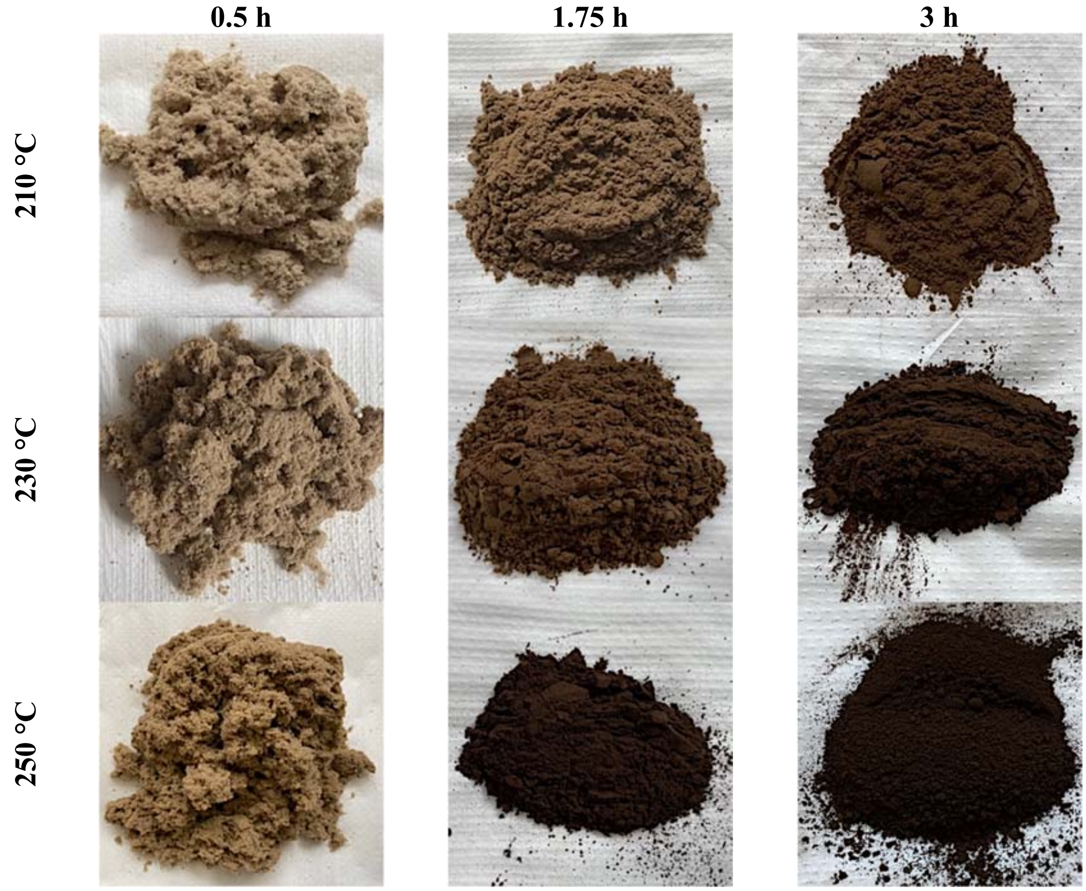

Figure B 3: Visual assessment of ground hydrochars obtained at different reaction severities for process optimisation.

References

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