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Hydrothermal Carbonization of Household Wet Waste – Characterization of Hydrochar and Process Wastewater Stream

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Outline

- **Background and Motivation**
- Aim and Objectives
- Materials and Methods
- Results
- Summary and Conclusions

BACKGROUND AND MOTIVATION

- Waste generation in India increased by 2.44 times in the last decade and is estimated to increase by 100 million tonnes by 2031 (Joshi and Ahmed, 2016; Ministry of New and Renewable Energy, 2016)
- In developing nations, ~50% of the waste comprises of wet biodegradable waste having 70-80% moisture content (Kaza et al., 2018)
- Conventional wet waste treatment processes include composting and anaerobic digestion
- Limitations of Biological processes:
  (i) High processing time
  (ii) Inhibition due to toxic compounds
  (iii) Odorous air emissions
  (iv) Require control of various parameters
- MSW is a source rich in carbon, can also be used as a renewable energy source
- Pre-treatment of waste is necessary to overcome heterogeneity, reduce moisture content and improve calorific value

HYDROTHERMAL CARBONIZATION

- Hydrothermal carbonization (HTC) concentrates 75-80% of the carbon in the solid; 15-20% in liquid, and ~5% is converted to gas (mainly CO_2)
- HTC produces homogeneous energy densified hydrochar and process wastewater (PW) with no need for pre-drying or chemicals, requires lesser time and space
- PW can be utilized to recover energy or value added chemicals such as organic acids, 5-HMF, phosphorus, proteins and humic like substances
- Hydrochar can be utilized as:
    i. **Co-fuel -** HHV upto 30 MJ/kg (Gupta et al., 2020)
    ii. **Soil amendment -** lower heavy metal content, increases soil microbial activity, improves nutrient sorption behavior of the soils (Bamminger et al., 2014; Chu et al., 2020)
    iii. **Adsorbent –** after pretreatment to increase oxygenated functional groups, cation exchange capacity (Parshetti et al., 2016)
- Lack of studies on HTC of household wet waste in developing countries

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AIM AND OBJECTIVES

AIM: To investigate the performance of HTC for energy and resource recovery potential from household wet waste (HWW)

The objectives were:

- To study the characteristics of HC and identify possible routes for its use (co-fuel, soil amendment)
- To characterize PW for identifying value added compounds produced during HTC
- To evaluate the biogas recovery potential of PW
- To determine the reaction kinetics of different possible reactions occurring during HTC

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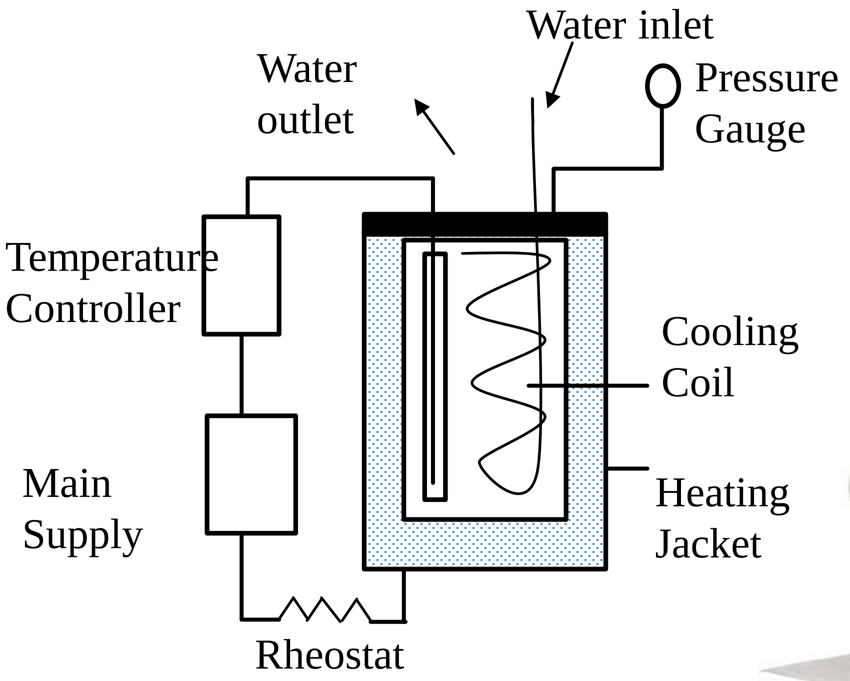
MATERIALS AND METHODOLOGY



2 L high pressure reactor
(Material : SS 316, design temperature = 250°C, design pressure = 100 bar)

- Source segregated HWW collected from residential buildings at Indian Institute of Technology (IIT) Bombay
- Average moisture content = 70%
- **700 g HWW subjected to HTC at 200°C for 1-8 h**
- HC and PW separated by vacuum filtration
- Oven dried HCs analyzed by CHNS, Boehm titration, chlorine content, and TGA
- H_2O_2 treatment of HCs using10% H_2O_2 (w/v) shaken at 110 rpm for 2 h
- PW analyzed for COD, BOD_5, TOC, NH_4^+-N, total carbohydrates, VFAs, 5-HMF, furfural, proteins and humic like substances

METHODS - BIOCHEMICAL METHANE POTENTIAL (BMP) OF PW AND HC POT EXPERIMENT

BMP Test

- 80 mL mixture of PW and inoculum (COD:VS = 1:1) was added to three 130 mL sealed bottles
- Control and sample bottles kept in a water bath at 35°C and gas measured at regular intervals using glass syringe
- The volume of gas and change in mass of the bottle (due to gas removal) were noted and used to calculate the approximate composition of biogas (Justesen et al., 2019)

Pot Experiment

- Pots containing 180 g of only soil (control), mixture of soil and HC_8 and mixture of soil and H_2O_2 treated HC_8 were prepared
- The HC percentage was varied from 1-5% by mass
- Ten germinated *Vigna radiata* seeds were added

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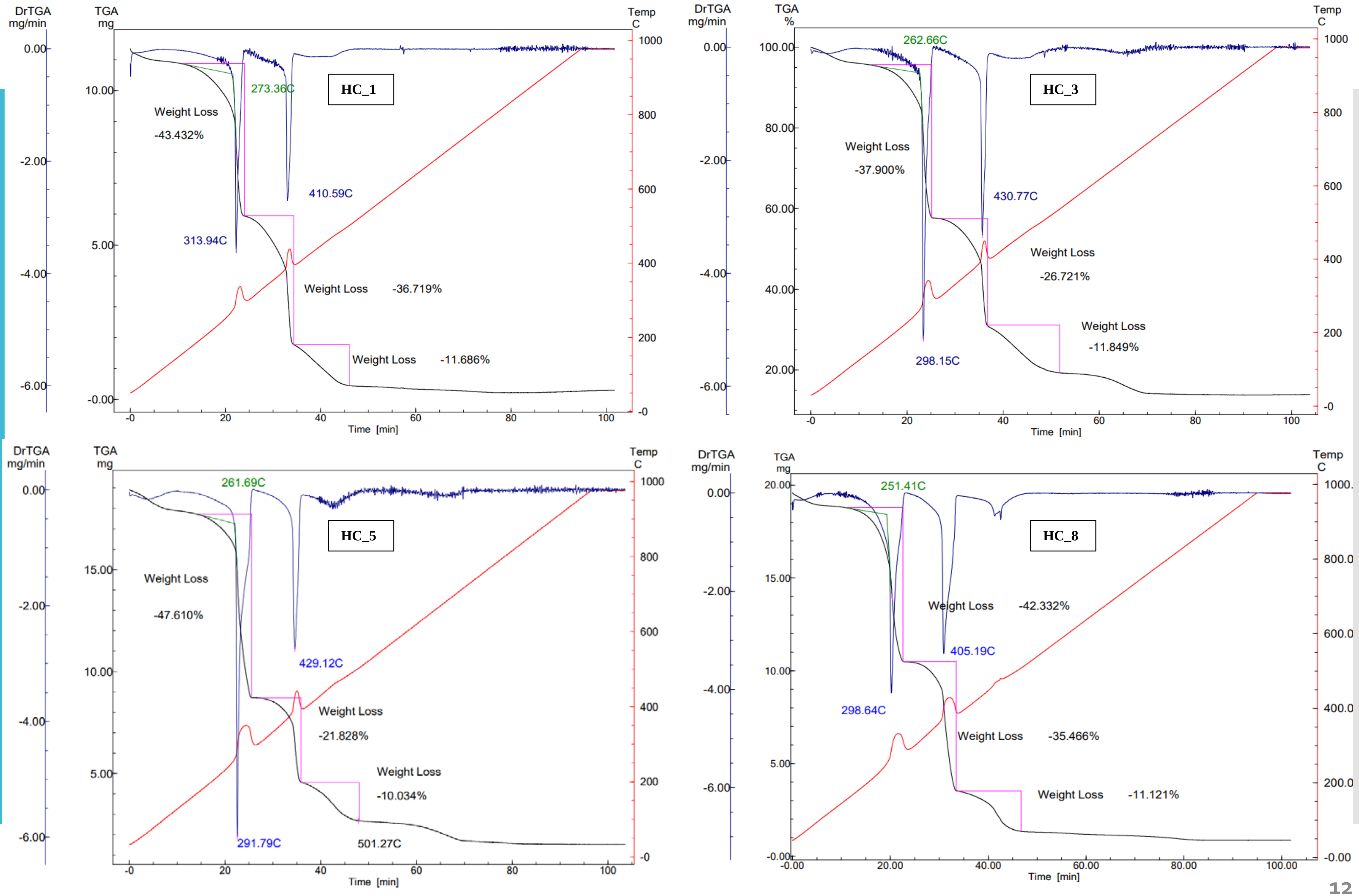
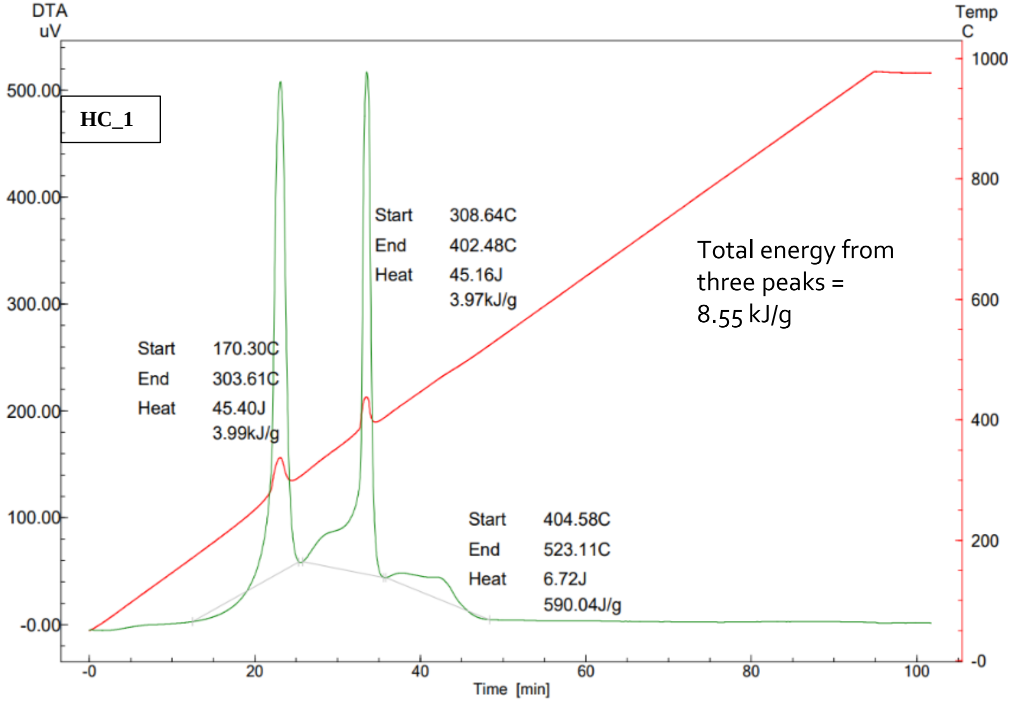
ULTIMATE AND PROXIMATE ANALYSIS

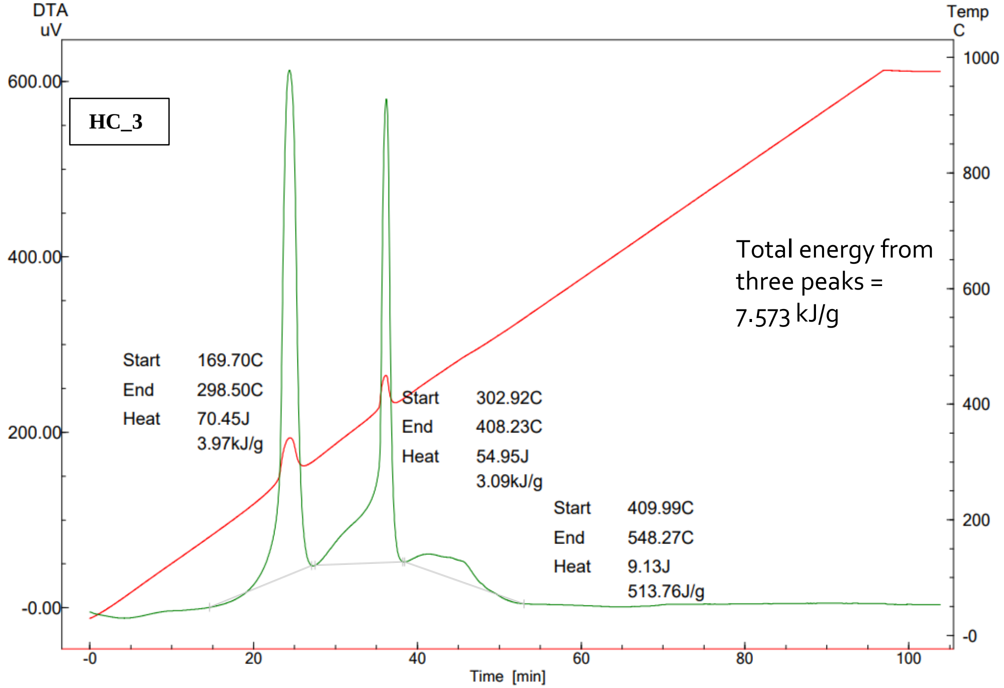
Parameter	HWW	HWW derived hydrochars			
		HC_1	HC_3	HC_5	HC_8
Solid yield (%)	-	50.0	47.8	53.7	48.5
Volatile solids (%)	93.6±0.64	91.4±0.6	91.5±2.8	92.3±0.9	92.8±0.1
Fixed carbon (%)	2.4±0.8	5.9±0.22	2.3±0.21	2.2±0.09	1.2±0.78
Ash (%)	4.0±0.02	2.7±0.18	6.2±0.04	5.5±0.19	6.0±0.78
C (%)	46.6	58.4	55.2	58.4	63.5
H (%)	7.3	6.4	6.5	6.1	7.2
O (%)	39.9	29.7	28.9	27.4	20.7
N (%)	2.2	2.8	3.2	2.6	2.6
Cl (mg/g)	11.6±0.35	5.5±0.07	4.7±0.21	3.8±0.18	4.6±0.09
LHV (MJ/kg)	2.5	-	-	-	-
HHV (MJ/kg)	18.2	22.7	22.4	22.5	26.6
Carbon densification	-	1.25	1.20	1.25	1.36
Energy densification (based on HHV)	-	1.3	1.2	1.2	1.5

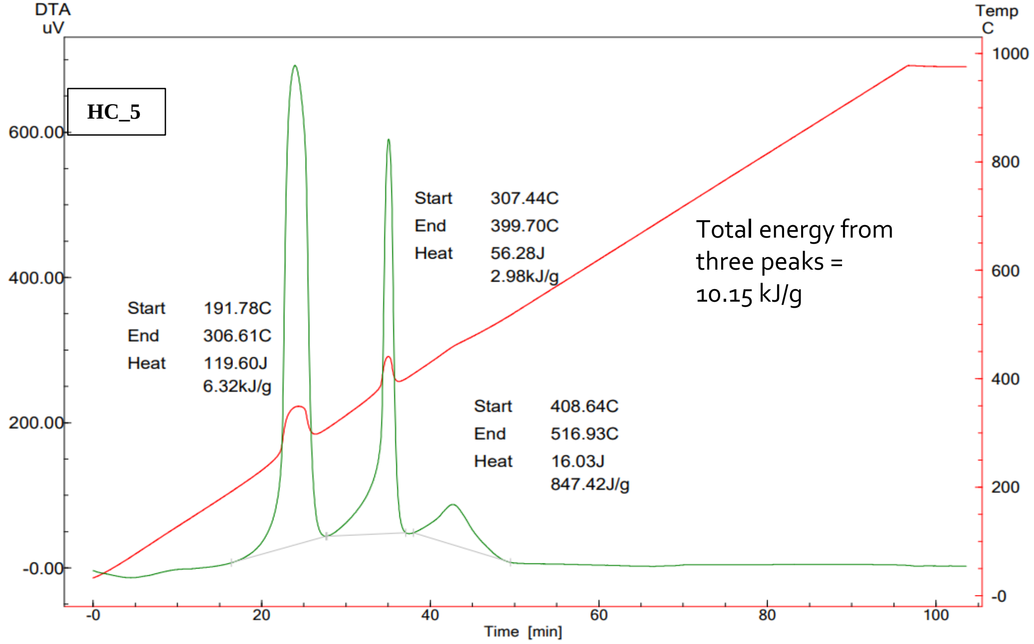
Thermal Behaviour of HC in air atmosphere : Thermo-gravimetric analysis (TGA)

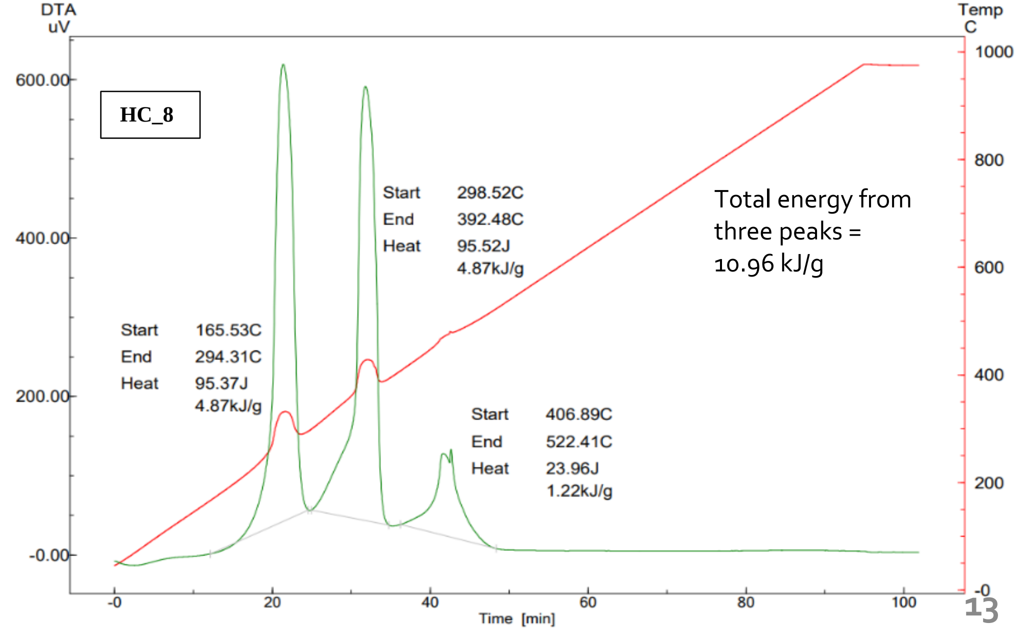


Thermal Behaviour of HC in air atmosphere : Differential Thermal Analysis (DTA)

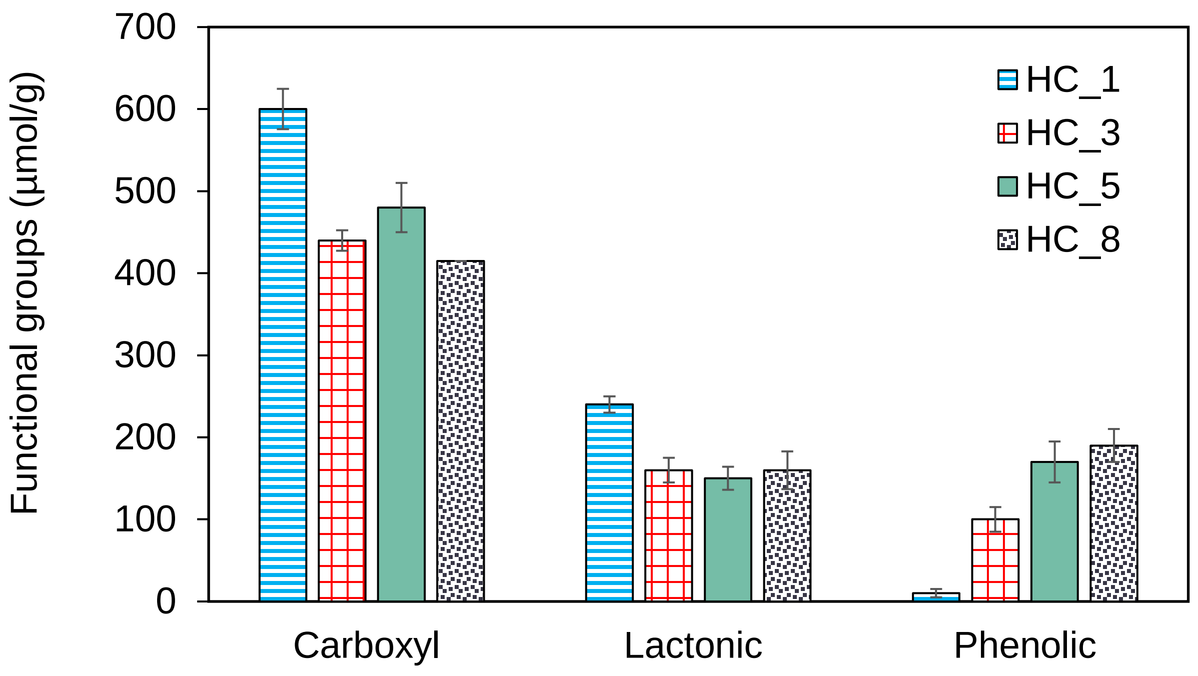




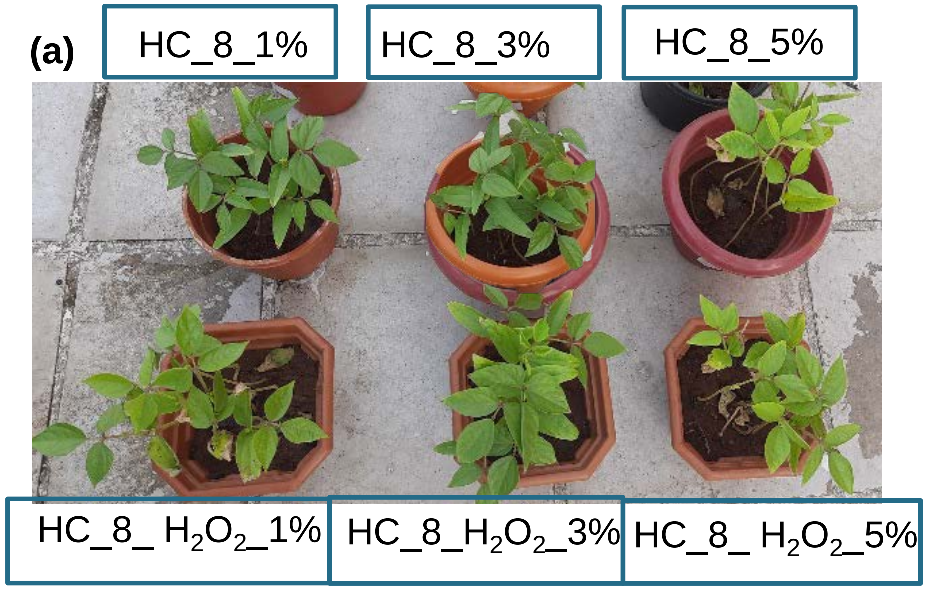




SURFACE FUNCTIONAL GROUPS ON HC AND ITS IMPACT ON PLANT GROWTH

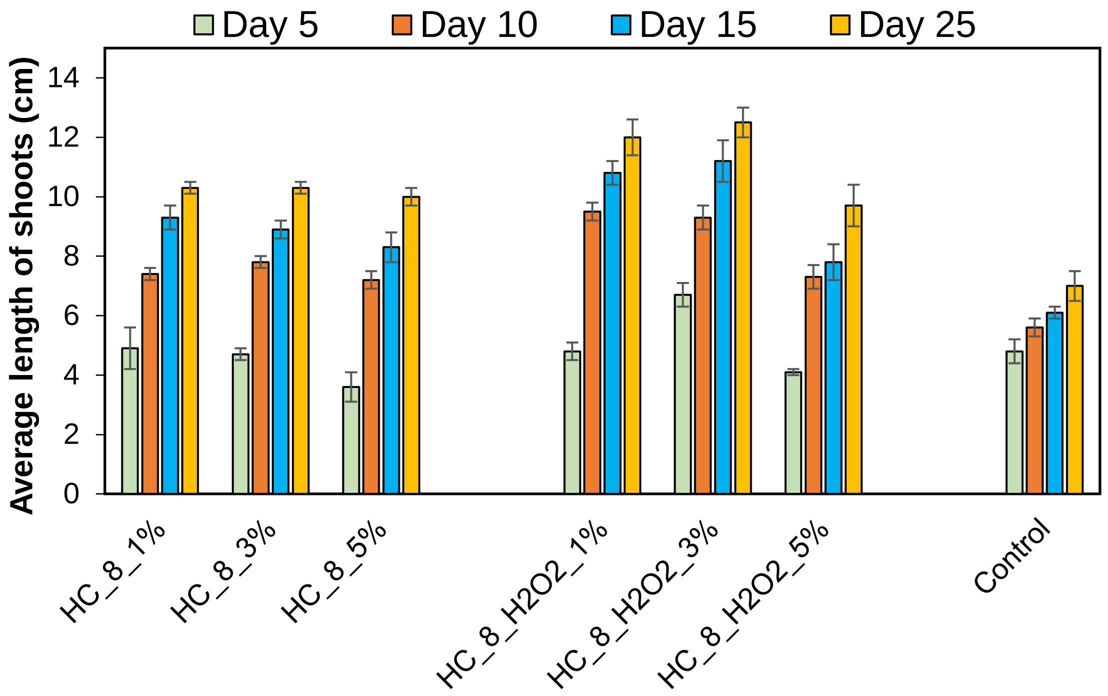


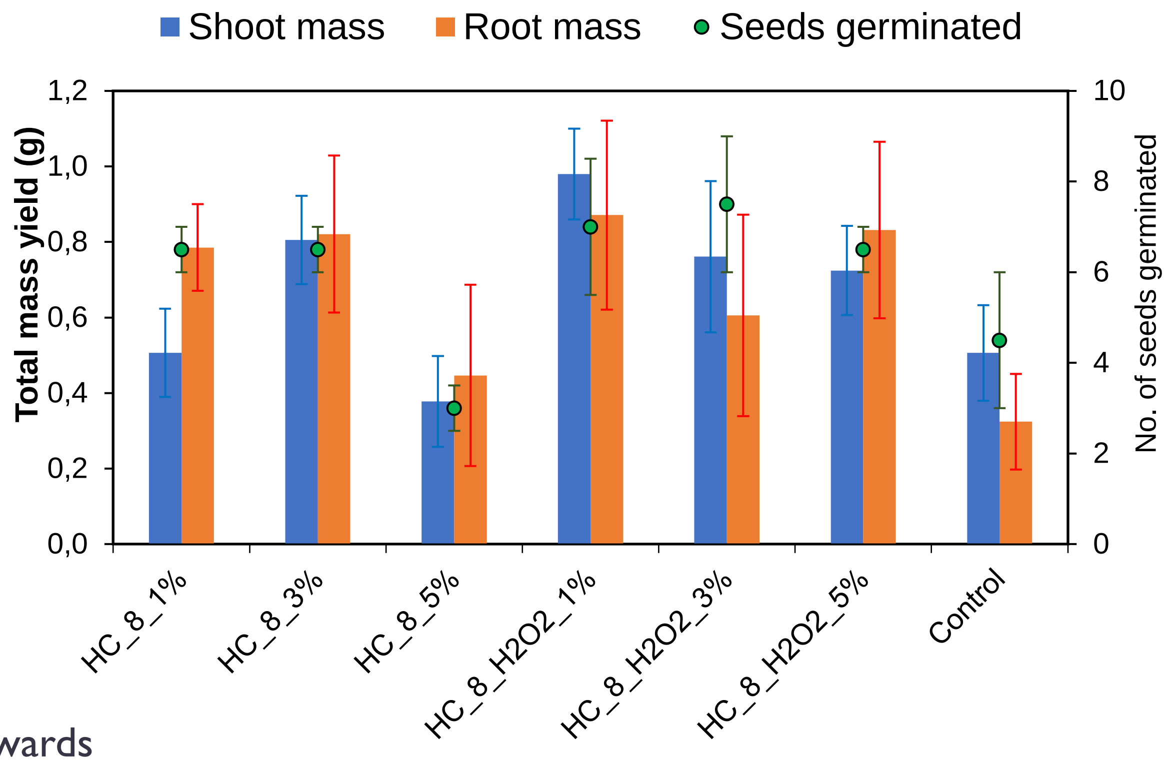
Acidic functional groups on the hydrochar surface



Pot Experiment of HC_8 and HC_8_H_2O_2 in 1-5% (w/w of soil) mass ratio

EFFECT OF HYDROCHAR ON PLANT GROWTH

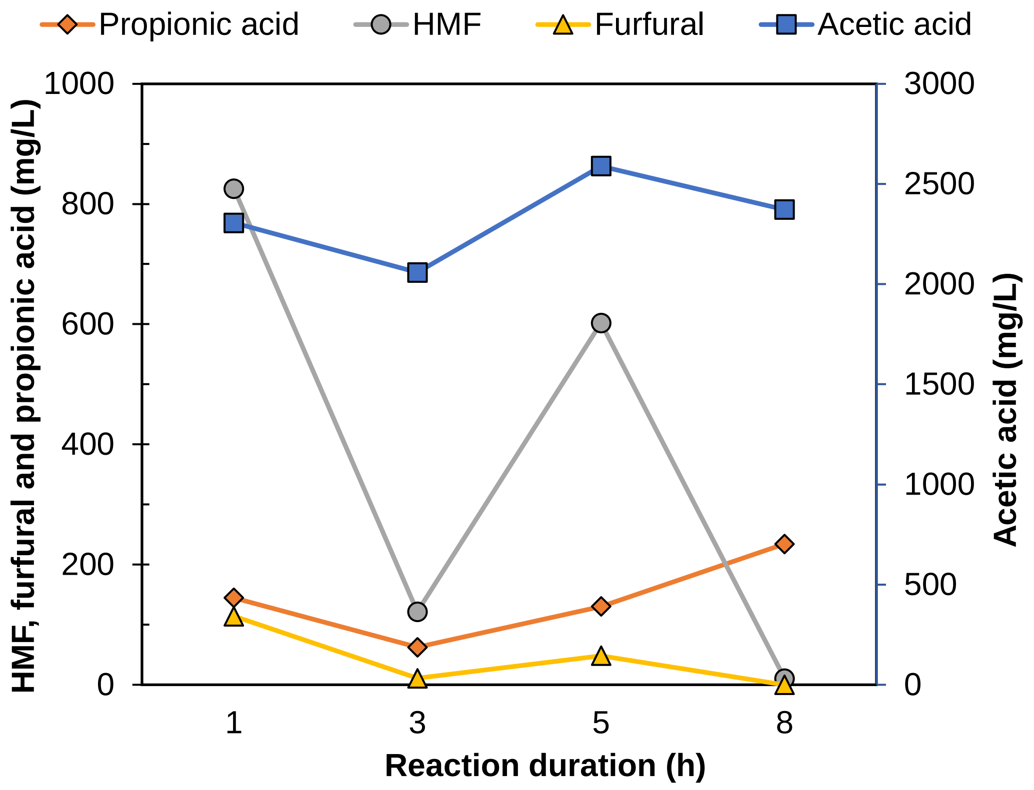




- Growth was slower during initial 5 days, but increased afterwards
- H_2O_2 treatment of HC samples resulted in highest shoot length
- At maximum application rate (5 wt%), slight decrease in length was observed
- Total average masses after 25 days were almost twice with HC_8_H_2O_2_1% than control
- H_2O_2 treatment removed growth inhibition and increased plant growth due to hydrochar application

PROCESS WASTEWATER CHARACTERISTICS

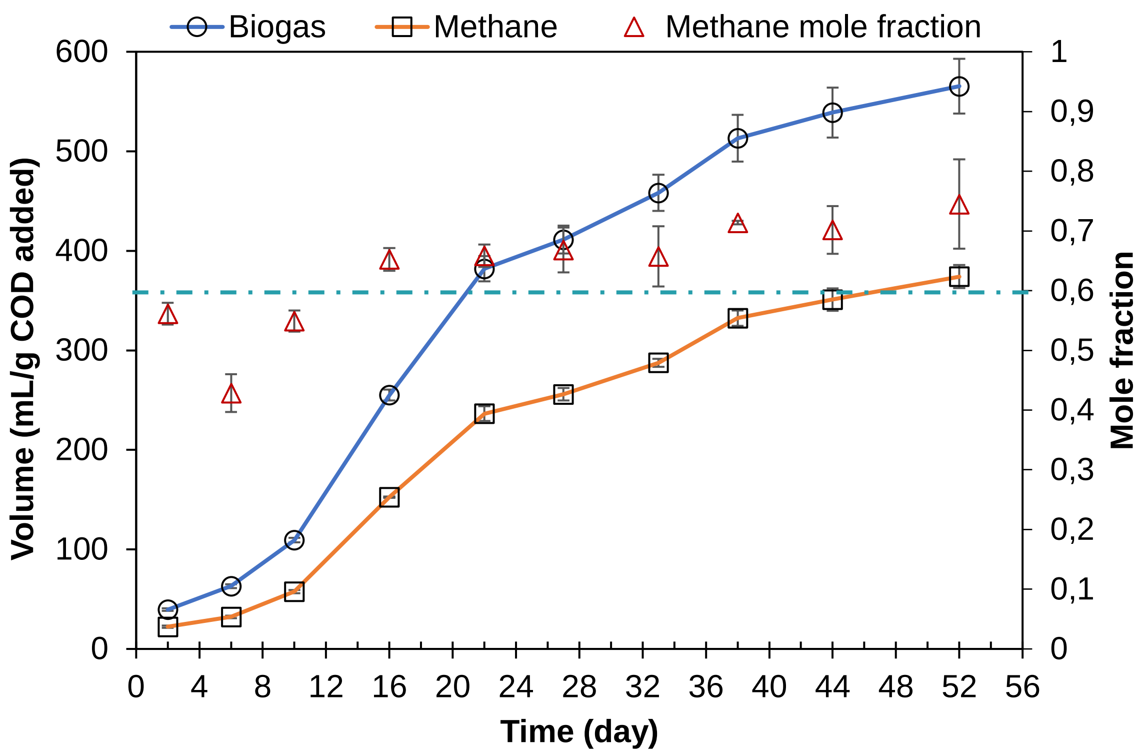
Analysis	PW_1	PW_3	PW_5	PW_8
PW yield (%)	66.6±4.3	70.9±6.2	67.7±5.6	80.5±7.8
COD (mg/L)	67,840±104	66,560±905	78,080±910	80,000±1358
BOD_5 (mg/L)	41,230±1198	36,693±560	36,490±652	37,594±407
TOC (g/L)	24,851±79.6	25,482±1841	28,6012±2601	29,305±2130
Carbohydrates (mg/L)	2,706±250	1,210±190	1,378±190	807±43
Ammonium-N (mg/L)	263±6.2	476±52	184±64	397±72
Proteins (mg/L)	6,424±1.83	6,267±0.36	6,279±0.84	5,846±0.79
Humic like substances (mg/L)	24,772±3.8	20,532±2.6	20,461±2.0	17,944±2.2



The pH of all PW samples was in the range of 3.5-3.7.

BIOCHEMICAL METHANE POTENTIAL OF PW_8

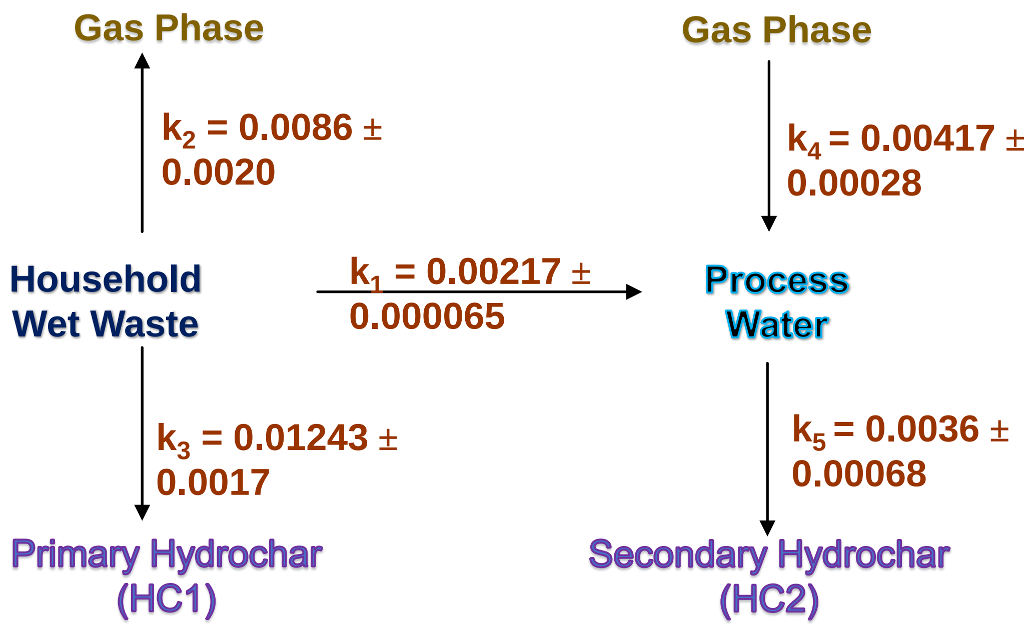
- Gas production increased rapidly after 10 days
- Significant gas production was observed until 38 days
- Methane concentration was more than 65% after 10 days
- 374 mL methane per g COD was obtained corresponding to more than 17.7 L methane or 575 kJ/kg HWW



Biogas production and methane mole fraction resulted from BMP test of PW_8

REACTION KINETICS – RATE CONSTANTS

Reaction Pathway



Reaction pathway modified from Lucian et al. (2019)

Rate Law Equations used in the model

$$\frac{dC_{HWW}}{dt} = -(k_1 + k_2 + k_3)^* C_{HWW} \quad (1)$$

$$\frac{dC_{PW}}{dt} = k_1 * C_{HWW} + k_4 * CG - k_5{}^* C_{PW} \quad (2)$$

$$\frac{dC_{HC1}}{dt} = k_3{}^* C_{HWW} \quad (3)$$

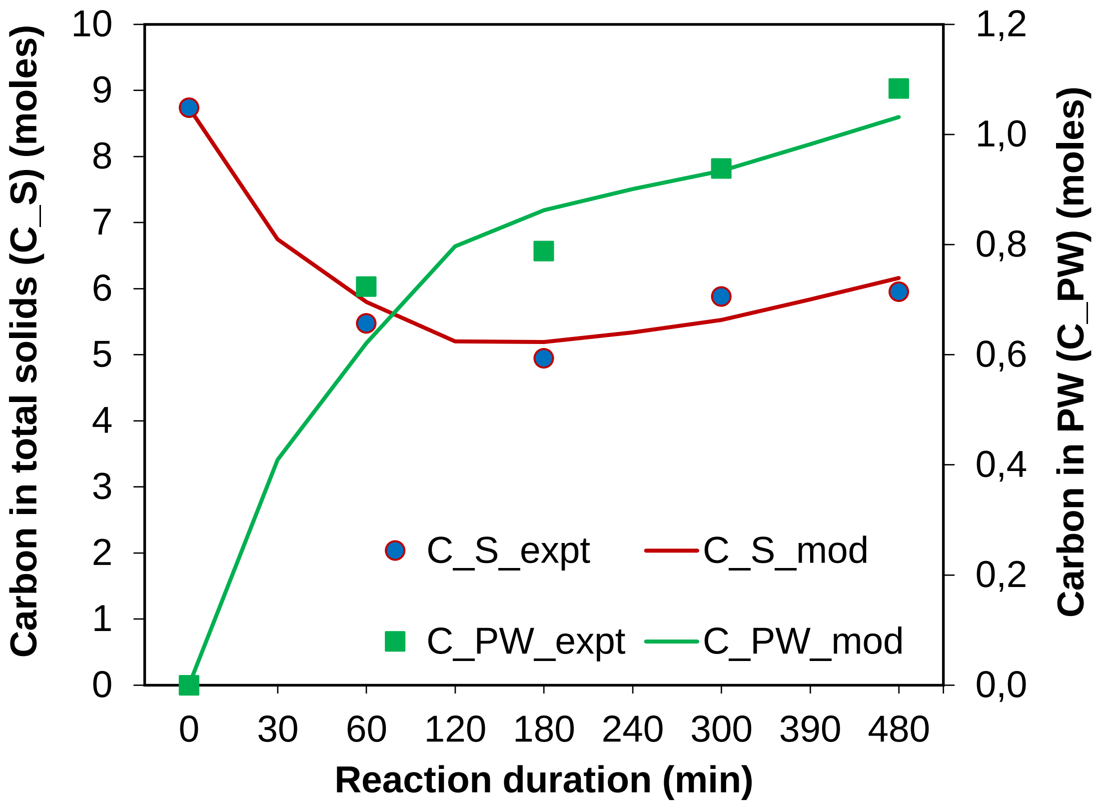
$$\frac{dC_{HC2}}{dt} = k_5{}^* C_{PW} \quad (4)$$

$$\frac{dC_G}{dt} = k_2 * CHW_W - k_4{}^* C_G \quad (5)$$

$$C_S = C_{HWW} + C_{HC1} + C_{HC2} \quad (6)$$

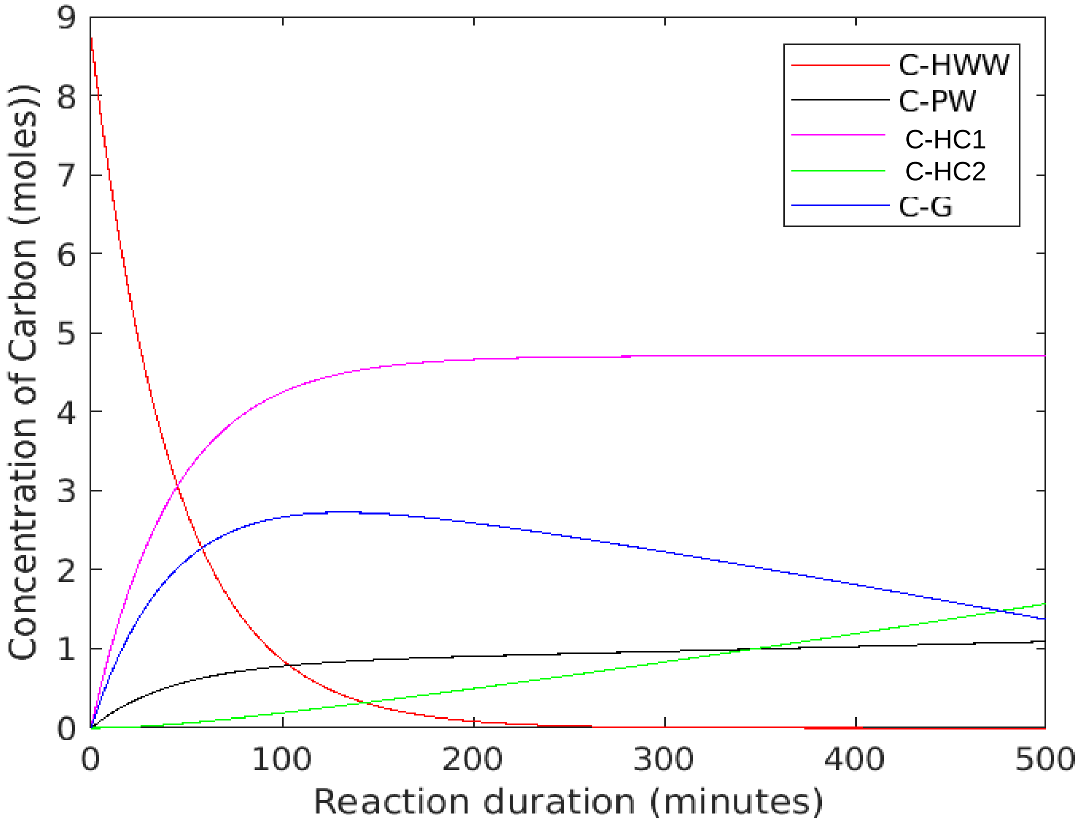
where, C_X = moles of carbon in X, where X can be HWW, PW, S (total solid phase), G (total gas phase), HC1 or HC2.

REACTION KINETICS – PREDICTED CONCENTRATIONS



Experimental and Model values of total carbon in Solid (C_S) and total carbon in liquid phase (C_PW) (Error tolerance < 10^{-6})

C_S = C_HWW + C_HC1 + C_HC2



Predicted Model concentrations of carbon in HWW (C_HWW), liquid phase (C_PW), primary HC (C_HC1) and secondary HC (C_HC2)

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SUMMARY AND CONCLUSIONS

- HTC of HWW produced a high calorific value HC (26.6 MJ/kg) with 1.5 times energy densification and 17% more carbon
- HTC can be used for generating waste to energy from HC (as co-fuel) and PW (biogas)
- HC also proved beneficial for plant growth, further enhanced by H_2O_2 pretreatment
- Decrease in carbohydrates and increase in short chain fatty acids observed with intermediate formation of HMF and furfural with increasing reaction duration
- The majority of solubilization occurred between 3 and 5 h after which repolymerization was more prominent
- Due to long durations required for HTC of HWW, further studies may be conducted on catalytic HTC of HWW

THANK YOU