Freie Universität Bozen
Libera Università di Bolzano
Free University of Bolzano

Integration of hydrothermal processes for fuels and hydrogen production from digestates

Marco Baratieri

Introduction

Cattle Manure

Anaerobic Digestion

DIGESTATE

BIOGAS

Introduction

In Europe, Directives 2016/2284/EU and 91/676/EEC ***regulate the distribution of digestate on agricultural land****, limiting the intake of N to 170 kg ha^{-1} year^{-1}*

- Water pollution: nitrate and nutrients leach into the groundwater causing eutrophication and hypoxia
- Air pollution: ammonia volatilization
- Very high water-content and residual biological activity ⇒ management issues
- Negative economic and environmental impacts

Introduction

Landfilling

Composting

- Long times
- Bad odor
- GHGs emissions
- Land availability

Pre-treatment step to decrease the moisture content

Incineration

HTC

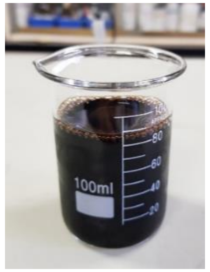
Hydrothermal Carbonization - HTC

(Pre)treatment of biomass in hot (180-250 °C) compressed water at residence times varying from minutes to several hours. Ideal for biomass with high moisture content (> 60 %).

Hydrothermal Carbonization - HTC

(Pre)treatment of biomass in hot (180-250 °C) compressed water at residence times varying from minutes to several hours. Ideal for biomass with high moisture content (> 60 %).

Hydrochar
(HC)

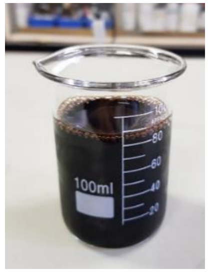


Aqueous HTC Liquid
(AHL)

Hydrothermal Carbonization - HTC

(Pre)treatment of biomass in hot (180-250 °C) compressed water at residence times varying from minutes to several hours. Ideal for biomass with high moisture content (> 60 %).

Hydrochar
(HC)



Aqueous HTC Liquid
(AHL)

→

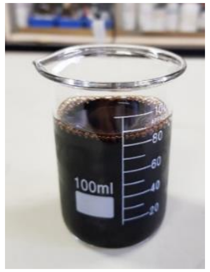
- Fuel
- Soil amelioration
- Carbon sequestration
- Wastewater treatment
- Carbon materials
- Energy storage

Hydrothermal Carbonization - HTC

(Pre)treatment of biomass in hot (180-250 °C) compressed water at residence times varying from minutes to several hours. Ideal for biomass with high moisture content (> 60 %).

Hydrochar (HC)

- Fuel
- Soil amelioration
- Carbon sequestration
- Wastewater treatment
- Carbon materials
- Energy storage



Aqueous HTC Liquid (AHL)

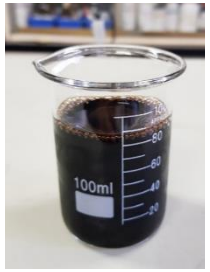
- Anaerobic digestion
- Fertilizers
- Recirculation
- Microalgae growth
- P recovery

Hydrothermal Carbonization - HTC

(Pre)treatment of biomass in hot (180-250 °C) compressed water at residence times varying from minutes to several hours. Ideal for biomass with high moisture content (> 60 %).

Hydrochar (HC)

- Fuel
- Soil amelioration
- Carbon sequestration
- Wastewater treatment
- Carbon materials
- Energy storage



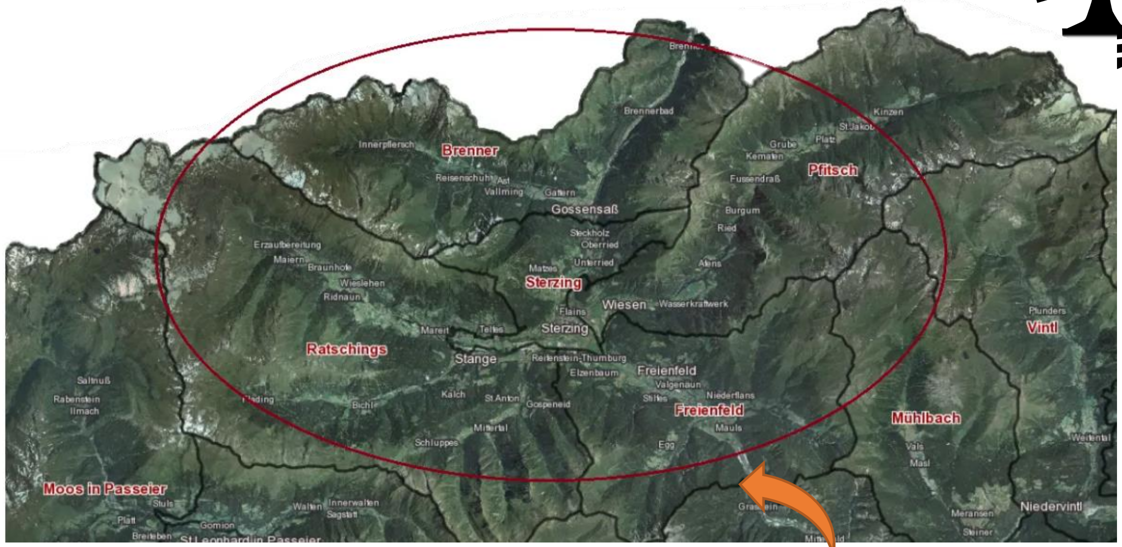
Aqueous HTC Liquid (AHL)

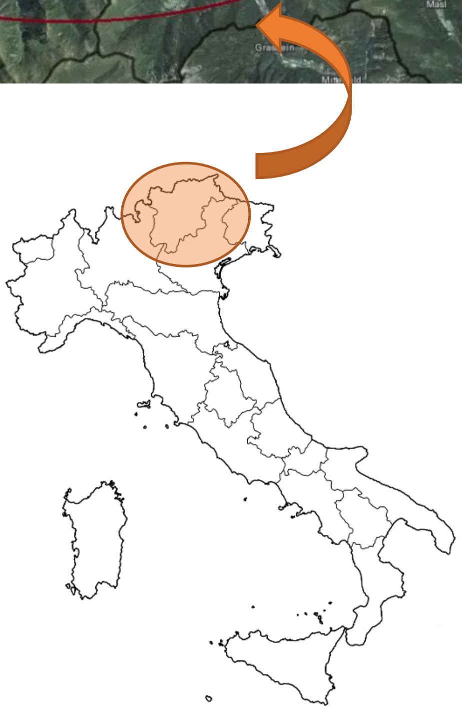
- Anaerobic digestion
- Fertilizers
- Recirculation
- Microalgae growth
- P recovery
- **SCWG**

Materials and Methods

Digestate

Source: courtesy of Biogas-Wipptal

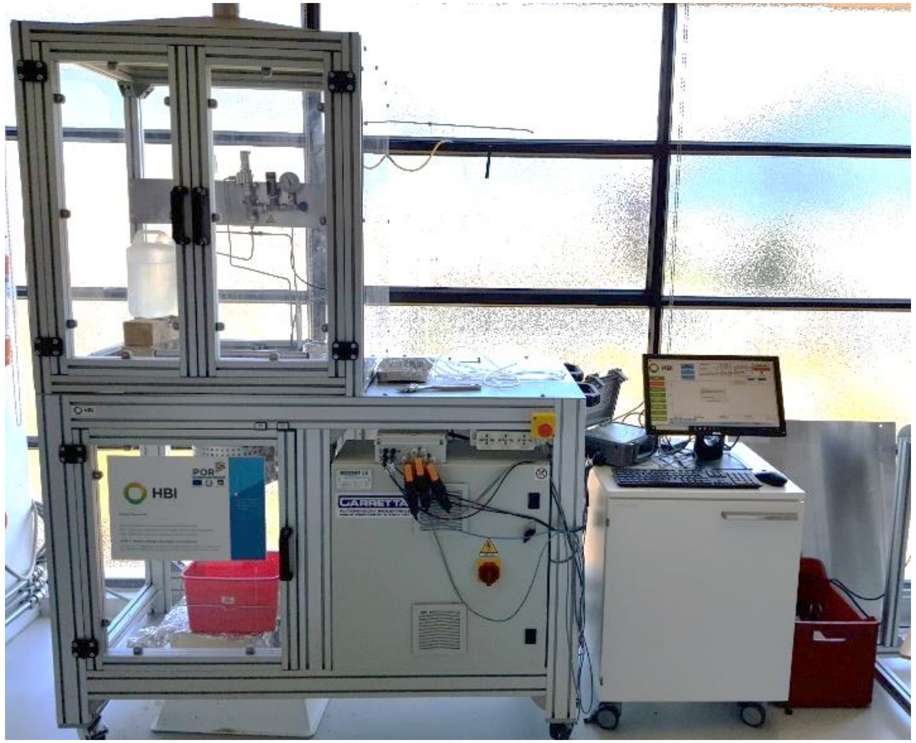




Digestate		
Ash content	[%wt]	26.83
C	[%wt]	39.11
H	[%wt]	4.87
O	[%wt]	26.56
N	[%wt]	1.94
S	[%wt]	0.68
HHV	[MJ/kg]	14.31
LHV	[MJ/kg]	13.24

- 2.5 kg per experiment
- Previously kept in refrigerator at 4 °C
- No pre-treatment

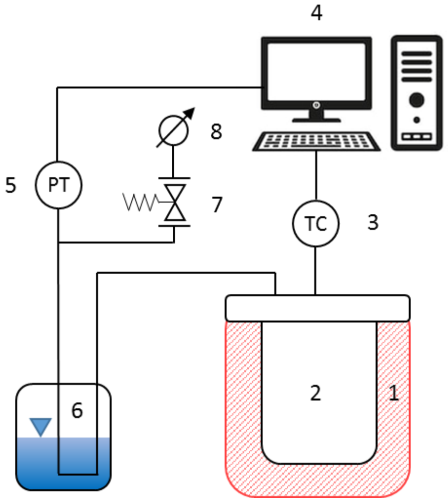
Materials and Methods



Batch reactor – 4 L

Hydrochar – oven-dried at 105 °C for 24 h

Aqueous HTC Liquid



1. Electric furnace
2. HTC reactor
3. Temperature controller
4. HTC controller
5. Pressure transducer
6. Cold trap
7. Safety valve
8. Manometer

Scheme of the experimental lay-out

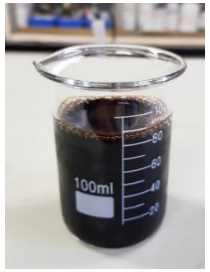
Operating condition	Experimental range		
Feedstock	digestate		
Temperature [°C]	180	220	250
Pressure	endogenous		
Residence time [h]	3		
Repetitions	3		

Hydrothermal Carbonization - HTC

(Pre)treatment of biomass in hot (180-250 °C) compressed water at residence times varying from minutes to several hours. Ideal for biomass with high moisture content (> 60 %).

Hydrochar
(HC)

- Fuel
- Soil amelioration
- Carbon sequestration
- Wastewater treatment
- Carbon materials
- Energy storage



Aqueous HTC Liquid
(AHL)

- Anaerobic digestion
- Fertilizers
- Recirculation
- Microalgae growth
- P recovery
- SCWG

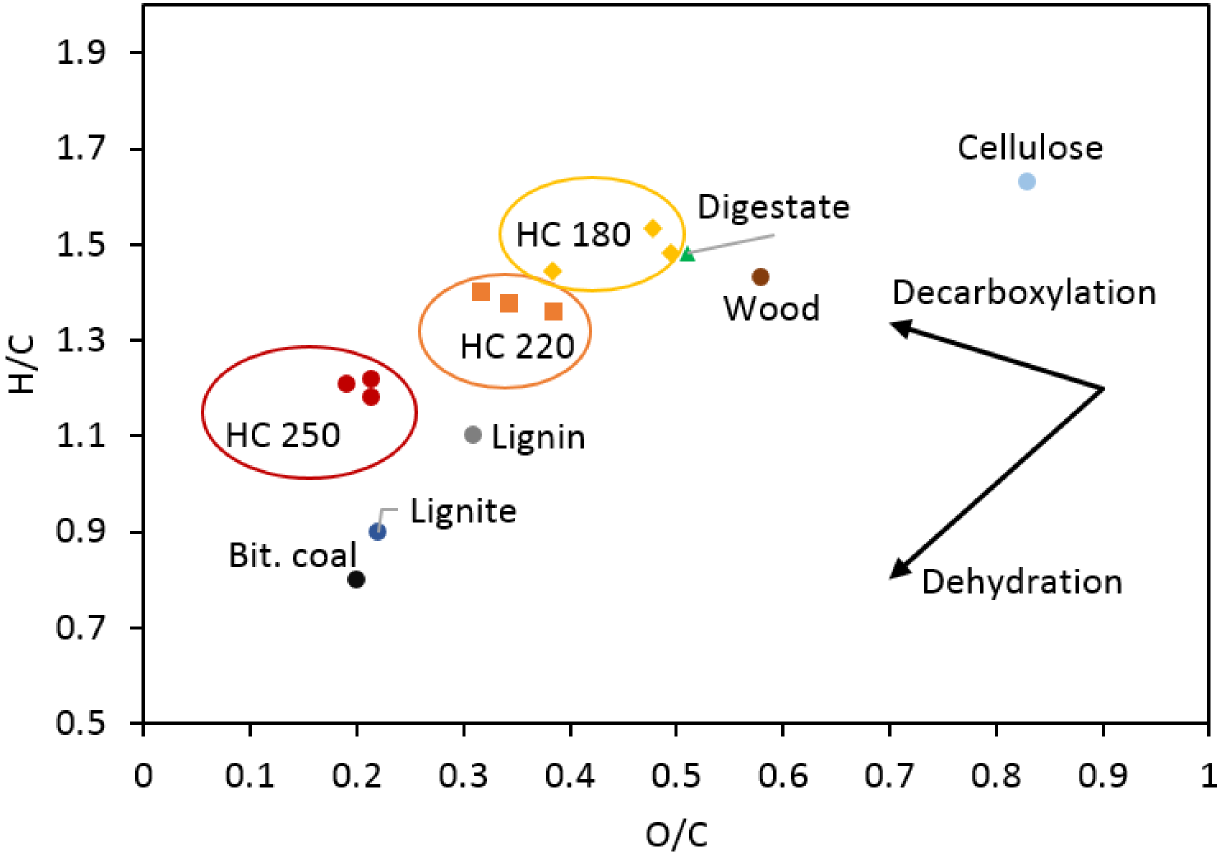
HC characterization results

		Digestate	HC180	HC220	HC250
Volatile matter	$\%wt_{dry}$	55 ± 1	55 ± 1	53 ± 1	46.7 ± 0.3
Fixed carbon	$\%wt_{dry}$	18 ± 1	17.9 ± 0.3	18.5 ± 0.4	20.7 ± 0.4
Ash	$\%wt_{dry}$	26.6 ± 0.5	27.2 ± 0.8	28.8 ± 0.8	32.5 ± 0.7
Fuel ratio	-	0.33	0.33	0.34	0.44
C	$\%wt_{dry}$	39.1 ± 0.5	40.1 ± 1.6	42.5 ± 0.8	45.0 ± 0.6
H	$\%wt_{dry}$	4.87 ± 0.05	5.01 ± 0.11	4.92 ± 0.15	4.54 ± 0.09
N	$\%wt_{dry}$	1.94 ± 0.09	2.03 ± 0.06	2.16 ± 0.03	2.59 ± 0.11
S	$\%wt_{dry}$	0.68 ± 0.03	0.71 ± 0.05	0.62 ± 0.01	0.59 ± 0.01
O*	$\%wt_{dry}$	26.56	24.09	19.71	12.35
HHV	MJ/kg	14.3 ± 0.5	15.9 ± 0.1	16.9 ± 0.2	18.2 ± 0.4

Benedetti et al., Combustion kinetics of hydrochar from cow-manure digestate via thermogravimetric analysis and peak deconvolution, Bioresource Technology 353 (2022) 127142

HC characterization results

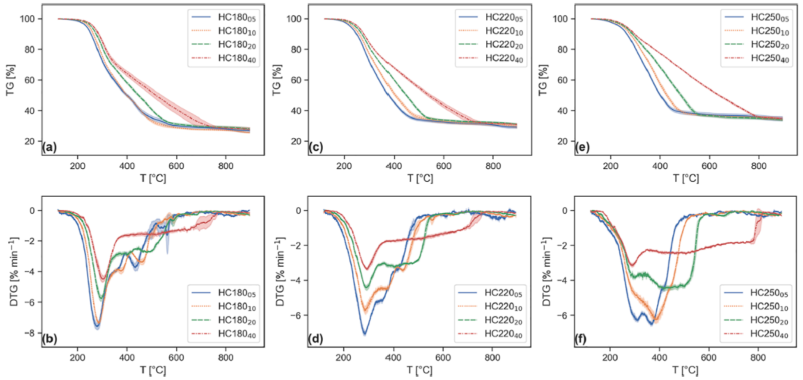
Van Krevelen Diagram



decarboxylation and **dehydration** reactions occur during the HTC process

Thermogravimetric analysis

- T: 40 - 900 °C
- Ramp rate (β): 5, 10, 20, 40 °C min^{-1}
- Purge gas: air, 20 mL min^{-1}
- Protective gas: N_2, 20 mL min^{-1}
- Replicates: 3



Combustion kinetics

Kissenger-Akahira-Sunose (KAS) method

$$ln\left(\frac{\beta}{T_\alpha^2}\right) = ln\left(\frac{A\,E_\alpha}{R\,g(\alpha)}\right) - \frac{E_\alpha}{R\,T_\alpha}$$

$$\alpha = \frac{m_i - m_t}{m_i - m_f}$$

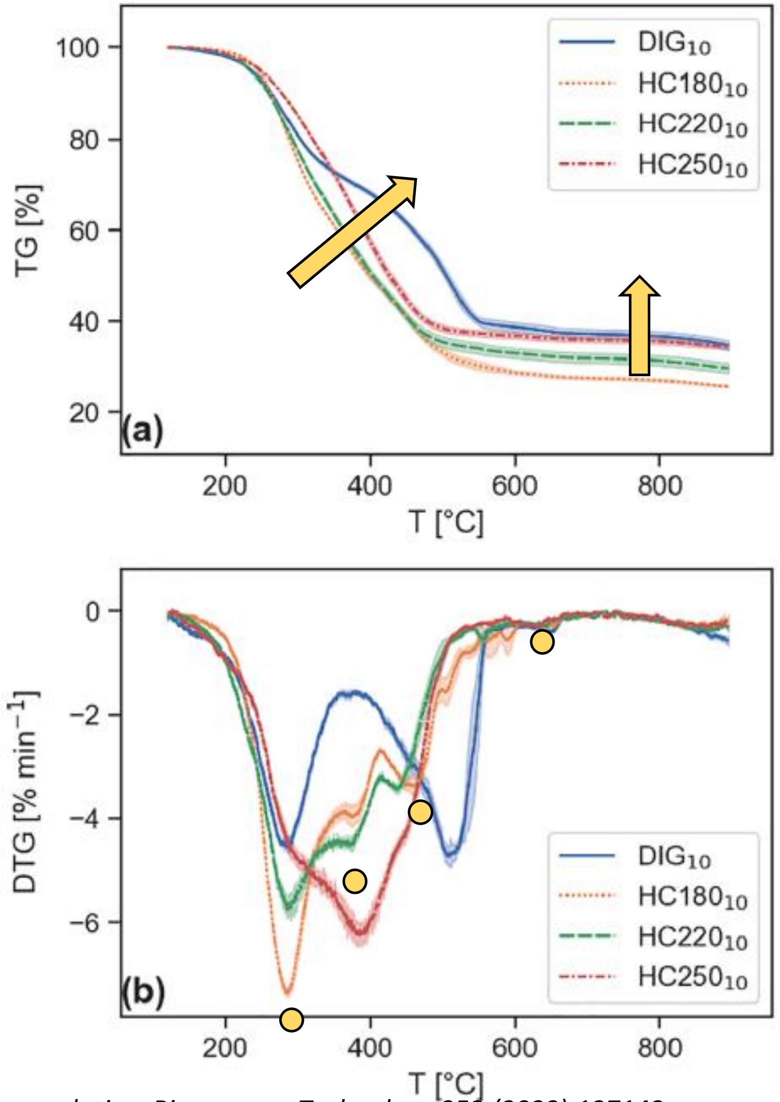
Benedetti et al., Combustion kinetics of hydrochar from cow-manure digestate via thermogravimetric analysis and peak deconvolution, Bioresource Technology 353 (2022) 127142

TG – DTG curves

Four main peaks:

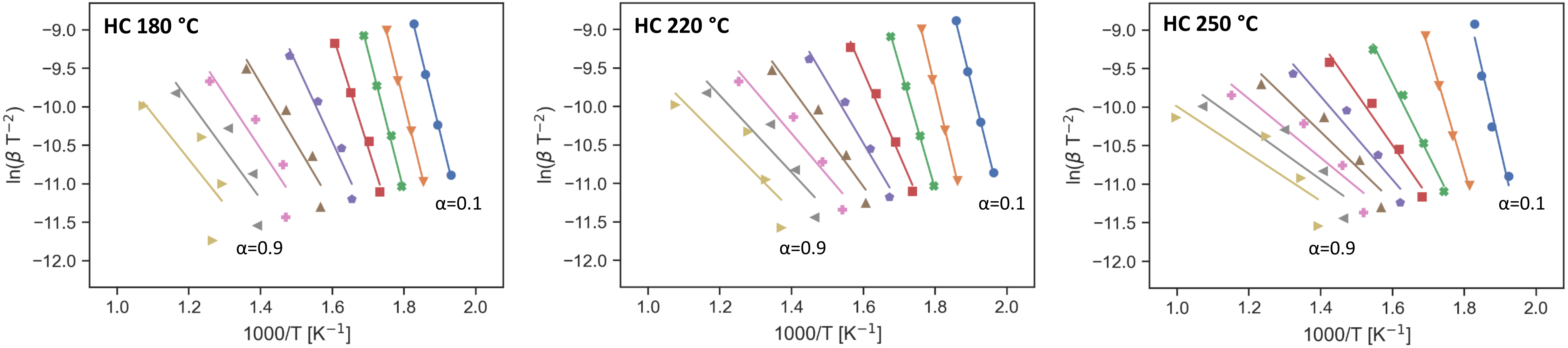
1. 290°C - Devolatilization
2. 370°C - Combustion
3. 450°C - Char combustion
4. 630°C - Secondary degradation reactions

Residual mass higher for HC obtained at higher T



Benedetti et al., Combustion kinetics of hydrochar from cow-manure digestate via thermogravimetric analysis and peak deconvolution, Bioresource Technology 353 (2022) 127142

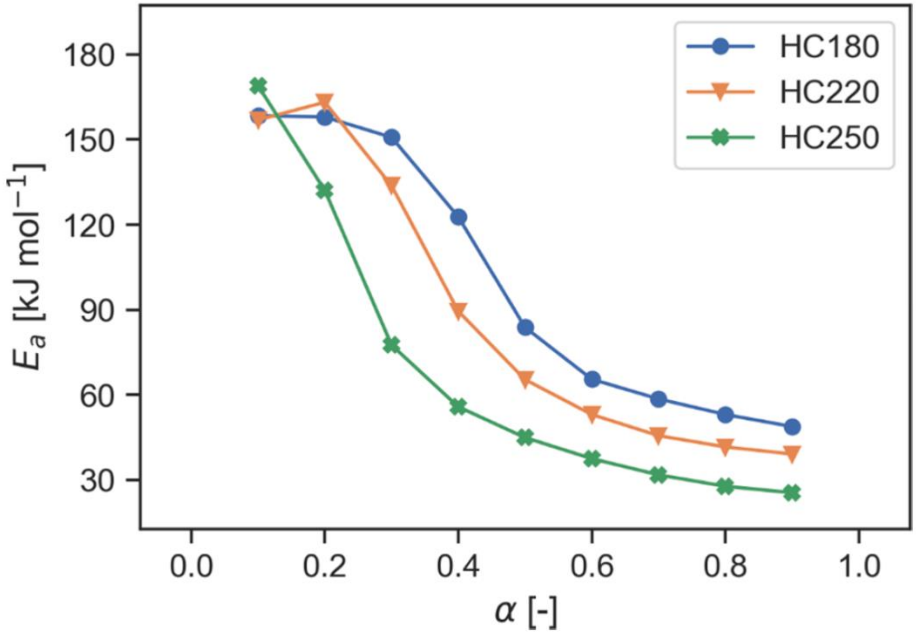
Isoconversional curves – KAS method



R^2	α								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
HC 180°C	0.9979	0.9990	0.9960	0.9877	0.9533	0.8989	0.8262	0.7985	0.5708
HC 220°C	0.9989	0.9985	0.9991	0.9874	0.9723	0.9439	0.9149	0.8620	0.7564
HC 250°C	0.9577	0.9968	0.9874	0.9684	0.9379	0.9052	0.8709	0.8196	0.7453

Benedetti et al., Combustion kinetics of hydrochar from cow-manure digestate via thermogravimetric analysis and peak deconvolution, Bioresource Technology 353 (2022) 127142

Activation energy



Sample	E_a average [kJ mol^{-1}]
HC 180°C	100
HC 220°C	88
HC 250°C	67

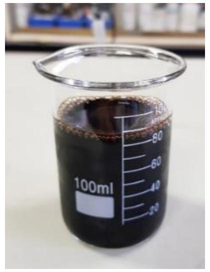
Benedetti et al., Combustion kinetics of hydrochar from cow-manure digestate via thermogravimetric analysis and peak deconvolution, Bioresource Technology 353 (2022) 127142

Hydrothermal Carbonization - HTC

(Pre)treatment of biomass in hot (180-250 °C) compressed water at residence times varying from minutes to several hours. Ideal for biomass with high moisture content (> 60 %).

Hydrochar (HC)

- Fuel
- Soil amelioration
- Carbon sequestration
- Wastewater treatment
- Carbon materials
- Energy storage



Aqueous HTC Liquid (AHL)

- Anaerobic digestion
- Fertilizers
- Recirculation
- Microalgae growth
- P recovery
- **SCWG**

AHL characterization

Characterization

AHL

Valorization

AHL characterization

TOC analysis

Feedstock	TOC	
AHL 180 °C	[g/L]	7.07
AHL 220 °C	[g/L]	7.43
AHL 250 °C	[g/L]	7.89

Semi-continuous analysis

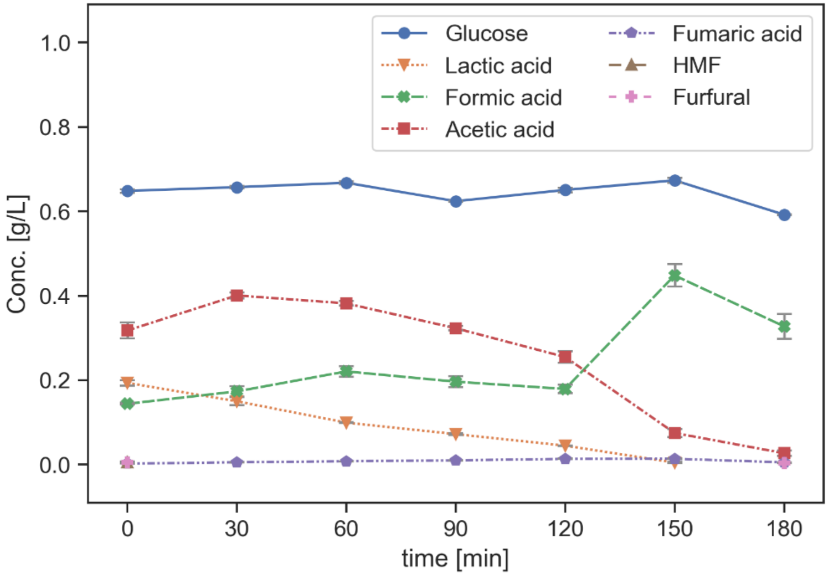
Spillages every 30 min during operation

HPLC analysis

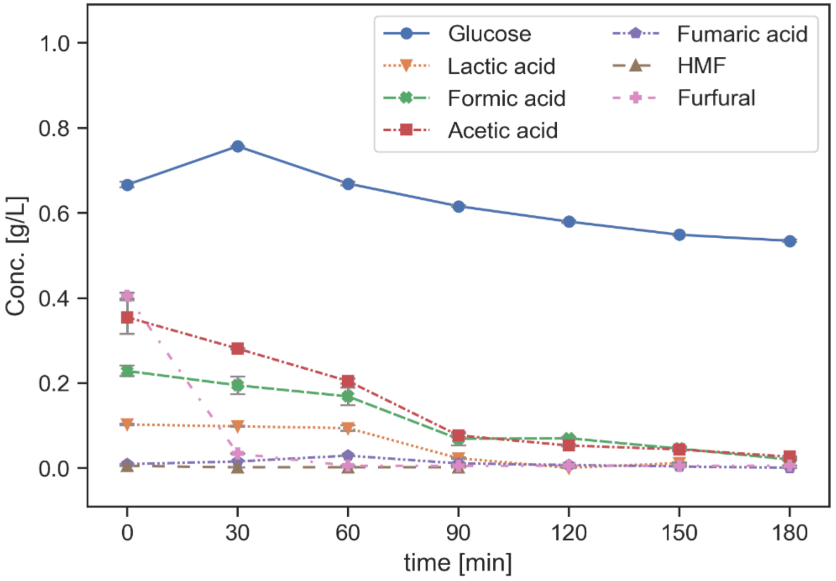
- Glucose
- Lactic, Formic, Acetic, Fumaric Acid
- Hydroxymethylfurfural (HMF), Furfural

AHL characterization

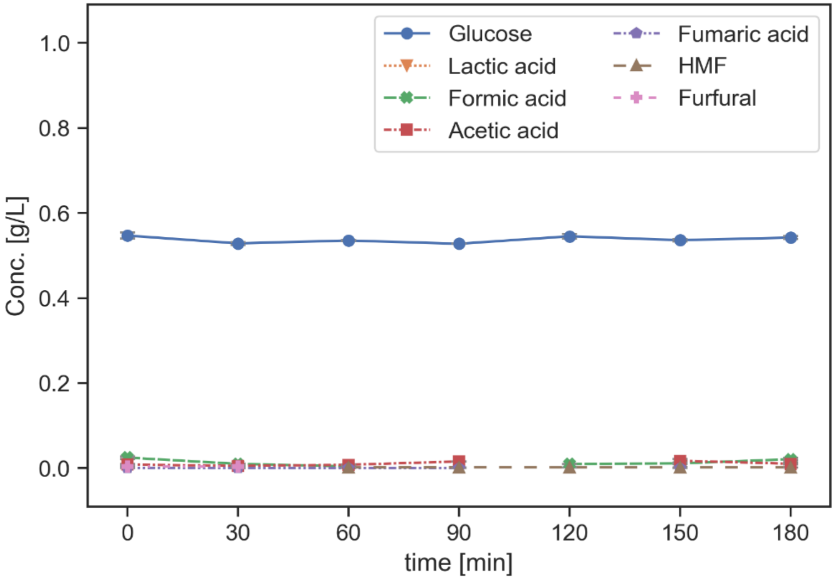
T_{HTC} = 180 °C



T_{HTC} = 220 °C



T_{HTC} = 250 °C



- Increased rate of **hydrolysis, decarboxylation** and **dehydration** that become the governing reactions of the process.
- Sugars, HMF and furfurals are **less stable at high temperature** and **residence time**.
- Polymerization and formation of secondary char.

AHL valorization

Characterization

AHL

Valorization

SCWG

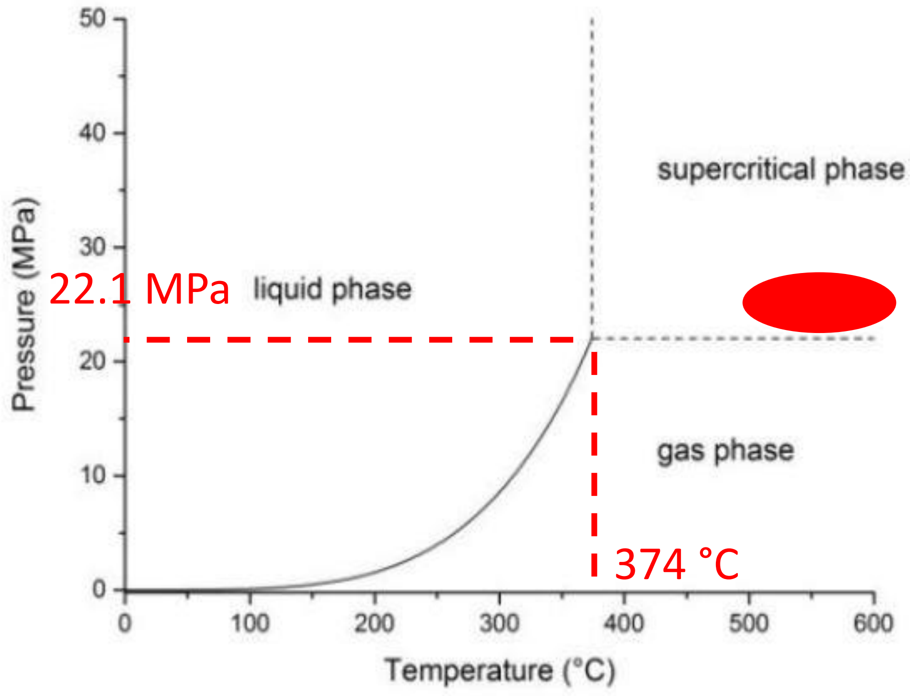
HIROSHIMA UNIVERSITY

AIM

- Obtain valuable gaseous product rich in H_2
- Minimize the waste, gasifying organic matter

Supercrtical water gasification: SCWG

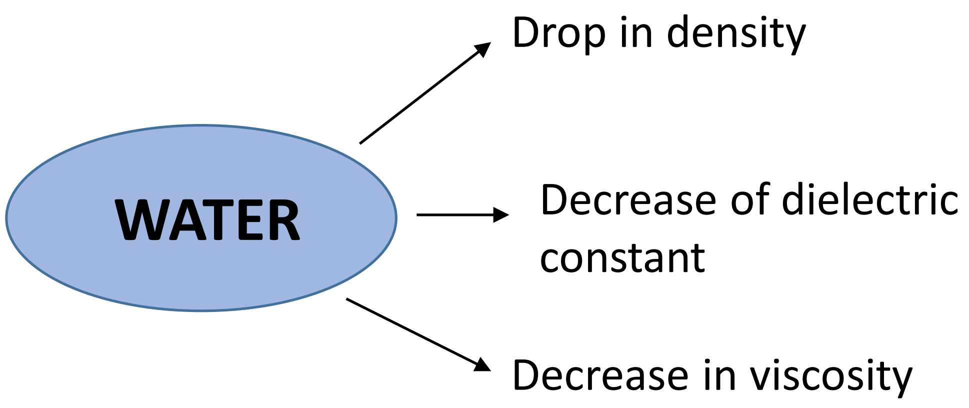
HIROSHIMA UNIVERSITY



Source: Yakaboylu et al., Supercritical water gasification of biomass

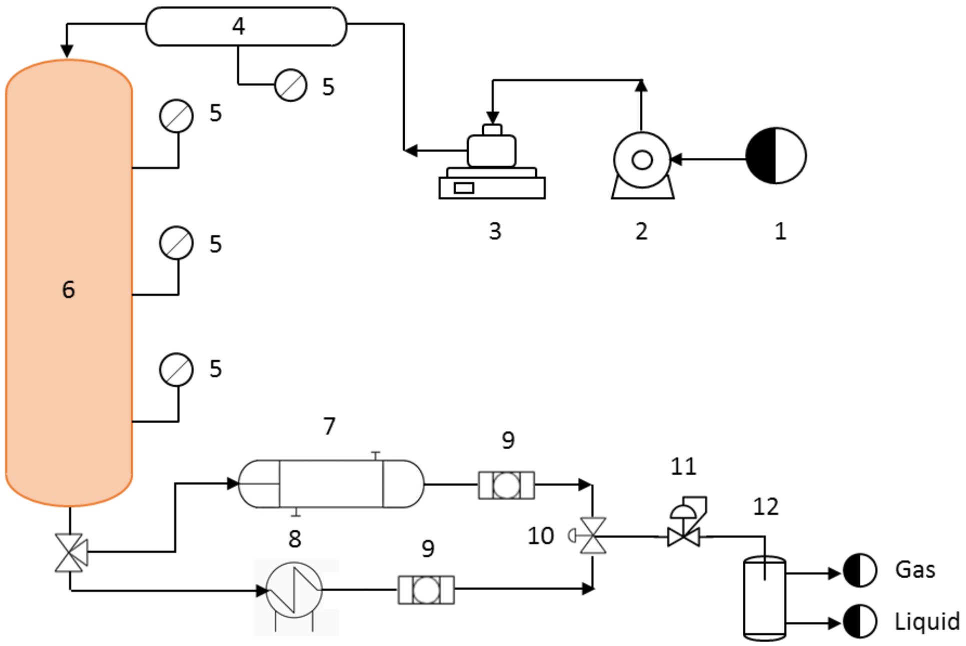
Hydrothermal process

- Alternative to conventional gasification and anaerobic digestion
- No need for pre-drying
- High temperature and pressure, low residence time
- Water in supercritical conditions becomes a very aggressive medium (and reactant)



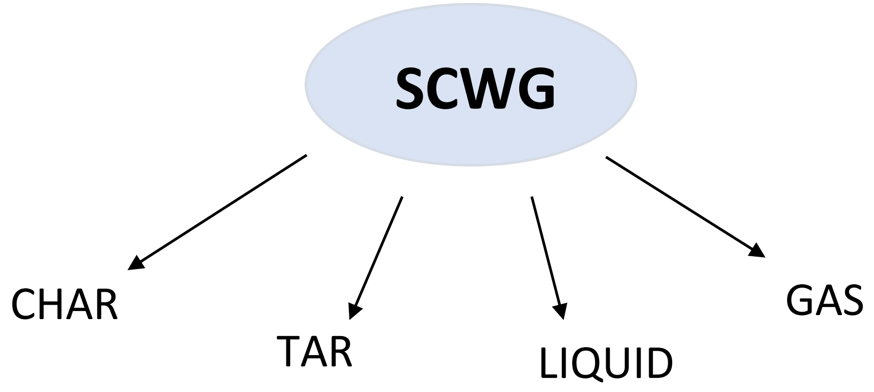
Materials and methods

HIROSHIMA UNIVERSITY



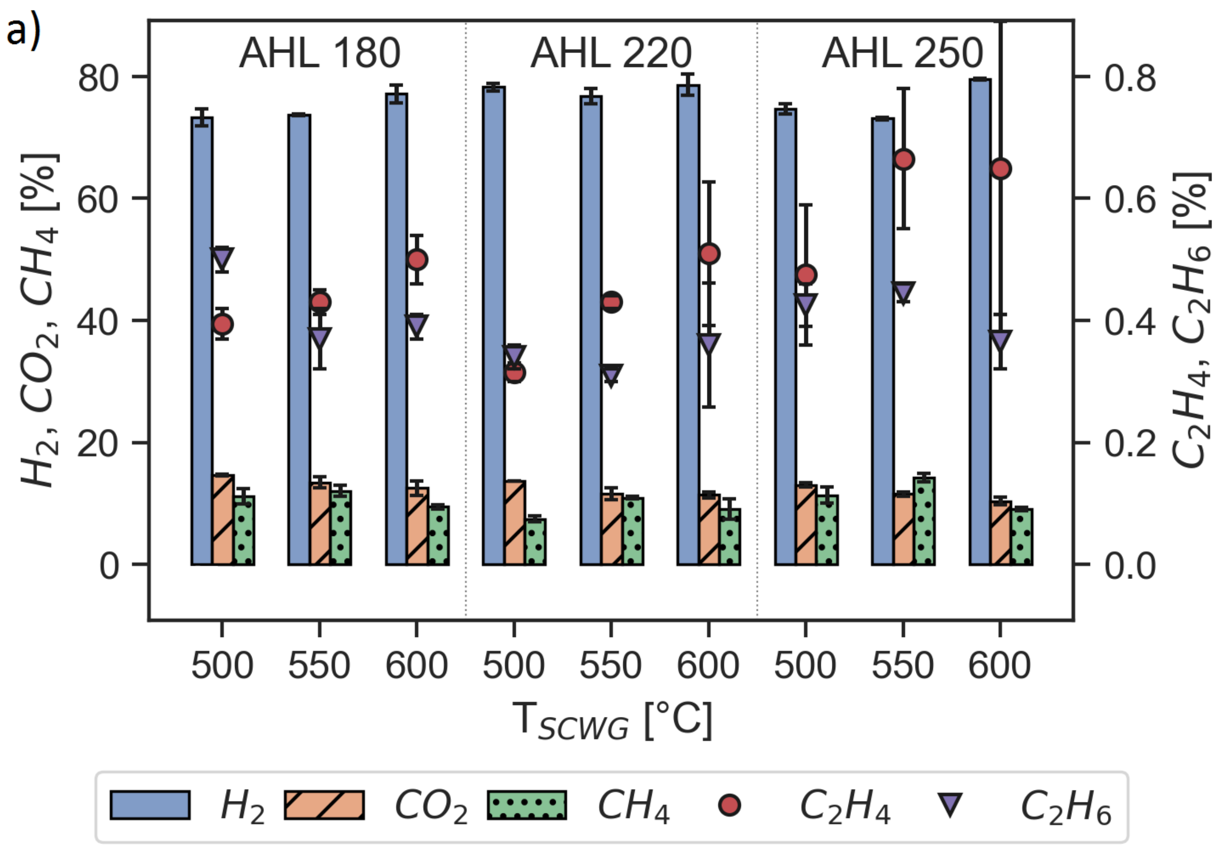
1. Water
2. Pump
3. Feeding system
4. Pre-heater
5. Temperature controller
6. Furnace
7. Heat exchanger
8. Cooling system
9. Filter
10. Ball valve
11. Back pressure regulator
12. Sampling port

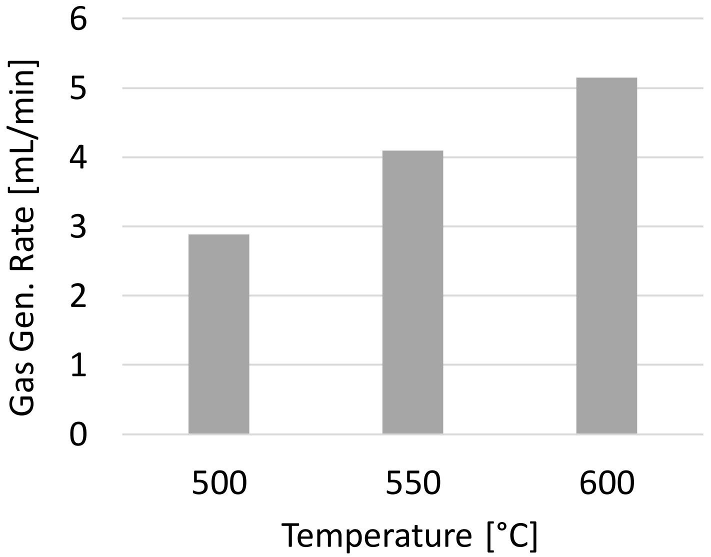
Feedstock	Temperature	Pressure	Residence time	Flow rate
	[°C]	[MPa]	[s]	[mL/min]
AHL 180 °C	500 550 600	25	30	8.0 7.0 6.3
AHL 220 °C	500 550 600	25	30	8.0 7.0 6.3
AHL 250 °C	500 550 600	25	30	8.0 7.0 6.3



Effect of Temperature

Gas composition





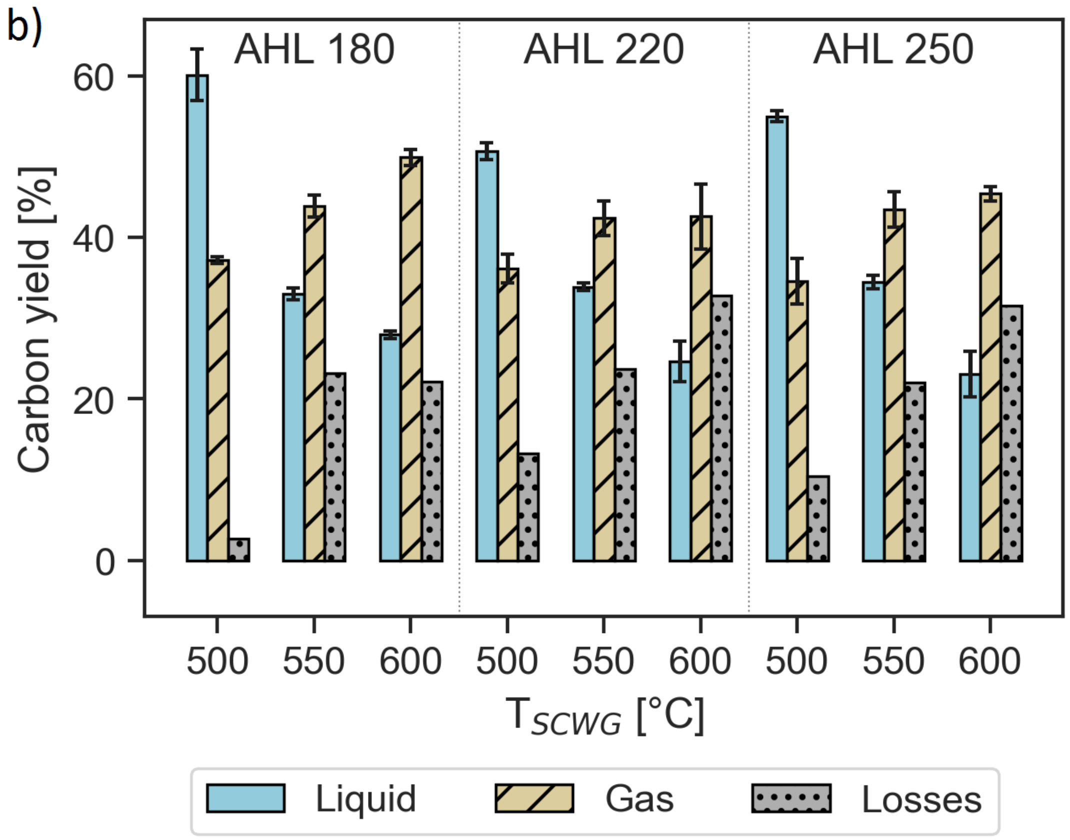
- No differences among AHLs
- Gas generation rate increases with T
- H_2 % increases with T

(other main gases: CO_2, CH_4)

Taufer et al., *Coupling hydrothermal carbonization of digestate and supercritical water gasification of liquid products, Renewable Energy 173 (2021) 934-941*

Effect of Temperature

Carbon balance



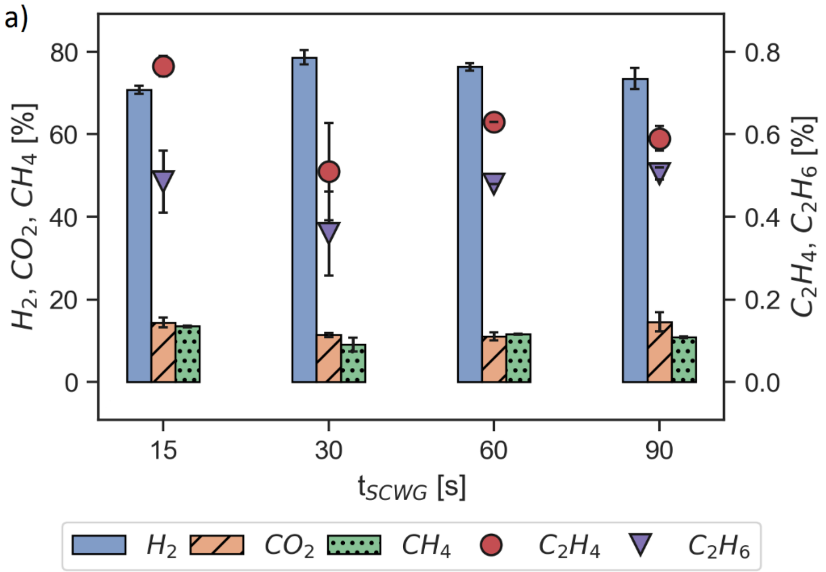
- SCWG 500: most of the carbon is in the liquid phase
- SCWG 600: most of the carbon is in the gas phase
- Amount of organic matter gasified increases with temperature

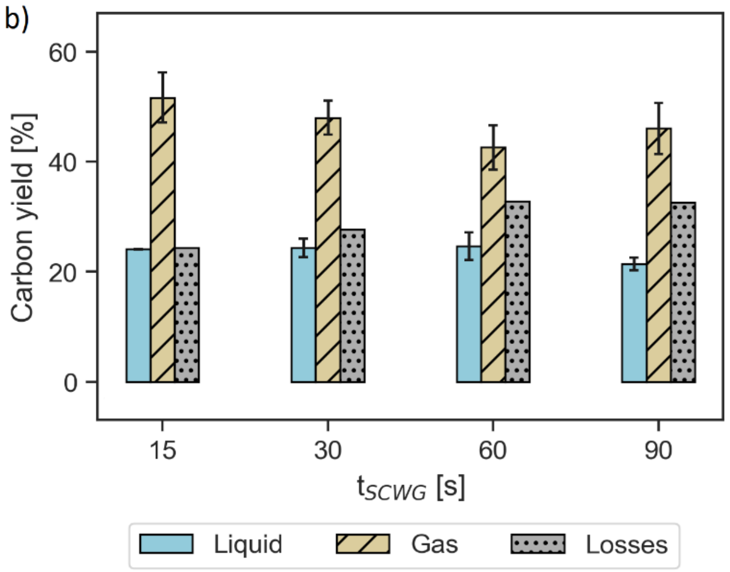
Taufer et al., Coupling hydrothermal carbonization of digestate and supercritical water gasification of liquid products, Renewable Energy 173 (2021) 934-941

Effect of Residence Time

Feedstock	Temperature	Pressure	Residence time	Flow rate
	[°C]	[MPa]	[s]	[mL/min]
AHL 220 °C	600	25	15	12.5
			30	6.3
			60	3.1
			90	2.1

- Minor effect of residence time
- H_2 % max at 30 s
- C yield % in the gas phase max at 15 s



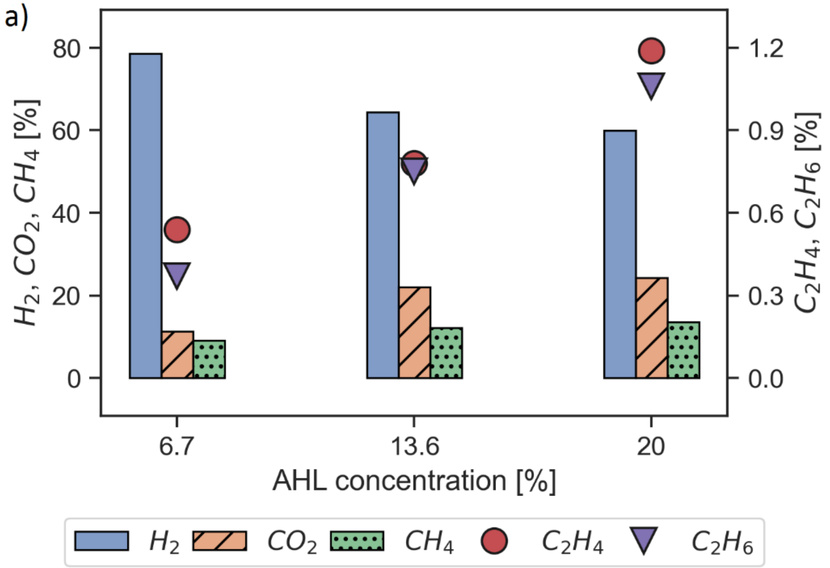


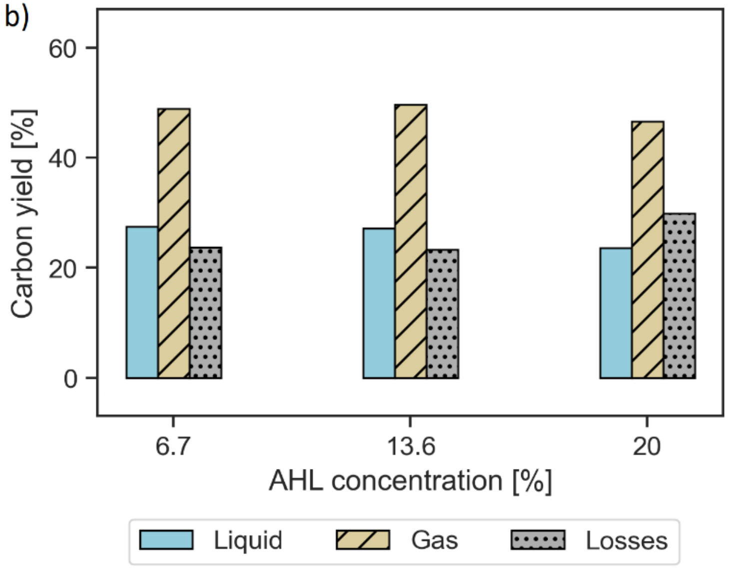
Taufer et al., Coupling hydrothermal carbonization of digestate and supercritical water gasification of liquid products, Renewable Energy 173 (2021) 934-941

Effect of Feedstock Concentration

Feedstock	Temperature	Pressure	Residence time	Concentration
	[°C]	[MPa]	[s]	[%]
AHL 180 °C	600	25	30	6.7 13.6 20.0

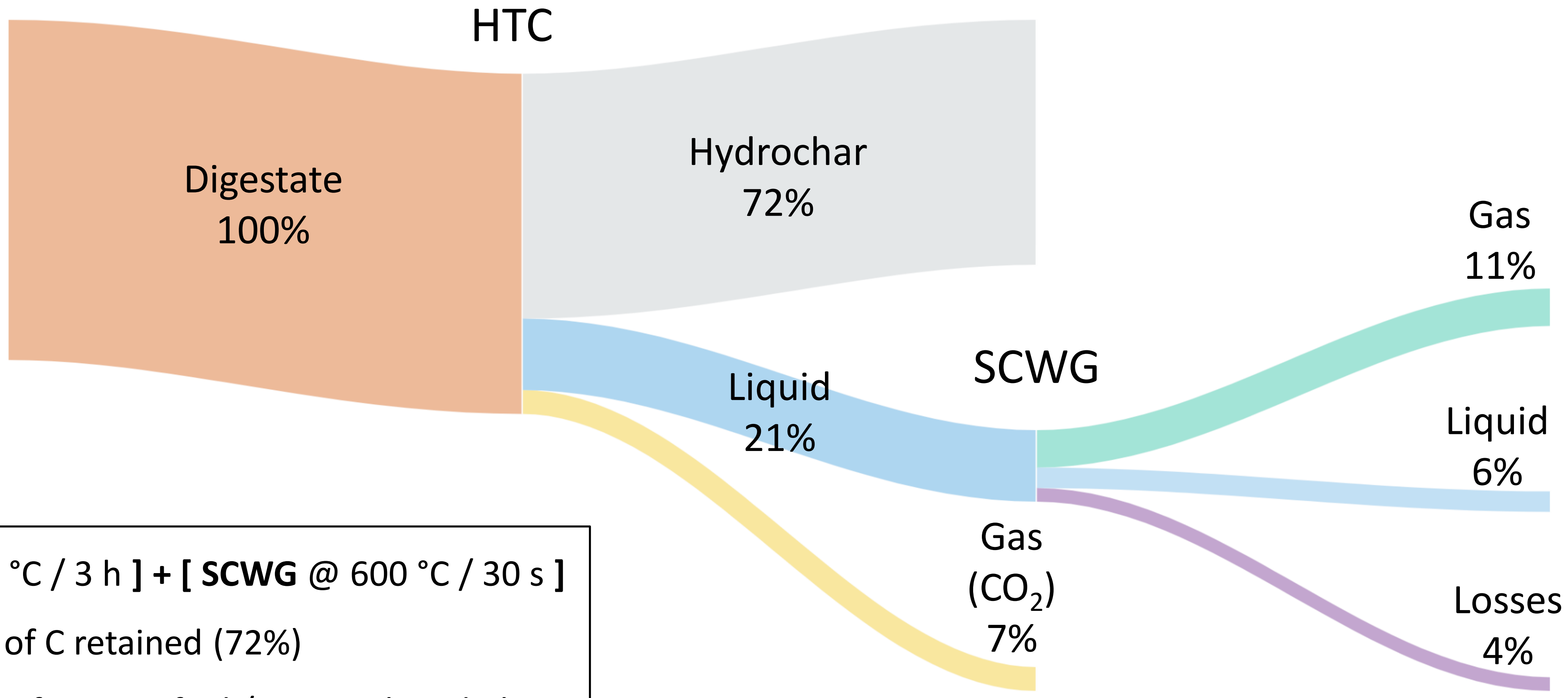
- CO_2 % and CH_4 % increases
- H_2 % decreases (from 80 to 60%)
- Carbon yield not affected





Taufer et al., Coupling hydrothermal carbonization of digestate and supercritical water gasification of liquid products, Renewable Energy 173 (2021) 934-941

Carbon Balance



[HTC @ 180 °C / 3 h **] + [SCWG** @ 600 °C / 30 s **]**

- HC: most of C retained (72%)
- AHL: 50% of C is gasified / 30% in liquid phase

Taufer et al., Coupling hydrothermal carbonization of digestate and supercritical water gasification of liquid products, Renewable Energy 173 (2021) 934-941

Remarks

- Hydrothermal carbonization (HTC) effectively treated digestate to produce hydrochar
- An HTC temperature of 250 °C converts the low-temperature volatiles to more stable compounds, producing a better fuel compared to 180 and 220 °C. This is supported by the high apparent activation energy at low conversions for HC250, but a lower apparent activation energy afterwards.
- Semi-continuous analysis of HTC liquids showed the presence of bio-inhibiting compounds
- Coupling with super-critical water gasification (SCWG) was possible, yielding a gas rich in H_2
- SCWG showed optimal results for operation at 600 °C and 30 s residence time
- Up to 50% of the carbon in the HTC liquids was valorised

Aknowledgements

People

unibz

- Vittoria BENEDETTI
- Francesco PATUZZI
- Matteo PECCHI
- Noah Luciano TAUFER

HIROSHIMA UNIVERSITY

Prof. Yukihiko MATSUMURA

HBI

Eng. Daniele BASSO

Aknowledgements

efre · fesr
Südtirol · Alto Adige
Europäischer Fonds für regionale Entwicklung
Fondo europeo di sviluppo regionale
EUROPEAN UNION
AUTONOME PROVINZ BOZEN SÜDTIROL
PROVINCIA AUTONOMA DI BOLZANO ALTO ADIGE

unibz
HBI

HB Ponics

Funding: Project **"HB Ponics"** (FESR1104; EFRE-FESR 2014-2020; CUP: B51B17000860008), financed by the European Regional Development Fund (ERDF) Investment for Growth and Jobs Programme 2014-2020.

https://www.hbigroup.it/hb-ponics/

Freie Universität Bozen
Libera Università di Bolzano
Free University of Bolzano

HIROSHIMA UNIVERSITY

Bioenergy & Biofuels LAB

Thank you for your attention

Integration of hydrothermal processes for fuels and hydrogen production from digestates

E-mail: marco.baratieri@unibz.it

Website: https://bnb.groups.unibz.it/