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Hydrothermal carbonization of biomass for production of densified solid fuel

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What is biochar?

Stable carbon-rich product obtained from the thermochemical conversion of plant- and animal-based biomass in an oxygen-limited environment

- Lower amount of volatile organic compounds (VOCs),
- No water
- Stored for many years without decay.
- The higher energy density

What is biochar made from?

Animal wastes

Agro wastes

Industrial wastes

Forest wastes

Algal biomass

- Solid fuel
- Low-cost adsorbent
- Carbon electrode
- Soil amendment
- Carbon based catalyst

How is biochar made?

Fuel Characteristics

- ✓ **High Yield**
- ✓ **High energy density**
- ✓ **High combustion reactivity**
- ✓ **Low volatile matter**
- ✓ **Low ash content**

<u>Pyrolysis</u>

High yield

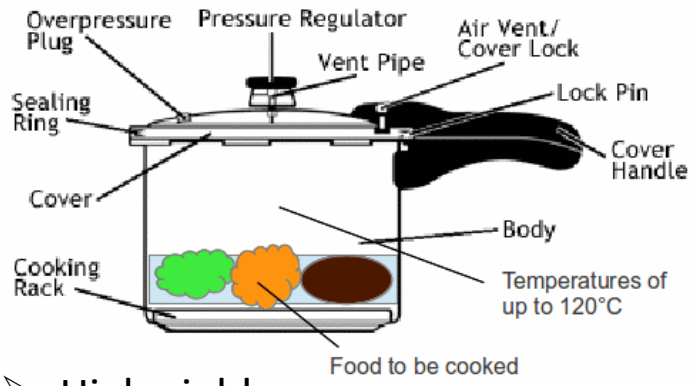
High ash content

Pretreatment of wet biomass

<u>Hydrothermal Carbonization (HTC)</u>

Under development

Pressure cooker principle



- ➢ High yield
- ➢ Applicable to wet biomass
- ➢ Relatively lower temperatures
- ➢ Smaller reactor volumes

Source: astarmathsandphysics.com

Objective

⇨ Investigation of biochar obtained from hydrothermal carbonization as energy feedstock.

⇨ Comparison with biochars derived pyrolysis process

Feedstock

Sunflower stalk (SS)

Poultry litter (PL)

Seaweed (AB)

	SS	PL	AB
Ultimate analysis (wt.%, dry basis)			
C	34.17	35.70	35.10
H	4.92	5.27	4.00
N	1.48	9.61	1.05
S	0.45	0.24	0.95
O	51.08	40.98	38.10
Proximate analysis (wt.%, dry basis)			
Volatile matter	74.6	68.3	58.4
Ash	7.9	8.2	20.8
Fixed carbon	17.5	23.5	20.8
High heating value (HHV), MJ kg^{-1}			
	13.50	15.10	11.60

Inorganic content of biomass, % wt.

	SS	PL	AB
Na_2O	0.19	**0.40**	**0.83**
K_2O	**0.47**	**0.63**	0.25
CaO	**4.09**	**7.83**	**4.33**
MgO	1.78	1.28	**3.16**
SiO_2	**4.08**	1.61	0.76
Al_2O_3	0.06	0.52	0.90

Methodology

- Hydrothermal carbonization (HTC)

Seaweed

Sunflower stalk

Poultry litter

CO_2, H_2O

HTC

Hydrochar

Liquid products
(Water soluble organics)

Parameters

- **Temperature**
- **Duration**
- **Biomass: water ratio**

Methodology

Experimental conditions

Objectives
- Maximum energy densified hydrochar with high yield
- Investigate the effect of parameters on HTC Results
- Optimization of experimental conditions
- Reduce # of experiments

Variables
- Temperature
- Duration
- Biomass: water ratio

Responses
- -Energy density
- -Mass Yield

Experimental design
- Central composite design
- ***20 Experiments***

Evaluation/ Analysis of Response
Optimimum conditions
- Design Expert Software 8.0
- Response Surface Methodology
- Anova test

Methodology

- Low Temperature Pyrolysis

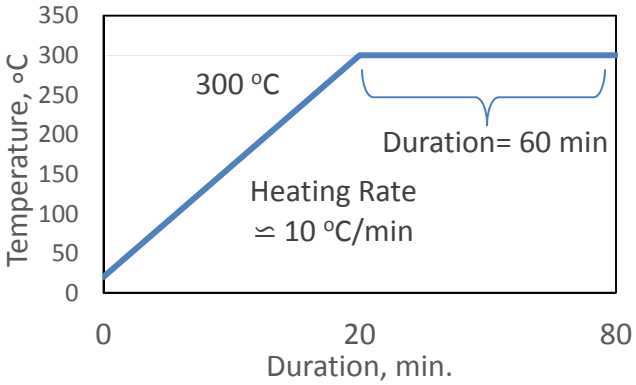
CO_2, H_2O

Pyrolysis

Biochar

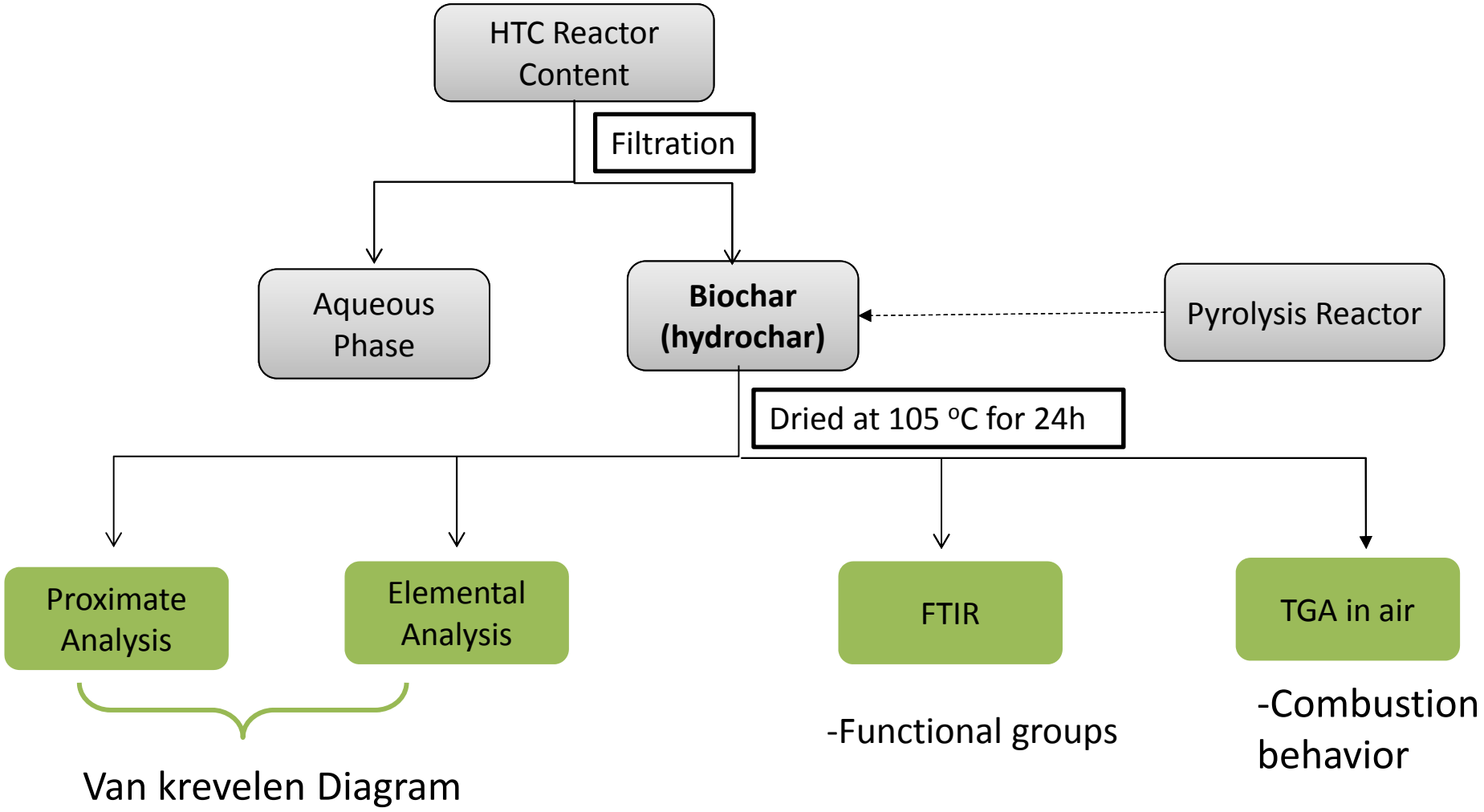
Liquid products
(Water soluble organics)

Conditions



Tag et al. Journal of Analytical and Applied Pyrolysis 120 (2016) 200–206

Biochar Analyses



HHV calculation*----------→ Energy density= $HHV_{biochar}/HHV_{biomass}$

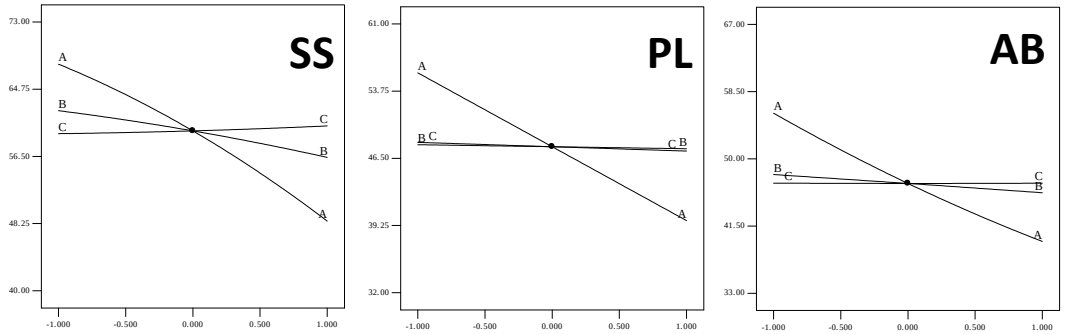
S.A. Channiwala, P.P. Parikh, Fuel 81 (2002) 1051–1063.

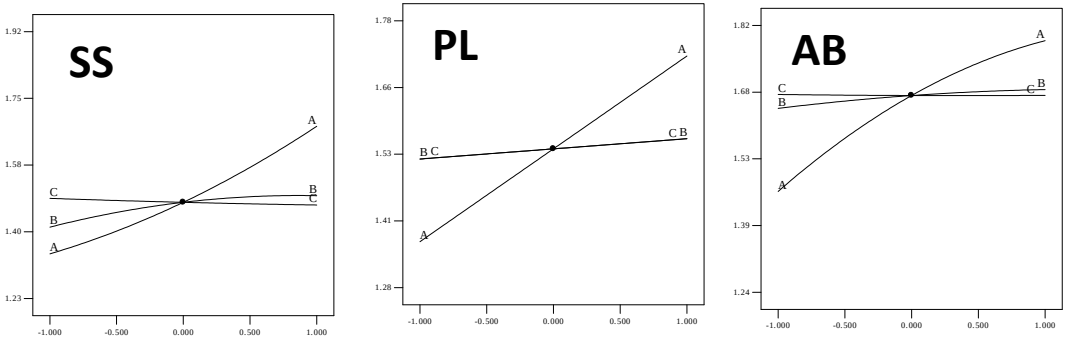
Results & Discussion

Yield and Energy Density

Factor	-1.68	-1	0	+1	+1.68
Temperature (°C)= X_1	150	175	212	250	275
Duration (min)= X_2	0	60	150	240	300
Biomass:water ratio =X_3	0.05	0.15	0.30	0.45	0.55

Yield





Energy Density

Results & Discussion

Optimization conditions

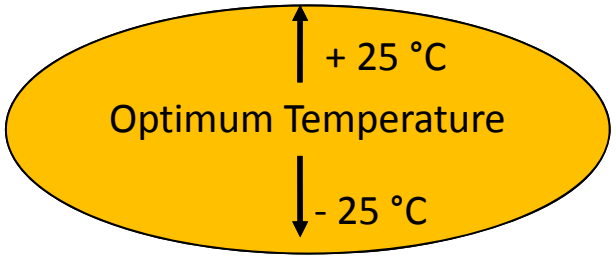
Maximize energy density

Mass yield > 40 %

	SS	PL	AB
Temperature, °C	250	250	225
Duration, min	150	120	120
Biomass:water ratio	0.30	0.30	0.30
Energy density	**1.68**	**1.76**	**1.73**
Mass yield, % wt.	**52.0**	**40.2**	**45.1**

Results & Discussion

Analyses of Biochars

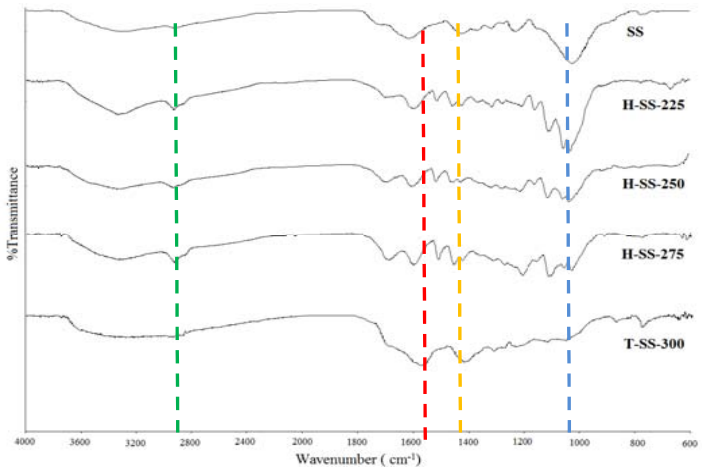


	Elemental analysis,wt %					Proximate analysis,wt %			HHV, MJ.kg^{-1}	Yield, % wt.	Energy Density
	C	H	N	S	O	Ash	VM	FC			
H-SS-225	51.3	5.71	0.82	0.08	36.19	5.9	69.6	24.5	20.77	55.1	1.54
H-SS-250	55.07	5.94	0.94	0.09	32.96	5.0	55.4	39.6	22.71	52.0	1.68
H-SS-275	58.16	5.64	0.91	0.04	32.25	3.0	53.3	43.7	23.54	41.0	1.74
T-SS-300	50.89	4.09	1.17	0.35	31.30	12.2	47.1	40.7	19.11	65.1	1.42
H-PL-225	57.57	4.66	4.12	0.41	26.94	6.3	60.2	33.5	22.65	42.2	1.50
H-PL-250	63.87	5.45	5.36	0.37	19.05	5.9	50.1	44.0	26.58	40.2	1.76
H-PL-275	62.01	6.32	5.70	0.26	21.41	4.3	48.2	47.5	26.73	32.8	1.77
T-PL-300	53.57	3.69	5.41	0.19	24.34	12.8	44.1	43.1	20.23	53.2	1.34
H-AB-200	48.06	4.56	1.68	0.21	34.69	10.8	55.4	33.8	18.33	51.6	1.58
H-AB-225	53.26	4.01	1.52	0.28	29.03	11.9	50.2	37.9	20.07	45.1	1.73
H-AB-250	54.29	4.09	1.56	0.36	30.70	9.0	47.2	43.8	20.42	41.2	1.76
T-AB-300	41.49	3.23	1.86	0.15	24.57	28.7	45.9	25.4	15.13	63.2	1.30

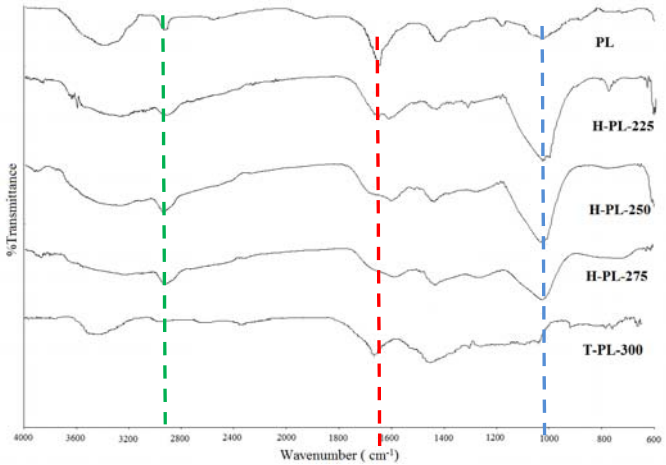
Results & Discussion

FTIR spectrum

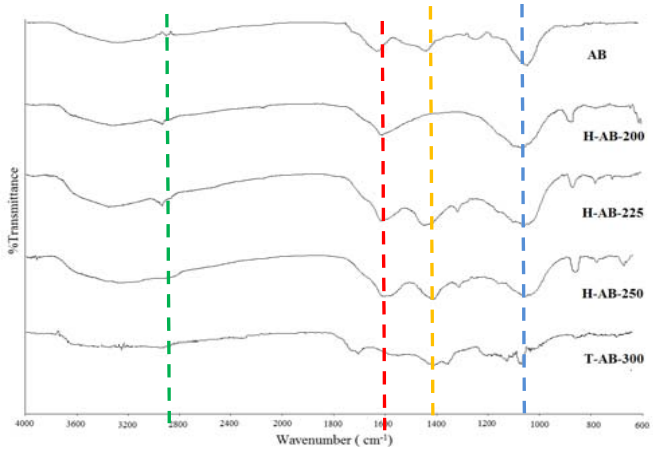
SS



PL



- aliphatic C-H stretching vibration
- alcohol C-O stretching vibration
- aliphatic C=O stretching vibration
- aromatic ring vibration



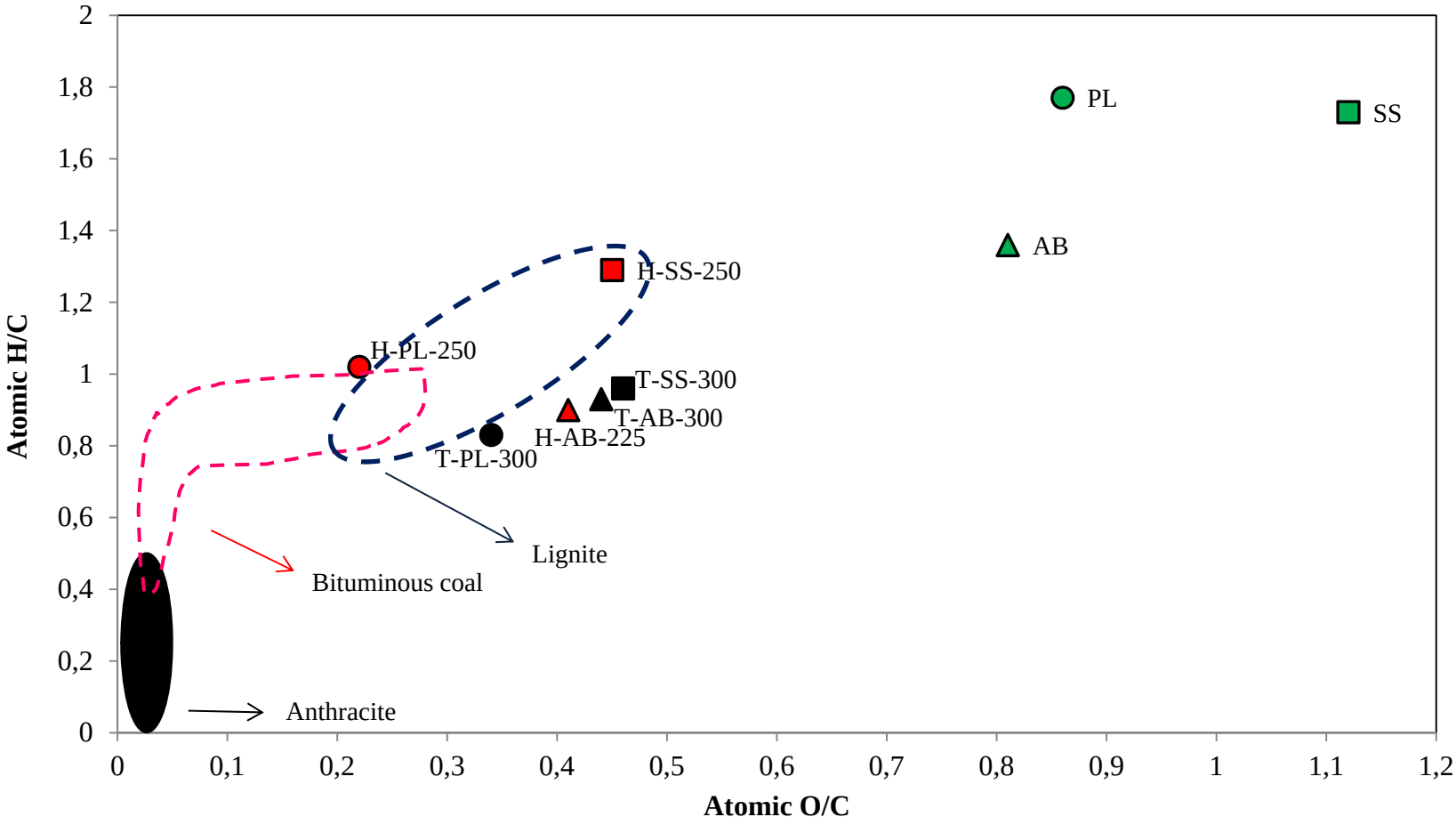
AB

Results & Discussion

Van Krevelen Diagram

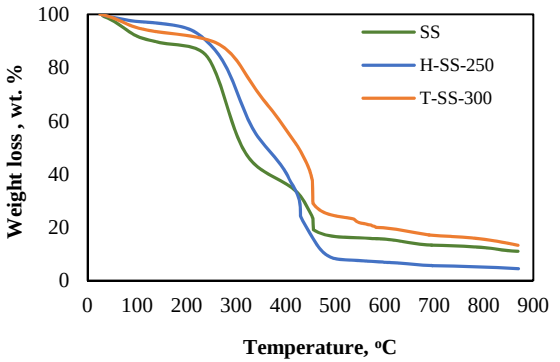
PL: Polultry litter
SS: Sunflower stalk
AB: Seaweed

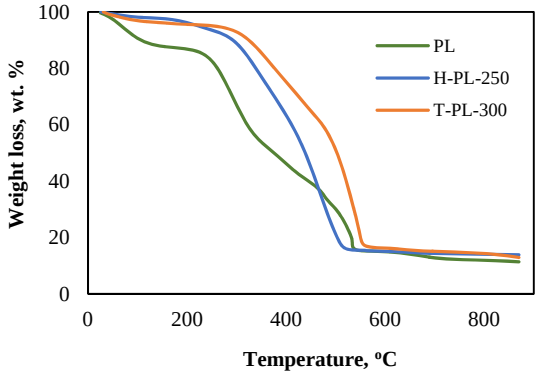
H: HTC biochar
T: Pyrolysis biochar

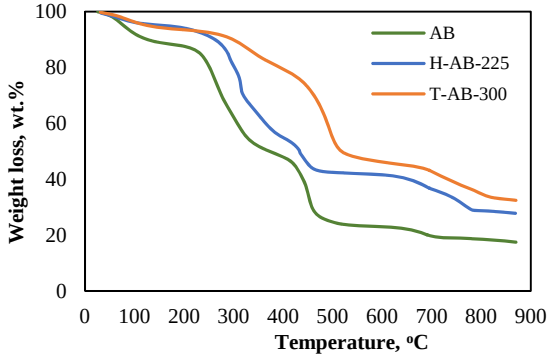


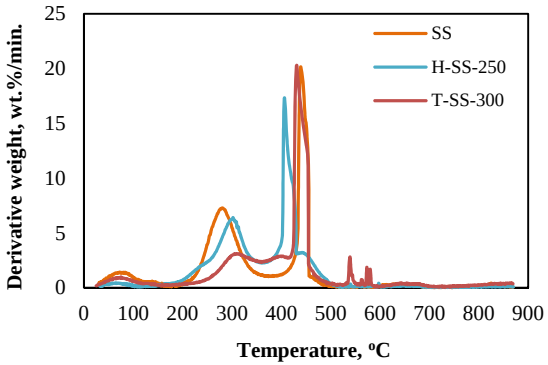
Results & Discussion

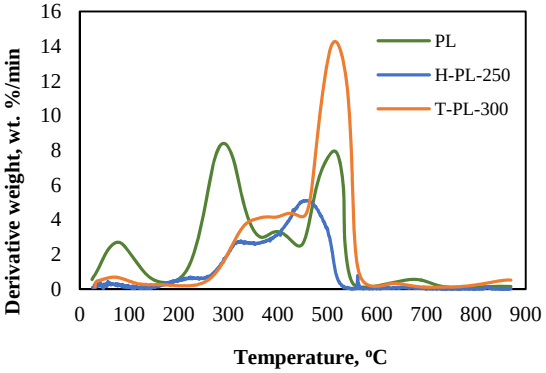
Combustion behavior

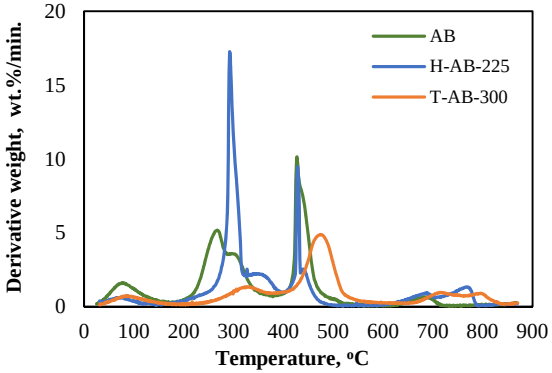












	SS	H-SS-250	T-SS-300	PL	H-PL-250	T-PL-300	AB	H-AB-225	T-AB-300
Peak temperature, ∘C	281;439	310;406	431	290; 513	454	515	266; 427	292; 429	474
Combustion	7.27;20.15	3.10;17.30	20.29	8.40; 7.96	5.1	14.27	5.16; 10.13	17.25; 9.47	4.88
Reactivity, %/min.∘C	3.589	2.631	4.708	2.224	1.123	2.771	2.156	4.057	1.03
Burnout, %/min	462	485	472	543	517	564	475	459	519
Ignition,∘C	233	218	258	235	268	282	228	261	273

Conclusion

- Hydrothermal carbonization is a promising method to produce biochar with high quality.
- The temperature is the main parameter effecting the yield and energy density
- Application on wet biomass
- Lower ash content biochar
- Higher energy density than biochar obtained from pyrolysis

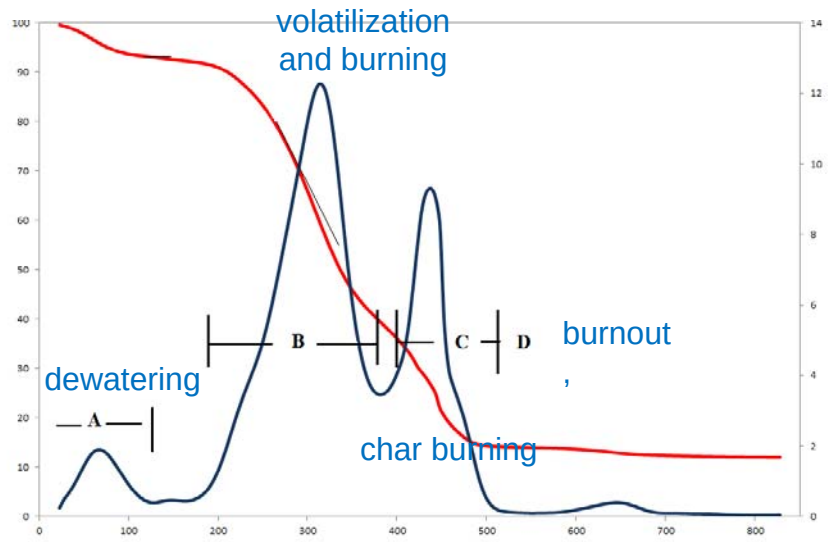
Thank you for listening !

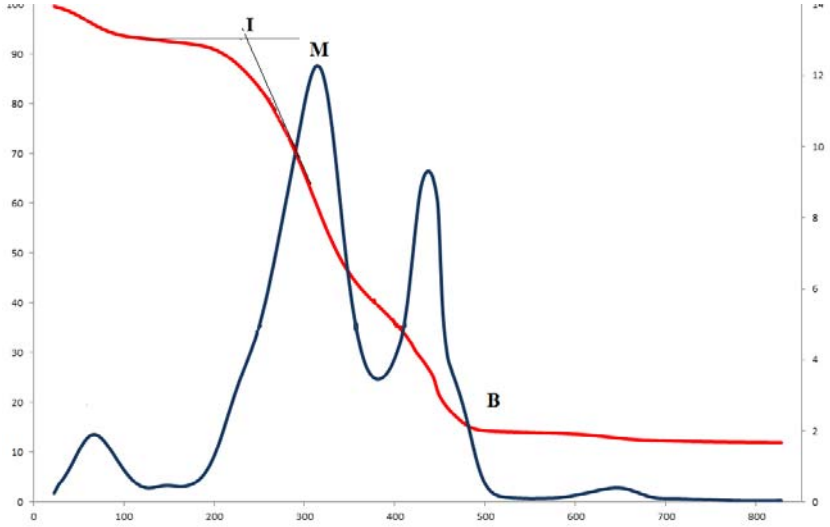
We would like to acknowledge the contribution of the COST Action TD1107 (Biochar as option for sustainable resource management)

The experiments designed by CCD

Run	Parameter 1 Temperature(^{0}C)	Parameter 2 Duration (min)	Parameter 3 Biomass: water ratio
1	150	150	0.30
2	175	60	0.15
3	175	60	0.45
4	175	240	0.15
5	175	240	0.45
6	212	0	0.30
7	212	150	0.05
8	212	150	0.30
9	212	150	0.30
10	212	150	0.30
11	212	150	0.30
12	212	150	0.30
13	212	150	0.30
14	212	150	0.55
15	212	300	0.30
16	250	60	0.15
17	250	60	0.45
18	250	240	0.15
19	250	240	0.45
20	275	150	0.30

Thermogravimetric analysis





Conditions

Heating rate: 20 °C /min

Combustion atmosphere: Air

Air flow: 100 mL / min

Sample amount:~ 5- 10 mg

I, ignition temperature

B, burnout temperature, the rate of weight loss become <1 wt.%/ min

M, highest d*m*/d*T* value

Reactivity = 100 x maximum combustion rate / peak temperature

Wang C, et al. Biomass and Bioenergy 2009, 33(1), 50-56.

Results & Discussion

Quadratic models

x_1: Temperature
x_2: Duration
x_3: Biomass: water

Y_i: mass yield, energy yield

$$Y_i = \beta_0 + B_1.x_1 + B_2x_2 + B_3.x_3 + B_{11}.x_1^2 + B_{22}.x_2^2 + B_{33}.x_3^2 + B_{12}.x_1.x_2 + B_{13}.x_1.x_3 + B_{23}.x_2.x_3$$

y_i		B_0	B_1	B_2	B_3	B_{12}	B_{13}	B_{23}	B_{11}	B_{22}	B_{33}
Mass Yield	AB	+46.89	**-8.11**	-1.15	-4.191E-3	-0.66	+0.19	-0.37	+0.78	-0.027	+0.039
	PL	+46.67	**-7.97**	-0.22	-0.47	+0.050	-0.33	+0.065	+0.48	+0.44	0.66
	SS	+59.63	**-9.63**	**-2.87**	+0.47	**-1.95**	-0.14	+0.055	**-1.44**	-0.39	+0.13
Energy Density	AB	+1.67	**+0.16**	+0.020	-9.985E-4	-0.025	-0.015	+0.000	-0.045	-0.007445	+1.379E-3
	PL	+1.54	**+0.17**	+0.019	+0.019	+1.250E-3	+1.250E-3	-0.016	+0.012	-5.359E-3	-2.367E-4
	SS	+1.48	**+0.16**	+0.041	-8.587E-3	+0.011	+0.016	+3.750E-3	+0.032	-0.024	+1.600E-3