

# Improvement of the physicochemical and combustion properties of hydrochars from hydrothermal carbonization of swine manure

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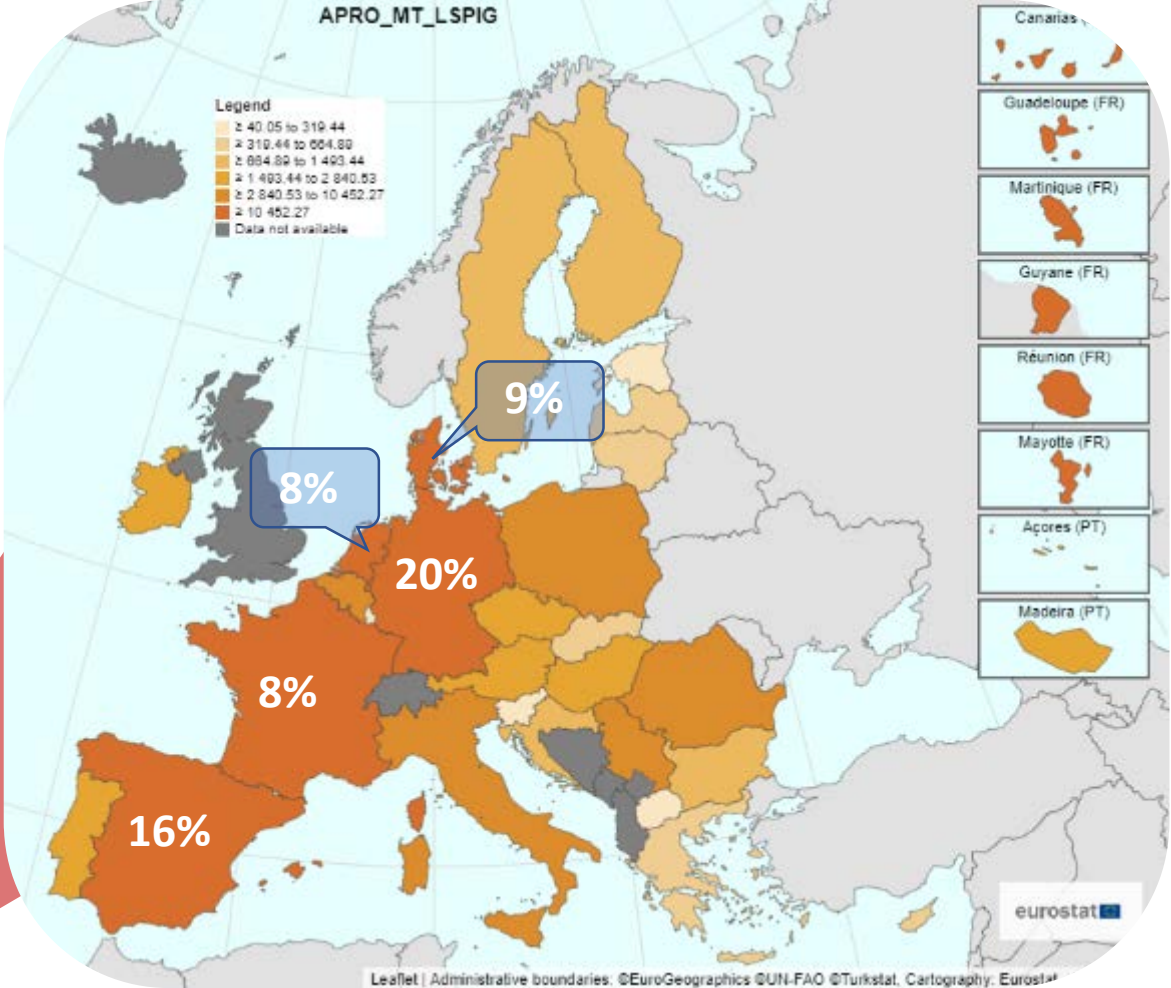
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# Swine crisis: Swine manure management key to tackling climate change

Swine manure population in EU

In the last 10 years the swine population increase  $\approx$  3%  
150·10<sup>6</sup> heads in 2020



Spain, France, Germany, Denmark and Netherlands account for up to 60% of the total swine population

# Swine crisis: Swine manure management key to tackling climate change

18·10<sup>6</sup> t swine manure (SM) d.b.

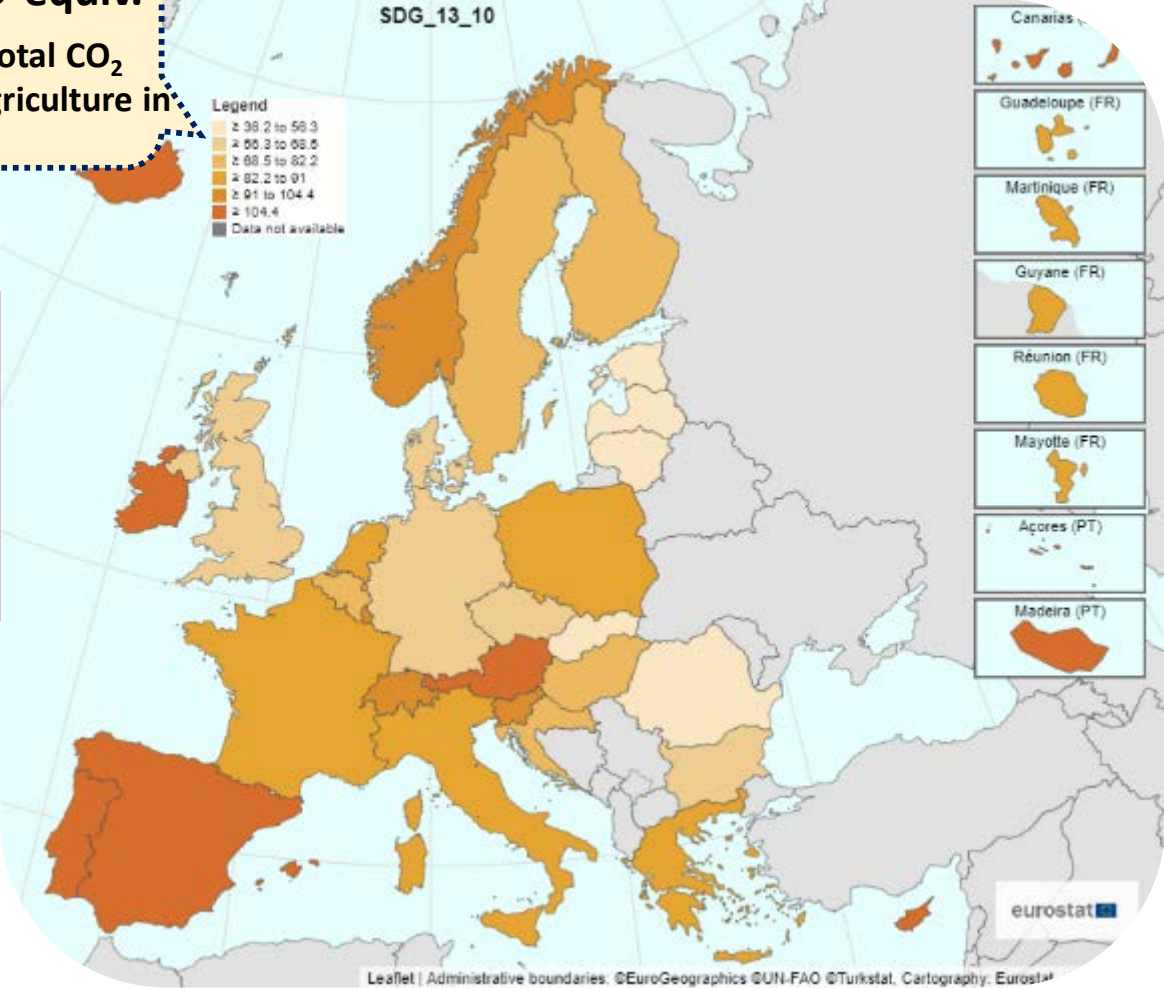


In the last 10 years the swine population increase ≈ 3%  
146·10<sup>6</sup> heads in 2019



25·10<sup>6</sup> t CO<sub>2</sub>equiv.  
≈ 7% of the total CO<sub>2</sub> generated by agriculture in EU

## Greenhouse gases emission in EU



3.3·10<sup>9</sup> t CO<sub>2</sub>equiv. was generated in EU



# Useful methods, insufficient for large-scale farms

## Aerobic compost

90%



- Stabilization of manure
- Reduce the volume of waste
- Compost rich in organic matter and nutrients

## Anaerobic digestion

6%



- Stabilization of manure
- Reduce the volume of waste
- Biogas rich in methane

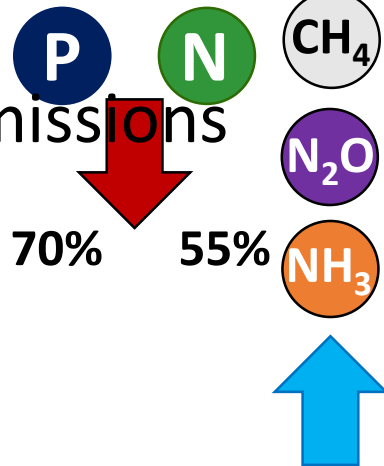
# Useful methods, insufficient for large-scale farms

## Aerobic compost



30%  
Composted

- Runoff of nutrients
- Greenhouse gases emissions
- Long period of time



## Anaerobic digestion

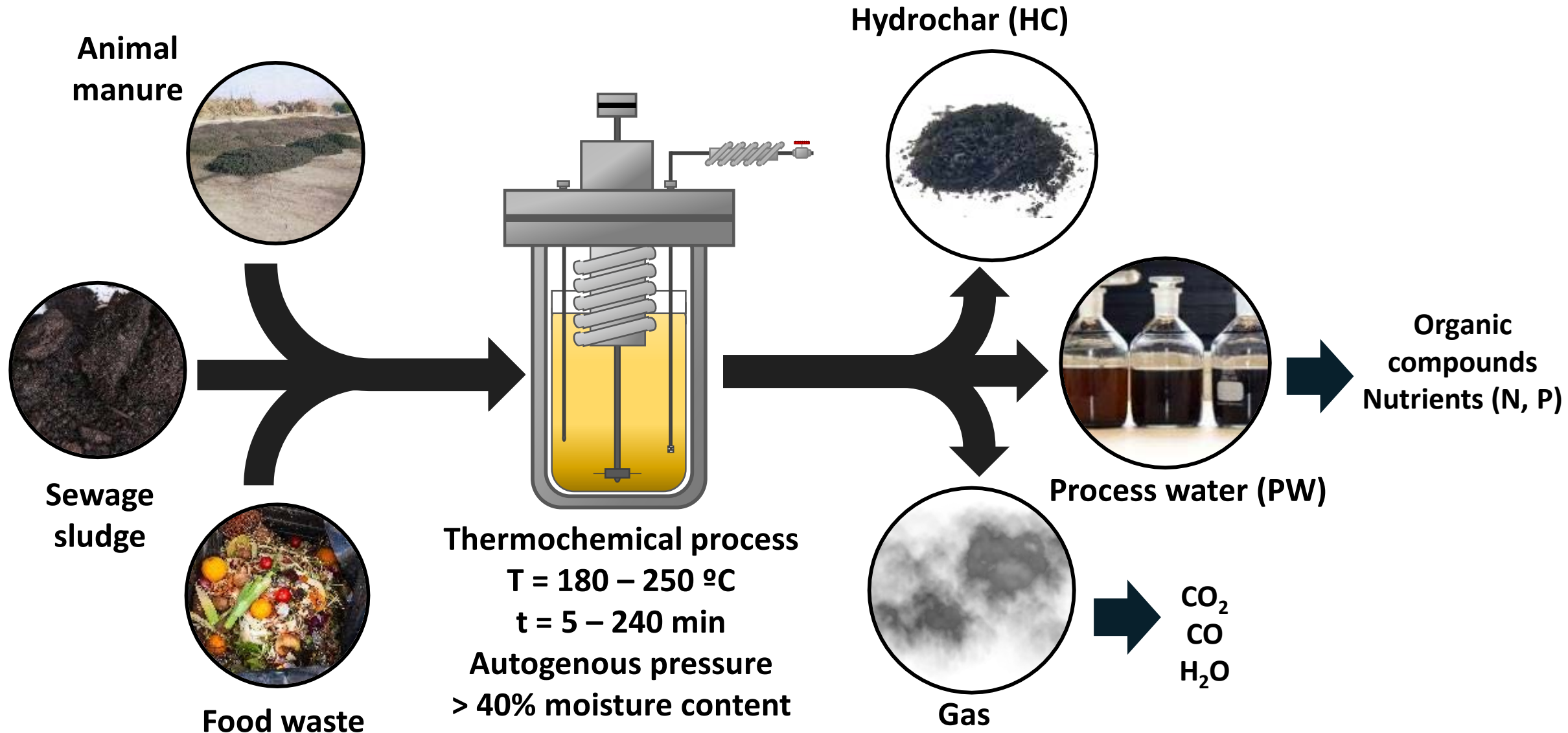


High  
investment

- Poor substrate biodegradability
- Low methane production
- Inhibition of the process



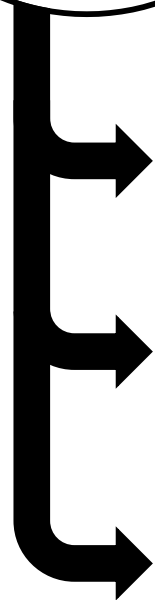
# Hydrothermal carbonization (HTC)





# Energy production

Hydrochar (HC)



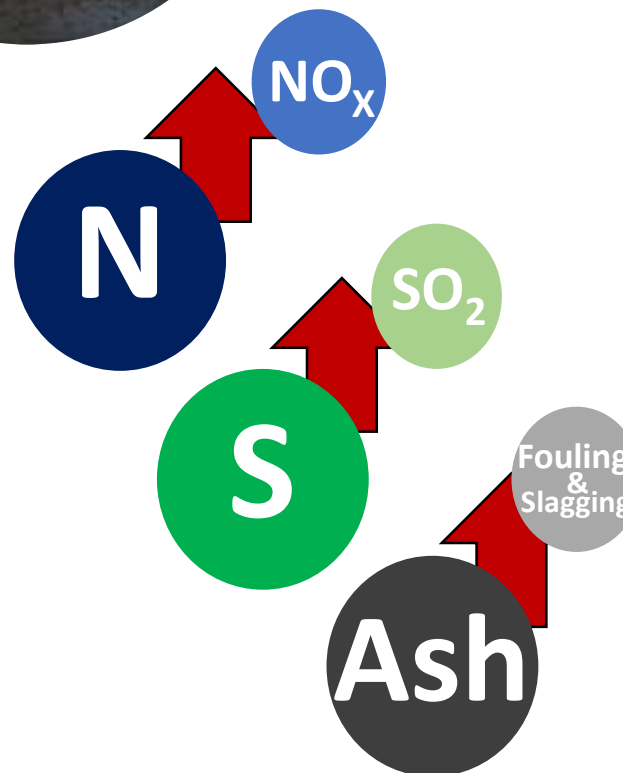
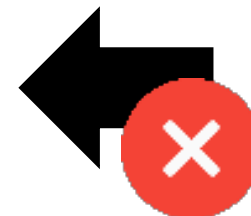
Microalgae



Animal manure



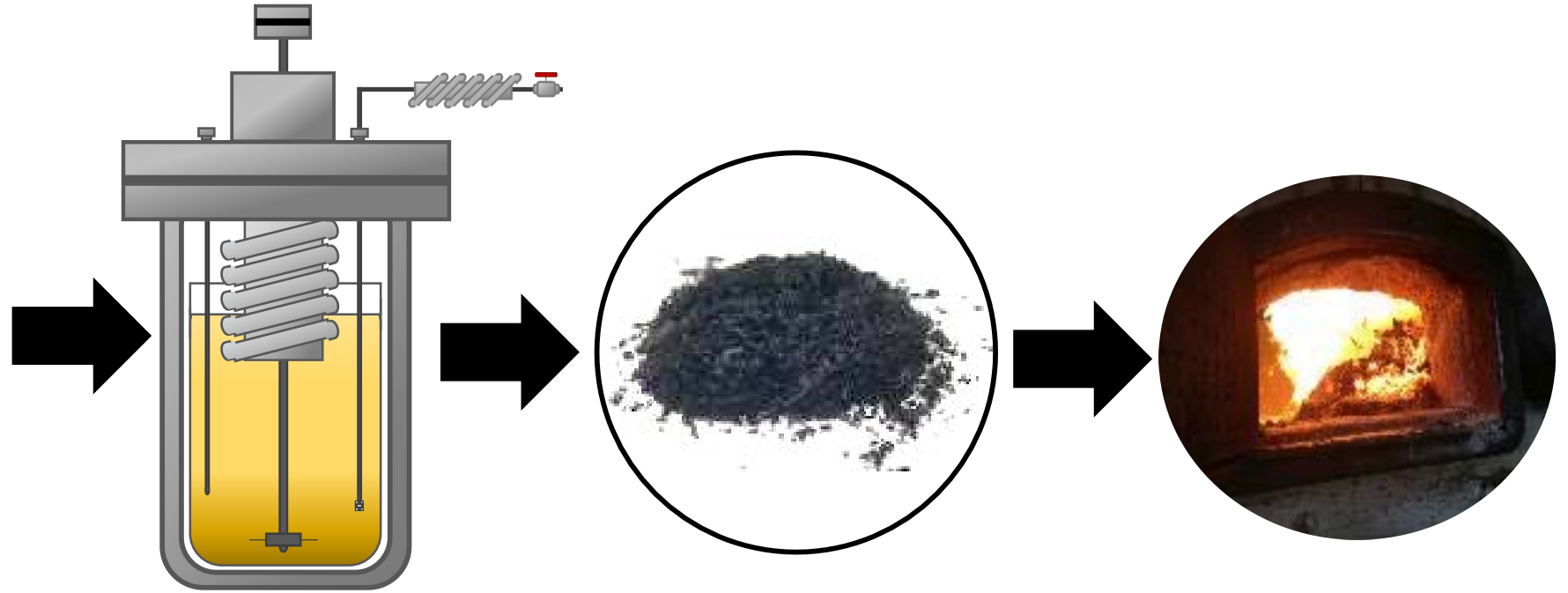
Sewage sludge



# Objective



Swine manure (SM)



$N < 3\%$   
 $S < 0.5\%$   
 $HHV > 17 \text{ MJ kg}^{-1}$

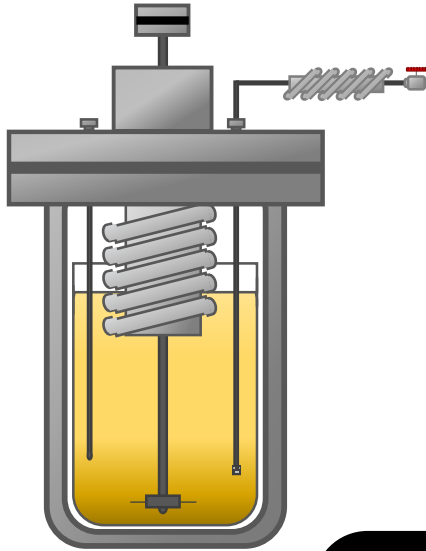
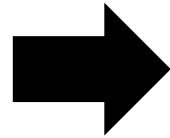
$VM < 75\%$   
 $Ash < 20\%$



# Experimental procedure



Swine manure (SM)



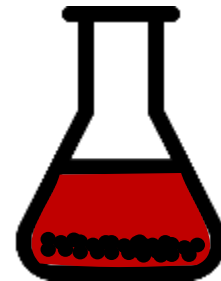
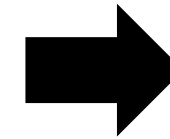
HTC

$T = 180, 210 \text{ and } 230 \text{ } ^\circ\text{C}$

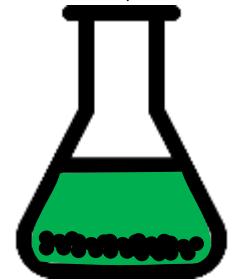
$t = 60 \text{ min}$



HC



HCl [5 M]  
HC-Wa

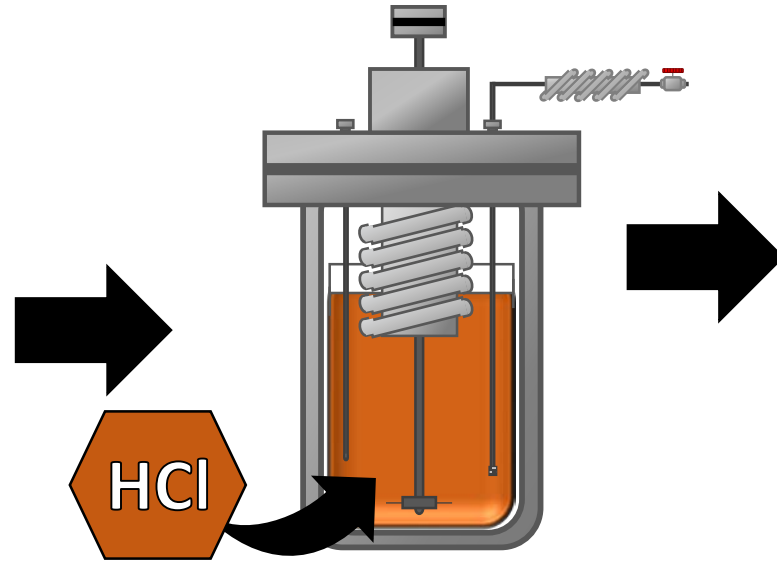


Acetone  
[20, 50 and 75% v:v]  
HC-Wb

# Experimental procedure



Swine manure (SM)



HTC assisted  
with acid  
HTC-A

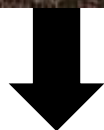
$T = 180, 210 \text{ and } 230 \text{ } ^\circ\text{C}$   
 $t = 60 \text{ min}$   
 $[\text{HCl}] = 0.1, 0.25, 0.5 \text{ and } 1.0 \text{ M}$



HC-A

# Swine manure origin and characteristics

## Swine manure (SM)



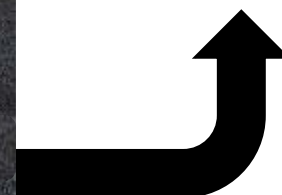
Avila – Spain



Swine manure (SM)	
C (%)	35.3 ± 0.6
N (%)	2.4 ± 0.1
S (%)	0.7 ± 0.0
HHV (MJ kg <sup>-1</sup> )	14.1 ± 0.3
Volatile matter (%)	60.0 ± 1.2
Fixed carbon (%)	15.7 ± 0.5
Ash (%)	24.3 ± 0.4

### Metals composition (g kg<sup>-1</sup>)

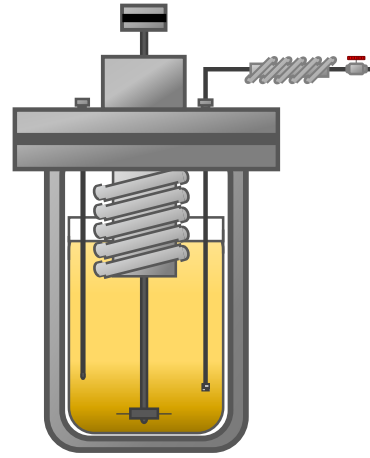
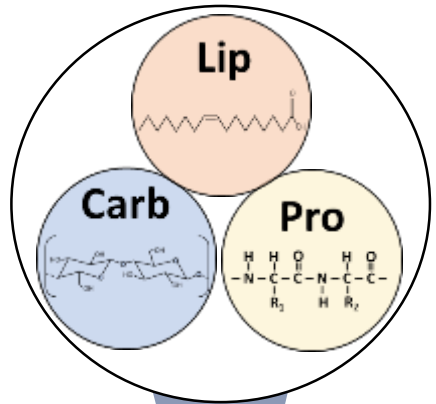
Ca	31.2 ± 0.2
Mg	13.5 ± 0.3
K	35.4 ± 0.2
Na	10.2 ± 0.1





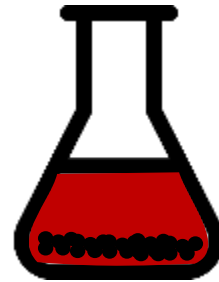
# Results

## Hydrochar characteristics; Mass yield



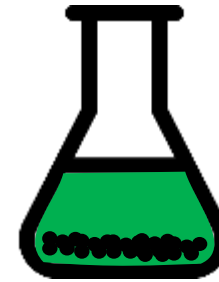
Plain HTC

$$Y_{\text{HC}} = 51 - 56\%$$



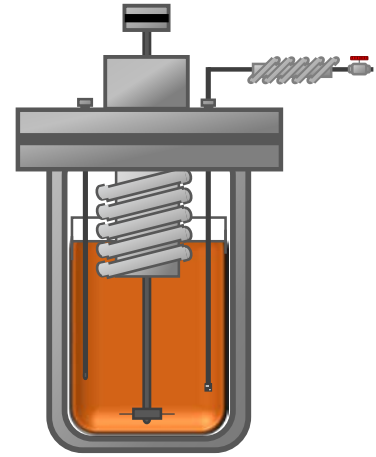
Acid washed

$$Y_{\text{HC}} = 28 - 39\%$$



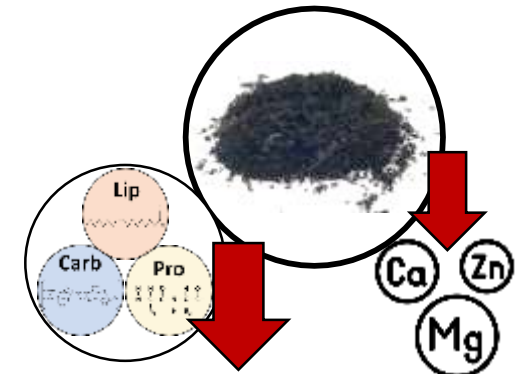
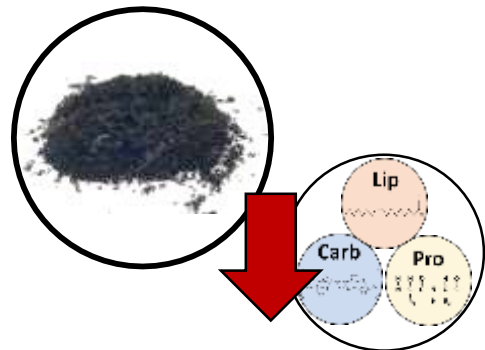
Acetone washed

$$Y_{\text{HC}} = \approx 44\%$$



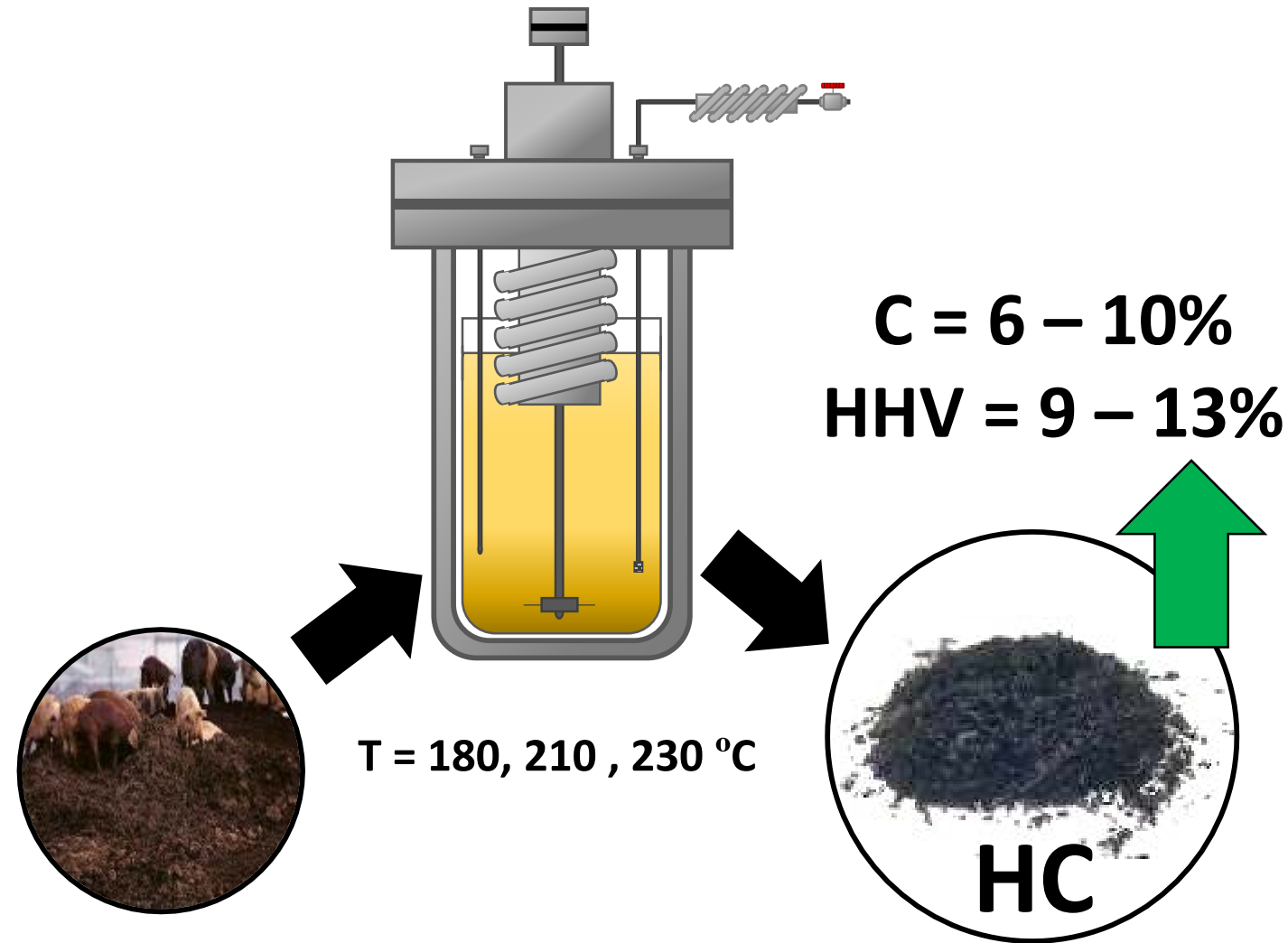
Acid-HTC

$$Y_{\text{HC}} = 26 - 43\%$$



# Results

## Hydrochar characteristics; Plain Hydrochar



**N = 1.8 – 2.1%**  
**VM  $\approx$  55%**



**HHV = 15 – 16 MJ kg<sup>-1</sup>**  
**S = 0.5 – 0.7**  
**Ash  $\approx$  32%**

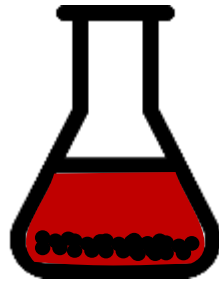


# Results

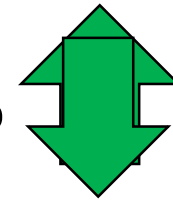
## Hydrochar characteristics; Washed hydrochars

Acid washed

HC-Wa



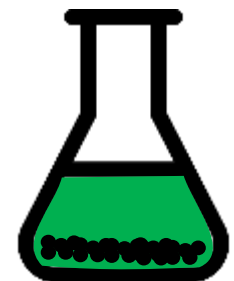
Ash = 50 – 60%



Ash ≈ 39%

Acetone washed

HC-Wb



HHV = 22 – 25 MJ kg<sup>-1</sup>

N < 3%

Ash < 10%

VM < 75%

HHV ≈ 19 MJ kg<sup>-1</sup>

N < 2%

Ash < 12%

VM < 75%



✗ S = 0.5 – 0.7%

S < 0.2%

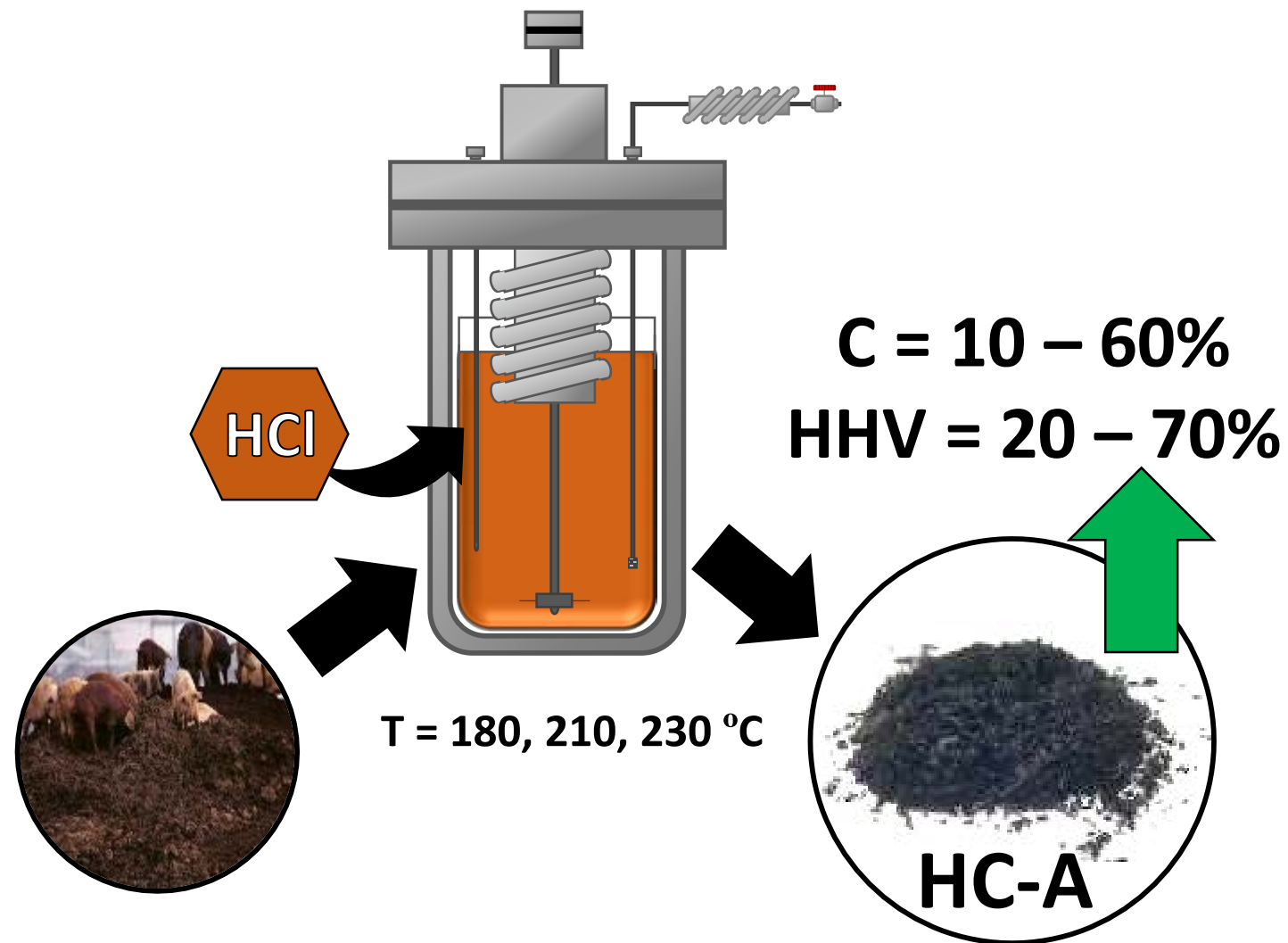


HC-W



# Results

## Hydrochar characteristics; Acid-Hydrochars



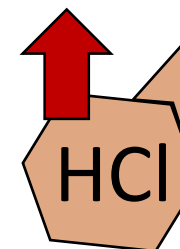
**HHV = 17 - 24 MJ kg<sup>-1</sup>**

**Ash = 8 - 15%**

**VM ≈ 70 %**

**S ≈ 0.7%**

**N = 2.8 - 4.0%**





**Nitrogen  
content**



# Results

## Ash agglomeration; Slagging and fouling indexes

**Not recommended for combustion**



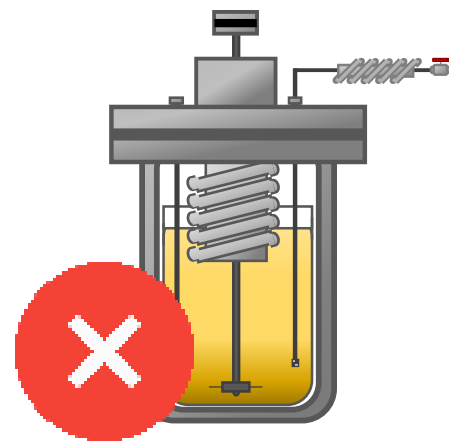
**Swine manure (SM)**

**FI = > 2000**

**SI = > 26**

**AI = > 4**

**Extremely high**



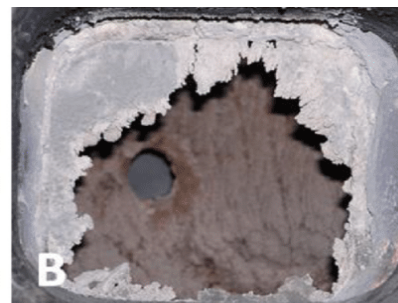
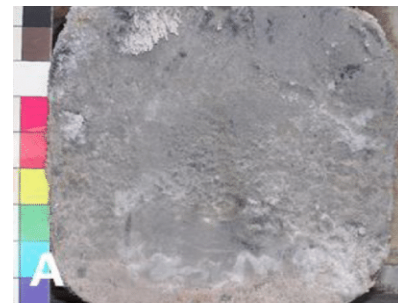
**Plain HTC**

**≈ 800**

**≈ 14**

**1.2 – 1.8**

**High**

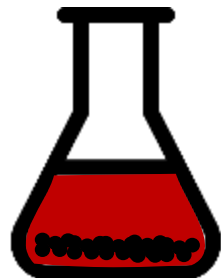


**Ash deposits forming during the combustion**

# Results

Ash agglomeration; Slagging and fouling indexes

Suitable for  
combustion



Acid  
washed

FI = 1.4 – 2.3  
SI = 0.9 – 1.8  
AI = 0.2

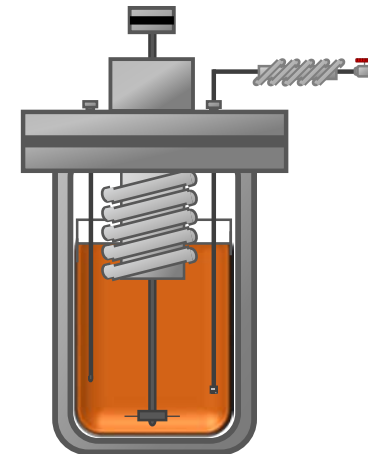
Low



Acetone  
washed

2.5 – 5.5  
0.1 – 0.3  
0.1

Low



HTC-Acid

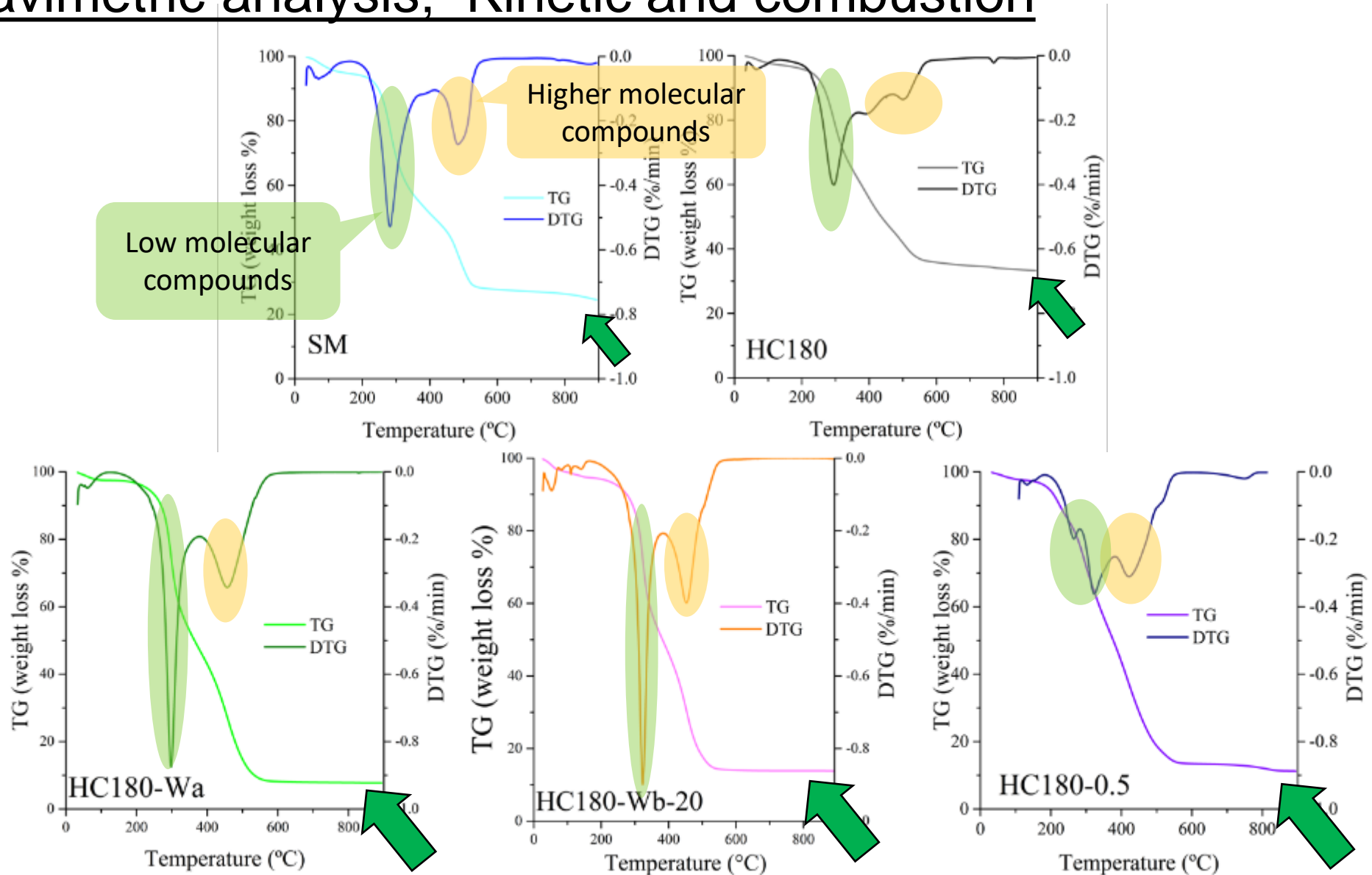
31 – 45  
2.5 – 5.0  
0.5 – 0.8

Low-medium



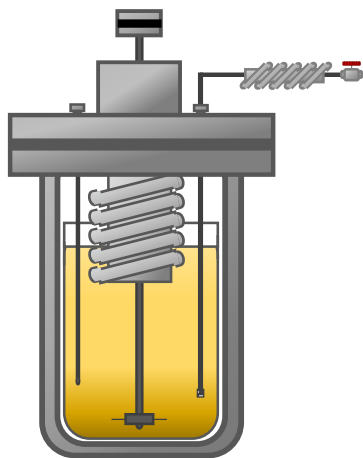
# Results

## Thermogravimetric analysis; Kinetic and combustion properties

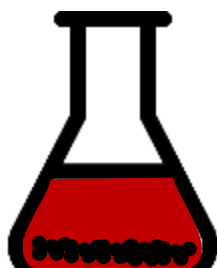


# Results

Thermogravimetric analysis; Kinetic and combustion properties



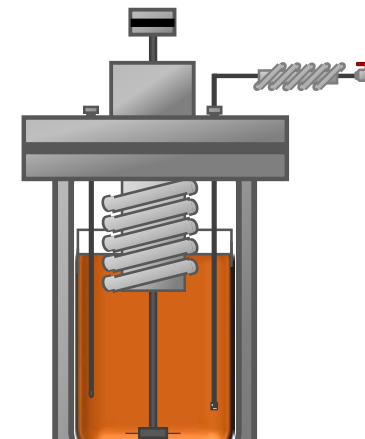
Plain HTC



Higher content of fixed carbon



Higher content of fixed carbon



Higher content of volatile matter

$E_a =$

55 – 68

104 – 184

110 – 118

44 – 49

$CCI \cdot 10^7 =$

5.6 – 6.2

6.3 – 8.9

$\approx 10.6$

7.5 – 9.9

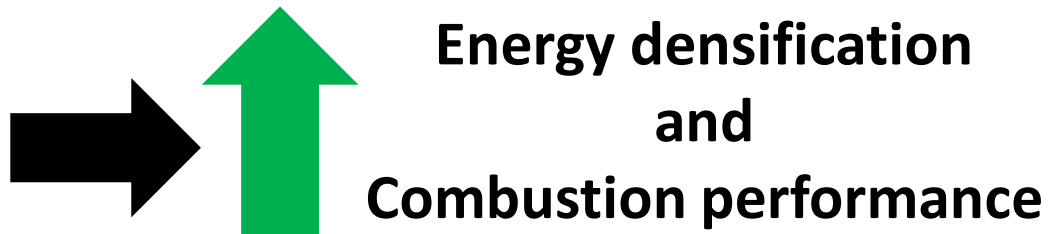
Higher and properly combustion stability


# In summary

- Plain HTC slight improved the hydrochar energy characteristics



- Hydrochar washing using hydrochloric acid




 **S > 0.5%**





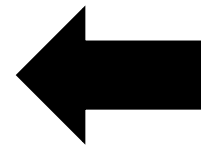
# In summary

- Hydrochar washing using acetone

 **N > 3%**  
**S > 0.5%**



 **Acid concentration**  
**and temperature**

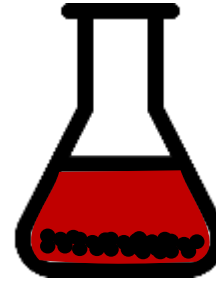


- Acid-assisted HTC

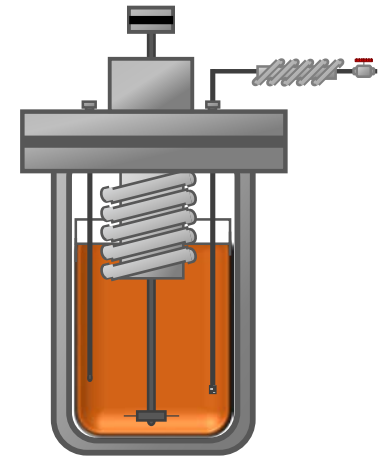


# In summary

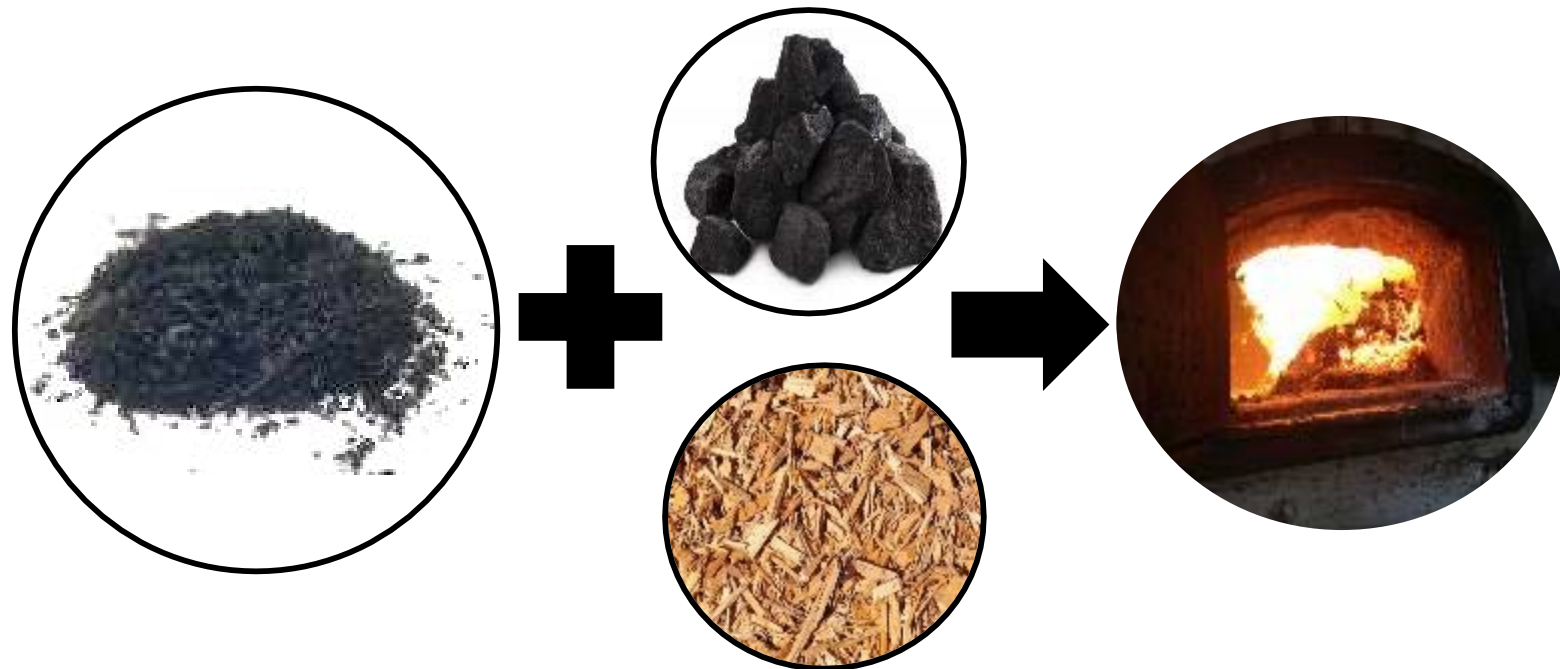
- Blending is necessary



Acid washed



HTC-Acid



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THANK  
YOU



### Acknowledgements

PID2019-108445RB-I00, PDC2021-120755-I00 and BES-2017-081515 (Spanish MINECO),  
S2018/EMT-4344 (Madrid Community)  
IND2019/AMB-17092 (Kerbest Company)



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Special Issue

Invitation to submit