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Biochar production through slow pyrolysis of different biomass materials: Seeking the best operating conditions

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Biochar production through slow pyrolysis of different biomass materials: seeking the best operating conditions

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Heat (heating rate < 30 K min^{-1})

Biomass →

Inert gas →

Slow Pyrolysis

→ Pyrolysis gas

→ Liquid fraction (aqueous and organic fractions)

Charcoal, Biochar, Biocarbon

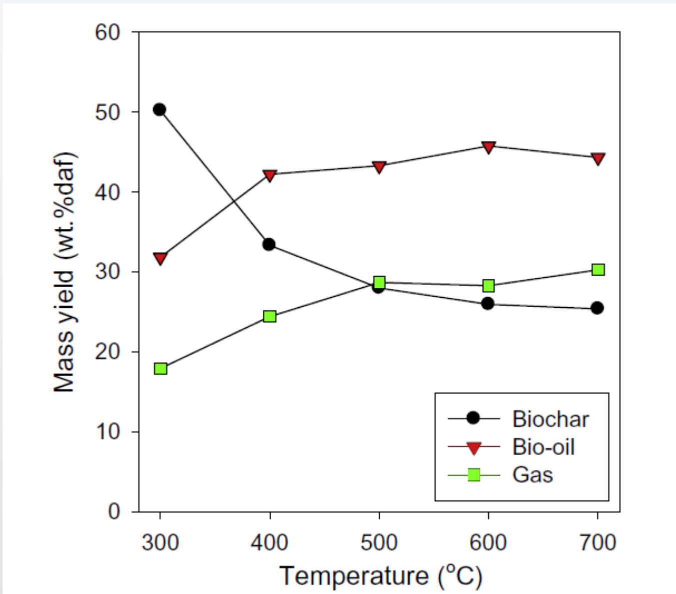
↓

High Yield

Parameters affecting biochar yield and properties

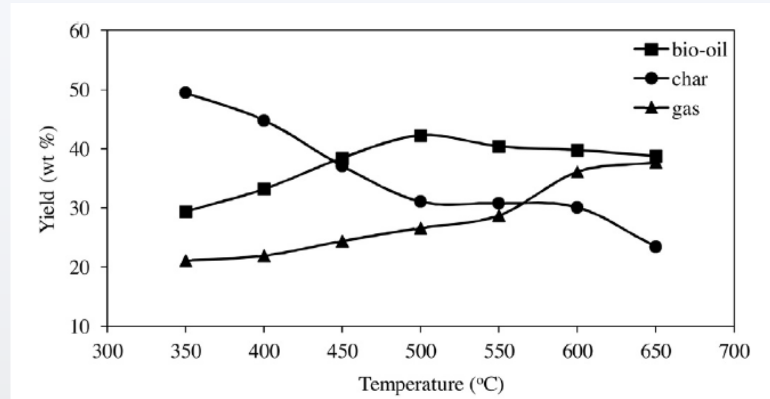
Peak Temperature (T_{peak})

Rice Straw



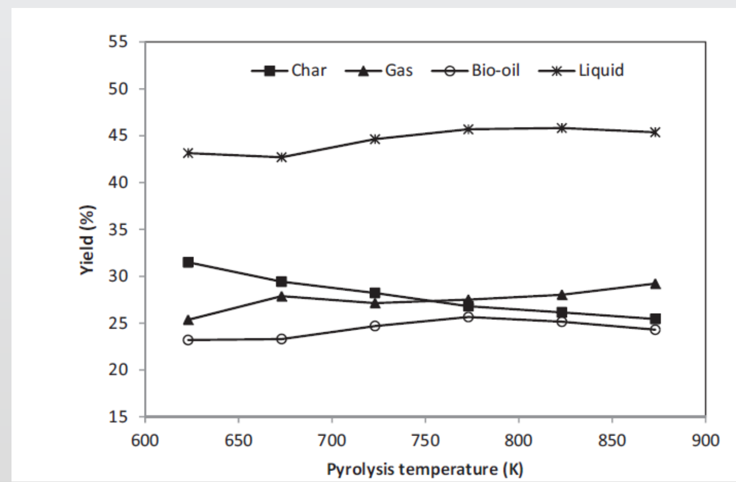
J. Park, et al. *Bioresour. Technol*. 2014, 155, 63–70

Sugarcane Bagasse



A.K. Varma, P. Mondal. *Ind. Crops Prod*. 2017, 95, 704–717

Paulownia wood



S. Yorgun, D. Yildiz. *J. Anal. Appl. Pyrolysis*. 2015, 114, 68-78

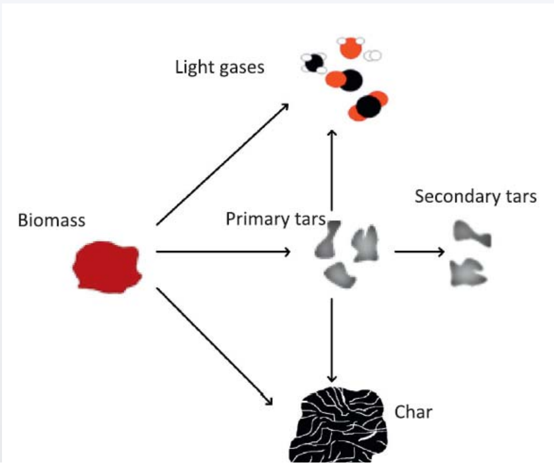
Biomass Feedstock dependence

↓

Lignin content, AAEM species…

Parameters affecting biochar yield and properties

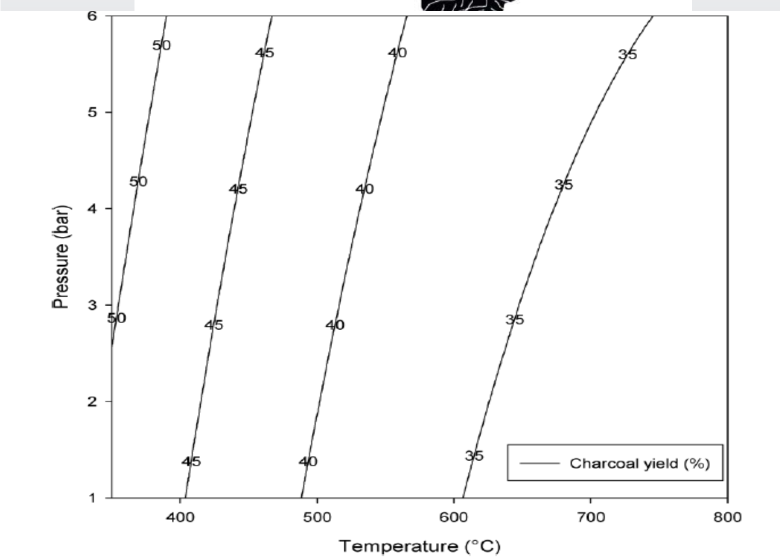
Pressure (P) Its effect is usually confounded with that of gas residence time (τ)



In packed-bed reactors, pressure can be raised:

1) By the carrier gas at **constant mass flow rate** (an increase in *P* leads to an increase in τ)

2) By the carrier gas at **constant gas residence time** (by adjusting the mass flow rate as a function of *P*).

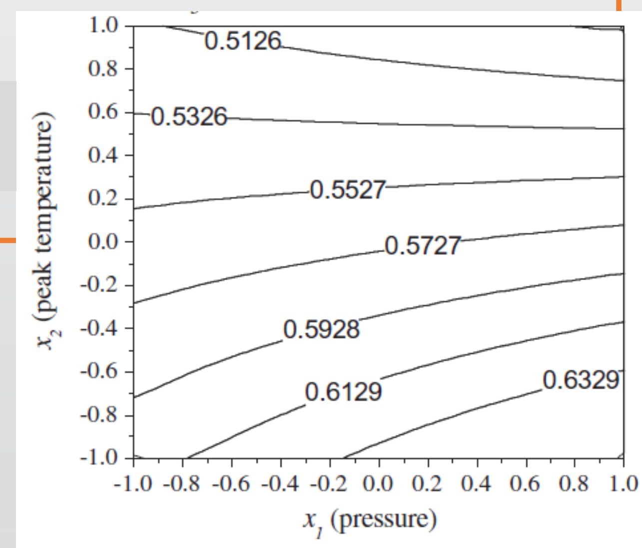


Vine shoots (y_{char})

J. J. Manyà, et al. *Fuel* 2014, 133, 163–172

Acacia wood

E. S. Noumi, et al. *Energy Fuels* 2015, 29, 7301–7308



Key properties in terms of potential biochar stability

- ✓ Proximate analysis: **Fixed-C content (x_{FC})** and **Fixed-C yield (y_{FC})** in a daf basis
- ✓ Elemental analysis: **molar ratios H:C and O:C** (Van Krevelen)
- ✓ Temperature programmed oxidation (TPO): **R_{50} index** proposed by Harvey et al. (*Environ. Sci. Technol*. 2012, 46, 1415−1421) to estimate thermal recalcitrance.
- ✓ Direct oxidation of biochars with H_2O_2: Edinburgh stability tool (Cross, A.; Sohi, S. P. GCB Bioenergy 2013, 5, 215–220) to estimate the **stable C fraction**.
- ✓ Percentage of **aromatic C**: estimated from solid-state ^{13}C NMR spectra.

Specific aim

- ➢ To analyze and compare the outcomes from previous studies, which were focused on determining the effects of certain operating conditions on the properties of the biochar produced from **three different sources**: corn stover (CS), two-phase olive mill waste (TPOMW), and vine shoots (VS).
- ➢ To analyze correlations among the **properties related to the potential stability** and suggest a suitable stability indicator.
- ➢ To analyze effects of operating conditions on the **produced gas**.

Biomass sources

Corn stover (CS)
corncob (15.5%), leaf (4.3%) and stalk (80.2 %)
Particle size: as received

Effect of T_{peak} and P
At constant gas residence time

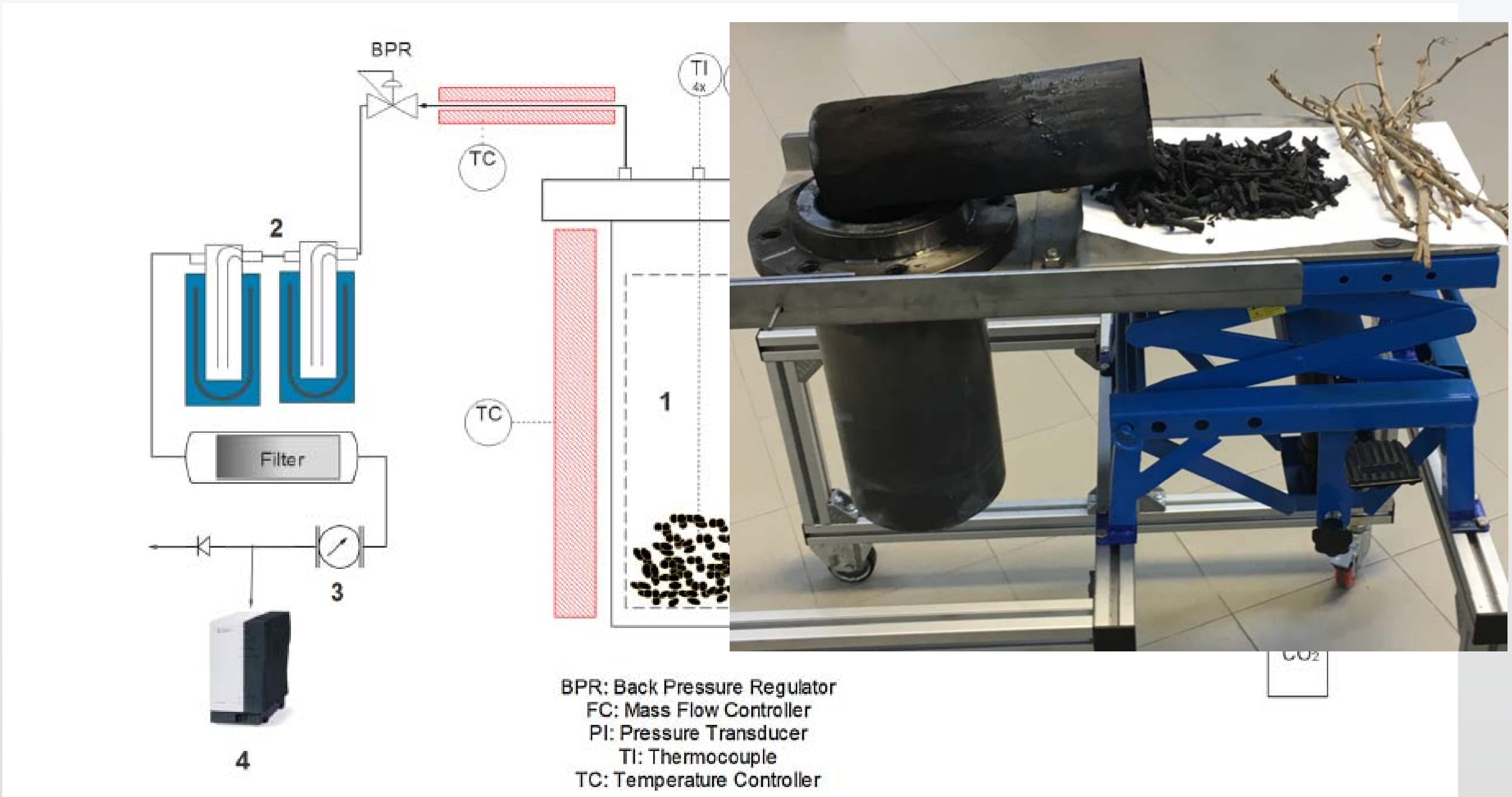
Dried two-phase olive mill waste (TPOMW)
Particle size: in the range of 0.32–3.0 mm

Effect of P and the addition of inorganics (AAEMs)
At constant gas residence time

Vine shoots(VS)
Particle size: in the range of 0.1–1.0 cm diameter and 1.0–3.5 cm long

Effect of T_{peak}, P, and carrier gas (N_2 or CO_2)
At constant gas residence time

Pyrolysis device



(1) fixed-bed pyrolysis reactor, (2) pyrolysis liquid condensation system, (3) volumetric gas meter and (4) micro-GC.

Potential stability for corn stover-derived biochars

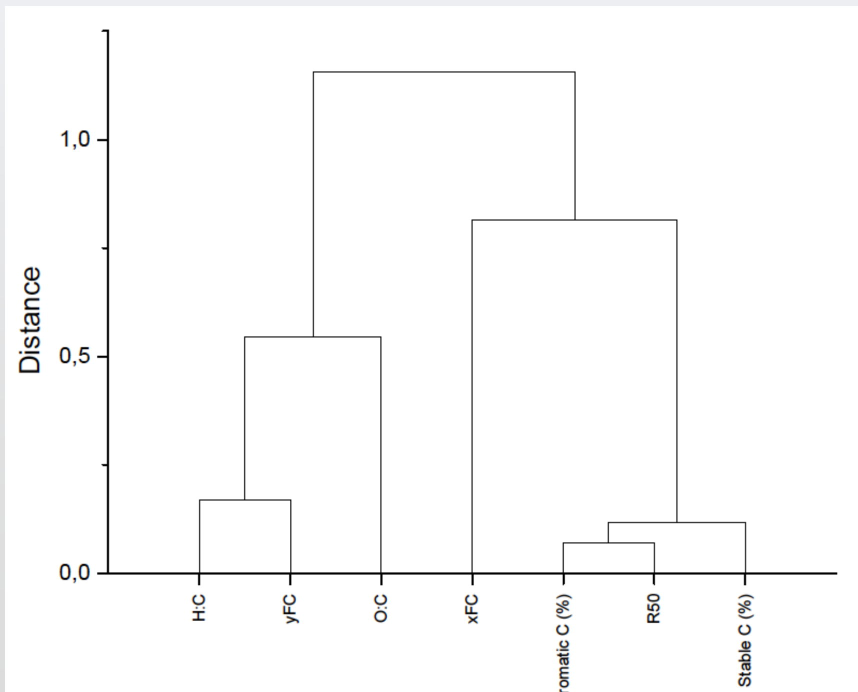
Carrier gas : N_2

	H:C	O:C	x_{FC}	y_{FC}	Aromatic C (%)	R_{50}	Stable C (%)
400 °C; 0.1 MPa	0.589	0.154	0.787	0.289	71,0	0.510	85.9
650 °C; 0.1 MPa	0.246	0.128	0.829	0.261	83.8	0.590	90,0
525 °C; 0.8 MPa	0.381	0.06	0.888	0.286	68.8	0.505	86,0
525 °C; 0.8 MPa	0.403	0.062	0.879	0.266	72.1	0.511	84.6
525 °C; 0.8 MPa	0.394	0.062	0.875	0.276	68.6	0.509	85.3
400 °C; 1.5 MPa	0.58	0.122	0.809	0.300	69.3	0.527	83.4
650 °C; 1.5 MPa	0.256	0.063	0.904	0.271	83.5	0.561	90.9

Statistically significant effects (α= 0.05)

- H:C → T_{peak} (−)
- O:C → T_{peak} (−), *P* (−), *Curv.*
- x_{FC} → T_{peak} (+), *P* (+), *Curv.*
- y_{FC} → *No effect*
- Aromatic C (%) → T_{peak} (+), *Curv.*
- R_{50} → T_{peak} (+), *P** T_{peak} (−), *Curv.*
- Stable C (%) → T_{peak} (−)

		H:C	O:C	xFC	yFC	Aromatic C (%)	R50	Stable C (%)
H:C	Pearson Corr.	1	0.49618	-0.67764	**0.83056**	-0.74437	-0.65205	**-0.79995**
	Sig.	--	0.2574	0.09438	**0.02067**	0.05499	0.11249	**0.03077**
O:C	Pearson Corr.	0.49618	1	-0.96205	0.32706	0.08333	0.24481	-0.03472
	Sig.	0.2574	--	52,8104	0.47398	0.85902	0.59675	0.94109
xFC	Pearson Corr.	-0.67764	-0.96205	1	-0.46483	0.16769	-0.02733	0.29944
	Sig.	0.09438	52,8104	--	0.29329	0.71931	0.95361	0.51413
yFC	Pearson Corr.	**0.83056**	0.32706	-0.46483	1	-0.667	-0.53537	-0.6202
	Sig.	**0.02067**	0.47398	0.29329	--	0.10171	0.21557	0.13732
Aromatic C (%)	Pearson Corr.	-0.74437	0.08333	0.16769	-0.667	1	**0.92885**	**0.92388**
	Sig.	0.05499	0.85902	0.71931	0.10171	--	**0.0025**	**0.00295**
R50	Pearson Corr.	-0.65205	0.24481	-0.02733	-0.53537	**0.92885**	1	**0.80626**
	Sig.	0.11249	0.59675	0.95361	0.21557	**0.0025**	--	**0.0285**
Stable C (%)	Pearson Corr.	**-0.79995**	-0.03472	0.29944	-0.6202	**0.92388**	**0.80626**	1
	Sig.	**0.03077**	0.94109	0.51413	0.13732	**0.00295**	**0.0285**	--



Potential stability for TPOMW-derived biochars

T_{peak} = 600 °C. Carrier gas : N_2

	H:C	O:C	x_{FC}	y_{FC}	Aromatic C (%)	R_{50}	Stable C (%)
OW at 0.1 MPa	0.3398	0.0324	0.616	0.231	85.8	0.564	89.4
OW at 1.0 MPa	0.2985	0.0166	0.946	0.305	86.6	0.605	86.3
OW+A at 0.1 MPa	0.308	0.0921	0.946	0.269	85.3	0.506	82.9
OW+A at 1.0 MPa	0.335	0.0919	0.947	0.283	86.7	0.559	81.9
OW+RC at 0.1 MPa	0.2524	0.083	0.906	0.286	85.4	0.634	94.6
OW+RC at 1.0 MPa	0.3979	0.0332	0.926	0.289	85.4	0.635	95.1

OW: TPOMW; OW+A: 5% K_2CO_3 + 5% CaO; OW+RC: 10% Rejected Material from Municipal Waste Composting

60% ash (Ca, K, Na)

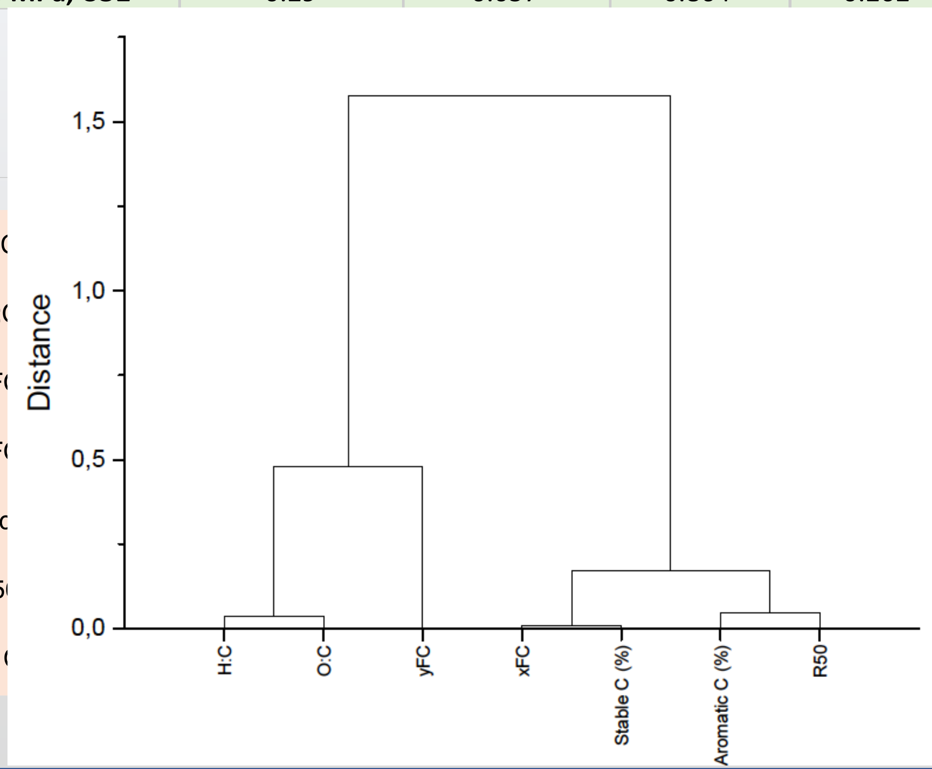
		H:C	O:C	xFC	yFC	Aromatic C (%)	R50	Stable C (%)
H:C	Pearson Corr.	1	-0,38246	-0,14557	-0,16147	-0,01364	0,02446	0,09676
	Sig.	--	0,45428	0,78319	0,75991	0,97954	0,96332	0,85531
O:C	Pearson Corr.	-0,38246	1	0,36319	-0,02178	-0,17738	-0,44698	-0,36889
	Sig.	0,45428	--	0,47917	0,96733	0,73672	0,37418	0,47176
xFC	Pearson Corr.	-0,14557	0,36319	1	**0,88139**	0,123	0,10601	-0,1968
	Sig.	0,78319	0,47917	--	**0,02027**	0,81643	0,84158	0,70861
yFC	Pearson Corr.	-0,16147	-0,02178	0,88139	1	0,29103	0,4766	0,05053
	Sig.	0,75991	0,96733	0,02027	--	0,57578	0,33923	0,92427
Aromatic C (%)	Pearson Corr.	-0,01364	-0,17738	0,123	0,29103	1	-0,04429	-0,55371
	Sig.	0,97954	0,73672	0,81643	0,57578	--	0,93361	0,25431
R50	Pearson Corr.	0,02446	-0,44698	0,10601	0,4766	-0,04429	1	**0,82557**
	Sig.	0,96332	0,37418	0,84158	0,33923	0,93361	--	**0,04299**
Stable C (%)	Pearson Corr.	0,09676	-0,36889	-0,1968	0,05053	-0,55371	**0,82557**	1
	Sig.	0,85531	0,47176	0,70861	0,92427	0,25431	**0,04299**	--

Potential stability for vine shoots-derived biochars

T_{peak} = 600 °C

	H:C	O:C	x_{FC}	y_{FC}	Aromatic C (%)	R_{50}	Stable C (%)
VS at 400 °C, 0.1 MPa, N2	0.74	0.16	0.709	0.269	56,0	0.513	64.2
VS at 400 °C, 1.0 MPa, N2	0.689	0.123	0.726	0.274	57.2	0.516	63.8
VS at 600 °C, 0.1 MPa, N2	0.401	0.068	0.855	0.277	69.5	0.528	81.8
VS at 600 °C, 1.0 MPa, N2	0.306	0.061	0.856	0.261	78.9	0.536	79.5
VS at 600 °C, 0.1 MPa, CO2	0.376	0.054	0.861	0.257	66.7	0.518	80.7
VS at 600 °C, 1.0 MPa, CO2	0.29	0.057	0.864	0.262	73.9	0.533	81.2

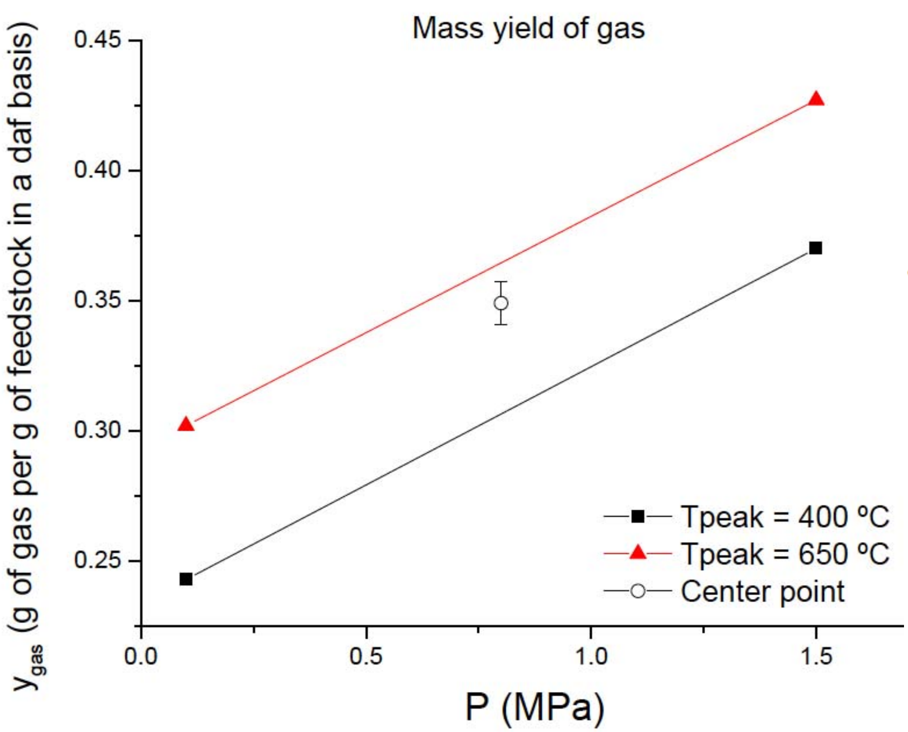
Effects of *Tpeak* and *P* (minor)

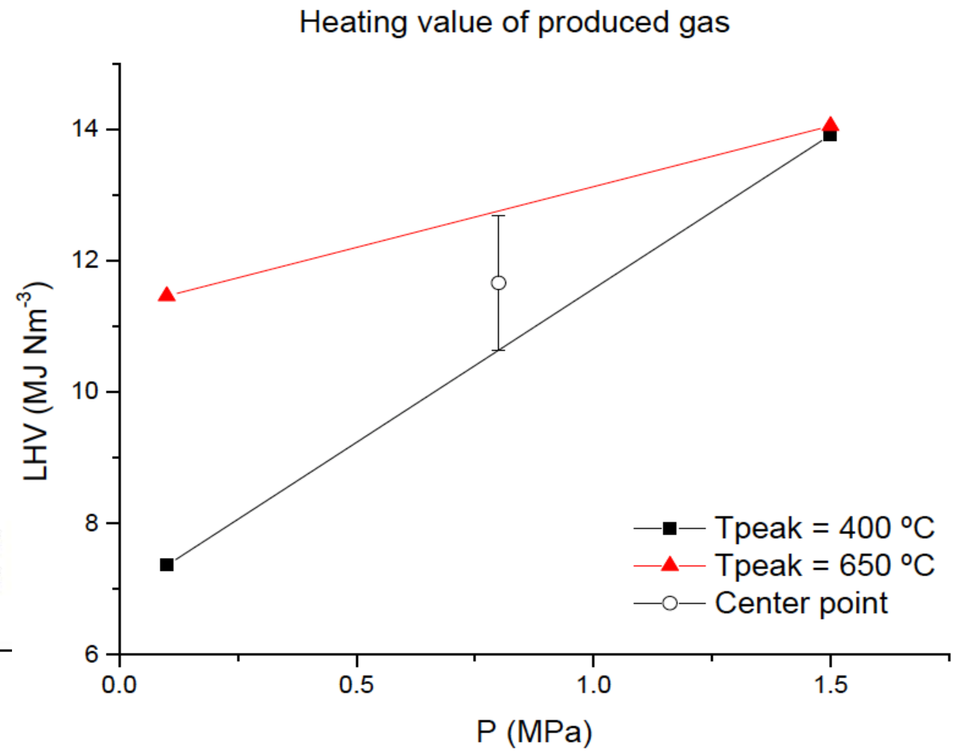


	romatic C (%)	R50	Stable C (%)
H:(	**-0,94561**	**-0,848**	**-0,95953**
	0,00436	**0,0329**	**0,00242**
O:(	**-0,85686**	-0,73453	**-0,94718**
	0,02927	0,09636	**0,00411**
xF(	**0,88589**	0,76455	**0,9919**
	0,01879	0,07663	**9,81148E-5**
yF(	-0,46845	-0,24969	-0,42527
	0,34872	0,63325	0,40055
Aromatic	1	**0,95305**	**0,85986**
	--	**0,00325**	**0,02808**
R5(	**0,95305**	1	**0,74345**
	0,00325	--	**0,09029**
Stable (	**0,85986**	**0,74345**	1
	0,02808	**0,09029**	--

Effects on produced gas

Corn stover





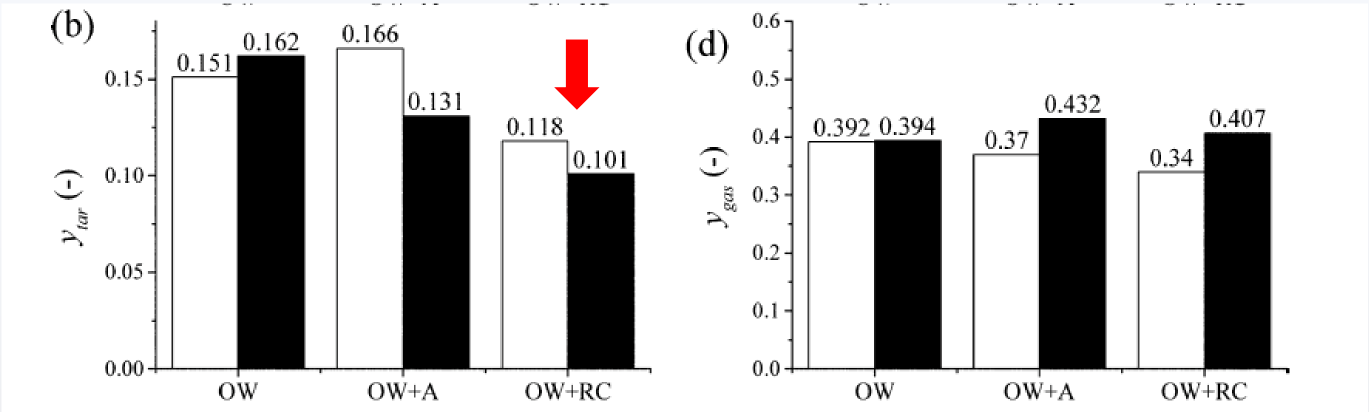
Yield of CO_2: *P* (+)
Yield of CO: T_{peak} (++); *P* (–)
Yield of CH_4: *P* (++)
Yield of H_2: T_{peak} (+); *P* (++)

number	reaction	ΔG^a (kJ mol^{-1}) 600 °C and 0.1 MPa	ΔG^a (kJ mol^{-1}) 600 °C and 1.0 MPa
1	$H_2O + CO \rightleftharpoons CO_2 + H_2$	−0.2794	−0.2594
2	$2CO \rightleftharpoons CO_2 + C$	−1.648	−2.675
3	$3H_2 + CO \rightleftharpoons CH_4 + H_2O$	12.43	−10.29
4	$C + 2H_2 \rightleftharpoons CH_4$	2.758	−14.05
5	$C + H_2O \rightleftharpoons CO + H_2$	−0.0604	1.486
6	$2H_2 + 2CO \rightleftharpoons CO_2 + CH_4$	10.99	−26.06

[a]Calculated by Aspen Plus 8.8 using the Peng−Robinson method and the equilibrium reactor (R_{equil}) module. The initial concentration in the molar fraction of reactants and products was taken equal to $1/n$, where n is the number of species involved.

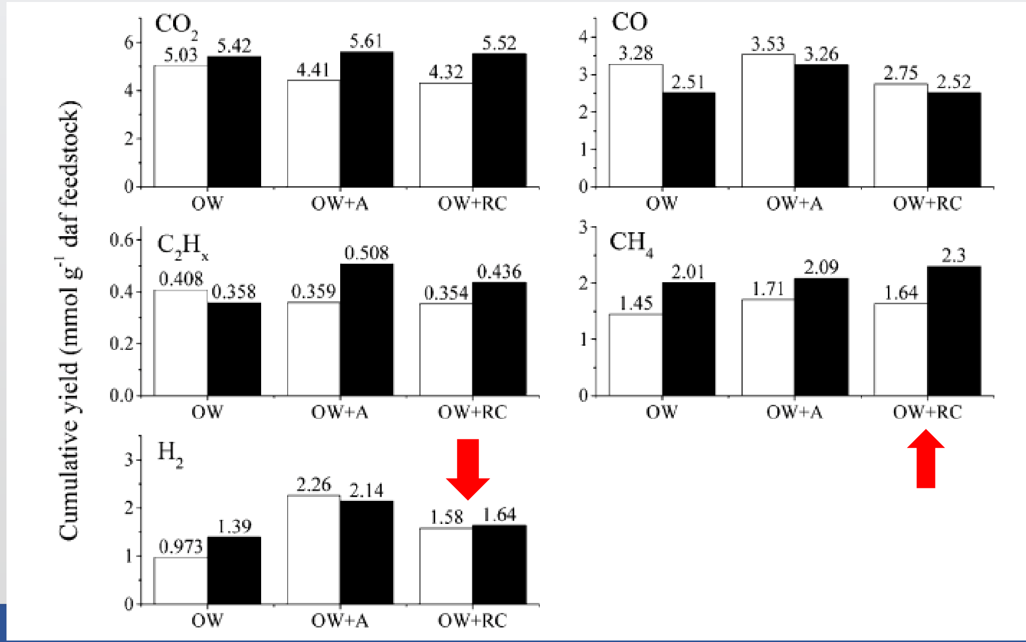
Effects on produced gas

TPOMW



Mass yields (on a daf basis) of (b) tar, and (d) gas. White columns correspond to pyrolysis runs at 0.1 MPa, whereas black columns refer to runs conducted at 1.0 MPa.

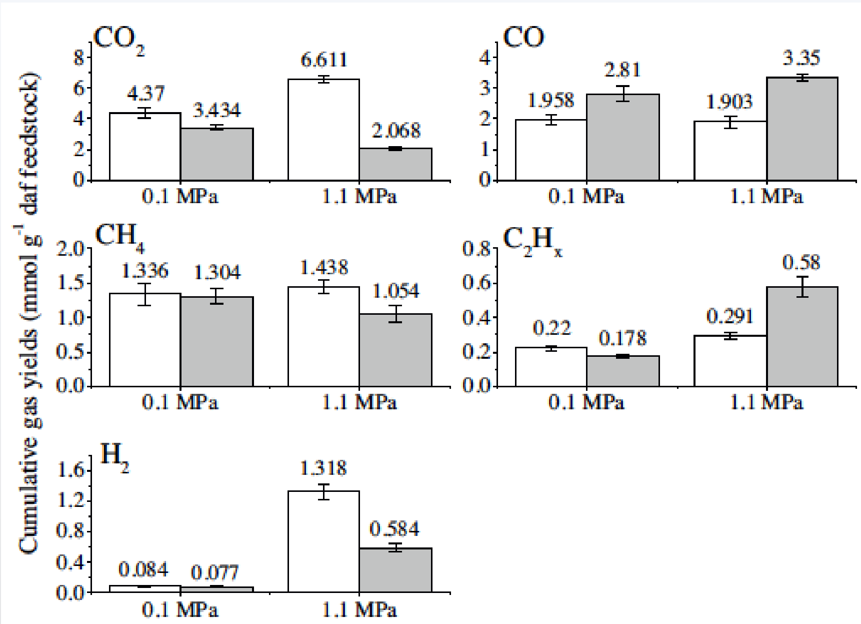
J. J. Manyà, et al. *Energy Fuels* 2016, 30, 8055–8064

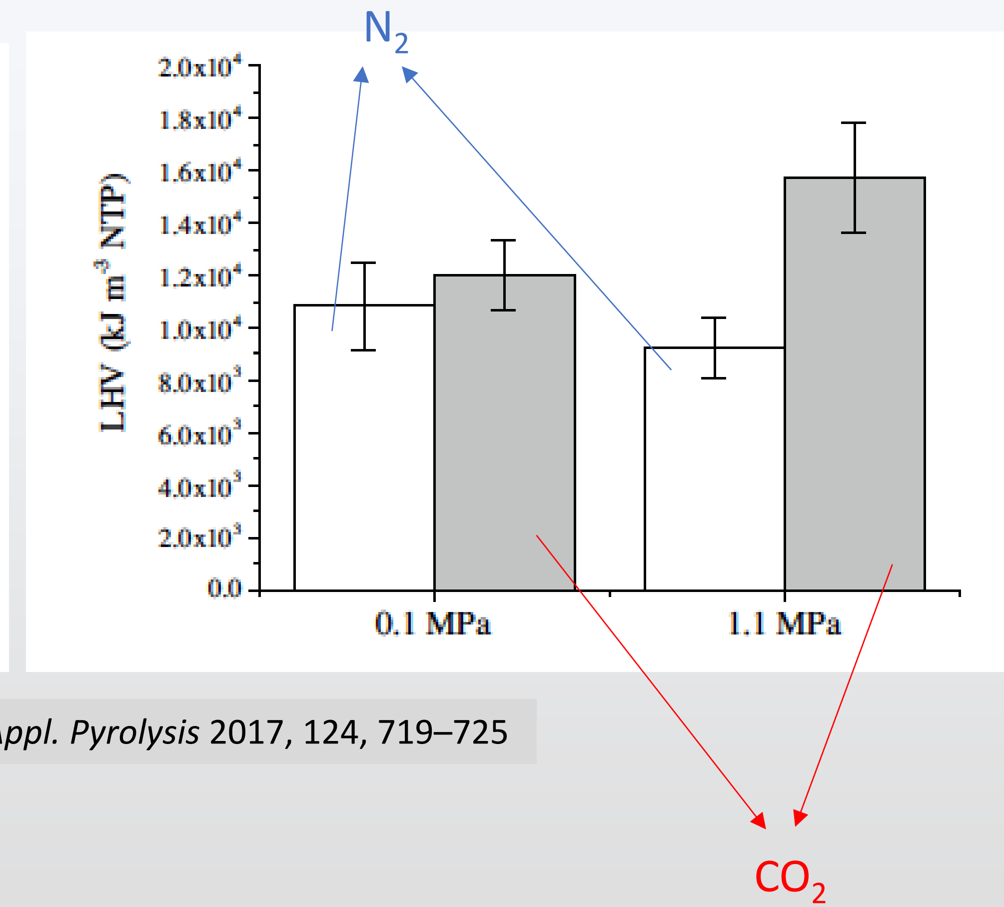


Addition of RC leads to a decrease in tar, and an increase in CH_4 and H_2

Effects on produced gas

Vine shoots





M. Azuara, et al. *J. Anal. Appl. Pyrolysis* 2017, 124, 719–725

Using CO_2 instead of N_2:
yields of **CO_2** ↓; **CO** ↑ ; **CH_4** ↓ (at pressure); **H_2** ↓(at pressure); **C2s** ↑ (at pressure)

- The ***R_{50} index*** and the ***stable C fraction*** (after oxidation with H_2O_2) appear as useful indicators of the potential stability of biochar. Both techniques are relatively fast and inexpensive compared to e.g. ^{13}C NMR.

- **Pressure** has a little effect on potential stability compared to Peak Temperature. However, working at moderate pressure (1.0−1.5 MPa) leads to higher yields of produced gas as well as an improvement of its composition.

- By adding a relatively small amount of **high-ash RDF (RC)**, it is possible to obtain biochars with higher potential stabilities. At the same time, the properties of the produced gas are improved.

- Using a **pyrolysis environment of CO_2** did not significantly affect neither the yield nor the potential stability of biochar. At moderate pressure, using CO_2 instead of N_2 can lead to a producer gas with very high heating value.

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