INTERMEDIATE PYROLYSIS OF AGRICULTURAL AND RESIDUAL LIGNOCELLULOSIC FEEDSTOCKS FOR BIOCHAR, BIOFUELS INTERMEDIATE AND BIOCHEMICALS PRODUCTION

Giacomo Lombardi[1,2], Arturo di Fraia[1], Giulia Lotti[1], Andrea Maria Rizzo[1,2], David Chiaramonti[1,3]

[1] Renewable Energy Consortium for Research and Demonstration (RE-CORD), Florence (Italy), [2] University of Florence, Department of Industrial Engineering (DIEF), Florence (Italy)

[3] Polytechnic of Turin, Energy Department (DENERG), Turin (Italy)

Tcbiomass2022 – April 19-21, 2022. Denver, Colorado, USA.

INTRODUCTION

The thermochemical technologies for the conversion of woody biomass are being rapidly developed in response to EU decarbonization policy of transport sector. The demand for biomass by advanced biofuels plant can be hardly met by crop residues alone, even though they are the most abundant EU biomass resources. Therefore, the introduction of dedicated annual and perennials crops is highly recommended to increase feedstock availability.

This work deals with the experimental valorization of agricultural and residual lignocellulosic feedstocks in a continuous auger-type pyrolyzer coupled with a condensation unit, where, where hot vapors can be condensed in multiple in-series, water-cooled, surface heat exchangers.

The present work was supported by the project BECOOL, "Brazil-EU Cooperation for Development of Advanced Lignocellulosic Biofuels" and aims at extending the present knowledge on intermediate pyrolysis, providing a quantitative and qualitative characterization of pyrolysis products (charcoal, oil and aqueous phases) from selected feedstocks and identifying their most suitable application.

MATERIALS AND METHODS

Feedstocks

Giant Reed – Bagasse – Eucalyptus – Sorghum – Lignin (2G EtOH)

Test Conditions

Pretreatment	Grinding, drying
Particle size	<8 mm
Temperature	550°C
Average feed rate	1.4 kg h^{-1}
Solid residence time	5 min

Solid product characterization

Ultimate, proximate and ICP-OES analysis

Oil phase characterization

CHN, Ash, Karl Fischer titration, GPC, GC-MS

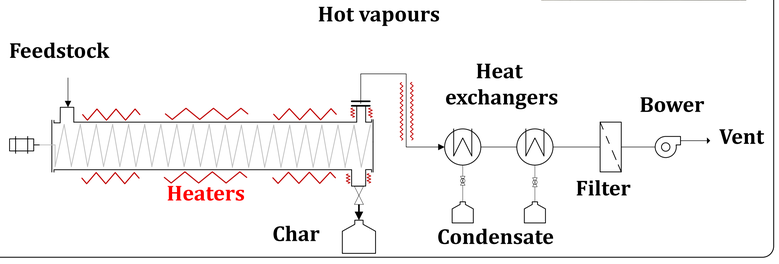
Aqueous phase characterization

HPLC, GC-MS

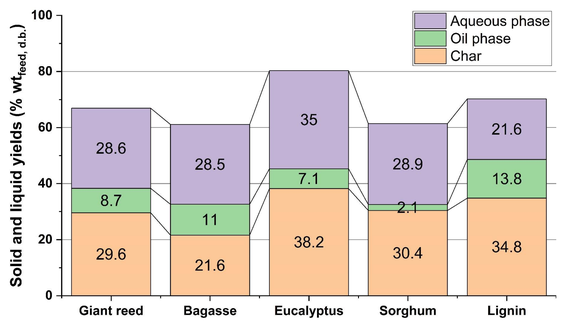
EXPERIMENTAL SETUP

SPYRO pilot unit

- Continuous auger-type pyrolyzers
- 2m long, 0.15 m inner diameter
- Design feed flow rate: 3 kg h^{-1}
- Externally heated - Allothermal reactor
- Variable auger speed
- Solid residence time achievable: 5-70 min
- T, p monitoring and acquisition
- Hot vapours extraction and condensation
- In-series shell and tube heat-exchangers
- Patent pending



RESULTS – SOLID AND LIQUID YIELDS



RESULTS – CHARCOAL

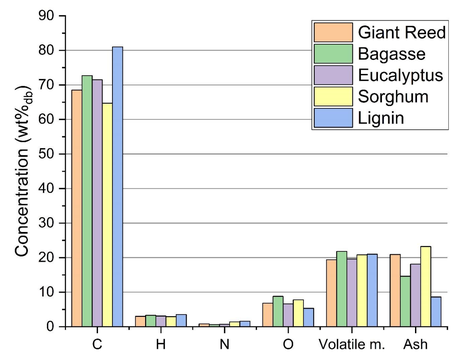
Proximate and ultimate analysis

Sample	Volatile matter	Ash	C	H	N	O*	O/C	H/C	HHV[a]	LHV[b]
	[wt%db]	[wt%db]	[wt%db]	[wt%db]	[wt%db]	[wt%db]	[-]	[-]	[MJ kg-1db]	[MJ kg-1db]
Giant Reed	19.4	20.9	68.5	3.0	0.8	6.8	0.07	0.53	*26.3*	*25.7*
Bagasse	21.8	14.6	72.7	3.3	0.6	8.8	0.09	0.54	*28.0*	*27.4*
Eucalyptus	19.6	18.1	71.5	3.1	0.7	6.6	0.07	0.52	27.5	26.9
Sorghum	20.8	23.2	64.7	2.9	1.4	7.8	0.09	0.54	24.7	24.1
Lignin	21.0	8.6	81.0	3.5	1.6	5.3	0.05	0.52	31.6	30.9

*evaluated by difference

[a] evaluated with: HHV = 0.3491·C + 1.1783·H - 0.1034·O - 0.0211·Ash + 0.1005·S - 0.0151·N, Channiwala, P.P. Parikh, A unified correlation for estimating HHV of solid, liquid and gaseous fuels, Fuel, Volume 81, Issue 8, 2002, Pages 1051-1063, ISSN 0016-2361, https://doi.org/10.1016/S0016-2361(01)00131-4.

[b] evaluated with: LHV = HHV-0.206·H



Inorganics concentration and comparison with Italian legislation and International biochar initiative

Parameter	Giant Reed	Bagasse	Eucalyptus	Sorghum	Lignin	ITA*	IBI
C [wt%db]	68.5	72.7	71.5	64.7	81.0	-	-
Corg [wt%db]	n.m.	n.m.	n.m.	n.m.	n.m.	Class 1: >60 Class 2: >30 & ≤60 Class 3: ≥20 & ≤30	Class 1: ≥60 Class 2: ≥30 & <60 Class 3: ≥10 & <30
Ash [wt%db]	20.9	14.6	18.1	23.2	8.6	Class 1: <10 Class 2: ≥10 & ≤40 Class 3: >40 & ≤60	Declaration
H/Corg *	0.53	0.54	0.52	0.54	0.52	≤0.7	≤0.7
O/Corg *	0.07	0.09	0.07	0.09	0.05	-	-
Al	974	2992	874	503	639	-	-
Ba	33	56	54	27	4	-	-
Ca	11017	3156	7830	12115	3699	-	-
Cd	bdl	bdl	bdl	bdl	bdl	<1.5	1.4-39
Co	bdl	bdl	bdl	bdl	bdl	-	34-100
Cr	53	65	24	52	25	-	93-1200
Cu	bdl	bdl	bdl	bdl	bdl	≤230	143-6000
Fe	1185	5637	919	781	1306	-	-
K	27634	6339	30003	39141	10765	-	-
Mg	2430	1733	2049	7899	516	-	-
Mn	134	204	92	94	14	-	-
Mo	bdl	bdl	bdl	bdl	bdl	Not required	5-75
Na	825	85	498	258	20051	-	-
P	755	0	743	2330	bdl	-	-
Pb	bdl	bdl	bdl	bdl	bdl	≤140	121-300
Si	1219	2976	2719	4549	614	-	-
Ti	25	625	50	37	18	-	-
Zn	bdl	bdl	bdl	98	62	≤500	416-7400

*D.L. 29 APRILE 2010 N. 75
bdl = below detection limit, 0.1 mg kg^{-1}
n.m. = not measured

CONTACT & INFORMATION

Prof. David Chiaramonti

DAVID.CHIARAMONTI@RE-CORD.ORG

+39 055 4796738

RESULTS – OIL PHASE

Oil phase properties

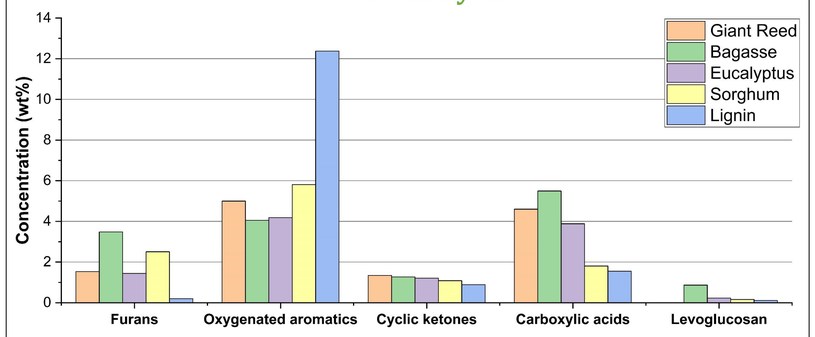
Sample	Water content	Ash	C	H	N	O*	Mw	HHV[a]	LHV[b]
	[wt%wb]	[wt%db]	[wt%db]	[wt%db]	[wt%db]	[wt%db]	[g mol-1]	[MJ kg-1db]	[MJ kg-1db]
Giant Reed	12.8	0.30	69.6	6.9	1.3	21.9	626.0	*30.2*	*28.7*
Bagasse	16.3	0.61	65.4	6.7	0.5	26.7	647.3	*28.0*	*26.6*
Eucalyptus	13.0	0.32	65.1	6.8	1.0	26.7	650.0	28.0	27.9
Sorghum	12.7	0.11	67.2	7.1	2.4	23.2	645.0	29.3	27.9
Lignin	11.7	1.38	64.8	7.1	2.1	24.6	484.3	28.4	27.0

*by difference

[a] evaluated with: HHV = 0.3491·C + 1.1783·H - 0.1034·O - 0.0211·Ash + 0.1005·S - 0.0151·N, Channiwala, P.P. Parikh, A unified correlation for estimating HHV of solid, liquid and gaseous fuels, Fuel, Volume 81, Issue 8, 2002, Pages 1051-1063, ISSN 0016-2361, https://doi.org/10.1016/S0016-2361(01)00131-4.

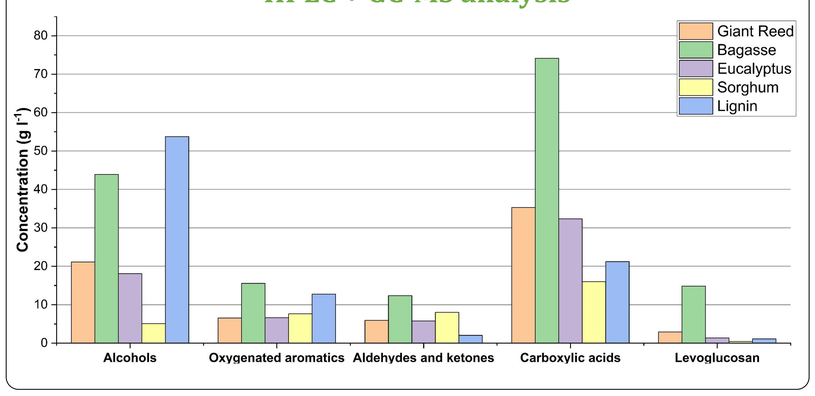
[b] evaluated with: LHV = HHV-0.206·H

GC-MS analysis



RESULTS – AQUEOUS PHASE

HPLC + GC-MS analysis



CONCLUSIONS

- The intermediate pyrolysis of the selected feedstocks was successfully carried out in an auger-type reactor (SPYRO).
- Eucalyptus resulted in the highest solid and aqueous phase yields, while lignin featured the highest oil phase yield.
- The results of ultimate and proximate analysis showed that lignin charcoal exhibited the highest total and fixed carbon contents, as well as the highest LHV and the lowest ash content.
- All the produced charcoal samples fitted at least the second quality class of the Italian legislation and IBI, concerning both the total carbon and ash content, exhibiting also good values for the estimation of charcoal stability and the concentration of the investigated contaminants.
- Lignin oil phase featured the highest concentration of oxygenated aromatics compound and the lowest averaged molecular weight, as well as the lowest water content (KF).
- Oxygenated aromatics compounds were the most present compound class observed in each oil phase sample, followed by carboxylic acids and furans.
- Light acids and alcohols were found at relatively high concentration in bagasse aqueous phase sample.
- The analytical results pointed out how the intermediate pyrolysis represents a renewed opportunity to produce biochar for agricultural purposes, biofuels intermediate and biochemicals.
- Lignin and bagasse resulted the most suitable feedstock for agriculture and for the extraction of chemicals through further separation techniques. While the former featured the highest charcoal quality, the latter resulted in the highest concentration of water-soluble organics.

The scientific work was supported by the project BECOOL, "Brazil-EU Cooperation for Development of Advanced Lignocellulosic Biofuels", which received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement No. 744821.