Stability and Safe Application of Fast Pyrolysis Biochars

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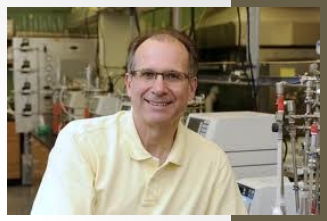
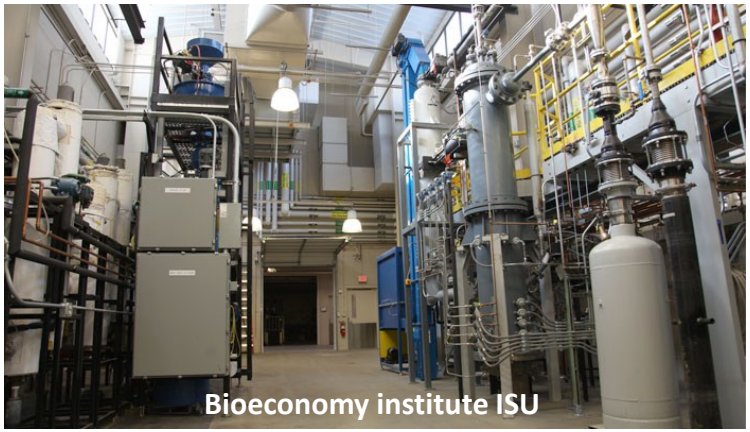
Acknowledgement: Phillips 66

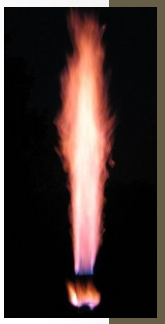
IOWA STATE UNIVERSITY

BEI Bioeconomy Institute at Iowa State University



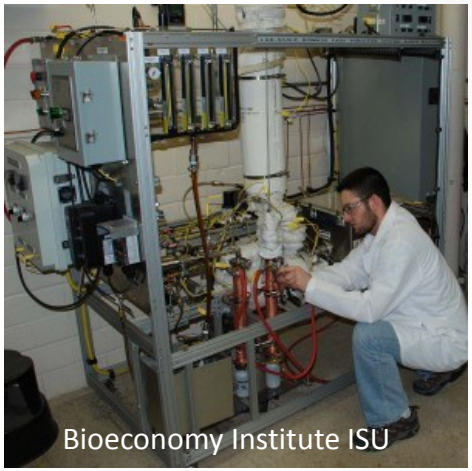
Introduction to Fast Pyrolysis



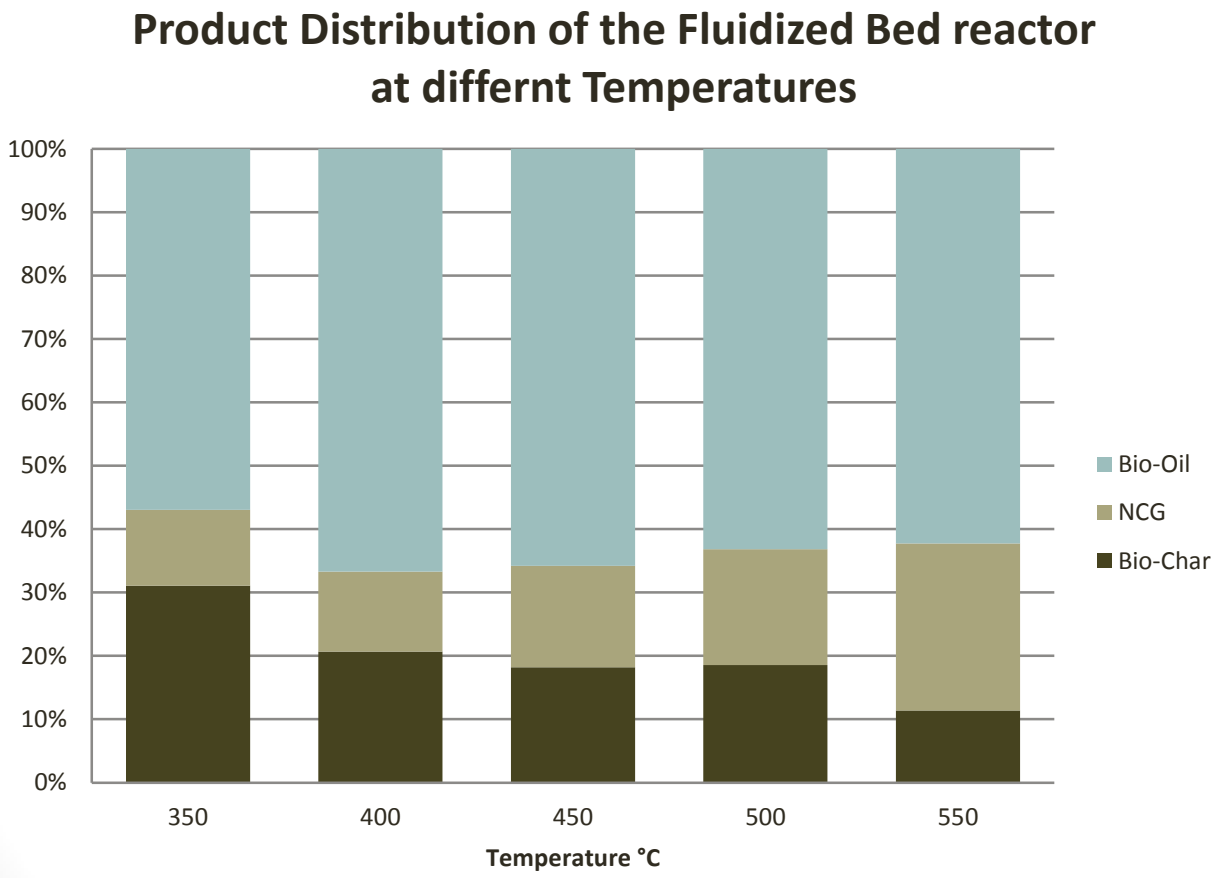


Bioeconomy Institute ISU

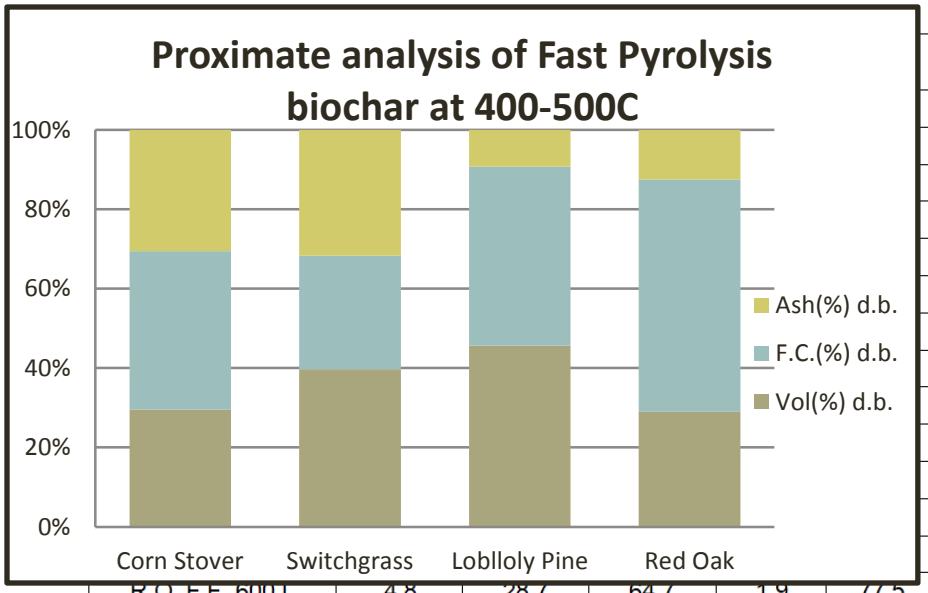
Different Reactors



Fast Pyrolysis products



Characterization



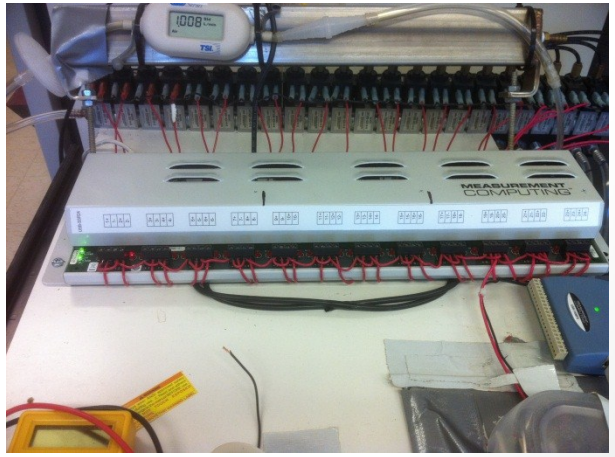
						H (wt %)	N (wt %)	O (wt %)	Particle ρ (g/cc)	S.A. (m^2/g)	HHV (MJ/kg)
						4.2	0.5	23.3	1.57	7.7	20.5
						2.9	0.6	16.3	1.88	8.7	14.4
						3.9	0.4	22.3	1.72	2.4	22.9
						4.1	0.5	22.9	1.55	2.4	23.6
						4.0	0.2	22.8	1.50	2.9	24.8
						4.0	0.3	20.2	1.53	2.2	24.1
						4.1	0.5				27.9
						2.7	0.1				18.4
						3.6	0.2				25.5
						2.3	0.1				18.6
						1.6	0.1				14.3
						3.8	0.3				29.0
						4.0	0.4				28.6
R.O. F.F. 600 L	4.8	28.7	64.7	1.9	77.5	3.9	0.4				29.0
R.O. F.F. 600 S	4.3	29.4	64.7	1.5	76.5	3.9	0.4	17.6	1.52	4.7	28.8
S.G. H3PO4	2.6	38.7	27.9	30.8	50.4	3.3	0.8	13.9	1.68	7.9	19.0

Treatment	Vol/FC	Char(%)
R.O. Biomass	6.4	
350°C	1.7	31.1
400°C	1.0	20.7
450°C	0.6	18.2
500°C	0.5	18.6
550°C	0.4	11.4

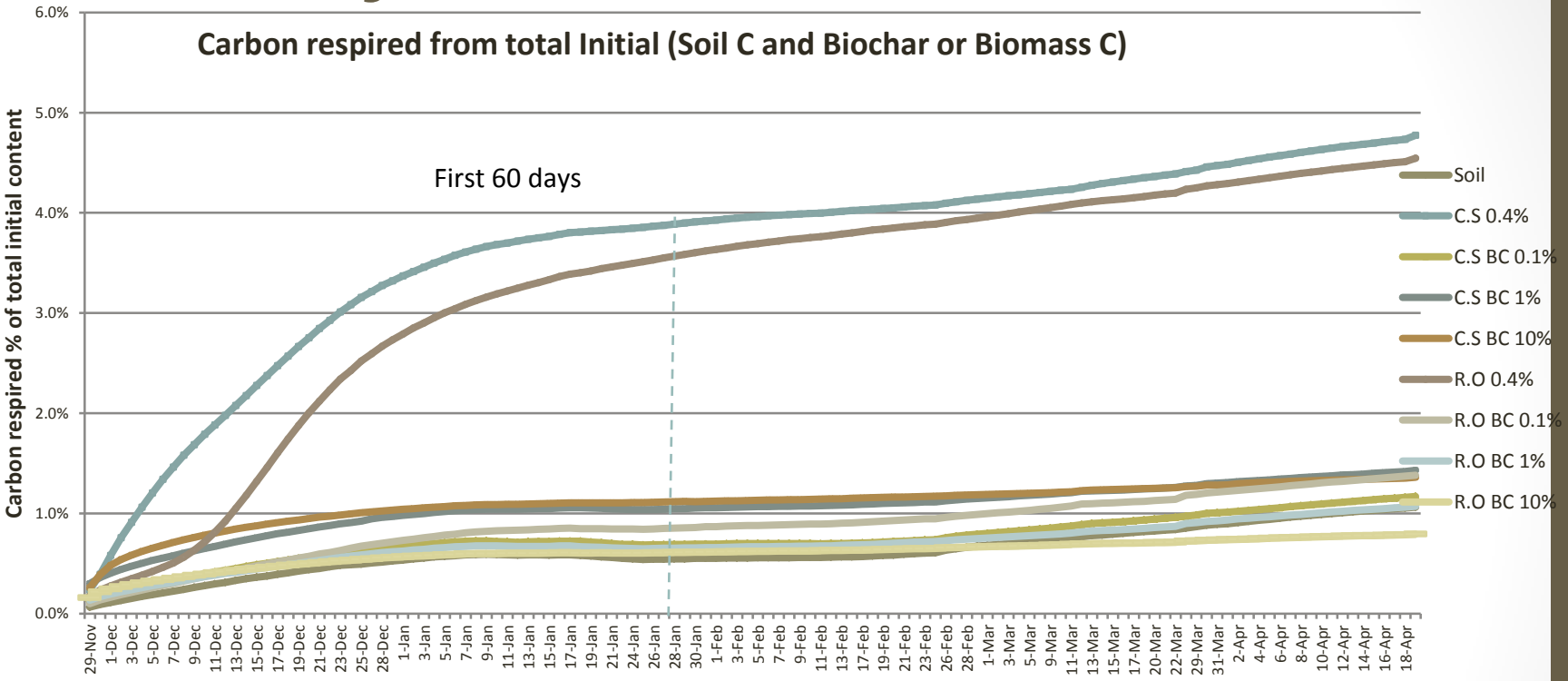
Corn stover Fast pyrolysis biochar 500°C with different harvest methods

	Vol.(%) d.b.	F.C.(%) d.b.	Ash(%) d.b.	C(%)	H(%)	N(%)	O(%) diff.	Particle ρ	S.A. (m2/g)	HHV (MJ/kg)
Clean	38.7	43.9	17.4	54.6	4.2	0.5	23.3	1.57	7.7	20.5
Regular	25.1	32.8	42.1	38.1	2.9	0.6	16.3	1.88	8.7	14.4

Respiration



Stability



		Corn Stover BM and BC at different rates				Red Oak BM and BC at different rates			
	Soil	**BM 0.4%**	**BC 0.1%**	**BC 1%**	**BC 10%**	**BM 0.4%**	**BC 0.1%**	**BC 1%**	**BC 10%**
Inital Carbon (g)	*10.3*	11.0	10.5	12.3	30.6	11.0	10.5	12.3	30.6
First 60 days	0.056	0.428	0.072	0.129	0.342	0.393	0.090	0.081	0.187
Daily Resp rate	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Proj. Annual	**0.290**	**0.841**	**0.293**	**0.333**	**0.661**	**0.848**	**0.332**	**0.306**	**0.429**
% of total C loss	2.82%	7.6%	2.8%	2.7%	2.2%	7.7%	3.2%	2.5%	1.4%
Carbon Initial C_{ini}	*10.3*	11.0	10.5	12.3	30.6	11.0	10.5	12.3	30.6
Years to *Soil* C_{ini}		**1**	**1**	**8**	**52**	**1**	**1**	**7**	**70**

Commercialization of Biochar

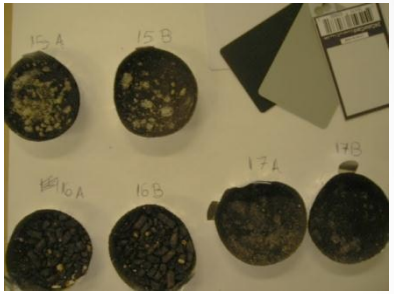
- Development of an MSDS
- Are BC Flammables?
- Self heating → spontaneous combustion?
- What is the auto-ignition temperature?

ASTM D4982-95: Flammability Potential Screening Analysis of Waste

Results ASTM D-4982

Test Method A-Test Sample Exposed to Heat and Flame

ASTM 4982	MOISTURE CONTENT						
Biochar feedstock	**0%**	**5%**	**10%**	**20%**	**30%**	**40%**	**50%**
Corn Stover 500°C	P	P	P	P	P	P	N
Mixed Woods	P	P	P	P	P	P	N
Switchgrass 500°C	P	P	P	P	P	N	N
Red Oak 500°C	P	P	P	N	N	N	N

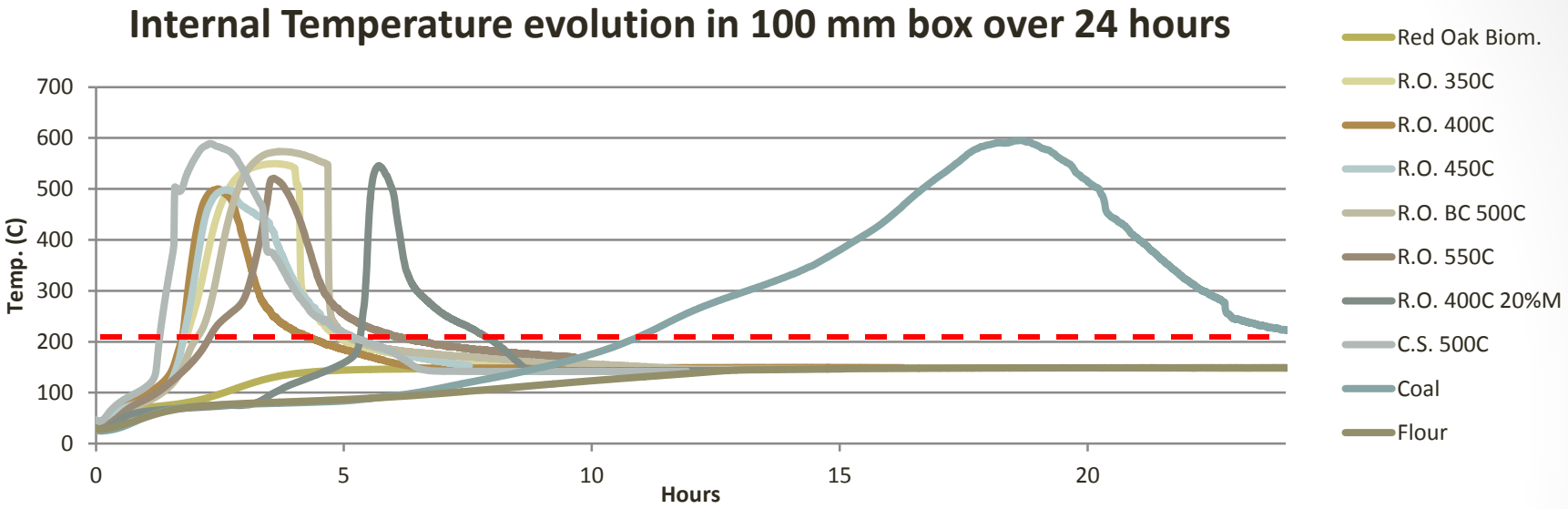


Test Method B-Test Sample Exposed to Spark Source

ASTM 4982	MOISTURE CONTENT						
Biochar feedstock	**0%**	**5%**	**10%**	**20%**	**30%**	**40%**	**50%**
Corn Stover 500°C	N	N	N	N	N	N	N
Mixed Woods	N	N	N	N	N	N	N
Switchgrass 500°C	N	N	N	N	N	N	N
Red Oak 500°C	N	N	N	N	N	N	N

Self-Heating; Test Method 1050C

Self reaction



Sample	100 mm cube Max Temp (°C)	Pass /fail	25 mm cube Max Temp(°C)	Pass /fail	Packing Group
C.S. Char 500C	550	Fail	149	Pass	III
R.O. Char 400C	513	Fail	146	Pass	III
R.O. Char 450C	505	Fail	146	Pass	III
R.O. Char 500C	561	Fail	145	Pass	III
R.O. Char 550C	568	Fail	150	Pass	III
R.O Char 20%M	545	Fail	142	Pass	III
Bituminous Coal	595	Fail	145	Pass	III
Red oak	148	Pass	142	Pass	Not a Division 4.2

Spontaneous combustion; UN/DOT Division 4.2 Classification

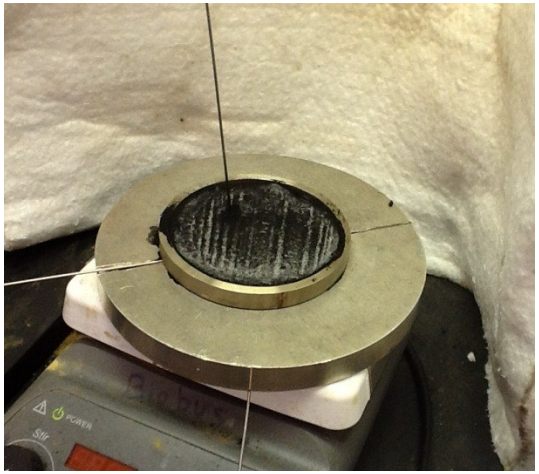
- UN/DOT Division 4.2 classification includes materials likely to spontaneous combust during shipping, such as:
  - Pyrophoric substances: ignite within 5 minutes of contacting air.
  - Self-heating substances: ignite without an energy source only in **large quantities** after **long time periods** in contact with air.

- UN/DOT Test Method 1050 determines material properties such that it can be classified in:
  - Packing Group I: most danger, most limitations
  - Packing Group II: intermediate danger/limitations
  - Packing Group III: least danger, some size/packaging limitations

What Packing Group III Means

- If packing group is known → US Code of Federal Regulations (CFR) describing how that material can be shipped.
- Biochars could potentially be classified as:
  - **Charcoal briquettes, shell, screenings, wood, etc. (Group III)**
  - Carbon, animal/vegetable origin (Group II)
  - **Carbon, animal/vegetable origin (Group III)**
  - Activated carbon (Group III)
- The next slide lists some of the ID numbers, relevant CFR document numbers, exceptions, and restrictions for these four materials; charcoals have the most exceptions (fewest restrictions) on shipping methods and size.

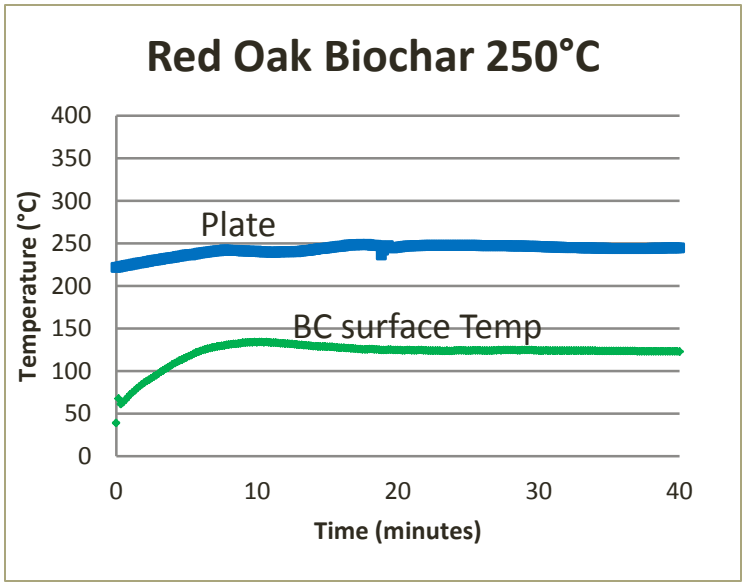
ASTM E2021: Surface Ignition

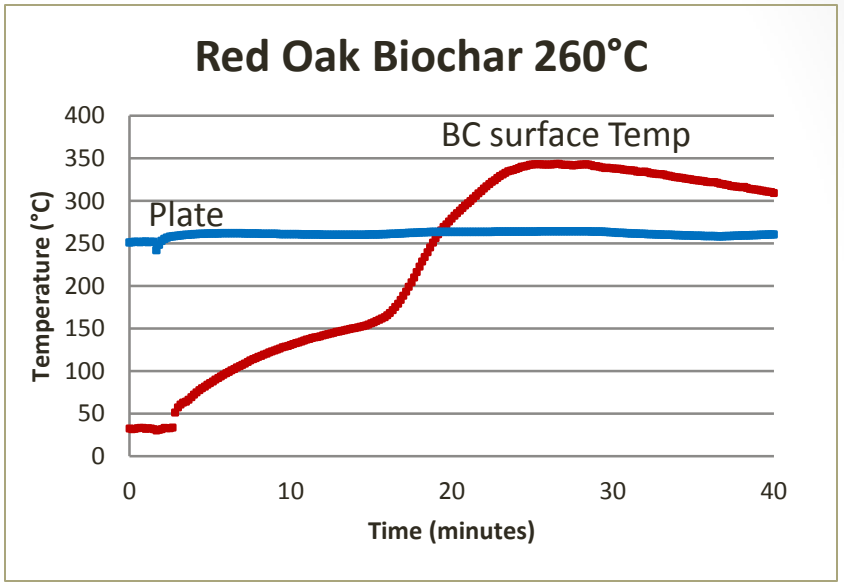


SECTION 5 – FIRE FIGHTING MEASURES

FLAMMABLE	Yes	**IF YES, UNDER WHAT CONDITIONS?**	**Fire** is possible at elevated temperature or by contact with an ignition source. **Explosion:** Fine dust dispersed in air in sufficient concentrations and in the presence of an ignition source is a potential dust explosion hazard.		
MEANS OF EXTINCTION	Dry chemical, carbon dioxide, water spray, fog or foam.				
FLASHPOINT & METHOD	NAV	**UPPER FLAMMABLE LIMIT**	NAV	**LOWER FLAMMABILITY LIMIT**	NAV
AUTO IGNITION TEMPERATURE	Min. 330°C	**SENSITIVITY TO IMPACT**	NAV	**SENSITIVITY TO STATIC DISCHARGE**	NAV
HAZARDOUS COMBUSTION PRODUCTS	Carbon dioxide and carbon monoxide				

Surface Ignition Results





Feedstock	Auto-ignition Temperature (°C)
Red Oak BC 500°C	260
Mixed Woods BC 500°C	230

Char Particle Size Distribution

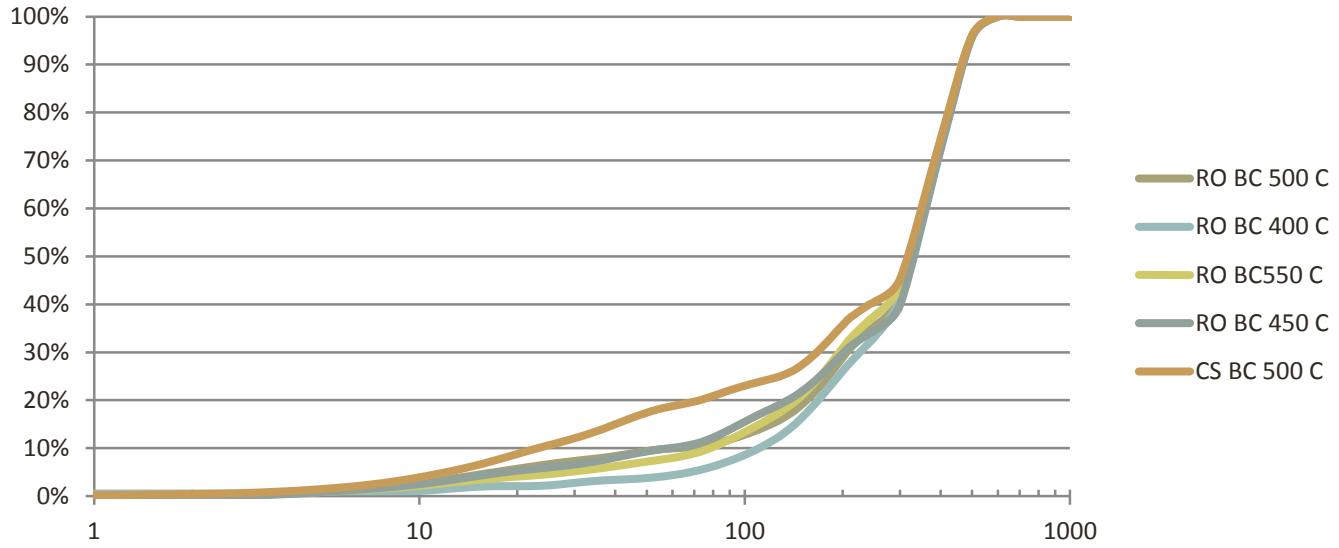
Laird (2008)

Biochar application Network

Laird (2007)

BlueLeaf Inc., Quebec,

Particle size with laser diffraction particle size analyzer



SECTION 11 – TOXICOLOGICAL INFORMATION

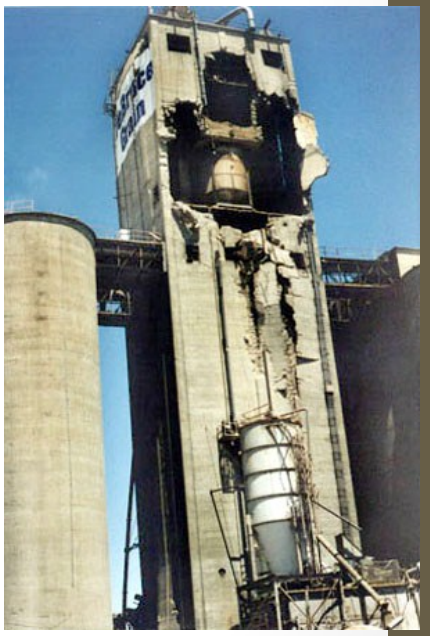
EFFECTS OF ACUTE EXPOSURE	May cause mild irritation to: skin, eyes, respiratory tract, and gastrointestinal tract.
EFFECTS OF CHRONIC EXPOSURE	May cause damage to the following organs: lungs.
IRRITANCY OF PRODUCT	NAV
RESPIRATORY SENSITIZATION	NAV

Laser diffraction particle size distribution supports sieve analysis data

Material	Red Oak Biochar				Corn Stover Biochar
Temp. (°C)	400°C	450°C	500°C	550°C	500°C
PM 1	0.6%	0%	0%	0.2%	0.2%
PM 10	1%	3%	3%	2%	4%
<100 um	9%	16%	13%	13%	23%
<250 um	33%	34%	35%	38%	40%
<500 um	96%	96%	96%	96%	96%
IBI Standard (<420; 420-2380; 2380-4760; >4760)					
<420	73%	74%	74%	72%	74%
420-2380	27%	26%	26%	28%	26%

Material	Corn Stover Biochar		
Moisture w.b.	0%M	20%M	40%M
PM 1	0.7%	0%	0%
PM 10	1%	0%	0%
<100 um	9%	0%	1%
<250 um	32%	4%	3%
<500 um	96%	33%	18%
IBI Standard			
<420	71%	24%	9%
420-2380	29%	76%	91%

Explosion hazard?



Heavy metal concentration

Analyte	Corn Stover	Red Oak	Loblolly Pine	Switchgrass	IBI Limit	Method
Arsenic	<4.15	<4.02	<4.17	<4.16	12 –100	SW 6010C
Cadmium	<1.04	<1.00	<1.04	<1.04	1.4 – 39	SW 6010C
Chromium	5.58	237	14.6	23.9	64 – 100	SW 6010C
Cobalt	<1.04	2.6	<1.04	<1.04	100 – 150	SW 6010C
Copper	13.3	7.68	8.95	19.5	63 – 1500	SW 6010C
Lead	<5.19	<5.02	<5.22	<5.20	70 – 500	SW 6010C
Mercury	<0.021	<0.020	<0.019	<0.021	5 –75	SW 7471B
Molybdenum	<2.59	24.5	<2.61	<2.60	1 – 17	SW 6010C
Nickel	9.18	171	9.67	20.8	47 – 600	SW 6010C
Selenium	<7.78	<7.53	<7.82	<7.80	1 – 100	SW 6010C
Zinc	38.8	10.1	49	152	200 – 2800	SW 6010C
Boron	10.6	8.37	14.5	12.7	Declaration	SW 6010C
Chloride	1820	<100	<104	1560	Declaration	SW 9056
Sodium	<51.9	137	130	52	Declaration	SW 6010C

PAH and PCB

Analyte	Corn Stover	Red Oak	Loblolly Pine	Switchgrass
Acenaphthene	<0.119	<0.108	<0.0390	<0.0794
Acenaphthylene	0.186	0.159	0.0642	0.0764
Anthracene	<0.105	<0.0955	0.0984	<0.0703
Benzo (a) anthracene	0.234	0.211	0.0835	0.149
Benzo (b) fluoranthene	<0.252	<0.228	<0.0843	<0.168
Benzo (k) fluoranthene	<0.302	<0.274	<0.101	<0.202
Benzo (a) pyrene	<0.398	<0.361	<0.133	<0.266
Benzo (g,h,i) perylene	<0.343	<0.311	<0.115	<0.229
Chrysene	<0.210	<0.191	<0.0705	<0.141
Dibenzo (a,h) anthracene	<0.334	<0.303	<0.112	<0.223
Fluoranthene	<0.0824	<0.0748	0.036	<0.0550
Fluorene	<0.128	<0.116	0.15	<0.0856
Indeno (1,2,3-cd) pyrene	<0.293	<0.266	<0.0981	<0.196
2-Methylnaphthalene	<0.421	<0.382	0.752	<0.281
Naphthalene	<0.233	<0.212	0.531	<0.156
Phenanthrene	<0.174	0.181	0.209	<0.116
Pyrene	<0.0961	<0.0872	0.0542	<0.06462

PAH and PCB

PAH Compounds measured by SIM GCMS

Analyte	Corn Stover	Red Oak	Loblolly Pine	Switchgrass
Maximum	<3.91	<3.56	<2.73	<2.56

IBI Standards Limit: 6-20 mg/kg TM

Polychlorinated Biphenyls by EPA Method SW 8082A

Analyte	Corn Stover	Red Oak	Loblolly Pine	Switchgrass
Total PCBs	<0.25	<0.21	<0.26	<0.23

IBI Standards Limit: 0.2-0.5 mg/kg TM

PCB Measured:

PCB-1016 PCB-1221 PCB-1232 PCB-1242
PCB-1248 PCB-1254 PCB-1260 PCB-1268

Thanks for your Charful attention!

Bernardo del Campo