Polymer Products from Lignin through De-aromatization and COOH Functionalization

BETO 2023 Peer Review
Feedstock Technologies Review Area

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Presenter: Mike Kent, Sandia National Labs

Ingevity Corporation
U. of South Carolina
Sandia National Laboratories

SAND2023-01427C

Project Overview

Heilmeier Catechism:

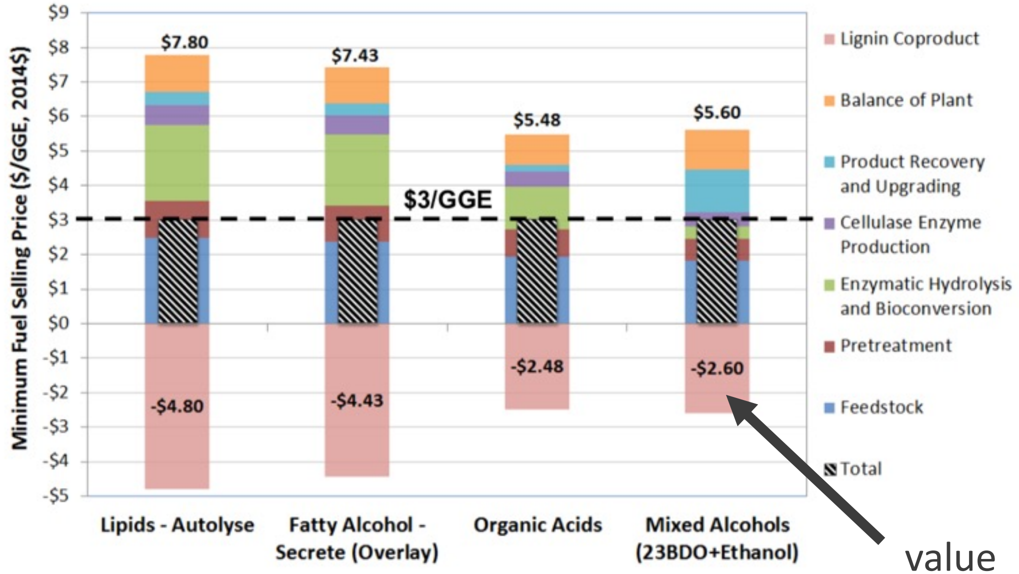
Goal: Commercial products from lignin that provide 20% reduction in feedstock cost (from FOA)

Today: lignin from pulp and paper is converted to polymer products through sulfonation

Importance: lignin coproducts must contribute $2-3/GGE to MFSP to meet DOE target of $3/GGE

Risks: must meet performance criteria and TEA metrics

NREL Technical Report 2018

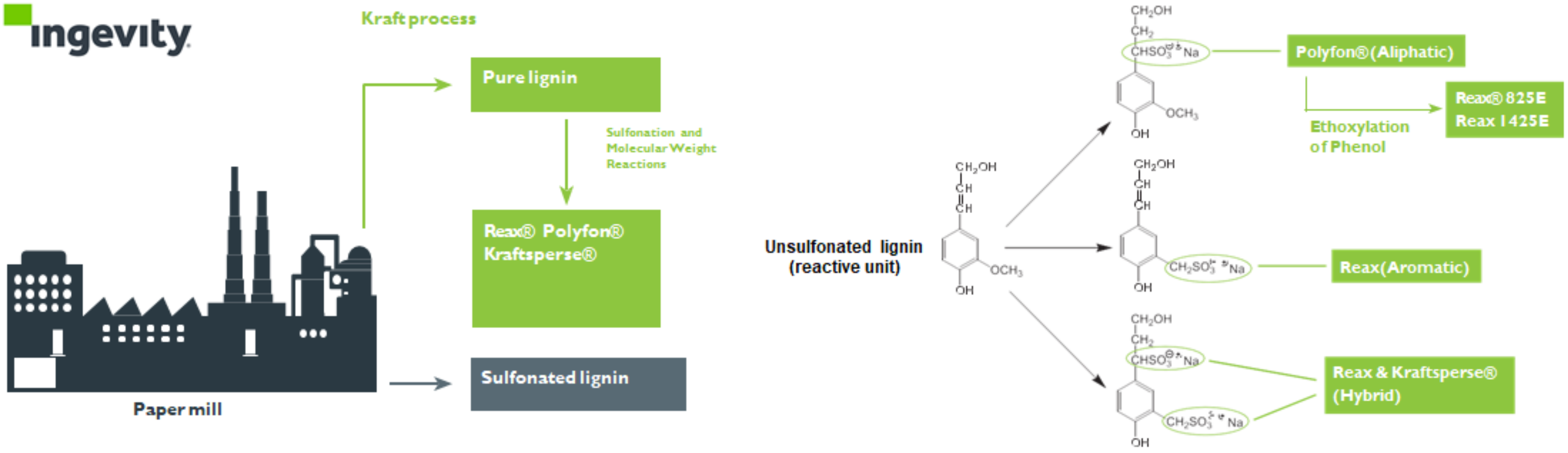


value needed from lignin

$0.34/lb lignin (100% yield)

Project Overview

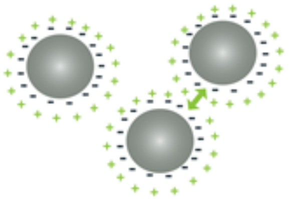
Ingevity: current lignin product line



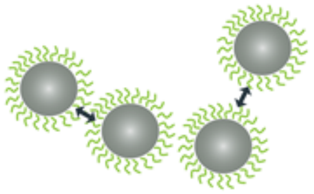
Agricultural Applications

- Water-dispersible granules (WDG)
- Suspension concentrates (SC)
- Wettable powder (WP)
- Oil dispersion (OD)
- Suspoemulsion (SE)
- Emulsifiable concentrate (EC)
- Capsule suspension (CS)

Dispersant Properties

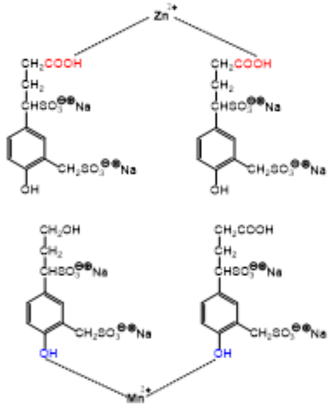


Ionic repulsion



Steric stabilization

Metal Chelation Properties



Project Overview

Use oxidative treatment to tailor chemical functionality and MW for specific product applications:

-dispersant

-water purification

-nutrient delivery

-hydrogels for agriculture (soil amendment)

many possible applications – mitigates risk

Project Overview

Use oxidative treatment to tailor chemical functionality and MW for specific product applications:

Ingevity's current business areas
- -dispersant
- -water purification
- -nutrient delivery

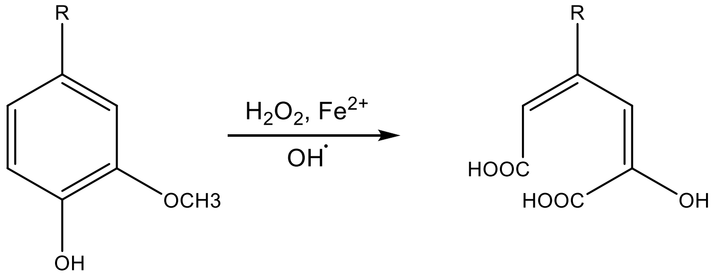
BETO interest in carbon sequestration, combine hydrogels with biochar
- -hydrogels for agriculture (soil amendment)

Risks: must meet performance criteria and TEA metrics

(from Ingevity's current product line and market analysis)

Project Overview

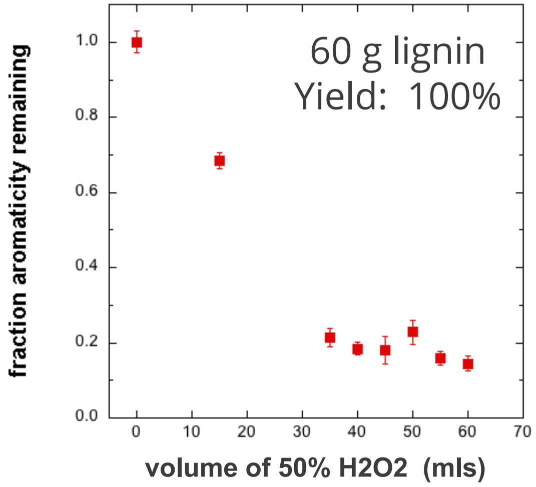
chelator-mediated Fenton (CMF) reaction

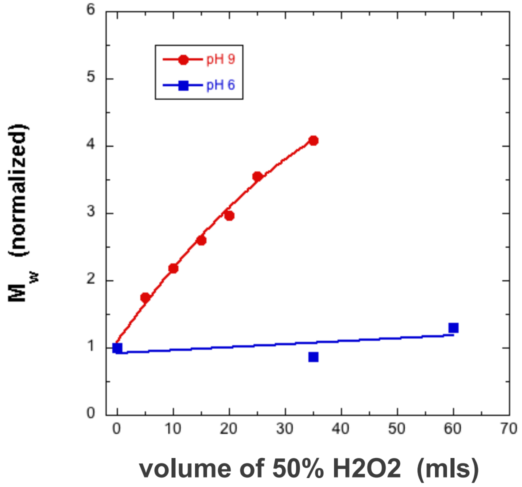


Fe chelator and Fe^{+3} reducer: 1,2-dihydroxybenzene (DHB)

CMF reaction allows control over hydrophobicity/hydrophilicity, COOH functionality, and MW

Can independently vary: aromaticity and molecular weight

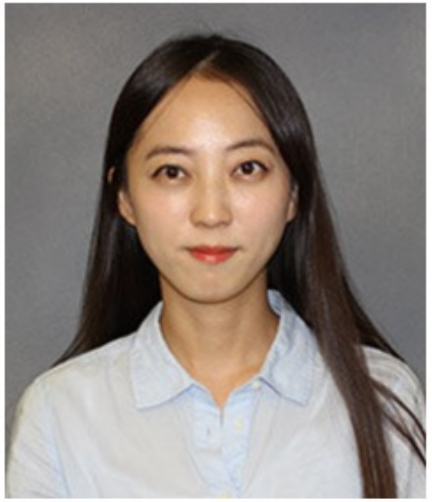




Project Overview

U of South Carolina - hydrogels

Chuanbing Tang
Role: project PI



JiHyuan Hwang

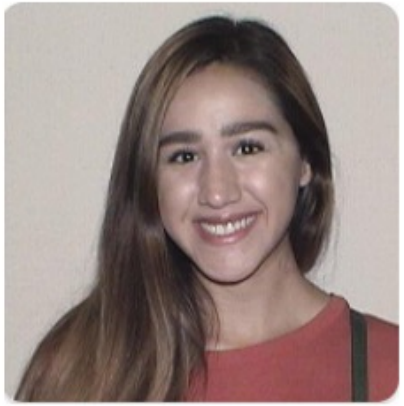
Ingevity Corp. – agrochemical applications

Mitra Ganewatta

Qi Wang

Sandia National Labs – CMF reaction

Mike
Kent



Daniella
Martinez

-Monthly meetings

-Quarterly meeting with BETO PMs

1 – Approach

Workflow:

-SNL prepares CMF-treated lignin samples, sends samples to:

Ingevity – dispersant, water purification, nutrient delivery testing
U of SC – crosslinking and hydrogel performance

-Ingevity performs TEA for all samples

Lignin feedstocks:

1. raw kraft lignin

30% solids

2. biorefinery lignin from NREL

freeze-dried powder

DMR-EH: deacetylation and mechanical refining, enzymatic hydrolysis

2 – Progress and Outcomes

Current status:

Met goals for Budget Phase 2

Completed verification for Budget Phase 3

Started Budget Phase 3: Mar 1, 2023

2 – Progress and Outcomes

Task 1. Kraft lignin sample set 1 for dispersant, micronutrient complexation, and water purification

Samples derived from raw **kraft** lignin

untreated

different reaction conditions

sample	% aromat. IR	COOH (mmol/g) titration	aromat. OH (mmol/g) titration	Mw* SEC
kraft lignin	100	1.03	2.47	1,960
R1	68	1.16	1.55	1,700
R2	25	1.50	1.29	2,560
R3	34	1.35	1.08	16,000
R3B	18	2.66	1.05	4,800
R4A	24	1.82	1.14	8100

*measured by SEC using UV 210 nm and 1 mM PO4 pH 9

All samples were tested for performance by Ingevity

2 – Progress and Outcomes

Task 2. Biorefinery lignin sample set 1 for dispersant, micronutrient complexation, and water purification.

Samples derived from **biorefinery** lignin

untreated

different reaction conditions

sample	% aromatic IR	COOH (mmol/g) titration	aromatic OH (mmol/g) titration	Mw* SEC
BL**	100	0.36	0.61	65,000
BL-BCD	-------	1.68	0.83	9,700
BL-CMF1	0.57	2.30	0.76	60,000
BL-CMF2**	0.04	1.70	0.72	56,000
BL-CMF3A**	0	1.23	0.70	104,000
BL-CMF3B	0	2.55	0.88	20,000
BL-BCD-CMF1	-------	1.47	0.60	21,000
BL-BCD-CMF2	-------	1.92	0.68	16,000
BL-BCD-CMF3	-------	1.83	0.54	34,000

*measured by SEC using UV 210 nm and 1 mM PO4 pH 9
**highly insoluble at pH 12 (analyzed soluble portion)

All samples were tested for performance by Ingevity

2 – Progress and Outcomes

BP2 go / no go criteria:

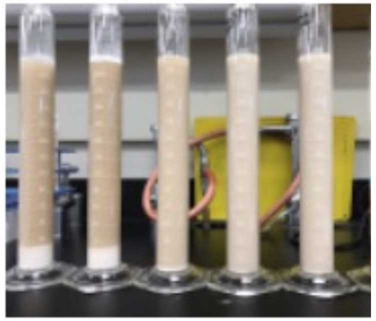
from Ingevity

Performance metric: At least one sample from kraft or biorefinery lignin meets at least one of the following minimum performance metrics:

Dispersant:

-suspensibility over 80%

-workable viscosity



initial and aged

Water Purification:

-adsorb > 14 mg Pb(II) and > 8 mg Co(II), Ni(II), Cu(II), and Zn(II) per gram of modified lignin at 100 ppm, pH 5-6, 24 h, room temperature

Water Absorption:

-adsorb > 18 g water per gram of modified lignin

TEA metric: viable pathway to $1.5/lb dry basis or better for at least one product application

2 – Progress and Outcomes

BP2 go / no go criteria

Performance metric: At least one sample from kraft or biorefinery lignin meets at least one of the minimum performance metrics:

Results for Kraft lignin

✅ = meets minimum performance metrics

	kraft lignin	R1	R2	R3	R3B	R4A
mesotrione dispersion		✅	✅	✅		
insoluble metal oxide dispersion		✅	✅	✅	✅	✅
soluble metal salt dispersion						
water purification Pb(II) Co(II) Ni(II) Cu(II) Zn(II)			✅		✅	
water absorption		✅	✅	✅	✅	

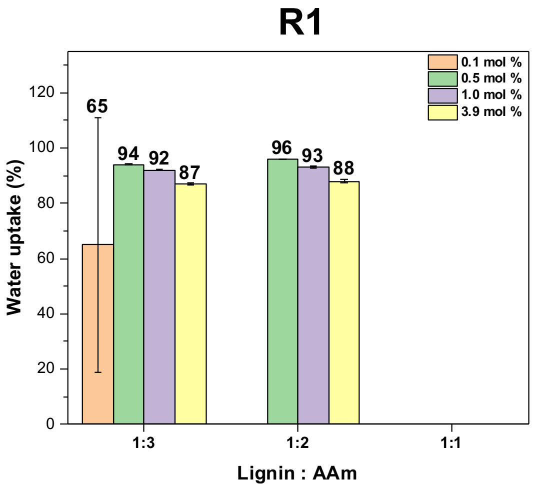
2 – Progress and Outcomes

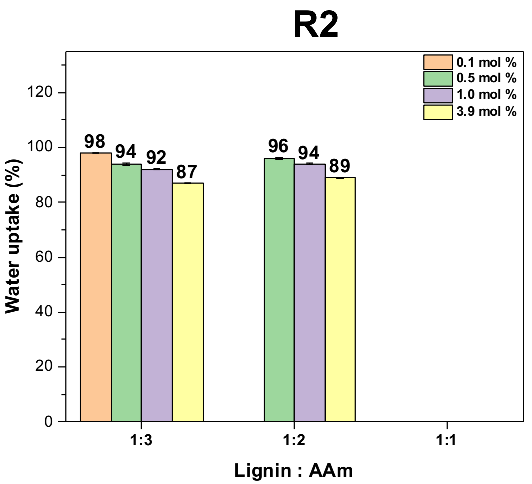
Kraft lignin/PAAm hydrogels

(95% - 18 g water, 1 g polymer)

68 % aromaticity
1.16 COOH mmol/g
1.55 Ph-OH mmol/g

M_w 1,700
M_z 9,600
M_{z+1} 28,700



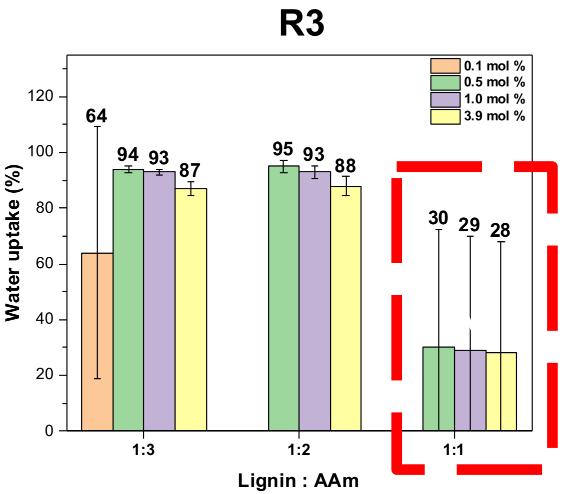


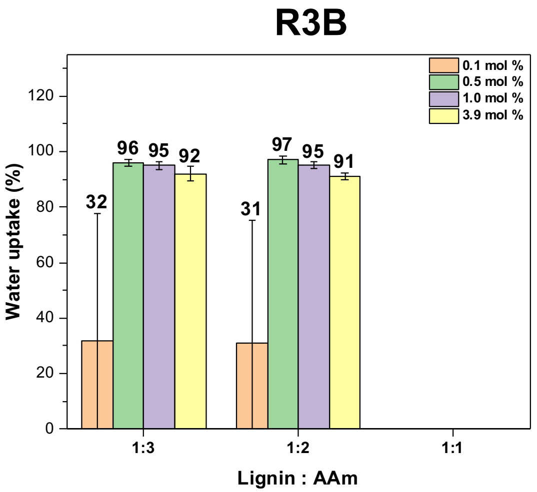
25 % aromaticity
1.50 COOH mmol/g
1.29 Ph-OH mmol/g

M_w 2,560
M_z 10,200
M_{z+1} 23,900

34 % aromaticity
1.35 COOH mmol/g
1.08 Ph-OH mmol/g

M_w 16,000
M_z 229,000
M_{z+1} 710,000





~20 % aromaticity
2.66 COOH mmol/g
1.05 Ph-OH mmol/g

M_w 4,800
M_z 22,100
M_{z+1} 93,400

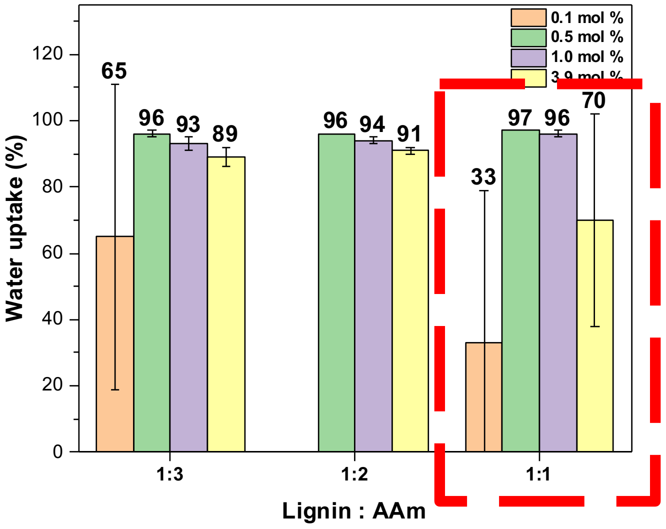
Best water uptake 98% (98 g water, 2 g lignin)

2 – Progress and Outcomes

Biorefinery lignin/PAAm hydrogels

(95% - 18 g water, 1 g polymer)

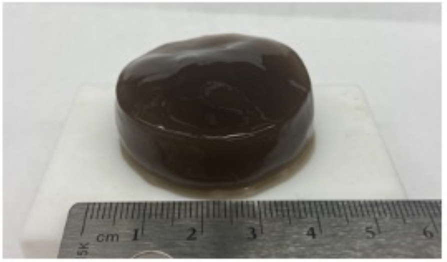
BL-CMF1



57 % aromaticity
2.30 COOH mmol/g
0.76 Ph-OH mmol/g

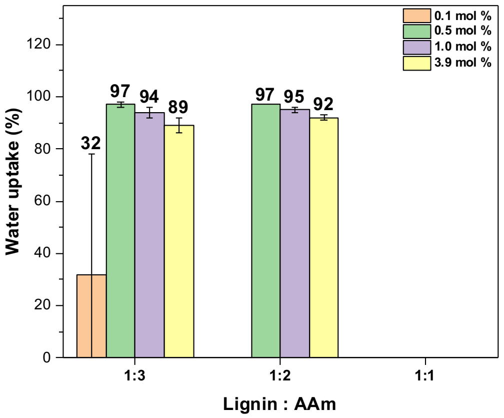
M_w 60,000
M_z 1.5 x 10^6
M_{z+1} 3.2 x 10^6

dry



swollen

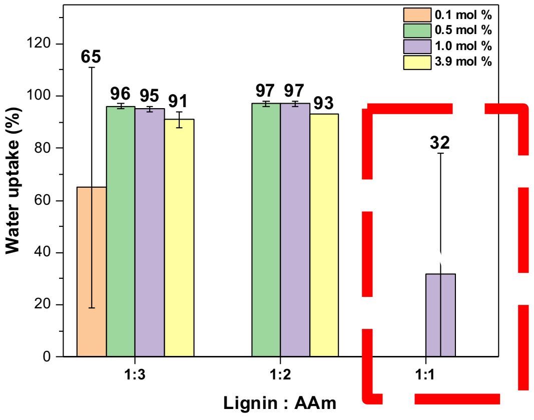
BL-BCD



?? % aromaticity
1.68 COOH mmol/g
0.83 Ph-OH mmol/g

M_w 9,700
M_z 0.32 x 10^6
M_{z+1} 0.93 x 10^6

BL-BCD-CMF3



?? % aromaticity
1.83 COOH mmol/g
0.54 Ph-OH mmol/g

M_w 34,000
M_z 0.55 x 10^6
M_{z+1} 1.3 x 10^6

2 – Progress and Outcomes

BP2 go / no go criteria

Performance metric: **At least one sample** from kraft or biorefinery lignin meets **at least one** of the minimum performance metrics:

Results for Biorefinery lignin (NREL DMR-EH)

	BL	BL-BCD	BL-CMF1	BL-CMF2	BL-CMF3A	BL-CMF3B	BL-BCD-CMF1	BL-BCD-CMF2	BL-BCD-CMF3
mesotrione dispersion									
insoluble metal oxide dispersion									
soluble metal salt dispersion									
water purification Pb(II) Co(II) Ni(II) Cu(II) Zn(II)									
water absorption		✅	✅						✅

2 – Progress and Outcomes

Biorefinery lignin ("BL" from NREL)

as-received

"DMR-EH" lignin
from corn stover

Isolated, freeze-dried

NREL compositional analysis: 40% lignin

Purity too low for high performance agrochemical applications

2 – Progress and Outcomes

TEA metric: TEA must show viable pathway to $1.5/lb dry basis or better for **at least one** product application.

Kraft lignin samples

Sample	Total Cost. ($/lb)	COOH content
R1	1.17	1.16
R2	1.22	1.50
R3	1.35	1.35
R3B	2.67	2.66
R4A	1.56	1.82

Biorefinery lignin samples

Sample	Total Cost. ($/lb)	COOH content
BL BCD	0.79	1.68
BL CMF1	1.30	2.30
BL CMF2	0.82	1.70
BL CMF3A	0.88	1.23
BL CMF3B	1.61	2.55
BL BCD CMF1	1.47	1.47
BL BCD CMF2	1.83	1.92
BL BCD CMF3	2.73	1.83

Viable pathway to $1.5/lb dry basis for all except those in RED

2 – Progress and Outcomes

Plans for BP3:

3.1. Kraft lignin sample set 2: Generate and evaluate materials from kraft lignin to optimize chemical functionalities and MW for dispersant (at least two biologicals) and micronutrient complexation applications

3.2. Lignosulfonate sample set: Generate and evaluate samples from lignosulfonate to optimize chemical functionalities and MW for dispersant (at least two biologicals) and micronutrient complexation applications

3.3. Hydrogels: Optimize crosslinking chemistries for generating hydrogels from COOH-functionalized kraft and biorefinery lignins for soil amendment applications

3.4. Process optimization: Optimize reaction and process conditions to minimize overall process cost for kraft and biorefinery lignins (at least one product application)

3.5. TEA: Perform TEA for each process and product to guide work in BP3

2 – Progress and Outcomes

Final Performance Criteria

Dispersant

-suspensibility over 95%
-workable viscosity
-small particle size (average < 5 μm at D50)
-good storage stability over 24 months (measured under accelerated aging conditions)

Water Purification

>18 mg Pb(II) and > 12 mg Co(II), Ni(II), Cu(II), and Zn(II) per gram of modified lignin at 100 ppm, pH 5-6, 24 h, room temperature

Water Absorption

>30 g water per gram of modified lignin

At least one commercially-viable product from CMF lignin will be identified with sufficient value to provide 20% reduction in feedstock costs

3 - Impact

Ingevity will pursue commercialization as warranted

- Agrochemicals – as dispersants for various actives, biologicals, and micronutrients

Potential market size 15,000 tons/yr

~$0.30/lb for biorefinery lignin

3 - Impact

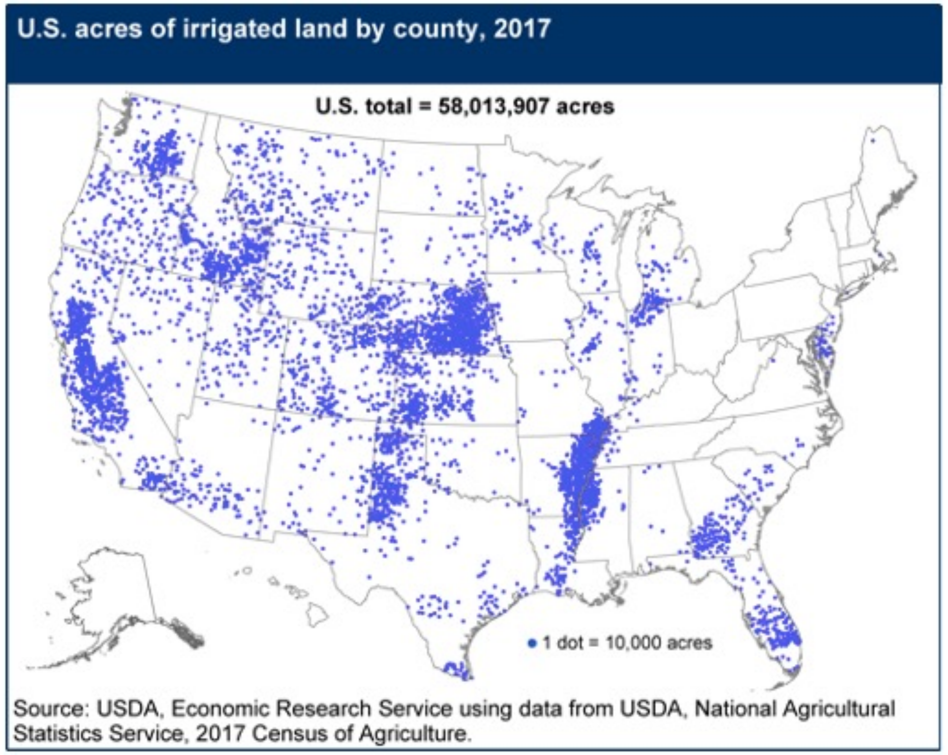
2. Lignin-based hydrogels for agriculture (mix with biochar)

Valorizing a waste product <u>and</u> improving carbon sequestration

For 10^9 ton biomass economy, >200 megatons of lignin/yr

If 2 tons of lignin-derived soil amendment per acre, more than 100 million acres of semi-arid land could be treated each year.

May facilitate application of biochar as soil amendment. A recent expert assessment estimates that biochar could sequester **0.5–2 GtCO2 per year by 2050** at a cost of $30–120 per ton of CO2.



Need field trials to evaluate $/lb for biorefinery lignin

4 - Summary

Met goals for Budget Phase 2

Focusing effort in BP3 on dispersant, nutrient complexation, and soil amendment hydrogel applications

Quad Chart Overview

Timeline

Project start date 10/1/2020

Project end date 7/31/2024

	FY22 Costed	Total Award
DOE Funding	*(10/01/2021 – 9/30/2022)* *$223,654*	*(negotiated total federal share)* *$879,000*
Project Cost Share *	$120,644	$250,722

TRL at Project Start: 2

TRL at Project End: 4

Project Goal

The goal of this project is to make polymer products from lignin through oxidation and crosslinking

End of Project Milestone

At least one commercially-viable product from CMF lignin will be identified with sufficient value to provide 20% reduction in feedstock costs

Funding Mechanism

FOA-0002029, Improving Economics and Development of Coproducts, 2019

Project Partners

U. Of South Carolina

Ingevity Corp.

Sandia National Labs.

23

Extra slides

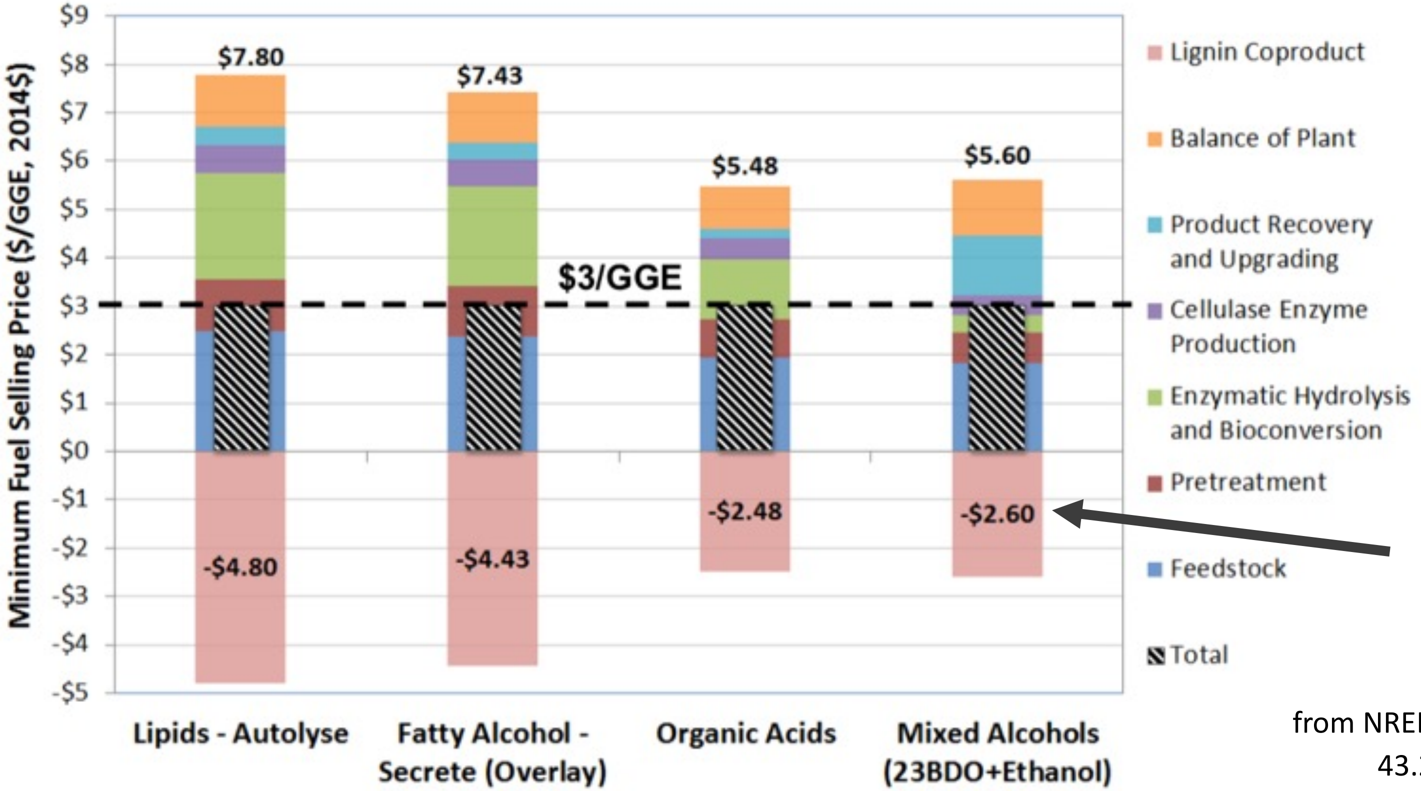
Papers, Patents, Presentations, Awards, and Commercialization

"Highly Swellable Hydrogels Prepared from De-aromataized Lignin", presented at Southeastern Regional Meeting of the American Chemical Society (Nov 10, 2021), Jihyeon Hwang, Dustin Goodlett, Mitra Ganewatta, Michael S. Kent, Chuanbing Tang.

"Highly Swellable Hydrogels Prepared from extensively oxidized lignin", **Giant** 10 (2022) 100106, JiHyeon Hwang, Daniella V. Martinez, Estevan J. Martinez, Gift Metavarayuth, Dustin Goodlett, Qi Wang, Mitra Ganewatta, Michael S. Kent, Chuanbing Tang.

Project Overview

Deriving Value From Lignin is Essential for Economic Viability of Lignocellulosic Biomass Conversion Industry



NREL Technical Report 2018

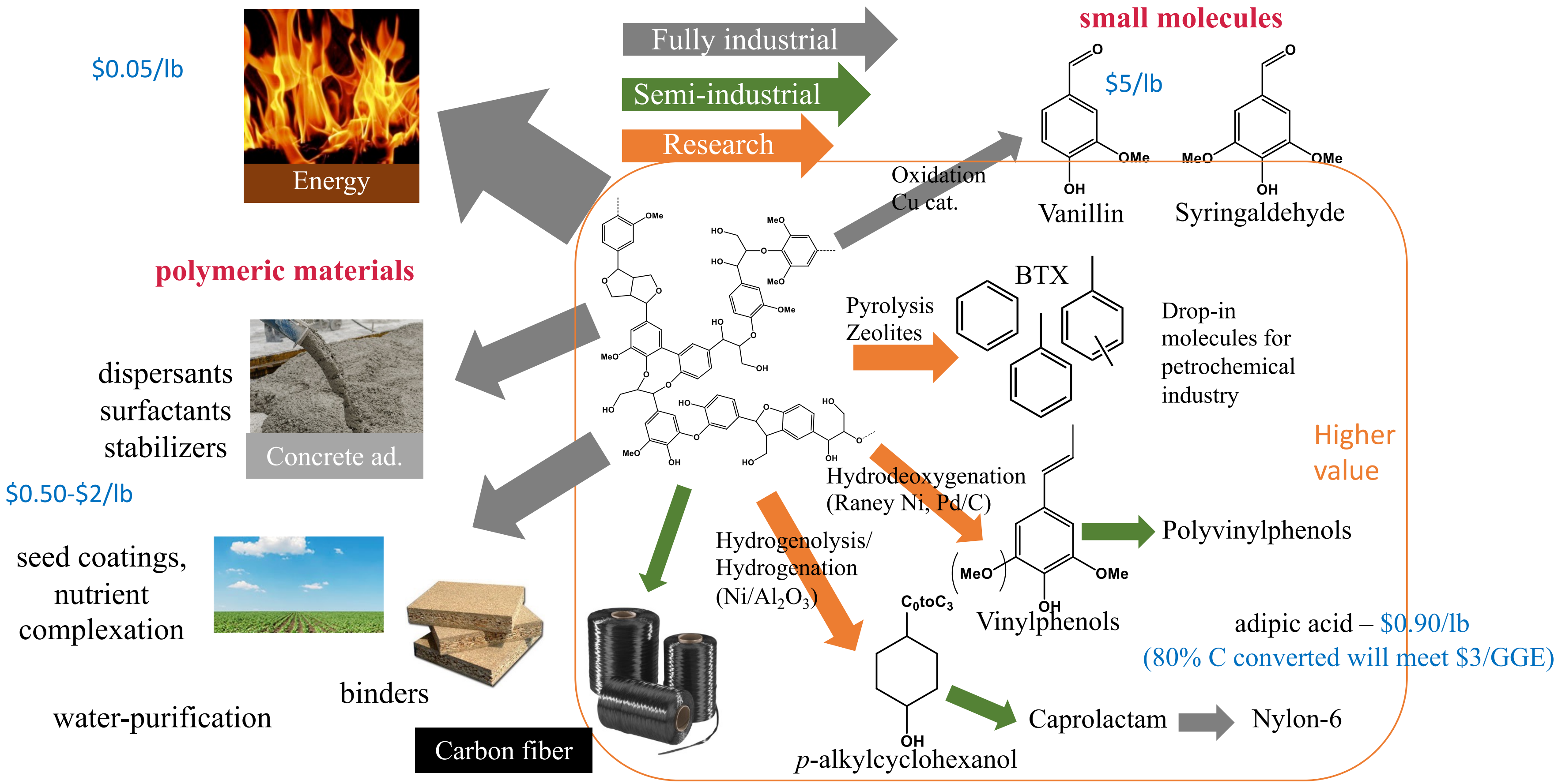
value needed from lignin

from NREL's 2018 Biorefinery TEA report:
43.2 GGE/dry U.S. ton feedstock
316 lb lignin / dry U.S. ton feedstock

$\boxed{\text{(\$0.34/lb lignin)}}$ x (316 lb lignin/43.2 GGE) = $2.5/GGE
(100% yield)

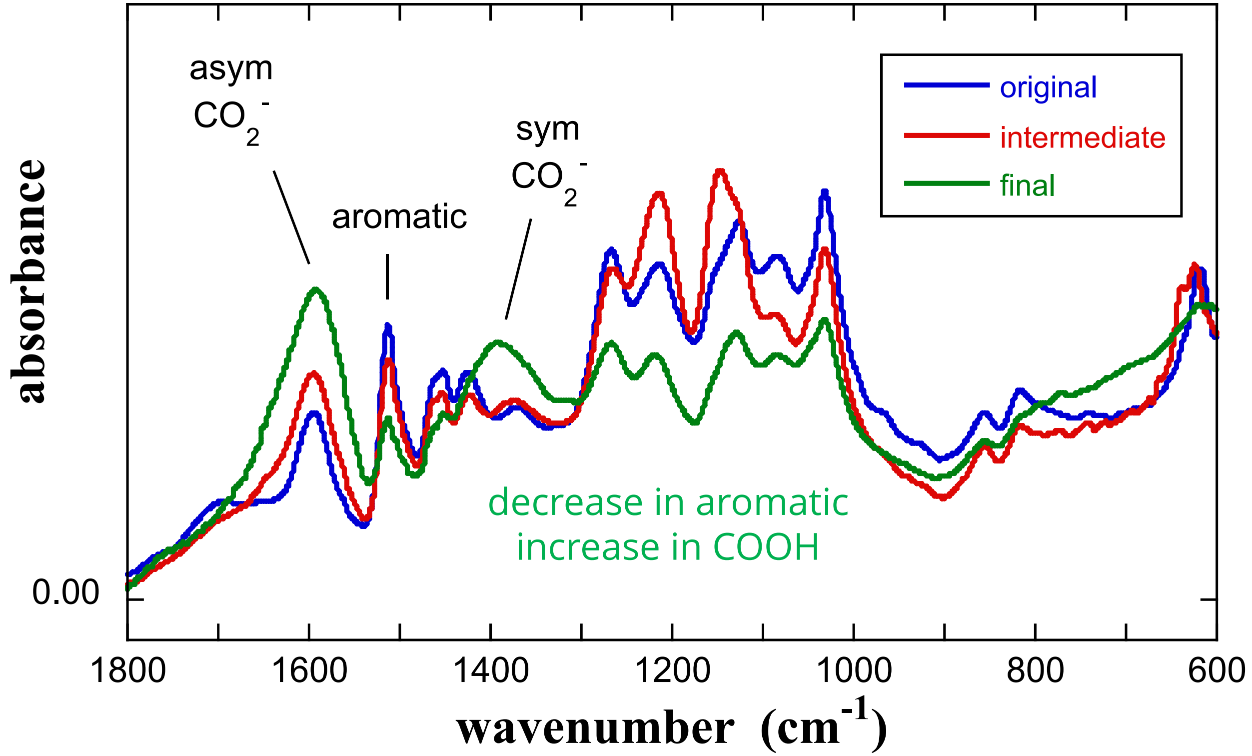
Project Overview

Current and Potential Future Applications for Lignin



Deriving Value From Lignin is Essential for Economic Viability of Lignocellulosic Biomass Conversion Industry

IR determination of aromaticity



Task 3. Evaluate CMF-processed materials from kraft lignin and biorefinery lignin for hydrogel formation

samples derived from **kraft** lignin sent to U of SC for crosslinking

untreated

different reaction conditions

sample	% aromatic IR	COOH (mmol/g) titration	aromat. OH (mmol/g) titration	Mw* SEC
kraft lignin	100	1.03	2.47	1,960
R1	68	1.16	1.55	1,700
R2	25	1.50	1.29	2,560
R3	34	1.35	1.08	16,000
R3B	18	2.66	1.05	4,800

samples derived from **biorefinery** lignin sent to U of SC for crosslinking

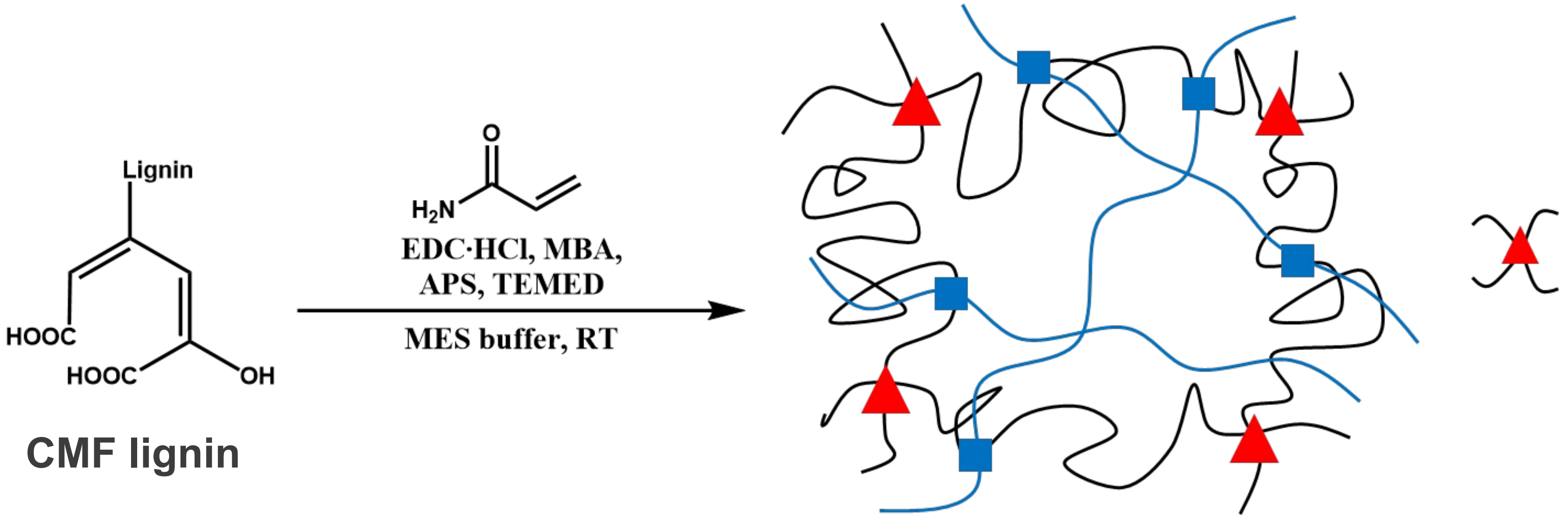
untreated

different reaction conditions

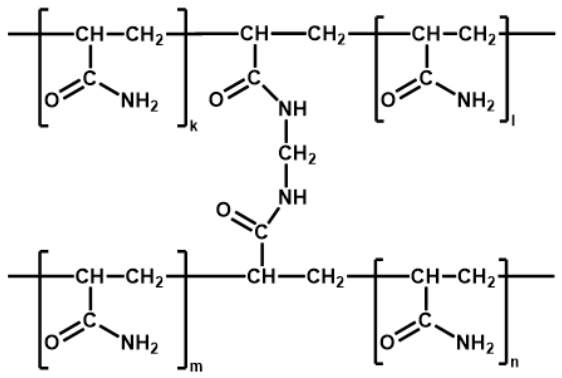
sample	% aromatic IR	COOH (mmol/g) titration	aromat. OH (mmol/g) titration	Mw* SEC
BL**	100	0.36	0.61	65,000
BL-BCD	-------	1.68	0.83	9,700
BL-CMF1	0.57	2.30	0.76	60,000
BL-BCD-CMF3	-------	1.83	0.54	34,000

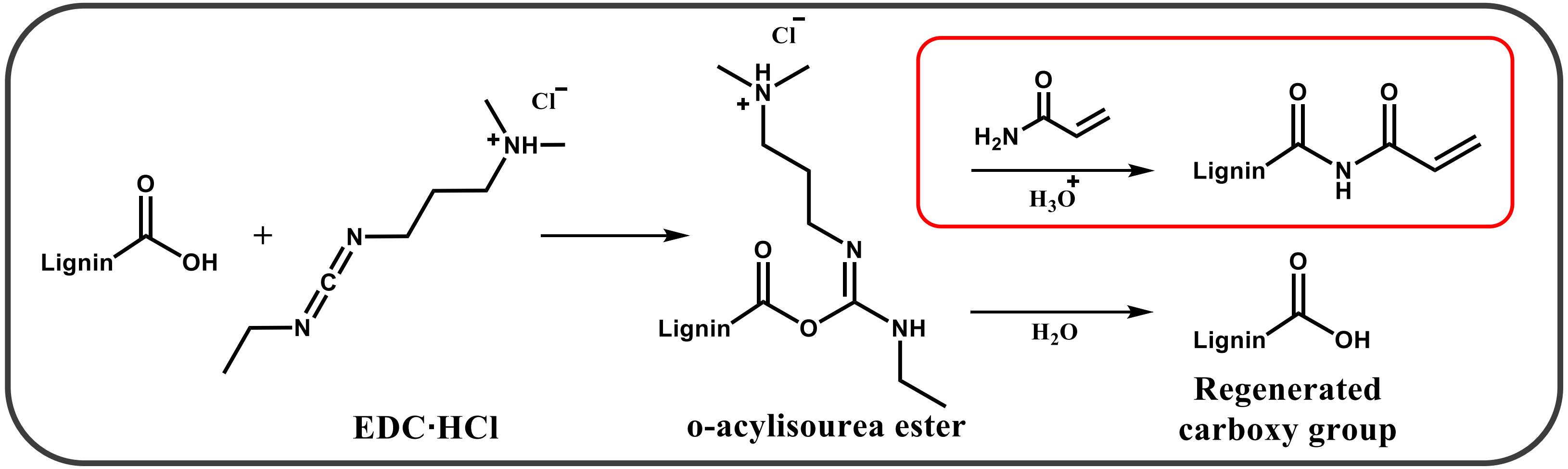
samples were crosslinked and tested for water absorption by U of SC

Schematics of lignin-based hydrogels

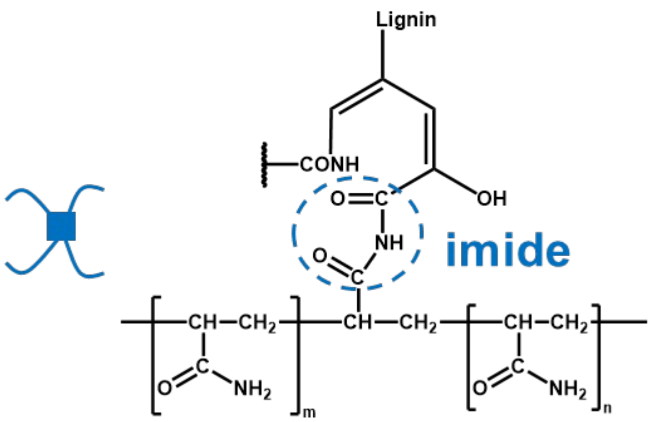


Acryl amide with MBA





Coupling of acryl amide to lignin

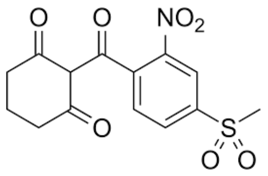


Giant 10 (2022) 100106

Kraft lignin samples: Mesotrione formulation

	Raw Lignin	CMF-R1	CMF-R2	CMF-R3	CMF-R3B	CMF-R4A
% Aromaticity (IR)	100	68	25	34	~20	24
COOH mmol/g (titration)	1.03	1.16	1.5	1.35	2.66	1.82
MW g/mol (SEC)	1960	1700	2560	16000	4800	8100
Initial suspensibility (%)	Gelled	99.3±0.7	100.0±1.42	100±0.28	100.7±0.41	96.9±3.81
Aged suspensibility		97.4±0.88	98±0.28	100±0.5	-	-
Initial blooming		Very well	Very well	Very well	Very well	Pass
Aged blooming		Very well	Very well	Very well	-	-
Initial particle size (µm, D50)		2.60±0.18	2.80±0.04	3.6±0.14	3.5±0.67	2.6±0.21
Aged particle size (µm , D50)		1±0.01	0.8±0.01	4.41±0.27	-	-
Initial particle size (µm, D90)		5.40±0.11	5.50±0.10	55±0.02	5.1±0.96	5.1±0.19
Aged particle size (µm, D90)		5.3±0.58	3.5±0.2	6.9±0.05	-	-
Initial viscosity		Workable	Workable	Workable	Workable	Workable
Aged viscosity (54 ^{o}C, 2 weeks)		Workable	Workable	Medium gel	Gelled	Gelled

meet performance specs



Mesotrione (herbicide)

Kraft lignin samples: Insoluble metal oxide SC formulation

	Raw lignin	CMF-R1	CMF-R2	CMF-R3	CMF-R3B	CMF-R4A
% Aromaticity (IR)	100	68	25	34	18	24
COOH mmol/g (titration)	1.03	1.16	1.5	1.35	2.66	1.82
Mw (SEC)	1960	1700	2560	16000	4800	8100
Initial suspensibility (%)	50.3±7.3	97.9±0.56	96.9±0.14	100.5±0.79	101.9±0.28	101.4±0.1
Aged suspensibiltiy (%)	90.3±0.8	97.4±1.24	98±0.37	90±0.31	99±0.73	101.1±0.01
Initial blooming	Pass	very well	very well	very well	very well	very well
Aged blooming	Pass	very well	very well	very well	very well	very well
Initial particle size (μm, D50)	4.00±0.75	0.855±0.01	0.834±0.07	0.9±0.02	0.8±0.02	0.7±0.00
Aged particle size (μm, D50)	2.90±0.71	1.00±0.02	0.84±0.01	4.9±0.18	2.1±0.58	0.8±0.03
Initial particle size (μm, D90)	8.30±0.08	4.465±0.22	3.6±1.02	2.9±0.1	3.4±0.3	2.0±0.05
Aged particle size (μm, D90)	8.4±1.76	5.35±0.81	3.47±0.28	17.2±2.13	5.9±1.23	2.6±0.045
Initial viscosity	Thin	Thin	Thin	Thin	Thin	Thin
Aged viscosity	Gelled	Soft gel	Medium gel	Medium gel	Thin	Soft gelled

meet performance specs

Kraft lignin samples: heavy metal adsorption

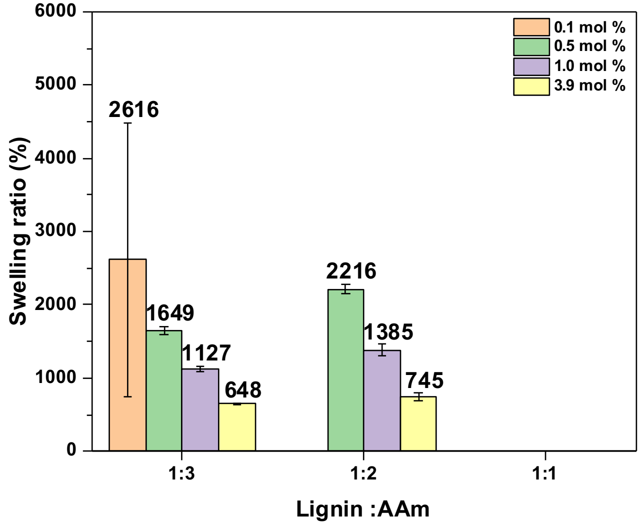
	Adsorption capacity (mg/g)				
	Cu	Co	Ni	Pb	Zn
kraft lignin	2.23±0.38	2.43±0.10	2.45±0.03	9.69±0.06	2.44±0.11
NREL	4.34±0.55	5.29±0.89	4.97±0.70	11.62±0.05	4.99±0.64
CMF-R1	5.10±0.01	7.00±0.84	6.96±0.47	19.16±0.22	8.44±0.59
CMF-R2	8.55±0.02	9.06±0.32	10.16±0.01	19.55±0.03	11.30±0.36
CMF-R3	15.83±0.32	16.99±0.06	16.17±0.08	>20	18.9±0.19
CMF-R3B	6.75±0.88	8.87±0.06	6.84±0.1	17.01±0.08	10.15±0.12

meet performance specs

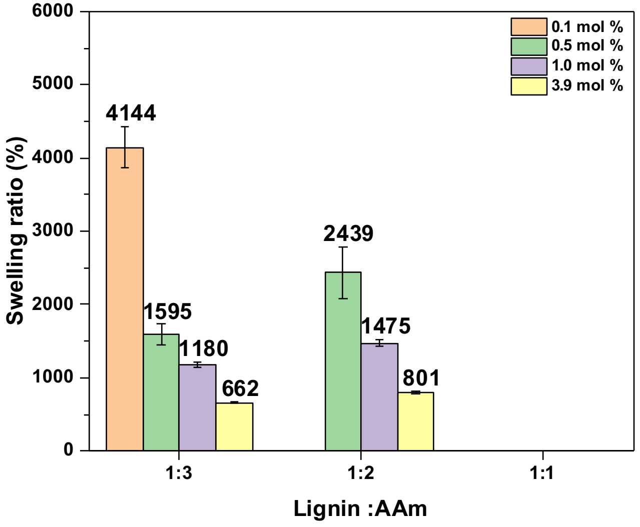
Metric: 14 mg/g Pb
8 mg/g Cu, Co, Ni, Zn

kraft

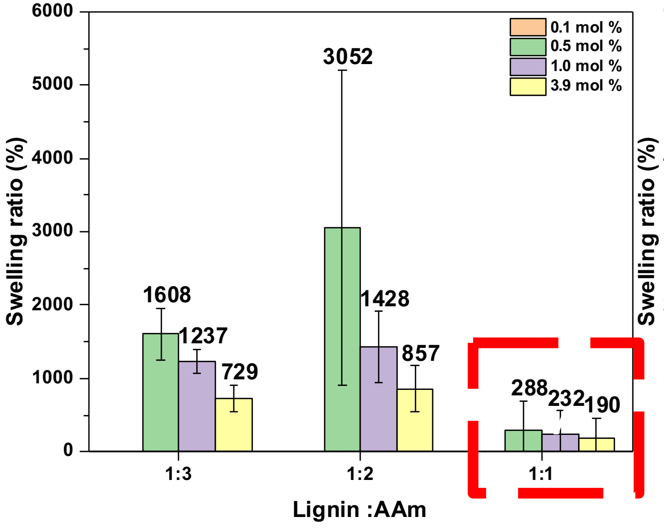
R1 M_w 1,700



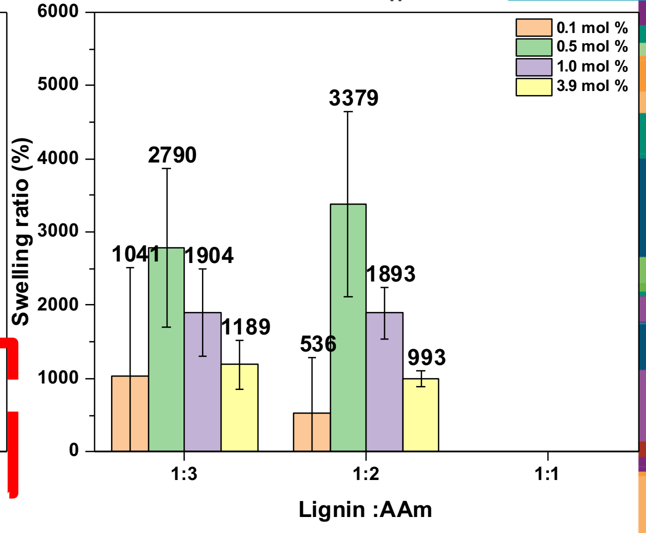
R2 M_w 2,560



R3 M_w 16,000

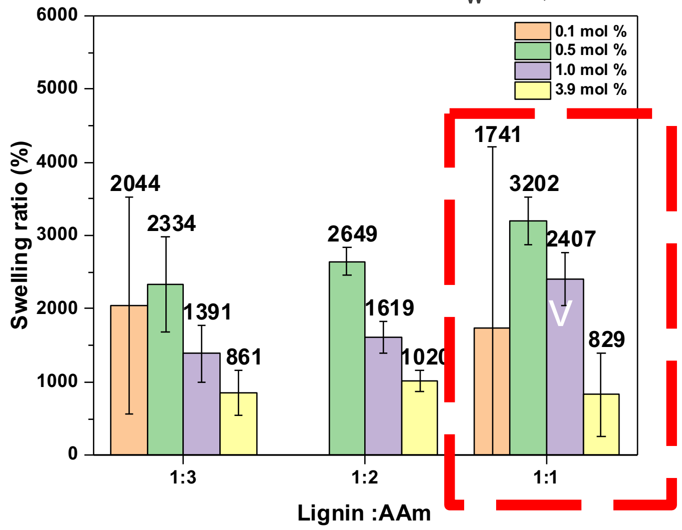


R3B M_w 4,800

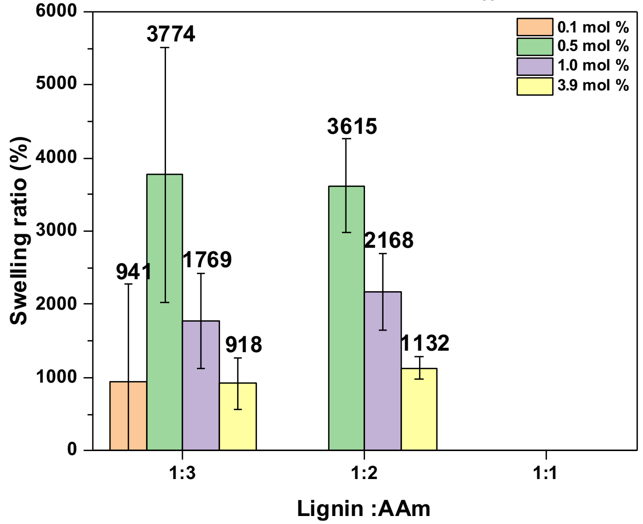


NREL DMR-EH (BL)

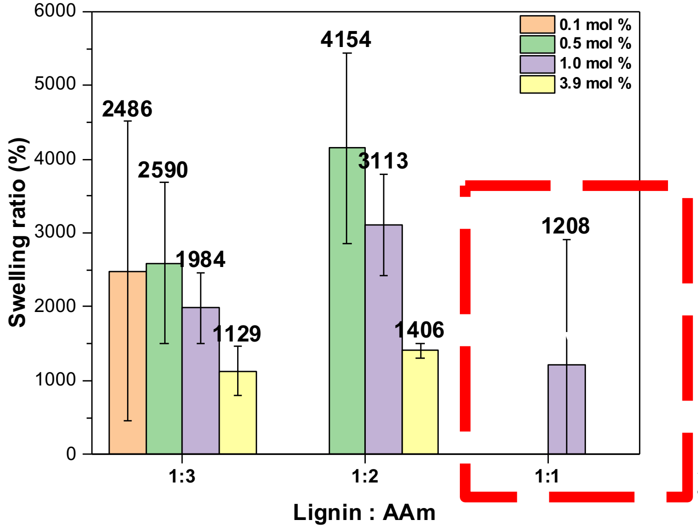
BL-CMF1 M_w 60,000



BL-BCD M_w 9,700



BL-BCD-CMF3 M_w 34,000



Hydrogels for soil application: Cost and performance metrics

Performance metrics for a product of that type to be viable in the marketplace
Benefits/Value Proposition: Same performance (soil water absorption, water permeability)
Improved biodegradability
Improve soil quality by increasing natural organic matter

Price for polyacrylamide gel (from distributor): $2.78/lb
Cost to produce a PA or PAM-based hydrogel for soil applications: ~$1/lb
Drawbacks: **Lack of biodegradation**
Microplastic pollution of soil
Based on petroleum resources

Cost to produce a lignin-based hydrogel product for soil applications (dried): $2.0/lb
Cost to produce a lignin-based hydrogel product for soil applications (wet): ~ $1.0/lb
Benefits: **Should be biodegradable**
Large volume of lignin available

Cost metric: ?? (price of water, or cost of crop failure? **Need field trials**)

- Proposed tests: 1) soil water absorption, 2) water permeability, 3) biodegradation
- Test soil: sandy loam

References: Engineering Reports 2.4 (2020): e12140; Microplastics – ECHA; Evonik STOCKOSORB 660; Soil Moist quotation

Mass of water adsorbed in the hydrogels

	g of absorbed water per g of lignin				g of absorbed water per g of lignin-based hydrogel (dried state)			
	R1	R2	R3	R3B	R1	R2	R3	R3B
1:3-0.1	NA	138 g/g of lignin	49 g/g of lignin	80 g/g of lignin	NA	45 g/g of lignin	18 g/g of lignin	31 g/g of lignin
1:3-0.5	61 g/g of lignin	55 g/g of lignin	50 g/g of lignin	44 g/g of lignin	16 g/g of lignin	17 g/g of lignin	13 g/g of lignin	17 g/g of lignin
1:3-1.0	41 g/g of lignin	40 g/g of lignin	46 g/g of lignin	46 g/g of lignin	11 g/g of lignin	12 g/g of lignin	12 g/g of lignin	14 g/g of lignin
1:3-3.9	24 g/g of lignin	24 g/g of lignin	25 g/g of lignin	24 g/g of lignin	6 g/g of lignin	6 g/g of lignin	6 g/g of lignin	7 g/g of lignin
1:2-0.1	NA	NA	NA	27 g/g of lignin	NA	NA	NA	16 g/g of lignin
1:2-0.5	43 g/g of lignin	30 g/g of lignin	26 g/g of lignin	30 g/g of lignin	21 g/g of lignin	21 g/g of lignin	13 g/g of lignin	17 g/g of lignin
1:2-1.0	27 g/g of lignin	30 g/g of lignin	16 g/g of lignin	25 g/g of lignin	13 g/g of lignin	14 g/g of lignin	9 g/g of lignin	14 g/g of lignin
1:2-3.9	17 g/g of lignin	16 g/g of lignin	16 g/g of lignin	17 g/g of lignin	7 g/g of lignin	8 g/g of lignin	6 g/g of lignin	8 g/g of lignin
1:1-0.1	NA	NA	NA	NA	NA	NA	NA	NA
1:1-0.5	NA	NA	2 g/g of lignin	NA	NA	NA	9 g/g of lignin	NA
1:1-1.0	NA	NA	4 g/g of lignin	NA	NA	NA	7 g/g of lignin	NA
1:1-3.9	NA	NA	4 g/g of lignin	NA	NA	NA	6 g/g of lignin	NA

Lignin:acryamide ratio – crosslinker mol% relative to AAm

Estimated cost of current hydrogels

Reagents	price range		median price	median price per lb
acrylamide	$ 1600 / metric ton	$ 2300 / metric ton	$ 1950 / metric ton	$ 0.88 / lb
methylene bis acrylamide	$ 48 / metric ton	$ 4500 / metric ton	$ 2274 / metric ton	$ 1.03 / lb
ammonium persulfate	$ 210 / metric ton	$ 220 / metric ton	$ 215 / metric ton	$ 0.10 / lb
sodium chloride	$ 40 / ton	$ 90 / ton	$ 65 / ton	$ 0.03 / lb
EDC HCl	$ 4.5 / kg	$ 6 / kg	$ 5 / kg	$ 2.38 / lb
TEMED	$ 1 / kg	$ 100 / kg	$ 51 / kg	$ 22.91 / lb
MES monohydrate	$ 1 / kg	$ 2 / kg	$ 2 / kg	$ 0.68 / lb
lignin				
water				

lignin:acrylamide-MBA mol% ratio	estimated price per lb without including the lignin price			
	R1	R2	R3	R3B
1:3-0.1	$0.98	$0.98	$0.98	$0.98
1:3-0.5	$0.98	$0.98	$0.98	$0.98
1:2-0.1	$0.72	NA	NA	$0.72
1:2-0.5	$0.90	$0.90	$0.90	$0.90
1:1-0.1	NA	NA	NA	NA
1:1-0.5	NA	NA	$0.69	NA

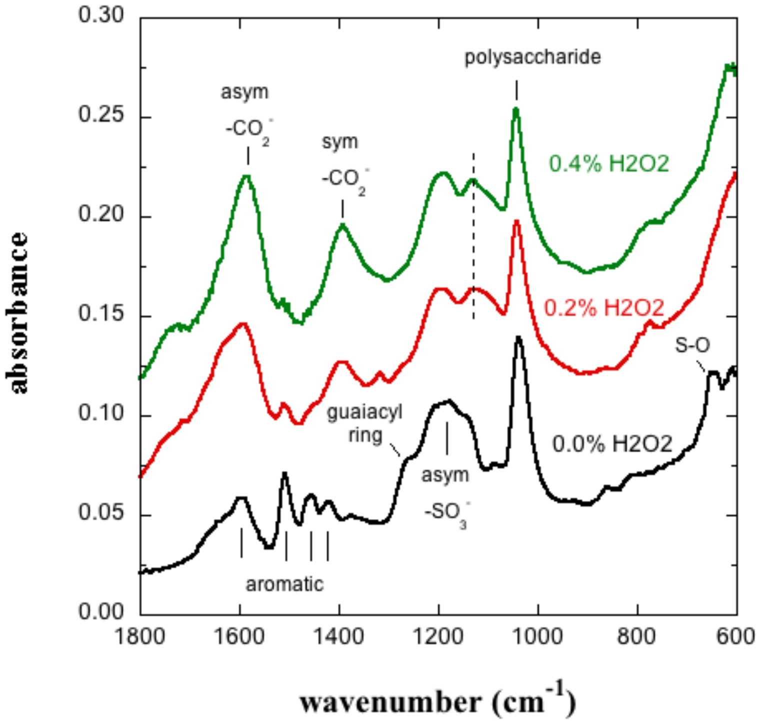
lignin:acrylamide-MBA mol% ratio	estimated price per lb including the lignin price			
	R1	R2	R3	
1:3-0.1	$2.15	$2.20	$2.33	
1:3-0.5	$2.15	$2.20	$2.33	
1:2-0.1	$1.89	NA	NA	
1:2-0.5	$2.07	$2.12	$2.25	
1:1-0.1	NA	NA	NA	
1:1-0.5	NA	NA	$2.04	

Commercial Producers Of hydrogels

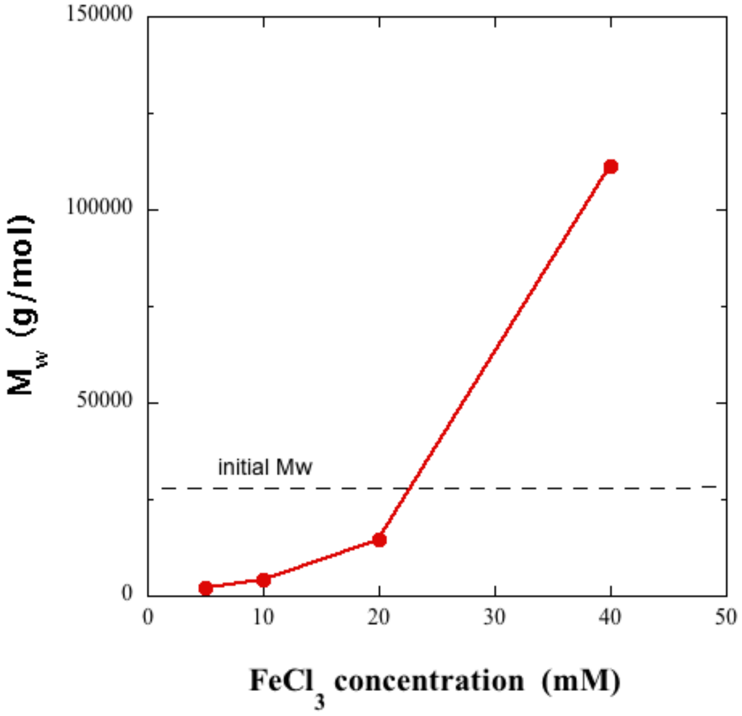
Company	Contacts	Contact Title	Contact email	Contact LinkedIn	Domestic?	Company Website	Company LinkedIn
Aquatrols	Darryl Ramoutar	Director of Research and Development	darryl.ramoutar@aquatrols.com	https://www.linkedin.com/in/darryl-ramoutar-a3084465/	Yes	https://aquatrols.com/	
Aqueus	Greg Rever	Business Development Independent Contractor		https://www.linkedin.com/in/greg-rever-2ba44a15/	Yes	https://www.aqueus.com/growthful/?gclid=EAIaIQobChMIi-bpvsPM-QIVJTizAB3mdgAcEAAYAiAAEgKcjPD_BwE	https://www.linkedin.com/company/aqueus/
BASF	https://agriculture.basf.us/crop-protection/contact-us.html				No	https://agriculture.basf.com/global/en/business-areas/crop-protection-and-seeds/use-areas/soil-management.html	https://www.linkedin.com/showcase/basfagriculturalsolutions/
Bios Hydrogel	https://www.bioshydrogel.com/#contact-us				No	https://www.bioshydrogel.com/	
Borregard	Jerry Gargulak	Global Business Development Director	jerry.gargulak@borregaard.com	https://www.linkedin.com/in/jerry-gargulak-b2149911/	No	https://www.borregaard.com/product-areas/lignin-biopolymers/?utm_term=lignins&utm_campaign=Product+Area+%7C+Lignin+Biopolymers+%7C+Global&utm_source=adwords&utm_medium=ppc&hsa_acc=3642184401&hsa_cam=13555587785&hsa_grp=126240300920&hsa_ad=528203487243&hsa_src=g&hsa_tgt=kwd-328562444388&hsa_kw=lignins&hsa_mt=p&hsa_net=adwords&hsa_ver=3&gclid=EAIaIQobChMI9bj4us_O-QIVhKjICh3UtwzGEAAYAiAAEgKcaPD_BwE	https://www.linkedin.com/company/borregaard/
Chemtex: Alsta Hydrogel	Jeff Taylor	BP Technology	jeff.taylor@chemtex.com	https://www.linkedin.com/in/jeff-taylor-9865bb12/	Yes	https://www.hydrogelagriculture.com/	https://www.linkedin.com/company/chemtex/
Evonik Industries AG	https://www.break-thru.com/en/contact-form/194416				No	https://corporate.evonik.com/en/products-and-solutions/markets/agriculture	https://www.linkedin.com/company/evonik/
Hydromer	Ravi Rangarajan	Strategic Global Business Executive	rrangarajan@hydromer.com	https://www.linkedin.com/in/ravi-rangarajan-491ba/	Yes	https://hydromer.com/hydrogels/	https://www.linkedin.com/company/hydromer-inc./
JRM Chemical Inc.	Scott Wiesler	VP	jrm@en.com	https://www.linkedin.com/in/scott-wiesler-27aa4428/	Yes	https://www.soilmoist.com/products/soil-moist.php	
Lebanon turf-roots	https://www.lebanonturf.com/contact-us				Yes	https://www.lebanonturf.com/brands/lebanonturf-grass-seed?utm_source=paidsearch&utm_medium=textad&utm_campaign=grassseed&utm_term=2022&gclid=EAIaIQobChMIpqGjna3O-QIVAb_ICh0-5gFpEAAYASAAEgJFwvD_BwE	https://www.linkedin.com/company/lebanon-seaboard/
Rain Soil	info@rainsoil.com					https://rainsoil.com/products/retain?variant=32680976711818	
Sanoway	info@sanoway.com				No	https://www.sanoway.com/en/	
Scotts Miracle-Gro	Anneke Chewning	Director of Business Development	anneke.chewning@scotts.com	https://www.linkedin.com/in/anneke-chewning-mba-573169108/	Yes	https://scottsmiraclegro.com/	https://www.linkedin.com/company/scottsmiraclegro/
Unicrop Biochem	https://unicropbiochem.com/contact/			https://www.linkedin.com/in/panchalakshay/	No	https://unicropbiochem.com/	https://www.linkedin.com/company/unicrop-biochem/

Preliminary data for CMF reaction with lignosulfonates

Green Chemistry 2022, 24, 1627

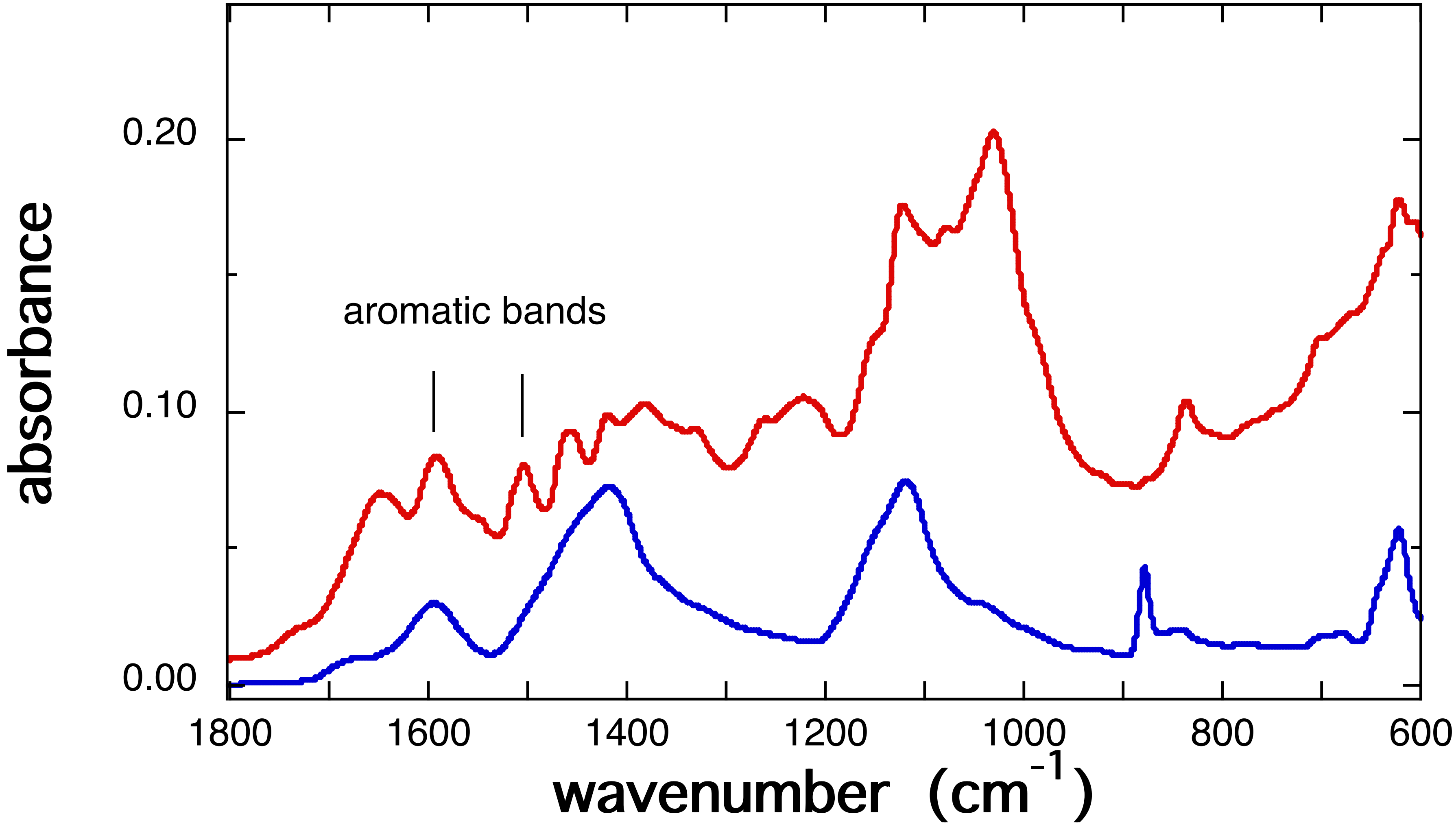


opens aromatic rings
generates COOH



can increase or decrease Mw

FTIR for BL and BL BCD



Biochar + hydrogel for soil amendment

Biochar is a by-product of biomass gasification and conversion to sustainable aviation fuel (SAF)

Biochar has great potential for increasing carbon sequestration in soils

Biochar can be mildly hydrophilic, but hydrogels are highly hydrophilic

Prior work indicates that for sandy soils a small amount of hydrogel can provide a synergistic benefit when combined with biochar

Das and Ghosh Energy 2022, 242, 122977

Riad et al 2018 Egyptian Journal of Horticulture, 45, 169-183

Hydrogels can be designed to retain and deliver nutrients in addition to improving water holding capacity

Das and Ghosh Energy 2022, 242, 122977

Hydrogels from acrylamide are not biodegradable but lignin-based hydrogels should be biodegradable

Lignin-based hydrogels are likely to greatly increase the use and efficacy of biochar as a soil amendment

MW distributions