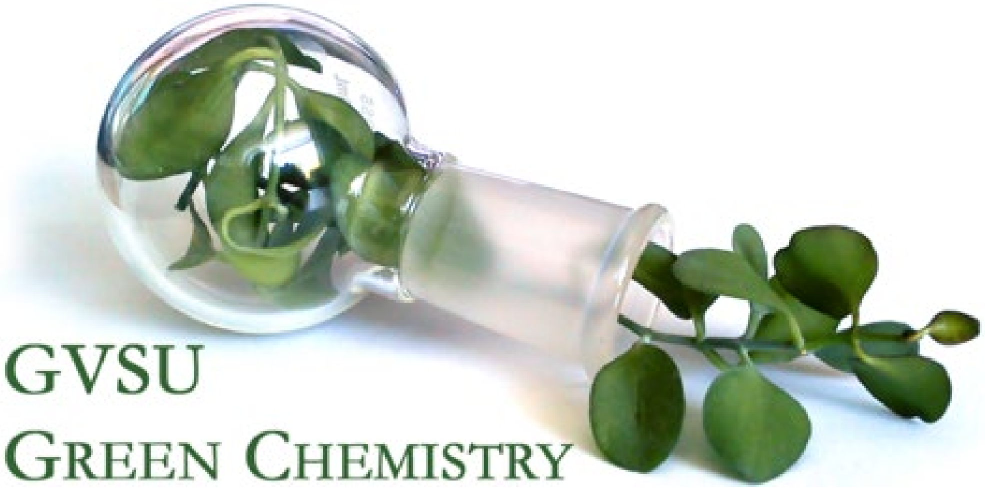
Biomass and biorefinery: a project for undergraduate laboratory

Andrew Philip Freiburger

Dalila Kovacs, Department of Chemistry
Jim Krikke, Department of Chemistry

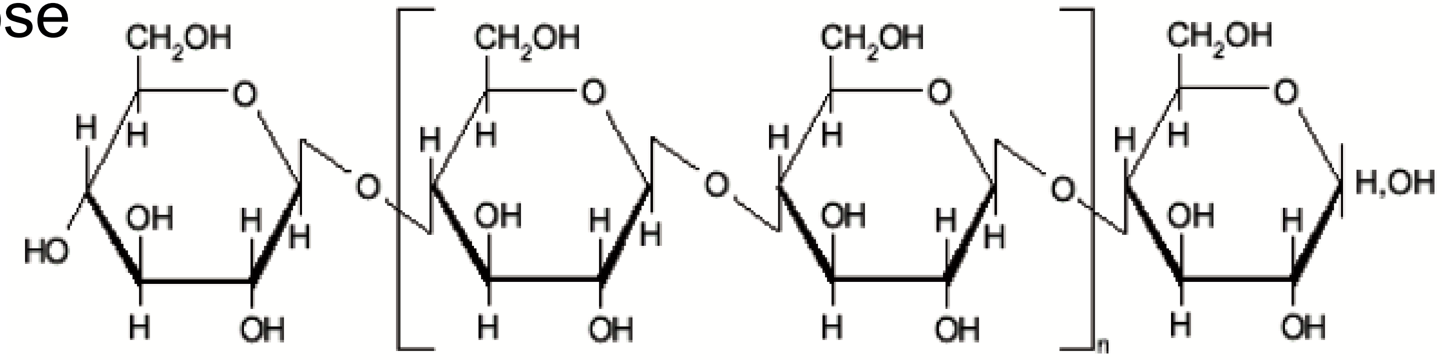
Erik Nordman, Department of Biology

Grand Valley State University, Allendale, MI



Lignocellulose

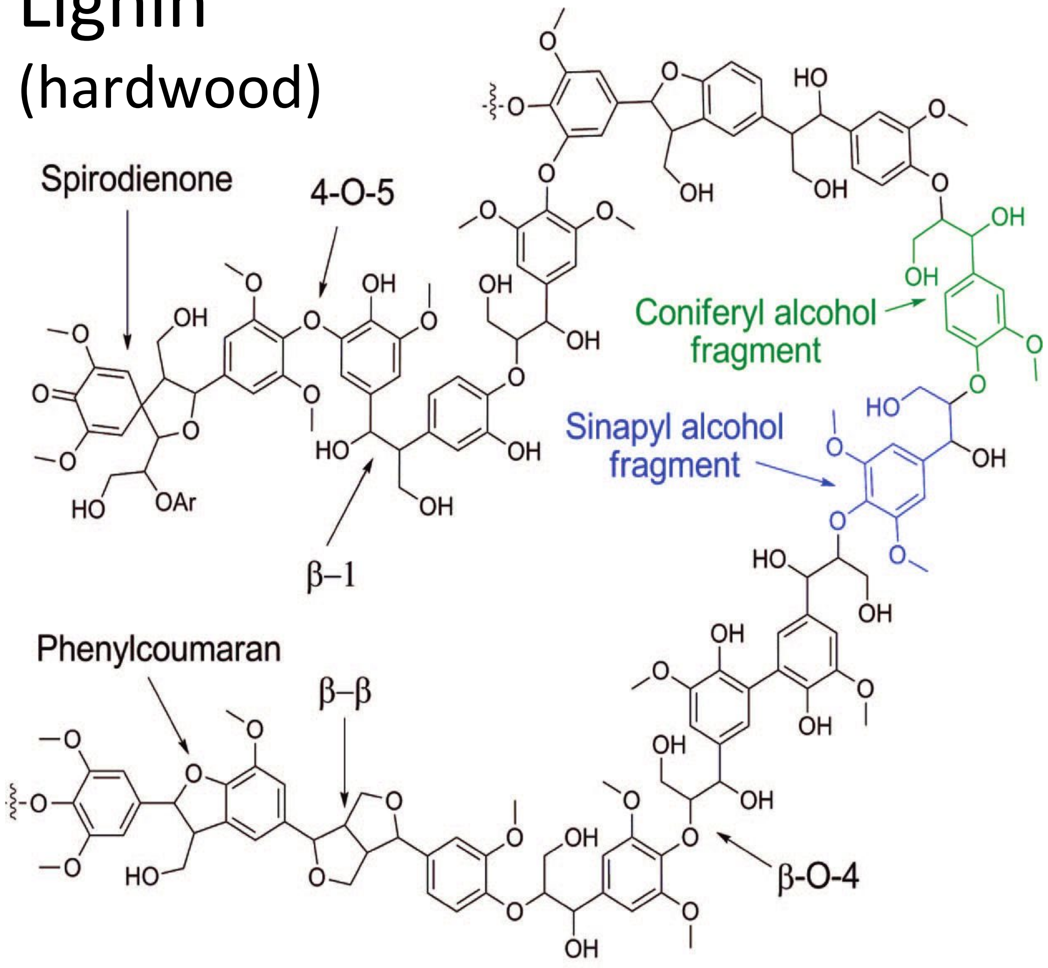
Cellulose



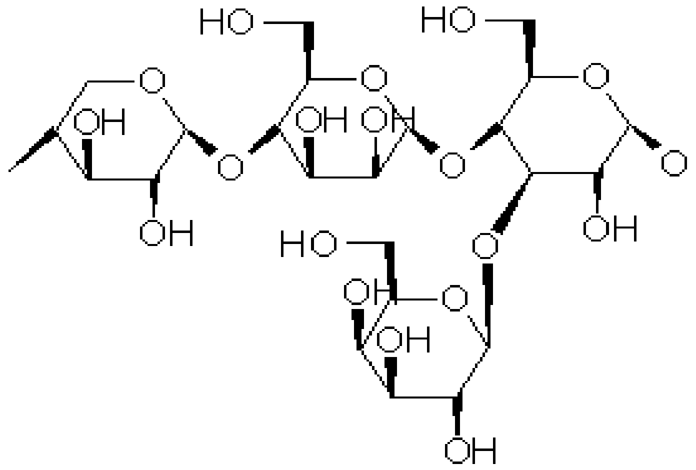
(a) Non-reducing end (b) Repeating cellulose unit (c) Reducing end

- **1.5 x 10^{12} tons** of cellulose alone is produced annually [Theo van de Ven and Louis Godbout. Cellulose – fundamental aspects. *InTech*. **2013**]

Lignin (hardwood)



Hemi-Cellulose



- Xylose - ß(1,4) - Mannose - ß(1,4) - Glucose -
- alpha(1,3) - Galactose

Hemicellulose

BerserkerBen, https://en.wikipedia.org/wiki/Hemicellulose#/media/File:Hemicellulose.png

Joseph Zakzeski, Pieter C. A. Bruijnincx, Anna L. Jongerius, and Bert M .Weckhuysen. The catalytic valorization of lignin for the production of renewable chemicals. *Chemical Reviews*.**2010**. 110, 3552-3599.

Woody **Biomass** (**Bio**logical **mass**)

Substance		**% fresh mass (variable)**	**Biological function**
Water		50	Solvent and reactant
Cellulose	**Lignocellulose**	20	Structure, cell wall
Hemicellulose		12	Structure, cell wall
Lignin		11	Binder and rigidity, middle lamella
Metabolites		6	Immune, hormonal, and metabolic function
Minerals		1	Catalysts and enzyme complexes

Industrial contributions => Green Chemistry

1. Prevent waste: Design chemical syntheses to prevent waste. Leave no waste to treat or clean up.
2. Maximize atom economy : Design syntheses so that the final product contains the maximum proportion of the starting materials. Waste few or no atoms.
3. Design less hazardous chemical syntheses : Design syntheses to use and generate substances with little or no toxicity to either humans or the environment.
4. Design safer chemicals and products : Design chemical products that are fully effective yet have little or no toxicity.
5. Use safer solvents and reaction conditions : Avoid using solvents, separation agents, or other auxiliary chemicals. If you must use these chemicals, use safer ones.
6. Increase energy efficiency : Run chemical reactions at room temperature and pressure whenever possible.
7. Use renewable feedstocks: Use starting materials (also known as feedstocks) that are renewable rather than depletable. The source of renewable feedstocks is often agricultural products or the wastes of other processes; the source of depletable feedstocks is often fossil fuels (petroleum, natural gas, or coal) or mining operations.
8. Avoid chemical derivatives : Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
9. Use catalysts, not stoichiometric reagents : Minimize waste by using catalytic reactions. Catalysts are effective in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and carry out a reaction only once.
10. Design chemicals and products to degrade after use : Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. Analyze in real time to prevent pollution : Include in-process, real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.
12. Minimize the potential for accidents : Design chemicals and their physical forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

https://www.epa.gov/greenchemistry/basics-green-chemistry

Valorization: the Biorefinery model

By Professional Sun Clouds Blue Sky background stock photos, license under CC0 Public Domain

hv

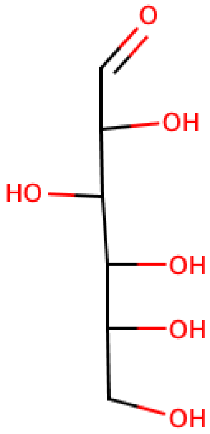
CO_2
H_2O

Biorefinery

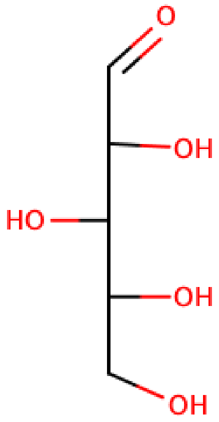
By Unknown Author is licensed under CC BY-SA

Fractionate

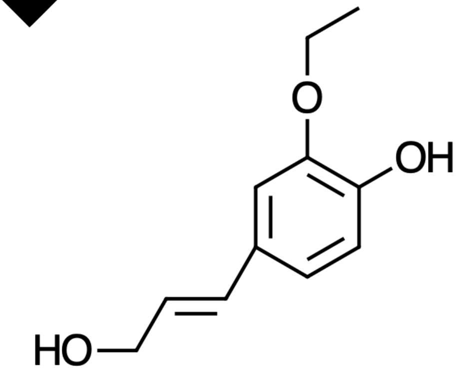
Derivatize



Cellulose



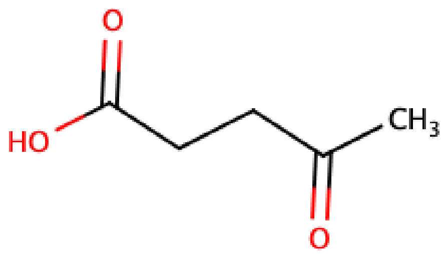
Hemicellulose



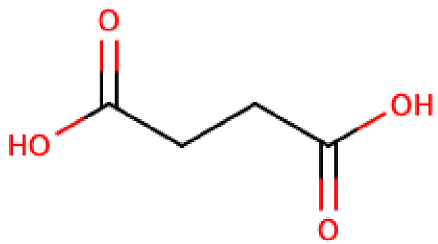
Lignin

Unknown author, licensed under CC BY

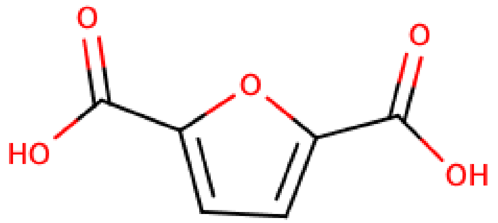
Top 12 value-added chemicals from biomass. *USDE,* **2004.**



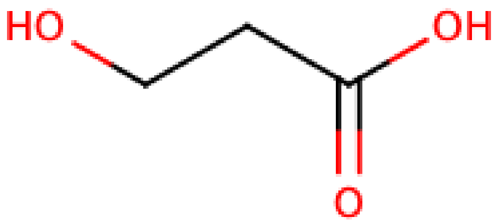
Levulinic Acid



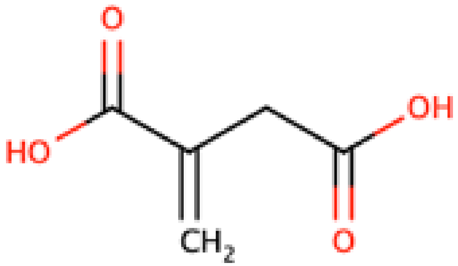
1,4 – diacids (e.g. Succinic Acid)



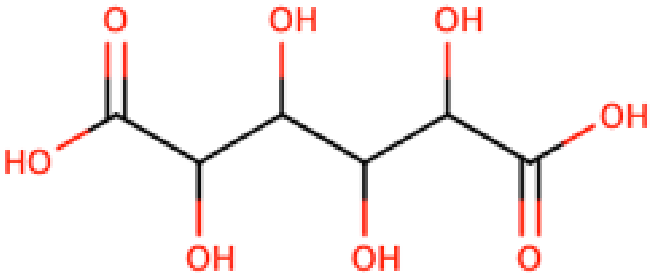
2,5 – Furandicarboxylic acid



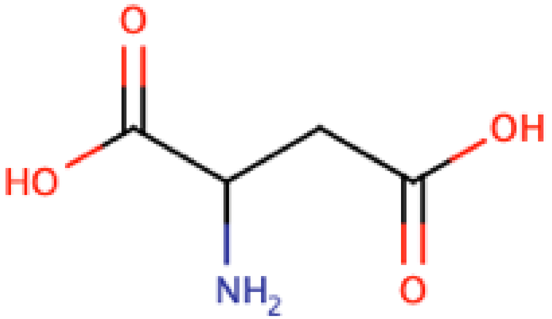
3 – hydroxypropionic acid



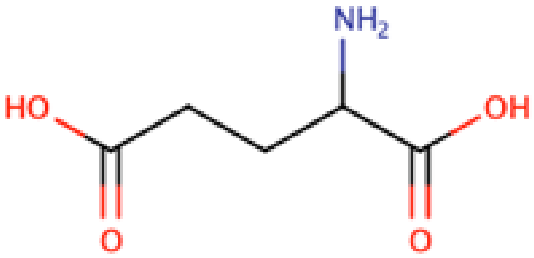
Itaconic Acid



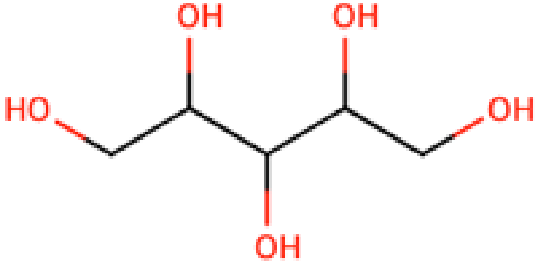
Glucaric Acid



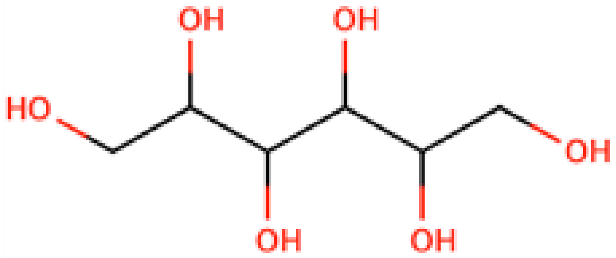
Aspartic Acid



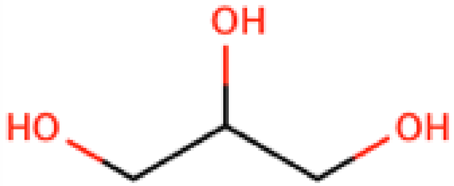
Glutamic Acid



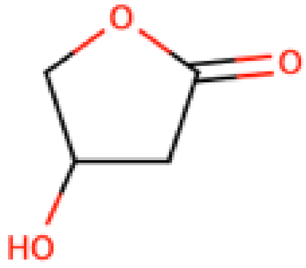
Xylitol



Sorbitol



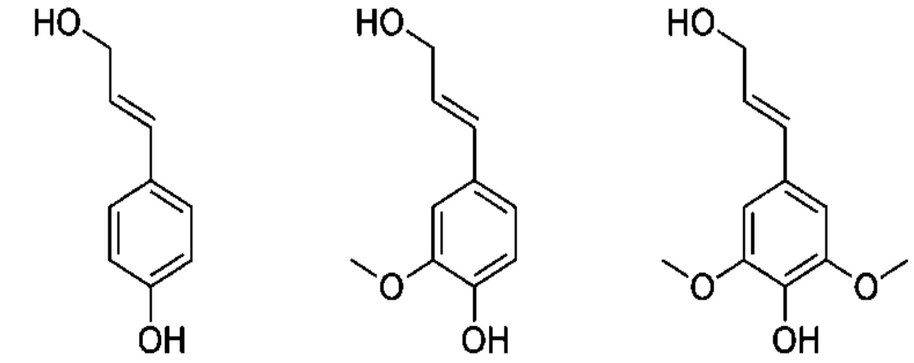
Glycerol



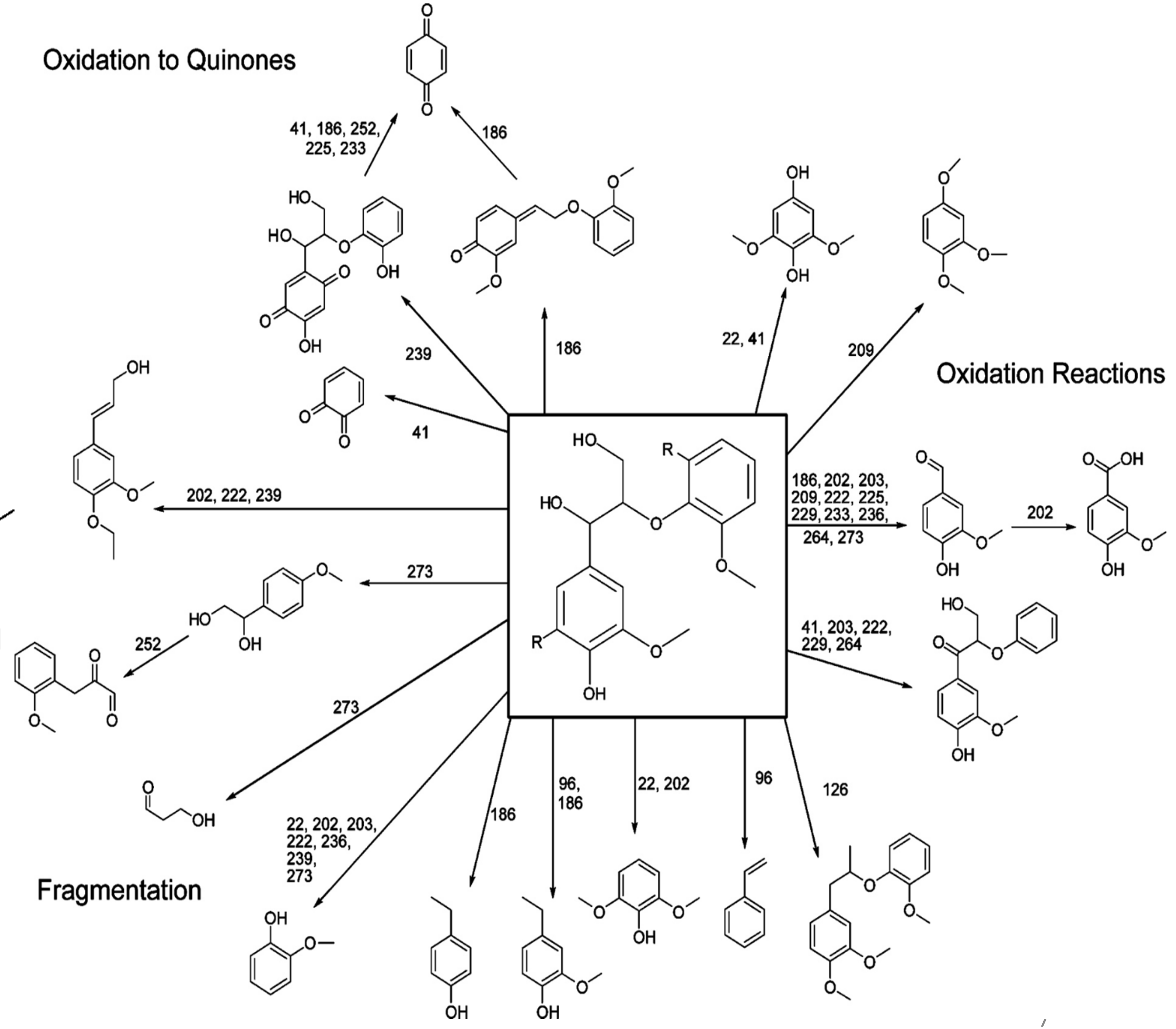
3-Hydroxybuyrolactone

Potential monomers

Lignin derivatives

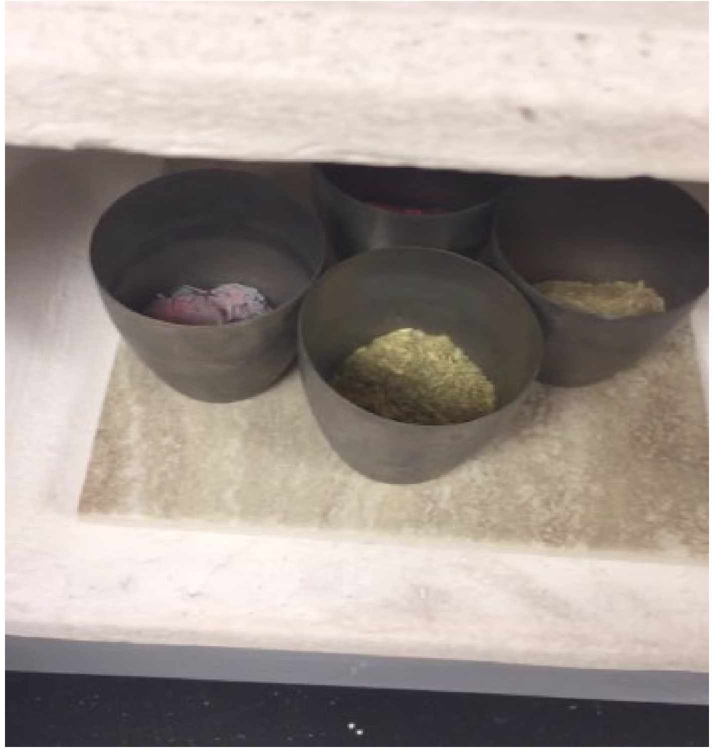


p-coumaryl alcohol   coniferyl alcohol   sinapyl alcohol



Joseph Zakzeski, Pieter C. A. Bruijnincx, Anna L. Jongerius, and Bert M .Weckhuysen. The catalytic valorization of lignin for the production of renewable chemicals. *Chemical Reviews*.**2010**. 110, 3552-3599.

Challenges with biomass



Ash

- Catalyzes side reactions
- Must be filtered [Livingston, 2006] *ThermalNet* Workshop. **2006.**
- Damages machinery [Dave Prouty, Heat Transfer International]

Lignin

- Unique to each plant
- Resistant ether bonds
  - **Carbon**iferous period (~360 – 300 mya) and coal forests

Biomass: Woody *vs.* "foody"

The annual agricultural requirements and global warming potential of low-lignin first generation and lignified second generation biomass energy crops.

Biomass source	Water requirements $\left(\frac{m^3\ of\ water}{L\ of\ biofuel \cdot year}\right)$	Land requirements $\left(\frac{m^2\ of\ land}{L\ of\ biofuel}\right)$	Fertilizer requirements $\left(\frac{kg\ of\ fertilizers}{Hectare\ of\ plot \cdot year}\right)$	Crop yield $\left(\frac{Kg\ of\ crop}{Hectare\ of\ plot \cdot year}\right)$	Growth cycles (annual or perennial)	Direct-effect greenhouse gas emission $\left(\frac{Grams\ of\ CO_2\ equivalents}{Megajoules\ of\ energy\ produced}\right)$
Corn	2.01[1]	4.75[1]	338[2]	5001[1]	Annual[3]	30.6[7]
Soybeans	15.63[1]	28.40[1]	ND	1720[1]	Annual[3]	ND
Shrub willow	ND	ND	100[5]	7,700[5]	Perennial[4], harvested in 3 year cycles for ~10 cycles	0.68[6]

[1]Sourced from Yang et al., **2009**

[2]Nitrogen contributes 162kg, Phosophate contributes 68kg, Potash contributes 90kg, and Sulfer contributes 18kg. Sourced from *USDA*,**2016**.

[3]Sourced from *USDA*, **1985**.

[4]Sourced from Heller et al., **2003**.

[5]Exclusively nitrogen fertilization; the addition of potassium and phosphorous fertilizers were not associated with increased growth rates. Sourced from Hytönen, **1995**.

[6]Sourced from Heller et al., **2003**

[7]Compared with for coal [Liska et al., **2009**]. Sourced from [Liska et al., **2009**].

Willow Biomass

GVSU's SAP May 31, 2017

September, 2017

November 3, 2018

15-25ft growth in each 3 year harvesting cycle

https://www.gvsu.edu/sustainableagproject/

Fishcreek – *Salix purpurea*, US plant patent 17,710

Doubleavineyards.com

Millbrook – *Salix purpurea* x *Salix miyabeana*, US plant patent 17,646

SX64 – *Salix miyabeana,* Developed at the University of Toronto

Fabius – *Salix viminalis* x *Salix miyabeana*

J. Chem. Ed. Literature

The first published undergraduate experiment of simulated biorefinery [Zhou et al., **2018**].

- From corncobs:
  - Lignin –> sunscreen
  - Cellulose –> ethanol
  - Hemicellulose –> biodiesel

Synthetic product	Citation
Benzaldehyde	• Lam et al., **2019**
Lidocaine	• Josephon et al., **2019**
Biosorbents (for water filtration)	• Samet and Valiyaveettil, **2018** • Garrison et al., **2014**
Paints	• Blatti, **2016**
Polymers	• Silverman, **2016** • Dintzner et al., **2012**
Amphiphiles	• Hwang et al., **2014**
Biodiesel	• Ault and Pomeroy, **2011** • Bladt et al., **2010**
Bioethanol	• Seters et al., **2011**
Mesotetraphenylporphyrin	• Warner et al., **2001**

Biomass refinery methods

- Degrade lignocellulosic material into monomers

Mechanical

- Physical
    - Drying or freezing
    - Cutting/chipping/grinding
- Gasification
    - Pyrolysis
- High energy cathode rays

Chemical

- Solvent
    - Deep Eutectic Solvents
    - Aqueous
        - Acid or Base **?**
    - Organic
        - e.g. ethanol, acetone, DCM
- Enzymatic depolymerization
    - Cellulases
    - Lignin peroxidases

Klason (acid) processing

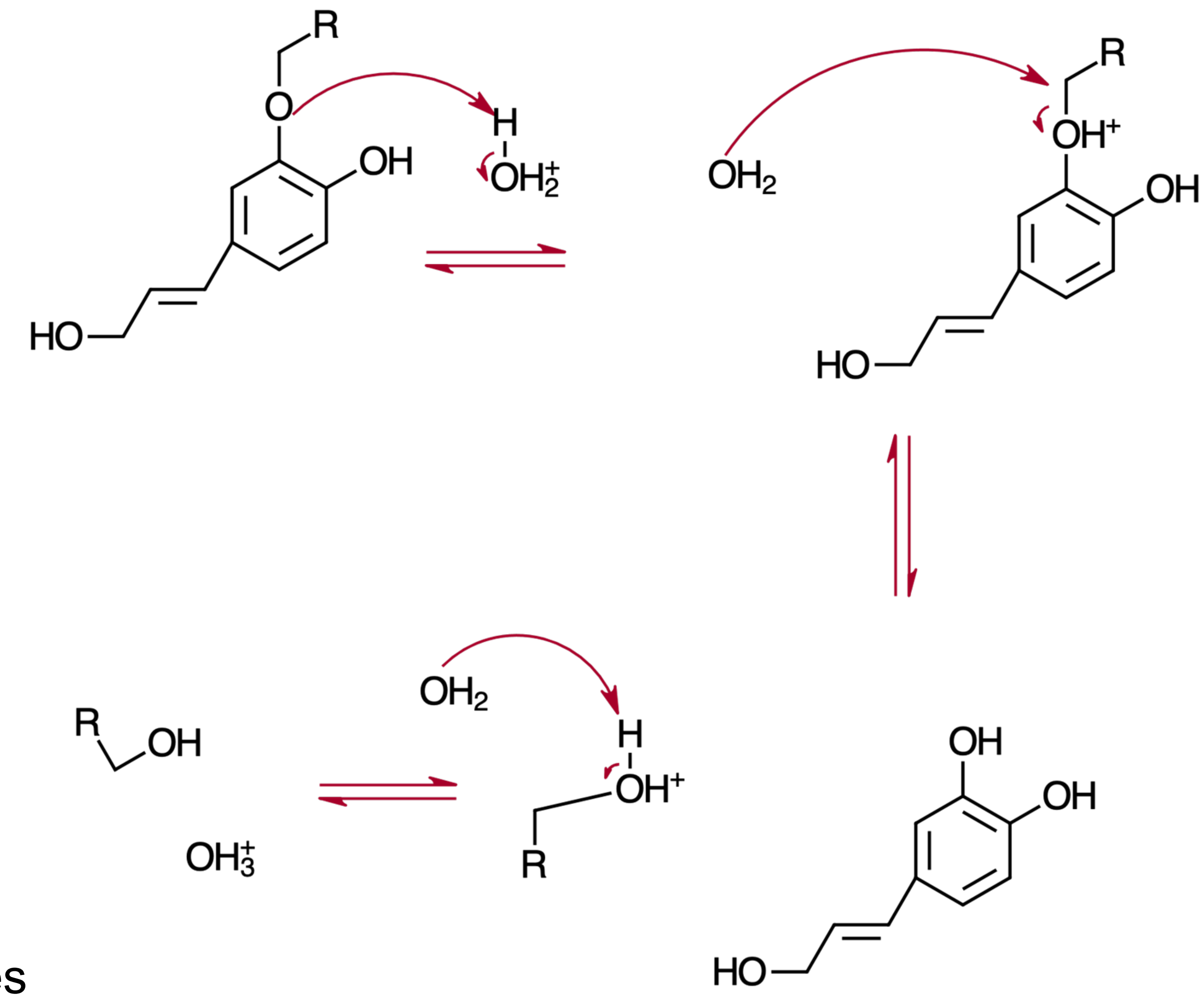
Common pulping method

Lalitha Devi Gottumukkala, Kate Haigh, François-Xavier Collard, Eugéne van Rensburg, Johann Görgens. Opportunities and prospects of biorefinery-based valorization of pulp and paper sludge. *Bioresource Technology*. **2016**, 215, 37-49.

Corrosive to machinery

Retschitzegger, Stefan; Thomas Brunner; Ingwald Obernberger. Low-temperature corrosion in biomass boilers fired with chemically untreated wood chips. **2015**. *Energy & Fuels*. 29(6), 3913-3921.

Depolymerizes carbohydrate residues



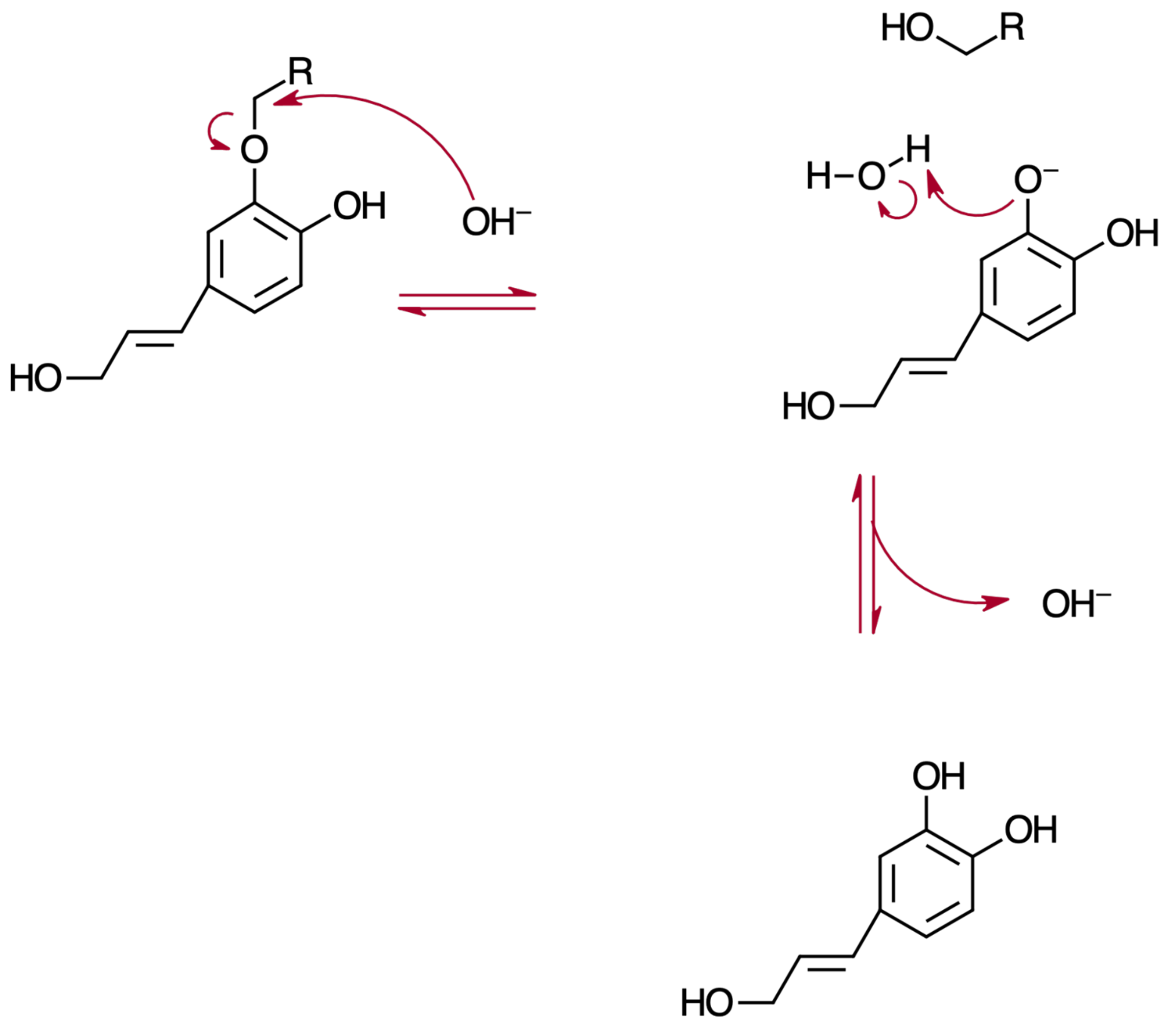
Kraft (alkaline) processing

>50 million tons of lignin are derived annually from the pulping industry, however, 98% is burned

Joseph Zakzeski, Pieter C. A. Bruijnincx, Anna L. Jongerius, and Bert M .Weckhuysen. The catalytic valorization of lignin for the production of renewable chemicals. *Chemical Reviews*.**2010**. 110, 3552-3599.

Selectively depolymerizes lignin and hemicellulose from the cellulosic fibers

Lalitha Devi Gottumukkala, Kate Haigh, François-Xavier Collard, Eugéne van Rensburg, Johann Görgens. Opportunities and prospects of biorefinery-based valorization of pulp and paper sludge. *Bioresource Technology*. **2016**, 215, 37-49.



Biomass refinery methods

- Degrade lignin from lignocellulosic material
- Separate monomers

Mechanical

- Physical
    - Drying or freezing
    - Cutting/chipping/grinding
- Gasification
    - Pyrolysis
- High energy cathode rays

Chemical

- Solvent extraction
    - Deep Eutectic Solvents
    - Aqueous
        - Acid or Base
    - Organic extraction
        - e.g. ethanol, acetone, DCM
- Enzymatic depolymerization
    - Cellulases
    - Lignin peroxidases

Mechanical pretreatment

Shrub willows @ GVSU Sustainable Agriculture Project , 09/ 2017

Hand garden loopers

Doubleavineyards.com/millbrook

Physical characterization

% moisture

Thermo Scientific Oven

Kitchen aid coffee grinder

% ash

Enthalpy of combustion

% moisture

- Oven drying
  - 3 days at 80°C
- Lyophilizing
  - ~24 hours @ -52°C and ~0.031 mBar

Sample	Average % moisture oven	Standard Deviation	Lyophilization % moisture
Old Mixed	19.76	0.26	
Wild	50.05	0.71	
Fishcreek	43.6	1.6	42.3
Fabius	52.2	2.0	53.6
Millbrook	51.6	1.2	51.1
SX64	50.1	2.2	50.4
Significant difference	No apparent difference between oven-drying and lyophilization		

% ash

- Platinum crucibles are cleaned for 1.5 hours at 575°C
- Trials were conducted at 575°C for 2.5 hours.

Sample	Average % ash	Standard Deviation
Old Mixed	2.44	0.27
Wild	2.86	0.37
Fishcreek	1.51	0.24
Fabius	2.39	0.37
Millbrook	2.72	0.53
SX64	2.53	0.37

Significantly lower ash concentration = less challenges with ash

Enthalpy of combustion

~0.55 grams of soxhlet extracted ground dry sample layered with ~0.45 grams of vegetable oil

Purged twice with 20 atm, and tested at 25 atm, of oxygen

Stable starting and ending temperatures (~7 total minutes)

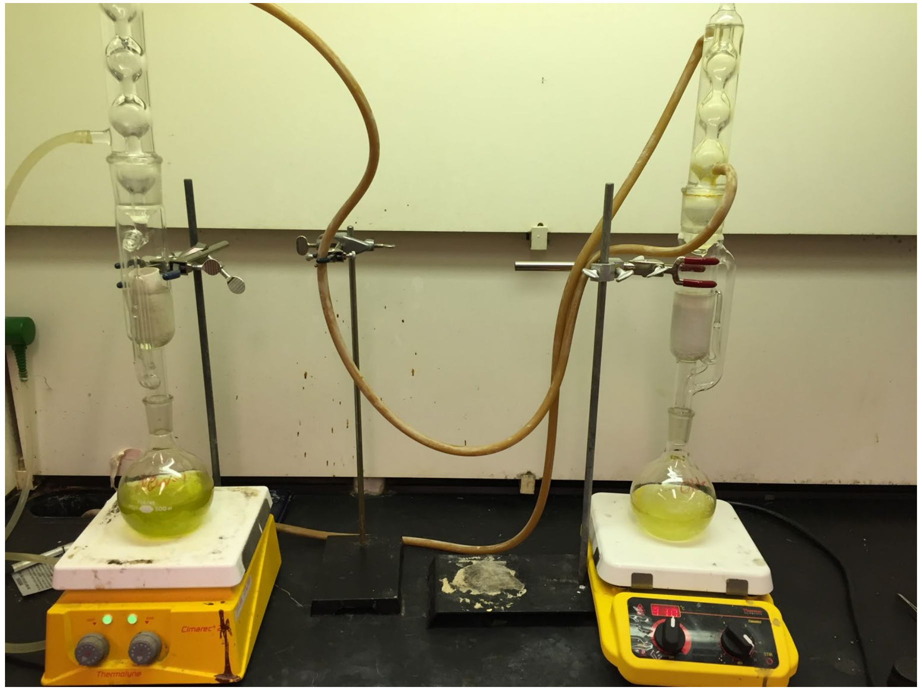
Unextracted *Salix babilonica* possessed 18,280 ± 350 joules per gram

Telmo, C.; J. Lousada. Heating values of wood pellets from different species. **2011**. *Biomass and Bioenergy*. 35, 2634-2639.

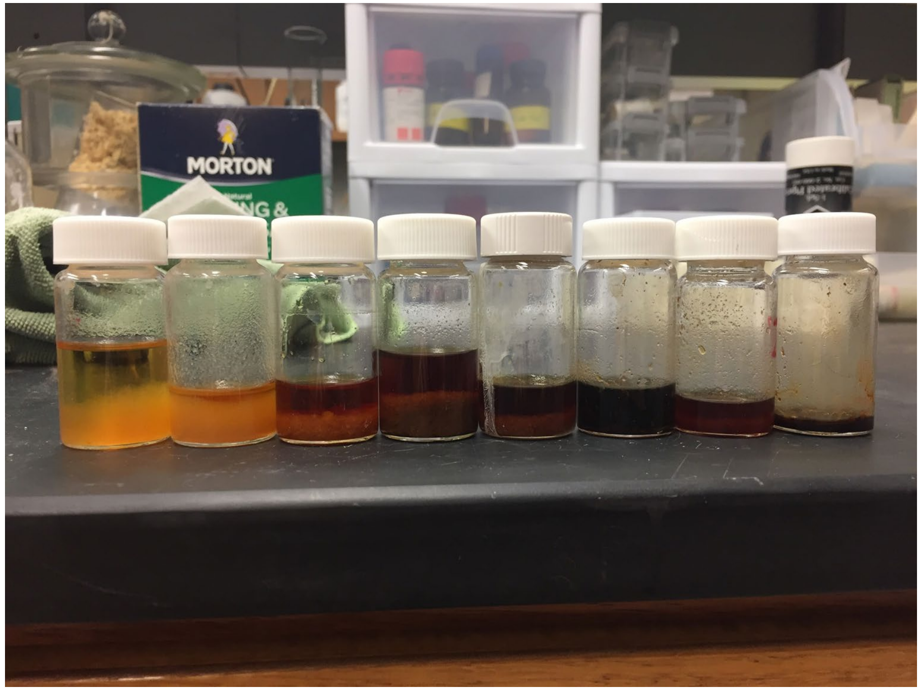
Millbrook has a significantly greater enthalpy of combustion

	Average Qcal (joules/gram)	**SD Qcal (joules/gram)**
Vegetable oil	43400	270
Fabius	14300	450
SX64	15600	540
Millbrook	17600	260
Fishcreek	15500	196

Chemical treatment and characterization

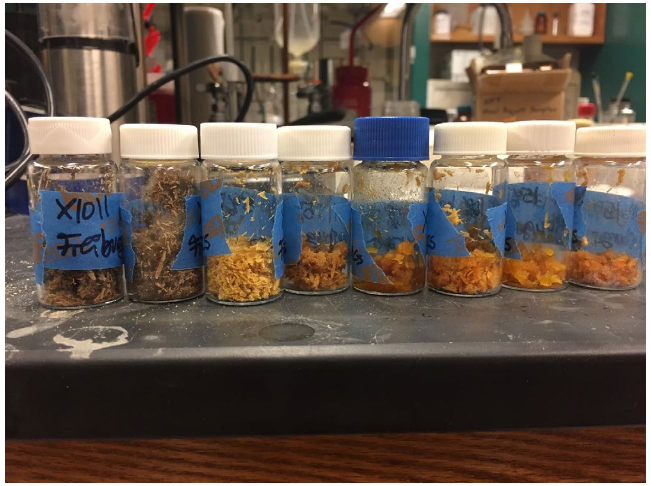


Soxhlet
extraction



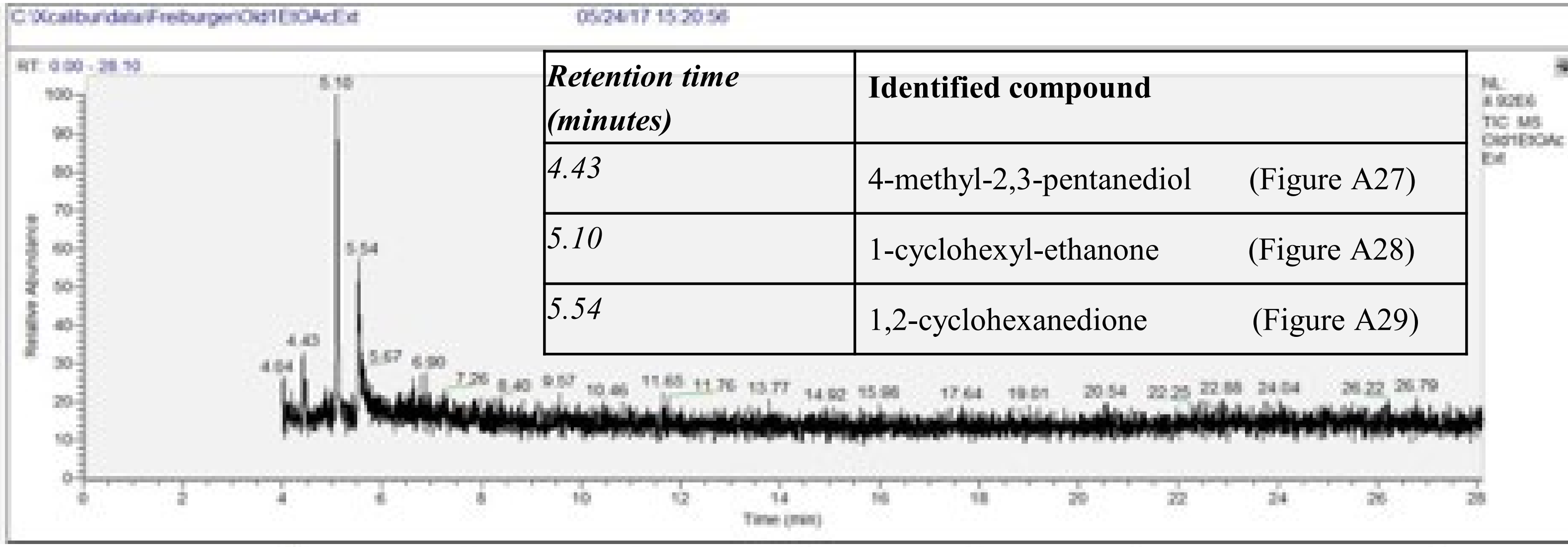
Steam
distillation

Kraft
treatment

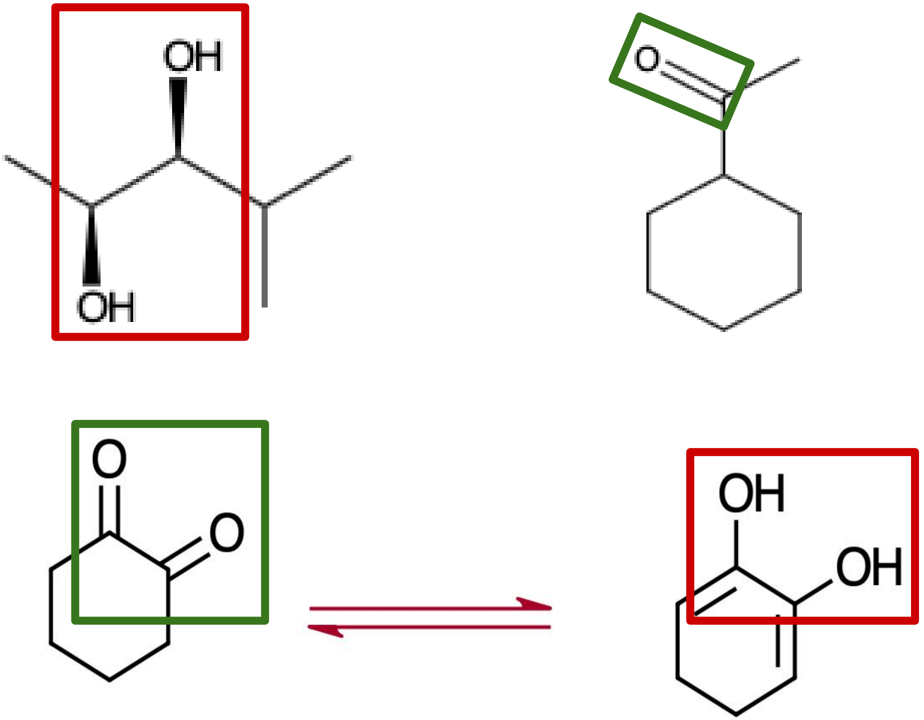


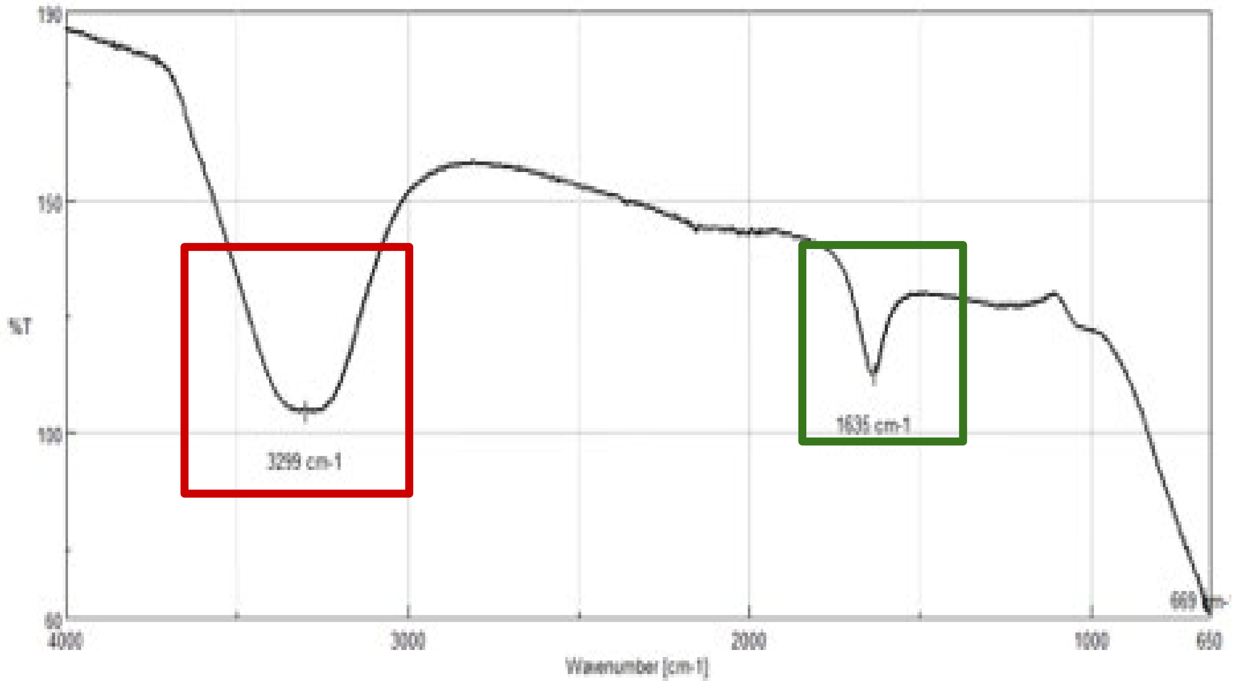
Steam distillation

- No organic layer observed
- Liquid-liquid extraction
    - Hexanes
    - Ethyl acetate



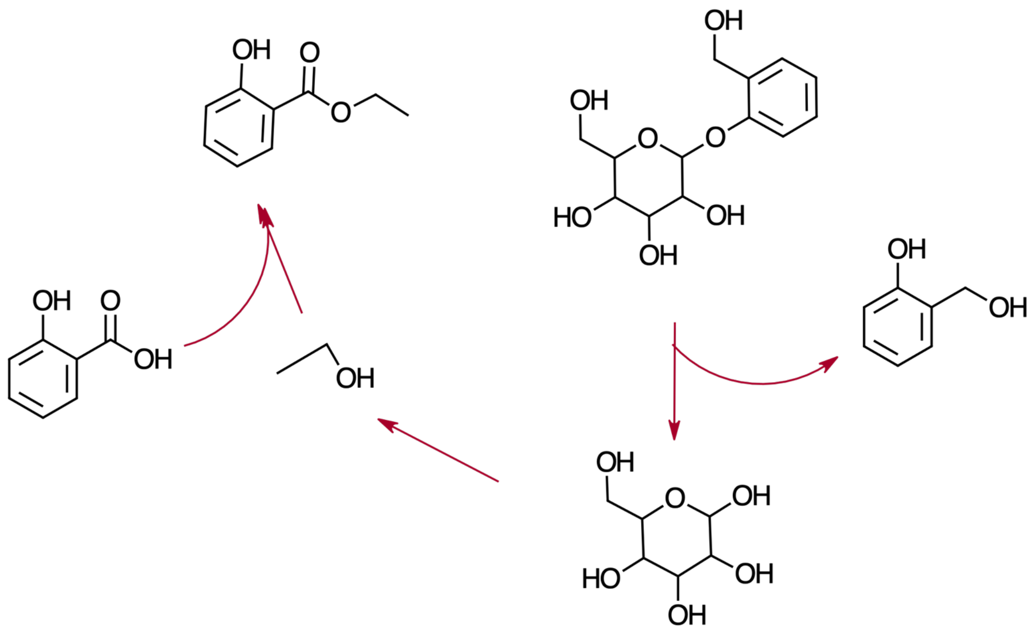
Retention time (minutes)	Identified compound	
4.43	4-methyl-2,3-pentanediol	(Figure A27)
5.10	1-cyclohexyl-ethanone	(Figure A28)
5.54	1,2-cyclohexanedione	(Figure A29)



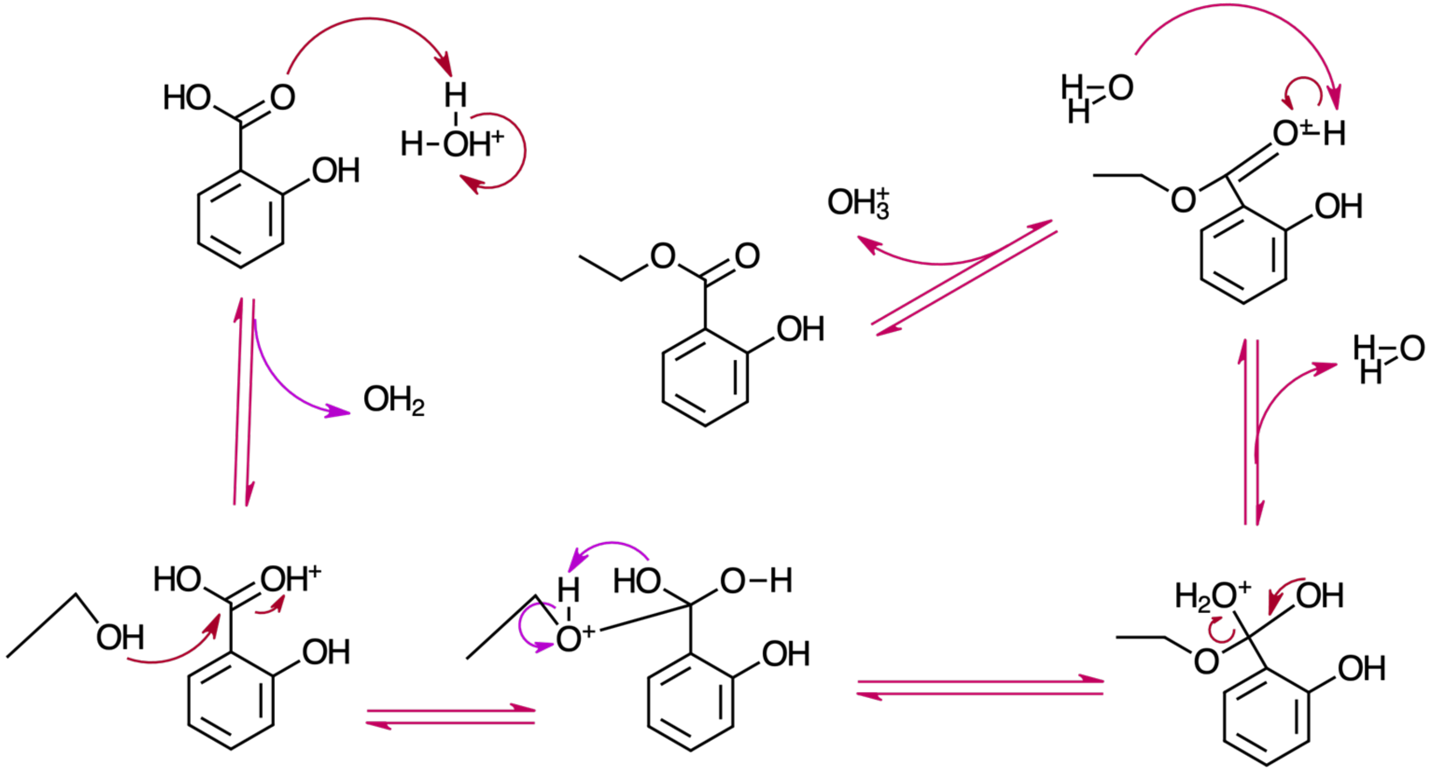


“fungis” are fun guys

Wintergreen agent



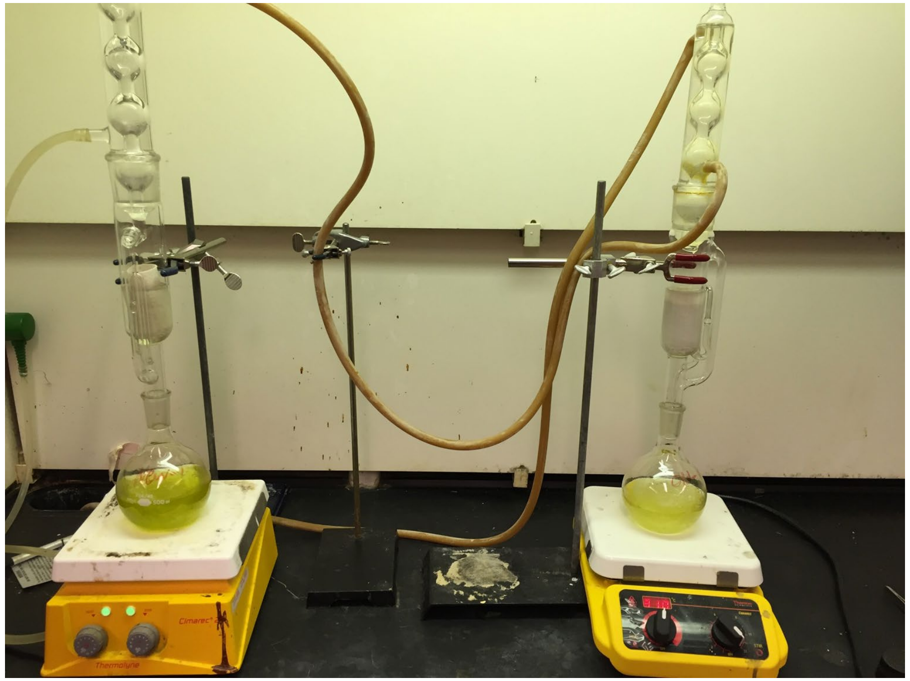
Fischer-esterification



Boiling resistant spores [Professor Aaron Baxter of GVSU]

Soxhlet procedure and solvent analysis

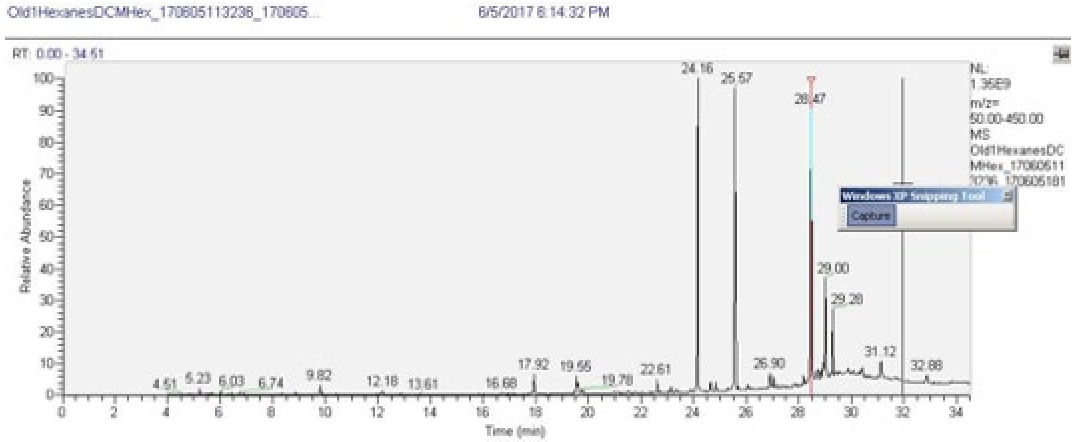
- 6.5 hour extraction period
  - ~50 reflux cycles
- ~275 mL of solvent
  - Hexanes, DCM, Acetone, and Ethanol



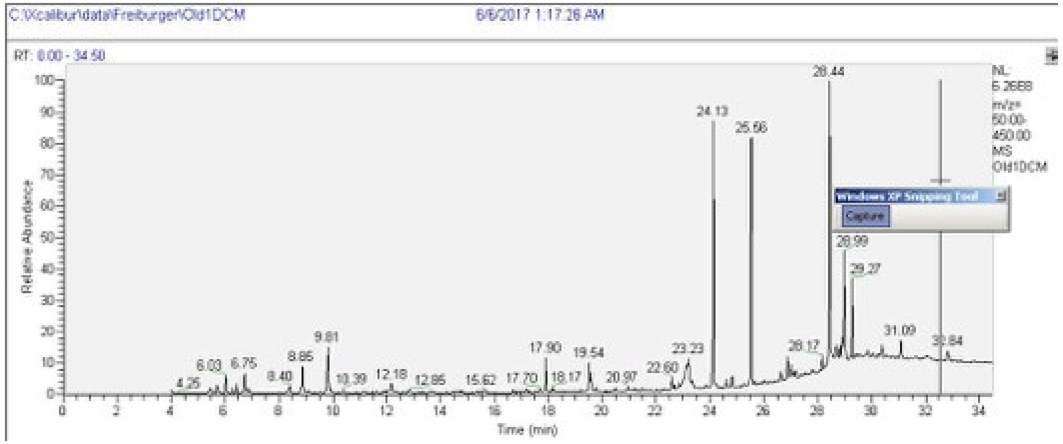
Sample	Acetone % extraction	Hexanes % extraction	Ethanol % extraction	DCM % extraction
Old Mixed	10.46	3.87	12.31	1.99
Wild	ND	3.55	11.05	1.69

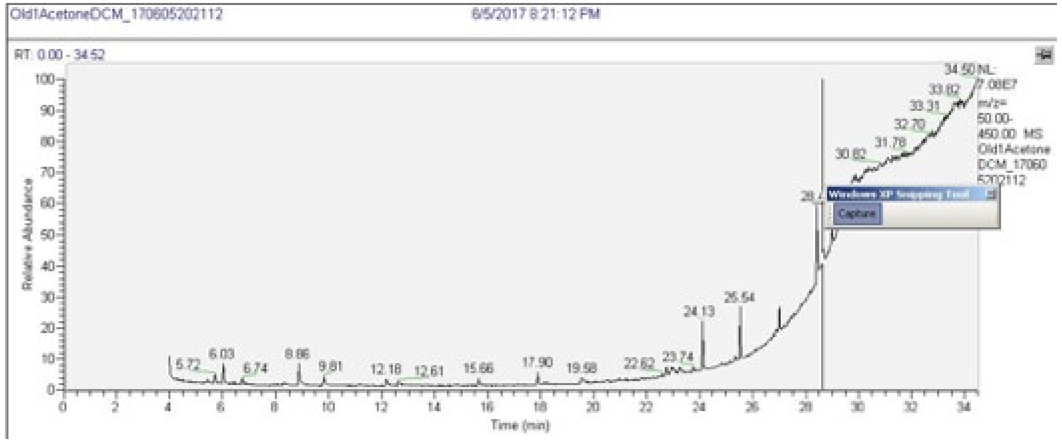
GC Spectra of Soxhlet extracts

Hexanes

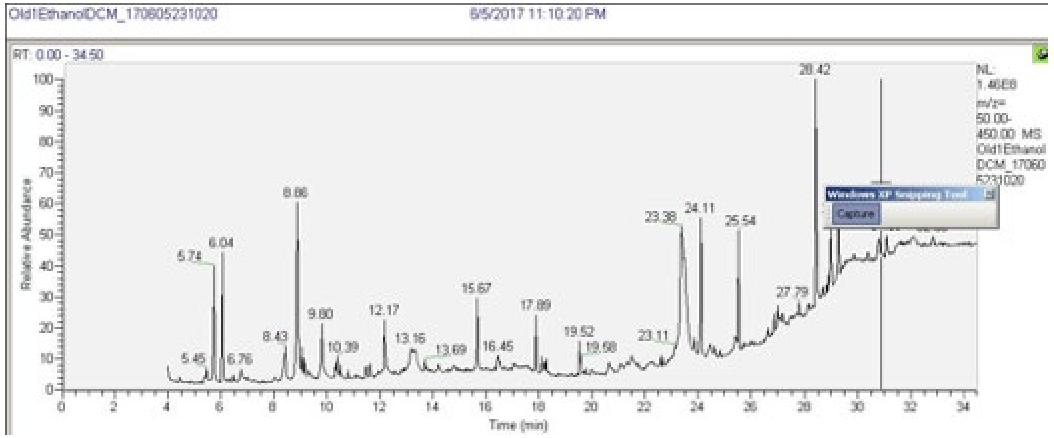


DCM





Acetone



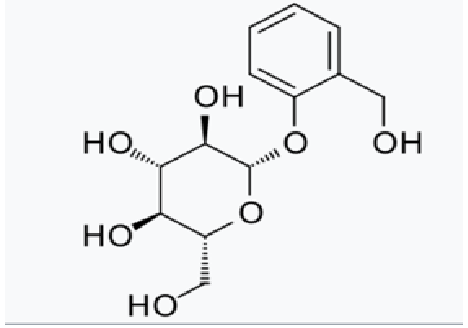
Ethanol

Extractable from different species

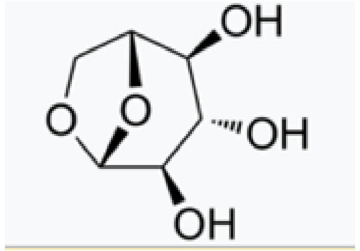
Sample	Average % extraction with ethanol	Standard Deviation
Old Mixed	12.31	
Wild	11.05	
Fishcreek	9.84	1.07
Fabius	11.22	0.90
Millbrook	10.72	0.70
SX64	12.42	0.40

SX64 has the greatest extractable concentration

Relative abundances via quantitative GC-MS



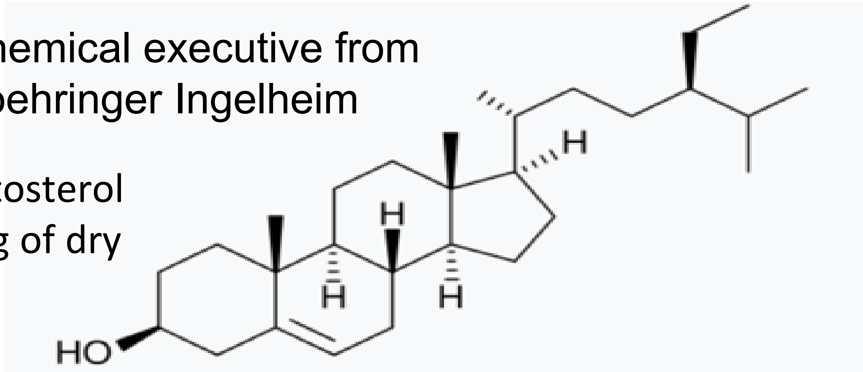
Salicin



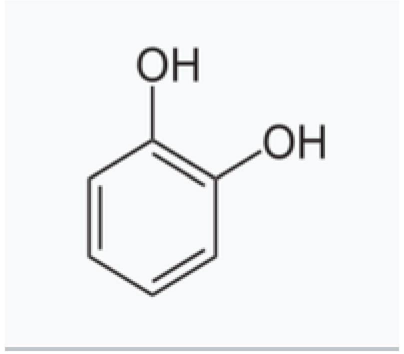
Levoglucosan

~1.5g sitosterol per 100g of dry fabius

Chemical executive from Boehringer Ingelheim



Sitosterol

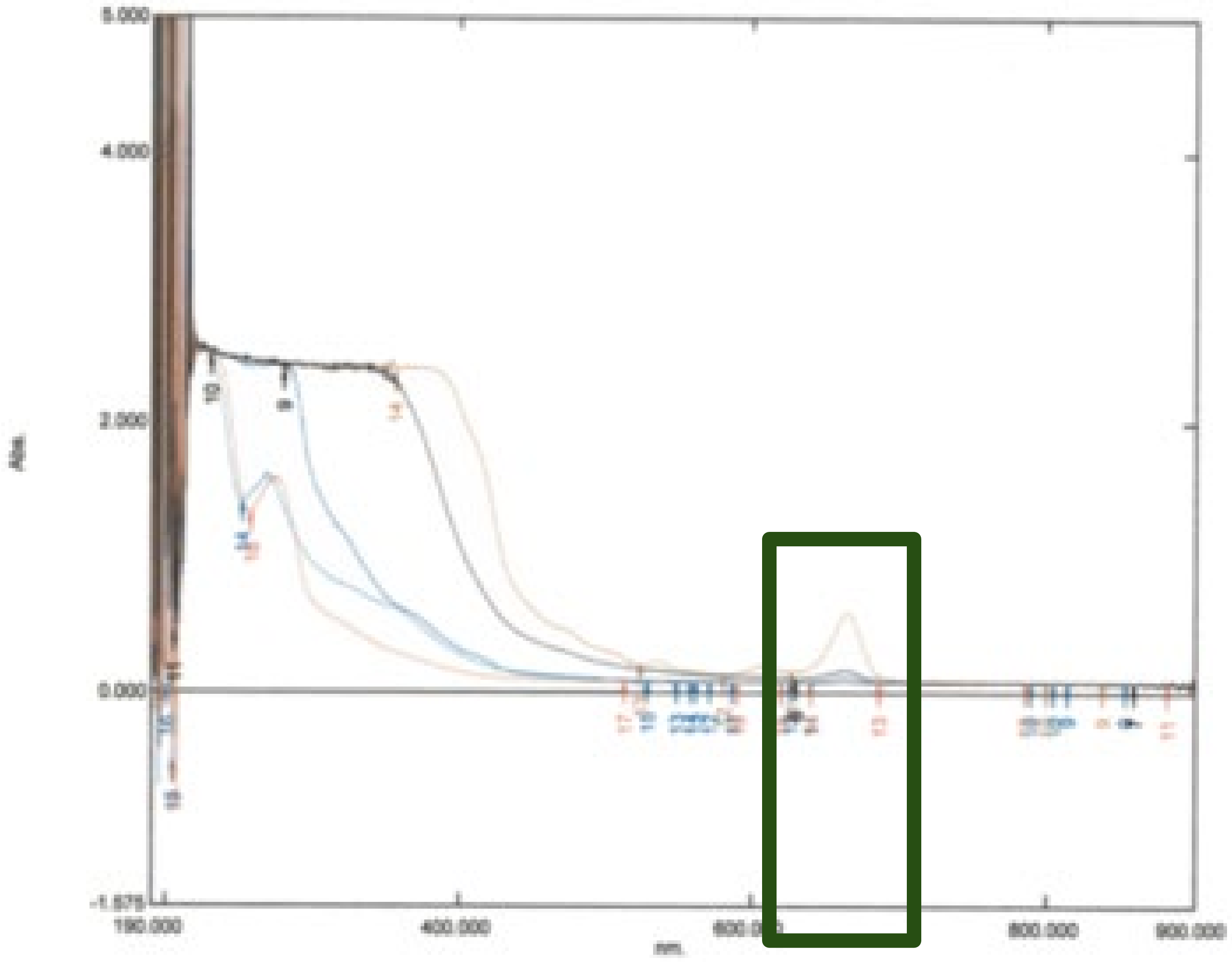


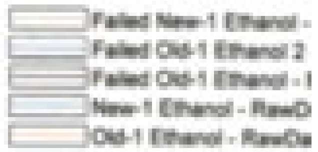
Catechol

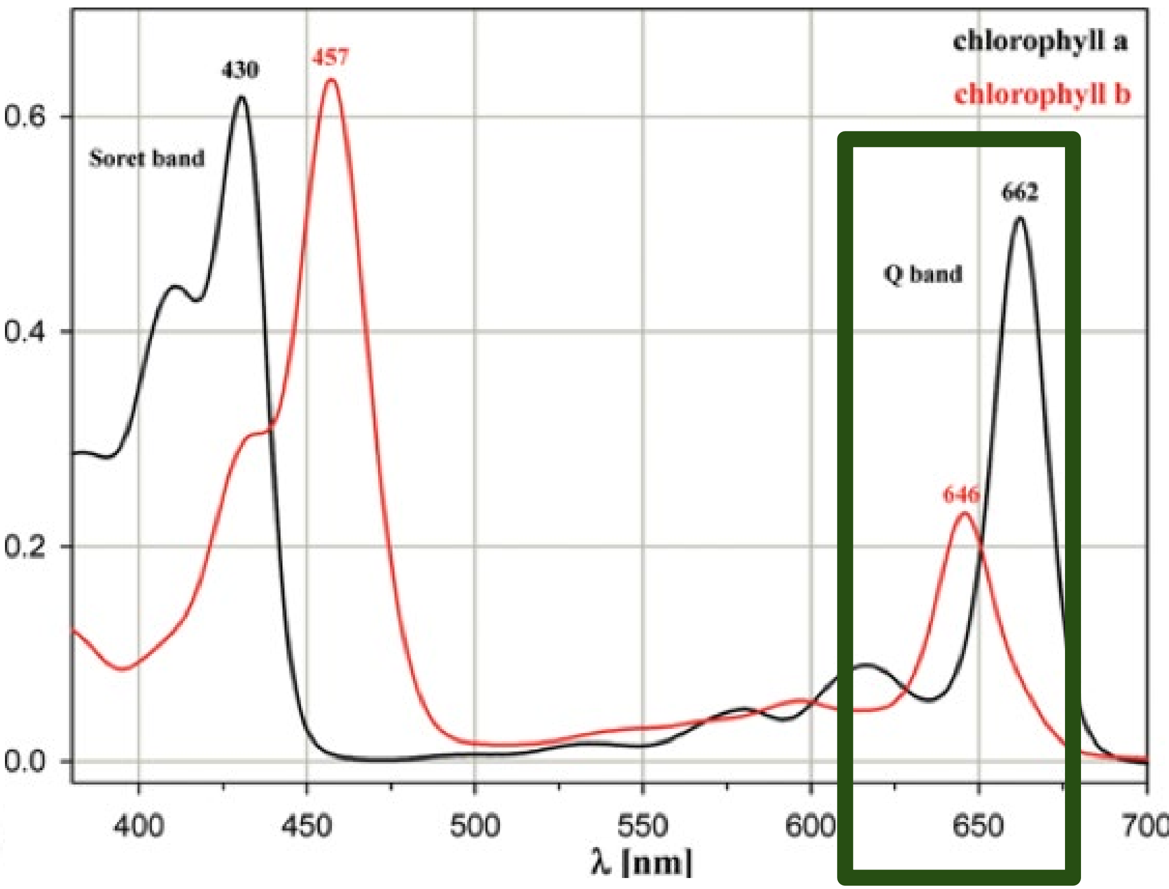
Compound / Sample	Catechol	Salicylic alcohol	2-hydroxy-Aceto-phenone	Levoglucosan	4-propeny syringol	Salicin	Heptacos-ane	c-Sitosterol	α-Amyrin	Astaxanthin
SX-64	8.52	3.76	10.09	9.68	3.73	22.23	ND	9.37	**1.97**	2.96
Fishcreek	4.03	2.86	ND	9.33	**1.88**	40.79	3.89	9.90	3.41	2.15
Millbrook	5.06	3.09	4.10	**0.75**	4.82	31.81	1.74	9.85	3.66	3.62
Fabius	9.55	2.27	5.14	10.35	5.29	14.04	2.89	**13.73**	3.02	2.29

Soxhlet UV-Vis analysis

Makarska-Bialokoz, Magdalena; Agniezka A. Kaczor. Computational analysis of chlorophyll structure and UV-Vis spectra: A student research project on the spectroscopy of natural complexes. **2014**.*Spectroscopy Letters*. 47, 147-152.







Organic extraction Brauns' lignin

- Depolymerization of lignin during hot ethanol extraction [Braun, **1939**].

Resembles protolignin (immature)

Precipitation

F. E. Brauns. Native Lignin I: Its isolation and methylation. *Journal of American Chemical Society*. **1939**. 61(8), 2120-2127.

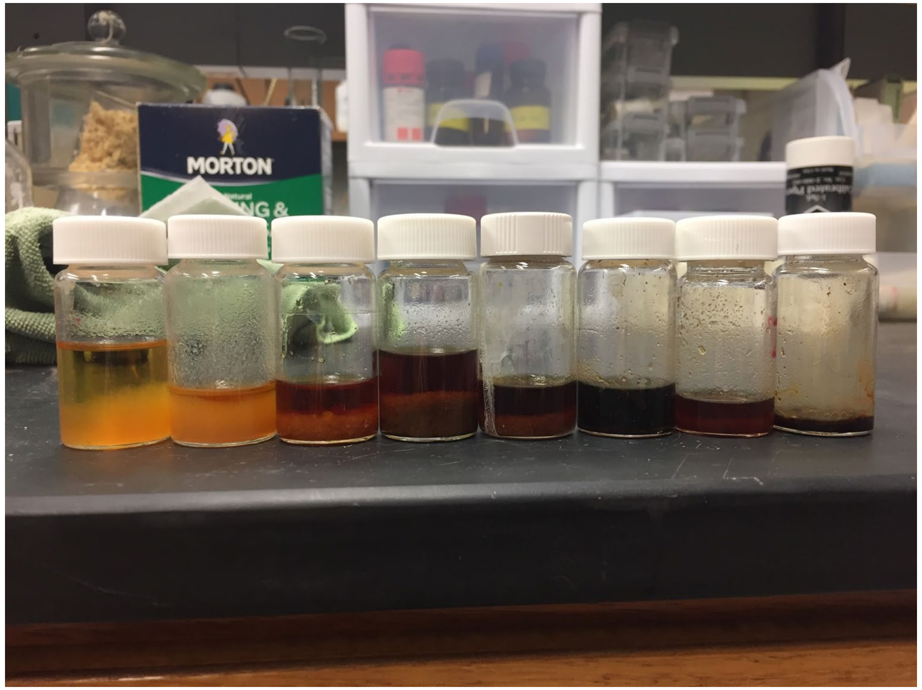
Kraft processing

0%, 5%, 10%, and 15% sodium hydroxide solutions were heated to boiling

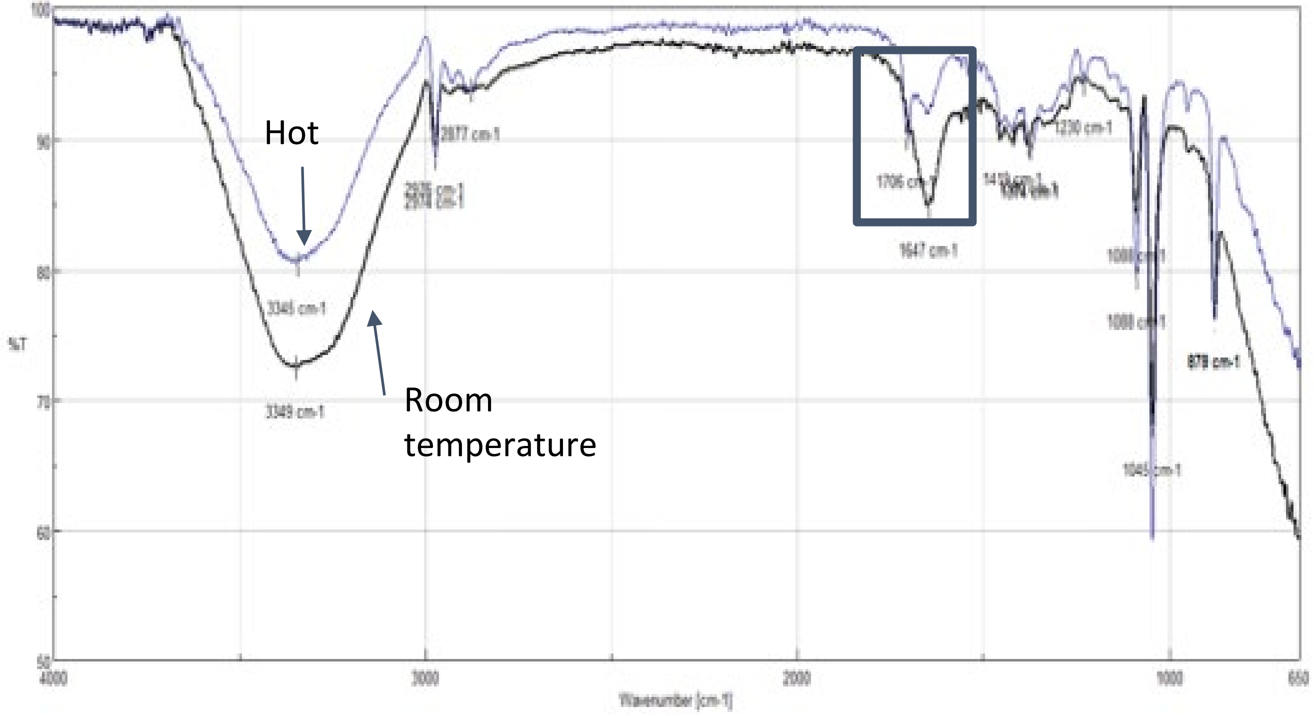
10 mL aliquots of each solution were added to two vials, each with 5g sample.

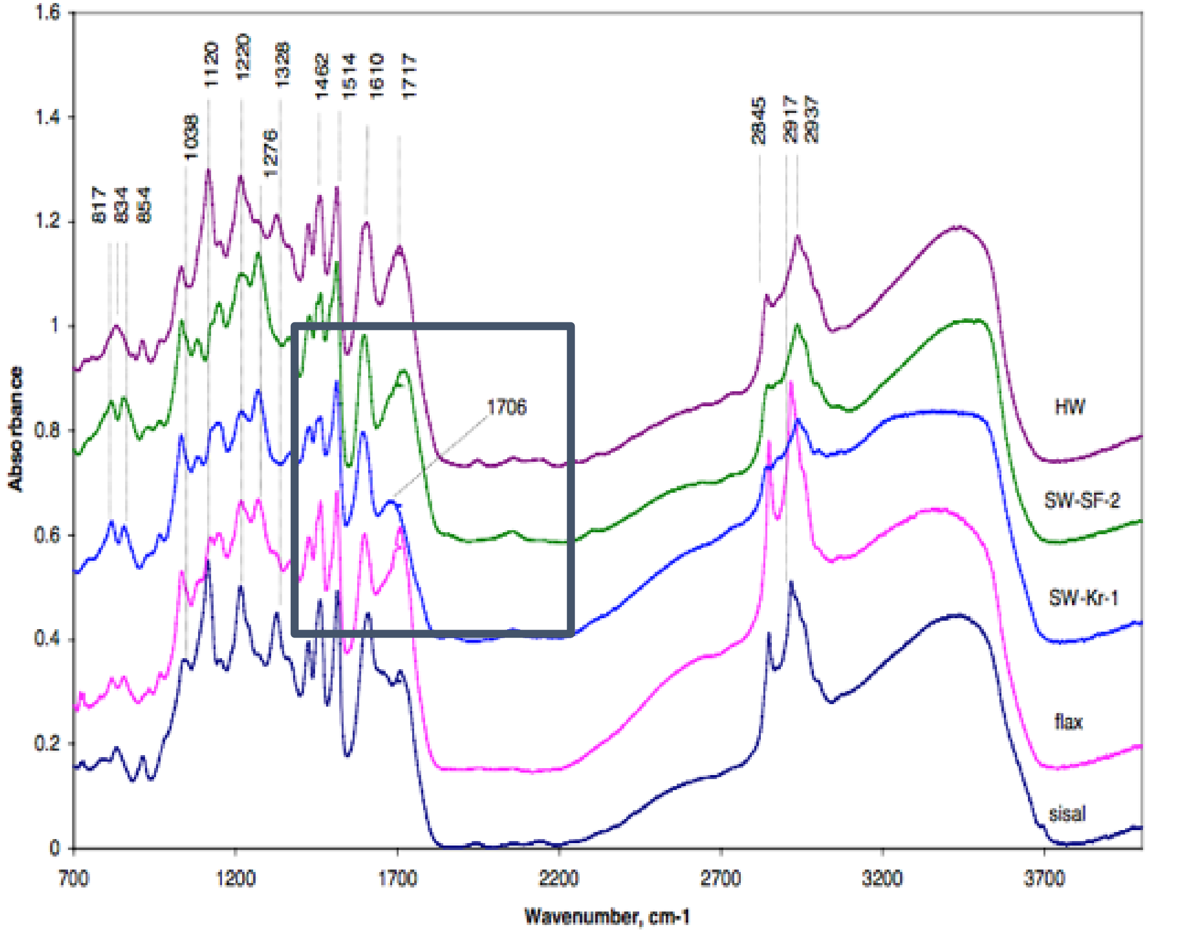
- one vial: heated below boiling for 2-4 hours
- the second vial: room temperature

The filtrate was separated after 20-80 hours of stirring at room temperature.



Kraft depolymerization





- Samples treated with 10% NaOH

- Literature data: same peak for kraft-treated wood (SW-Kr-1 = soft wood Kraft 1)
- C. G. Boeriu, D. Bravo, R. J. A., J. E. G. van Dam. Characterization of structure-dependent functional properties of lignin with infrared spectroscopy. *Industrial Crops and Products*, **2004.** 20, 205-218.

Adapting for the classroom

Interdisciplinary Chemical project

- Organic, green, physical, environmental, and analytical chemistries

Organic Chemistry

- Steam distillation, Soxhlet extraction, UV-Vis spectroscopy, and GCMS
  - Soxhlet extraction vs steam distillation
  - Solvent comparison for Soxhlet extraction

Physical Chemistry

- Bomb calorimetry for enthalpy of combustion

Adapting for the classroom

Analytical/Environmental Chemistry

- Moisture and ash content
- Analytical techniques: e.g. sample massing, instrumentation, and calculations of percent change and statistical analyses.
- Elemental analysis (future work)
  - Procedure: dissolve ash in hot acid and subsequently analyze with ICP-MS

Microbiology/Biotechnology

- Synthesis of ethyl salicylate via wild microbiota fermentation

Genetics

- Investigating heredity of metabolite production

Conclusions

Undergraduate experiments were devised (no student data)

- Introduce natural lignocellulosic polymers, renewable feedstocks for monomers, biorefinery concepts, and systems-level thinking

- Green chemistry metrics and laboratory techniques

- Single experiments or multidisciplinary projects

Conclusions

<u>Fishcreek</u> appears to be preferable for biorefinery: lowest ash and moisture.

<u>SX64</u> possesses the greatest concentration of extractable content

<u>Fabius</u> possesses the greatest concentration of Sitosterol

<u>Millbrook</u> appears to be preferable as a fuel: highest enthalpy of combustion

Hot ≥10% alkaline solution are supported to delignify willow lignocellulose

Air-drying sample can reduce % moisture without affecting % extractable

Willow appears to be a promising alternative feedstock

The rest is still unwritten

Natasha Bedingfield

Apply in labs to acquire student data

Derivatize high-value chemicals

Pyrolysis

- Potential industry partner (D. Prouty, Heat Transfer International)

ICP-MS of ash for Bioremediation

Depolymerize cellulose

Acknowledgements

- Dalila Kovacs
- Jim Krikke
- Erik Nordman
- Michelle
- Laurie Witucki
- George McBane
- Diane Laughlin

Appendix

Ubiquitous biomass

Etc...

Green Chemistry metrics

Roger A. Sheldon. The E factor: fifteen years on. **2007**. *Green Chemistry*. 9(12), 1261-1384.

E-factor – Waste mass (kg) : Product mass (kg)

- E.g. Soxhlet extraction
  - Rotavaped ethanol is GC-MS pure: i.e. recyclable and not waste
  - Biomass residues may be considered waste

Reaction Mass Efficiency – Product mass (kg) : Reactant mass (kg)

- E.g. Alkaline kraft treatment
  - Product is lignin

Polymerization literature for cellulosic-derivatives

Succinic acid: Inna Bechthold; Karlheinz Bretz; Stephan Kabasci; Rodion Kopitzky; Andrea Springer. Succinic Acid: A new platform chemical for biobased polymers from renewable resources. **2008**. *Chem. Eng. Technol.* 31(5), 647-654

Glucaric acid: Donald E. Kiely; Liang Chen; Tsu-Hsing Lin. Hydroxylated nylons based on unprotected esterified D-Glucaric acid by simple condensation reactions. **1994**. *J. Am. Chem. Soc.* 116, 571-578

Itaconic acid: P. Lanthong; R. Nuisin; S Kiatkamjornwong. Graft copolymerization, characterization, and degradation of cassava starch-g-acrylamide/itaconic acid superabsorbents. **2006**. *Carbohydrate Polymers.* 66, 229-245

Levulinic acid: Joseph J. Bozell; L. Moens; D.C. Elliott; Y. Wang; G.G. Neuenscwander; S.W. Fitzpatrick; R.J. Bilski; J.L. Jarnefeld.Production of levulinic acid and use as a platofrm chemical for derived products. **2000**. *Resources, Conservation, Recycling.* 28, 227-239

Aspartic acid: Masayuki Yokoyama; Mizue Miyauchi; Noriko Yamada; Teruo Okano; Yasuhisa Sakuari; Kazunori Kataoka; Shohei Inoue. Polymer micelles as novel drug carrier: Adriamycin-conjugated poly(ethylene glycol)-poly(aspartic acid) block copolymer. **1990**. *Journal of Controlled Release.* 11, 269-278

Glutamic acid: Chun Li. Poly(L-glutamic acid)–anticancer drug conjugates. **2002**. *Advanced Drug Delivery Reviews.* 54, 695-713.

Polymerization literature for cellulosic-derivatives

3-hydroxypropionic acid: Donghui Zhang; Marc A. Hillmyer; William B. Tolman. A new synthetic route to poly[3-hydroxypropionic acid] (P[3-HP]): Ring-opening polymerization of 3-HP macrocyclic esters. **2004**. *Macromolecules.* 37, 8198-8200.

Xylitol: Joost P. Bruggeman; Christopher J. Bettinger; Christian L.E. Nijst; Daniel S. Kohane; Robert Langer. Biodegradable Xylitol-based polymers. **2008**. *Advanced Materials.* 20, 1922-1927

Sorbitol: Hiroshi Uyama; Ellen Klegraf; Satoshi Wada; Shiro Kobayashi. Regioselective polymerization of sorbitol and divinyl sebacate using lipase catalyst.. **2000**. *Chemistry Letters.* 800-801

Glycerol: Somaieh Salehpour; Marc A. Dubé. Reaction monitoring of glycerol step-growth polymerization using ATR-FTIR spectroscopy. **2012**. *Macromolecular Reaction Engineering.* 6, 85-92

3-hydroxybutyrolactone: Furkan H. Isikgoe; C. Remzi Becer. Lignocellulosic biomass: a sustainable platform for production of bio-based chemicals and polymers. **2015**. *Polymer Chemistry.*

2,5-hydroxyfurandicarboxylic acid: A. F. Sousa; C. Vilela; A. C. Fonseca; M. Matos; C. S. R. Freire; G. iJ. M. Gruter; J. F. J. Coelho; Armando J. D. Silvestre. Biobased polyesters and other polymers from 2,5-furandicarboxylic acid: a tribute to furan excellancy. **2015**. *Polymer Chemistry.*

Instrumentation

- Labconco Freezone Lyophilizer
- Heratherm Thermo Scientific oven
- Thermo Focus DSQ GC-MS
- Jasco 4100 FTIR with a Pike ATR.
- Thermo Scientific Nicolet is5 FTIR with an id7 ATR

GCMS settings

Instrument setting	**Instrument value**
Column	ThermoScientific TG-5ms (5% diphenyl, 95% dimethyl polysiloxane)
Column dimensions	15m x 0.25mm, 0.5 um film
Inlet temperature (°C)	220
Mass spectra transfer line (°C)	250
Split flow ()	42
Split ratio	1:42
Mobile phase ()	1.0 of Helium
JKEoil	
Oven temperature (°C)	50°C for 2 mins, to 250°C, 250°C for 5 minutes
JKEoilht	
Oven temperature (°C)	40°C for 2 mins, to 325°C, 325°C for 2 minutes

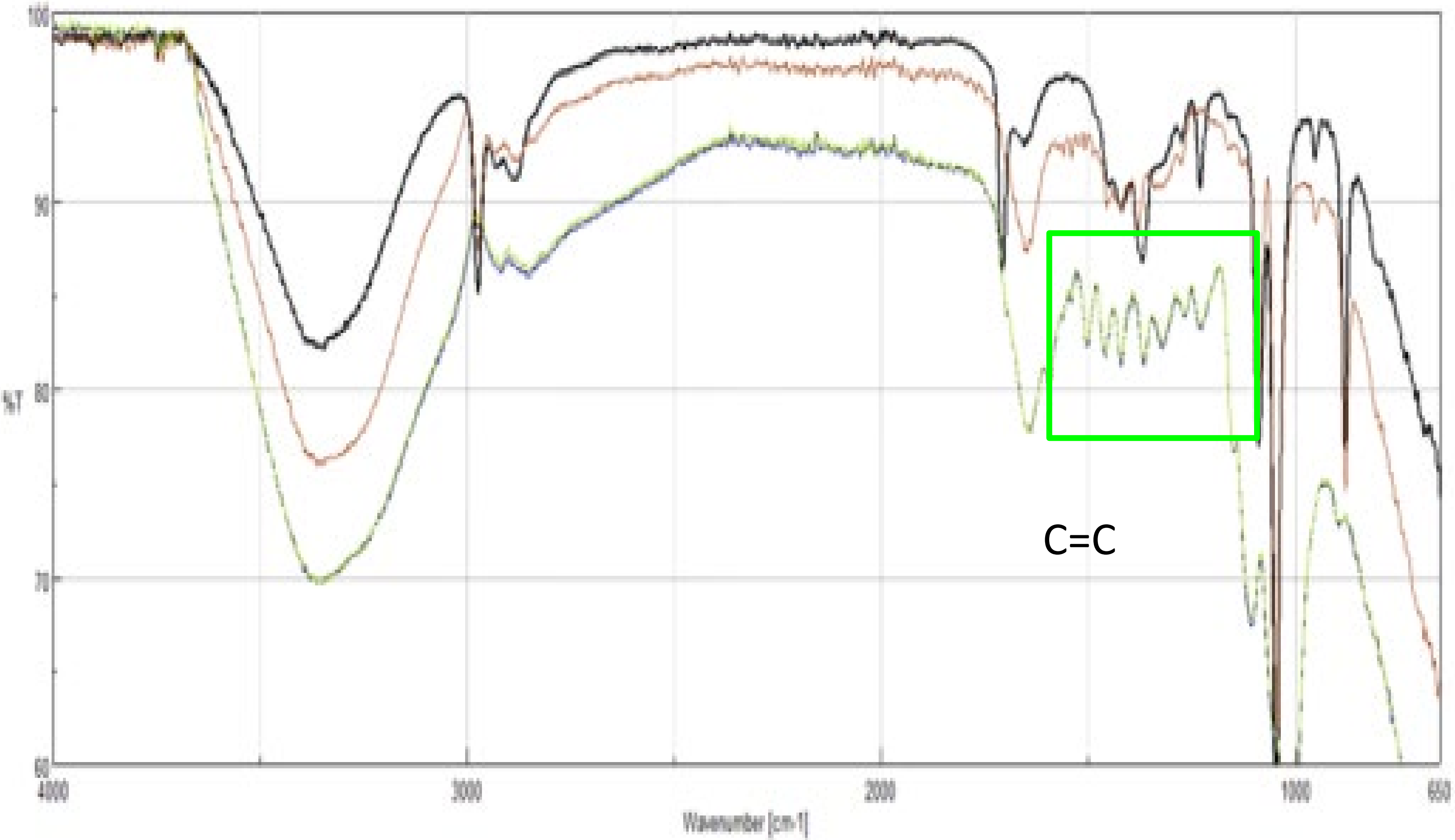
Why high value chemicals in lieu of biofuels?

By Professional Sun Clouds Blue Sky background stock photos, license under CC0 Public Domain

hv

By AleSPA, https://en.wikipedia.org/wiki/Solar_panel#/media/File:Photovoltaik_Dachanlage_Hannover_-_Schwarze_Heide_-_1_MW.jpg, is licensed under CC BY-SA

Kraft depolymerization

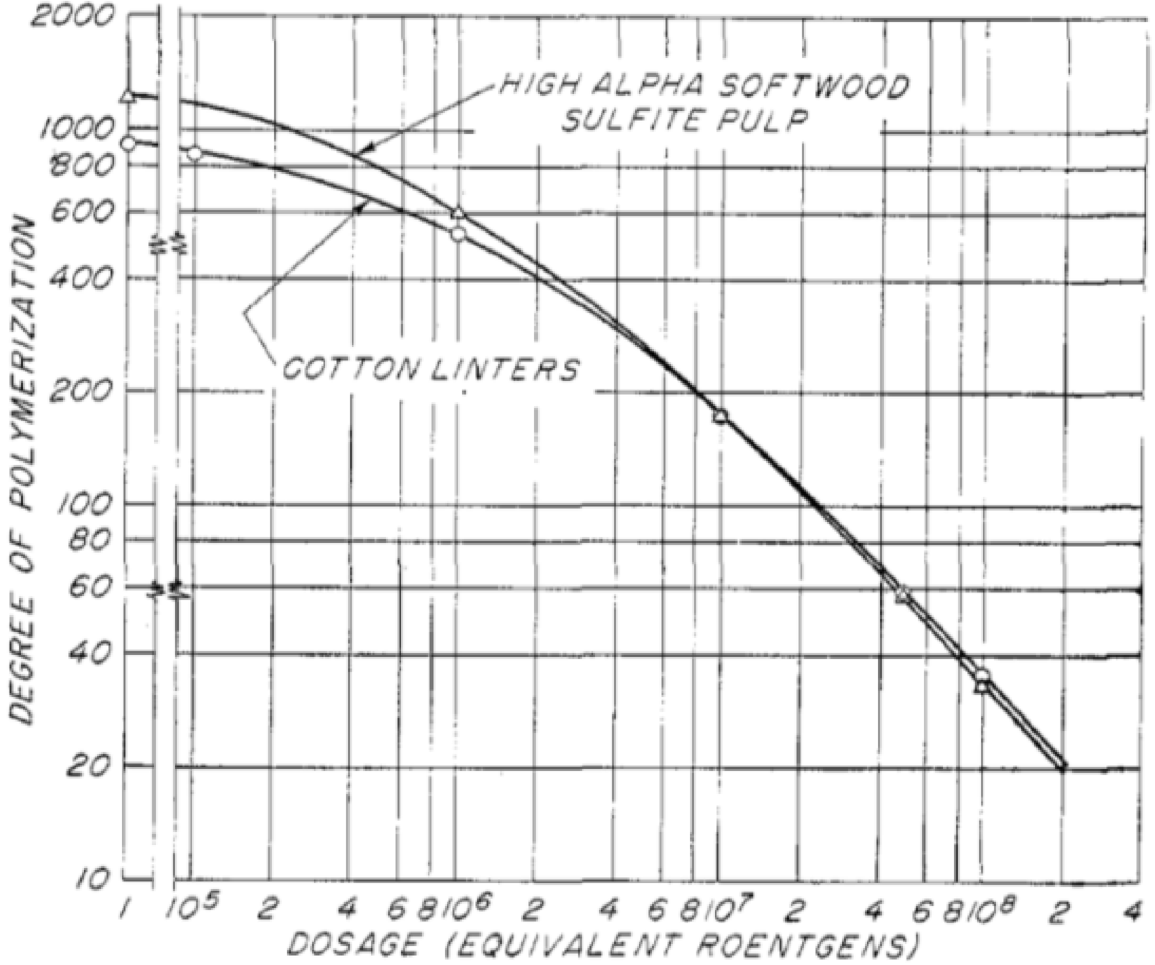


- X906 15%
- black = hot
- red = RT
- Green = RT solid
- Blue = hot solid

Cathode ray

- 800 kv peak voltage and 143,000 roentgens (1 R = 2.58E-4 C/kg) per second @ a distance of 10 cm.
- 5E8 roentgens produced water soluble derivatives of cellulose (~400 gray – chemo treatments are ~20-60 gray).

  - Wood pulp hydrolyzed quicker than cotton
  - >70% glucose yield after acid hydrolysis



Xyleco

Jerome F. Saeman, Merrill A. Millett, Elliott J. Lawton. Effect of high energy cathode rays on cellulose. *Industrial Engineering Chemistry*. **1952**, 44(12), 2848-2852.

Gasification

- Between combustion (100% oxygenating environment) and pyrolysis (0% oxygenating environment).
  - Water, volatiles (oil if cooled), and fixed carbon (i.e. coal).

- Thermally degrades
  - Distills separately hemicellulose, cellulose, and lignin at different temperatures

- Syn-gas, town gas, imbert cars in WWII

Bundesarchiv, Bild 183-V00670A
Foto: o.Ang. | 1946

https://www.lowtechmagazine.com/2010/01/wood-gas-cars.html

Enzymes

- Cellulose: cellulases
- Lignin: Lignolytic peroxidases (heme peroxidase)

Francisco J. Ruiz-Dueñas and Ángel T. Martínez. Microbial degradation of lignin: how a bulky recalcitrant polymer is efficiently recycled in nature and how we can take advantage of this. *Microbial Biotechnology*, **2009**, 2(2), 164-177.

- Cons:
  - High dilution is required
  - Generally slow reactivity
  - Costly to produce

- Pros:
  - Optimum selectivity
  - low waste

Deep Eutectic Solvents (DES)

~90% pure lignin with >70% yields from woody biomass

Carlos Alvarez-Vasco; Ruoshui Ma; Melissa Quintero; Mond Guo; Scott Geleynse; Karthikeyan K. Ramasamy; Michael Wolcott; Xiao Zhang. Unique low-molecular-weight lignin with high purity extracted from wood by deep eutectic solvents (DES): a source of lignin for valorization. *Green Chem*, **2016**, 18, 5133-5144.

DES lewis/bronsted acids and bases that create a eutectic system

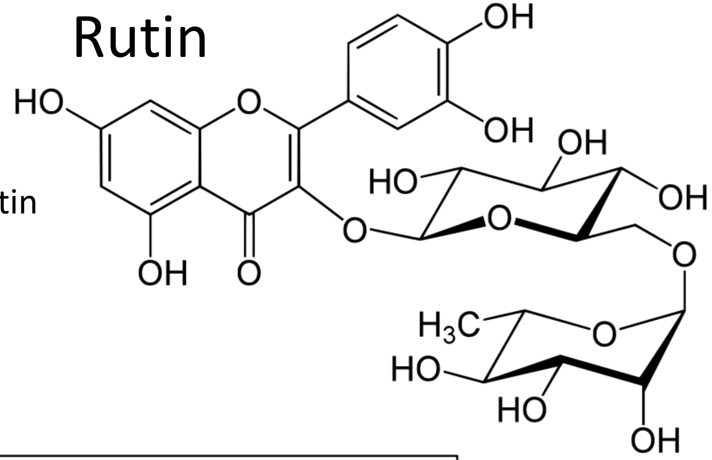
- Choline chloride (MP = 303°C) and Urea (MP = 134°C) 1:2 creates DES (MP = 12°C)

Emma L. Smith, Andrew P. Abbott, and Karl S. Ryder. Deep Eutectic Solvents (DESs) and their applications. *Chemical Reviews*. **2014.** 114, 11060-11082.

Ionic liquid (liquid salts at room temperature)

Natural Deep Eutectic Solvents

Flavonoid
Rutin

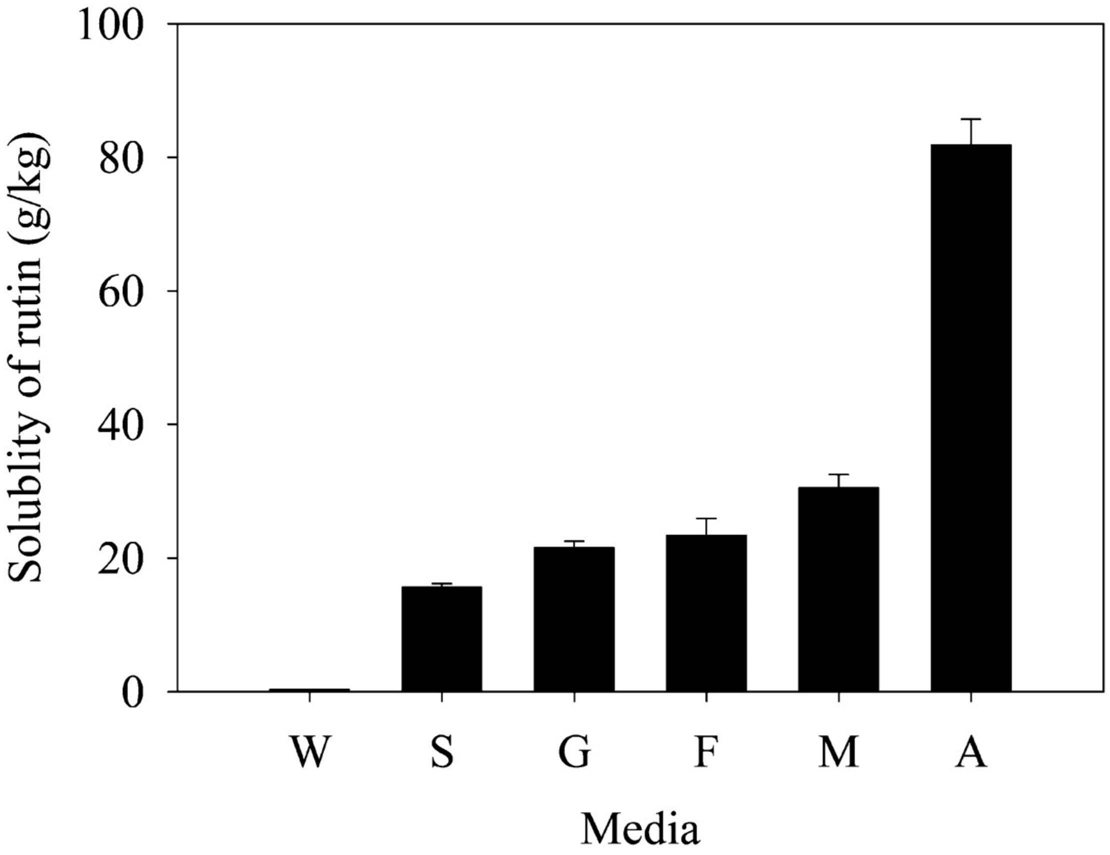


Yikrazuul,
https://en.wikipedia.org/wiki/Rutin

- Proposed third phase of life: water, lipids, and "natural" deep eutectic solvents [Choi et al., 2011].

W = water
S = Sucrose-choline chloride
G = Glucose-choline chloride
F = Fructose-choline chloride
M = Malic acid-choline chloride
A = Aconitic acid-choline chloride

[Choi et al., 2011]



Young Hae Choi, Jaap van Spronsen, Yuntao Dai, Marianna Verberne, Frank Hollmann, Isabel W.C.E. Arends, Geert-Jan Witkamp, and Robert Verpoorte. Are natural deep eutectic solvents the missing link in understanding cellular metabolism and physiology?.*Plant Physiology.***2011**. 156, 1701-1705.

Citations for the fertilizer data table

Yang, Hong; Yuan Zhou; and Junguo Liu. Land and water requirements of biofuel and implications for food supply and the environment in China. *Energy Policy*, **2009**, 37, 1876-1885.

USDA. Annual and Perennial crop list. **1985**.

NASS-USDA. 2016 Argicultural chemistry use survey – Corn. *USDA*.**2016**.

Heller, Martin C.; Gregory A. Keoleian; Timothy A. Volk. Life cycle assessment of a willow bioenergy cropping system. *Biomass and Bioenergy*. **2003**. 25, 147-165.

Liska, Adam J.; Haishun S. Yang; Birgil R. Bremer; Terry J. Klopfenstein; Daniel T. Walters; Galen E. Erickson; Kenneth G. Cassman. Improvements in life cycle energy efficiency and greenhouse gas emmisions of corn-ethanol. **2009**. *Journal of Industrial Ecology*. 13(1), 58-74.

Hytönen, Jyrki. Effect of fertilizer treatment on the biomass production and nutrient uptake of short-rotation willow on cut-away peatlands. *Silva Fennica*. 29(1), 21-40.

Anthropocene => new geologic age

Simon L. Lewis and Mark A. Maslin. Defining the Anthropocene. *Nature*, **2015**, 519, 171-180.

- Contaminating ecosystems
  - New world meet Old world (e.g. tomatoes in Italy, potatoes in Ireland, wheat in Americas)

- Agriculture
  - The Haber-Bosch process has created the greatest disturbance in the nitrogen cycle since microbial equilibrium was establish 2.5 billion years ago

    Donald E. Canfield, Alexander N. Glazer, Paul G. Falkowski. The evolution and future of Earth's nitrogen cycle. *Science*. **2010**, 330, 192-196

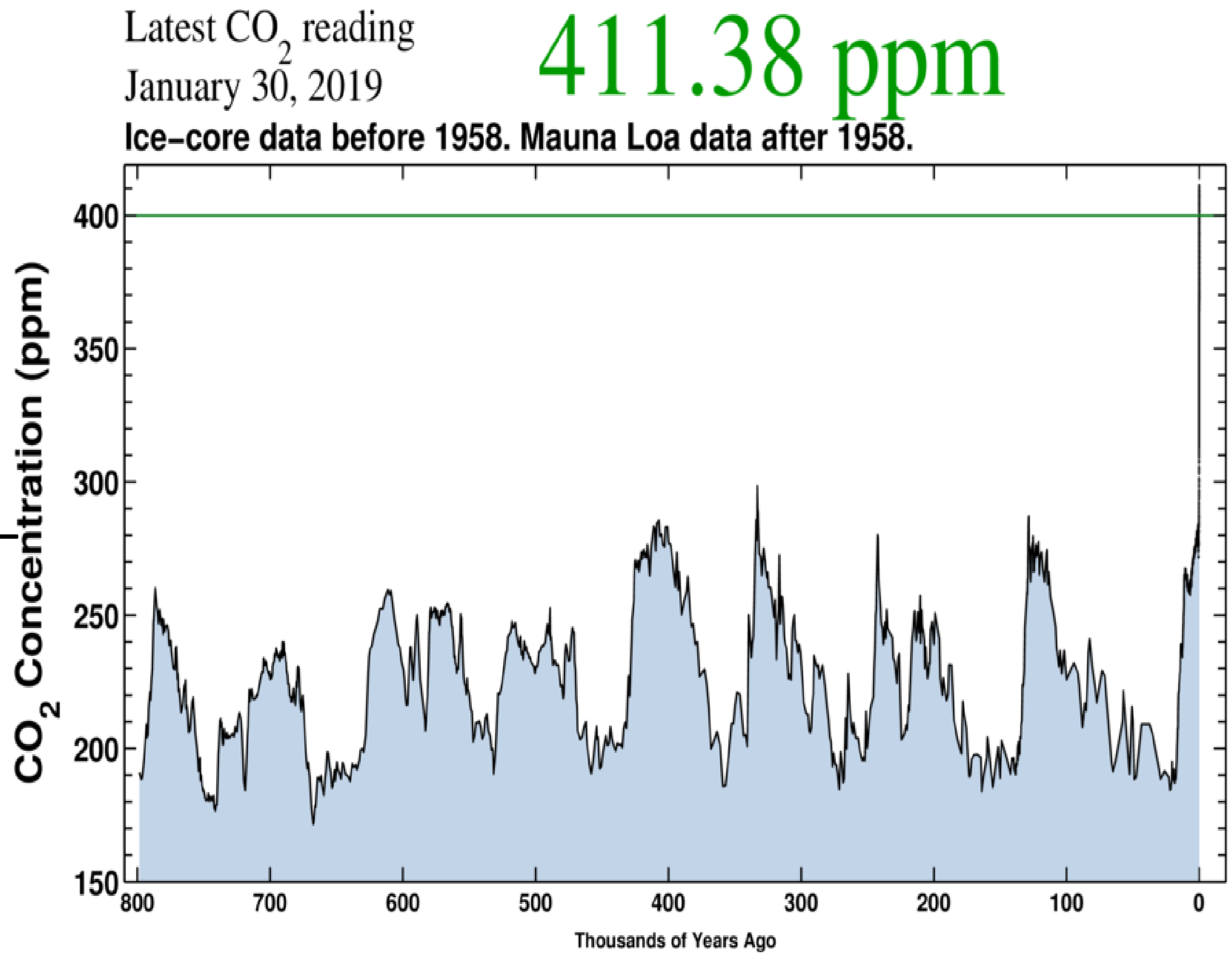
- Industrial pollution
  - Plastic, nuclear, PFAS, ethylene oxide, et cetera

Global climate change

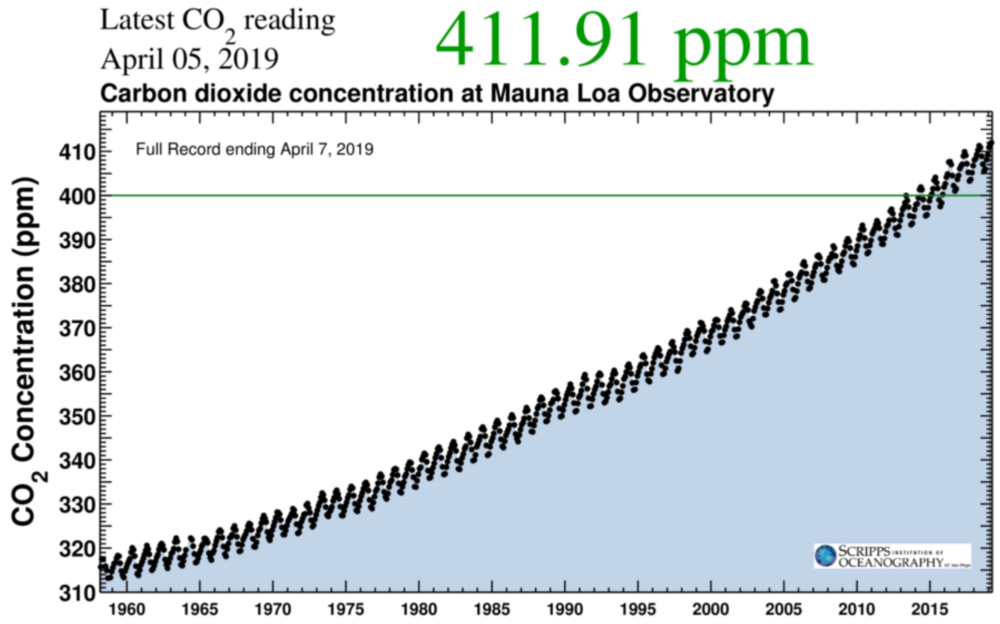
"High confidence" of reaching 1.5°C above pre-industrial levels between 2030 and 2052 at the current rate [IPCC, 2018].

Intergovernmental Panel on Climate Change (IPCC). Global Warming of 1.5°C. **2018**

Lower photosynthetic rate —> lower food security



https://scripps.ucsd.edu/programs/keelingcurve

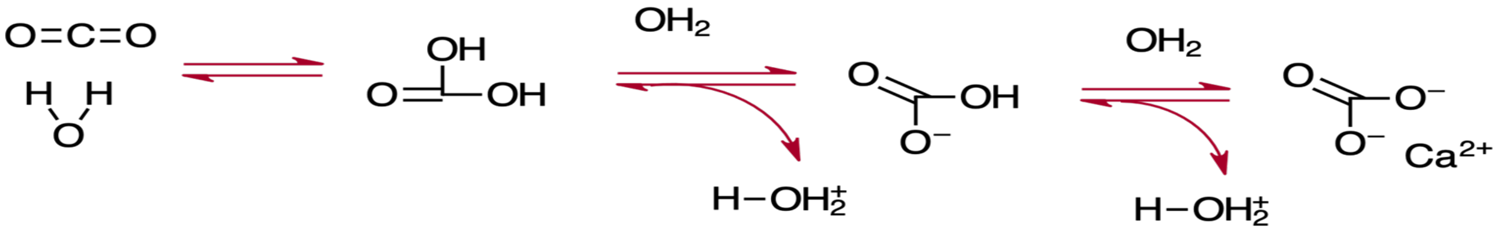


Miocene

Paul N. Pearson and Martin R. Palmer. Atmospheric carbon dioxide concentrations over the past 60 million years. *Nature*. **2000**, 406, 695-699.

Mass extinction (6th)

- 1000x to 10,000x preindustrial [De Vos et al., 2014].
    - Greatest in 65 million years
- Coral reefs – home to ~32% of all marine species [Costello, 2015] – may be extinct by 2100 [Carpenter et al., 2008]; >99% extinction @ 2°C warming [IPCC, 2018].



Acropora, https://en.wikipedia.org/wiki/Coral_bleaching#/media/File:Bleachedcoral.jpg

Gerardo Ceballos, Paul R. Elrlich, Anthony D. Bamosky, Andrés García, Robert M. Pringle, Todd M. Palmer. Accelerating modern human-induced species losses: Entering the sixth mass extinction. *Environmental Sciences*, **2015**.

Jurriaan M. De Vos, Lucas N. Joppa, John L. Gittleman, Patrick R. Stephens, Staurt L. Pimm. Estimating the normal background rate of species extinction. *Conservation Biology*. **2014**, 29(2), 452-462

Rodolfo Dirzo, Hillary S. Young, Mauro Galetti, Gerardo Ceballos, Nick J. B. Isaac, Ben Collen. Defaunation in the Anthropocene. *Science*. **2014**, 345 (6195), 401-406

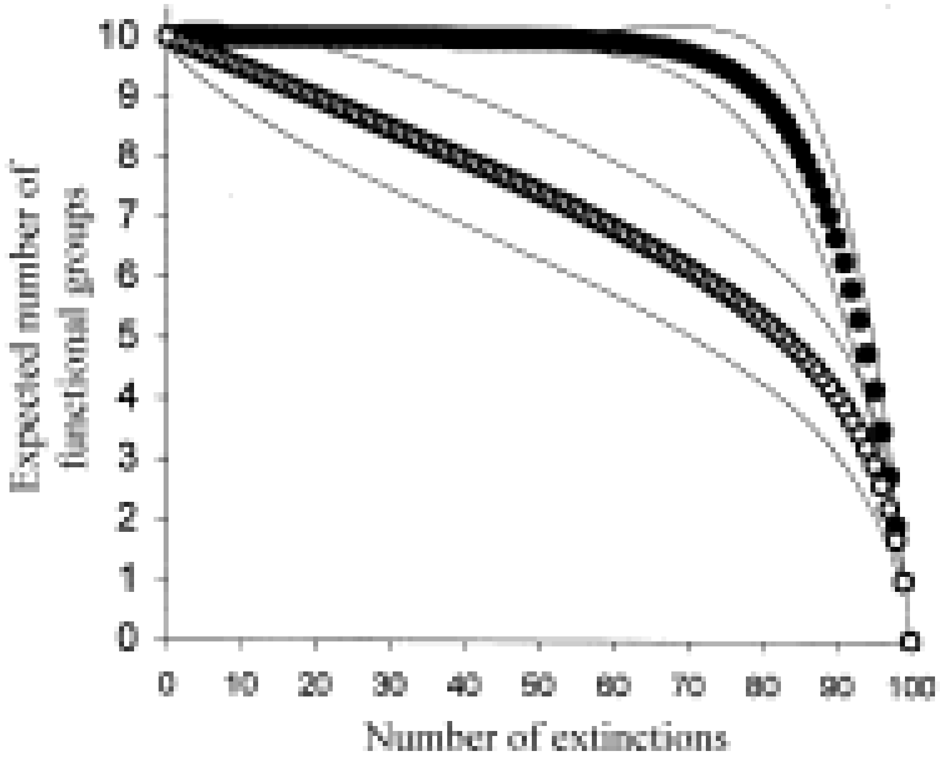
Mark J. Costello. Biodiversity: the known, unknown, and rates of extinction. *Current Biology*.**2015**, 25, 368-371.

Kent E. Carpenter, Muhammad Abrar, Greta Aeby, Richard D. Aronson, Stuart Banks, Andrew Bruckner, Anglet Chiriboga, Jorge Cortés, J. Charles Delbeek, Lyndon DeVantier, Graham J. Edgar, Alasdair J. Edwards, Douglas Fenner, Héctor M. Guzmán, Bert W. Hoeksema, Gregor Hodgeson, Ofri Johan, Wilfredo Y. Licuanan, Suzanne R. Livingstone, Edward R. Lovell, Jennifer A. Moore, David O. Obura, Domingo Ochavilla, Beth A. Polidoro, William F. Precht, Miledel C. Quibilan, Clarissa Reboton, Zoe T. Richards, Alex D. Rogers, Jonnell Sanciangco, Anne Sheppard, Charles Sheppard, Jennifer Smith, Simon Stuart, Emre Turak, John E. N. Veron, Carden Wallace, Ernesto Weil, Elizabeth Wood. One-third of reef-building corals face elevated extinction risk from climate change and local impacts. *Science*. **2008**, 321, 560-563

Functional redundancy hypothesis

By Narong Khueankaew, royalty-free

- Analogy to janga: each block is a species
  - Loss in biological diversity transpires an accelerating loss in ecological function



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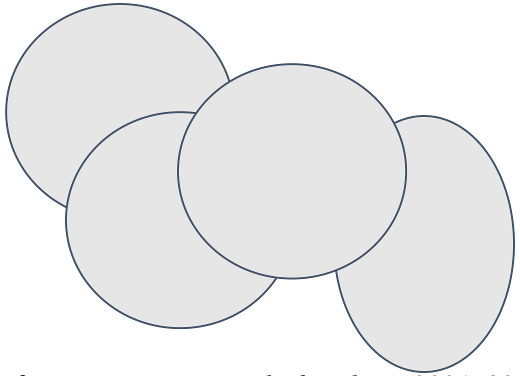

Carlos Roberto Fonseca and Gislene Ganade. Species functional redundancy, random extinctions, and the stability of ecosystems. *Journal of ecology*. **2001**, 89, 118-125.

The evolution of research goal

- Fall 2016 undergraduate research fair
- “Biofuels from willows at the SAP”

Andrew Freiburger <freibura@mail.gvsu.edu> Thu, Oct 6, 2016, 7:12 AM

to nordmane

Hi Dr. Nordman,

I glanced over your renewable energy research at the Undergraduate Research Fair this past week, and I am interested to know more about it and any opportunities that exist for undergraduates. I was told by Youseff at the SAP that some willow trees are apart of your research into biomass energy, however, this is the extent of my knowledge about your research. Let me know if there is anything that I can do or if there is someplace that I should go to learn about your research.

Thanks!

Andrew

- Dr. Witucki —-> Dr. Kovacs <– –> Professor Krikke

- Starting from scratch
  - Develop methods for an undergraduate lab
  - Investigate and characterize willow biomass

Personal contributions => consumer choices

- Reducing Carbon footprint [Jones and Kammen, 2011]
  - Transportation
  - Diet
    - 30% of European greenhouse gas emissions are agricultural [Petrovic, **2015**]
  - Electricity

Jones, Christopher M. and Kammen, Daniel M. Quantifying carbon footprint reduction opportunities for U.S. households and communities. *Environmental Science Technology*. **2011**, 45, 4088-4095

Petrovic, Zoran; Vesna Djordjevic; Dragan Milicevic; Ivan Nastasijevic; Nenad Parunovic. Meat production and consumption: environmental consequences. **2015**. *Procedia Food Science*. 5, 235-238.

Abstract

Biomass, and specially lignocellulose, is very rarely discuss in the chemistry undergraduate curriculum or constitutes the subject of routinely run laboratory experiments. Modeled after an independent undergraduate research project pertaining to valorizing willow-shrub biomass, the proposed lab project has been developed in which students would have the personal opportunity to follow the life-cycle of biomass feedstock from the source, through biorefinery, and to industrial intermediates. The experience will heighten student awareness of a resources' footprint and provide an opportunity to apply green chemistry metrics. The project could be conducted as a series of experiments, or individually integrated into the typical analytical, environmental, or organic lab courses. The flexibility of the experiments enables the usage of any readily available biomass resource. Students will directly harvest the biomass, mechanically process it, characterize the physical properties, and chemically pretreat the samples in steps toward valorization. By performing these experiments, students will employ techniques in determining moisture and ash content; ash elemental analysis via ICP-MS; extractions – from Soxhlet and steam distillation to sub-critical CO_2; IR and GC-MS analyses of the extracts; degradation, like Kraft delignification and pyrolysis; and chemical conversion processes.

These series of experiments, for use individually or holistically, have the potential to contextualize the complexities of evaluating a resource' potential as a biorefinery feedstock, while exploring lifecycle analysis, system-thinking, and green chemistry principles.

Series

Polymers & Plastics in the Classroom: Educational Materials Demonstrating Life Cycle Thinking

The topic of plastics, both society's dependence on them and their effect on human health and the environment, is one that resonates with students of all ages. Plastics are uniquely familiar as materials that, in some cases, can be recycled, yet most are accumulating in alarming quantities on land and in our oceans. New green and sustainable chemistry innovations in polymers and nanomaterials provide compelling lessons to engage learners in systems thinking. This symposium will share educational materials which illustrate components/examples of "closing the loop" through use of renewable feedstocks, green reaction conditions, applications in areas such of remediation or more environmentally-friendly products, and end-of-life considerations such as design for degradation and/or recycling. Case studies will include K-12, undergraduate, and graduate instruction as well are outreach initiatives