

Advanced Biofuels: Back to Fundamentals

Robert C. Brown
Iowa State University
Ames, IA

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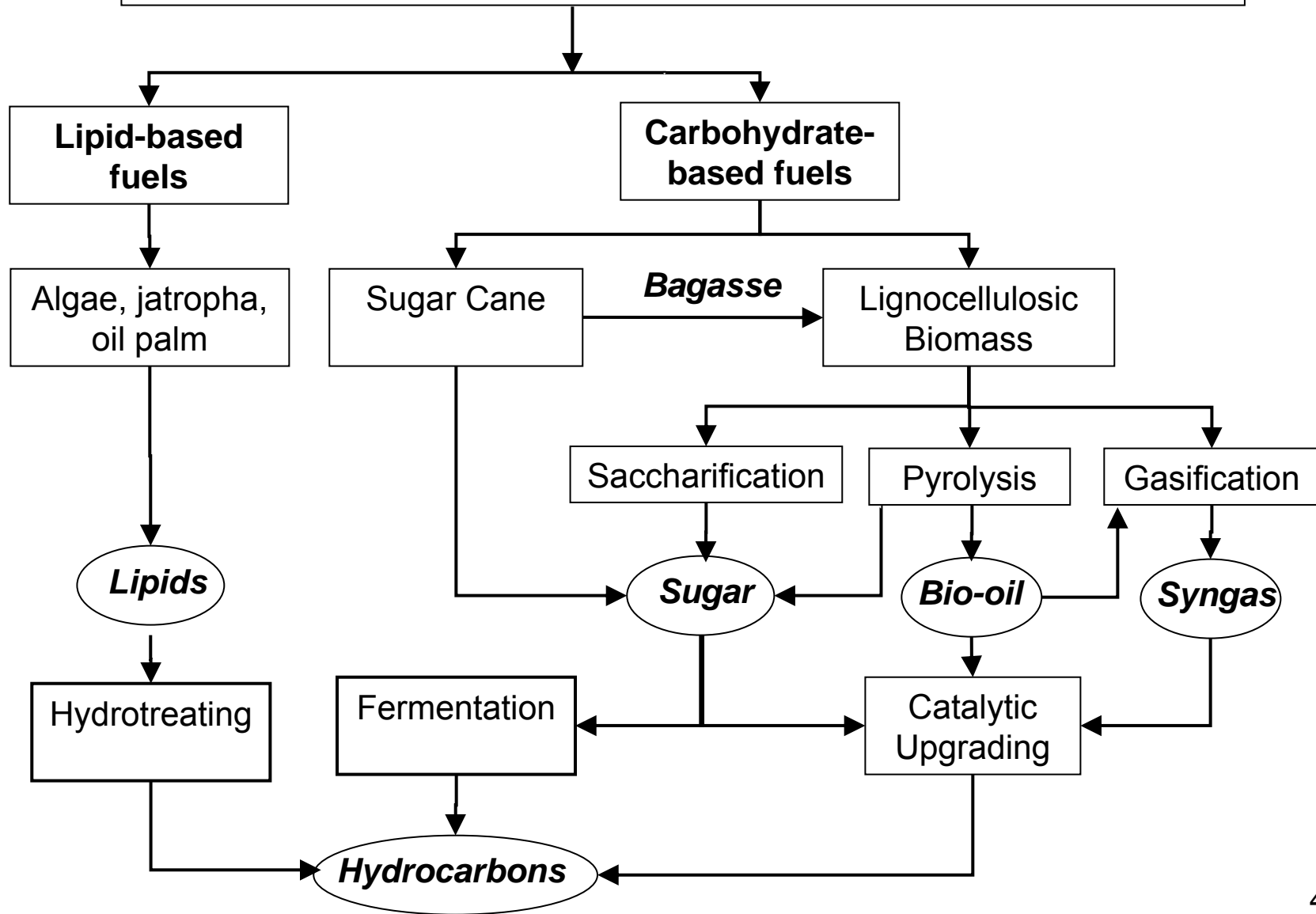
What is the Perfect Fuel?

- Liquid at ambient conditions
- Immiscible in water
- Low toxicity
- High energy density
- Cold weather operability
- Stable during long-term storage
- Efficient production from a primary energy source

Drop-In Fuels

- Fully compatible with existing fuel infrastructure
 - Hydrocarbons (alkanes and aromatics)
 - Possibly butanol
- Are drop-in fuels also the “perfect fuel?”
 - Might be close enough

Hydrocarbon fuels from biomass



Lipids vs. Lignocellulose

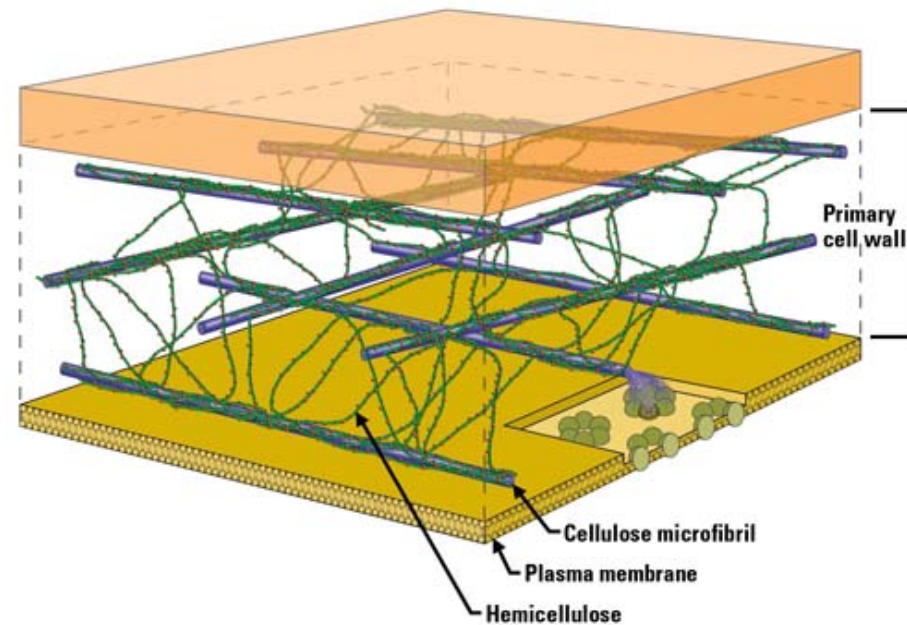
- **Lipids**

- Advantage: Upgrading to drop-in fuels relatively easy
- Disadvantage: Sourcing inexpensive lipid feedstocks

- **Lignocellulose**

- Advantages: Plentiful and relatively inexpensive
- Disadvantages: Difficulty of depolymerizing plant polymers and deoxygenating carbohydrate

Challenge of Lignocellulose: Deconstructing Natural Composite



Whereas starch is a *storage polysaccharide* designed by nature as an energy reservoir, cellulose is a *structural polysaccharide* that in combination with lignin resists microbial degradation

Biochemical vs. Thermochemical for Processing Lignocellulose

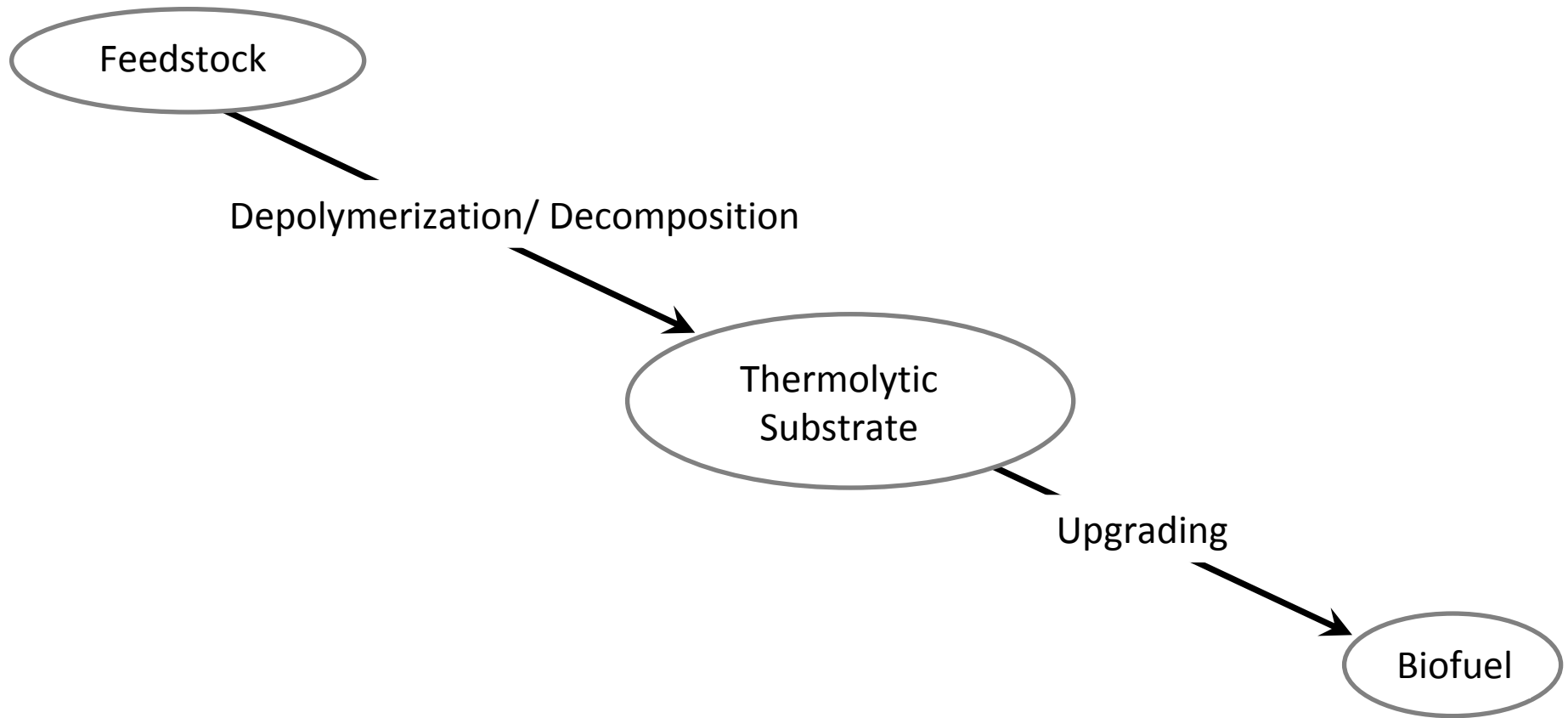
- **Biochemical**

- Advantages: Selectivity and promise of biotechnology advances.
- Disadvantages: Difficulty of depolymerizing biomass and fermenting multiple monosaccharides.

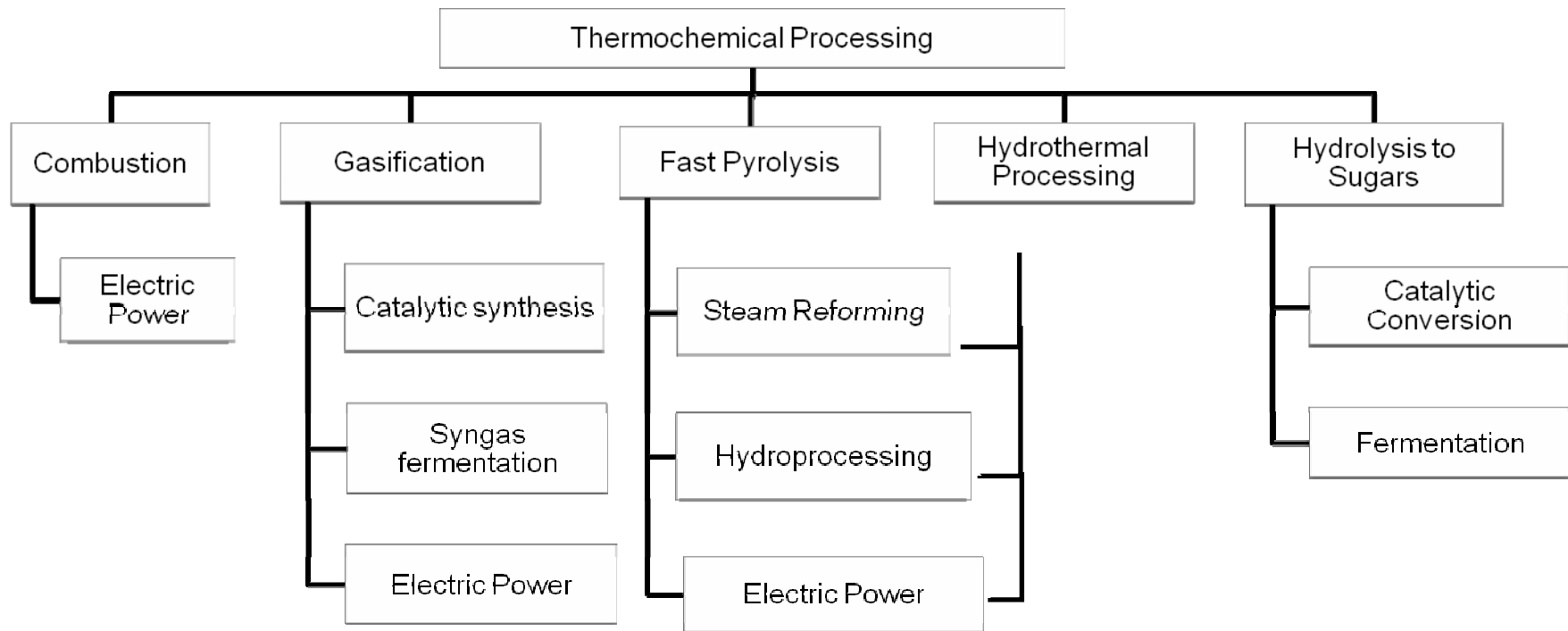
- **Thermochemical**

- Advantages: Rapid biomass deconstruction; many processes are feedstock agnostic.
- Disadvantages: Catalyst deactivation; high hydrogen demand for deoxygenation.

Generalized Thermochemical Process



Thermochemical Pathways



Gasification vs Pyrolysis

- **Gasification**

- Advantages: Feedstock agnostic; uniform syngas product; commercially demonstrated.
- Disadvantages: Large scale of operation; high production cost.

- **Pyrolysis**

- Advantages: Liquid feedstock intermediate; distributed preprocessing; attractive economics.
- Disadvantages: Bio-oil unstable and corrosive; upgrading technology not fully developed.

Bio-oil Upgrading has Attractive Costs

2000 tpd plant capacity	Capital	Production	Feedstock
gge=gallons gasoline equivalent	Cost	Cost	Cost
capital cost is based on annual capacity	(\$/gge)	(\$/gge)	
Grain Ethanol ¹	0.94	1.74	\$3.00/bu
Lignocellulosic Ethanol ²	7.52	5.50	\$75/ton
LT gasification Fischer-Tropsch liquids ³	15.43	4.75	\$75/ton
HT gasification Fischer-Tropsch liquids ³	14.52	4.25	\$75/ton
Motor fuels from bio-oil ⁴	7.82	3.04	\$75/ton
Motor fuels from bio-oil + merchant H ₂ ⁴	3.30	2.09	\$75/ton

References :

1. A. McAloon, F. Taylor, W. Yee, K. Ibsen, and R. Wooley (2000) Determining the Cost of Producing Ethanol from Corn Starch and Lignocellulosic Feedstocks, National Renewable Energy Laboratory Report, October.
2. Kazi, F. K., Fortman, J., Anex, R. P., Hsu, D. D., Aden, A., Dutta, A., Kothandaraman, G. (2010) Techno-economic comparison of process technologies for biochemical ethanol production from corn stover, Fuel 89, Supplement 1, S20-S28.
3. Swanson, R., Platon, A., Satrio, J., Brown, R.C. (2010) Technoeconomic analysis of biomass-to-liquids production based on gasification, Fuel 89, Supplement 1, S11-S19.
4. Wright, M. M., Daugaard, D. E., Satrio, J. A., Brown, R. C. (2010) Techno-economic analysis of biomass fast pyrolysis to transportation fuels, Fuel 89, Supplement 1, S2-S10.

Fast Pyrolysis

Rapid thermal decomposition of organic compounds in the absence of oxygen to produce predominately liquid product

- Dry feedstock: <10%
- Small particles: <3 mm
- Moderate temperatures (400-500°C)
- Short residence times: 0.5 - 2 s
- Rapid quenching at the end of the process

Py Products

- Gas – non-condensable gases like carbon dioxide, carbon monoxide, hydrogen; yields of 13-25%.
- Solid – mixture of inorganic compounds (ash) and carbonaceous materials (charcoal); yields of 12-15%.
- Liquid – mixture of water and organic compounds known as *bio-oil* recovered from pyrolysis vapors and aerosols (smoke); yields of 60-70%.



Bio-Oil

Composition of Bio-Oil from Oak Wood (wt %)

Saccharides	14.1
Aldehydes	16.3
Furans	1.4
Ketones	3.2
Carboxylic acids	4.7
Phenolic compounds	7.3
Other GC/MS Detected	2.2
Lignin oligomers	22.4
Water	28.4

Source: ISU (2010)



- Advantages:

- Liquid product
- Easier to transport and store than raw biomass
- Upgrading resembles petroleum refining
- Attractive economics compared to other biomass conversion processes

- Disadvantages

- High oxygen and water content makes bio-oil inferior to petroleum
- Phase-separation, polymerization, and corrosiveness make storage difficult
- Appropriate catalysis for upgrading bio-oil molecules are still being identified

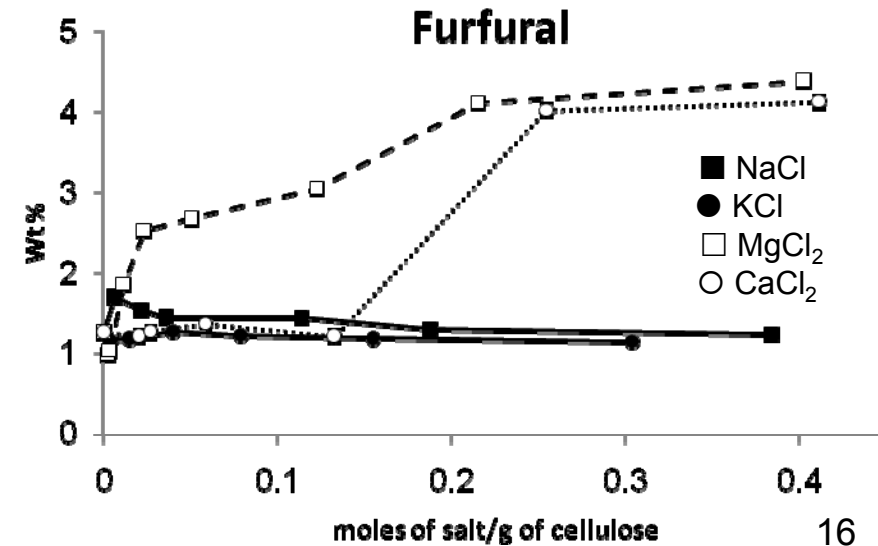
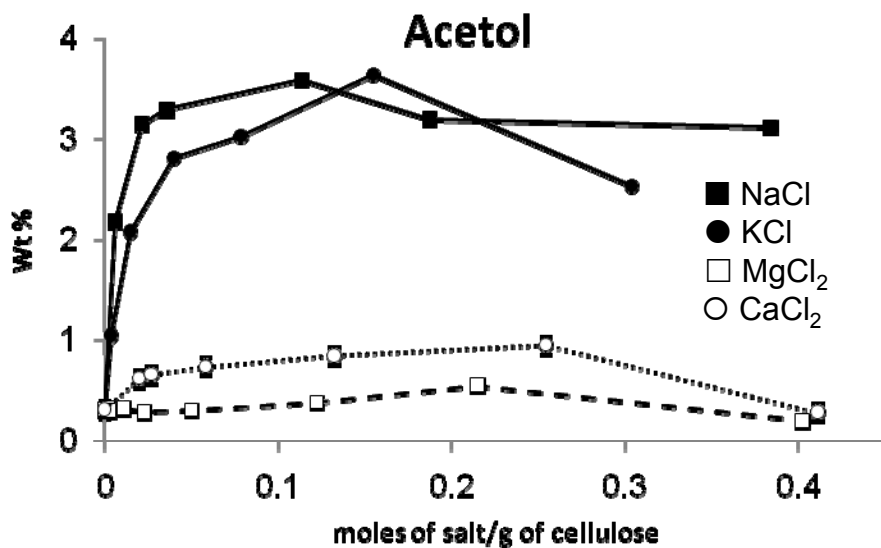
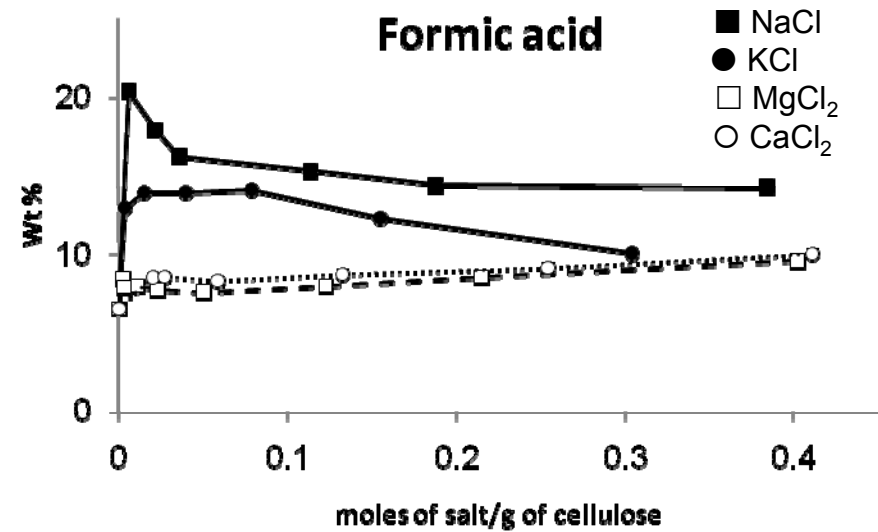
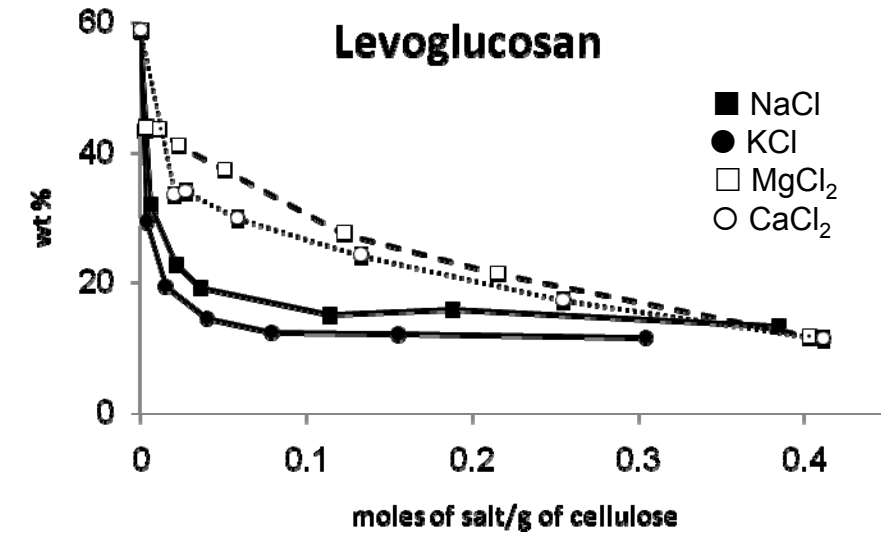
Challenging Conventional Wisdom about Pyrolysis

- Working hypotheses on carbohydrate
 - Pure holocellulose *depolymerizes* to thermally stable monomeric anhydrosugars;
 - Alkali and alkali earth metals catalyze *decomposition* of holocellulose to undesirable “light oxygenates” in competition with depolymerization;
 - Alkali and alkali earth metals can be “passivated” through pretreatments.
- Working hypotheses on lignin
 - Lignin readily depolymerizes to monomers that immediately begin to recondense in the gas phase to aerosols;
 - Condensation can be controlled to produce predominantly lignin-derived monomers instead of undesirable high molecular weight “pyrolytic lignin.”



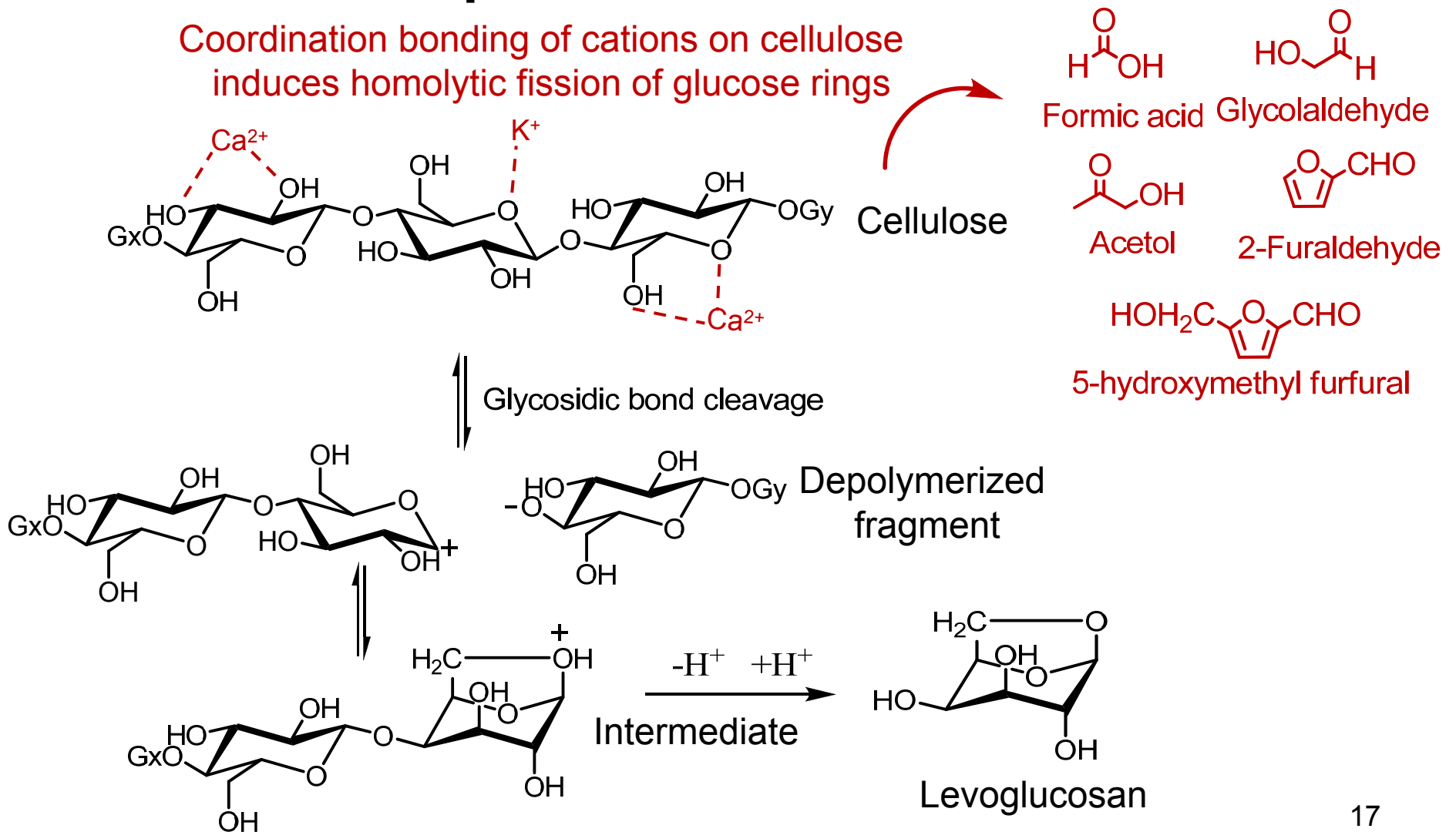
Thermolytic Molasses

Effects of Cations on Deconstruction of Cellulose



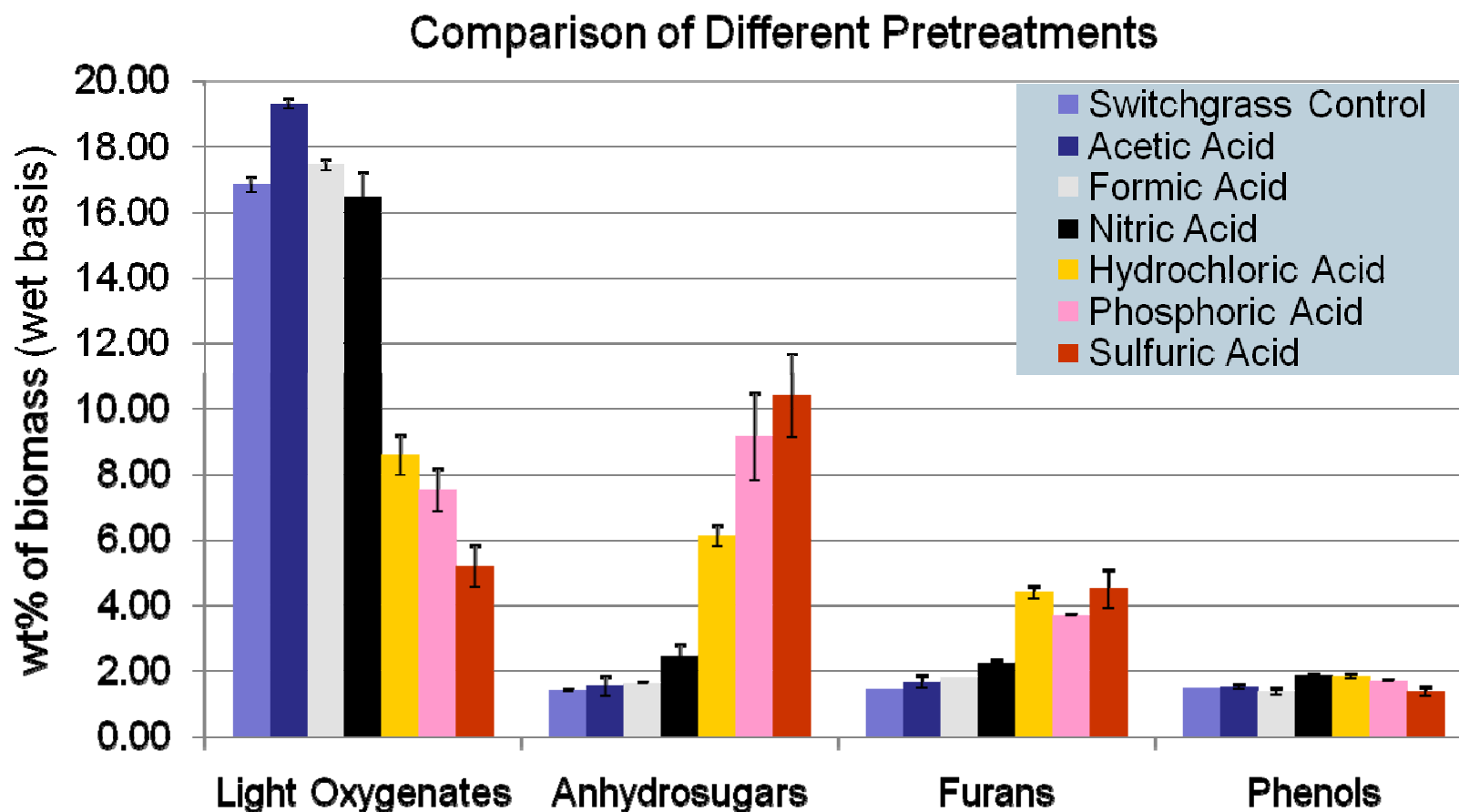
Mechanism of Cellulose Decomposition Via Cations

Coordination bonding of cations on cellulose induces homolytic fission of glucose rings



Passivating Alkali in Biomass

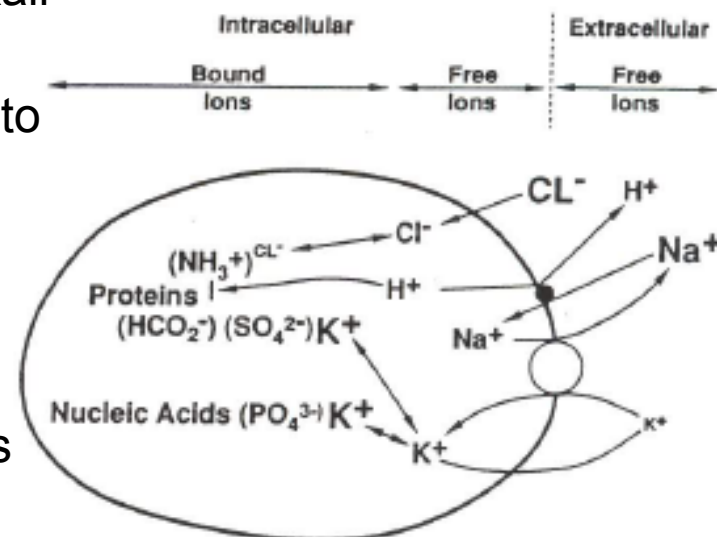
Pretreating switchgrass with most mineral acids (with the exception of nitric acid) significantly increases yields of anhydrosugars and decreases yields of light oxygenates. Organic acids and nitric acid had little affect on pyrolysis. Why?



Source: Brown et al (2010) Manuscript in preparation

Passivating Alkali in Biomass

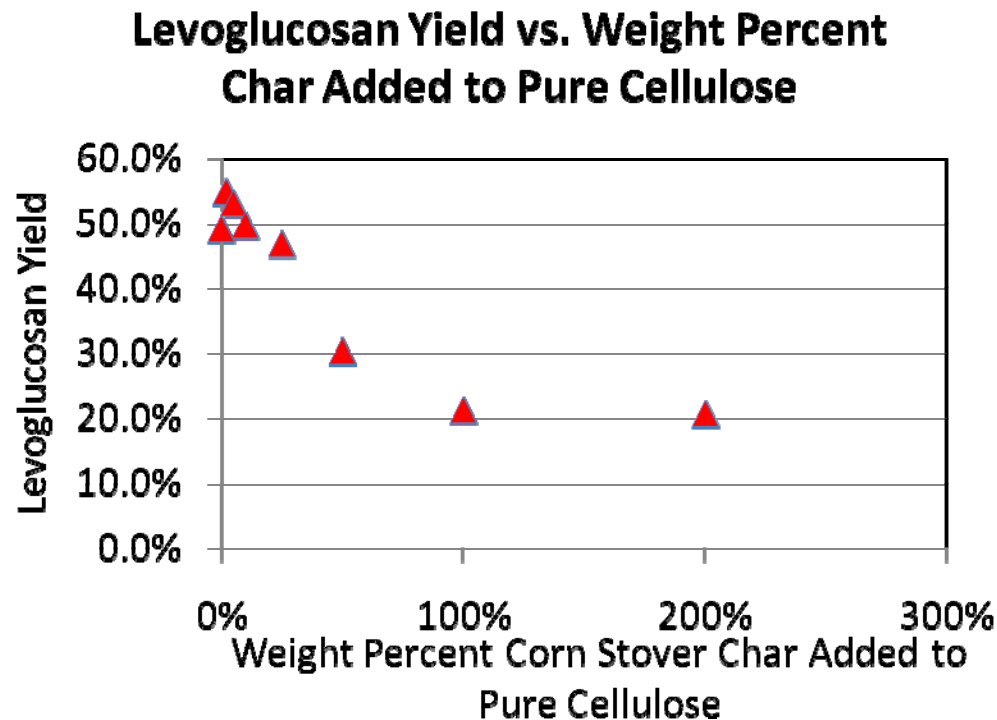
- Uncertainty about the forms of alkali in biomass:
 - Inorganic salts: Potassium exists as highly mobile K^+ ions accompanied by NO_3^- and Cl^- anions (Marchner 1995, Mengel and Kirkby 2001, Barker and Pilbeam 2007)
 - Organic complexes: K^+ is complexed to organic compounds such as proteins and nucleic acids by anionic functional groups: phosphate, sulfate, and $COOH$ (Cameron et al 1998)
- Hypotheses:
 - During pyrolysis organically (or nitrate) bound alkali is released and becomes catalytically active.
 - Acid infusions before pyrolysis convert this alkali to salts. Those that are stable against thermal decomposition reduce catalytic activity of alkali.
- Goal: Manage alkali in biomass:
 - Reduce alkali accumulation in biomass
 - Chemically complex the alkali before pyrolysis



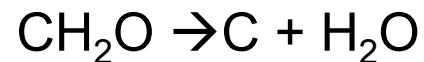
Cameron et al 1998

Effect of char on deconstruction of cellulose

Micropyrolysis of cellulose mixed with different levels of char

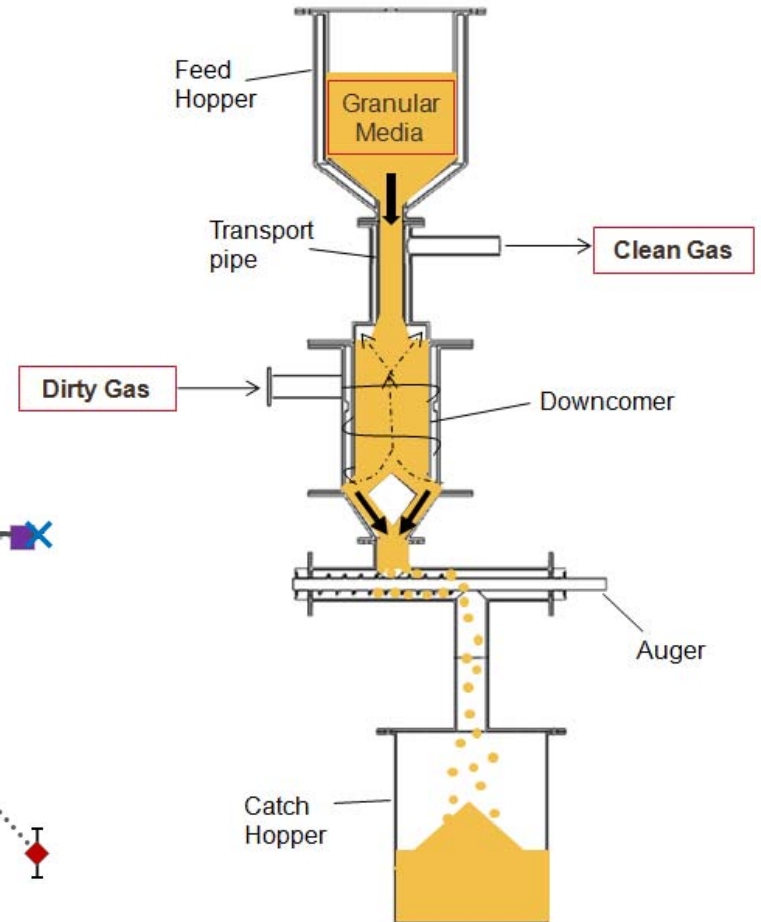
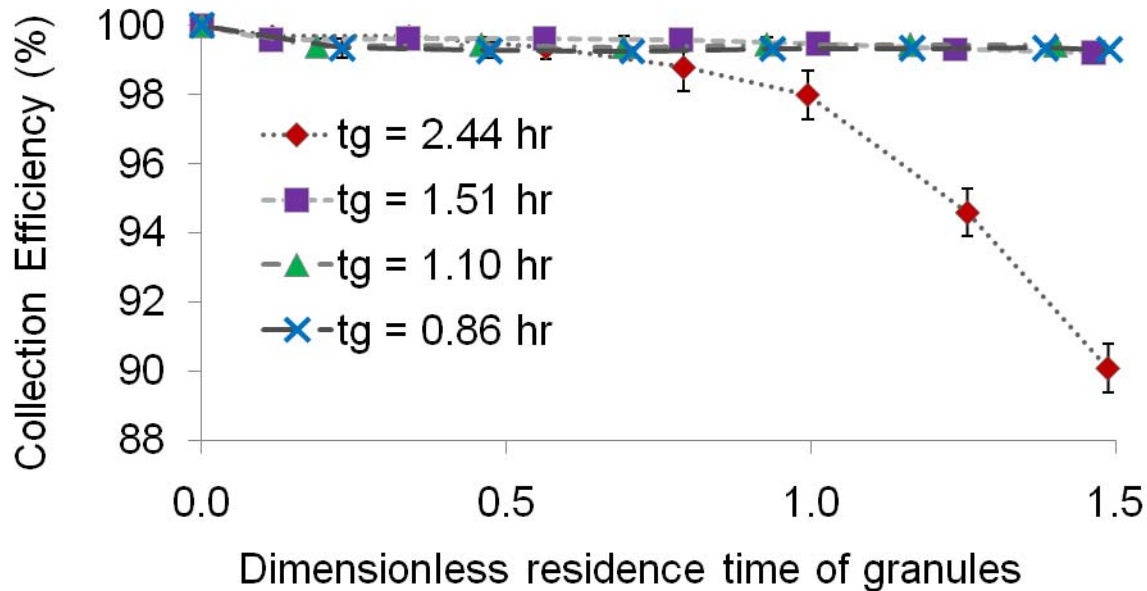


Secondary reactions of oxygenated vapors in presence of char particles:



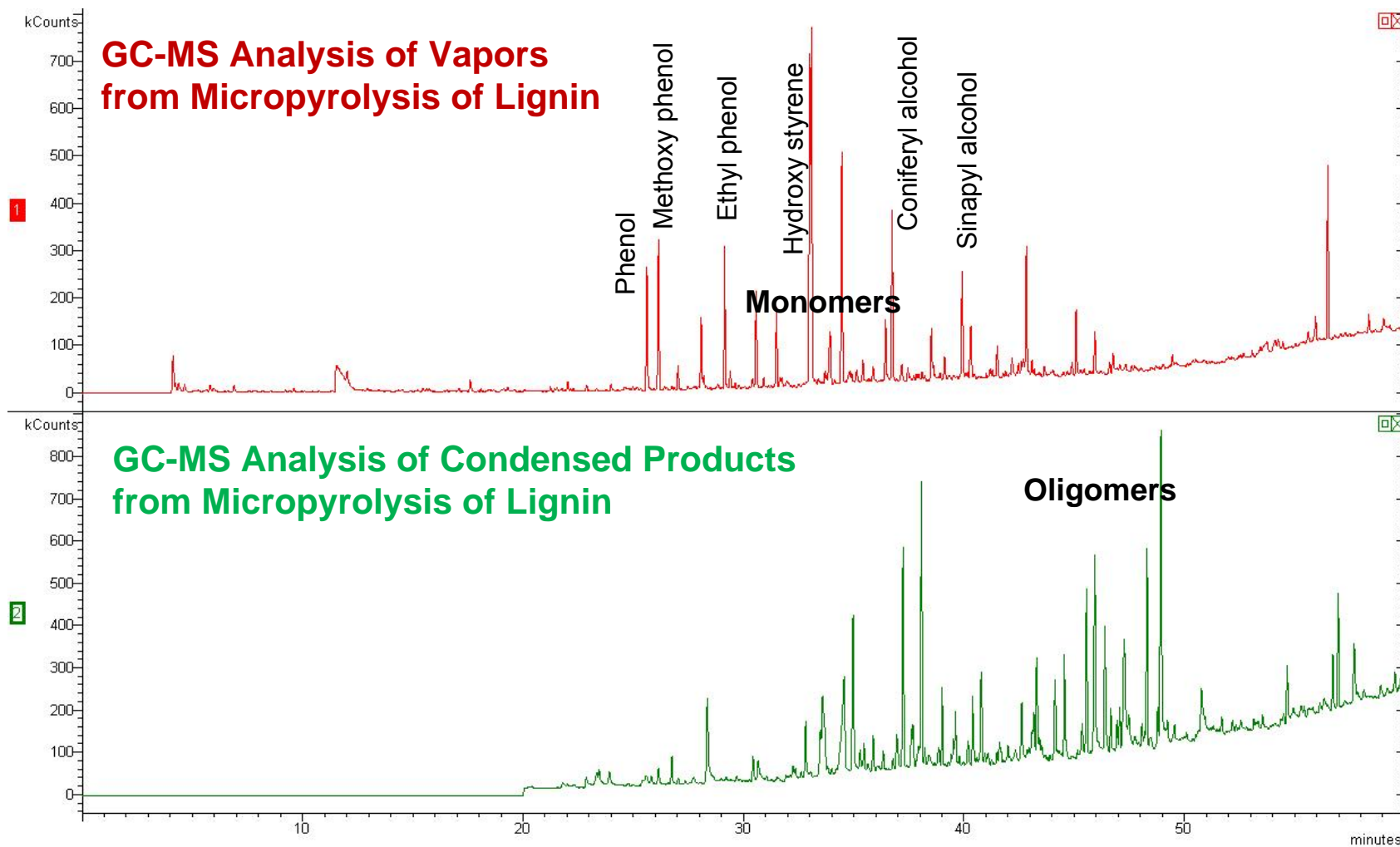
Hot Vapor Filtering

- Problem: Hot gas filtration compromised by char-vapor reactions, which reduce bio-oil yields and quality
- Approach: Moving bed granular filter, which constantly refreshes filter media
 - Char hold-up controlled by granular flow rate
 - Filtration efficiencies exceed 99% for sufficiently high granular flow rates

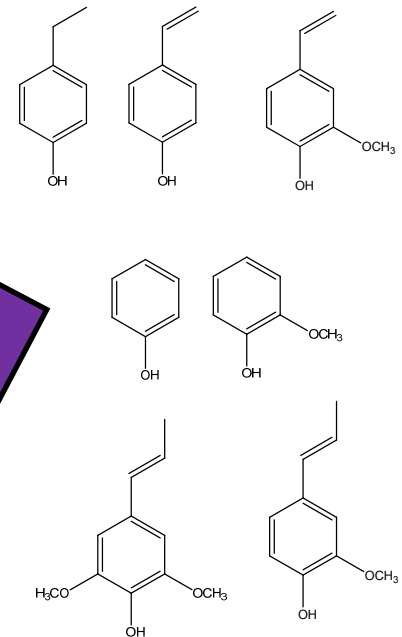
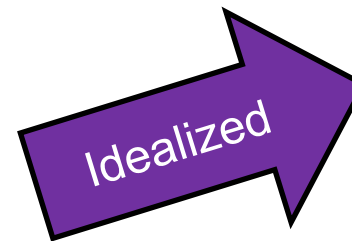
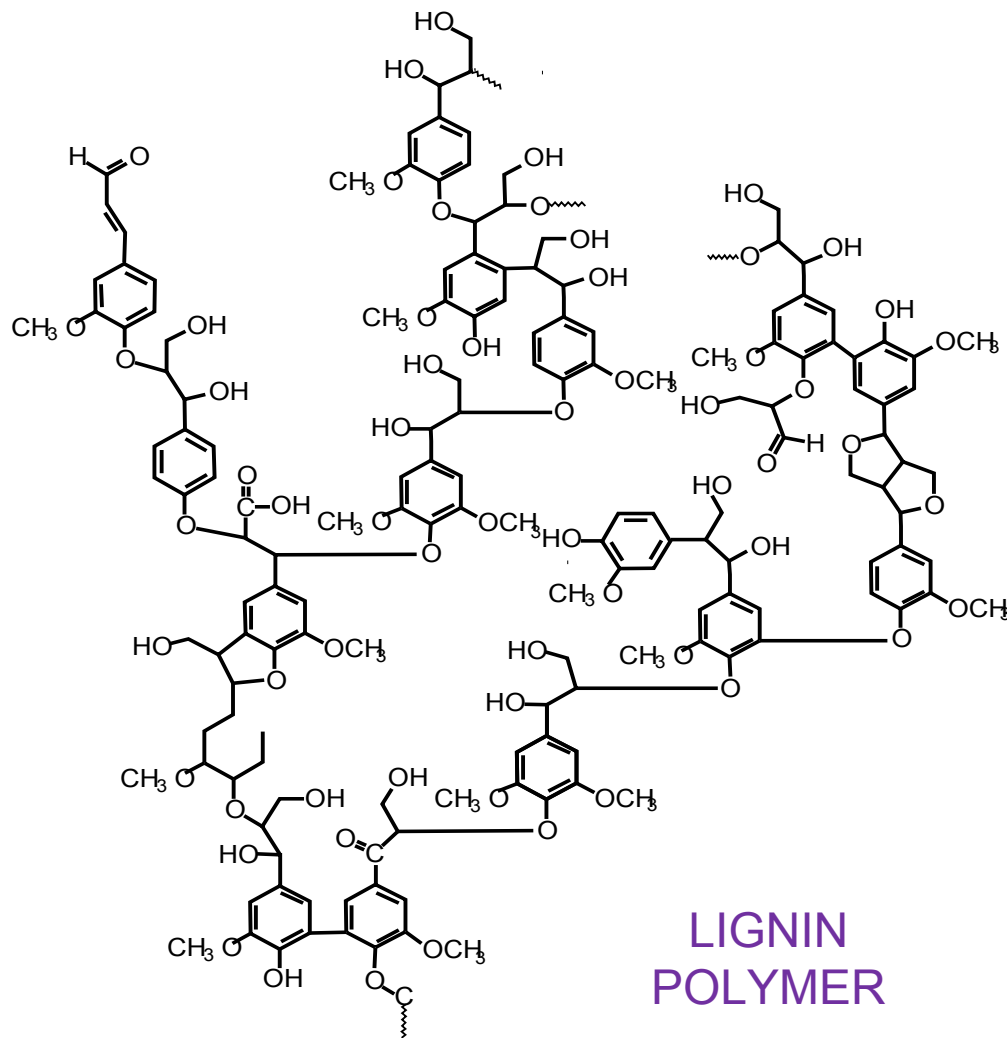


Micropyrolysis of Lignin

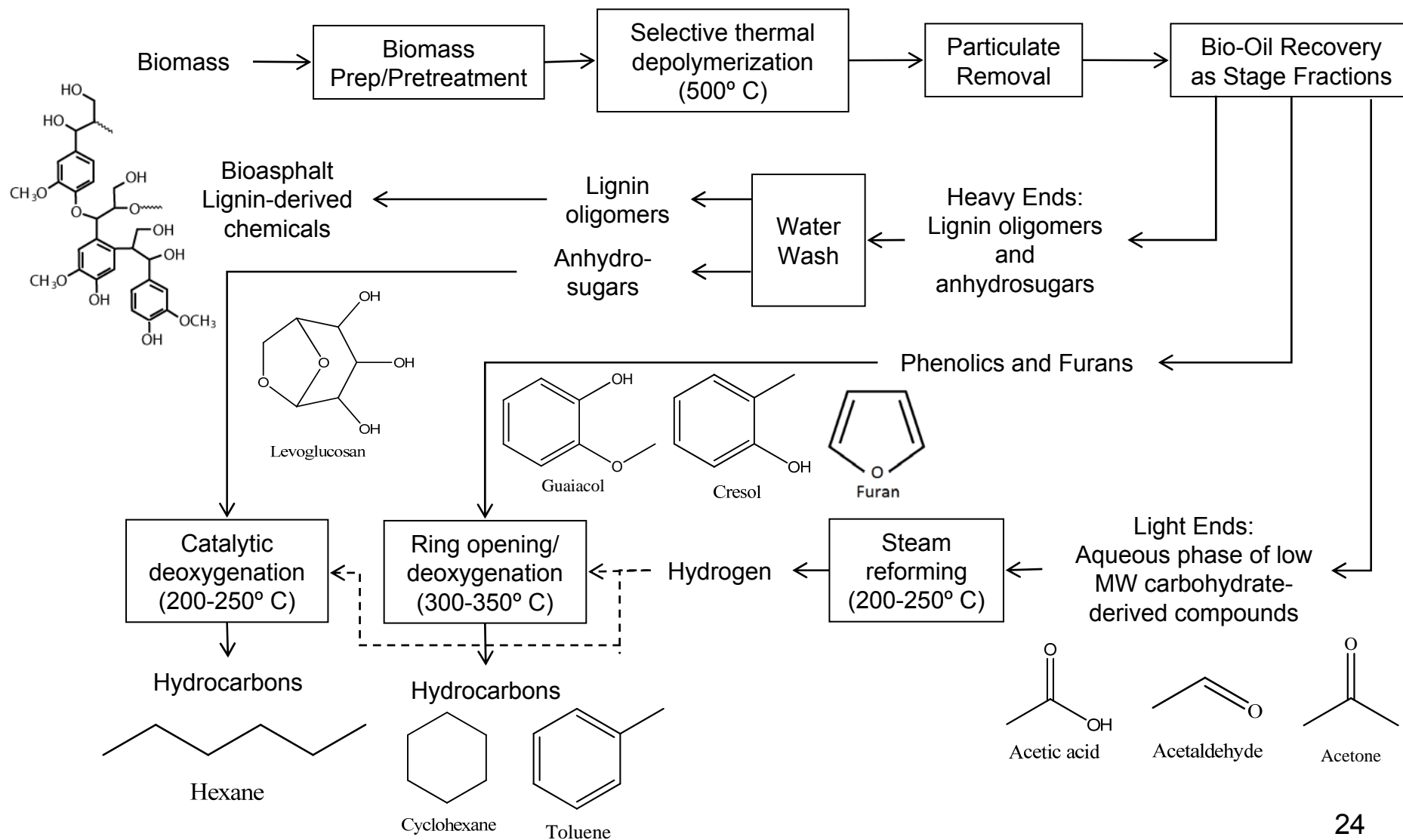
Initial lignin pyrolysis products are phenolic monomers!



Pyrolysis of Lignin



ISU's Vision for Bio-Oil Upgrading

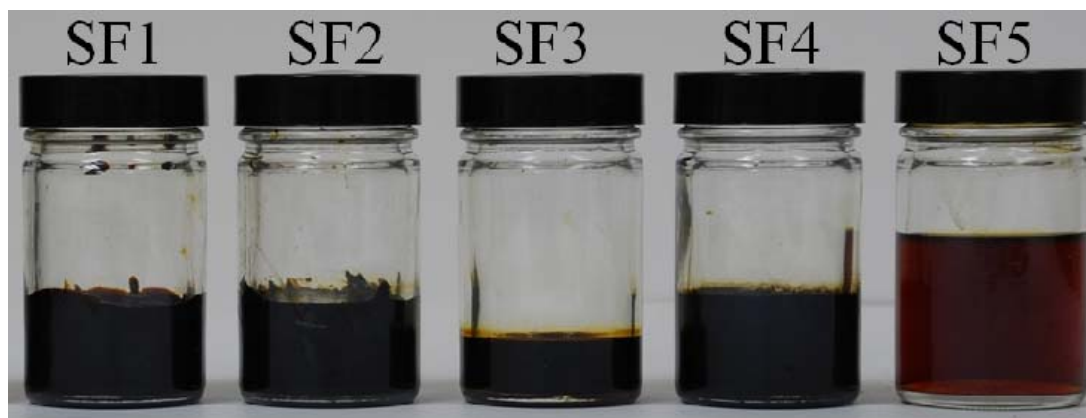


Process Development Unit to Evaluate Recovery of Bio-Oil Stage Fractions



Rethinking Strategy for Bio-Oil Upgrading

Recover bio-oil as distinctive fractions that can be upgraded separately.



	Stage Fraction 1	Stage Fraction 2	Stage Fraction 3	Stage Fraction 4	Stage Fraction 5
Fraction of bio-oil yield (wt%)	21	26.6	5.5	11	35.9
Moisture (wt%)	6.5	7.8	8.8	14.8	62.9
Modified acid number (mg KOH/g)	34.9	31.6	79.1	117.1	116.8
Levoglucosan (wt%)	10	6	1.5	1.0	0.5
Water Insoluble Content (wt%)	43.8	46.8	8.6	14.4	0.83
Oxygen Content (wt% m.f. basis)	28.6	29.1	41.1	39.6	53.7

Other Biobased Products from Fast Pyrolysis

- **Bio-Oil Heavy Ends**
 - Bioasphalt from lignin oligomers
 - Sugars from carbohydrate depolymerization
- **Bio-Oil Light Ends**
 - Renewable hydrogen from light oxygenates
 - Acetic acid
- **Biochar for carbon sequestration and soil amendment**

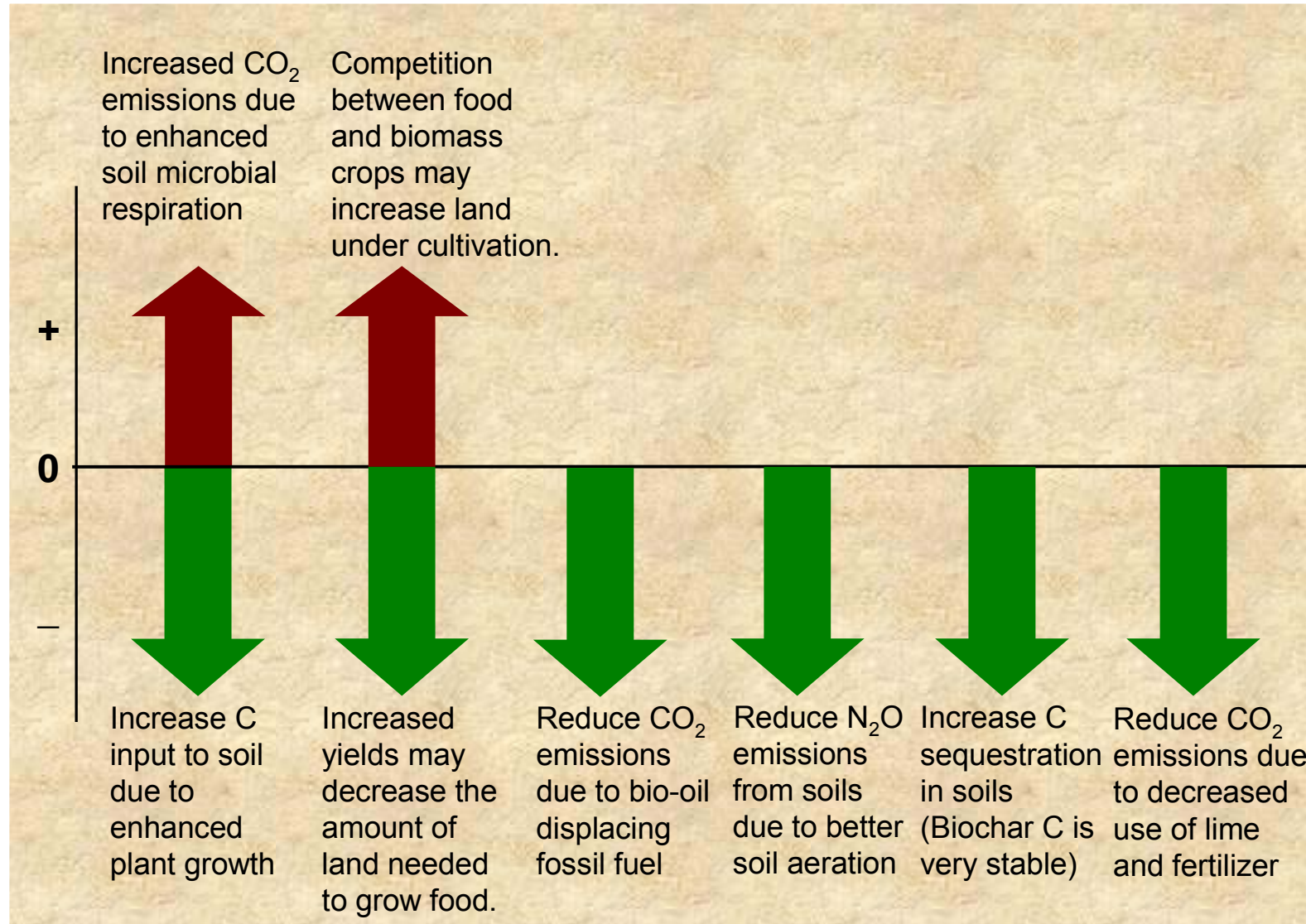


Pyrolytic molasses—sugars extracted from bio-oil

Pyrolysis Peppers grown on biochar, Summer 2010



GHG Impacts of Soil Application of Biochar



Conclusions

- Fast pyrolysis offers attractive costs for advanced biofuels
- Fundamental studies of fast pyrolysis can contribute toward improved strategies for fuel production
- Recovery of bio-oil as fractions with distinctive chemical compositions and physical properties may improve the prospects for bio-oil stabilization and upgrading

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