Thermochemical Biofuels: Challenges and Opportunities

June 14, 2012

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Some Context

- **Petroleum at $90/bbl**
  - **Gasoline, wholesale & untaxed ~$2.70/gal**
  - **Diesel, wholesale & untaxed ~$3.00/gal**
  - **Grain Ethanol, corn at $3 & $6.50/bu $2.40 & $3.80/gge**

Usage *(in billions of bushels)*	**2002/03**	**2007/08**	**2012/13**
Ethanol	**1.10**	**3.00**	**5.00**
Returned from ethanol to feed	0.36	1.00	1.66
Feed, export, residual, other	8.40	9.80	9.79
Total available for other uses	**8.76**	**10.80**	**11.45**

Biofuels Digest, May 11, 2012

Technology Comparison*

- Requires consistent capital cost and evaluation bases
- Comparative economics, not business-case economics
- Considered commercial or "near-commercial" technology where possible
- Material and energy balances by Aspen Plus, generally
- Location U.S. Gulf Coast, 2011 $
- Biomass at $5.4/GJ (limit 1 million t/yr/plant)
- Coal at $2/GJ
- Estimates for N^{th} of a kind plants (N = 5-7)
- Stand-alone plant: Feedstock in; Finished fuels out
- Comparisons are based on best available data; design basis and data are often not very complete

* *Jim Katzer (ExxonMobil retired, Iowa State University)*

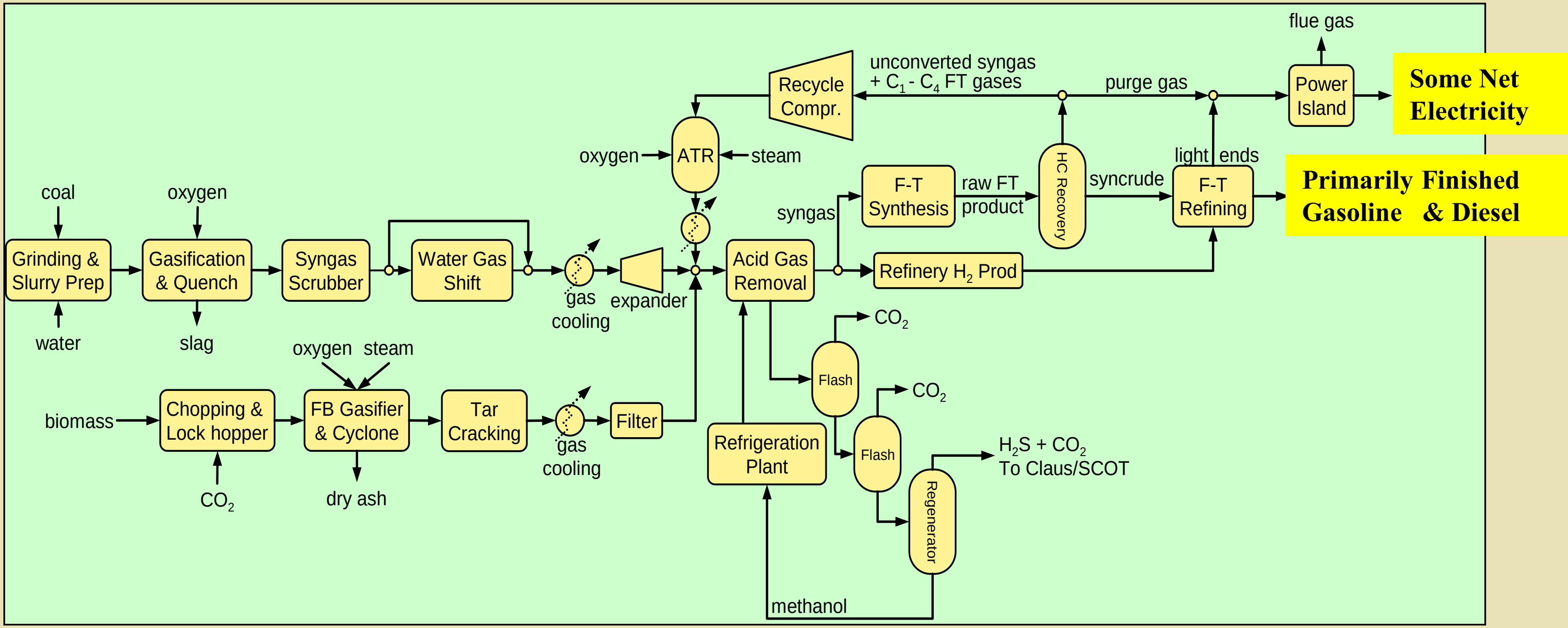
Biomass Properties & Fuel Cost Component

Material:	Grain (corn)	Corn Stover	Wood (poplar)
Starch, wt %	72.0	n/m	n/m
Cellulose, wt %	2.4	36	40
Hemicellulose, wt %	5.5	26	22
Lignin, wt %	0.2	19	24
Ash, wt %	1.4	12	0.6
Bio-Conversion:			
Typical Yields: gge/dry tonne	72	48	50
Thermal-Conversion:			
Gasification Yield, gge/dry tonne	-	67	72
Pyrolysis Yield, gge/dry tonne	-	55	60
Feedstock Cost, $/dry tonne:	255	95	80
Feedstock Cost Component:			
Bioconversion, $/gge	3.50*	$2.00	$1.60
Gasification, $/gge	-	$1.40	$1.10
Fast Pyrolysis, $/gge	-	$1.75	$1.30

Red numbers are first-cut indicator of feedstock cost contribution to product cost

* For Corn at $6.50/bu, DDGS netback reduces this to ~$2.60/gge

Thermochemical: Gasification

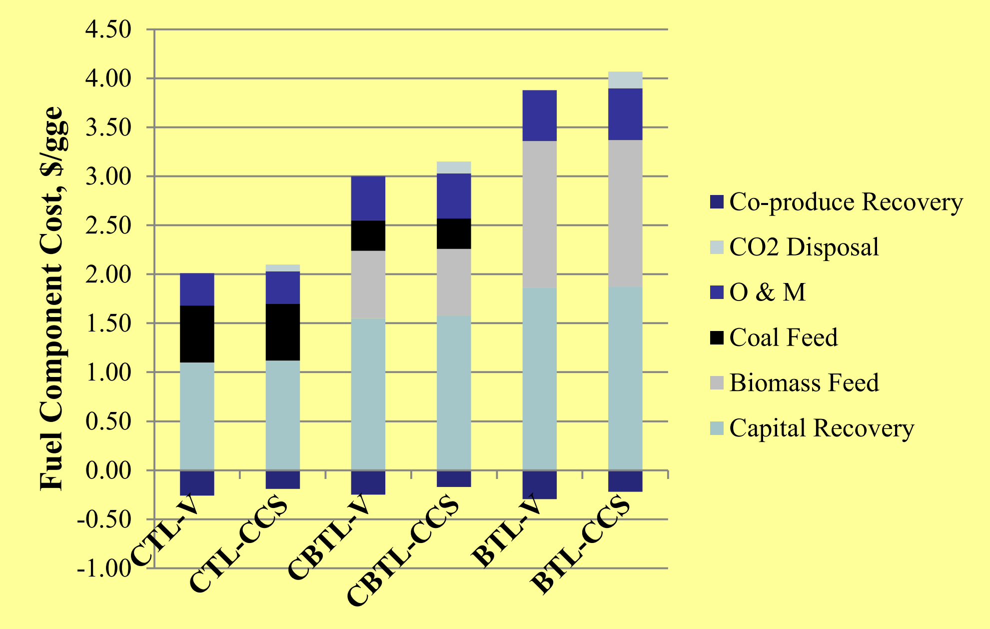


- **Coal: all components are commercially robust**
- **Biomass gasification is "essentially commercial"**
- **Options: Methanol synthesis followed by MTG to produce mainly gasoline, DME**

Liquid Transportation Fuels from Coal and Biomass: Technological Status, Costs, and Environmental Impacts, NRC, 2009.

Thermochemical: Gasification

Feedstock	Mode	Fuel Price, $/gge
– Coal (CTL)	Vent CO_2	1.75
– Coal	CCS	1.90
– Coal/Biomass (40%) (CBTL)	Vent CO_2	2.75
– Coal/Biomass (40%)	CCS	3.00
– Biomass (BTL)	vent CO_2	3.60
– Biomass	CCS	3.85

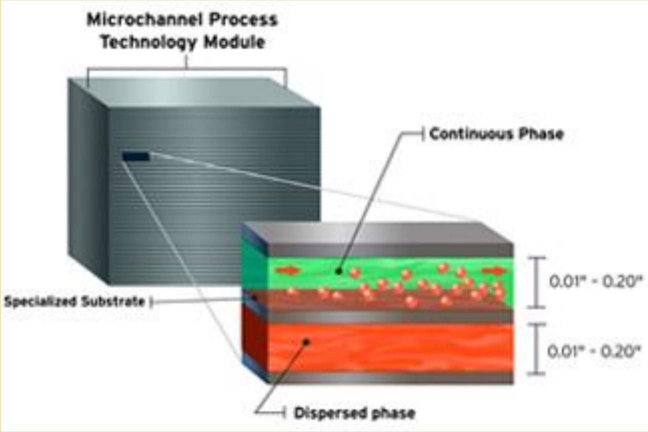


Fuel Component Cost

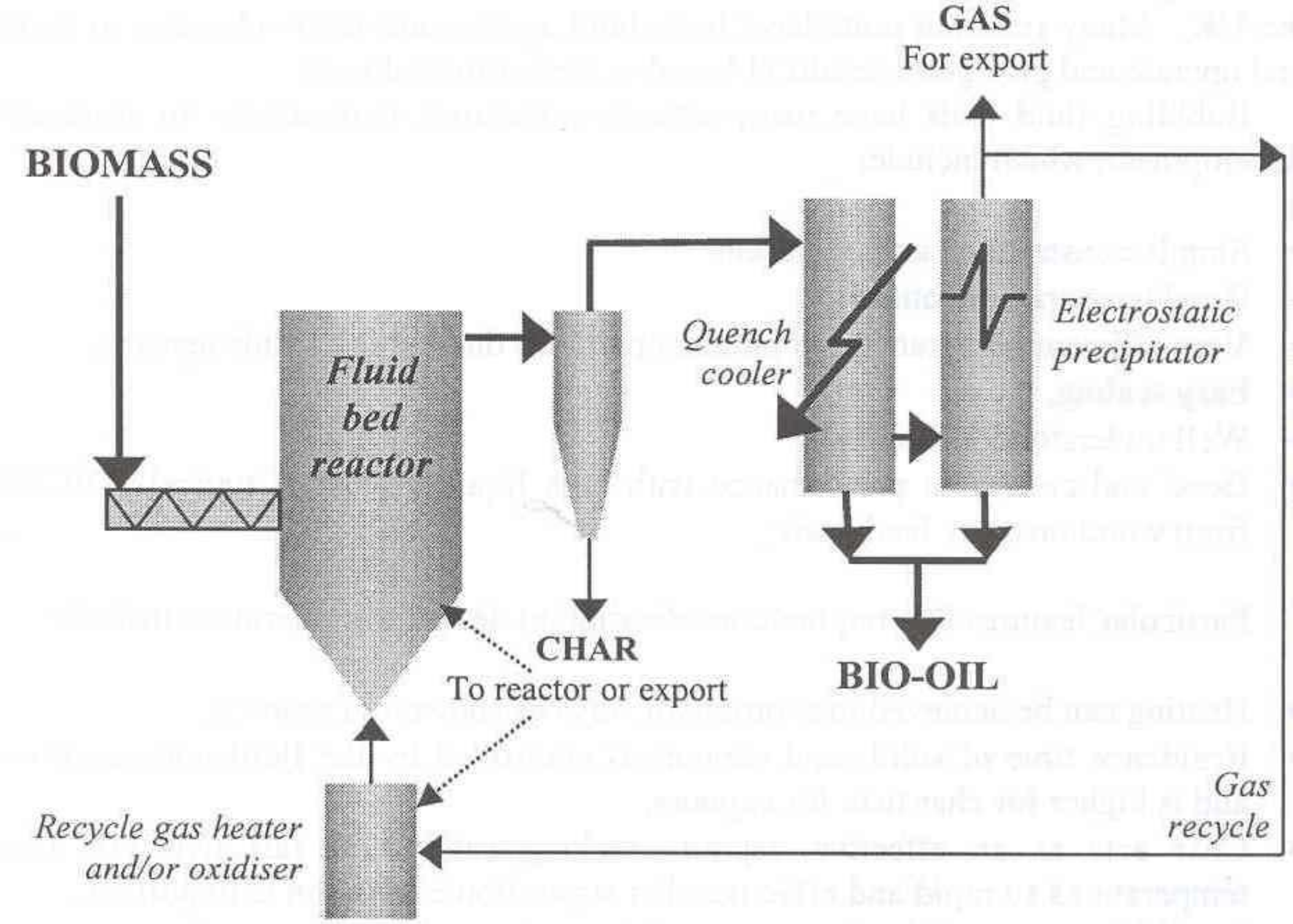
Biomass Gasification Challenges

- Ash management
- "Tars" conversion
- Scalability

- Reactor technology
  - CompactGTL, Syntroleum
  - Velocys (25 bpd, May, 2012)



Biomass Fast Pyrolysis*



*Bridgwater et al. in Progress in Thermochemical Biomass Conversion, Bridgwater, ed. (2001) 977.

Fast Pyrolysis

Corn stover

(~1.5 GJ m^{-3})

~500°C →

Gas

(~6 MJ kg^{-1})

+

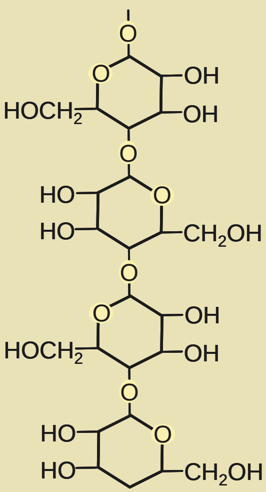
Bio-oil

(~22 GJ m^{-3})

+

Biochar

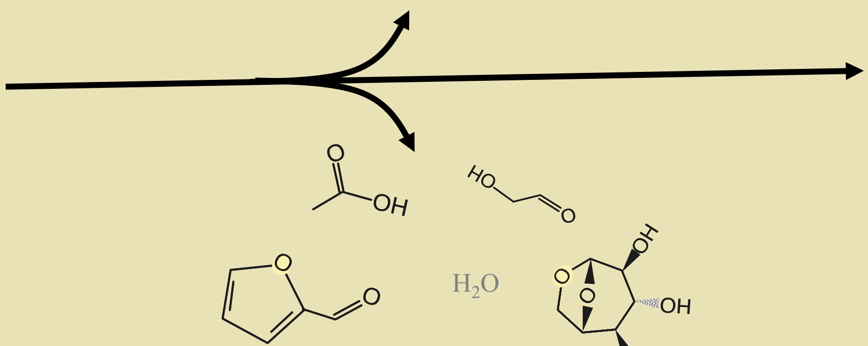
(~21 MJ kg^{-1})



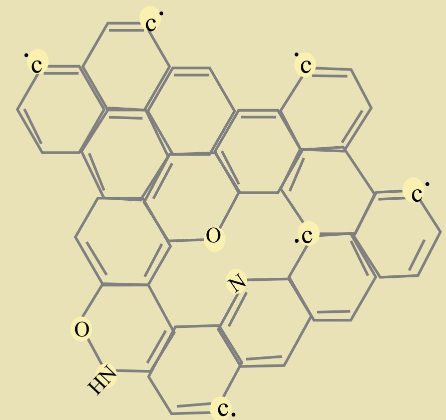
Cellulose

Gas

H_2, CO, CH_4, CO_2



Bio-oil



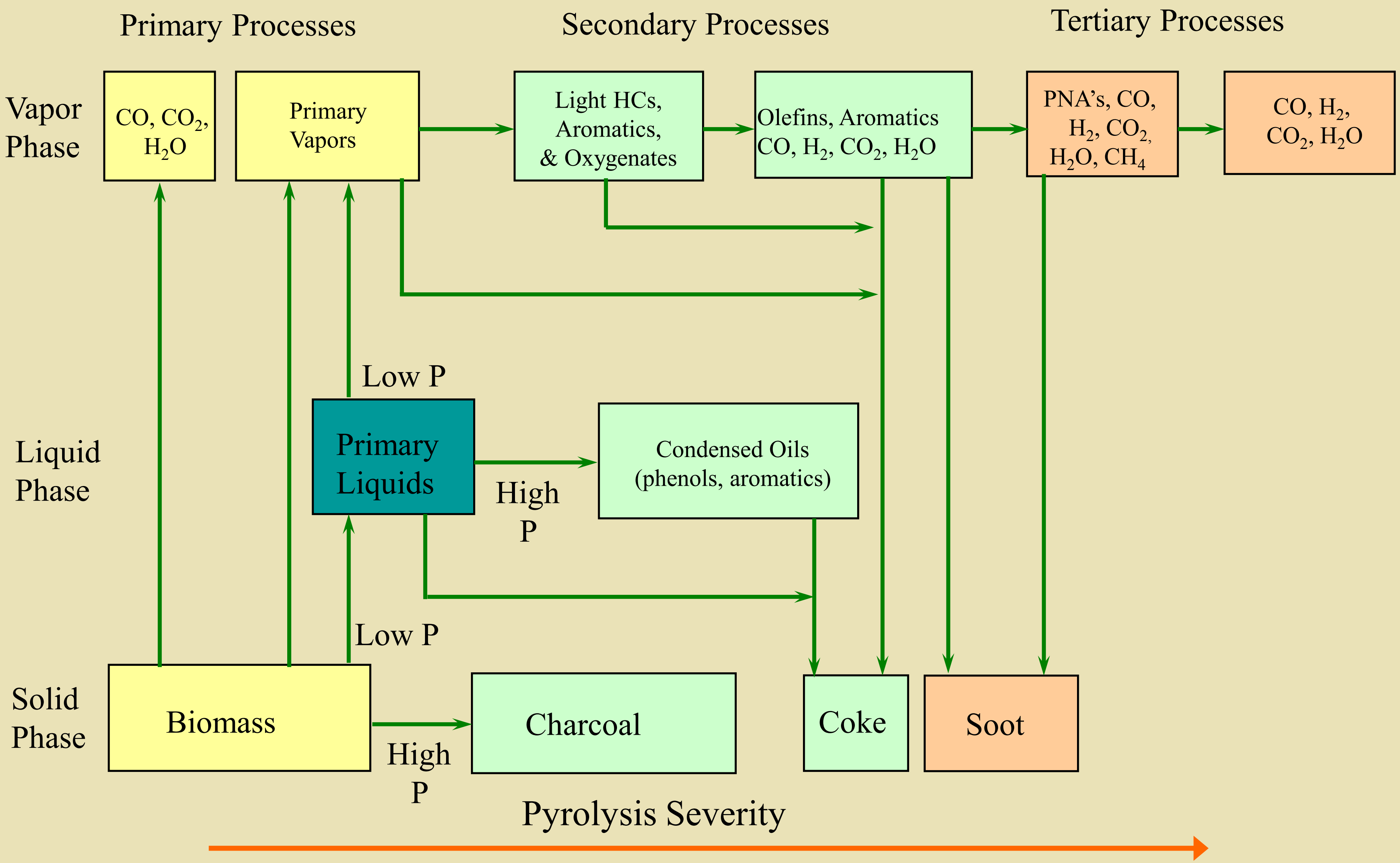
Biochar

Composition: Fast Pyrolysis Bio-Oil*

	Wt%
Water	20-30
Lignin fragments: insoluble pyrolytic lignin	15-30
Aldehydes: formaldehyde, acetaldehyde, hydroxyacetaldehyde, glyoxal	10-20
Carboxylic acids: formic, acetic, propionic, butyric, pentanoic, hexanoic	10-15
Carbohydrates: cellobiosan, levoglucosan, oligosaccharides	5-10
Phenols: phenol, cresol, guaiacols, syringols	2-5
Furfurals	1-4
Alcohols: methanol, ethanol	2-5
Ketones: acetol (1-hydroxy-2-propanone), cyclopentanone	1-5

*Bridgwater et al.; in Progress in Thermochemical Biomass Conversion, Bridgwater, ed. (2001) 977.

Thermal Conversion Reactions

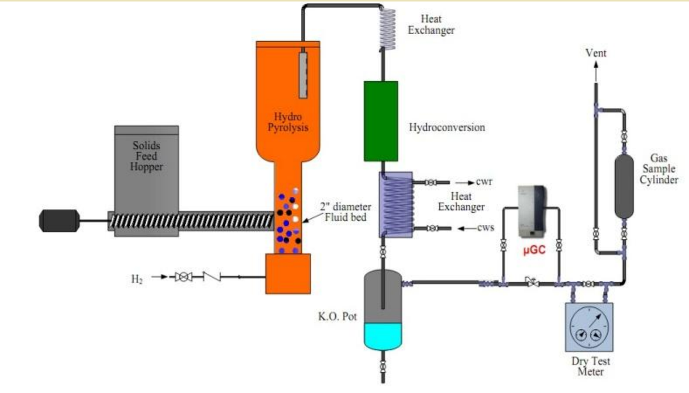


Thermochemical: Pyrolysis

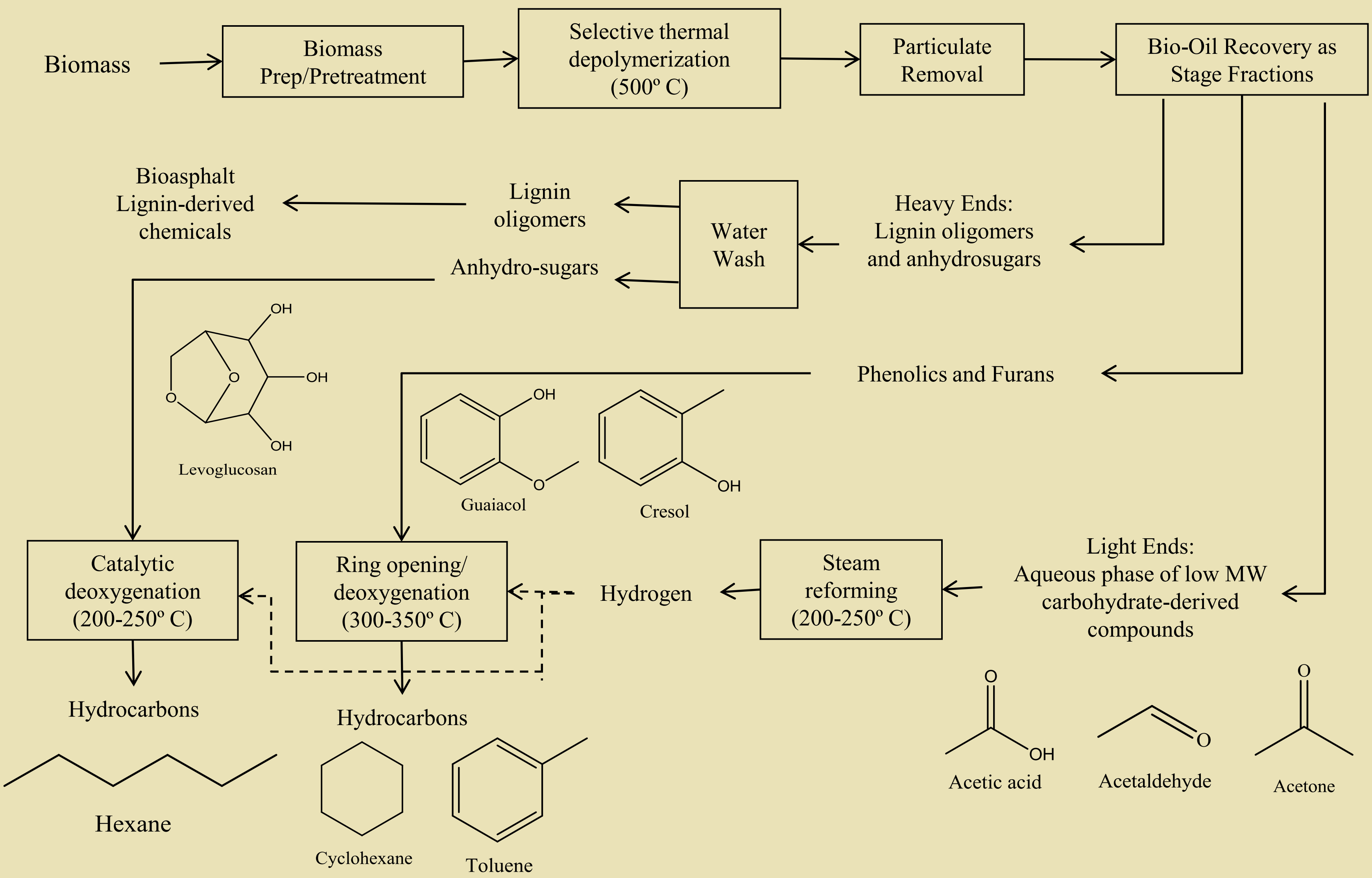
- **Fast pyrolysis**
  - **Dynamotive, ENSYN**
  - **Avello**
- **Catalytic pyrolysis**
  - **KIOR**
  - **Anellotech**
- **Hydropyrolysis**
  - **GTI**

ENSYN, 40 tonne/day

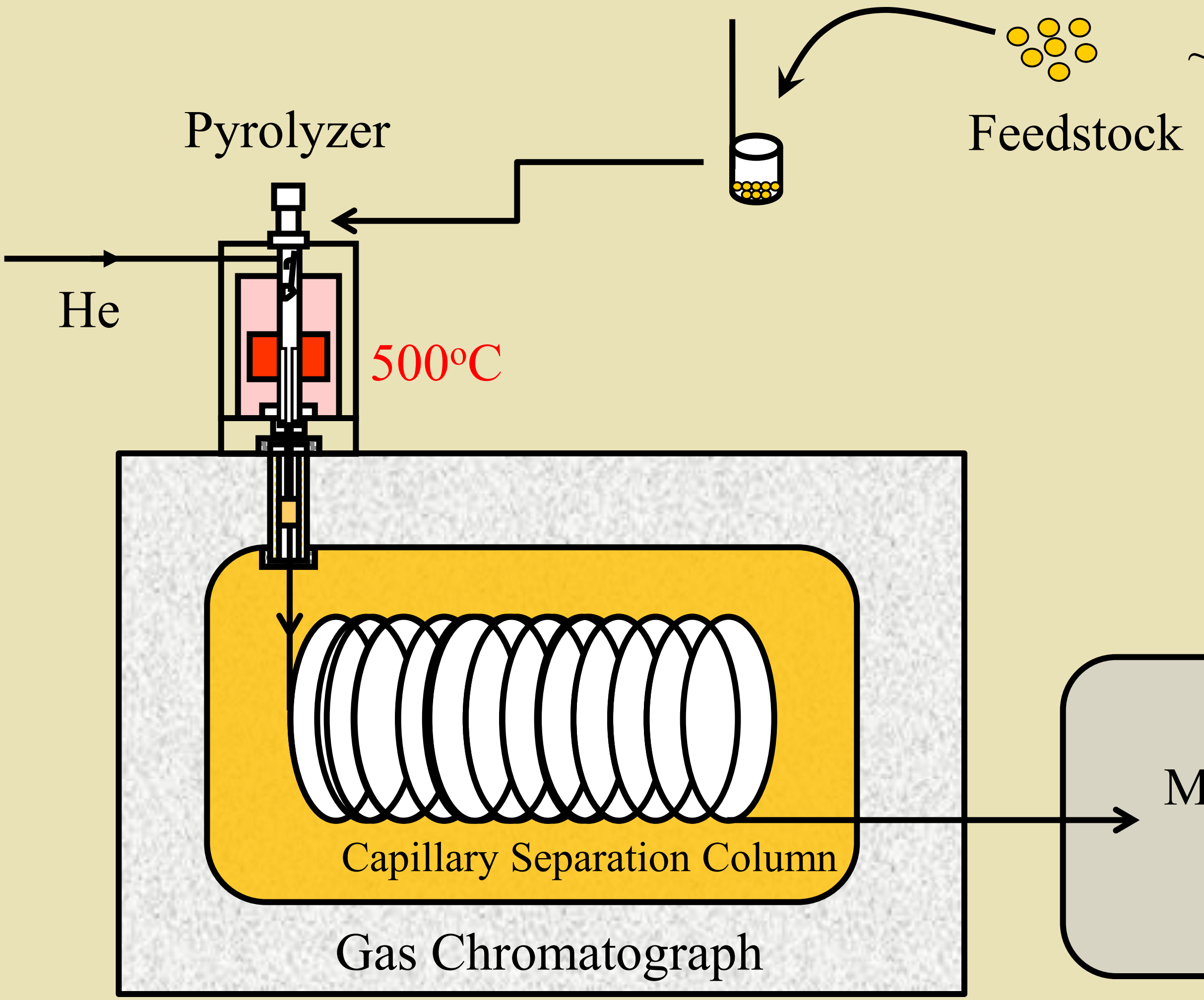
KIOR, 50 ton/day



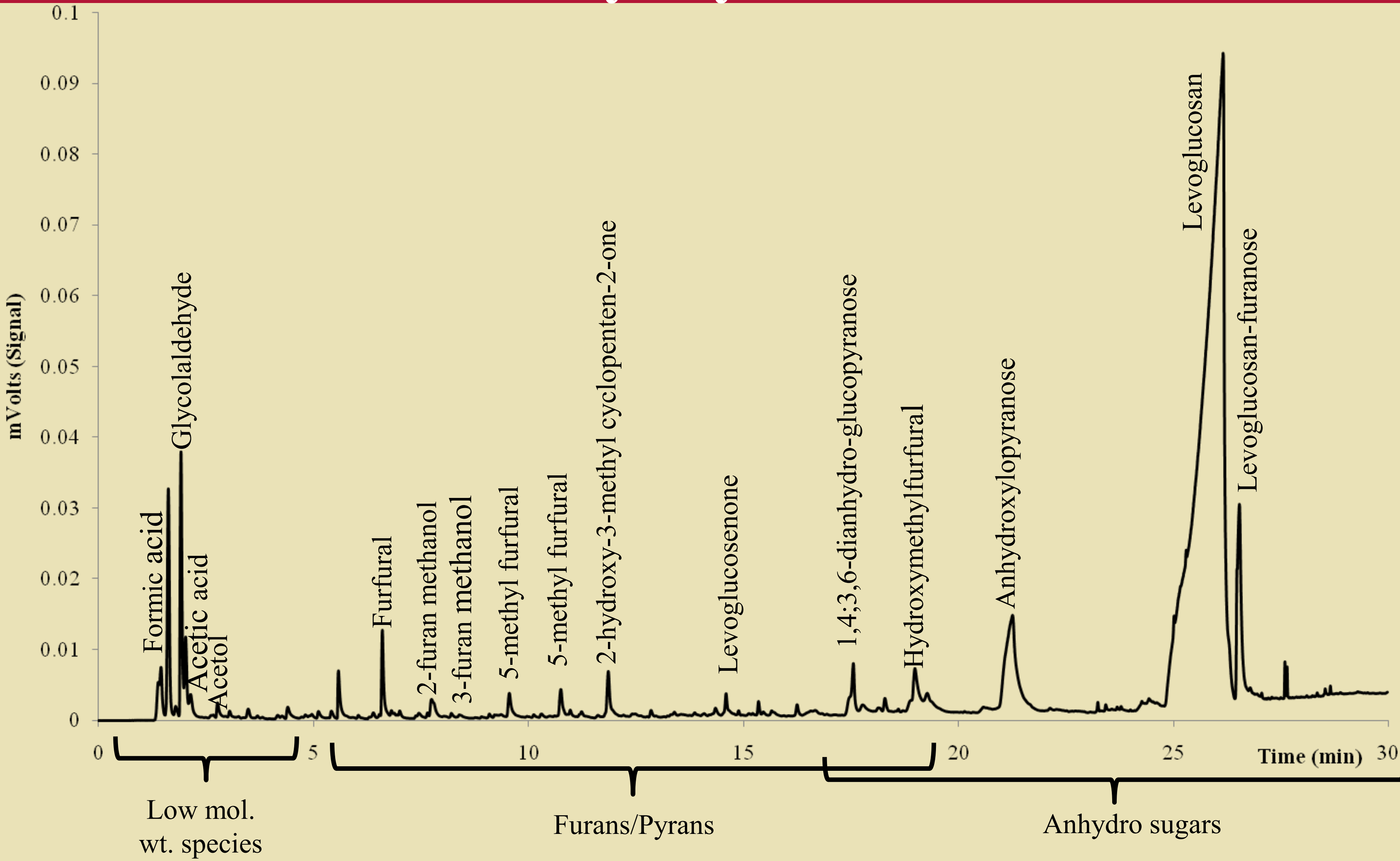
Bio-Oil Upgrading Approach



Schematic of Pyrolyzer–GC/MS System



Cellulose Pyrolysis Products



Patwardhan, P.; et al. *J. Anal. Appl. Pyrolysis* 2009, *86*, 323

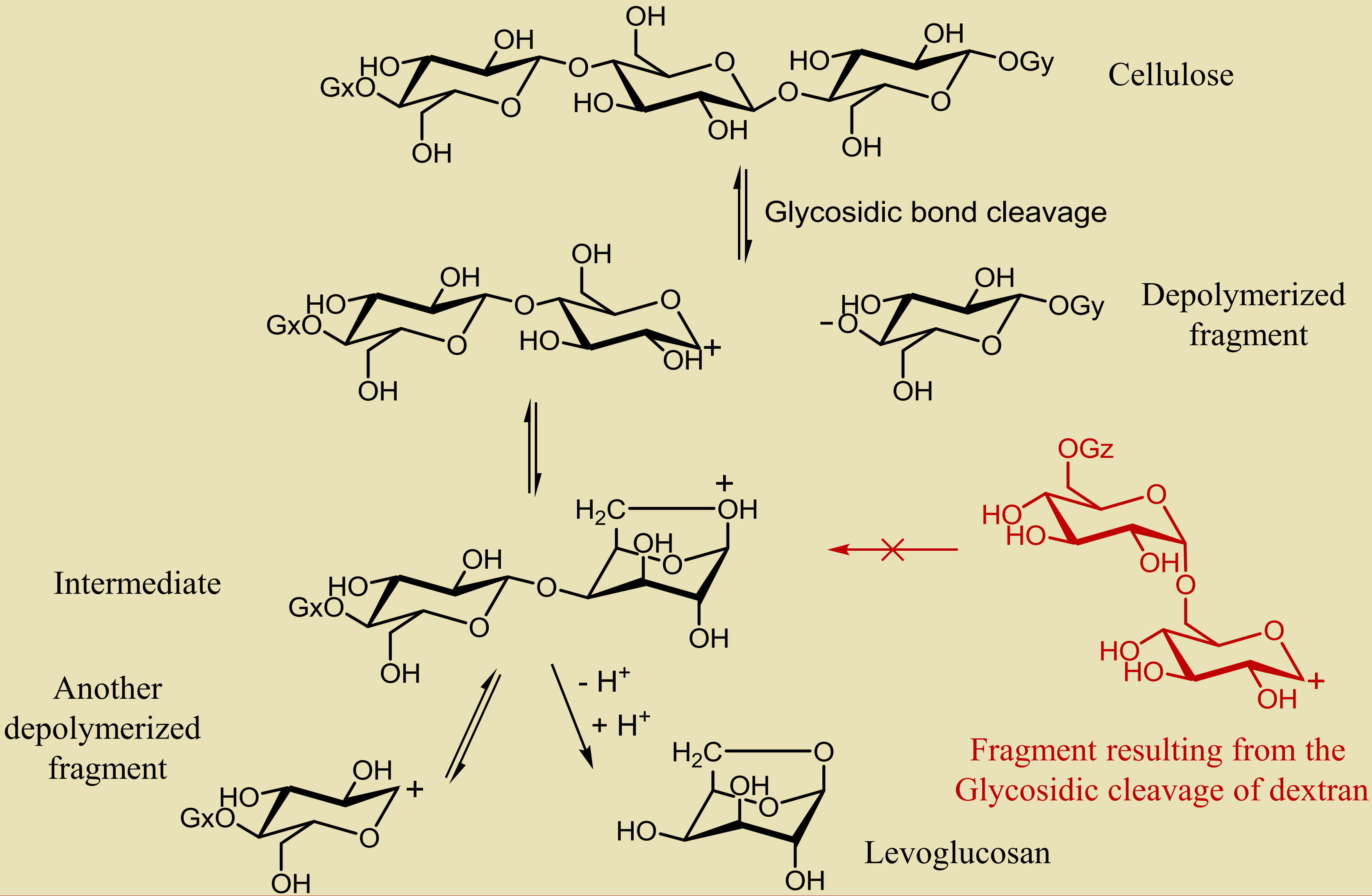
Effect of Chain Length

	Glucose	Cellobiose	Maltohexaose	Cellulose
LMW	**57.42**	42.16	41.01	21.42
Furans	19.08	17.44	13.85	5.63
Anhydrosugars	13.65	30.69	40.33	**67.59**
Levoglucosan	7.01	24.36	33.11	58.78

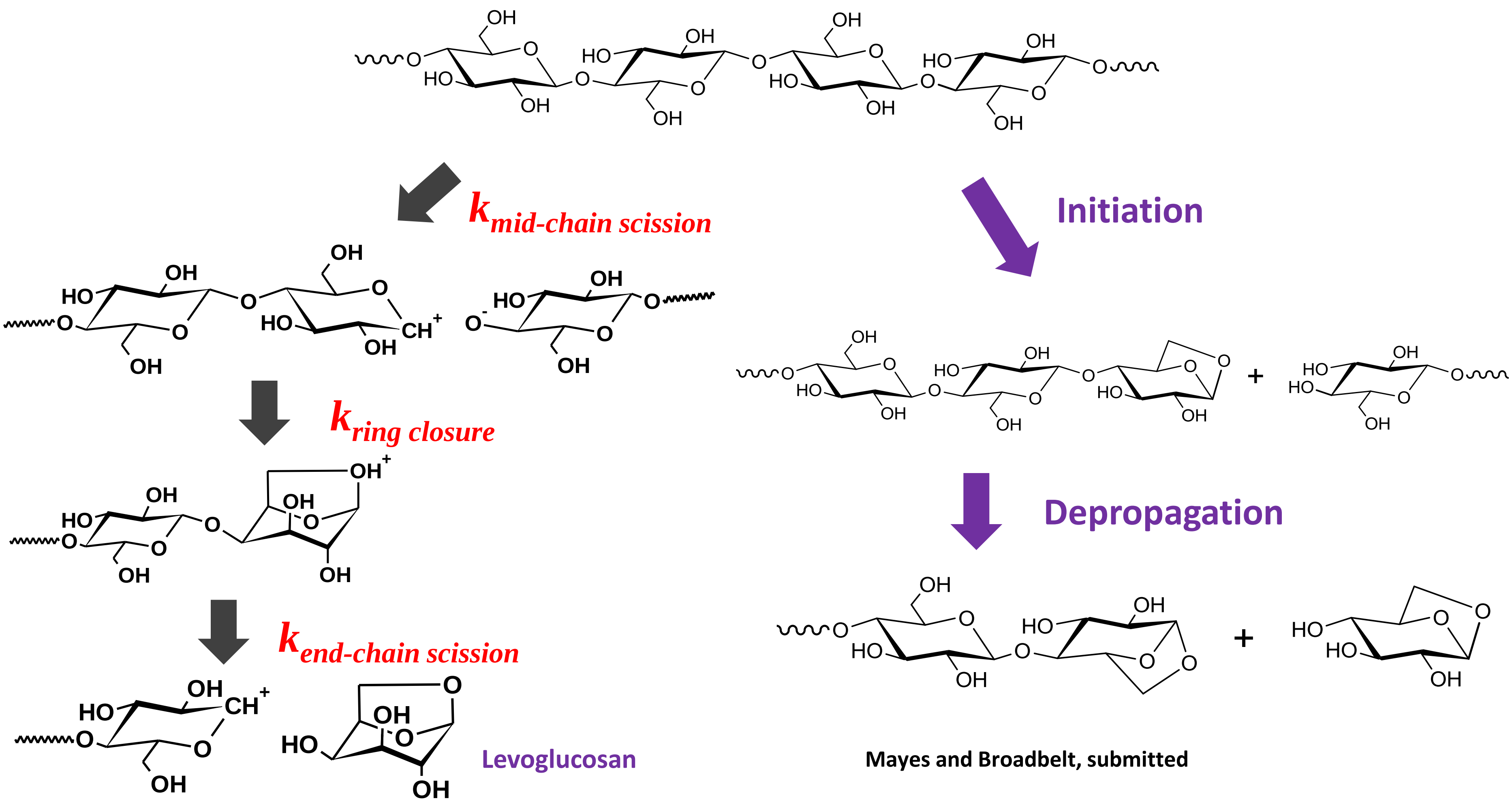
All numbers are wt%
LMW – Low molecular weight compounds

Patwardhan, P.; et al. *J. Anal. Appl. Pyrolysis* 2009, *86*, 323

Proposed Mechanism



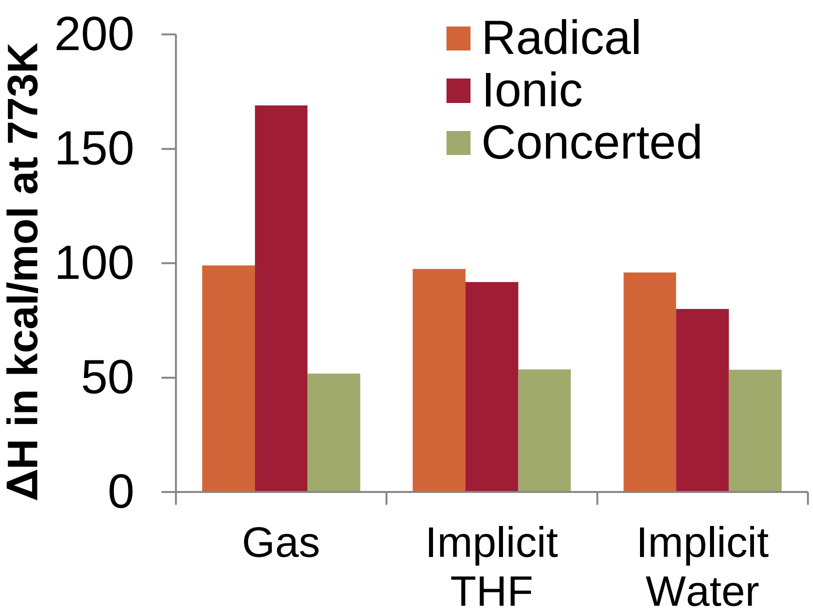
Quantum Chemistry Investigations



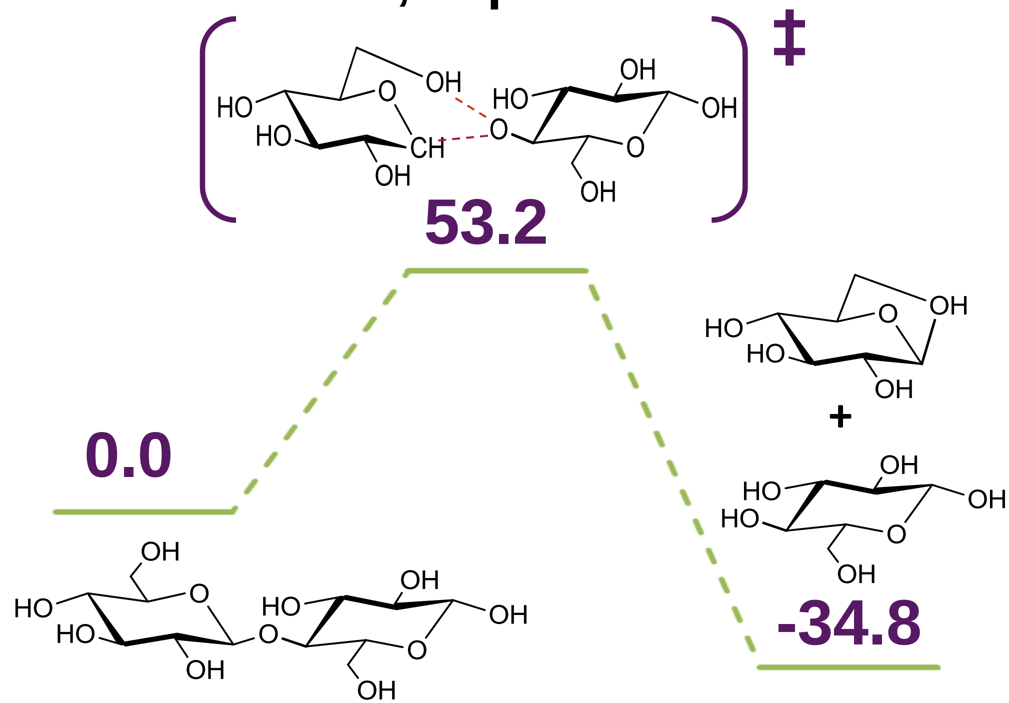
Mayes and Broadbelt, submitted

Ponder *et al.*, *J. Anal. Appl. Pyrolysis* 1992, 22, 217-229.

Quantum Chemistry Investigations Results



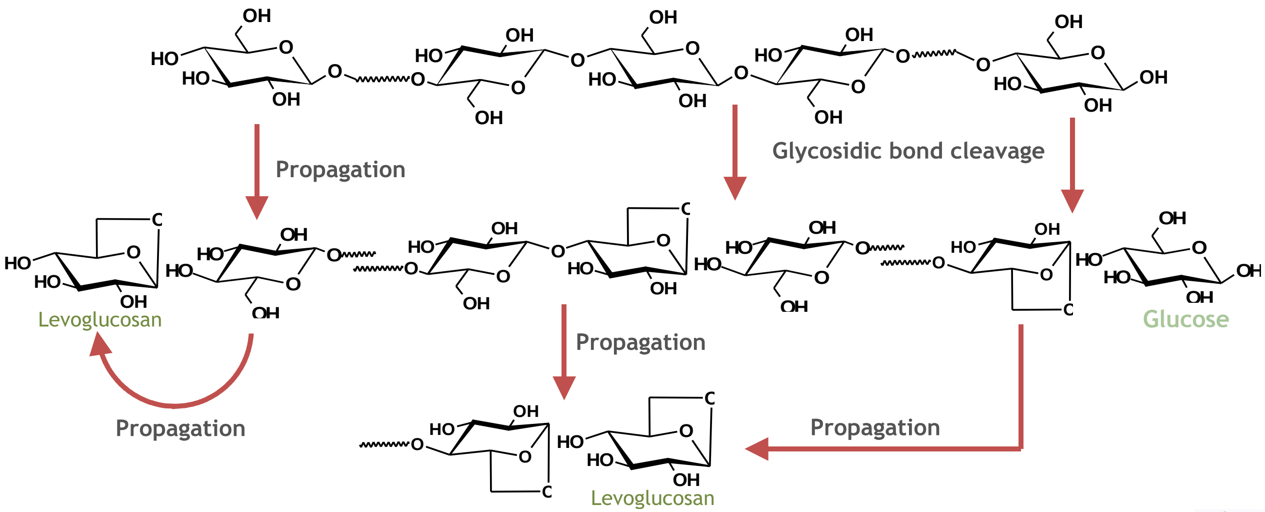
Concerted Mechanism ΔG in kcal/mol 773K, Implicit THF



$$k = 5 \times 10^{13} \frac{1}{s} \times e^{(-54.7kcal/mol)/RT}$$

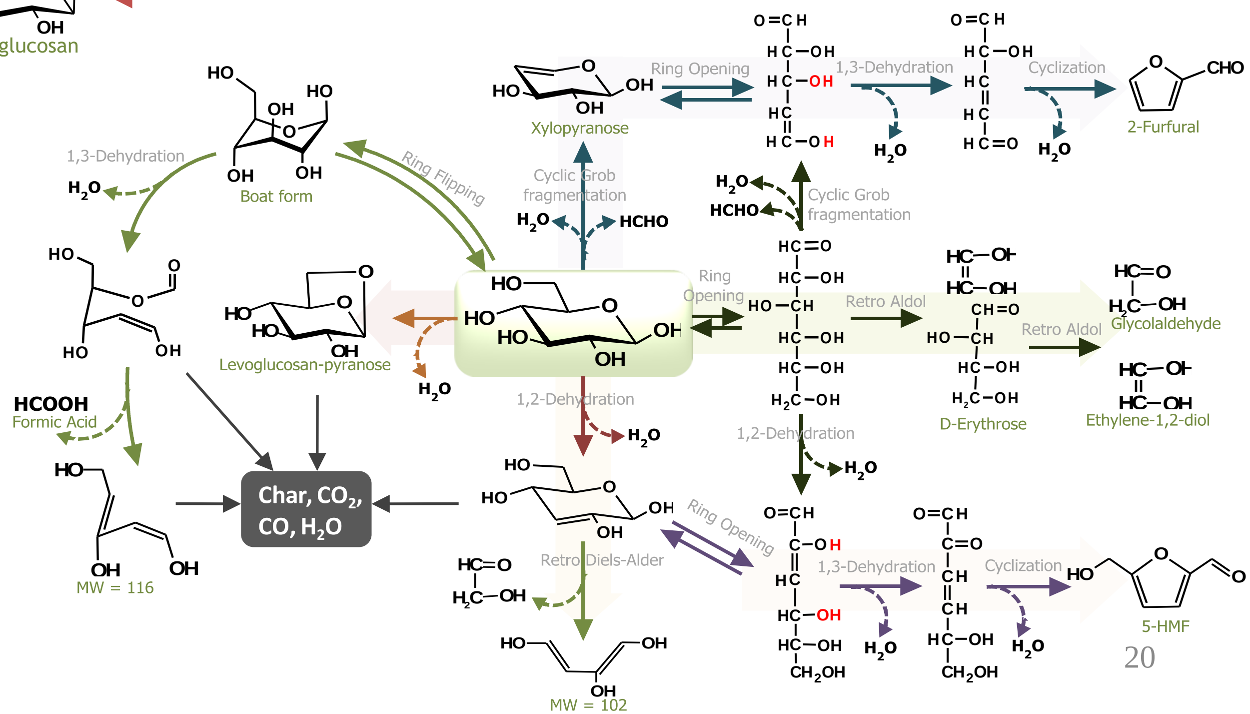
Mayes and Broadbelt, "Unraveling the Reactions that Unravel Cellulose," submitted.

Reaction pathways included in cellulose fast pyrolysis

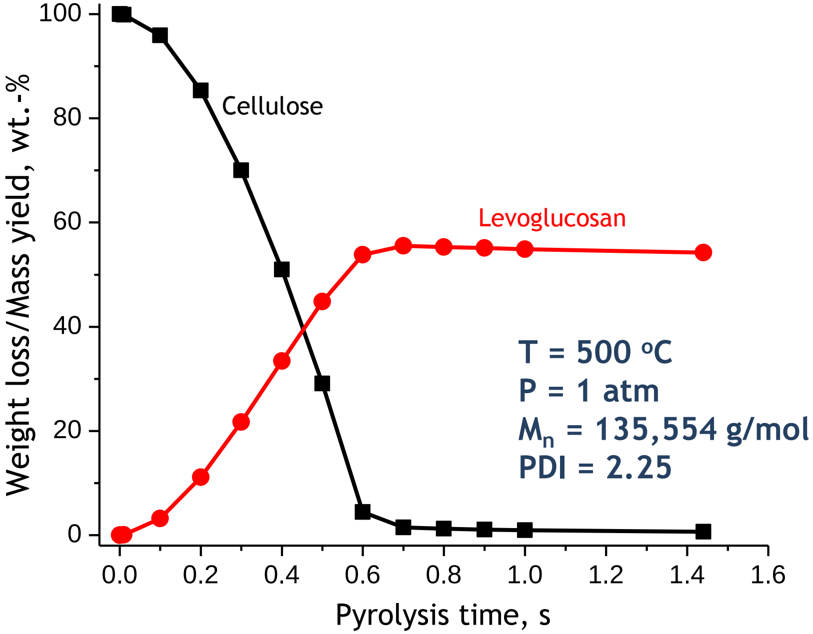


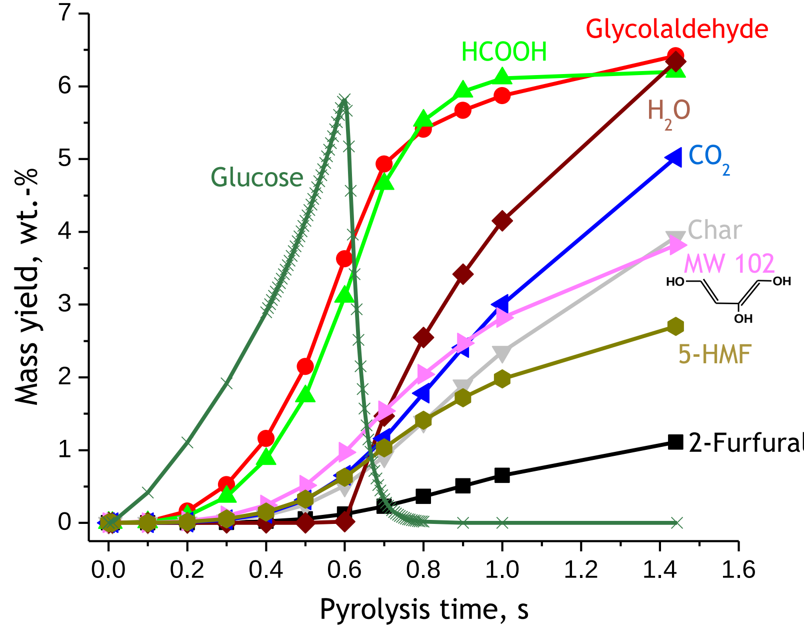
Levoglucosan is formed by concerted, glycosidic bond cleavage reactions in the mid and end of cellulose chains

All other low molecular weight products are formed from glucose through various reactions like dehydration, ring opening, ring flipping, retro aldol, retro Diels-Alder and Grob fragmentation

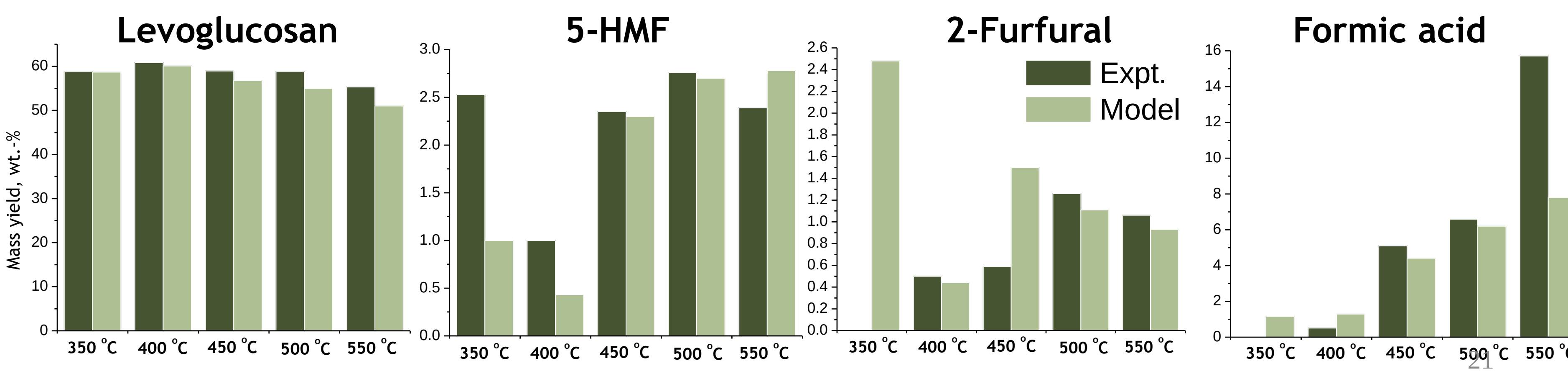


Time evolution of products of cellulose fast pyrolysis



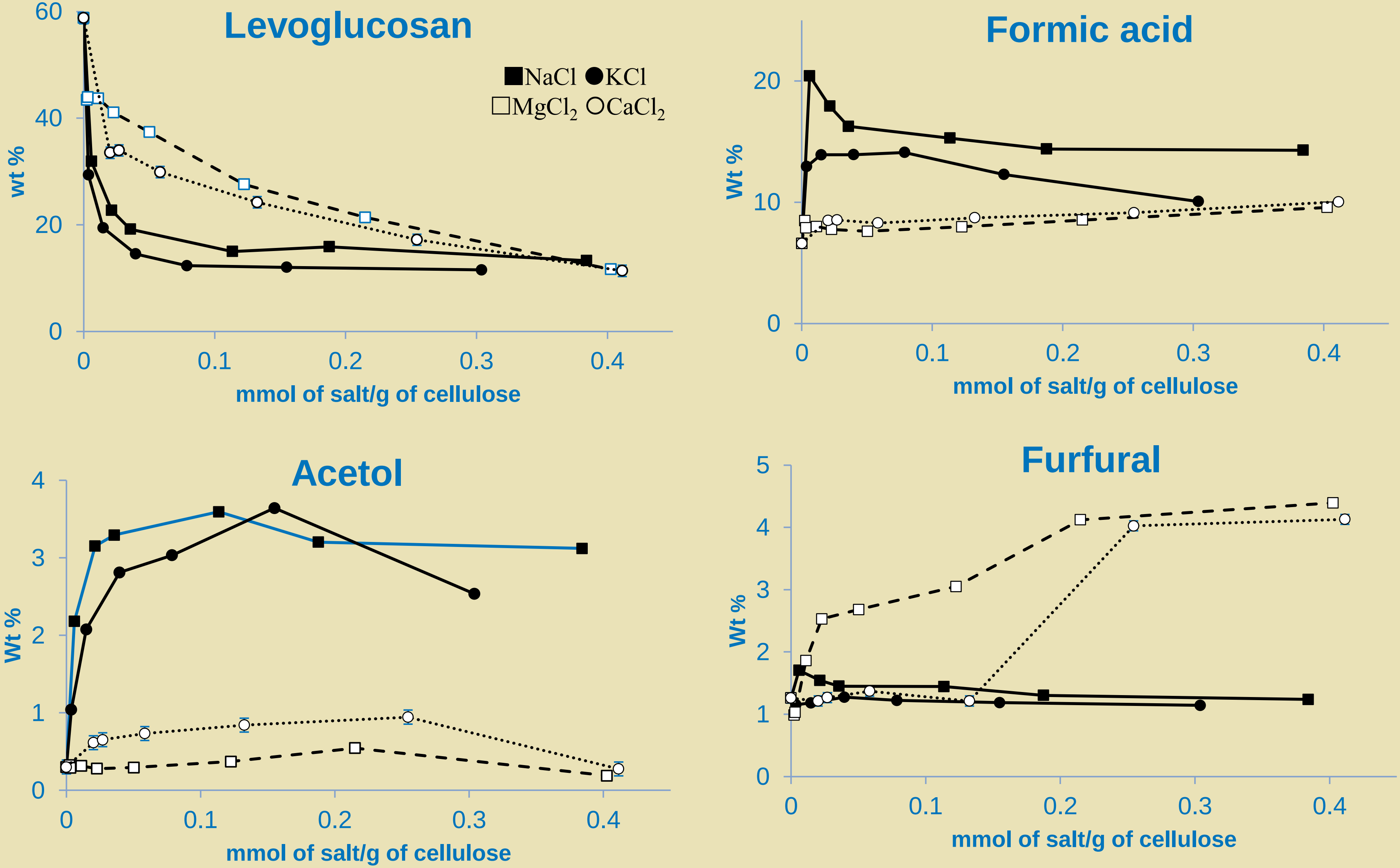


Effect of temperature on cellulose fast pyrolysis products

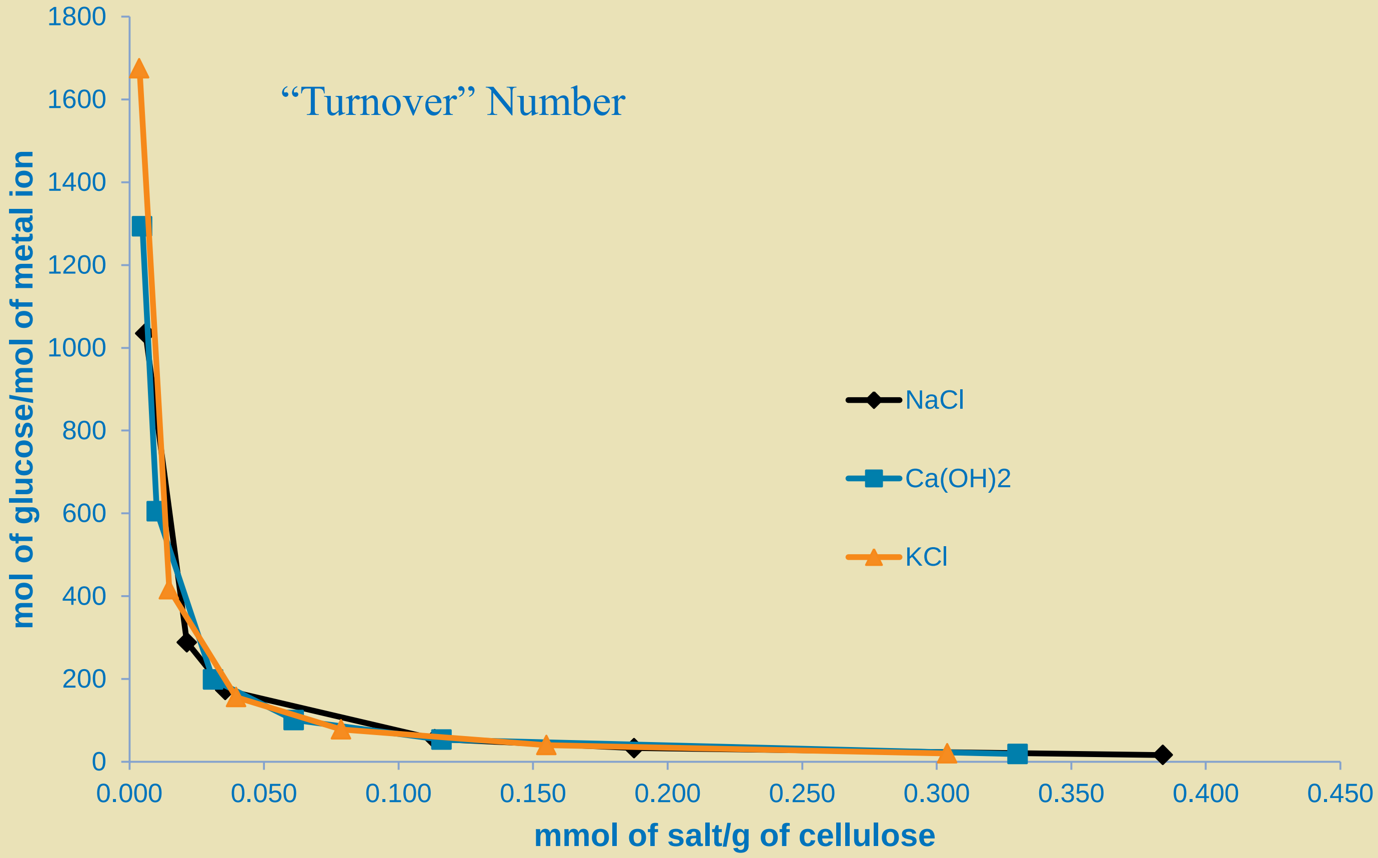


Experimental data corresponds to Patwardhan *et al.*, *Biores. Technol.* 2010, 101, 4646-4655

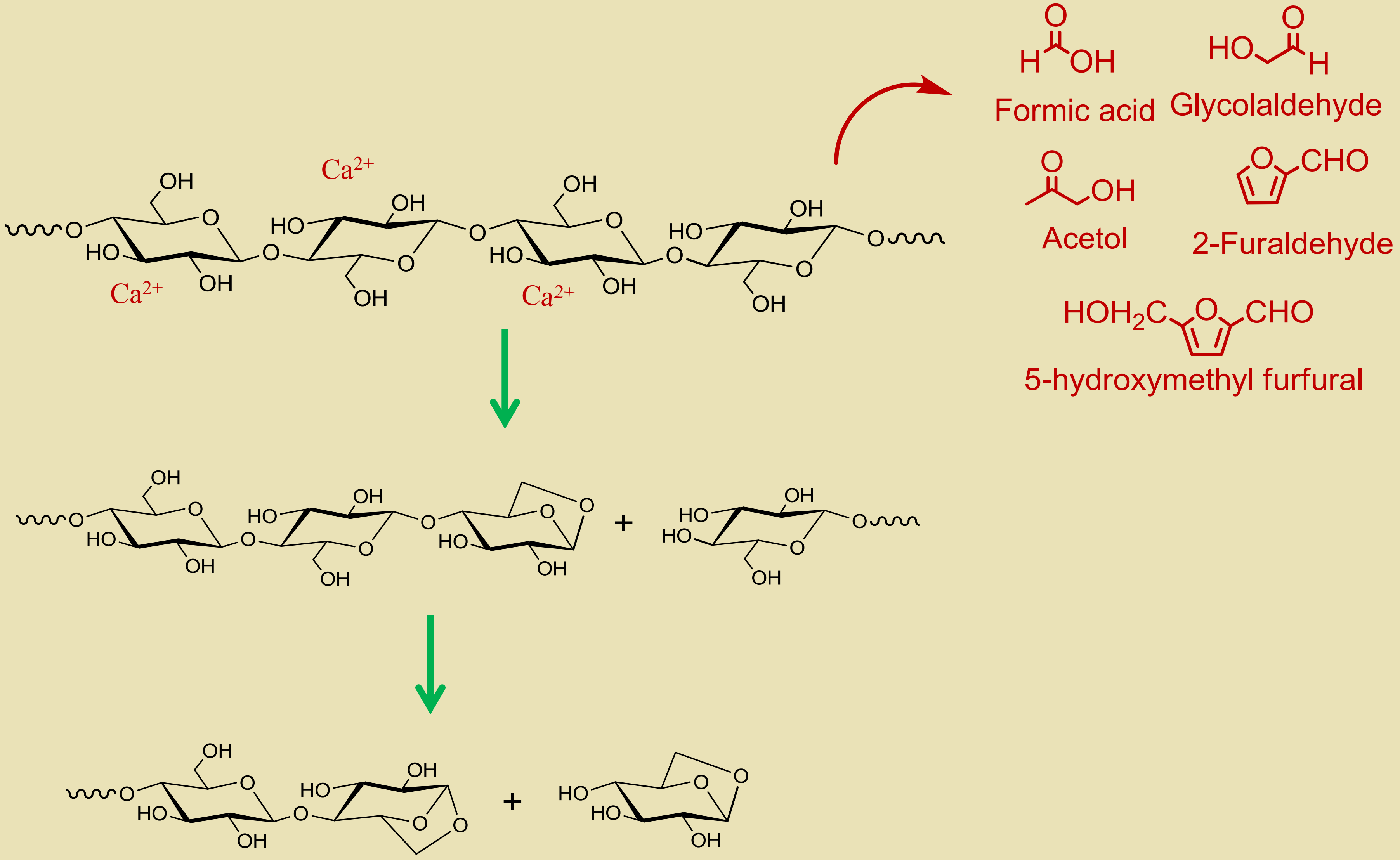
Alkali/Alkaline Earth Effects



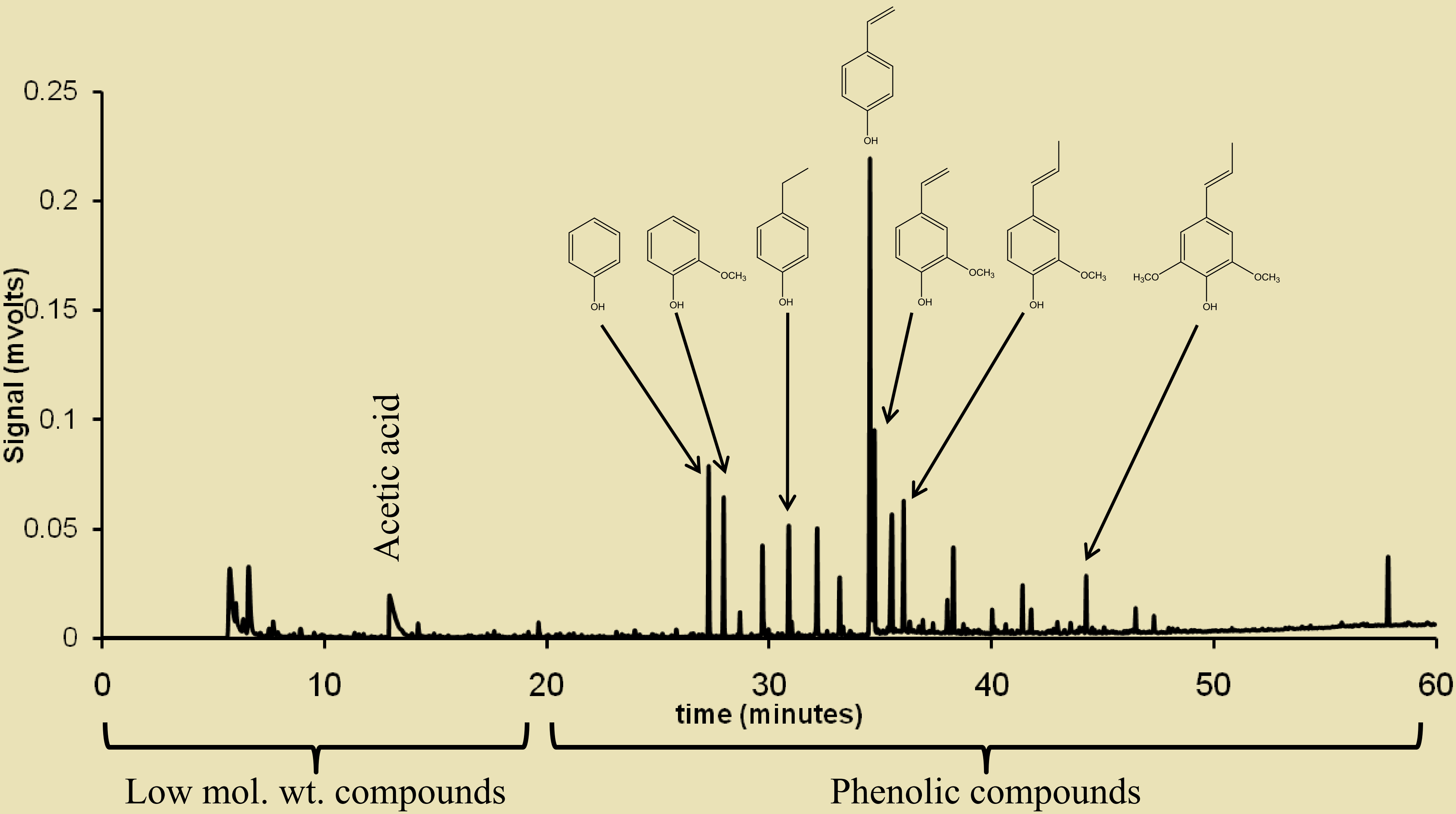
Effect of Alkali/Alkaline Earth



Proposed Mechanism

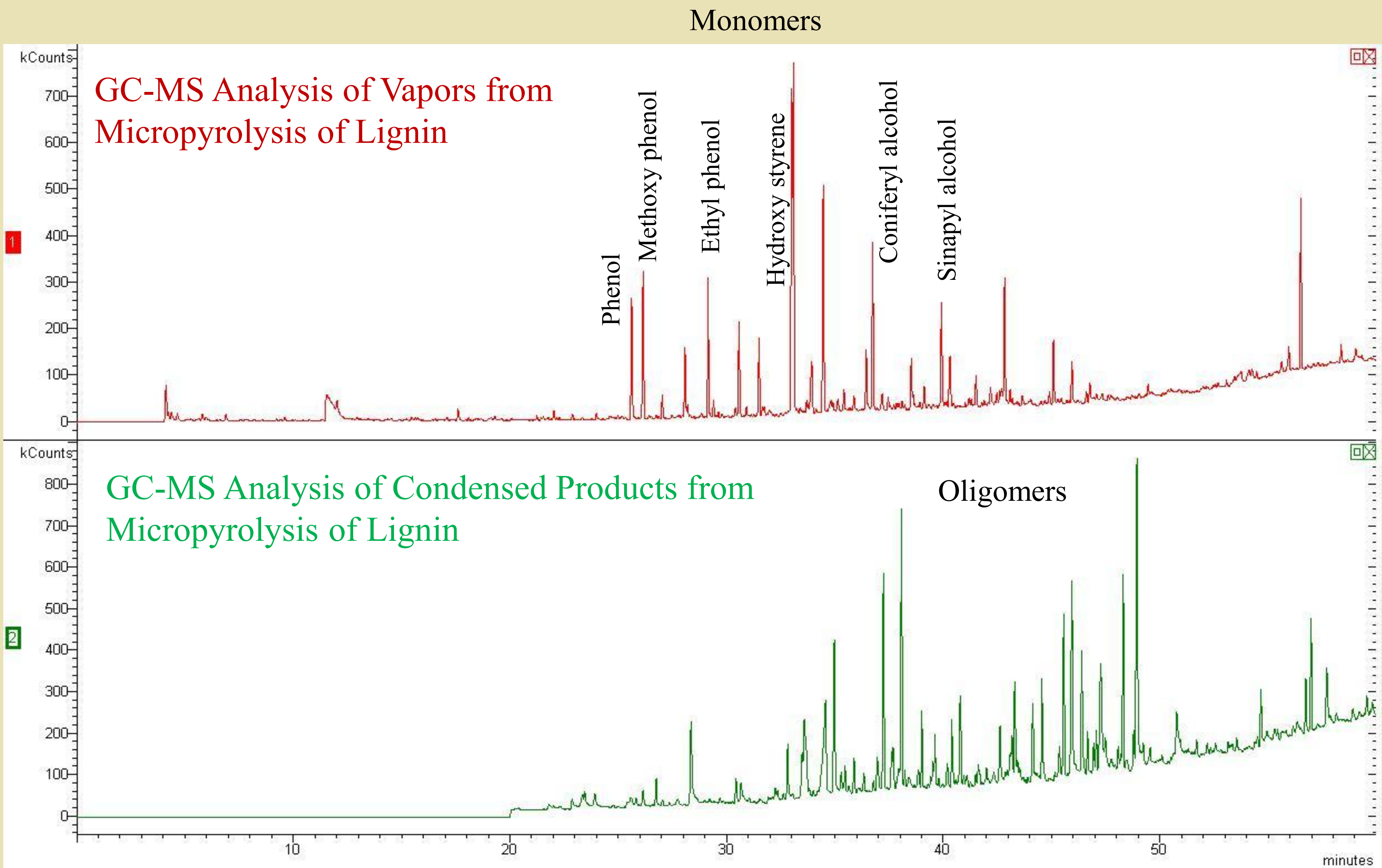


Lignin Pyrolysis

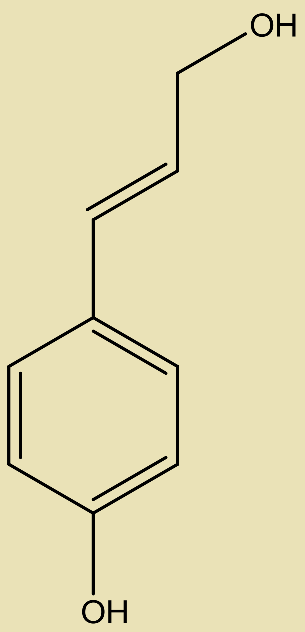


Patwardhan, P.; et al. *submitted 2011*

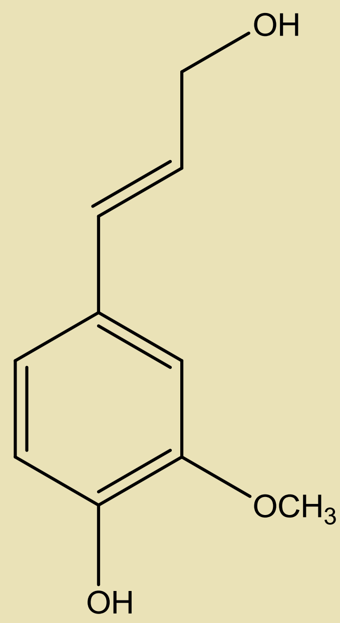
Micropyrolysis of Lignin



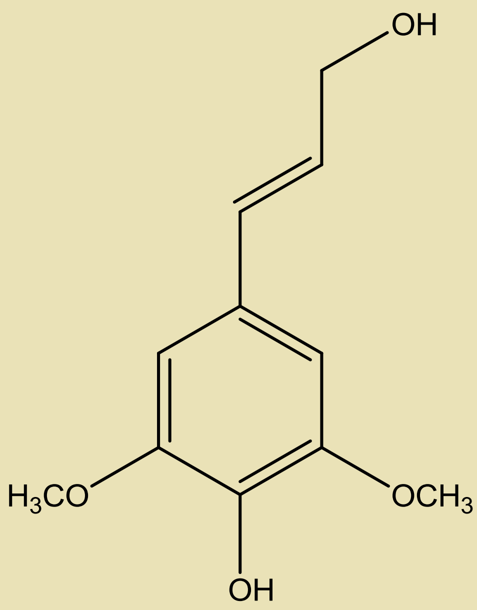
Lignin Monomers



coumaryl alcohol

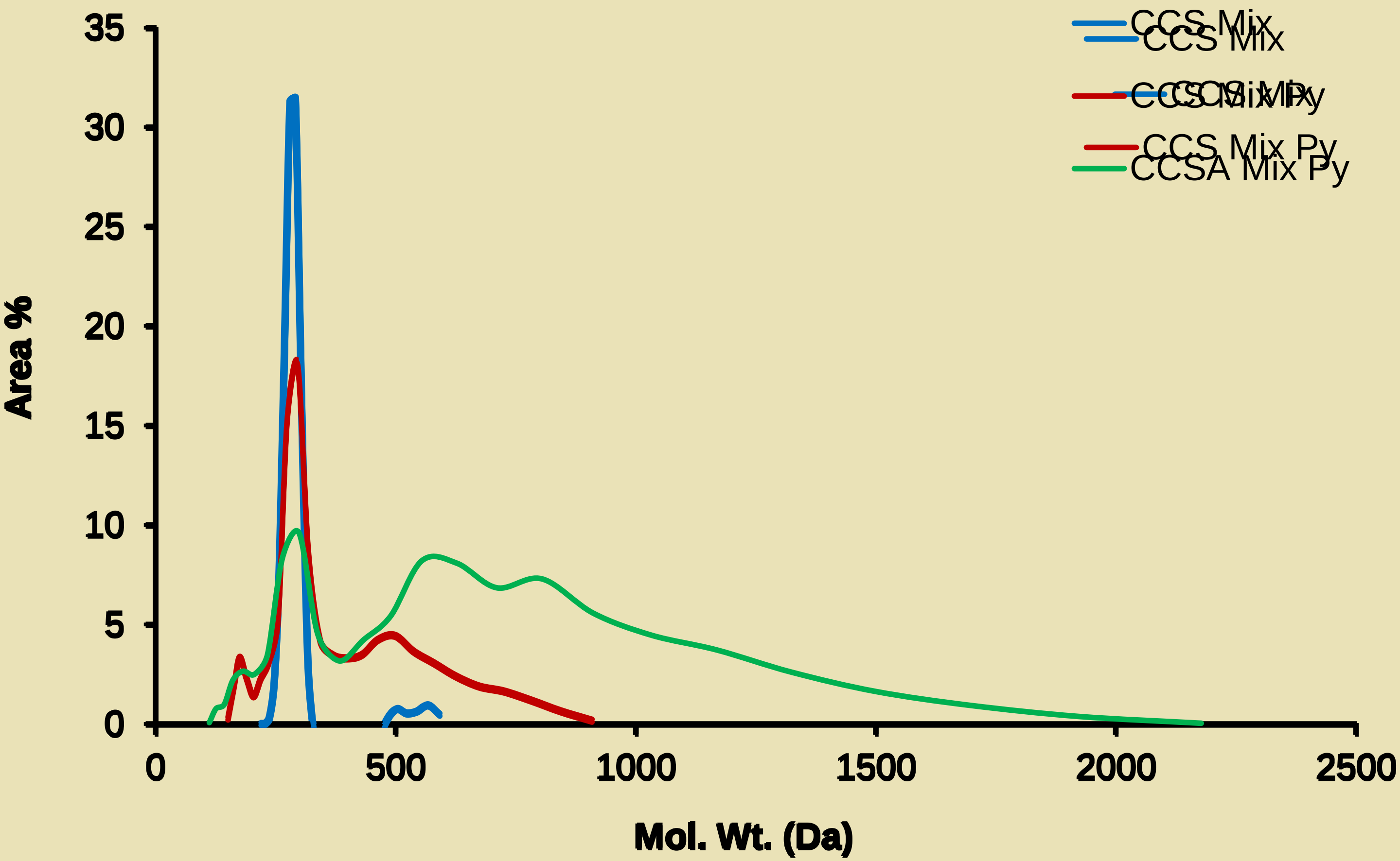


coniferyl alcohol



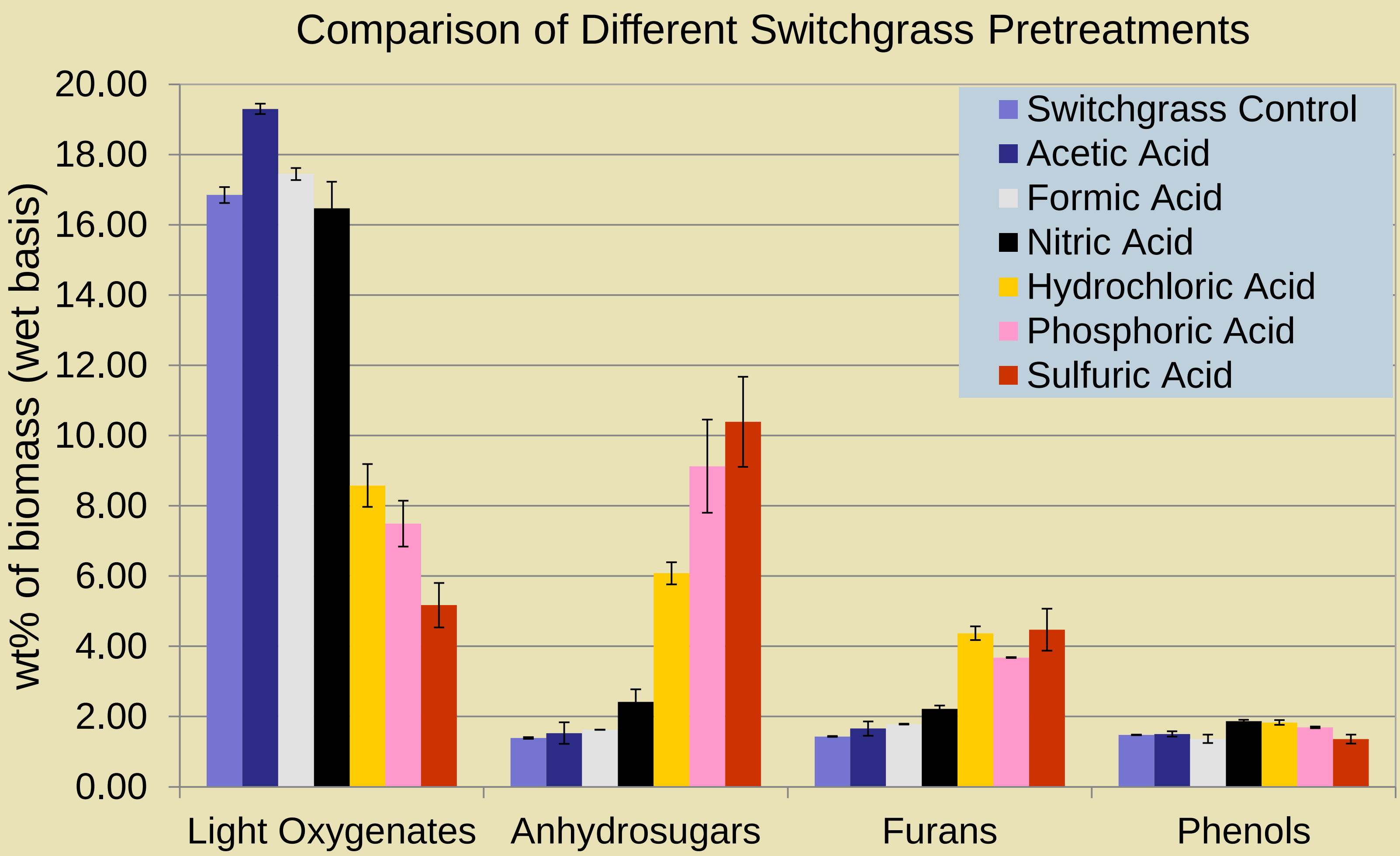
sinapyl alcohol

GPC of Lignin Monomers



Patwardhan, P.; et al. *ChemSusChem 2012*

"Passivating" Alkali in Biomass



Kuzhiyil et al. (2012) submitted

Biochar Application

Increases:

Nutrient Availability

Microbial Activity

Soil Organic Matter

Water Retention & Quality

Crop Yields

Decreases:

Fertilizer Needs

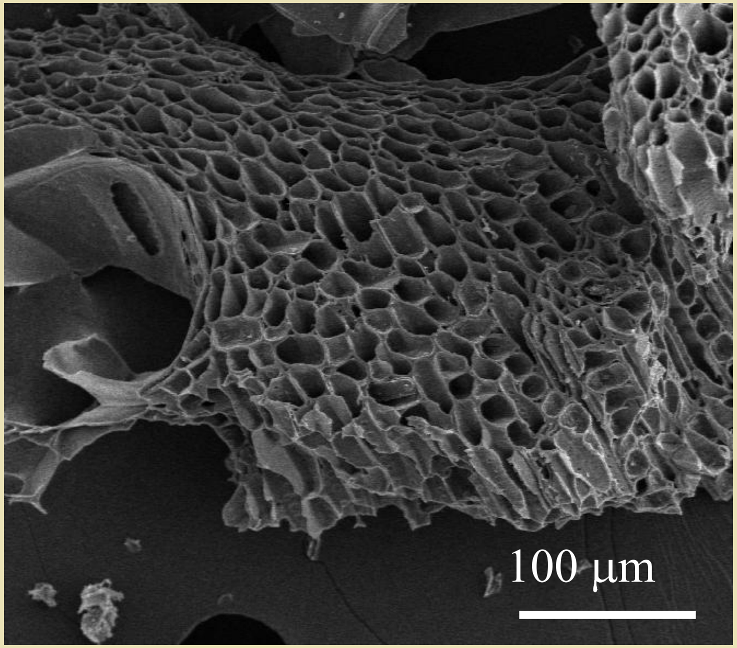
Greenhouse Gas Emissions

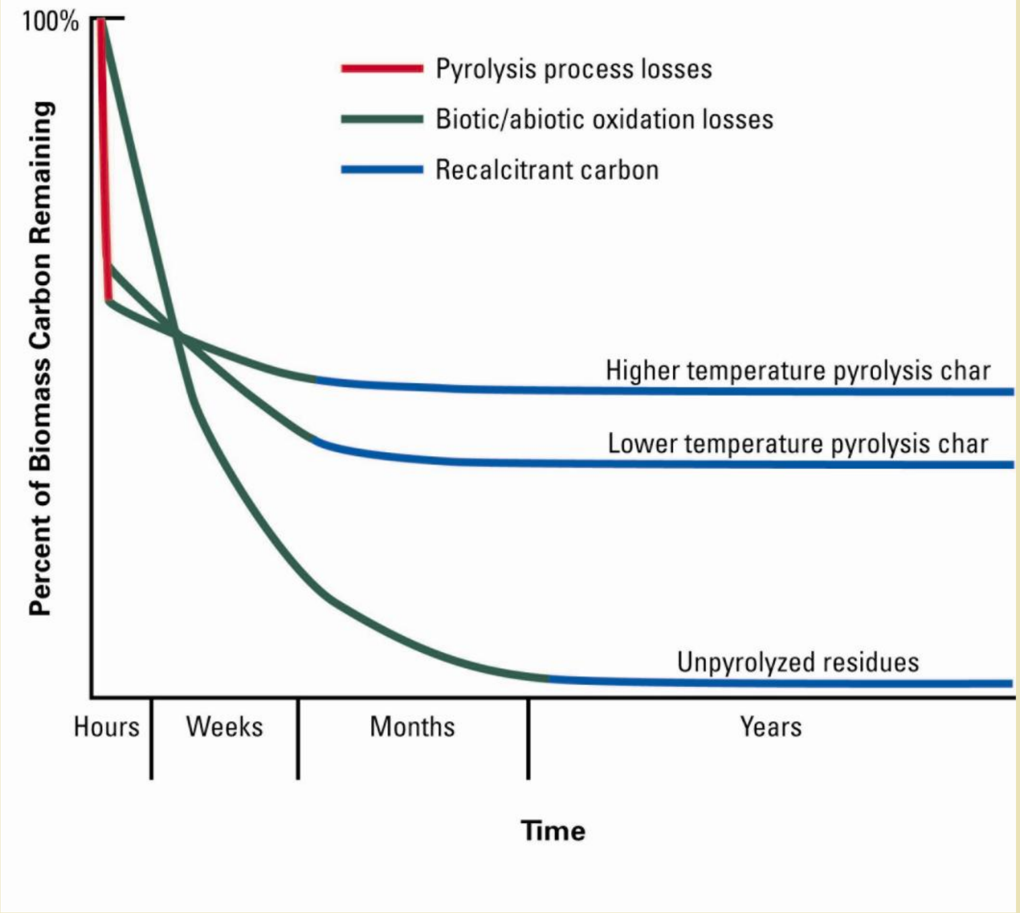
Nutrient Leaching

Soil Bulk Density

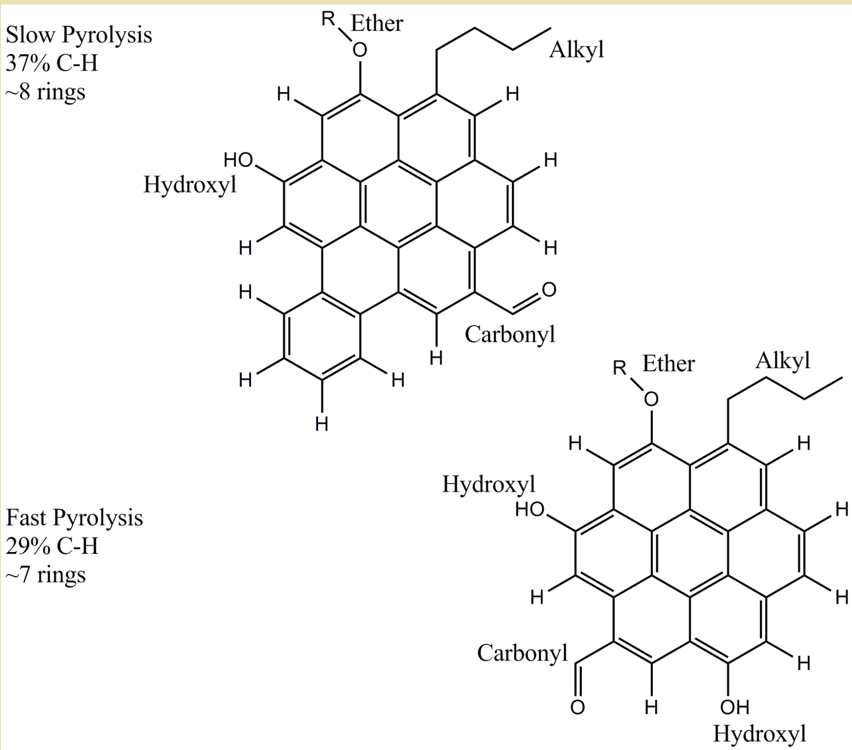
Terra Preta | Oxisol

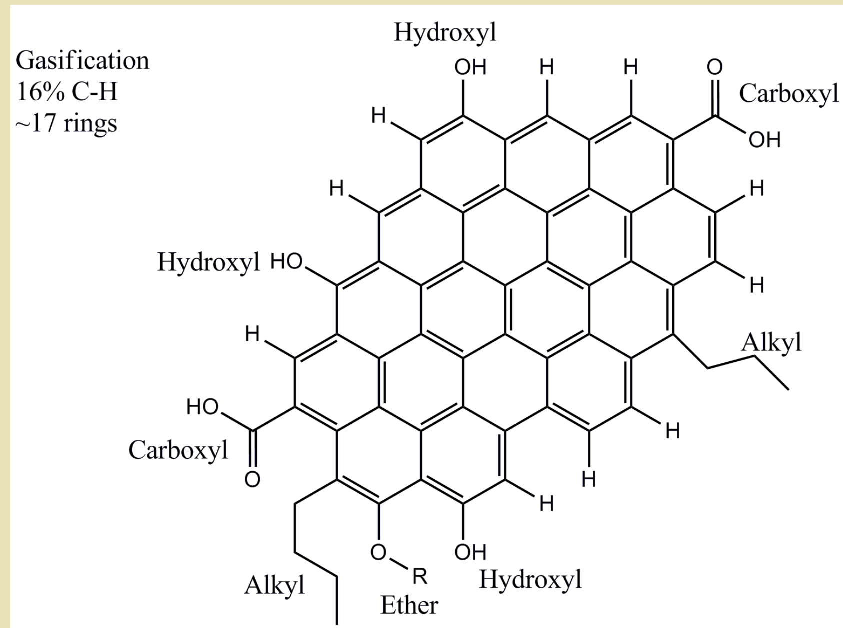
Carbon Residence Time





Biochar "Average" Structure





Moderate Temperature

High Temperature

Brewer, et al. *Environ. Prog. Sustainable Energy* **2009**, *28*, 386-396.

Key Challenges

- Gasification

  → *issue of scale*

- Pyrolysis

  → *issue of product quality*

Acknowledgements

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- U.S. Department of Energy

National Advanced Biofuels Consortium