



Aalto University

Department of Bioproducts and Biosystems
School of Chemical Engineering

Introduction to Lignin Chemistry and Technology

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Outline – Deliverables

- ❖ Lignin Structure
- ❖ Lignin analysis
- ❖ Technical lignins
- ❖ Lignin Engineering
- ❖ Lignin utilizations:
 - ❖ Fuel
 - ❖ Macromolecular material
 - ❖ Aromatic monomers
- ❖ Market issues

Lignin Chemistry in Biorefinery

- ❖ The structure of lignin is the key point in understanding:
 - ❖ the reactivity of the substrates
 - ❖ the reaction mechanisms
 - ❖ utilization of technical lignins
- ❖ Variety of lignocellulosic substrates:
 - ❖ Different lignocellulosics (wood, agricultural residues, wastes etc.)
 - ❖ Breeding programs
 - ❖ Genetic engineering
- ❖ Variety of technical processes

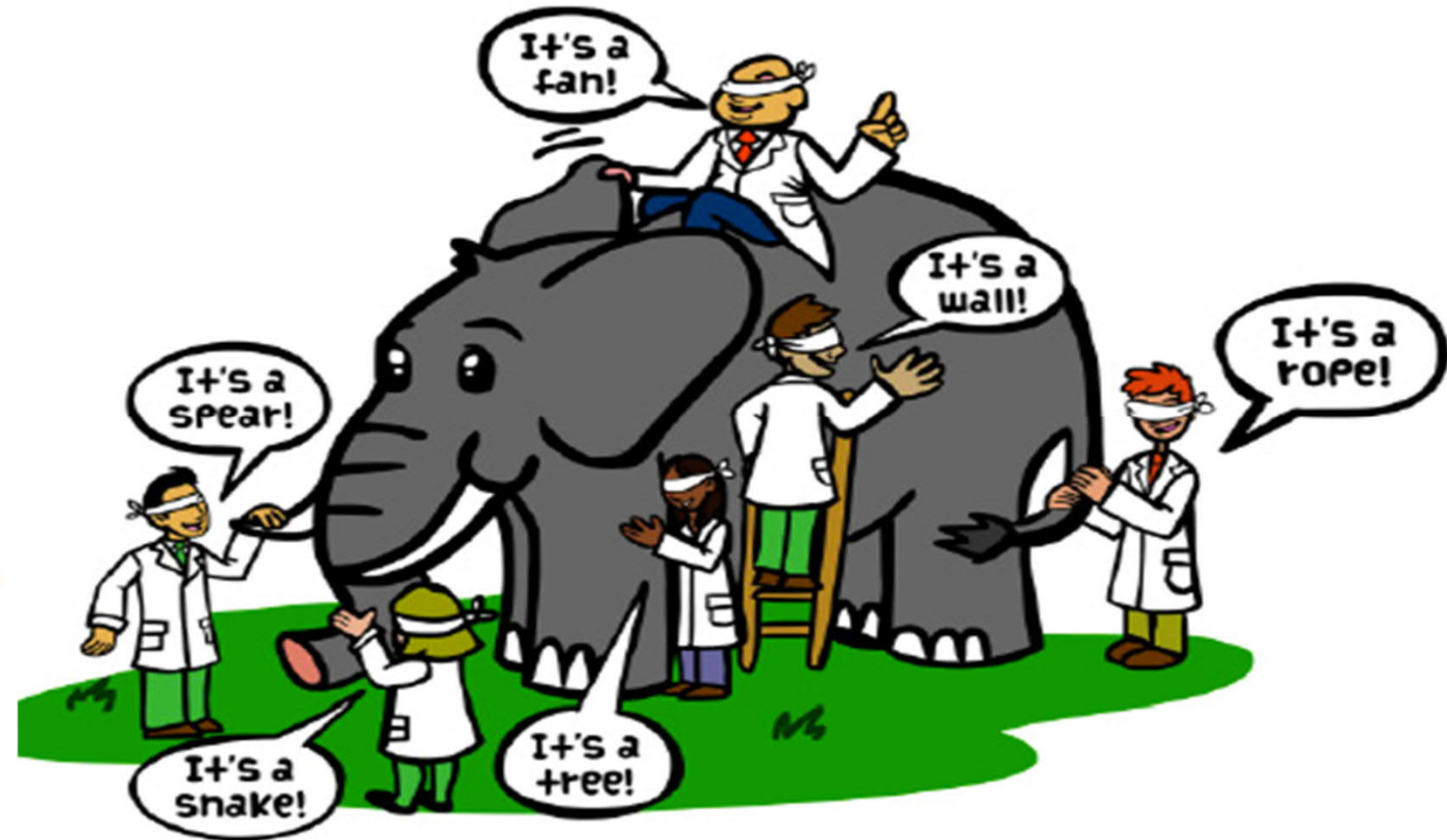
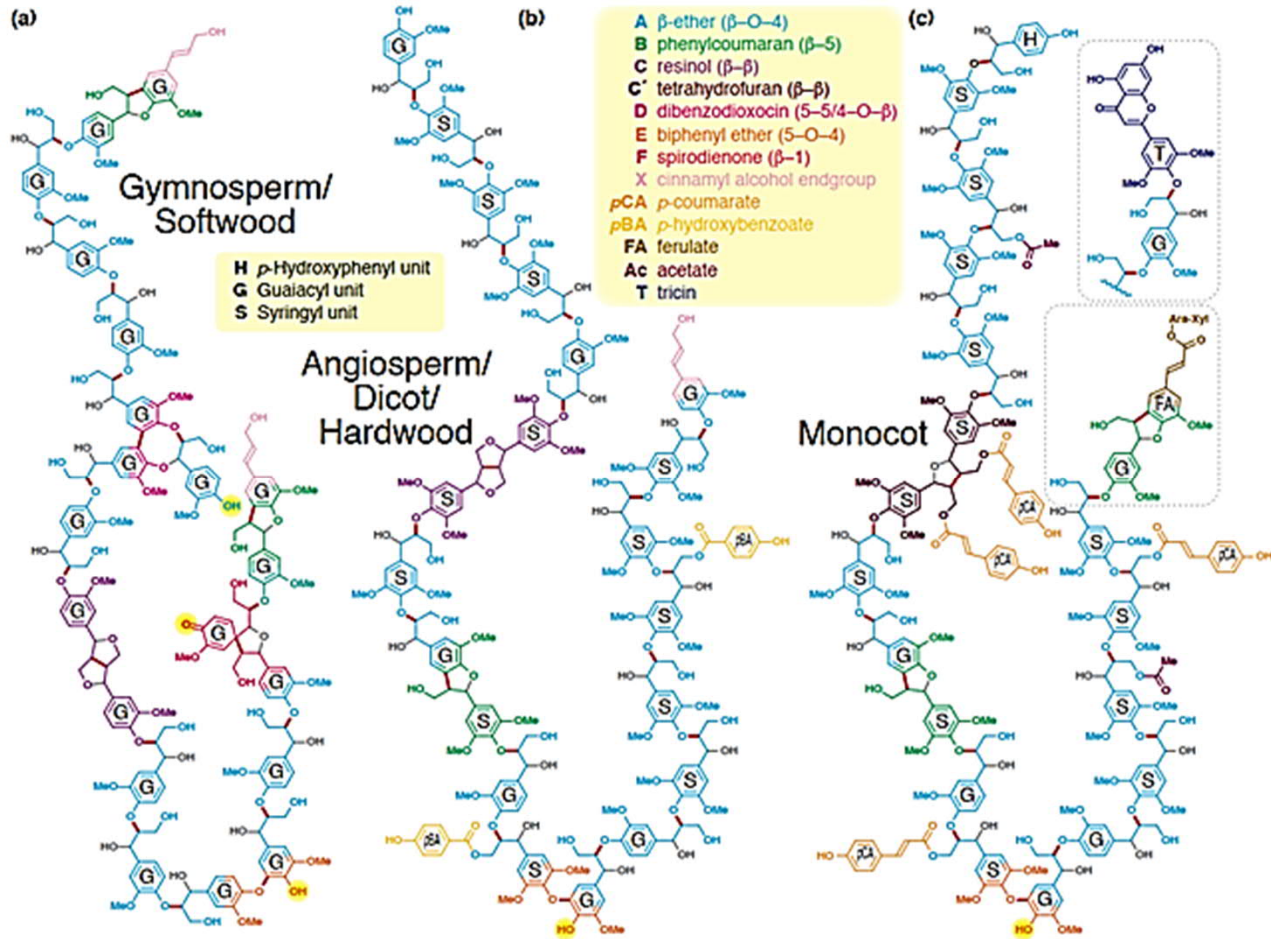
Lignin Variety

The same word “Lignin” is used for quite different materials. It is like wine



There is no perfect lignin; best lignin candidate is application dependent (similar to paper)

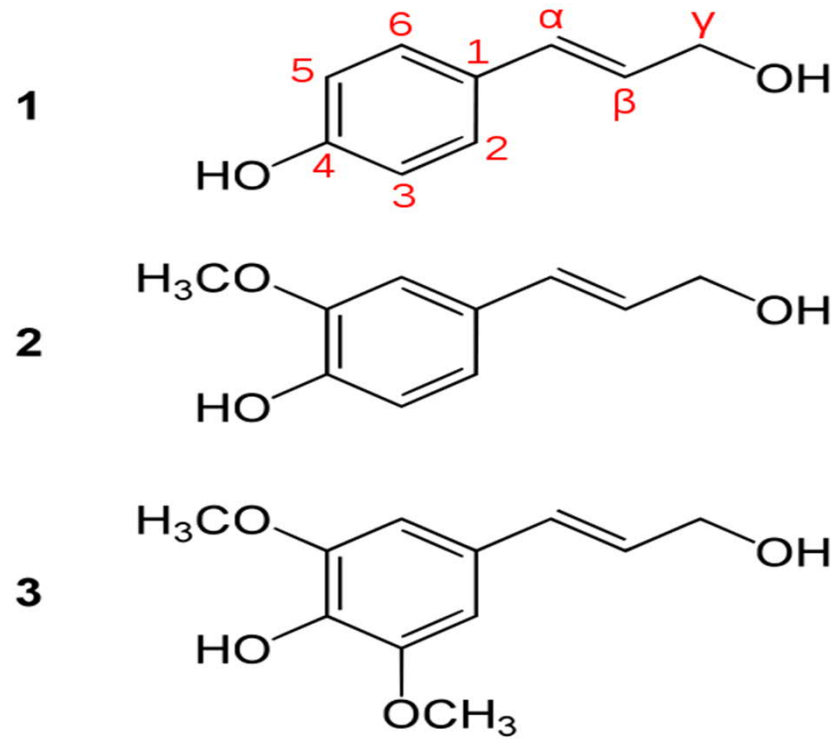
Lignin is Very Complex



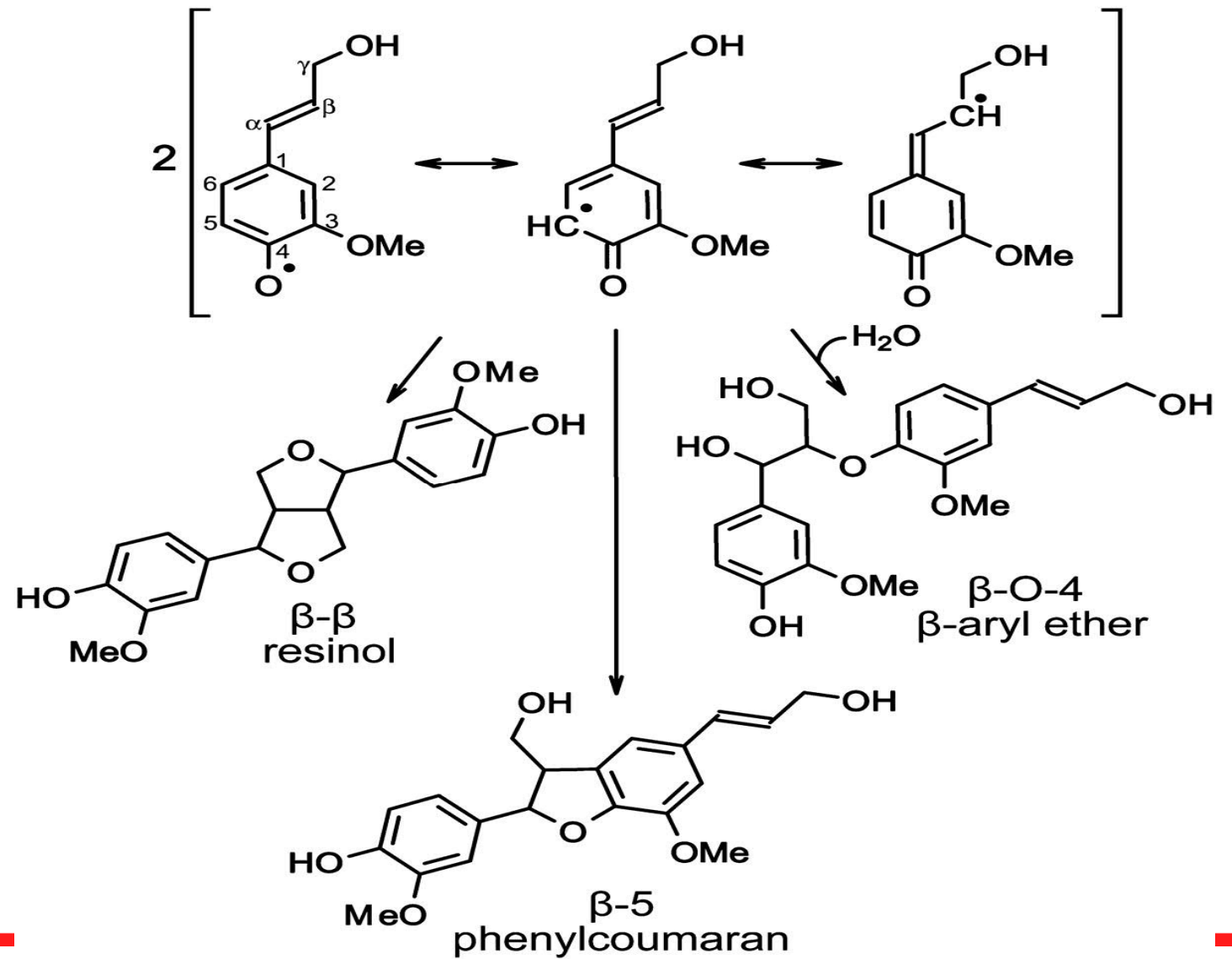
Ralph et al. 2019

- ❖ High variety of structural units and inter-unit linkages
- ❖ Comprehensive approach for lignin characterization is required

Lignin Polymerization



- 1: *p*-coumaryl alcohol (H-units)
 2: coniferyl alcohol (G-units)
 3: sinapyl alcohol (S-units)



Structural Model of Native Lignin (MWL)

Green Chemistry



CRITICAL REVIEW



Cite this: *Green Chem.*, 2020, **22**, 3985

Spruce milled wood lignin: linear, branched or cross-linked?

Mikhail Balakshin, ^{*a} Ewellyn Augsten Capanema, ^b Xuhai Zhu, ^{†a} Irina Sulaeva, ^c Antje Potthast, ^c Thomas Rosenau ^c and Orlando J. Rojas ^{a,d}

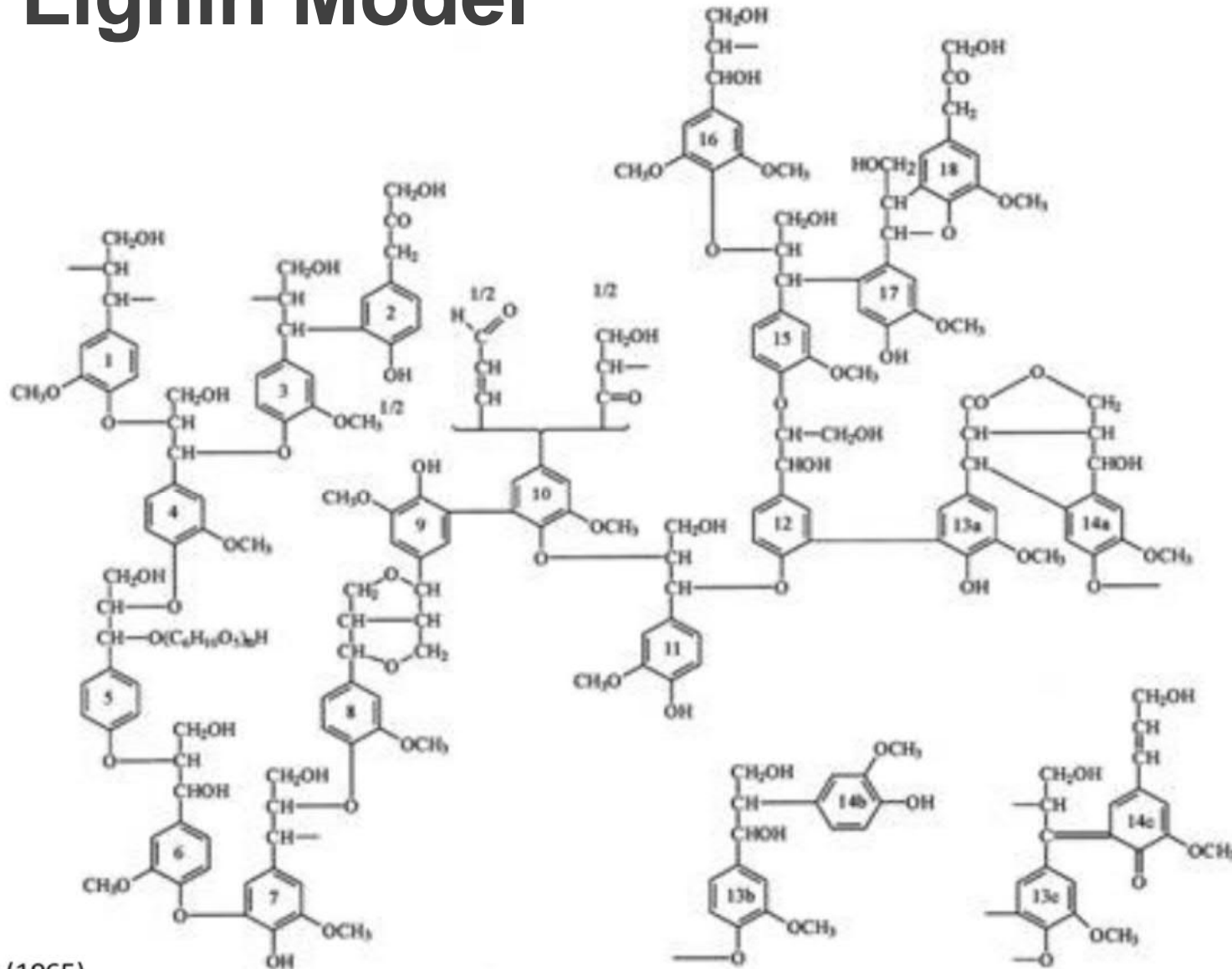
The subject of lignin structure, critical for fundamental and practical reasons, is addressed in this study that includes a review of the methods applied to elucidate macromolecular branching. The recently available approaches for determination of the absolute molecular mass of spruce milled wood lignin (MWL) along with the quantification of terminal groups clearly indicate that MWL is significantly branched and cross-linked (with ~36% lignin units partaking in these linkages). Results from independent methods imply that about half of the branching and crosslinking linkages involve aromatic rings, predominantly 5–5' etherified units; meanwhile, a significant number of linkages are located in the side chains. Quantitative ¹³C NMR analyses suggest that the branches involve different aliphatic ether (alkyl-O-alkyl) types at the α - and γ -positions of the side chain, with intact β -O-4 linkages. While the exact structures of these moieties require further investigation, our results point to the fact that conventional lignification theory disagrees with the presence of such key moieties in softwood MWL and the observed high degree of branching/crosslinking. Potential reasons for the noted discrepancies are discussed.

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rsc.li/greenchem

First Lignin Model



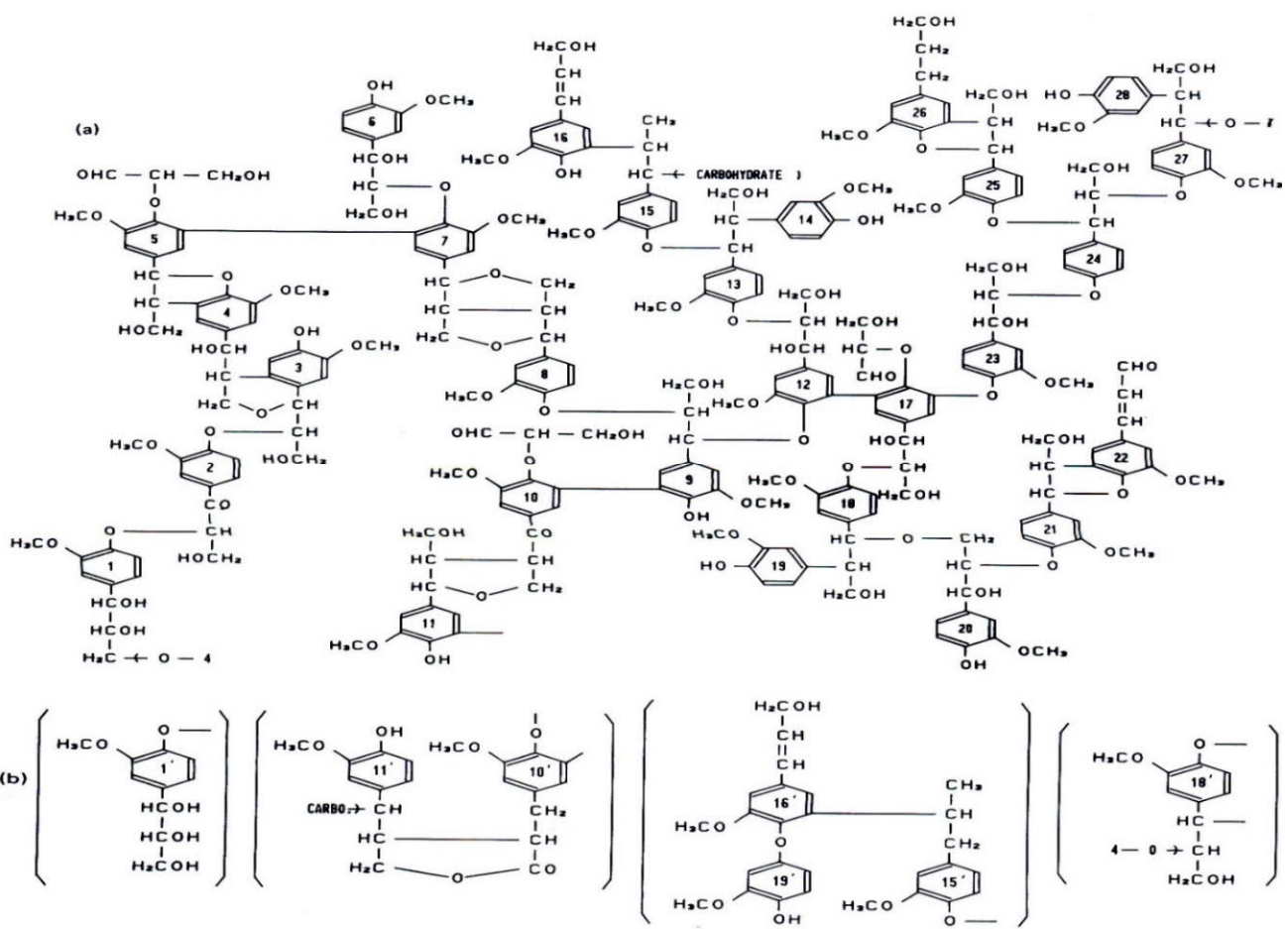
Freudenbrerg (1965)



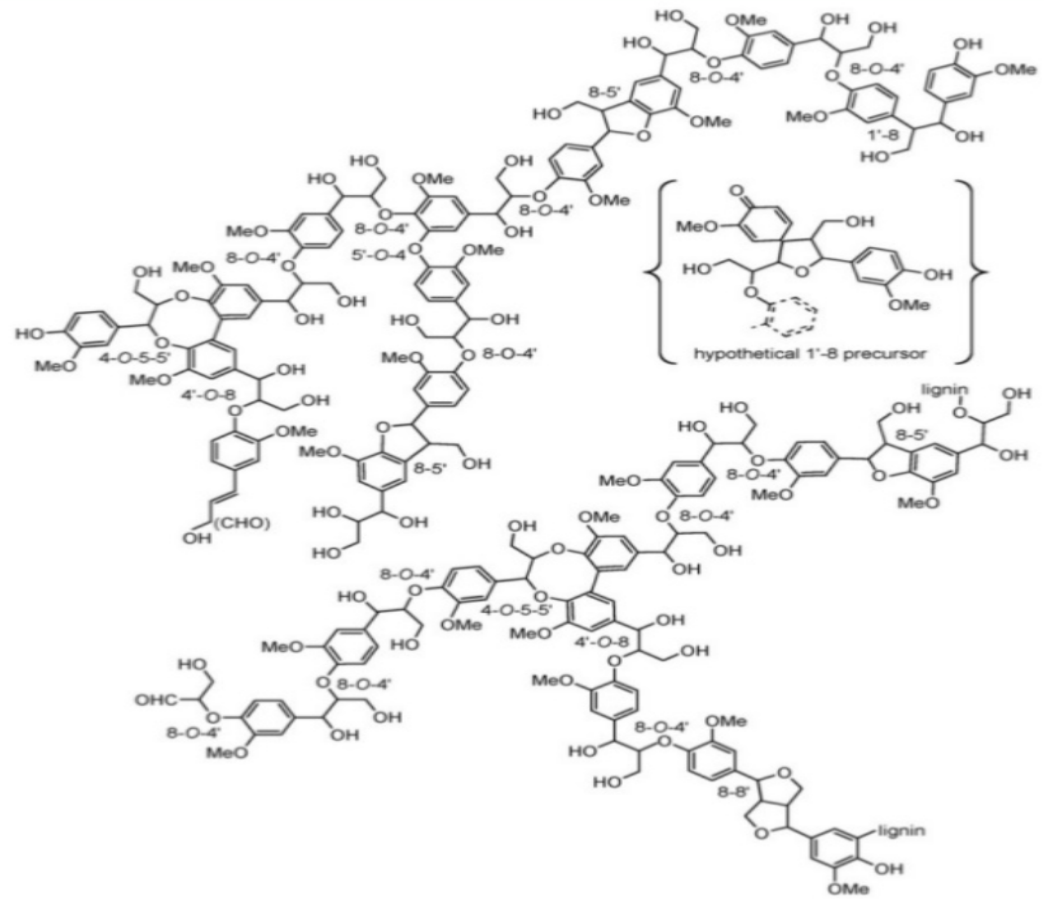
K. Freudenberg
Heidelberg Univ.
1965

❖ This is not a real lignin structure, but rather visualization of certain structural features

Recent Models of Native Softwood Lignins

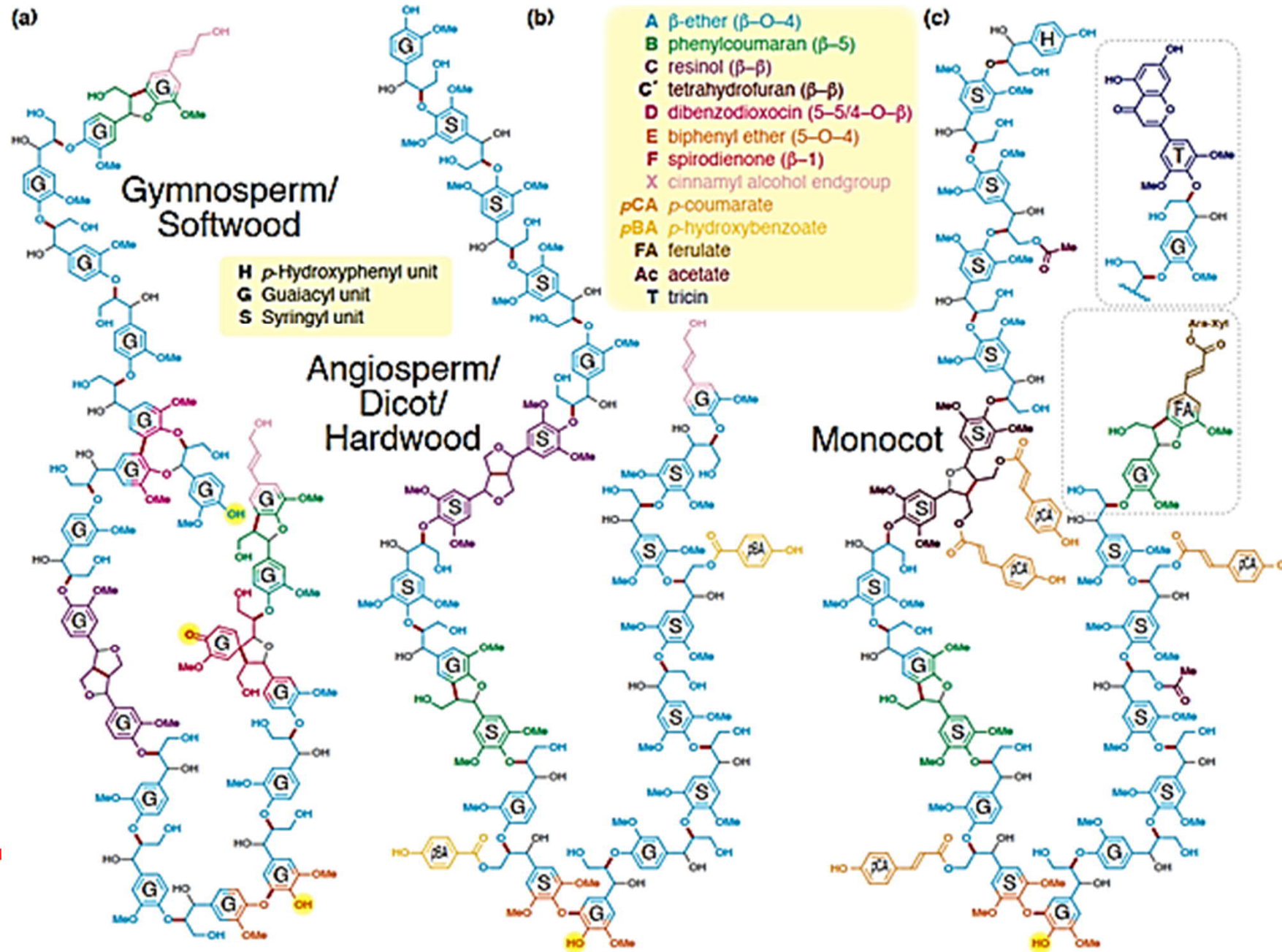


Quantitative Sakakibara's model (1991)



Brunow's model 1998 (non-quantitative)

Recent Models of Native Lignins



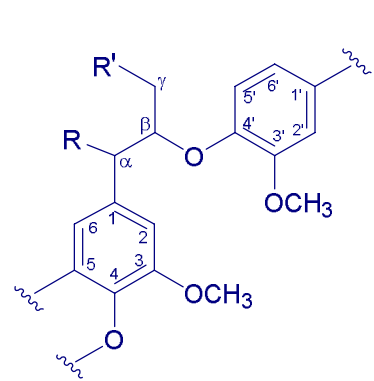
Ralph et al. 2019
Very linear

Based on the current lignification theory

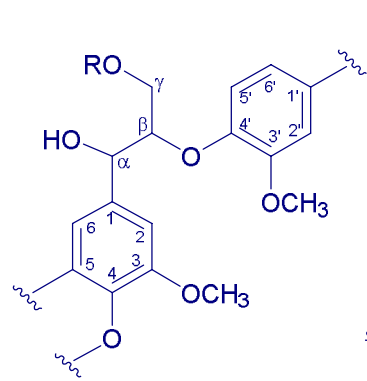
This are not real lignin structures

MWL Major Units (per 100 Ar):

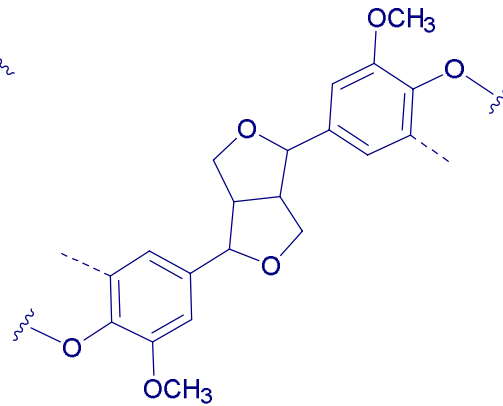
What is New after Sakakibara?



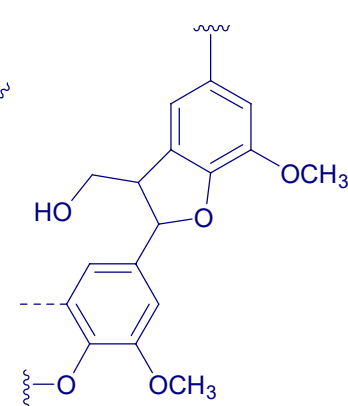
Total β -O-4
 ~50
45



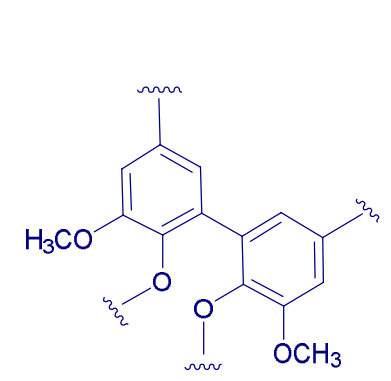
β -O-4/ α -OH
 36
16



β - β
 2
14

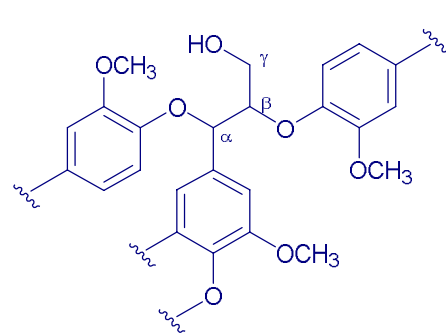


β -5
 10
14

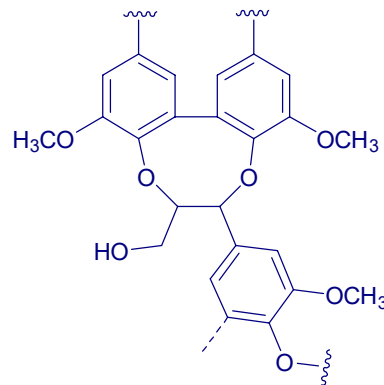


5-5'
 12
11

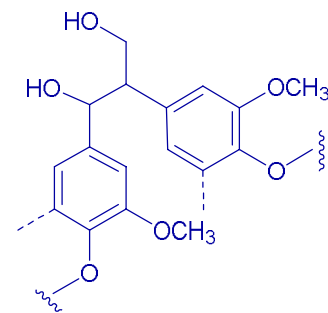
Current
Sakakibara



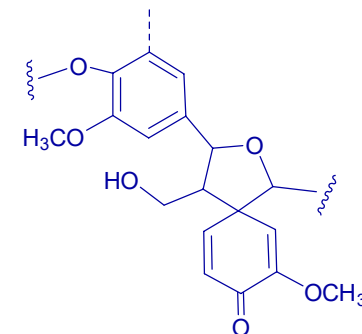
β -O-4/ α -O-4
 <1
10



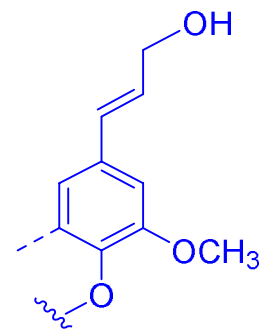
DBDO
 4
NA



β -1/ α -OH
 1-2
10



SD
 2
NA



CA
 2
3

Current
Sakakibara

Functional Groups and Interunit Linkages in Spruce MWL (per 100 Ar)

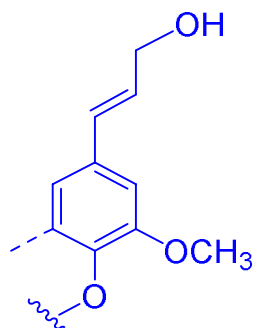
Structure	Amount	Structure	Amount
β -O-4	44-53	Total carbonyl	15-21
Total OH	130-138	aldehyde	3-9
Aliphatic OH	100-107	ketone	10-17
primary	68-79	α -CO	6-10
benzylic	38	non-conjugated	5-10
Phenolic OH	25-32	Alk-O-Alk	38-46
Total COOR	2-5	Alk-O-Ar	61-67
conjugated	2	5-5'	20-27
aliphatic	3	Degree of conden.	37-45

Lignin: Linear, Branched or Cross-linked?

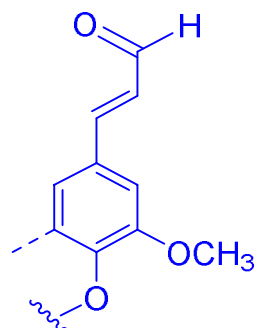
- Lignin reactivity
 - More cross-linked, implies less reactive
- Lignin applications:
 - Linear – preferable for carbon fiber
 - Highly cross-linked – preferable for sorbents
 - Moderately cross-linked – preferable for wood adhesives (PF)
- **Classical version:** lignin is 3-dimensional cross-linked polymer
- **Recent claim:** Lignin (MWL) is linear (Crestini et al. 2011, Ralph et al. 2019)

Terminal Units (per 100 Ar)

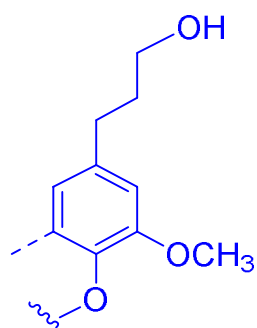
- Side Chain:



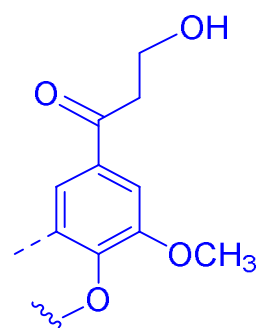
2



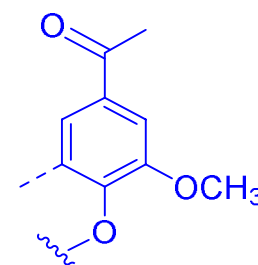
4



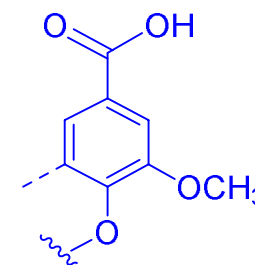
2



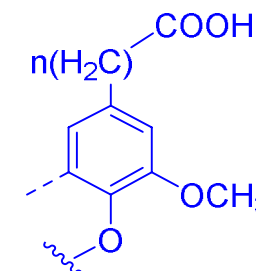
2



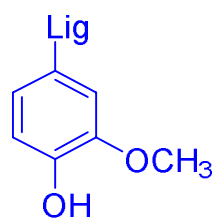
4



1



3



26

Total Terminal units
T = 44%

Linear Polymer:

DP=2: T – T T=100%

DP=3: T – I – T T=67%

DP=4: T – I – I – T T=50%

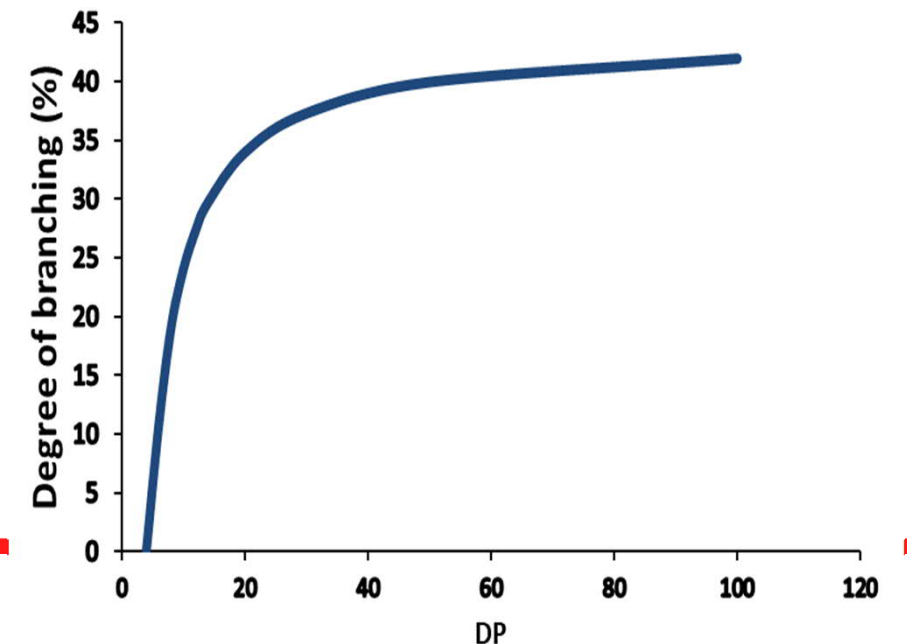
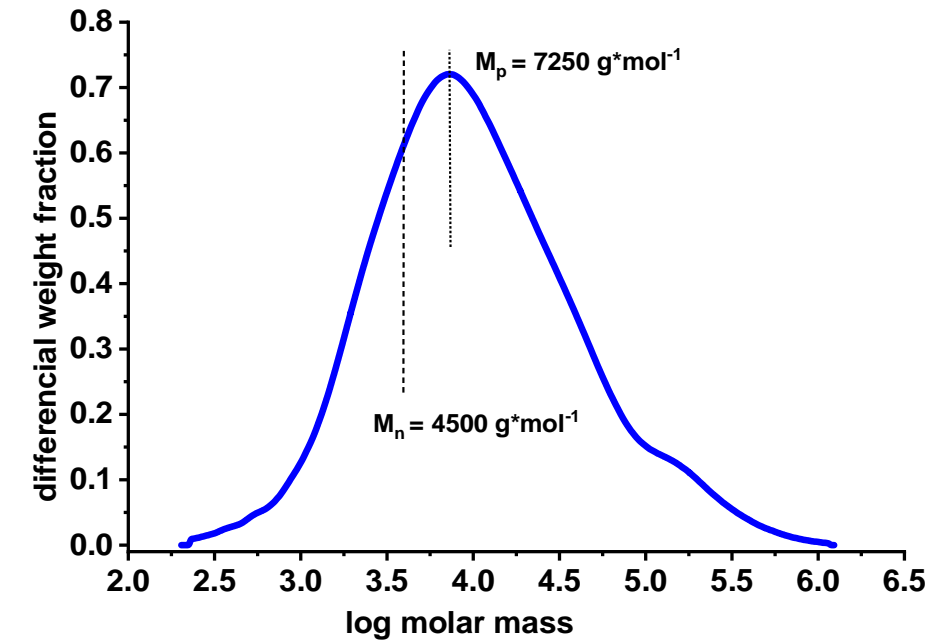
DP=5: T – I – I – I – T T=40%

By different independent NMR and wet chemistry methods

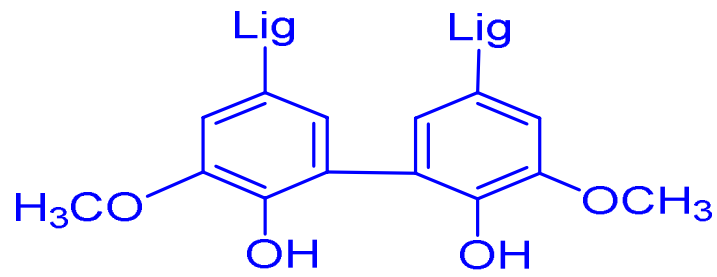
Macro-Features of MWL

- Average Molecular weight (M_n) of Spruce MWL is about 4,500 Da; DP ~ 25
- Terminal units ($T=44\%$) 11 per 25 units :
 - Main chain: 2 T
 - Each branching: 1T extra
 - Each crosslinking: 2T extra
- Branching (B) and crosslinking (X) points in the model:

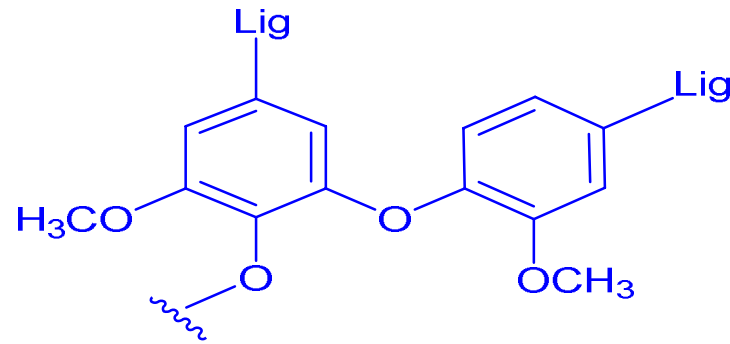
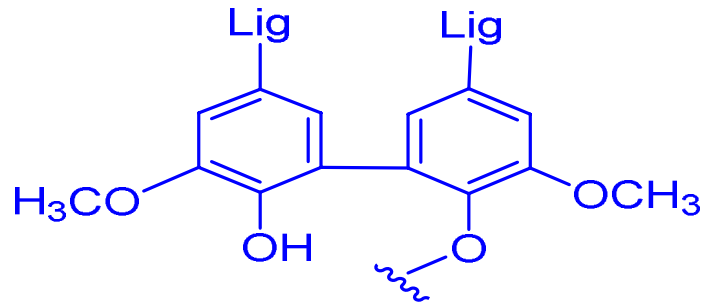
$$B + 2X = T - 2 = 11 - 2 = 9$$



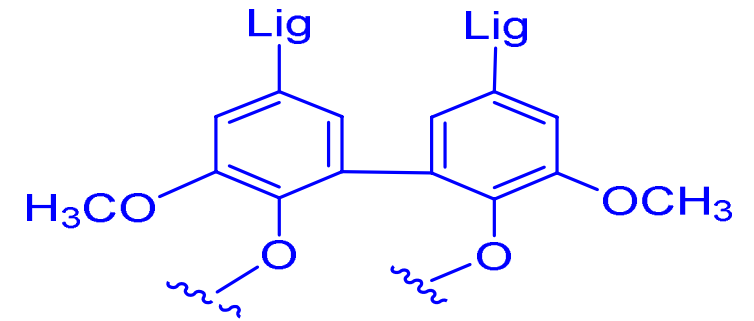
Common Branching and Cross-linking Points



Linear



Branched



Cross-linked

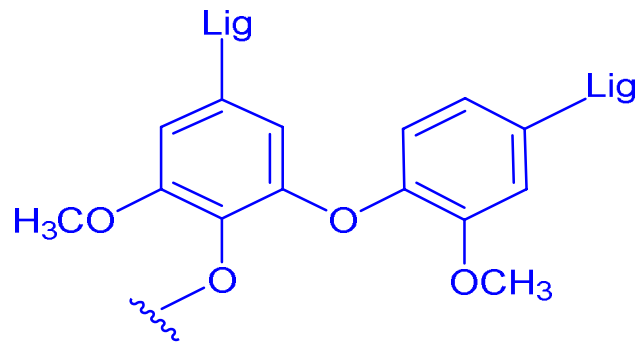
Quantification of 5-5' and 4-0-5' Units

Units (per 100 Ar)	CuO-PO	TA - ³¹ P NMR	DFRC - ³¹ P NMR	¹³ C NMR (A)	¹³ C NMR (B)
5-5' ne	5-6			5-8	5
4-0-5' ne	2				
5-5' et	14-16		6-8**	19	
incl. DBDO			6-8	7***	7***
4-0-5' et	2		<DL		
(5-5'+4-0-5) et	16-18		6-8**	20	23
Total 5-5'	19-22	16 (21*)		24-27	28
Total 4-0-5'	4	5 (7*)		~1***	~1***

*after correction; **claimed as DBDO only; *** by HSQC

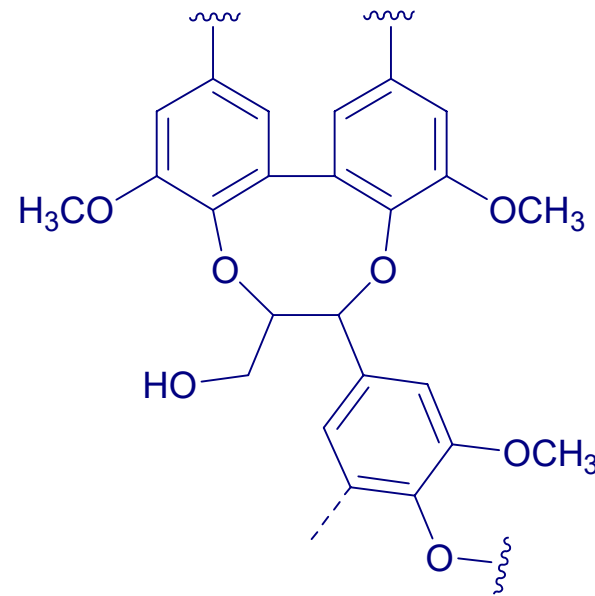
Branching and Cross-Linking in the Aromatic Ring (per 25 C9-unit model)

$$\text{Total: } B + 2X = 9$$



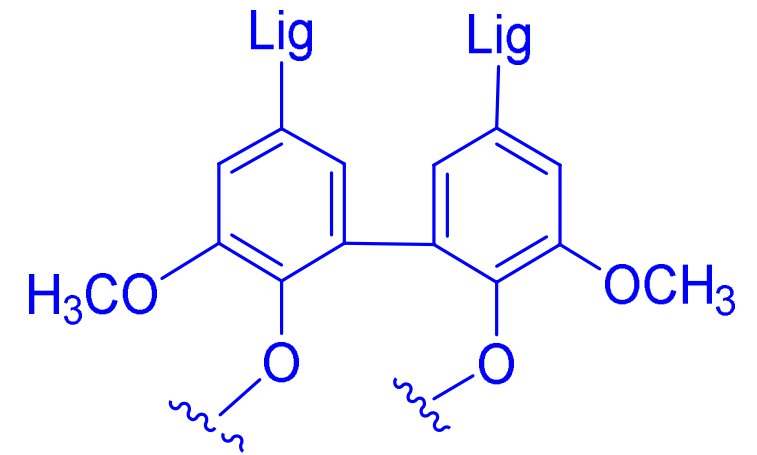
<1

Branched (B)



1

Branched (B)

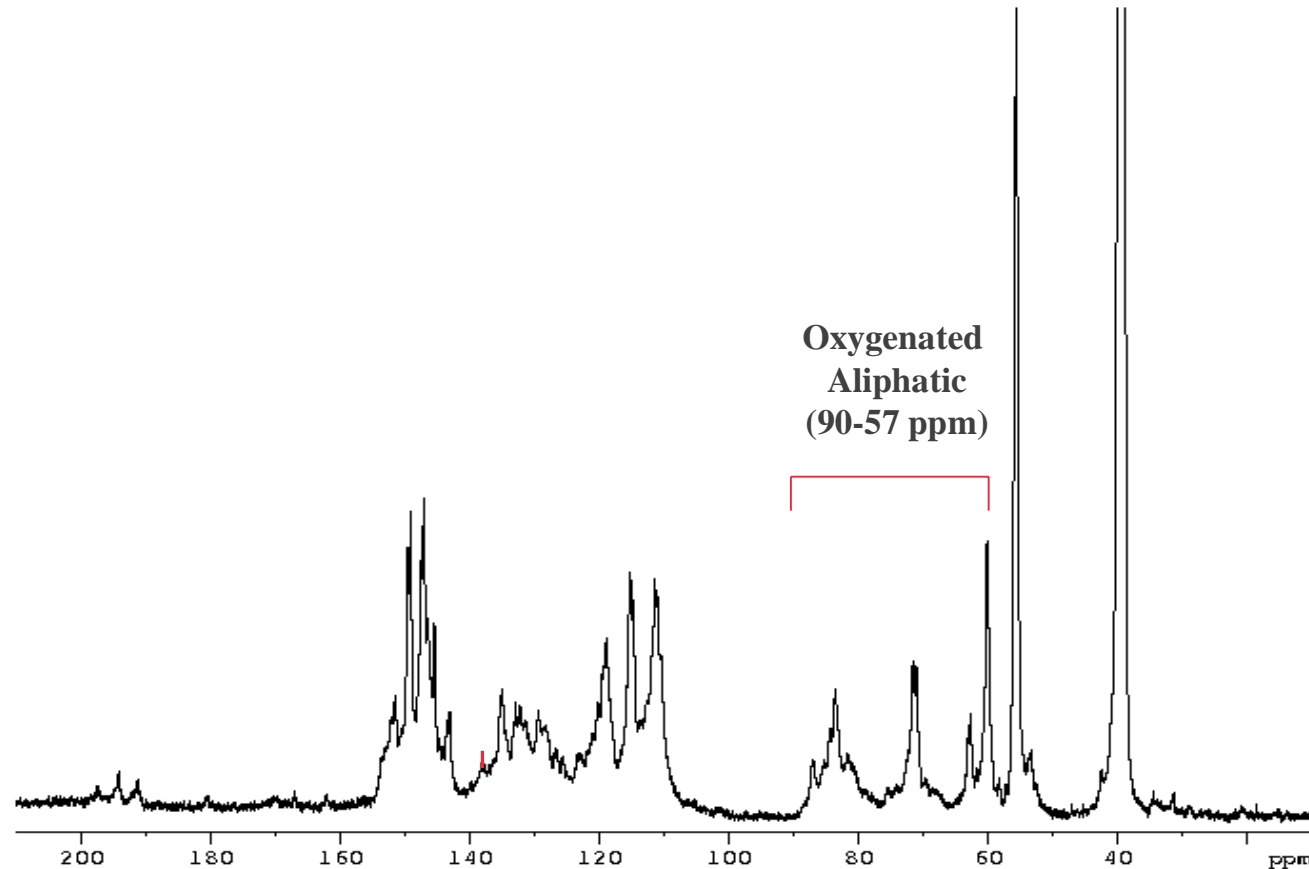


2

Cross-linked (X)

2 cross-linking points are still missing

Material Balance in the Oxygenated Aliphatic Region (per 100 Ar)



Oxygenated Aliphatic = AliphOH + Alk-O

$$\text{Alk-O-} = 214 - 107 = 107$$

$$\text{Alk-O-Ar} = 100 - \text{PhOH} - \text{SD} = 100 - 31 - 2 = 67$$

$$\text{Alk-O-Alk} = 107 - 67 = 40$$

8 are identified (pinoresinol + SD)

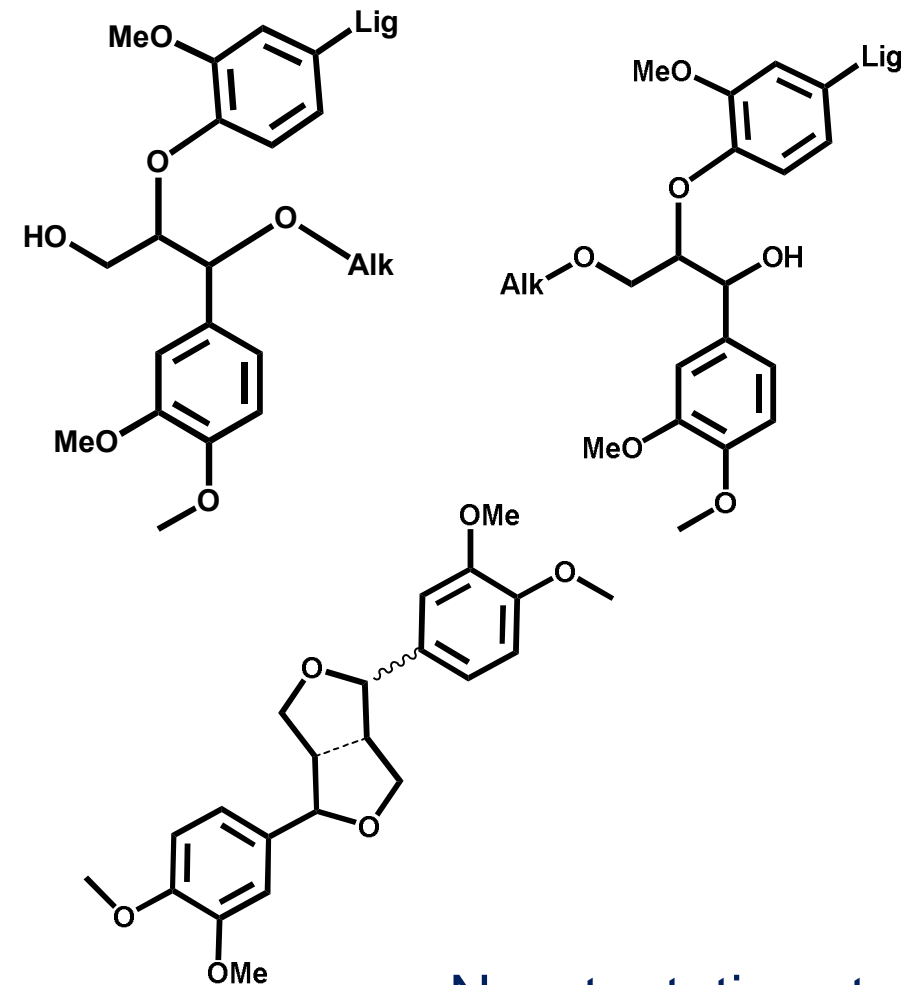
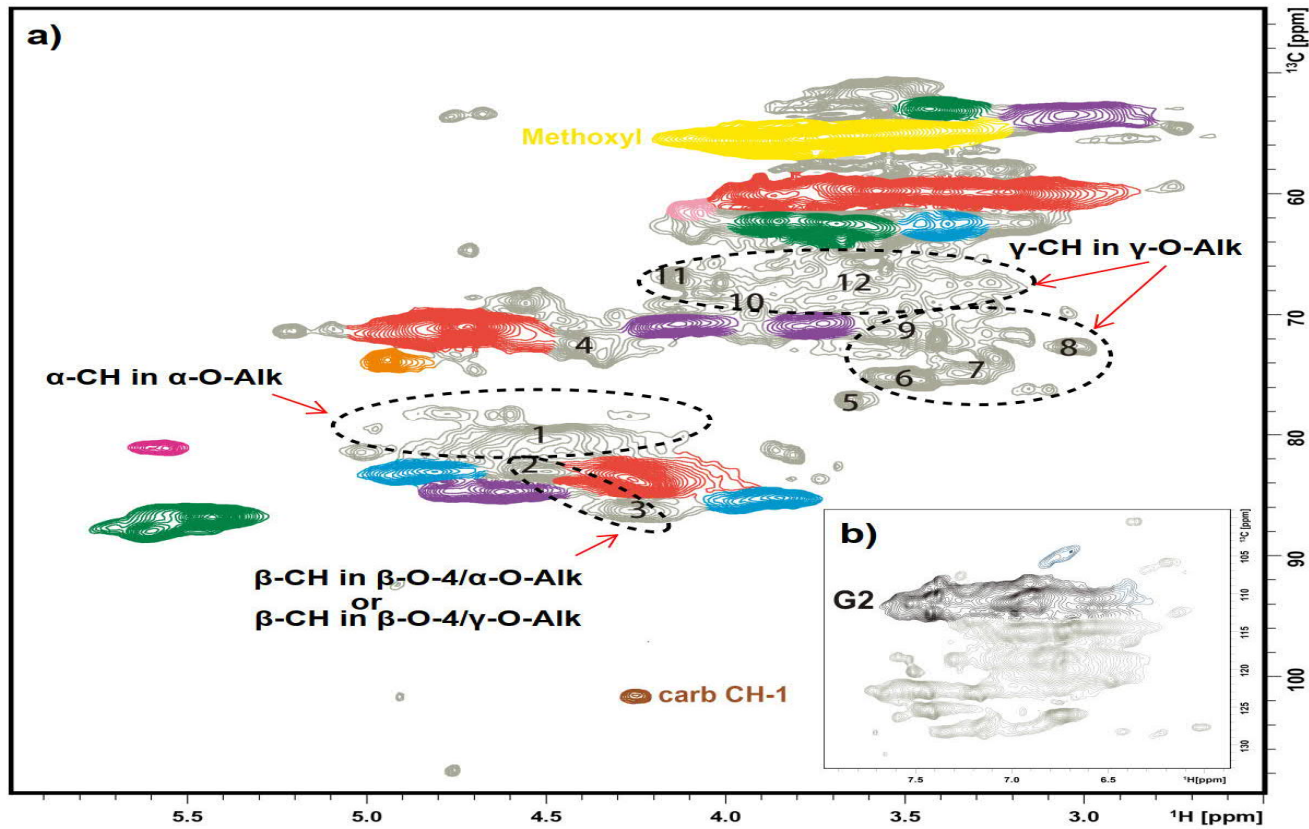
32 are not identified yet (Capanema et al. 2004);

tentatively α -O-Alk and γ -O-Alk (16 each)

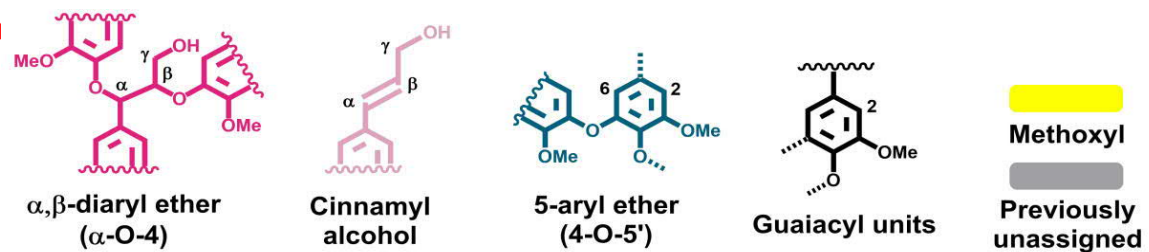
Supported by:

- Glasser and Glasser (1974) – computer modeling
- Terashima et al. (1991) – ¹³C enrichment of γ - and α -positions

Alkyl-O-Alkyl Structures



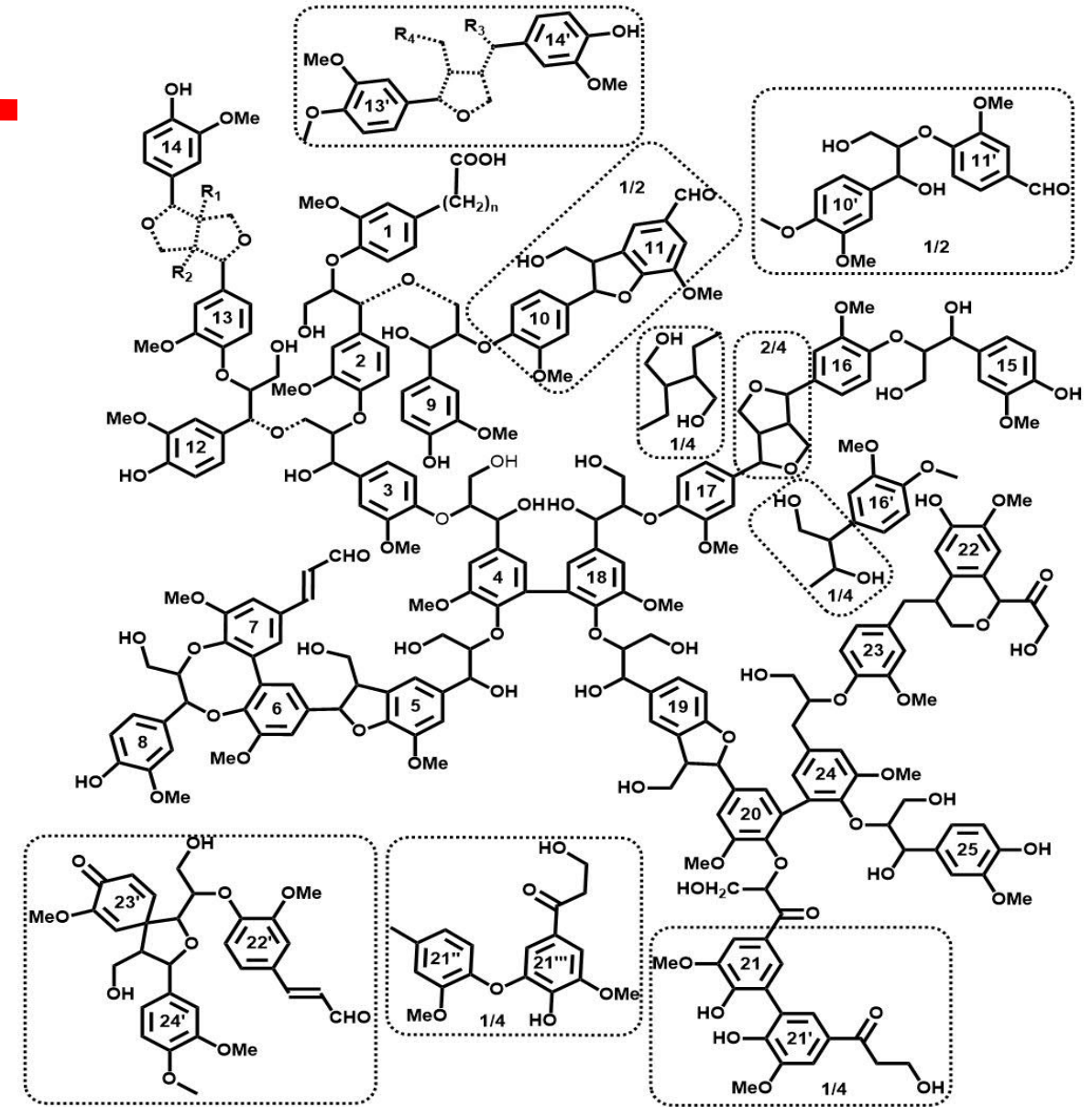
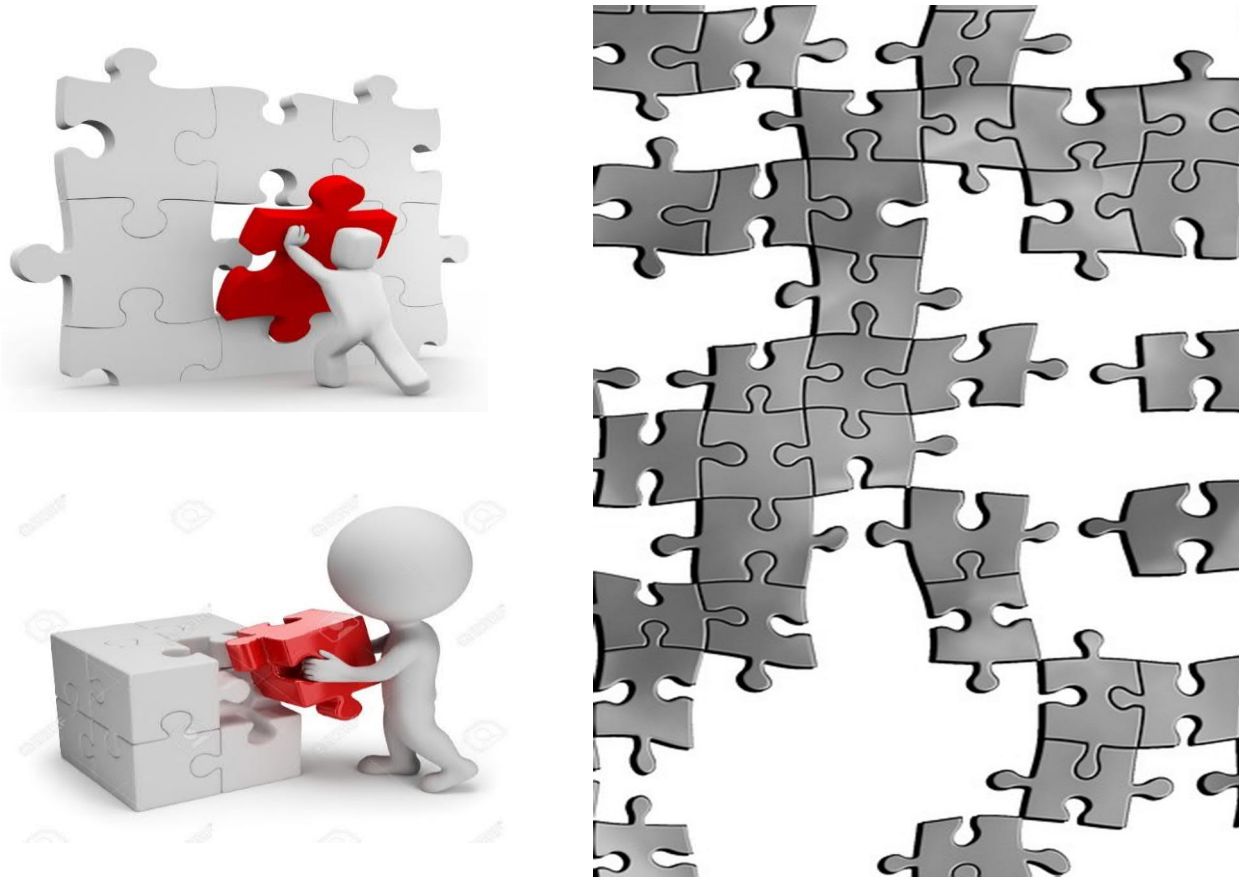
New tentative structures



Material Balance as Specific Positions (per 100 Ar)

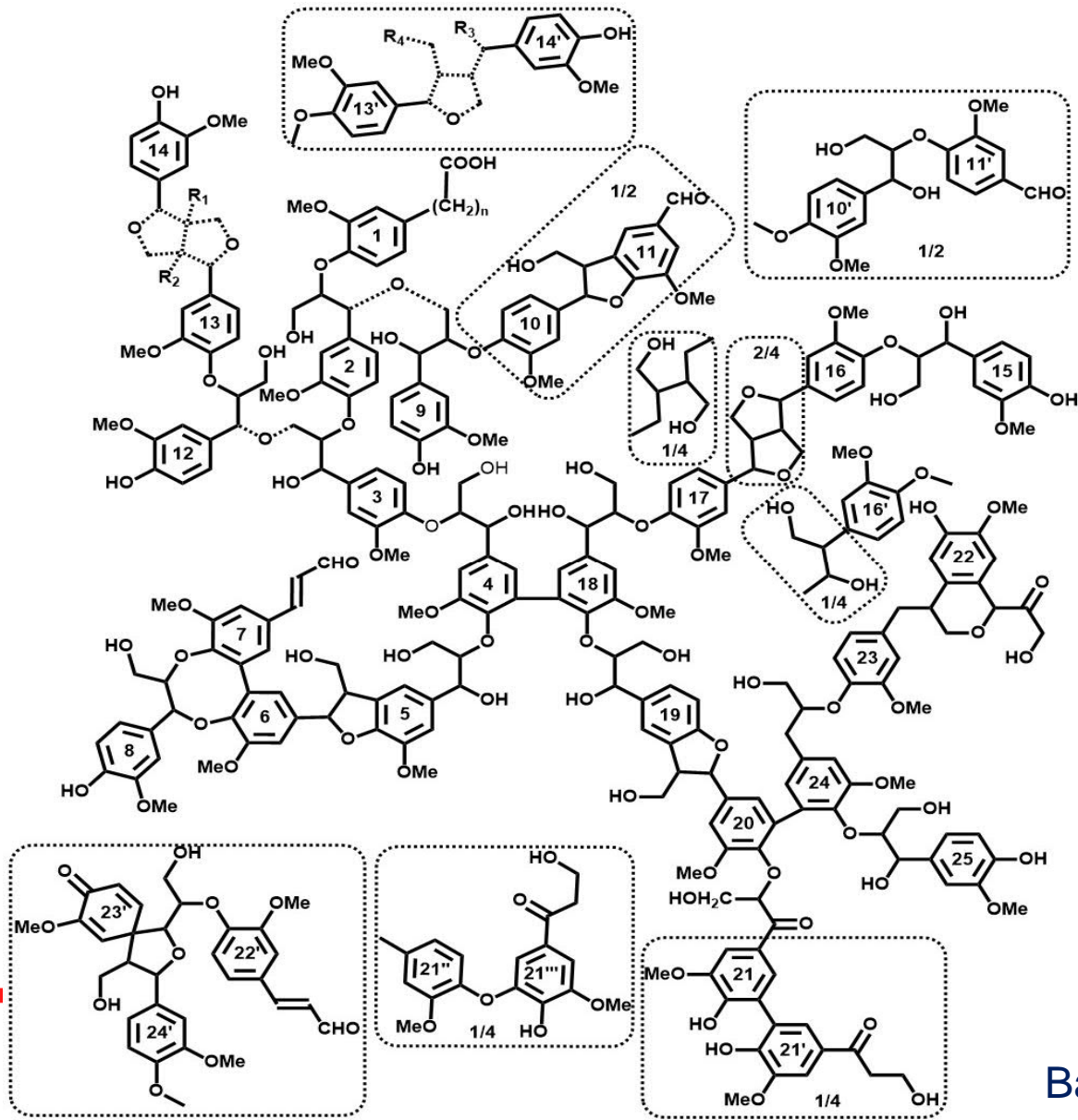
γ		β		α		Ar-4	
OH-total	68	β -O-4 total	50	OH	38	OH	31
		Phenylcoumaran	10	Phenylcoumaran	10	Spirodienone	2
Pinoresinol	4	Pinoresinol	4	Pinoresinol	4	Etherified in	67
Coniferaldehyde	4	Coniferaldehyde	4	Coniferaldehyde	4	β -O-4 total	50
		Coniferyl alcohol	2	Coniferyl alcohol	2	DBDO- α	4
		Spirodienone	2	Spirodienone	4	Phenylcoumaran	10
		Secoisolariciresinol	2	Secoisolariciresinol	2		
		Dihydroconiferyl alcohol	2	Dihydroconiferyl alcohol	2		
		Ar-CO-CH ₂ -CH ₂ OH	2	Ar-CO-CH ₂ -CH ₂ OH	2		
		β -1/ α -OH	1	DBDO	4		
Short chain (Vanillin +COOR)	10	Short chain (Vanillin +COOR)	10	Short chain (Vanillin +COOR)	10		
		Carbonyl (non-conjugated)	5	β -O-4/ α -CO	2		
Total identified	86	Total identified	94	Total identified	84	Total identified	97
<i>γ-O-Alk (tentative)</i>	<i>14</i>	<i>β-Alk (tentative)</i>	<i>6</i>	<i>α-O-Alk (tentative)</i>	<i>16</i>	<i>Others (4-O-5, α-O-4 etc.)</i>	<i>3</i>

Constructing Lignin Molecule



An attempt to compose a picture-puzzle with an incomplete number of pieces, more than one way to reassemble the pieces.

Our Model for Spruce Milled Wood Lignin



This is not a real lignin structure

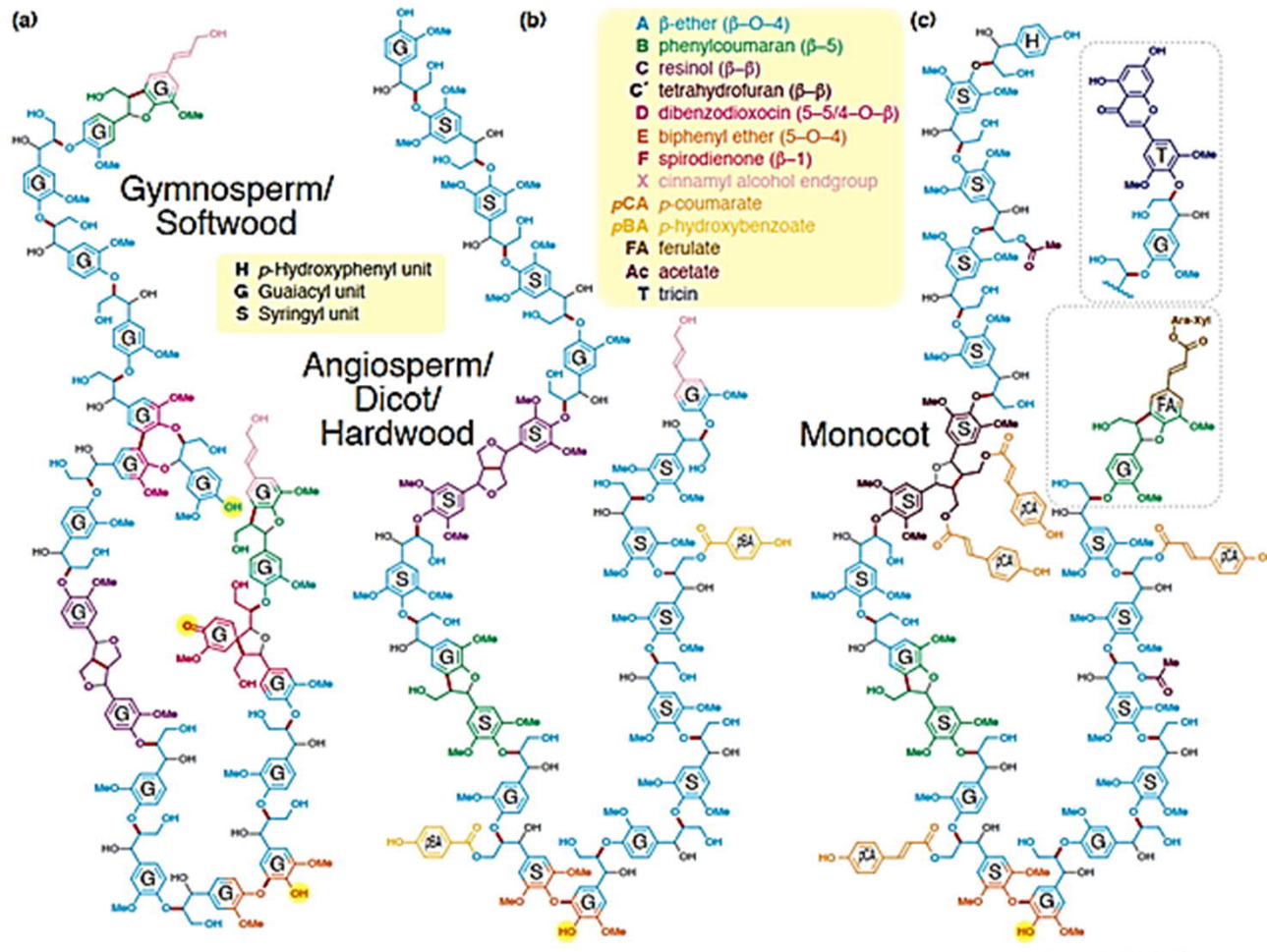
In agreement with all available quantitative data as well as absolute molecular mass measurements

- Comprehensive review of all available analytical data
- Spruce Milled Wood Lignin (MWL) is heavily crosslinked (36% units involved)
- About half of crosslinking points are in the aromatic ring (5-5' etherified units) while the other half is in the side chain (Alk-O-Alk linkages)
- The exact structures of new Alk-O-Alk moieties (of high variety) are not known yet

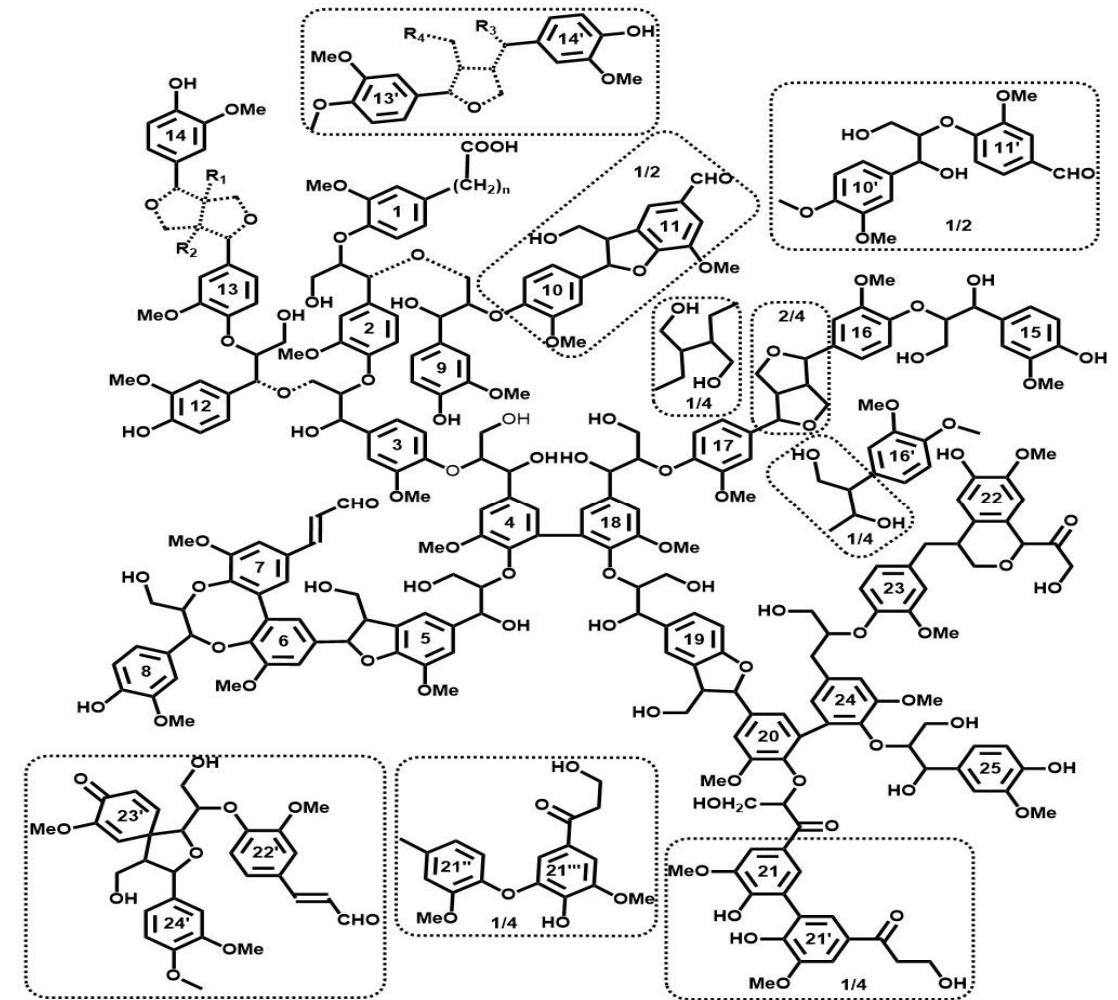
Balakshin et al. Green Chem. 2020, 22 (13), 3985–4001



Lignification Theory vs Analytical Data



In situ lignin based on lignification theory
Ralph et al. 2019



MWL based on comprehensive analytical data
Balakshin et al. 2020

- The lignification theory may require an update to include new biosynthetic route(s)
- Some structural changes during isolation of native lignin (as MWL) to be considered

Lignin Analysis



Analysis of Lignin

There are a large variety of methods to analyze lignin

There are no perfect universal method and it is necessary to use a combination of different methods in order to obtain the whole picture on the structure of lignin

Requirements for Analytical Methodology

- ❖ Reliable
- ❖ Informative
- ❖ Productive (reasonably fast)

Structural Analysis of Lignin

- ❖ Wet chemistry
- ❖ Spectroscopic and Spectrometric techniques:
 - ❖ NIR, FTIR, MS (MALDI, ESI), Raman etc.
 - ❖ NMR Spectroscopy
 - ❖ ^1H , ^{31}P NMR (express methods)
 - ❖ 2D and 3D NMR (qualitative and semi-quantitative)
 - ❖ ^{13}C NMR (qualitative and quantitative)

Wet Chemistry Methods

- ❖ Functional groups analysis (OMe, PhOH, AlOH, COOH, CO etc)
- ❖ Degradation techniques for specific functionalities:
 - ❖ β -O-4 units (other Alk-O-Ar)
 - ❖ S/G ratio
 - ❖ substitution pattern in Ar ring
- ❖ Dedicated, accurate, but 1 method = 1 number (not very productive)
- ❖ Good to specific purposes
- ❖ Often do not require lignin isolation

Spectroscopic Techniques

- 1- Infrared and near infrared
- 2- Ultra-violet
- 3- Raman-spectroscopy
- 4- Nuclear magnetic resonance
 - Correlation techniques:
 ^1H - ^1H ; ^1H - ^{13}C NMR
 - Quantitative:
 ^1H , ^{31}P , ^{19}F , ^{13}C

Spectroscopic techniques are non destructive methods and allow direct detection of lignin moieties

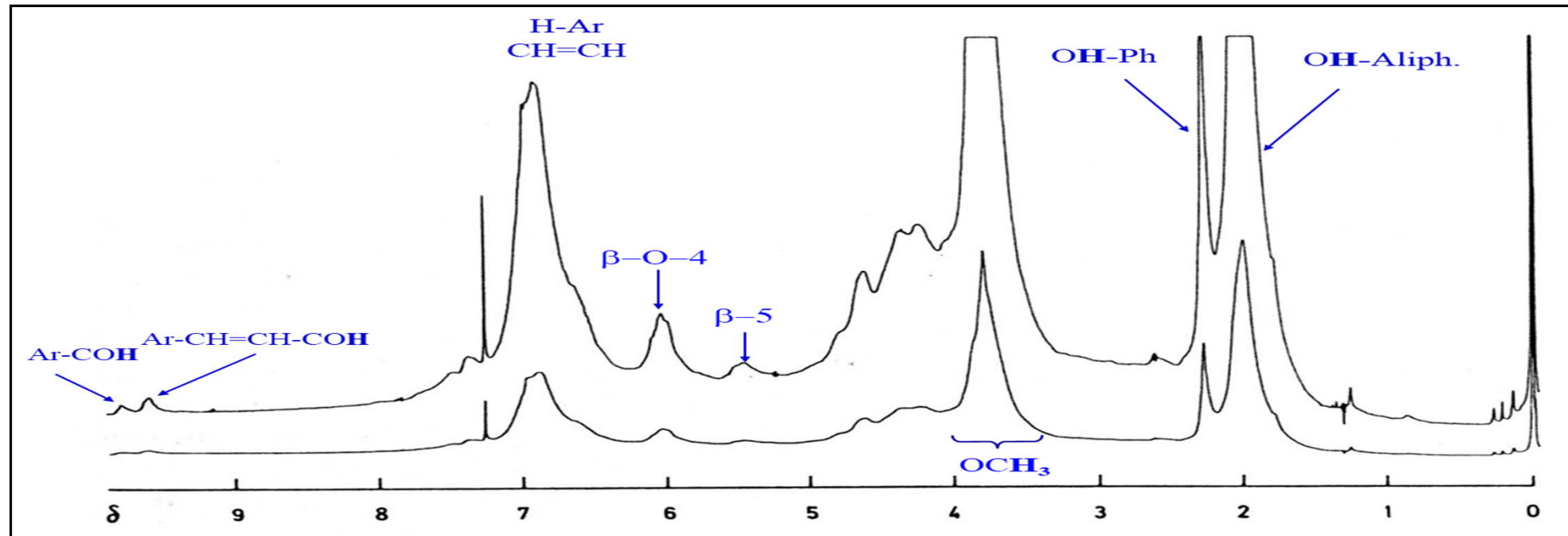
Provide information of isolated lignin as a whole

Technological Frontiers in NMR Spectroscopy



Superconducting magnets with field approaching 21 T (920 MHz)

^1H NMR of Acetylated Lignin



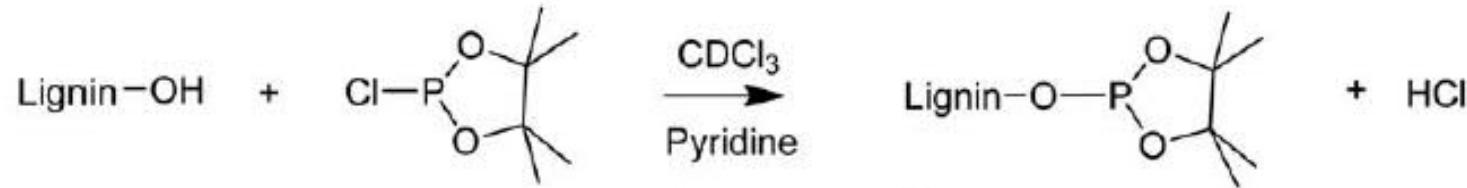
❖ Advantages:

- ❖ High sensitivity (fast experiment)
- ❖ Some quantitative information is possible

❖ Disadvantages:

- ❖ Acetylation is required (tedious procedure)
- ❖ Resolution is not good for comprehensive analysis

^{31}P NMR Spectra of Lignin

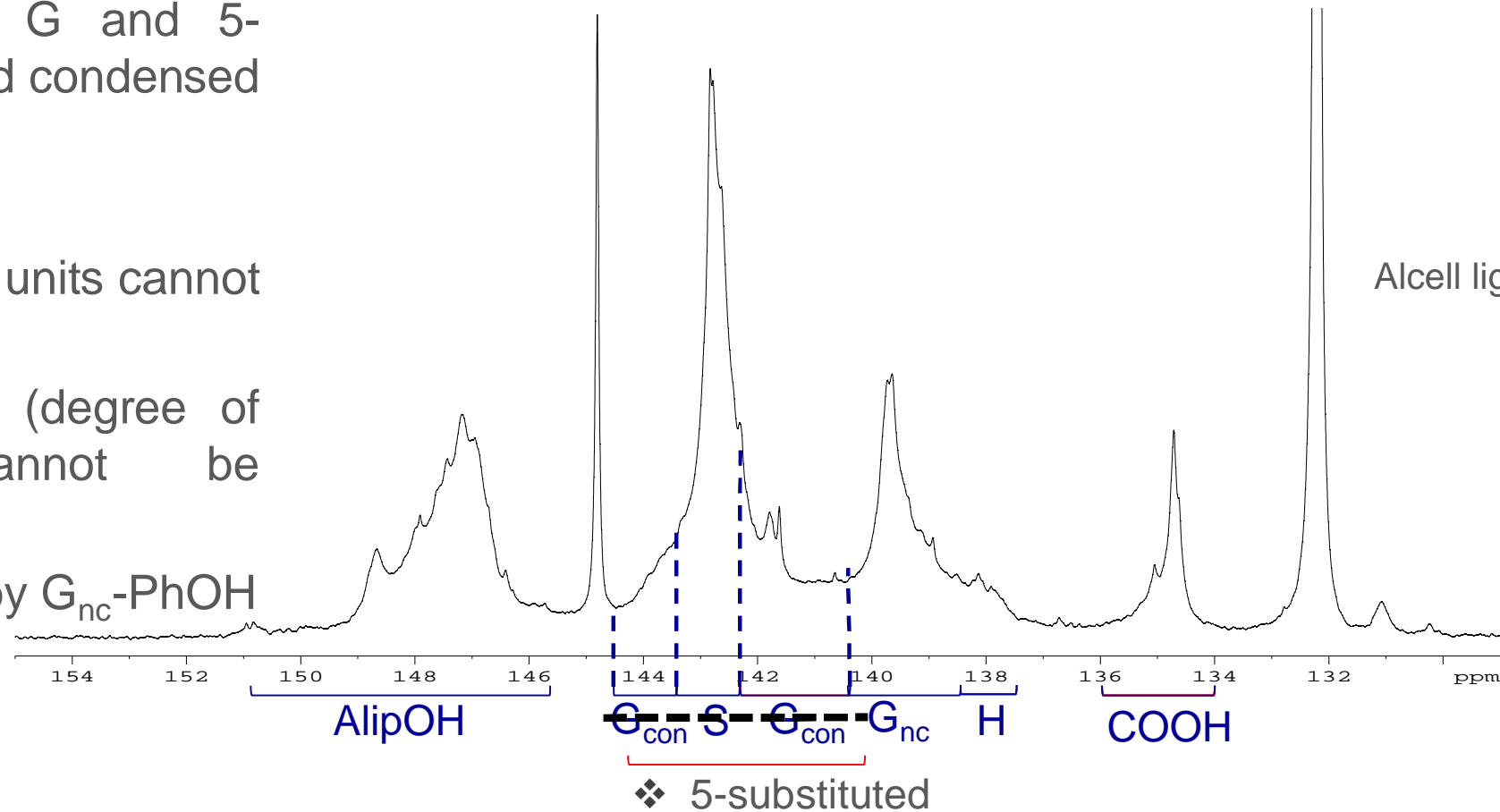


Kostukevich et al 1993
Granata and Argyropoulos 1995

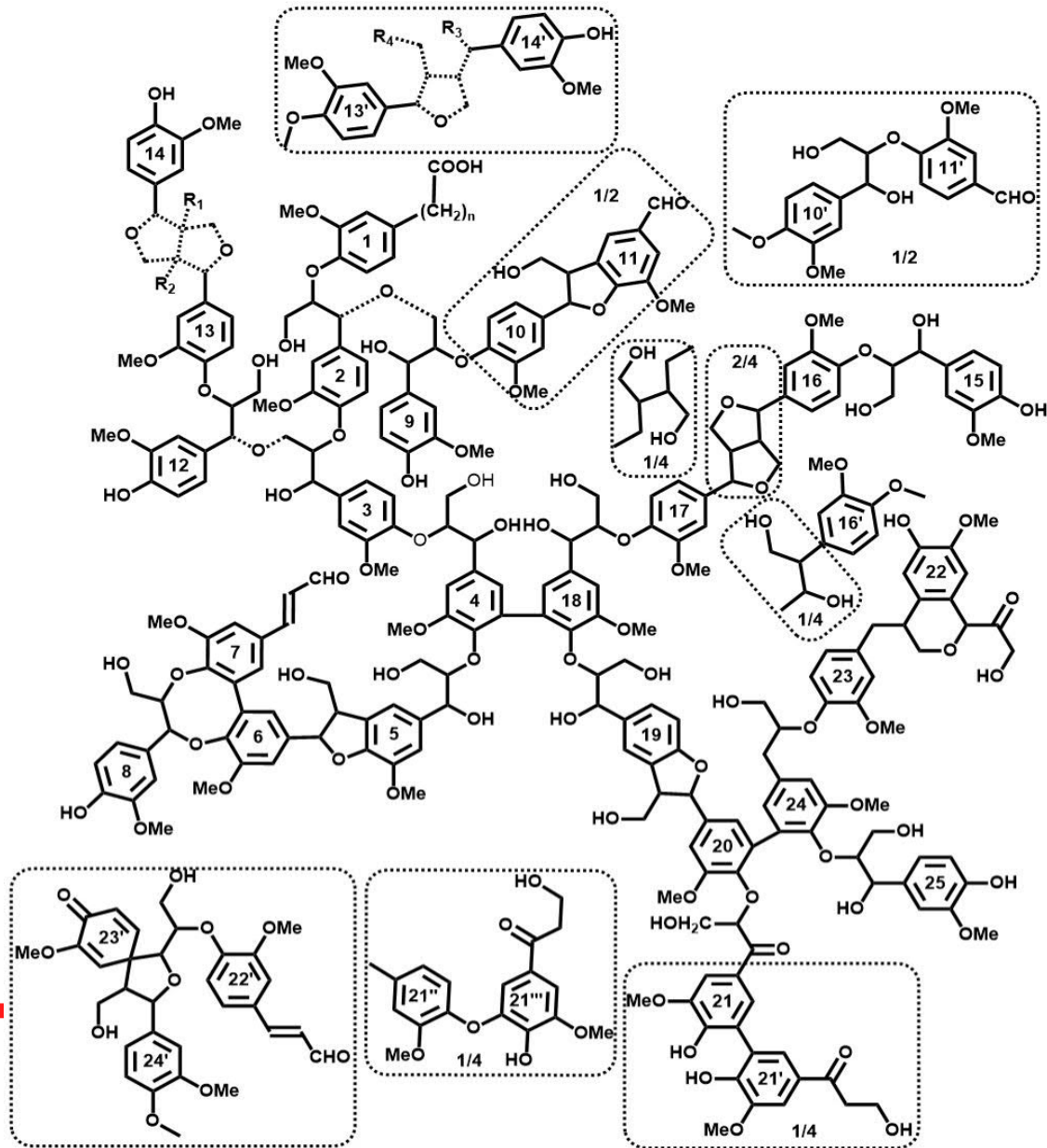
- ❖ Reports 4-5 main OH types (Aliphatic, Phenolic H, G and 5-substituted (sum of S and condensed G) and COOH)

❖ Caution:

- ❖ G-condensed and S units cannot be separated
- ❖ S/G ratio and DC (degree of condensation) cannot be determined
- ❖ H-units are inflated by $\text{G}_{\text{nc}}\text{-PhOH}$



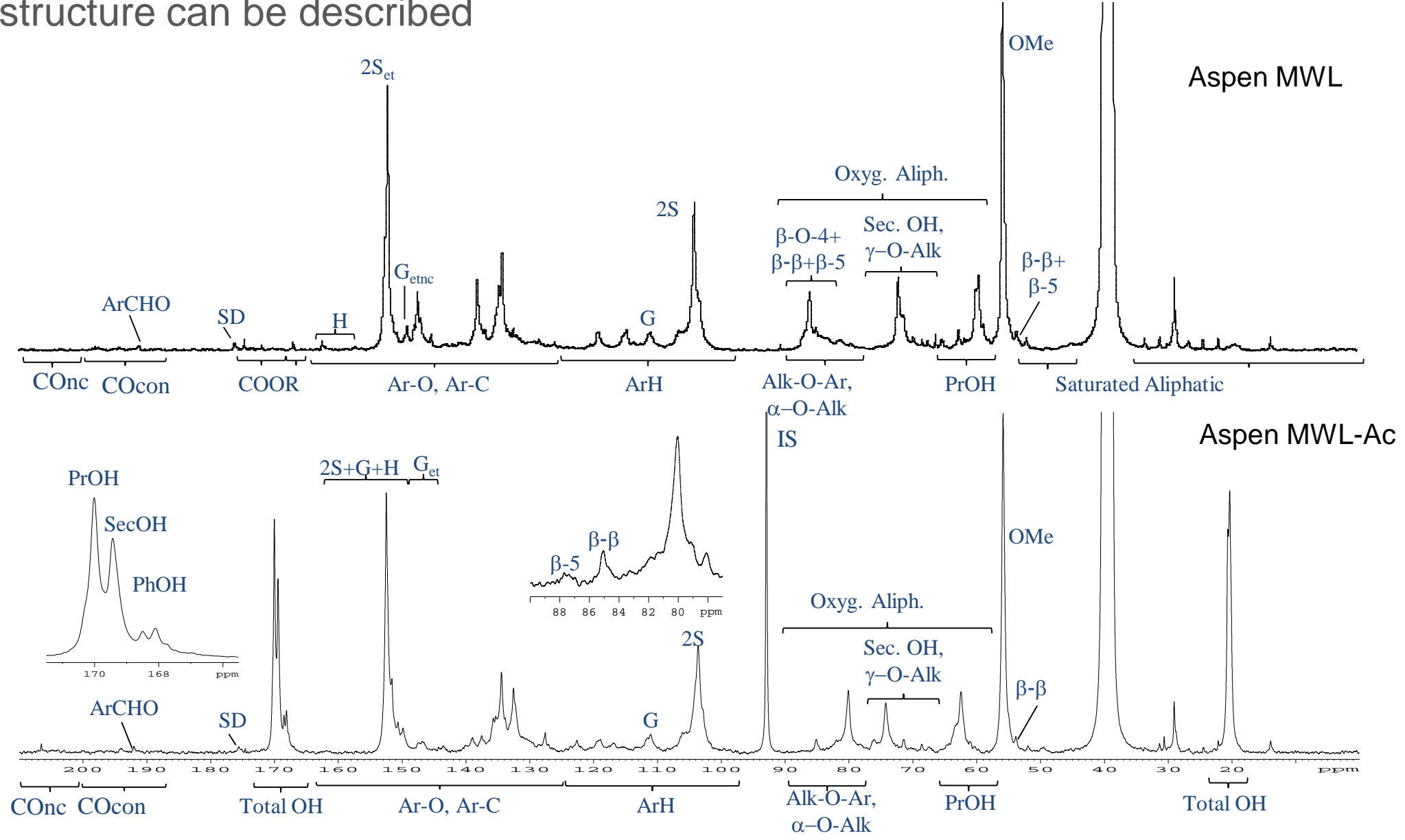
Methodology Should be Comprehensive



- A few parameters are not enough to describe lignin structure
- Need for advanced method

Advanced ^{13}C NMR Analysis of Lignin

Whole lignin structure can be described



¹³C NMR Provides Large Amount of Information

Routine mode

Quantitative

- ❖ OMe
- ❖ Total OH
 - ❖ PhOH
 - ❖ AIOH
 - ❖ Primary
 - ❖ Secondary
- ❖ COOR
 - ❖ Aliphatic
 - ❖ Conjugated
- ❖ S
- ❖ G
- ❖ S/G ratio
- ❖ ArH
- ❖ Oxygenated Aliph.
- ❖ β -O-4 total
- ❖ Ar-CHO

Semi-quantitative

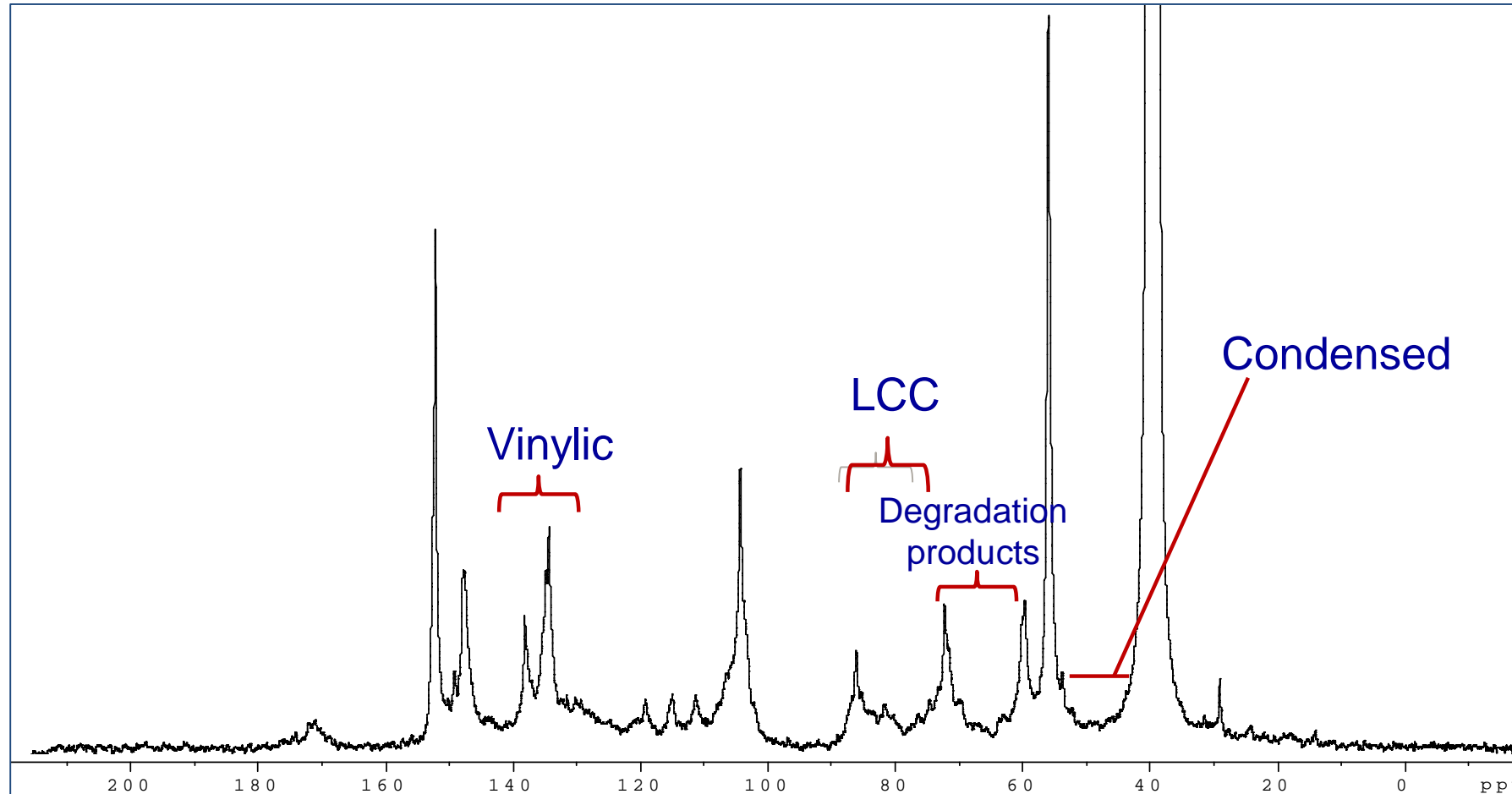
- ❖ Total Carbonyl
 - ❖ Conjugated
 - ❖ Non-conjugated
- ❖ β - β
- ❖ β -5
- ❖ Spirodienone
- ❖ DBDO
- ❖ β -O-4/ α -OH
- ❖ Degree of condensation
- ❖ Saturated Aliphatics
- ❖ H-units
- ❖ 5-5'
- ❖ 5-free PhOH
- ❖ 5-substituted PhOH
- ❖ Sugar content

Special cases

- ❖ EtO- (Organosolv lignins)
 - ❖ Ethers
 - ❖ Esters
- ❖ Grass lignins:
 - ❖ FA/CA acids
 - ❖ FA/CA esters
 - ❖ H-units:
 - ❖ Phenolic
 - ❖ Etherified
 - ❖ Conjugated
 - ❖ Non-conjugated
- ❖ Derivatized/Functionalized Lignins

40+ values/sample

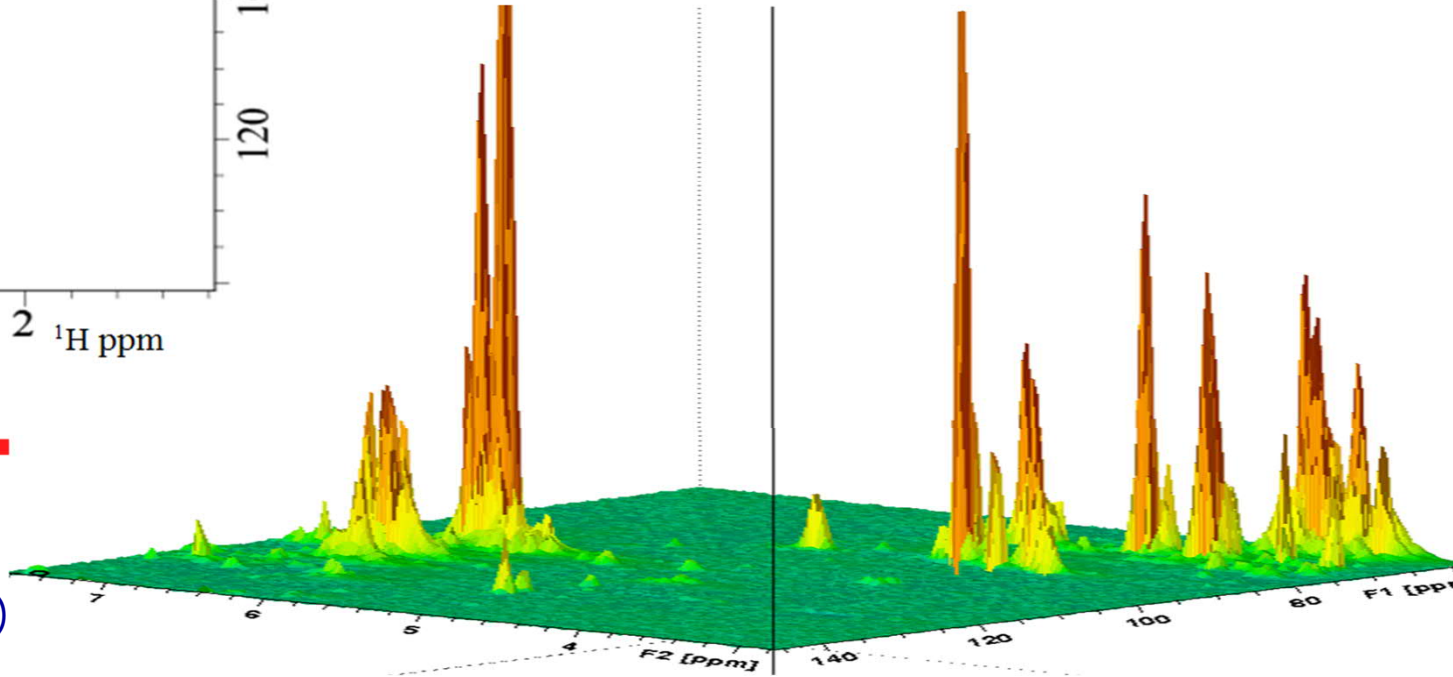
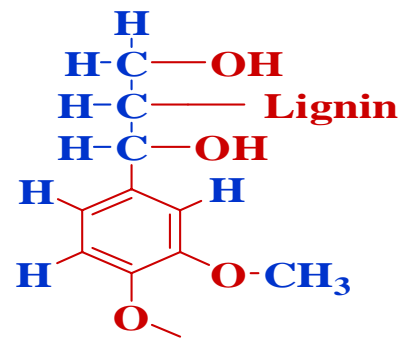
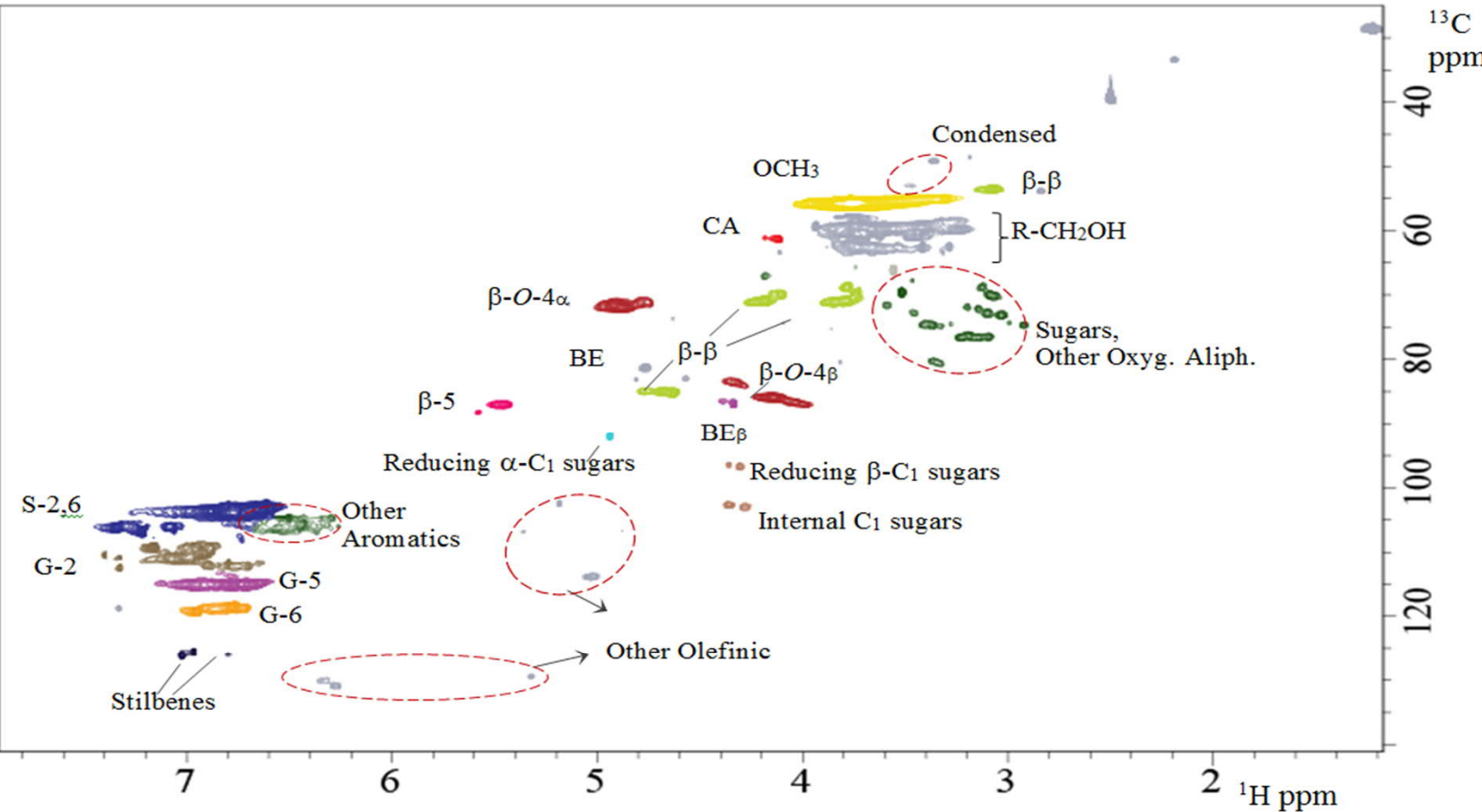
Limitations of 1D Methods



Signals overlapped in 1D ^{13}C NMR and cannot be accurately quantified, however this limitation is overcome in 2D spectra

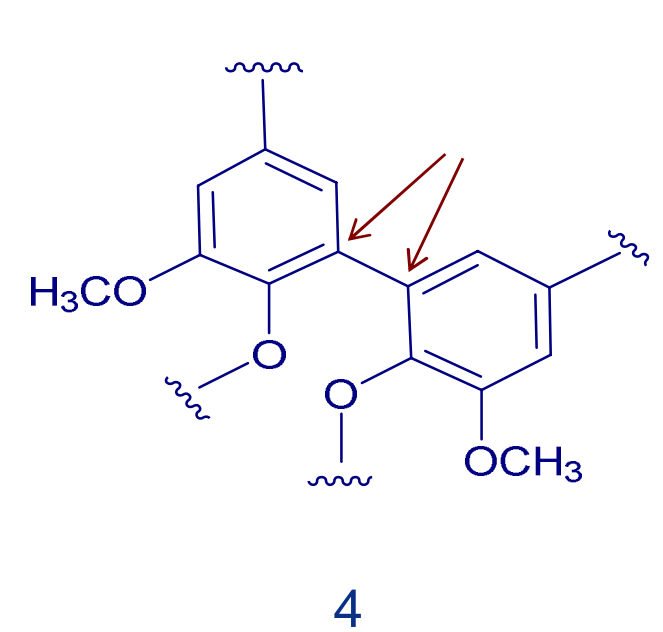
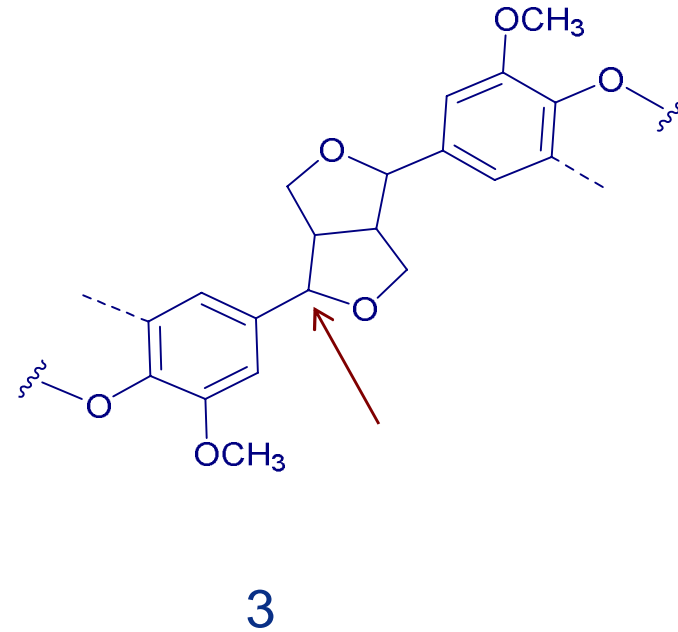
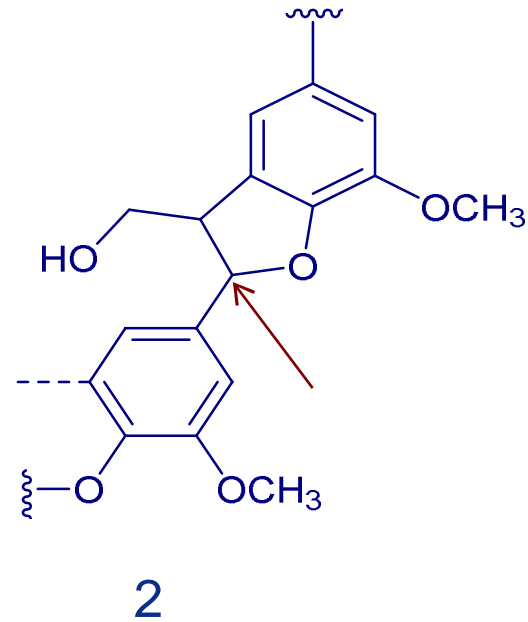
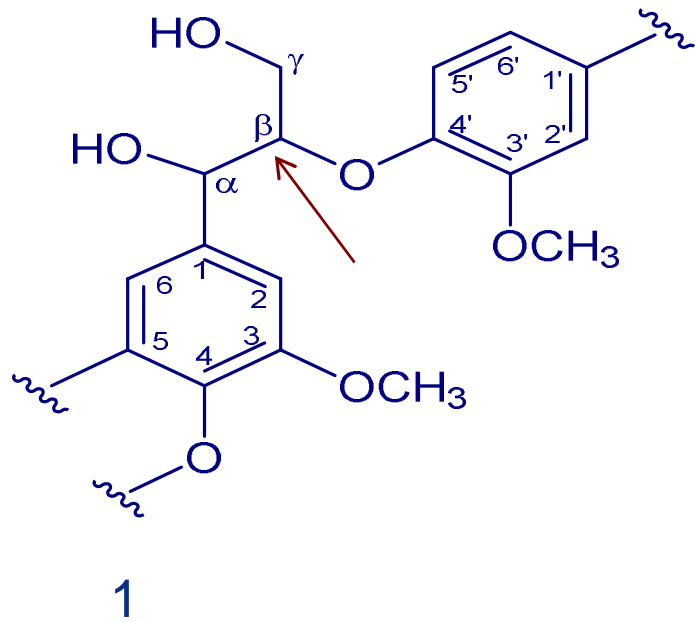
Heteronuclear Single Quantum Coherence (HSQC)

Correlation between ^1H and ^{13}C atoms via $^1J(\text{C},\text{H})$



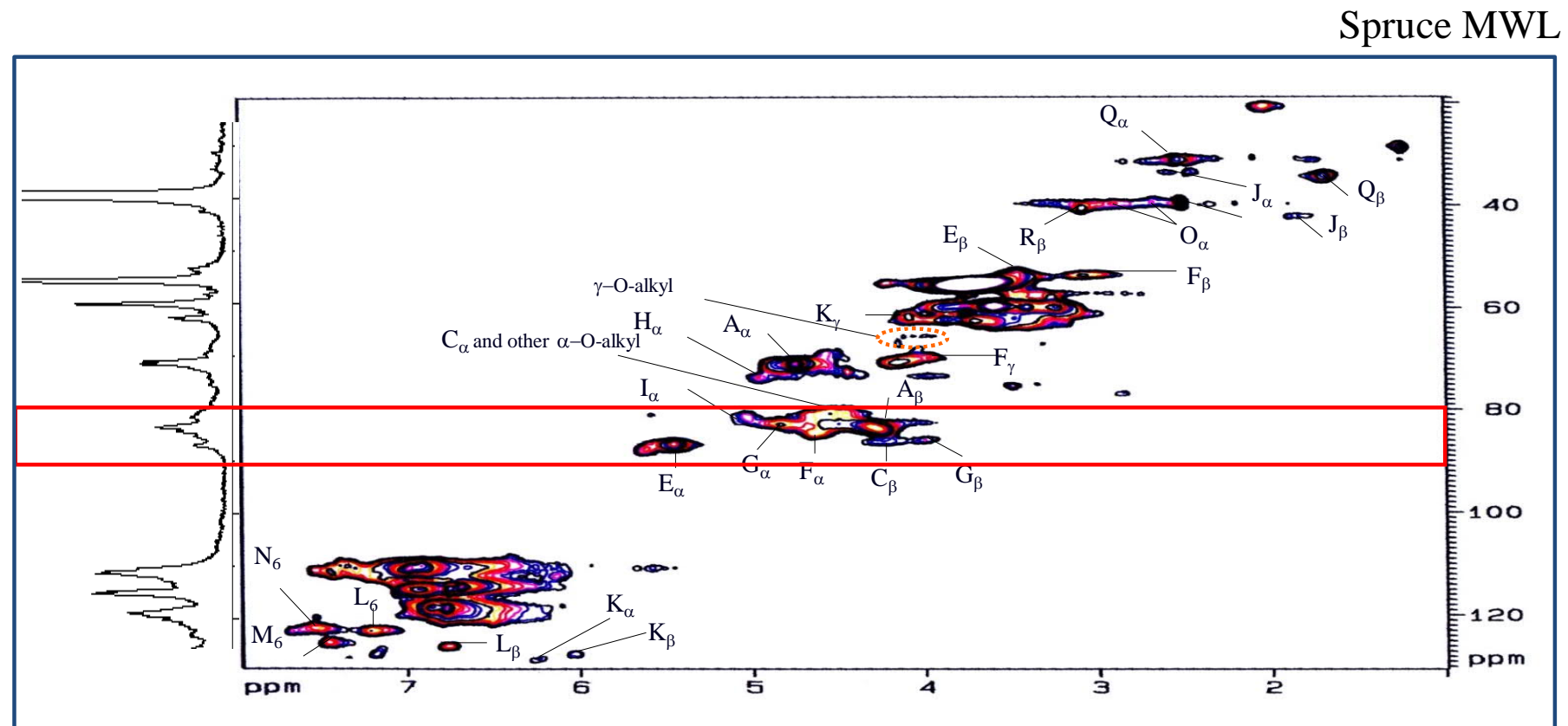
- Signals (cross-peaks) are assigned based on:
- Model compounds
 - Other 2D correlation techniques (HMBC, COSY, TOCSY etc.)

Which Moieties Can't be Identified by the HSQC Method?



Homework

Advantage of HSQC NMR Technique

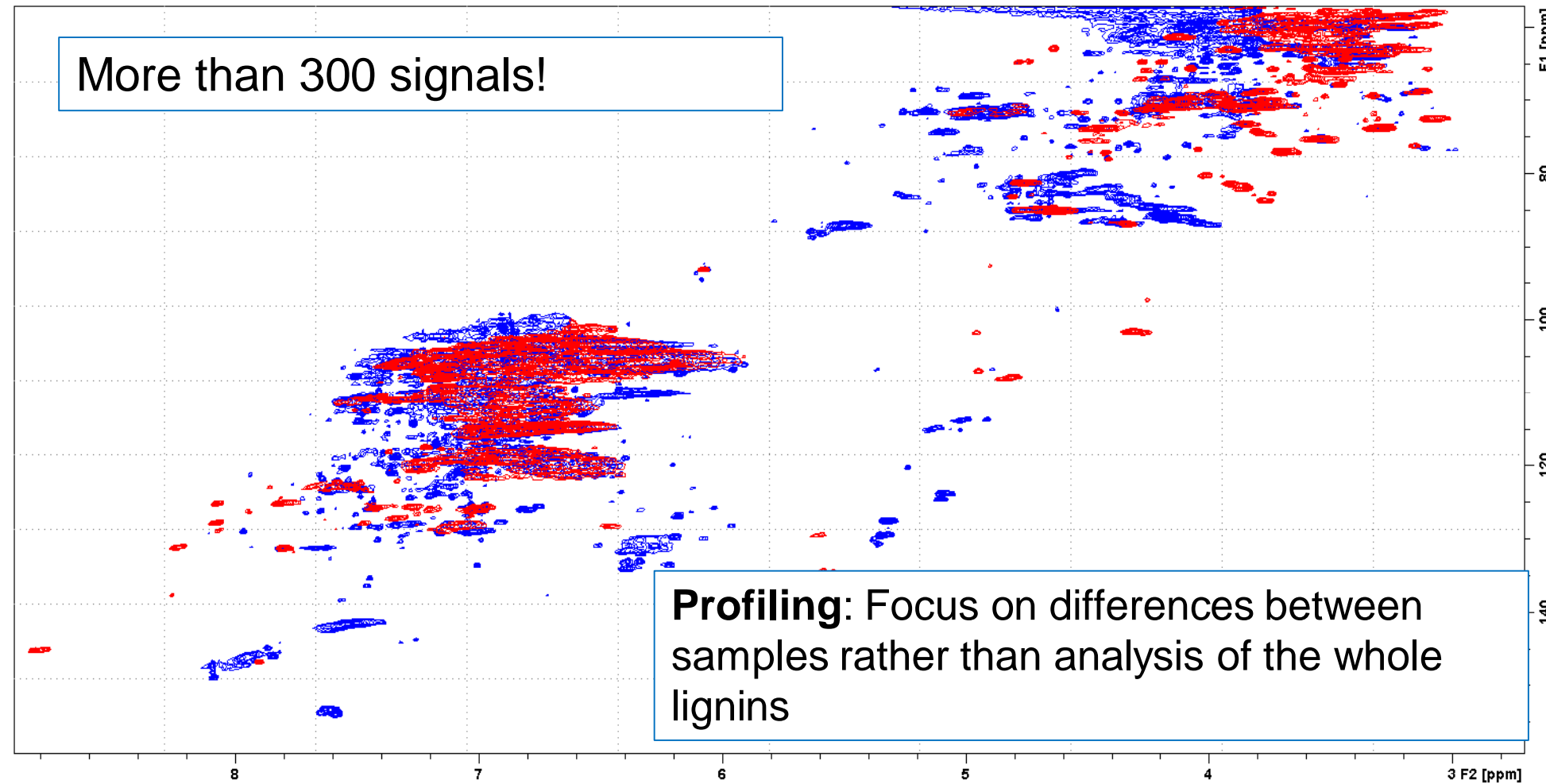


Good separation of signals overlapping in the 1D spectra (7 separated signals in 2D spectrum vs 1 cluster in ^{13}C NMR)

Better interpretation of signals (from the chemical shift values for the ^1H and ^{13}C dimensions)

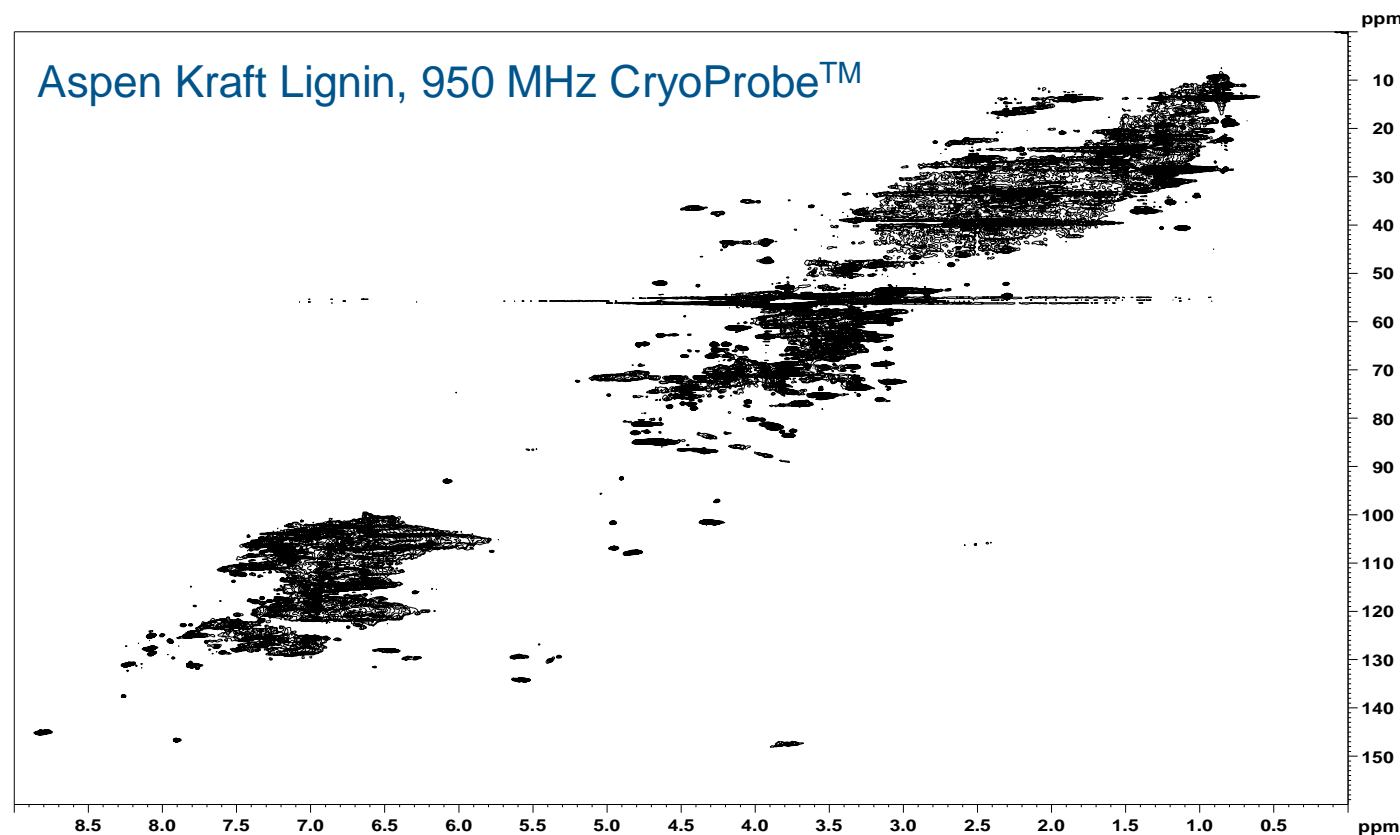
Lignin Fingerprinting with 2D HSQC NMR

Alcell (blue) vs Kraft aspen (red) lignins



950 MHz Bruker NMR with CryoProbe™

Analysis of Technical Lignins by a HSQC NMR Method



- ❖ A few hundreds signals; most of them of low intensity
- ❖ Native lignin moieties (β -O-4, β - β , β -5 etc) is 5-15% (mol)
- ❖ Advanced characterization allows for the quantification of 20-30% units
- ❖ Great for fingerprinting, but the quantification for the whole lignin is very challenging

Summary: Possibilities and Limitations of 2D NMR

❖ Possibilities:

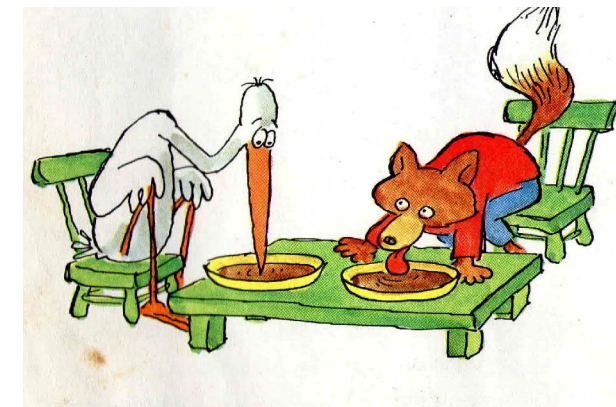
- ❖ Good separation of signals, reliable interpretation (important for complex lignin/LCC preparations)
- ❖ Quantification of specific moieties using ^{13}C NMR as reference
- ❖ Excellent lignin fingerprinting

❖ Limitations:

- ❖ Certain precautions to be considered for quantification
- ❖ Not suited for analysis of functional groups and quaternary C moieties

Comparison of Different NMR Methods

	^1H	^{31}P	^{13}C	2D (HSQC)
NMR time	Few minutes	0.5-1h	Overnight	0.5-20h
Number of signals	~10	~5	~100	Up to ~300
Fingerprinting	Maybe	no	Good	Excellent
Molecular Structure	no	no	Some	Excellent
Functional groups	Some	OH-groups	Comprehensive	no
Best use	Express	Express	Comprehensive	Comprehensive



The best method is dependent on the research task (and substrate type)

High Resolution NMR Approach

- ❖ Observation of the lignin as a whole, not only specific moieties
- ❖ Absolute values for amounts of lignin structural moieties
- ❖ Characterization of side chain moieties on structural level
- ❖ Allows comprehensive picture of lignin structure in a short experimental time with a small amount of sample
- ❖ Limitation: requires soluble preparation

Practical Outcome: Patenting the Structures of Specific Lignins

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International Bureau



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61/233,345 12 August 2009 (12.08.2009) US

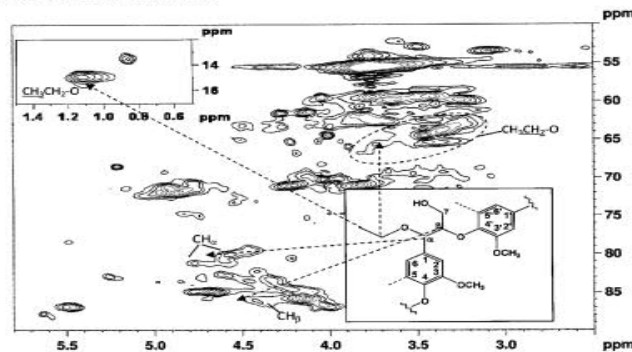
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[Continued on next page]

(54) Title: DERIVATIVES OF NATIVE LIGNIN



Balakshin et al. 2010

(19) United States

(12) Patent Application Publication
Capanema et al.

US 20140275501 A1

(10) Pub. No.: US 2014/0275501 A1
(43) Pub. Date: Sep. 18, 2014

(54) HIGH PURITY LIGNIN, LIGNIN COMPOSITIONS, AND HIGHER STRUCTURED LIGNIN

Related U.S. Application Data

(60) Provisional application No. 61/802,087, filed on Mar. 15, 2013.

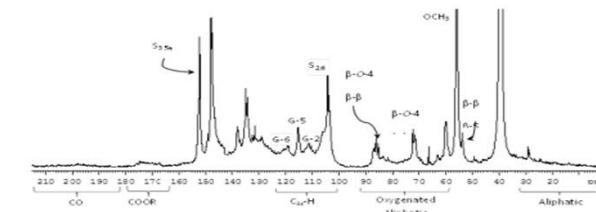
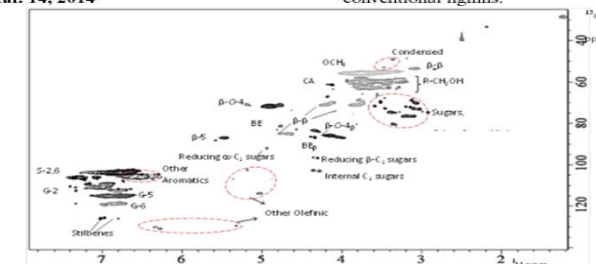
Publication Classification

(51) Int. Cl. C07G 1/00 (2006.01)
(52) U.S. Cl. C07G 1/00 (2013.01)
CPC C07G 1/00 (2013.01)
USPC 530/500

(57) ABSTRACT

Disclosed are lignins and lignin compositions having high purity. Also disclosed are lignins having unique structural characteristics, including less structural degradation than conventional lignins.

(21) Appl. No.: 14/213,680
(22) Filed: Mar. 14, 2014

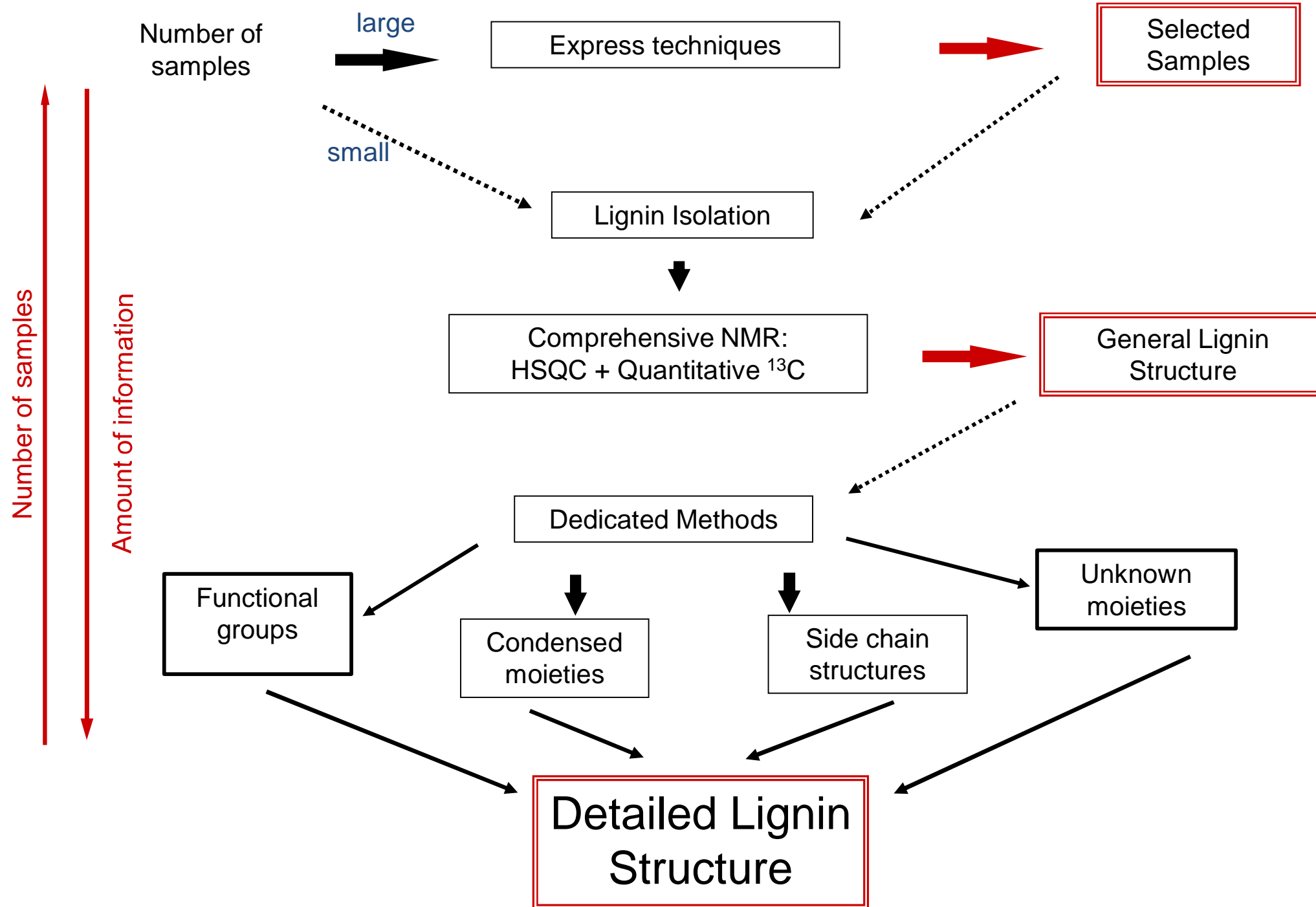


Capanema and Balakshin 2013

- ❖ Structural patents also cover lignin production processes and lignin applications
- ❖ Advanced methods are critical for patenting



STRATEGY FOR LIGNIN ANALYSIS



Lignin Analysis - Summary

- ❖ Lignin is a complex and chemically heterogeneous polymer; its complexity dramatically increases during technical processes
- ❖ Lignin analysis requires a comprehensive “toolbox” of various analytical methods and the use the correct “tool” in a specific situation
- ❖ Combination of quantitative ^{13}C and HSQC NMR methods allows comprehensive lignin fingerprinting and detailed characterization

Lignin Valorization

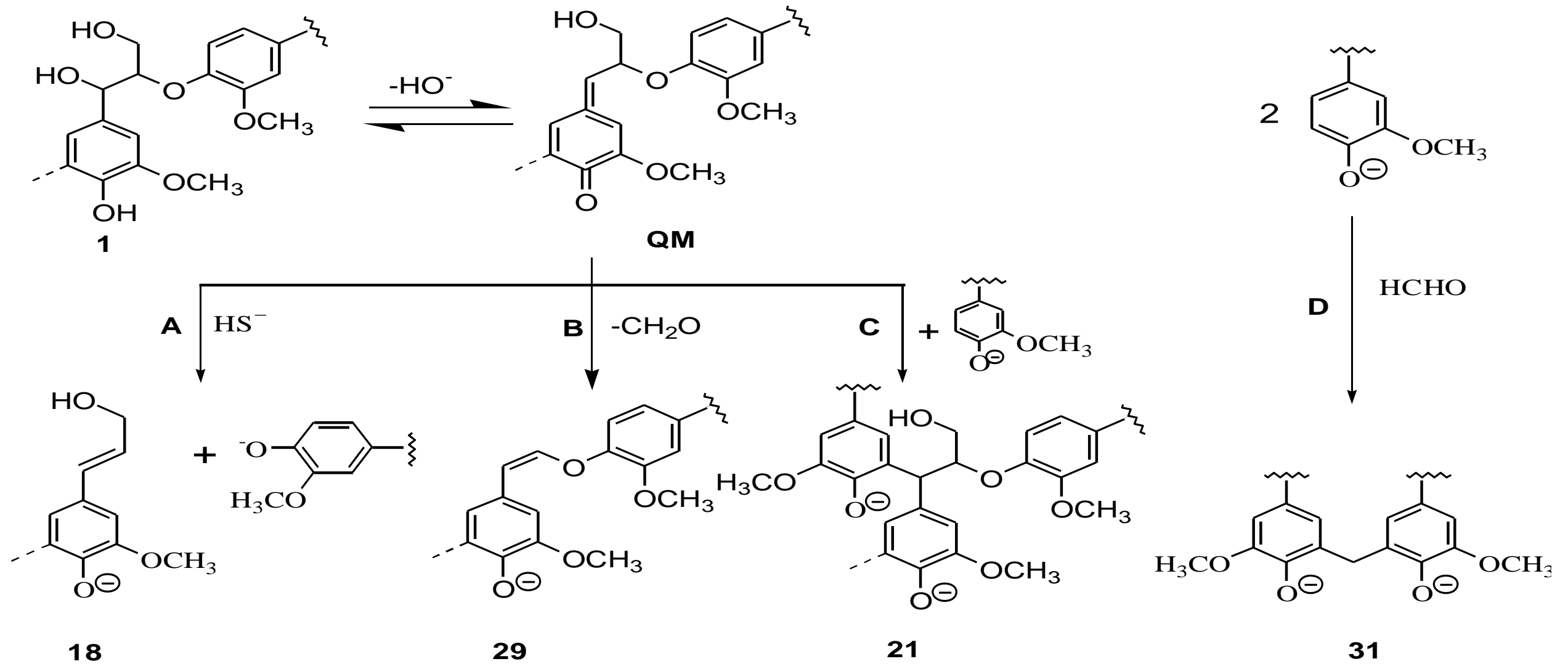


Comparison of Different Technical Lignins

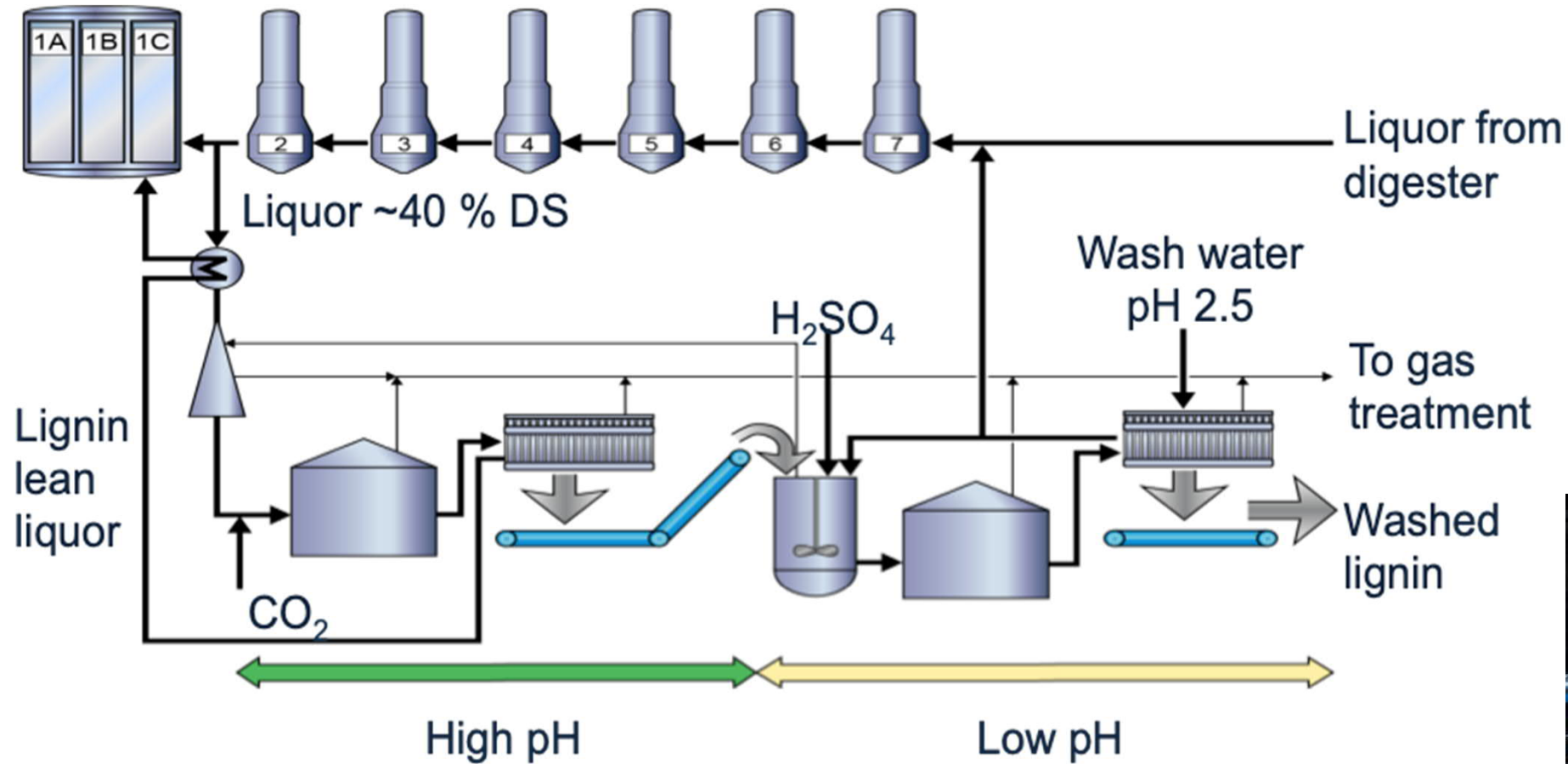
Lignin type	Feedstock	Scale	Production Chemistry	Sulfur content	Carbohydrates	Ash
Kraft	HW, SW	Industrial	Alkaline	1-3%	0.2-3%	0.5-5%
Soda	HW, Non wood	Industrial	Alkaline	Free*	0.2-3%	0.5-5%
Lignosulphonates	HW, SW	Industrial	Acid	4-8%	1-35%	0-20%
Organosolv	All	Pilot	Acid	Free*	<0.5	<0.2
Acid Hydrolysis	All	Industrial/pilot	Acid	Low-free*	1-20%	...
Steam Explosion	?	Pilot	Acid	Low-free*	1-5	...
SCW Hydrolysis	All (data for HW)	Pilot	SC	0.1-0.9%*	0.8-40%	0.1-1%

* Dependent on washing efficiency during lignin isolation

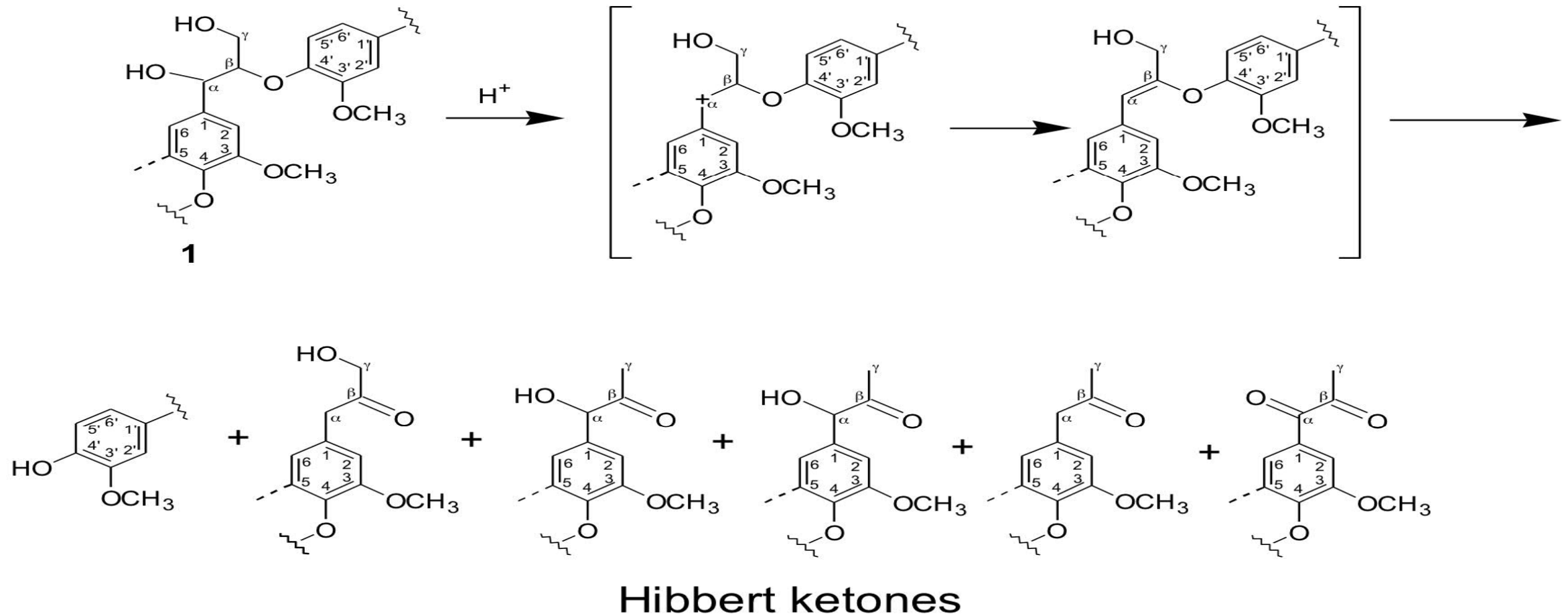
Lignin Reactions in Alkaline Pulping



LignoBoost Recovery Process



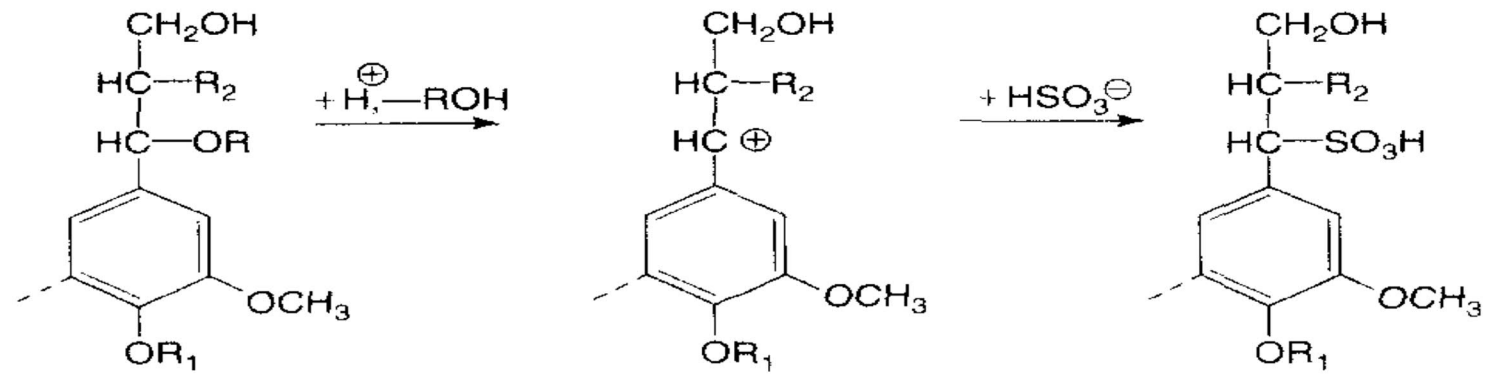
Acidic Lignin Degradation



Major reaction of lignin degradation under acidolysis (in acidic aqueous organic solvent) conditions is cleavage of β -O-4 structures (1) resulted in formation of free phenolic moieties and Hibbert ketones.

Lignosulphonates Chemistry

- Information is “old-fashioned”
- Ca 0.5 HSO₃ group/Ar (range of 0.2-0.65)
- Very wide MWD (MW 1,000 – 150,000)
- No Tg
- High solubility in water
- Low solubility in organics



R = H, alkyl, aryl
R₁ = H, neighbouring lignin unit
R₂ = neighbouring lignin unit

Current Sugar-Based Biorefinery

- ❖ The main products are sugars (ethanol, etc)
- ❖ Lignin is:
 - ❖ Waste
 - ❖ Fuel
 - ❖ Low value feedstock for high value chemicals (aromatic monomers, BTX, etc)
- ❖ Biorefineries are optimized for sugars production, lignin is a leftover
- ❖ Biorefinery faces significant economic challenges

Lignin: To Make the Biorefinery Great Again!

Sugars income:	\$150 – 200/t biomass
Lignin as fuel:	\$20 – 60/t biomass
Lignin as high-value product:	\$100 – 750/t biomass

- Variations in process conditions affect sugars (ethanol) yields, but not their properties
- Lignin can be sold as a high-value product only if required characteristics are achieved

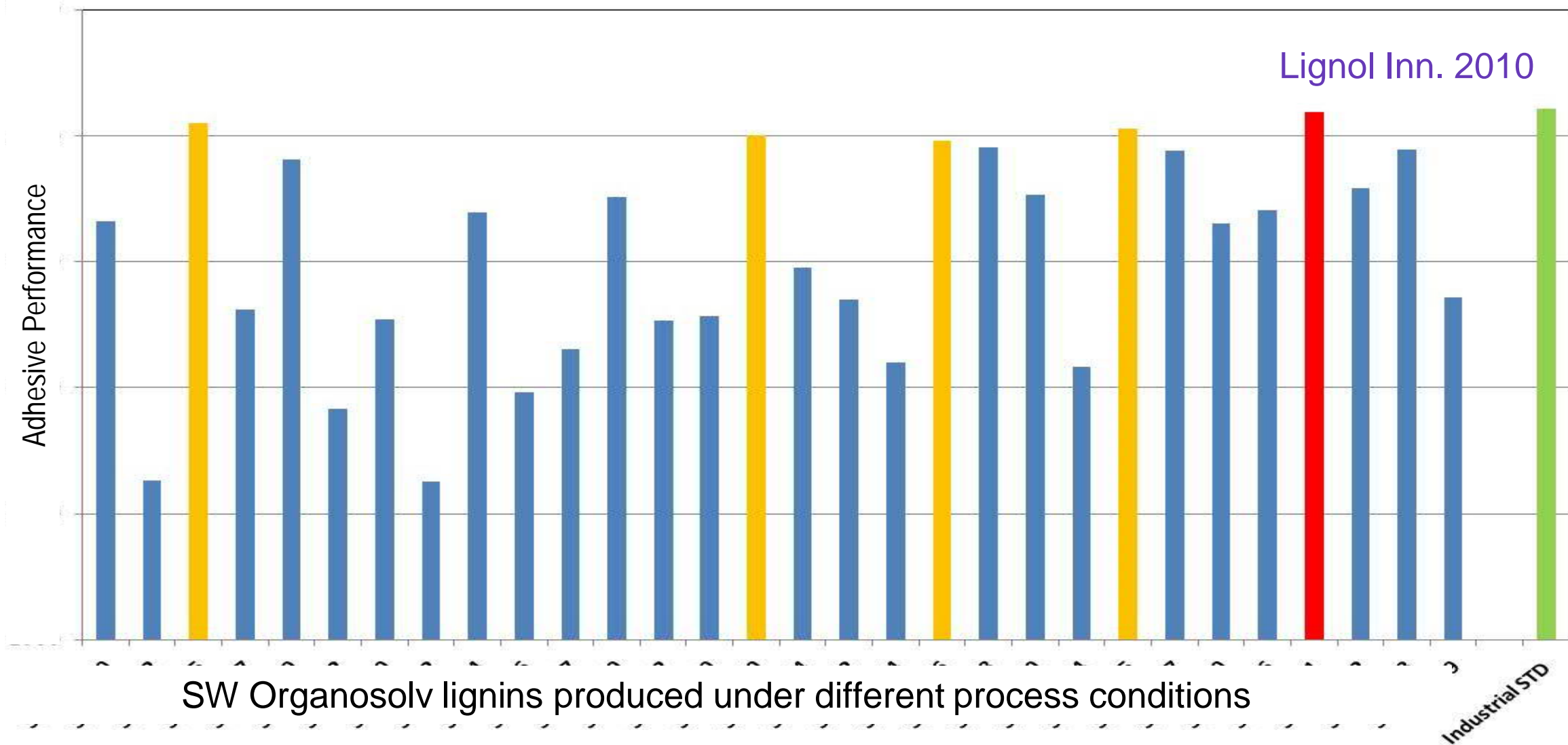
To make sugar biorefinery economically successful, the process optimization should be focused on lignin engineering



Lignin Engineering



Lignins Were not Born Equal

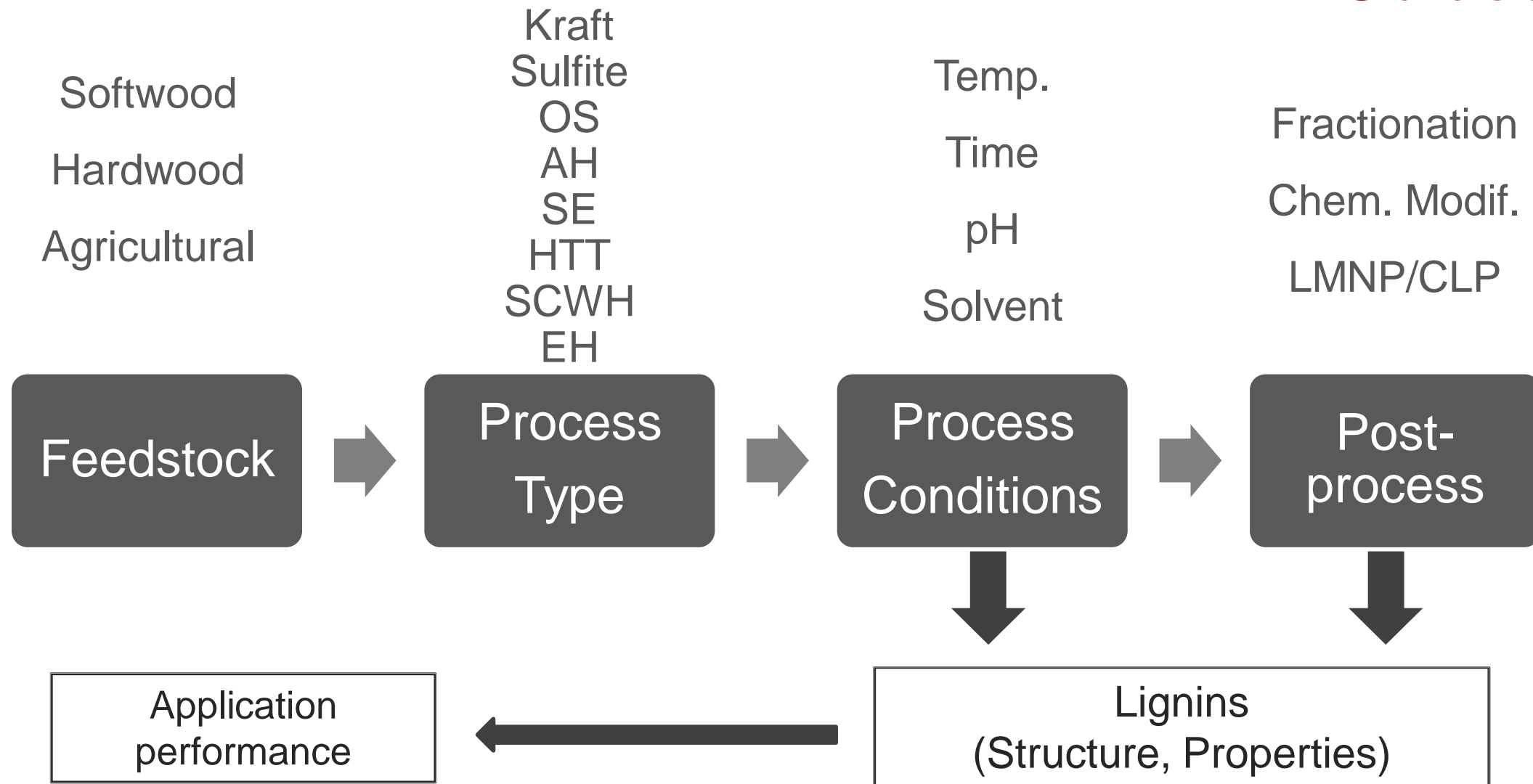


Only one lignin fits the standard requirement, 4 are close, the rest fail

Lignin Engineering is Required!

Lignin Engineering

Guided by AI



Large number of lignins to be evaluated requires efficient analytical methodology

Biorefinery Lignins vs Pulping Lignins

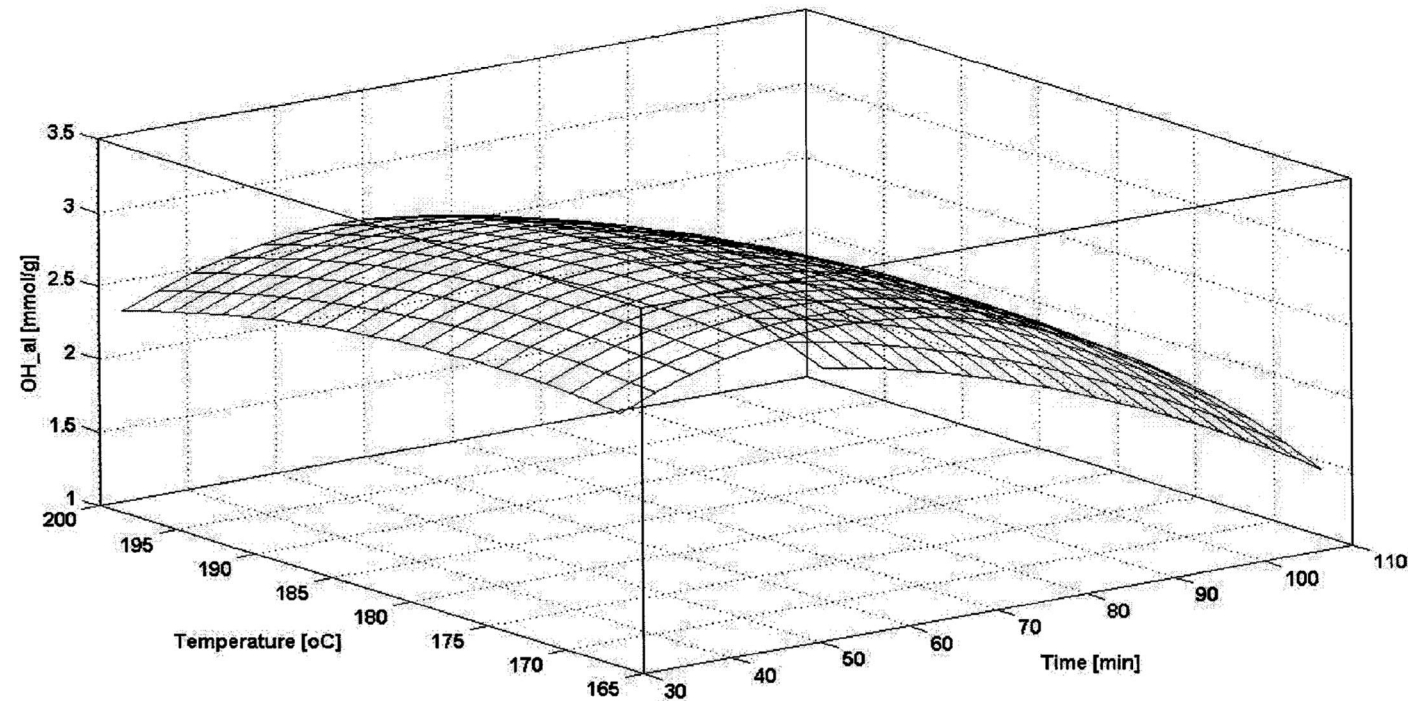
Lignin source	Potential production, Mt/y	Purity	Feedstock range	Process flexibility	Cost	Application value
Pulping	5-8	med.-high	narrow	narrow	med.-high	med.-high
Biorefinery	>200	low	wide	wide	low	low-high*

*our opinion

- ❖ Lignin Engineering (Structure - Performance correlations):
 - ❖ By feedstock
 - ❖ By process conditions
 - ❖ By post-processes (purification, fractionation, functionalization)

More flexibility in optimization of biorefinery lignins

Process – Structure Correlation



Example:

$$\text{Al-OH} = 19.79 - 11.22 \cdot \text{pH} - 0.153 \cdot \text{Time} - 2.40 \cdot \text{pH}^2 + 0.088 \cdot \text{pH} \cdot \text{Time} + 0.102 \cdot \text{pH} \cdot \text{Temp.} + 0.0203 \cdot \text{pH} \cdot \text{EtOH} + 0.000537 \cdot \text{Time}^2 - 0.000706 \cdot \text{Temp.}^2 - 0.00047 \cdot \text{EtOH}^2$$

Similar models were built for all structural parameters

Structure – Performance Correlations

- ❖ Structural lignin analysis is quite reliable, informative and productive
 - ❖ Performance evaluation is the bottleneck:
 - ❖ Large lignin quantity is needed
 - ❖ Time/labor consuming tests
 - ❖ Low productivity (few samples can be tested)
 - ❖ Lack of reliable fast bench screening methods
-

ABES Test: Example of a Screening Method

- ❖ Automatic Bond Evaluation System (ABES) test for wood adhesives
- ❖ Small amounts (< 1g), good productivity (1-3 samples/day)
- ❖ Good correlation with pilot performance tests
- ❖ Similar tests are needed for other applications



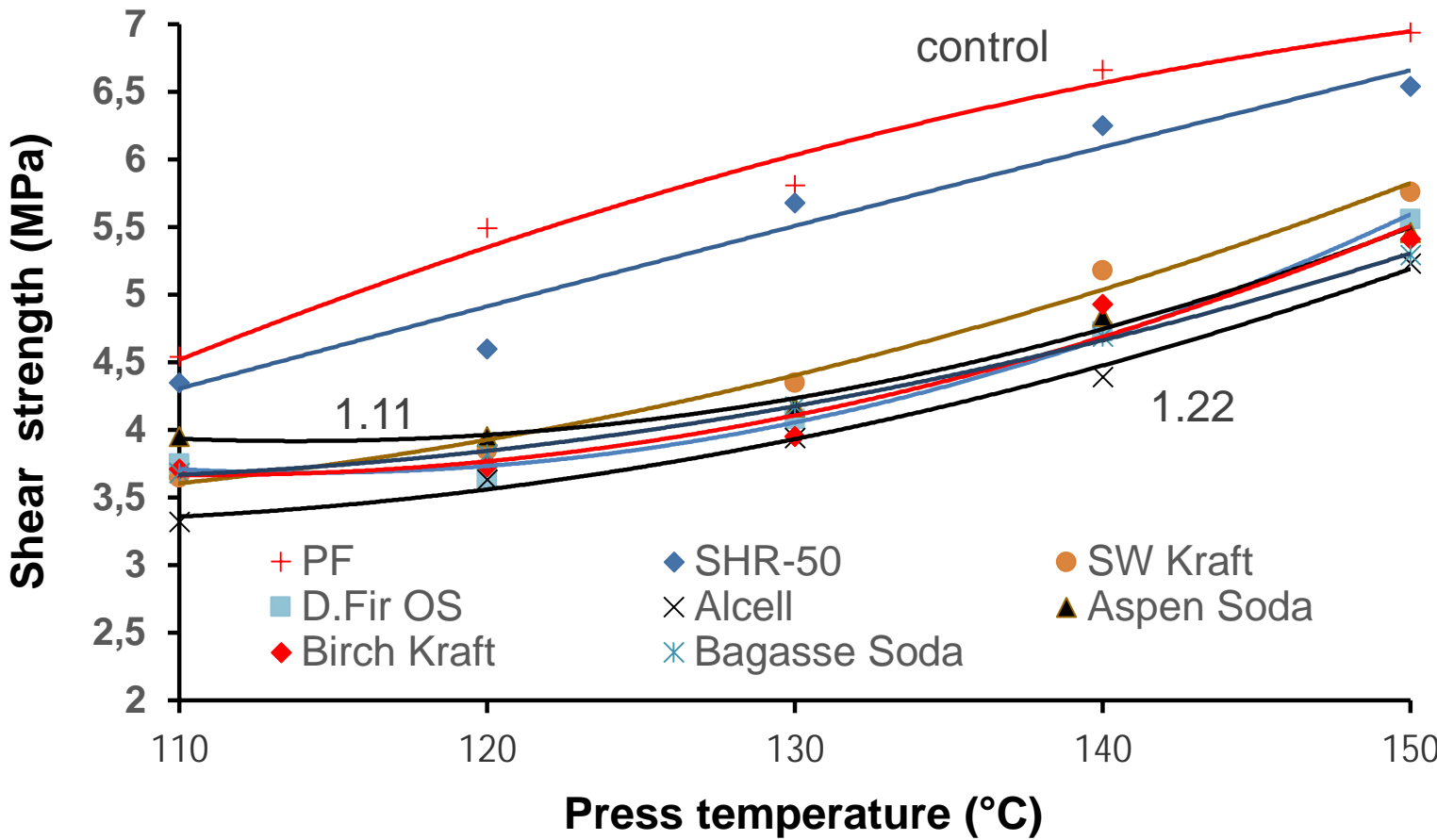
Bench test (50 samples)



Pilot trials (2 samples)

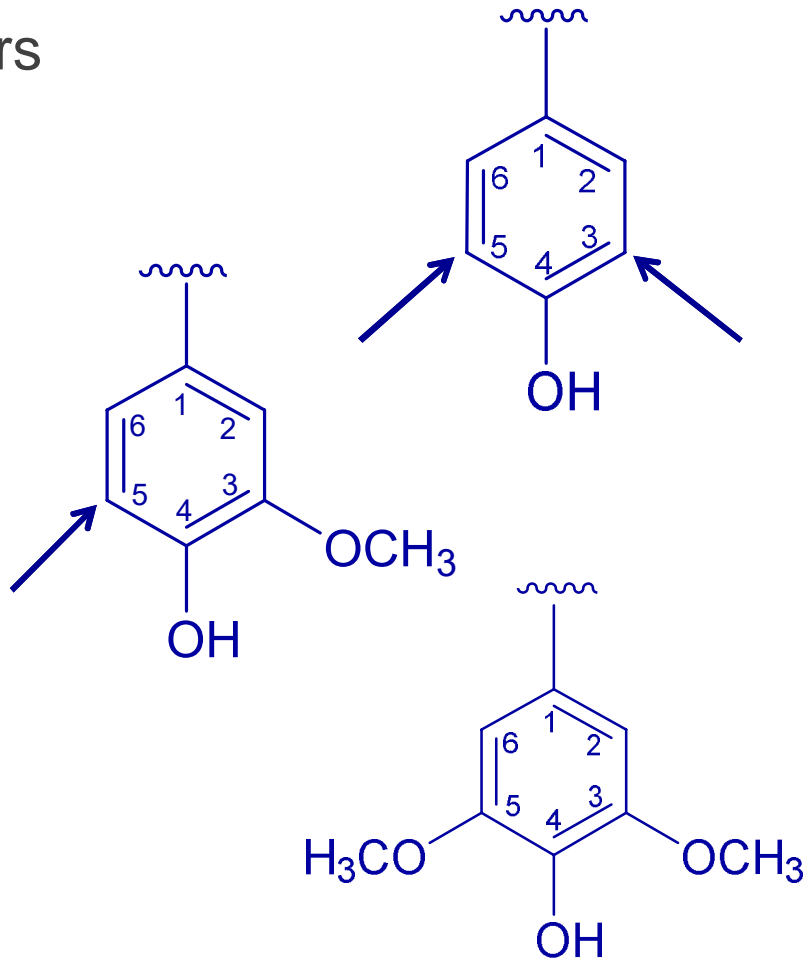
Example of Structure - Performance Correlation (PF Adhesives)

ABES test, 30% plywood PF substitution, Press time 90 sec.



Reactive centers

- mmol/g
- 0.65
- 2.36
- 2.61
- 1.04
- 2.26



Balakshin and Capanema, 14th EWLP, V.I, 63 (2016)

- No correlation with the amount of reactive centers or molecular mass
- Other variables should be more important

Dogmas Around Biorefinery Lignins

- ❖ Low purity causes low performance
- ❖ Challenges in production of high-purity lignins from crude biorefinery lignins
- ❖ Inferior performance of HW lignins as compared to SW lignins

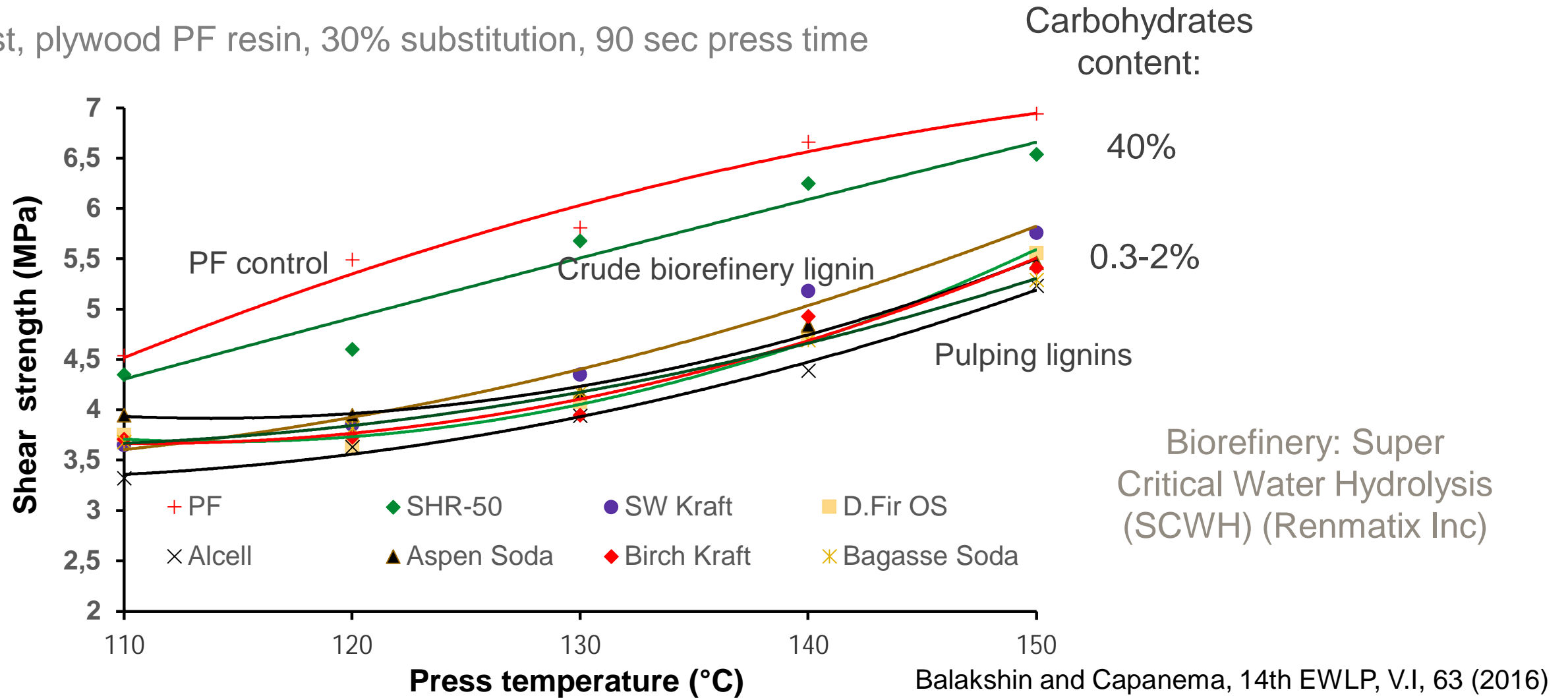


Biorefinery Lignins are considered as low-value products

These dogmas are challenged with our recent achievements

Is Lignin Purity a Must?

ABES test, plywood PF resin, 30% substitution, 90 sec press time



Crude biorefinery lignin (Cello-Lignin) performs better than high-purity lignins

Lignin – Cellulose Synergism

- ❖ Other examples of lignin – cellulose synergisms:
 - ❖ Lignin-cellulose carbon fiber (Hummel et al.; Rojas et al.; Chalmers – RISE)
 - ❖ Lignin - CNC in thermoplastics (Fortunatti et al., 2016)
 - ❖ Lignin improves CNC and CNF performance (Rojas et al.)
- ❖ Similar effect can occur in the case of biorefinery lignins containing crystalline cellulose, but at dramatically lower costs
(~\$100-200/t vs ~\$5,000-7,000/t CNC)
- ❖ Cellulose component has to be optimized

Balakshin and Capanema, 14th EWLP, V.I, 63 (2016)



Dogma:
**Upgrade of crude biorefinery lignins is
technically and economically challenging**

?

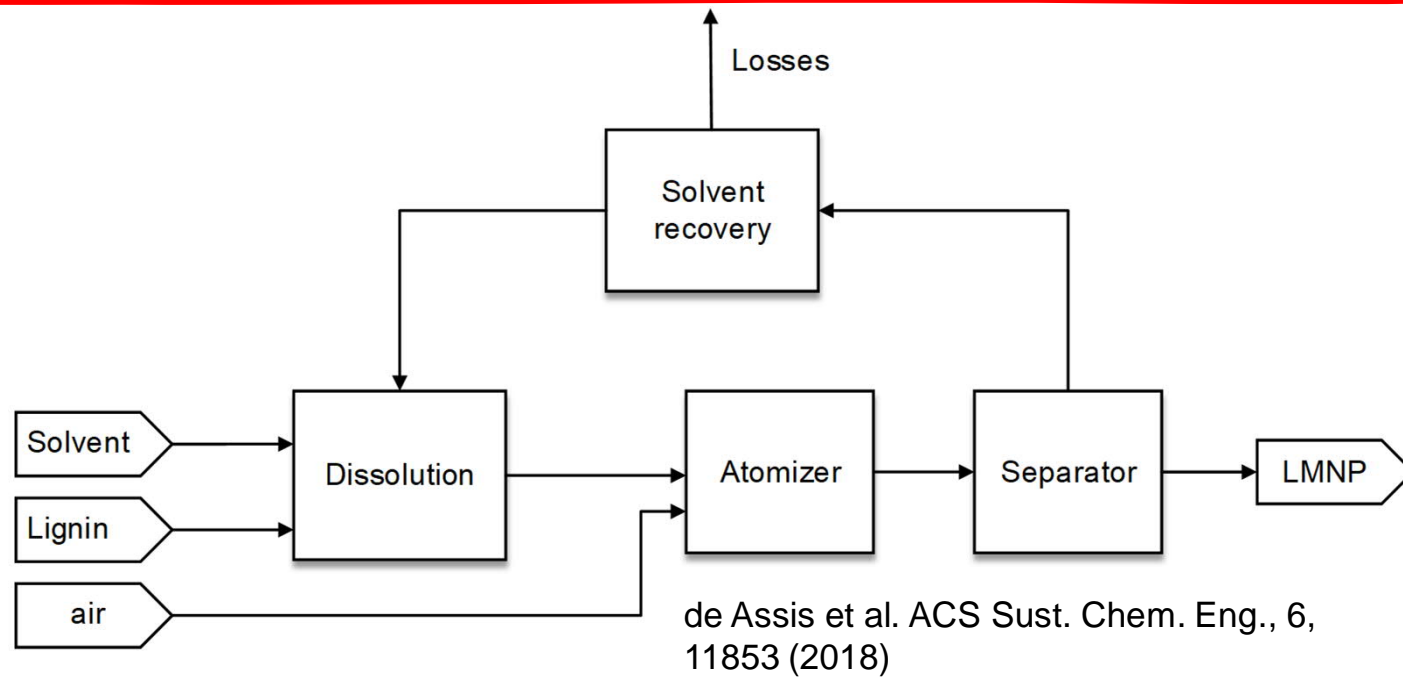
- ❖ Purification
- ❖ Fractionation
- ❖ Functionalization

One Pot Purification, Fractionation and Derivatization

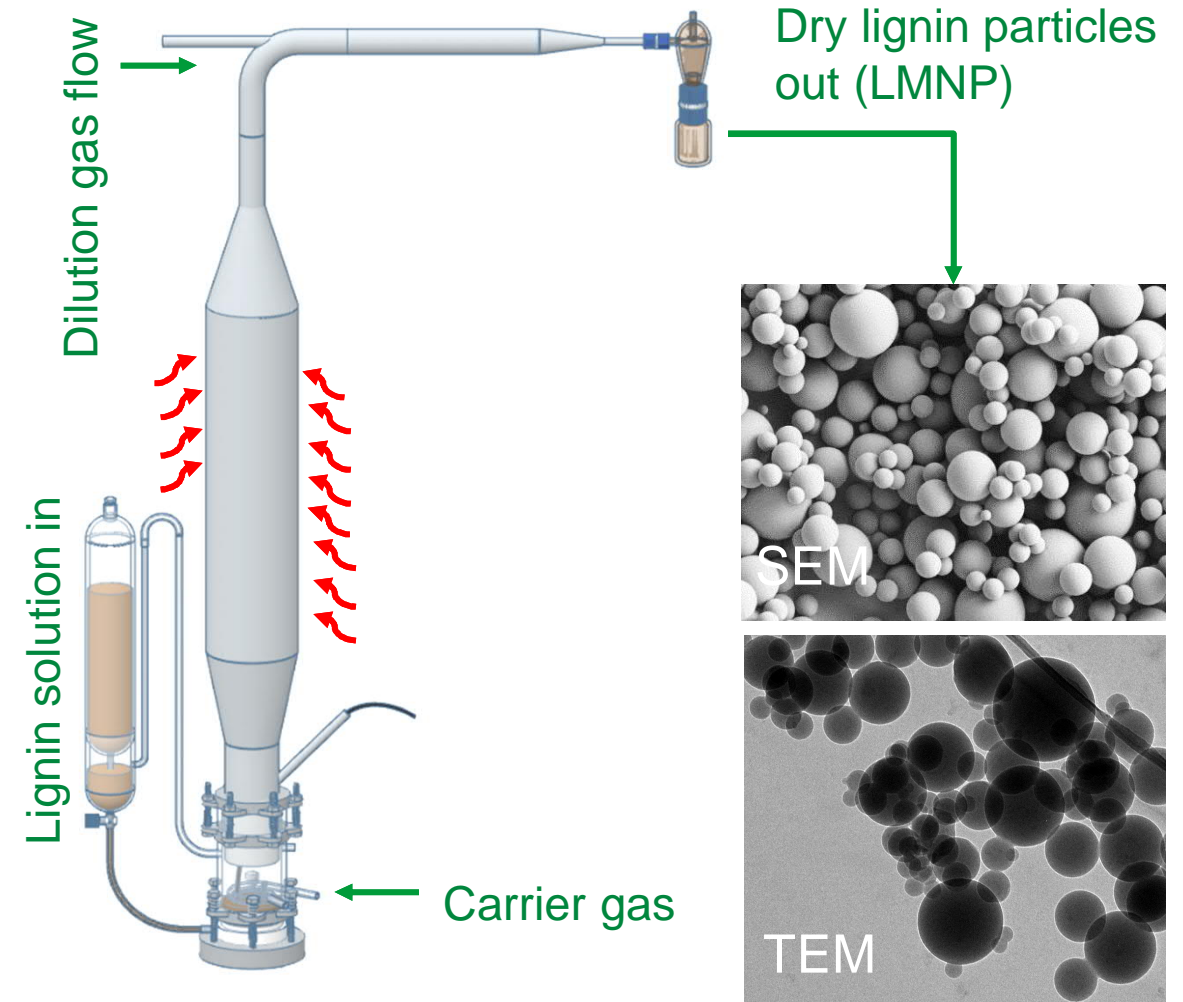


- ❖ Purification: Very high purity (>99.5%) and extraction yield (~90%)
- ❖ Fractionation: Specific and narrow MW and T_g fractions by manipulating solvent; very similar lignin structure
- ❖ Partial lignin functionalization during lignin extraction/fractionation under very mild conditions :
 - ❖ Alkylation (ethylation)
 - ❖ Acylation (acetylation)
 - ❖ Others
- ❖ Technically very simple, low hazard, very affordable economically

Lignin Micro- and Nanoparticles (LMNPs)



- ❖ Strongly enhance useful lignin properties (antioxidant and UV-protection, antimicrobial properties, thermal stability)
- ❖ New properties (mechanical reinforcement, good miscibility, emulsion stabilization, etc)
- ❖ Alternative to chemical lignin modification
- ❖ Green processes



LMNP can be easily incorporated into biorefinery lignin processing

Production cost is reduced from 900 - 1200 USD/t (kraft lignins, LS) to ~750 USD/t

de Assis et al. ACS Sust. Chem. Eng., 6, 11853 (2018)

Rethinking Biorefinery Lignins

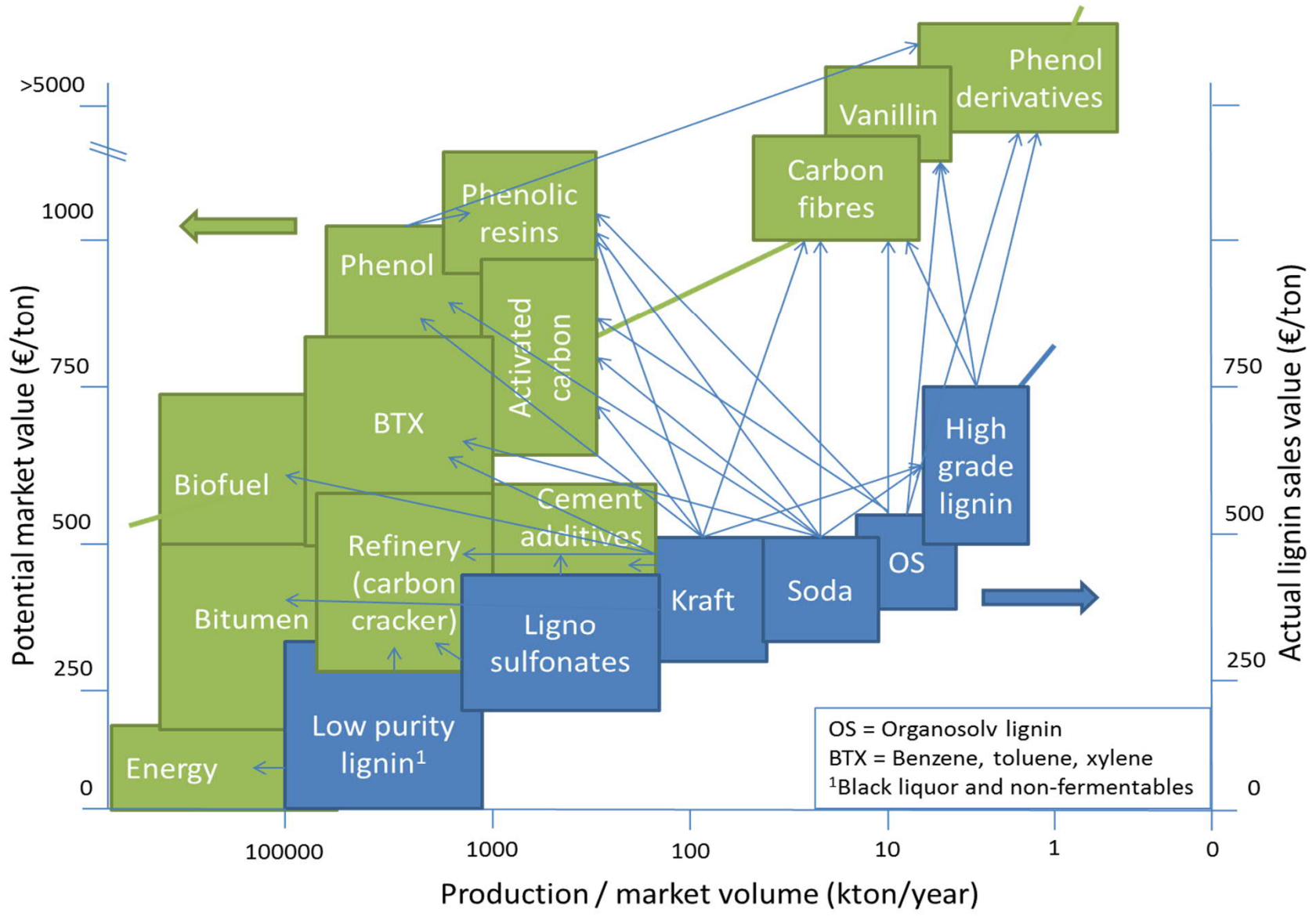
- ❖ High lignin purity is not a must:
 - ❖ Cellulose-containing lignins may have similar or superior performance
- ❖ When needed, crude biorefinery lignins can be easily upgraded to higher value products in green, technically feasible and cost efficient ways comprising:
 - ❖ Purification
 - ❖ Fractionation
 - ❖ Functionalization
 - ❖ Lignin micro- and nanoparticles

Biorefinery lignins can be used in various high-value applications

Market Aspects

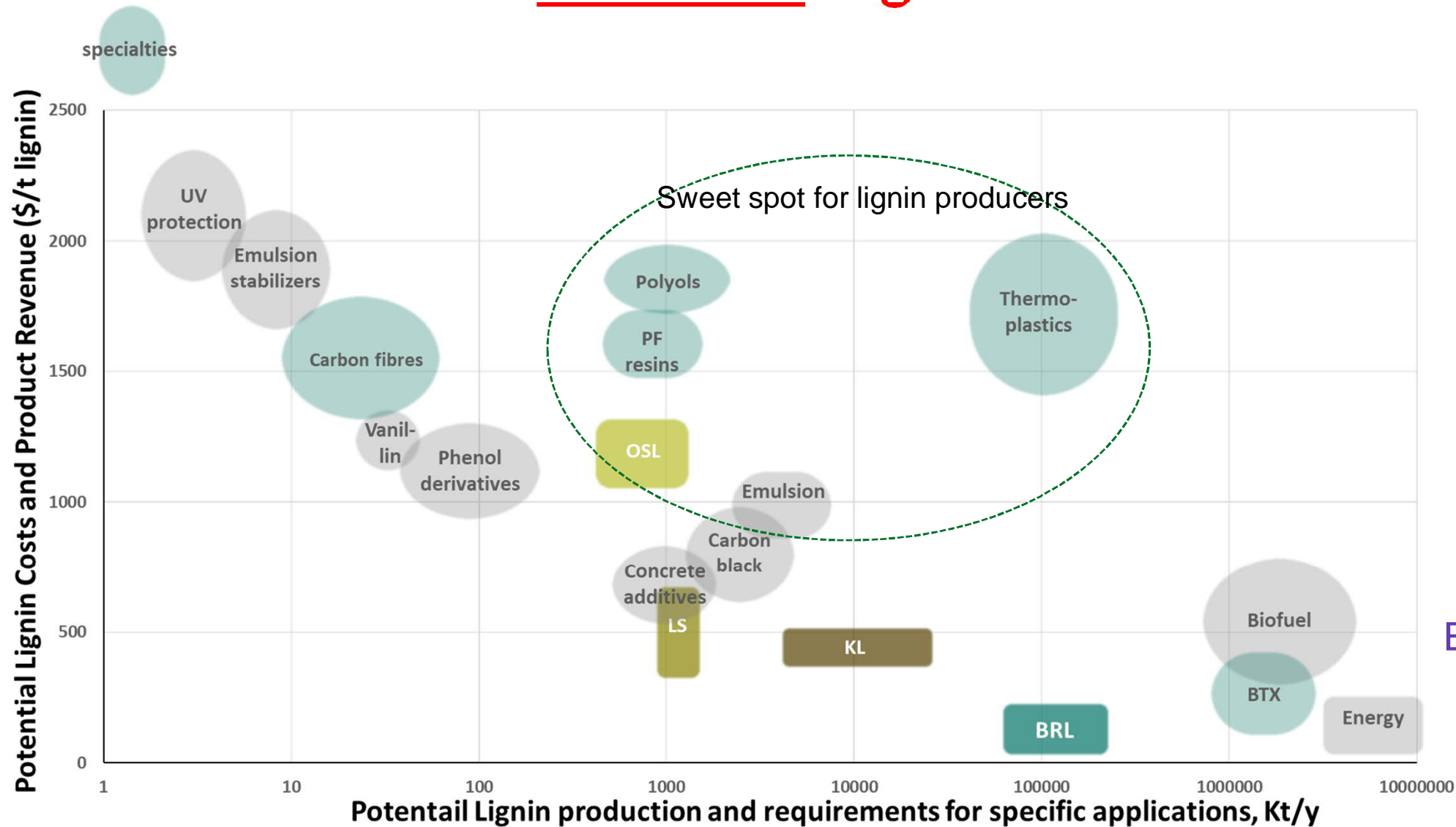


Lignin Production vs Utilisation



Gosselink R.J.A. 2011

Potential Lignin Market



OSL = organosolv lignins
 LS = Lignosulfonates
 KL = Kraft lignins
 BRL = biorefinery lignins (crude)

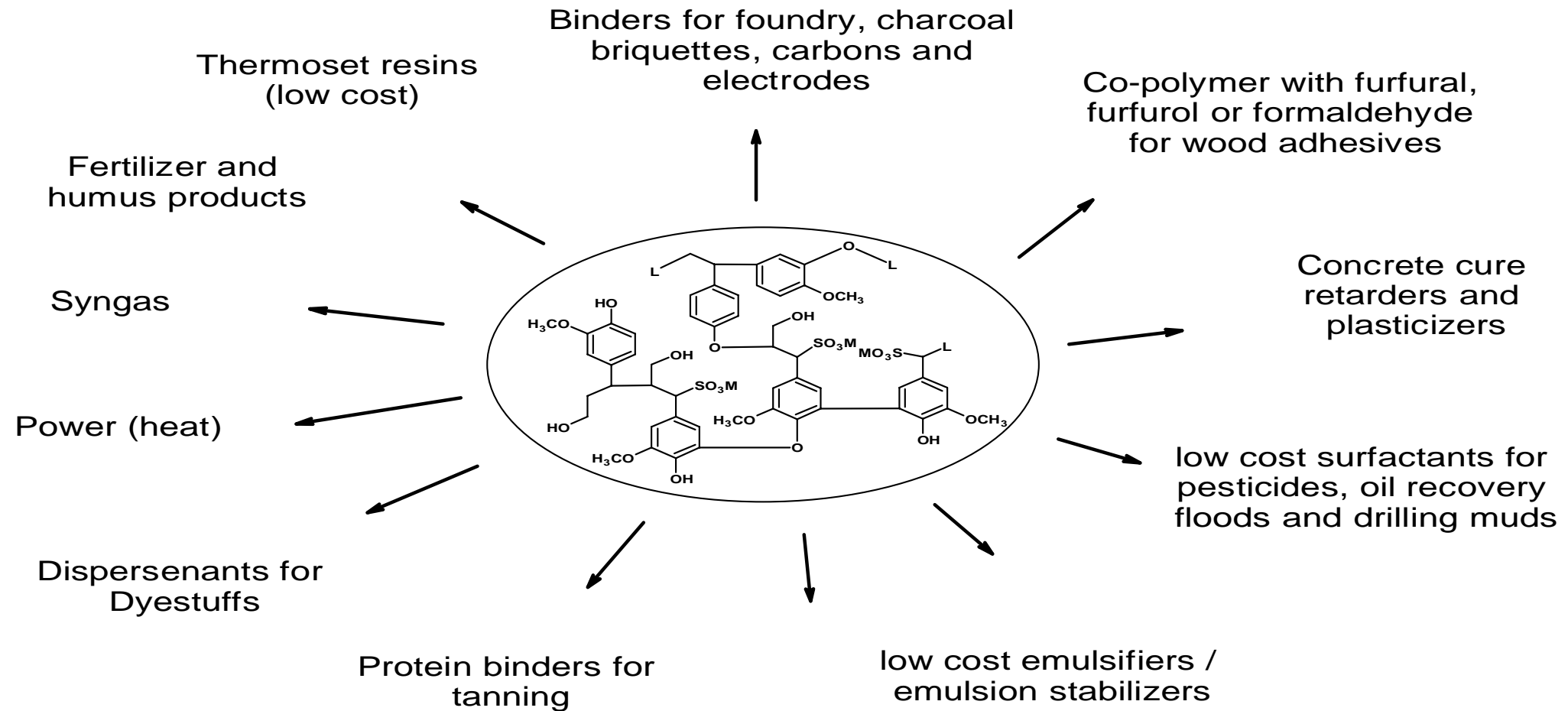
Balakshin et al. 2020 submitted

- All values are very approximate due to undeveloped lignin market
- Revenue and requirement values consider product yields from lignin (e.g., 5-20% for BTX) and replacement ratios (e.g., 30-70% for PF resins)
- Optimum business case: Best Revenue @ Market size for specific producer/customer

Lignin Applications



Traditional Lignin Market



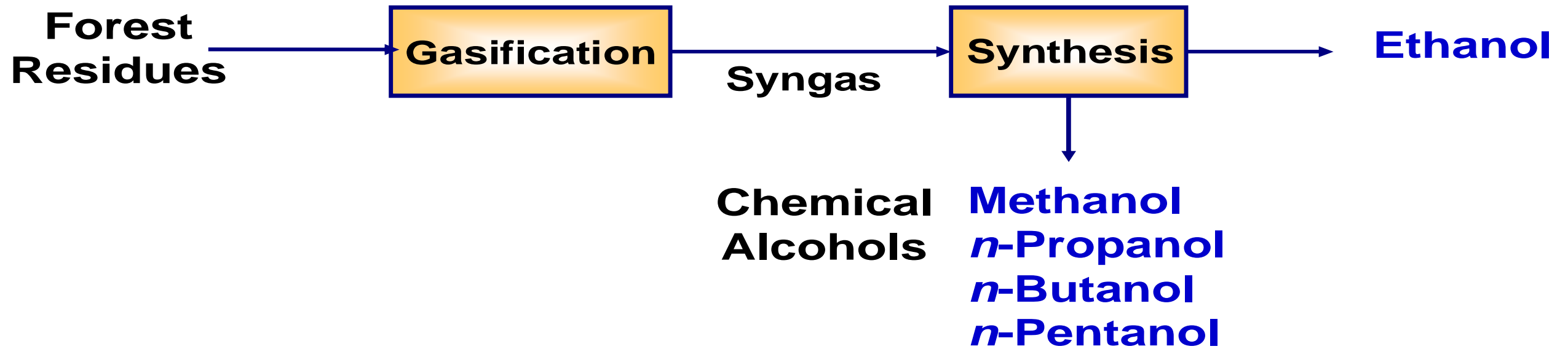
Current use of lignosulphonates and sulphonated kraft lignin

Holladay et al. 2007

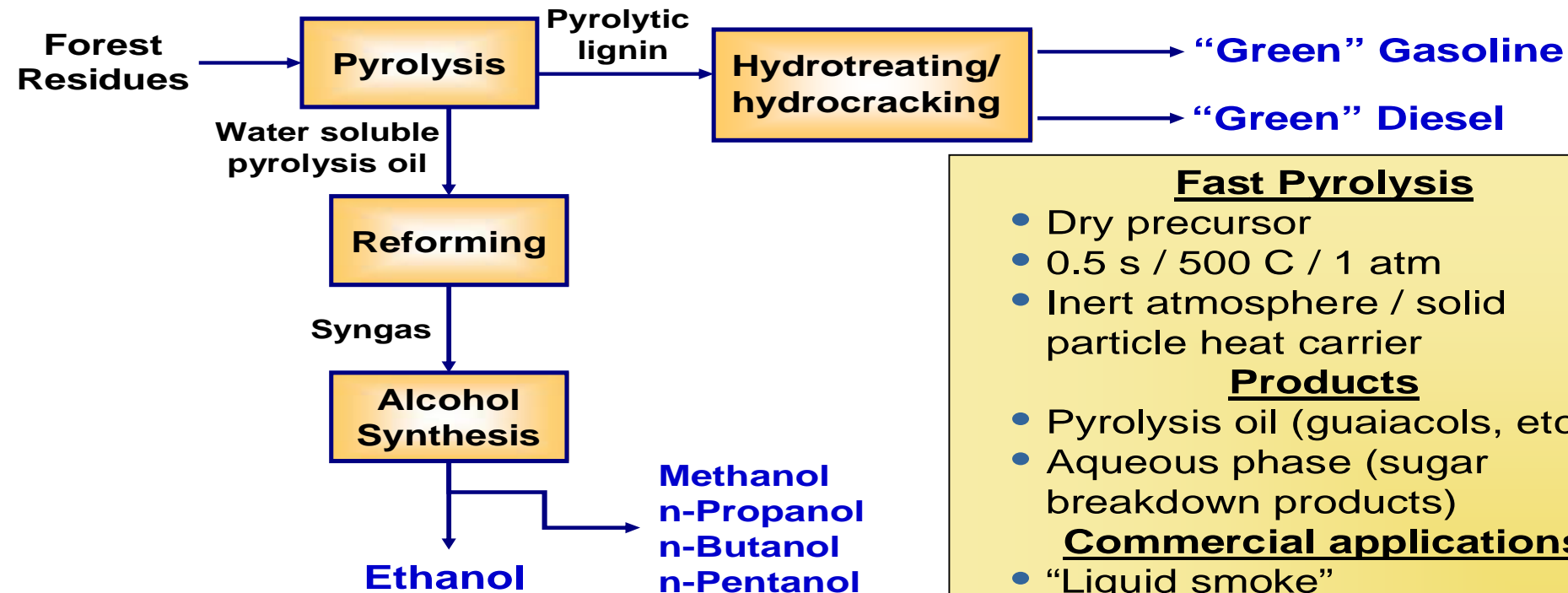
Lignin-to-Power & Fuel

Near-Term Opportunity

Gasification



Pyrolysis Integrated with Gasification



Fast Pyrolysis

- Dry precursor
- 0.5 s / 500 C / 1 atm
- Inert atmosphere / solid particle heat carrier

Products

- Pyrolysis oil (guaiacols, etc)
- Aqueous phase (sugar breakdown products)

Commercial applications

- “Liquid smoke”
- “resins” not commercial
- “mixtures” not pure cpds

Lignin as a Fuel in the Lime Kiln

- Prior work at UBC demonstrated the technical feasibility of burning lignin in a pilot lime kiln.
- RISE recently conducted trials at a Swedish mill replacing the fossil fuel with dry lignin.
- Market size (100%): enormous
- Lignin value: \$150/t at a natural gas price of \$6/GJ and \$300/t at oil price of \$100/barrel



Lignin as a Fuel in Power Plants

- Lignin pellets successfully used as a supplementary fuel in a coal-fired power boiler
- Efforts being made to qualify lignin as a fuel for coal-fired power plants in Ontario
- Lignin used as a binder in wood pellets at FPInnovations
- Market size (2%): 240,000 t/y
- **Lignin value > \$800/tonne**



Challenges: Lignin-to-Power & Fuel

Technology	Product Examples	Technology Challenges
Lignin combustion	Process heat	Engineering and process integration
Gasification	MeOH/DME Green fuels olefins	Economic gas purification; process scale-up
Gasification	Fischer-Tropsch green fuels	Economic gas purification; catalyst and process improvements for methane and heavies reduction; process scale-up
Gasification	Fuel ethanol, propanol, butanol	Economic gas purification; catalyst and process improvements to produce 2-carbon and larger alcohols; process scale-up
Pyrolysis	Pyrolysis oil suitable for integration into petroleum refinery; process for green fuel and chemicals	Economical stabilization of pyrolysis oil for transport and compatibility in petro-refinery; process scale-up
Lignin fuels	Reformulated gasolines	Process demonstration; catalyst life; reducing number of process steps; process scale-up

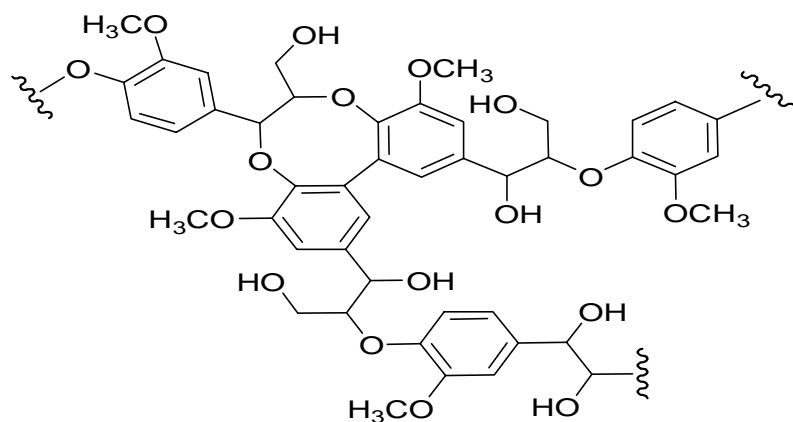
Holladay et al. 2007

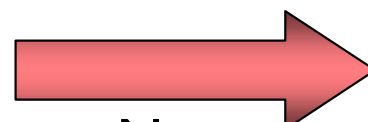
Aromatic Monomers from Lignin

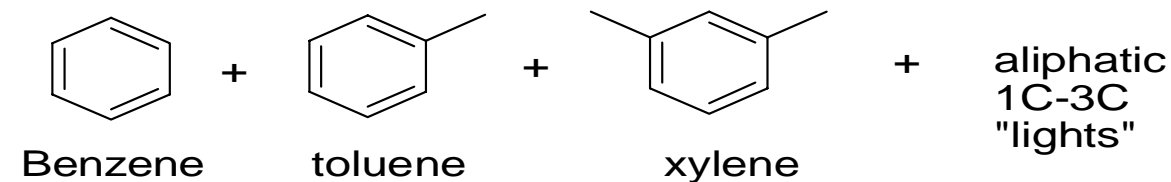
Long-Term Opportunity



Conversion of Lignin to BTX Chemicals




New
technology

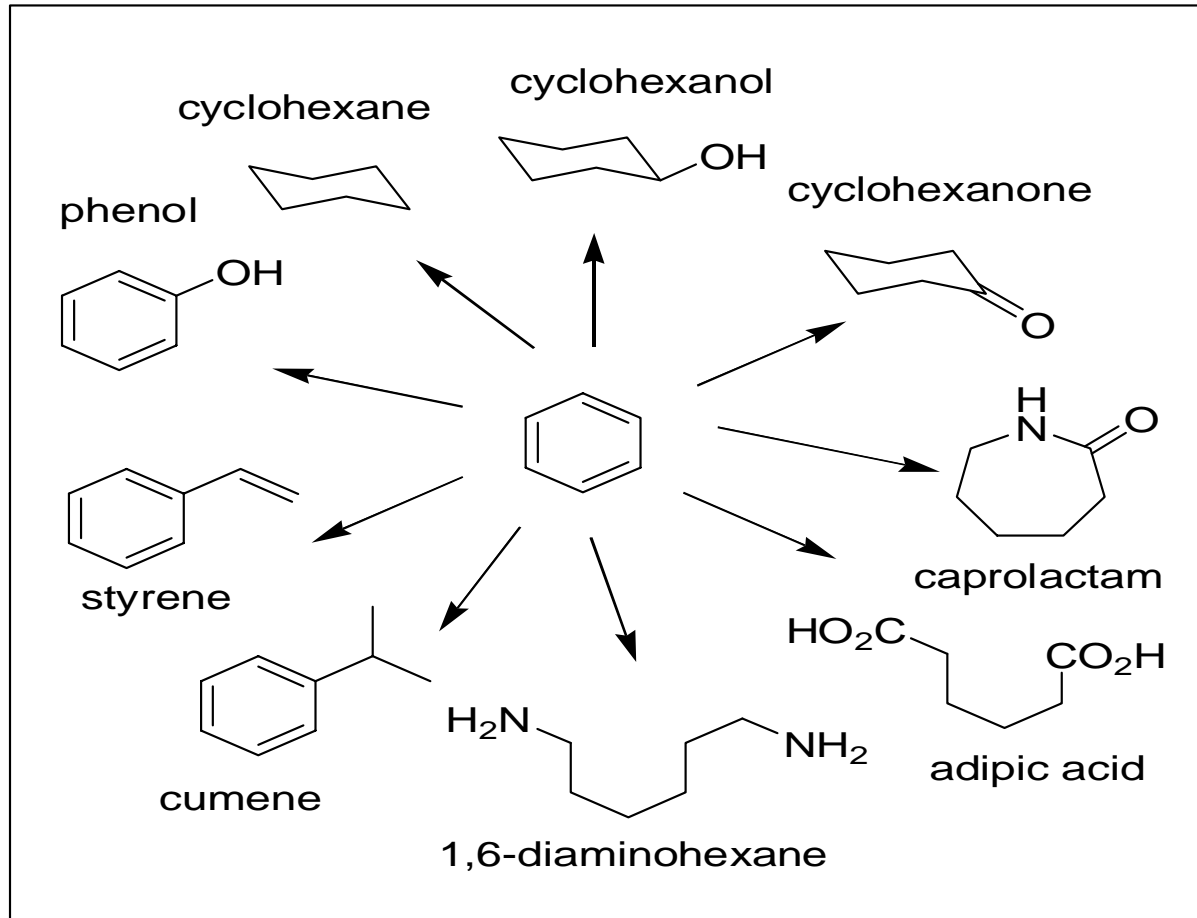



Current technology

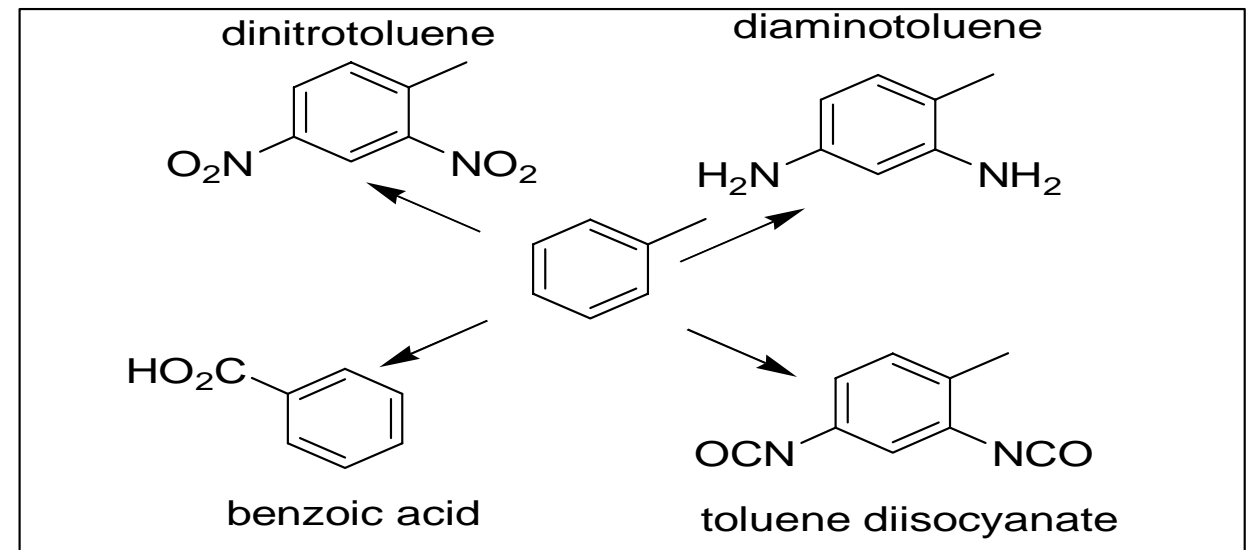
Aromatic chemicals, nylon intermediates,
resins and many others

Holladay et al. 2007

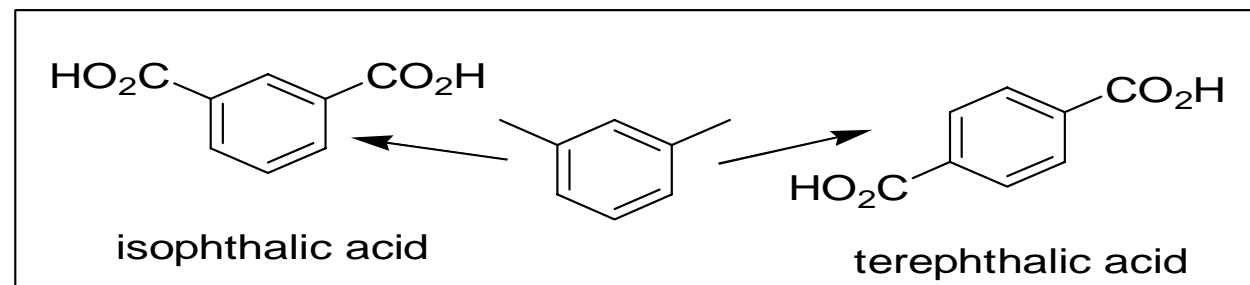
Examples of BTX Derived Chemicals



Examples of Benzene Derived Chemicals



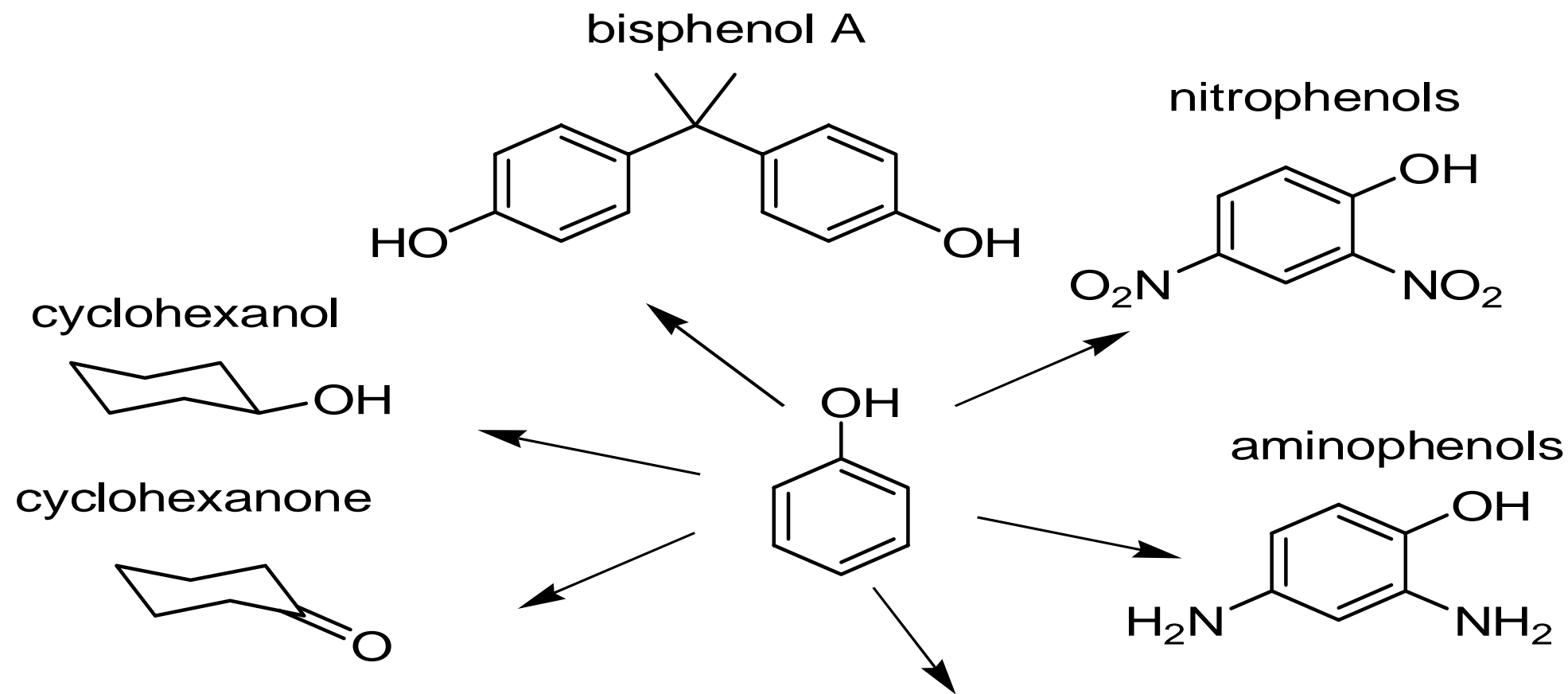
Examples of Toluene Derived Chemicals



Examples of Xylene Derived Chemicals *

Holladay et al. 2007

Phenol Derivatives (Current Technology)



pigments, dyes, resol resins, antioxidants, urea resins, formaldehyde resins, alkyl phosphites and others

Lignin-to-Aromatics: Challenges

BTX Chemicals <ul style="list-style-type: none">• Benzene• Toluene• Xylene	Catalysis – selective dehydroxylations and demethoxylations; dealkylations. Application of catalytic-reforming chemistry from petrochemical industry
Phenol	Catalysis – selective dehydroxylations and demethoxylations; hydrogenolysis; dealkylations. Application of catalytic reforming chemistry from petrochemical industry
Lignin monomer molecules (substituted coniferols) <ul style="list-style-type: none">• Propylphenol• Eugenol• Syringols• Aryl ethers• Alkylated methyl aryl ethers	Catalysis – selective hydrogenolysis; formylation, hydrotreating, understanding of reactivity ratios, polymerization technology, formulations; catalytic dealkylation, demethoxylation, hydrolysis; control of side chain structure; controlled reduction, preservation of aromaticity; aromatic side chain cleavage, applications for mixtures; demethylation; ether cracking
Oxidized lignin monomers <ul style="list-style-type: none">• Syringaldehyde• Vanillin• Vanillic Acid	Catalysis – selective oxidation

Macromolecules

Medium-Term Opportunity



Lignin to Substitute of Phenol in Phenolic Wood Adhesives

- Advantages of lignin:
 - Rich in phenolic structures
 - Lower cost
- Disadvantages of lignin
 - Slower cure rate at high substitution rate
 - Increased swelling in some wood products
- Market size (30%): 100,000 tonne/y
- **Lignin value: >\$1500/tonne**



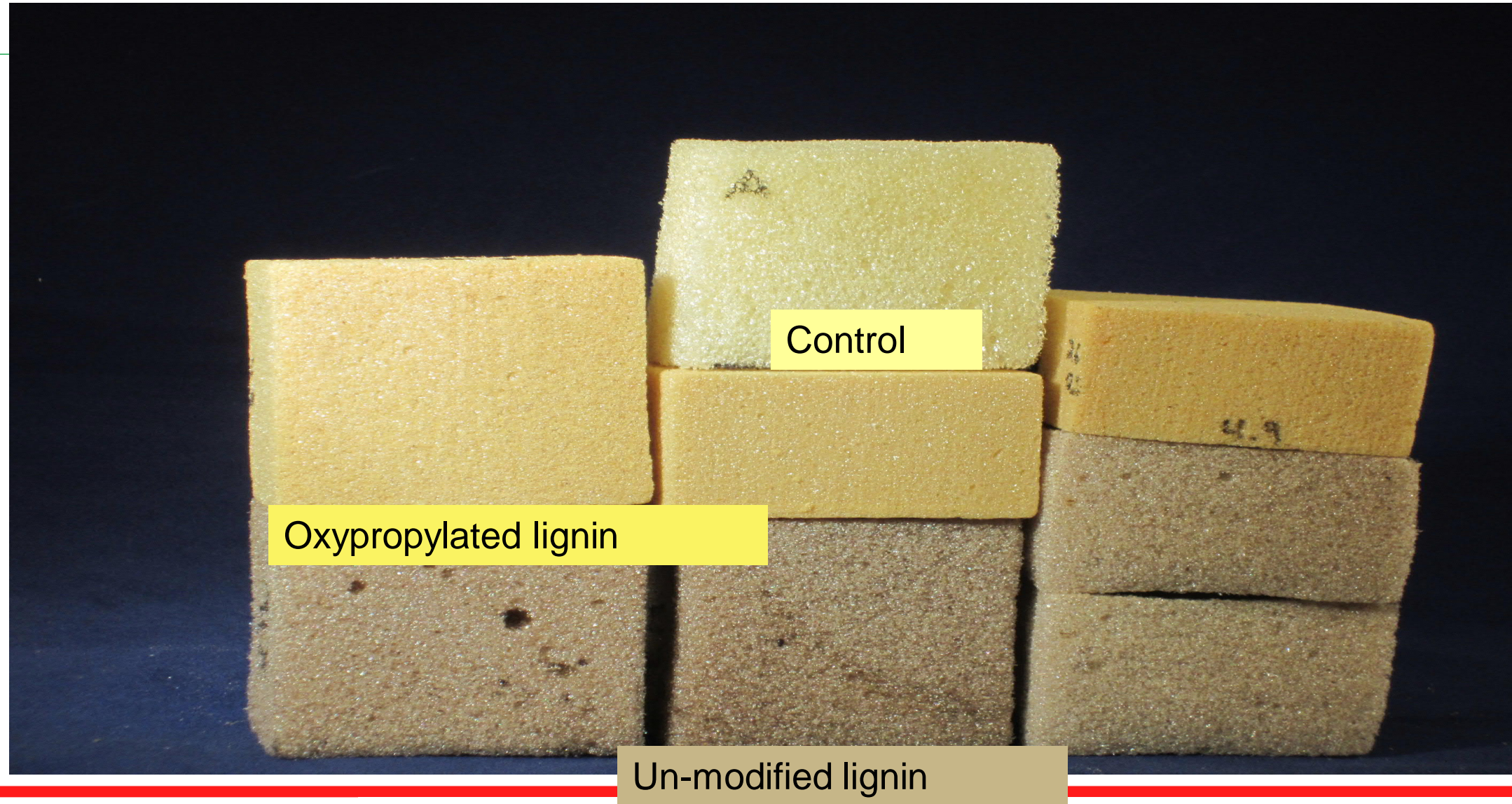
Lignin in Rigid Polyurethane Foams

- To make polyurethane foams isocyanate is reacted with petroleum-based polyols
- Lignin is a natural polyol as a result of its numerous phenolic and aliphatic hydroxyl groups
- Lignin modification is required to increase accessibility of lignin OH groups
- Lignin-based polyols are viewed as potentially useful for making rigid polyurethane foams with beneficial thermal degradation (fire-resistant) properties
- Market size (20%): 220,000 tonne/y
- Lignin value: >\$2000/tonne

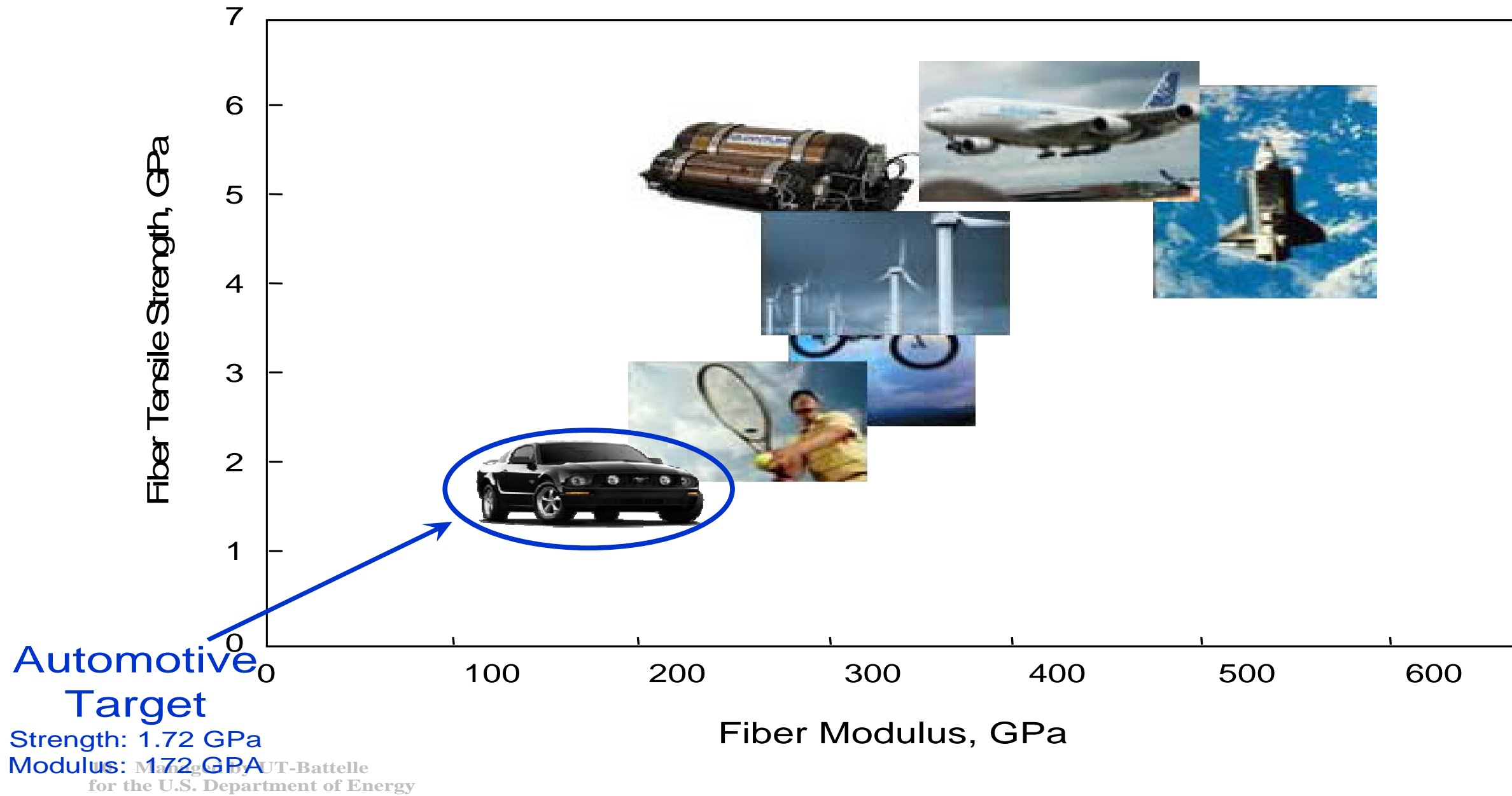


Solid substrate

Rigid Polyurethane Foams



Structural Applications of Carbon Fibers



Ultimate Example of “Vehicle” Lightweighting

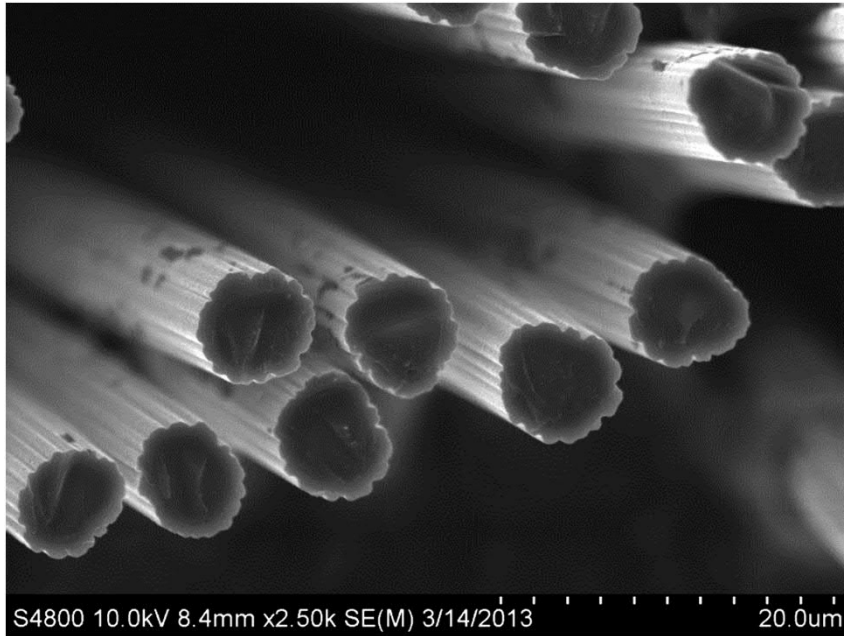
The Boeing 787 Dreamliner comprises 50% by weight carbon fiber composite materials

- Five (5) tons of weight saved on the wings alone
- Ultimate-load tests completed April 7, 2010: wings were flexed upward by 25 feet (7.6 meters) during tests!

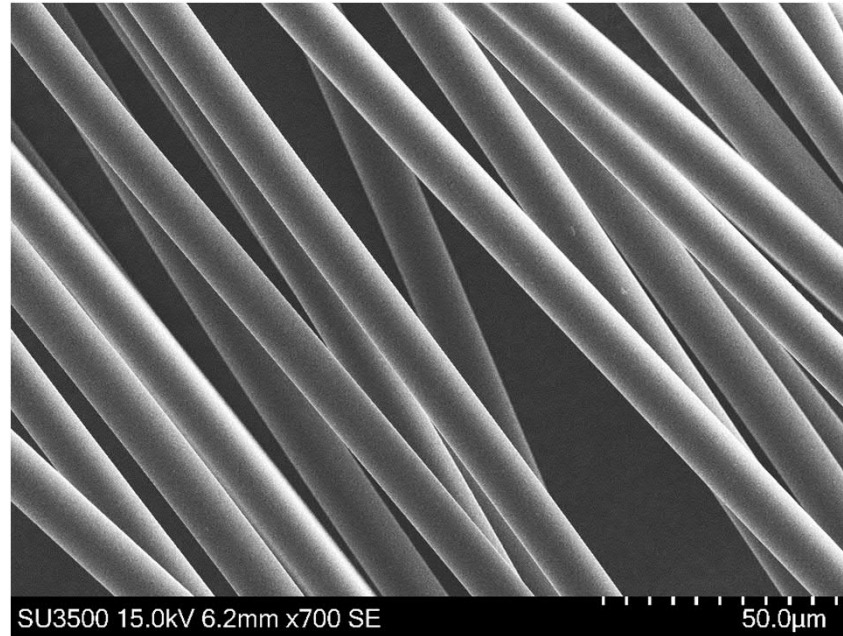


First flight: December 15, 2009

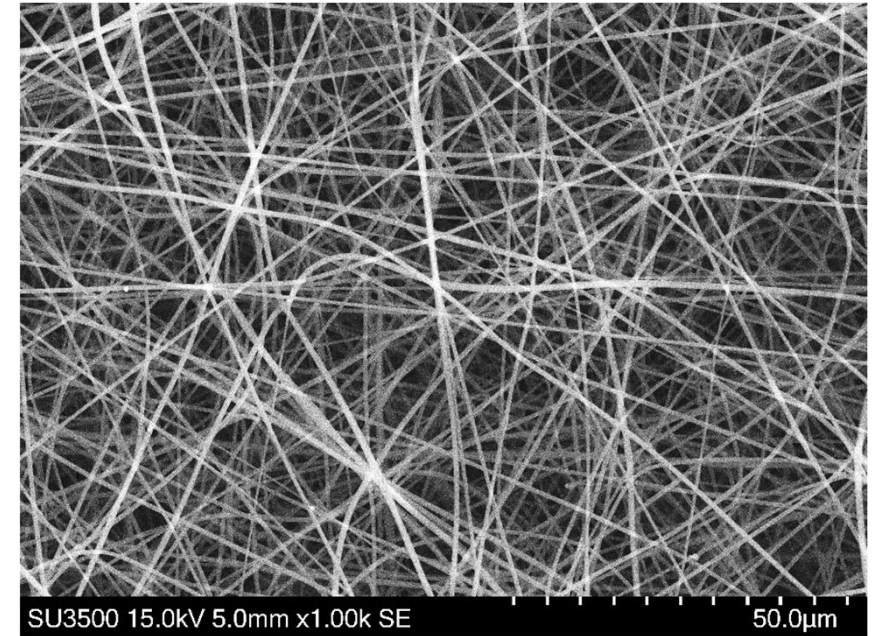
Lignin spinning: different methods



Solution spinning:
Zhang and Ogale 2016; acetylated
SWK



Melt spinning:
Softwood kraft lignin (RISE)



Electrospinning:
Fractionated SWK (RISE)

■ Solution spinning

■ Melt-spinning

■ Electrospinning

Carbon Fiber is in Some US Cars Today

Ford GT



Carbon fiber composite rear deck lid and seat (4500 units total)



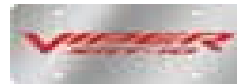
Carbon fiber fenders, wheel house, and floorpan (7000 units/year)



2006 Z06 Corvette



2006 Dodge Viper



Carbon fiber LH/RH fender/sill supports, LH/RH door inner reinforcements, windshield surround reinforcement (2000 units/year)



But not yet Affordable for high volume production vehicles!

Lignin in Thermoplastics and Composites

- Incorporation of lignin into thermoplastics represents by far the largest market opportunity
- PP + PE market size: 130 million t/y
- Market size (1%): 1.3 million t - 74 mills producing 50 t/d of lignin would be needed to meet this demand
- Lignin value: \$1500-2000/t



Macromolecular Lignin: Challenges

Carbon fiber	<ul style="list-style-type: none">• Economical purified lignin sources• Economical modifications to allow high-melt spin rates• High carbon yields• Application to varied lignin sources
Polymer fillers	<ul style="list-style-type: none">• Economical modifications to improve solubility and compatibility with other polymers• Controllable alteration of molecular weight• Control of polymer color• Control of polyelectrolyte character• Functional group enhancement
Thermoset resins Formaldehyde-free resins Adhesives and binders	<ul style="list-style-type: none">• Molecular weight and viscosity control• Functional group enhancement (carbonylation, carboxylation, de-etherification) to improve oxidative stability, thermal stability, consistent lignin properties, cure rate consistency and lignin color

Holladay et al. 2007

Final Remarks

- ❖ Lignin is a very complex irregular aromatic polymer; the structure is getting much more heterogeneous during technical processes.
- ❖ Lignin as a high-value product can renaissance the whole sugar-based biorefinery
- ❖ Understanding structure – performance correlations is critical for lignin engineering; analytical methodology is of primary importance
- ❖ Educated guesses in lignin structure - performance correlations should be avoided; experimental evidences are needed
- ❖ Economical issues should be considered for industrial lignin valorization