Characterization of LignoBoost lignin to predict possible utilization

Matyas Kosa

07-17-2009

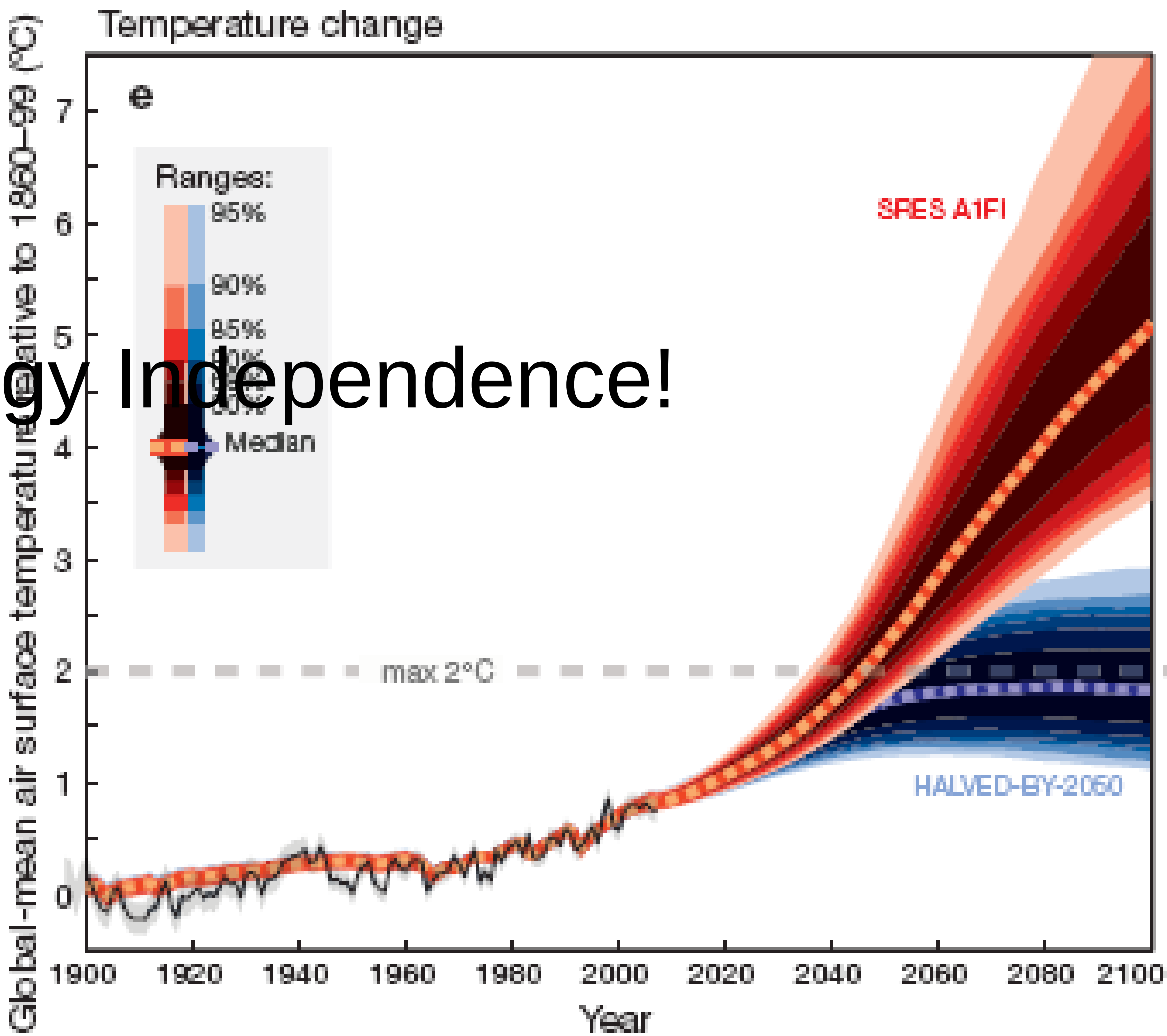
Georgia Institute of Technology
School of Chemistry and Biochemistry

OUTLINE

- The need for biofuels
- Lignin as a potential source, biosynthesis
- Kraft-cycle, LignoBoost, 2nd gen. bioethanol pretreatm.
- Results (so far): Purification, GPC, NMR

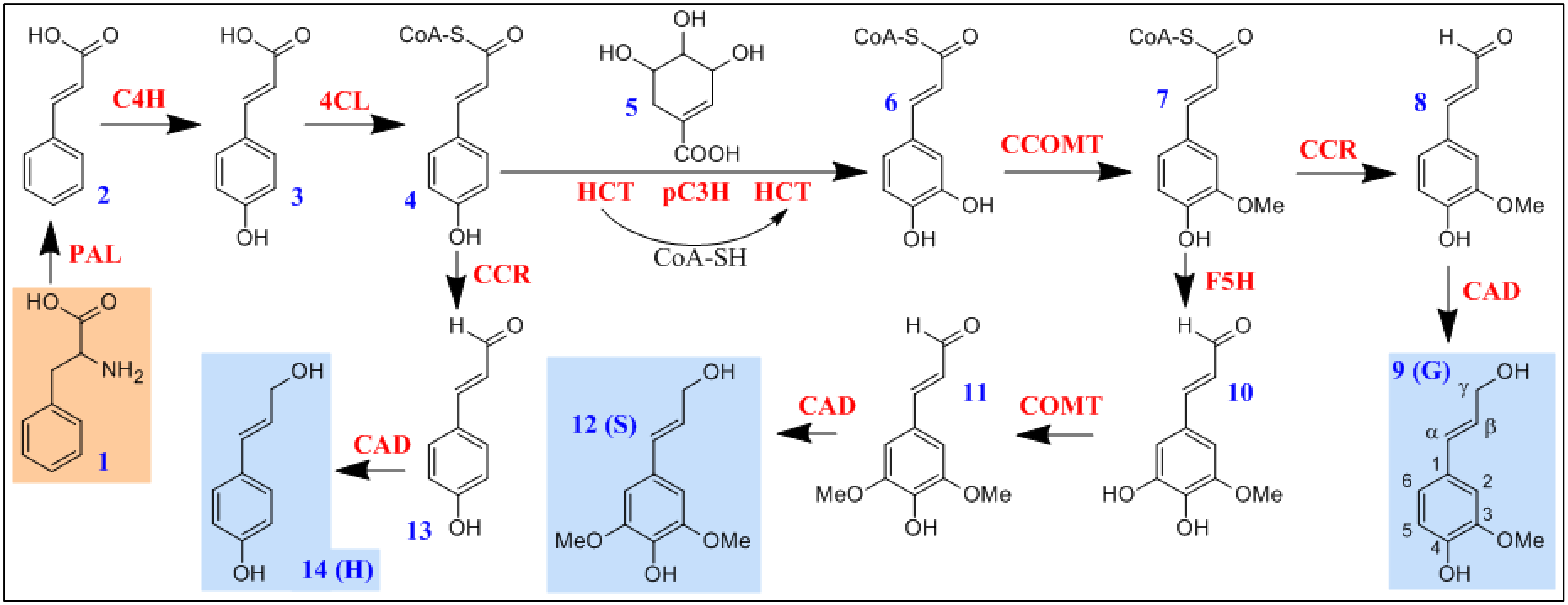
WHY BIOFUELS?

- Unpr… …rices?
- Glob…
- Energy Independence!



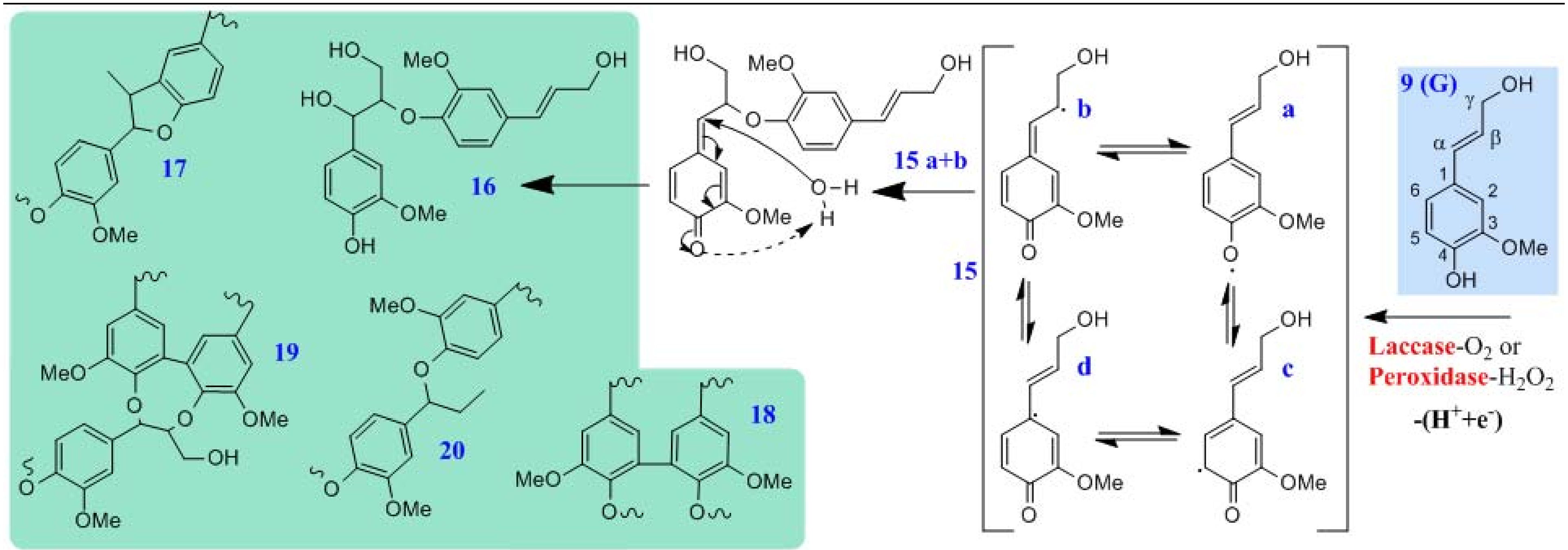
M. Meinshausen et al, *Nature*, 2009, **458**: 1158-1163

PHENYLPROPANOID PATHWAY



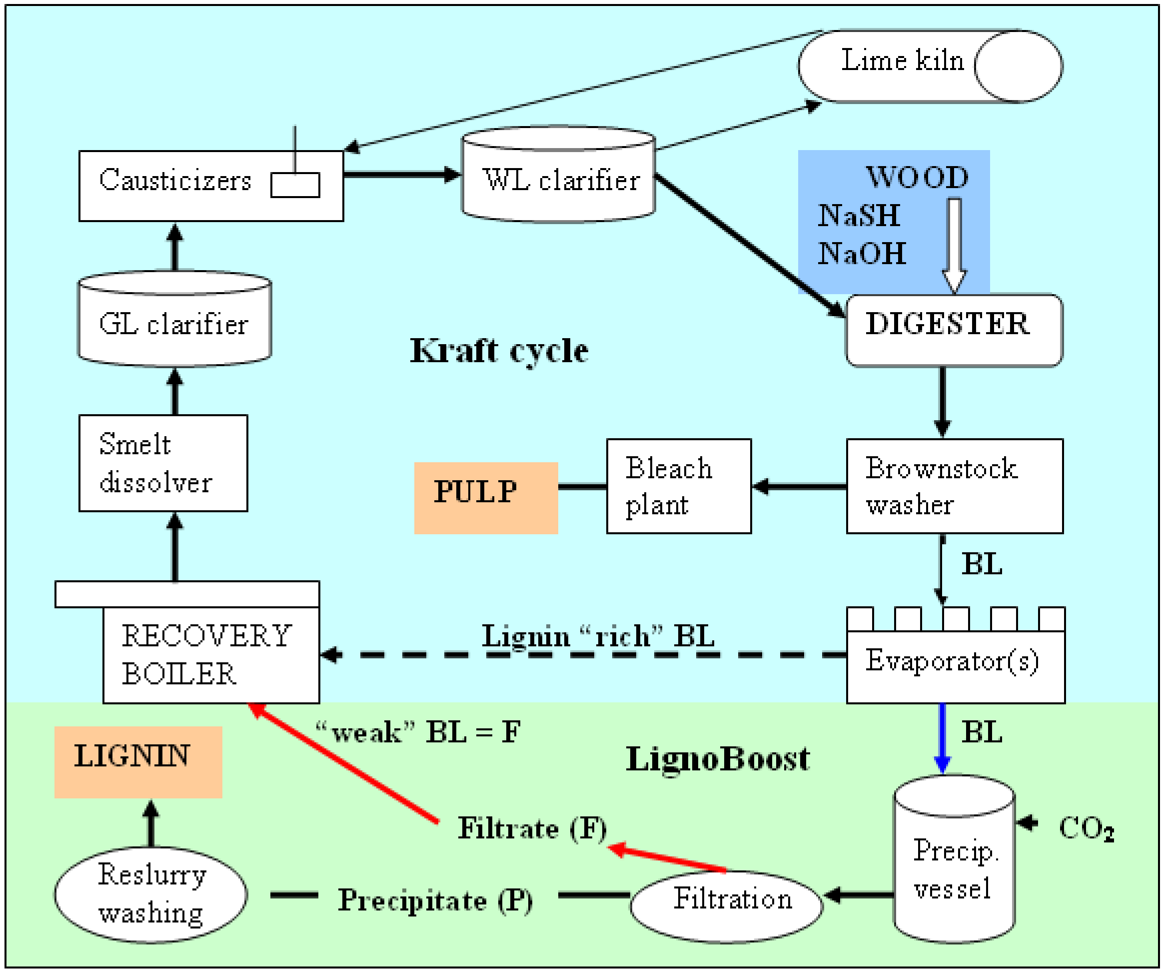
Wout Boerjan et al, *Annu. Rev. Plant Biol.*, 2003, **54**: 519-46
Laurence B. Davin et al, *Natural Product Reports*, 2008, **25**: 1015-1090

LIGNIN POLYMERIZATION



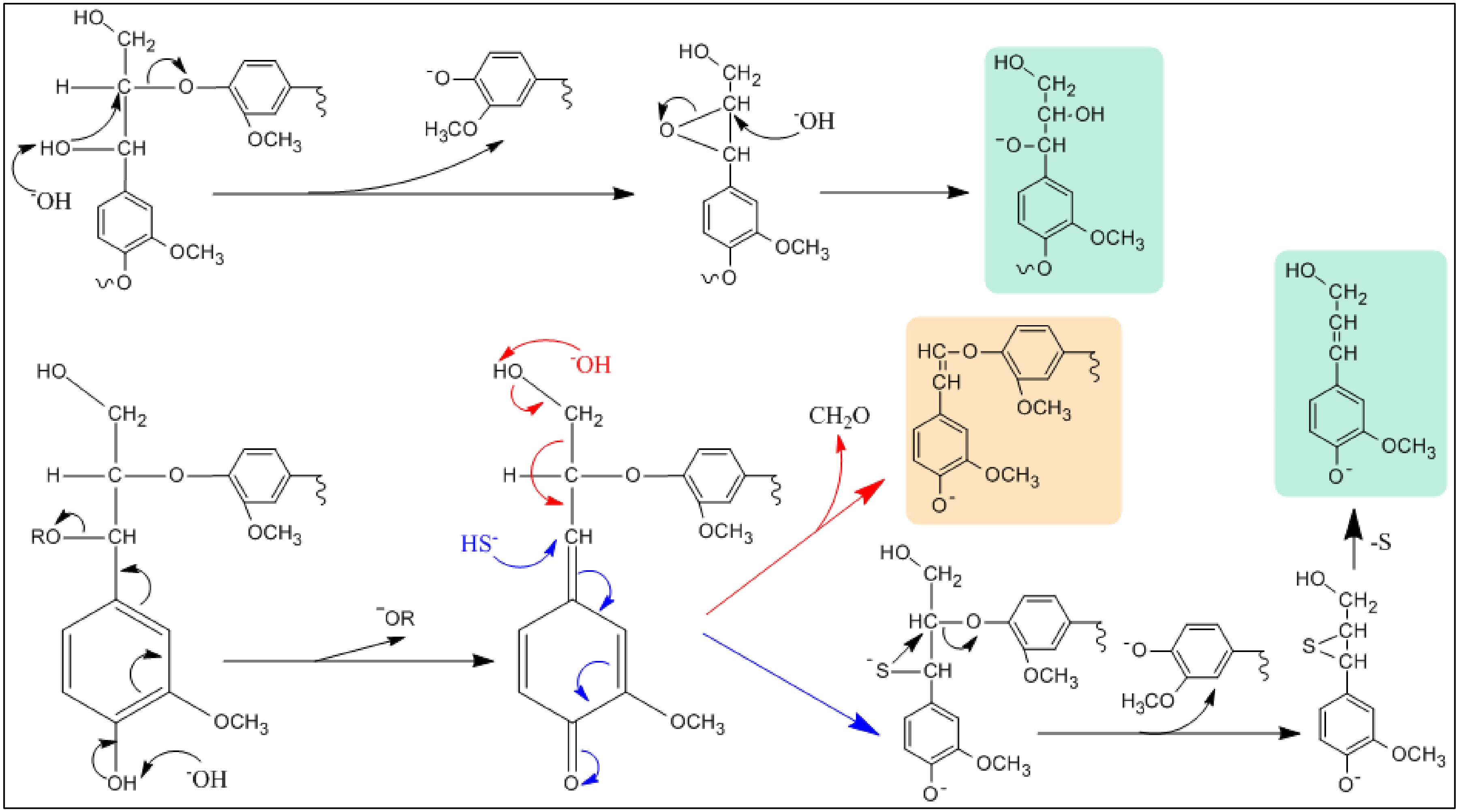
Wout Boerjan et al, *Annu. Rev. Plant Biol.*, 2003, **54**: 519-46
Laurence B. Davin et al, *Natural Product Reports*, 2008, **25**: 1015-1090

KRAFT CYCLE-LIGNOBOOST



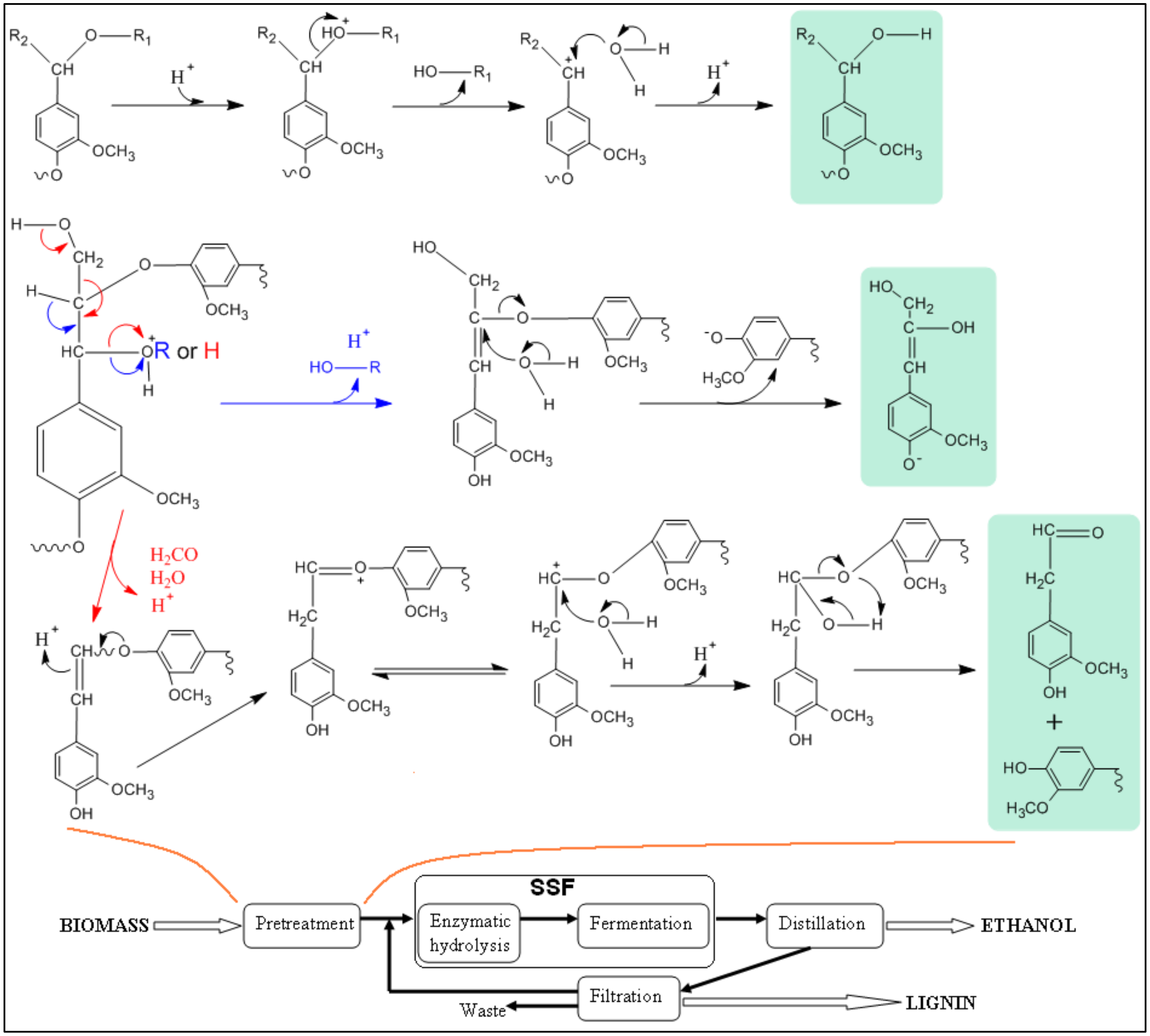
Johan Gullichsen and Carl-Johan Fogelholm: CHEMICAL PULPING, *Papermaking Science and Technology series, Book 6A*, **1999**, TAPPI

PULPING CHEMISTRY



Johan Gullichsen and Carl-Johan Fogelholm: CHEMICAL PULPING,
Papermaking Science and Technology series, Book 6A, **1999**, TAPPI

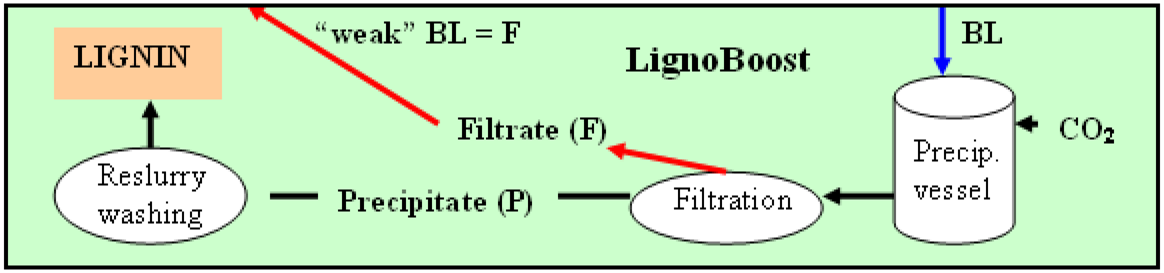
ORGANOSOLV PROCESS

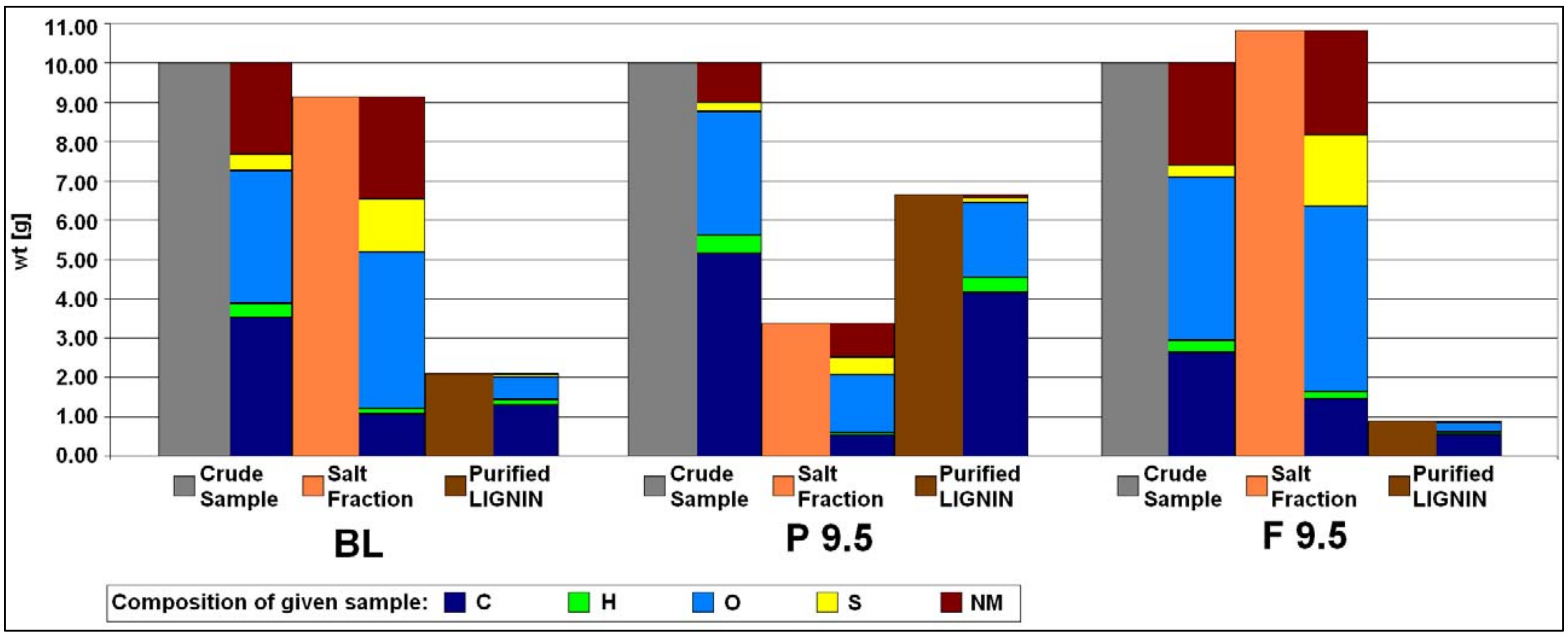


T. J. McDonough
TAPPI
Solvent Pulping Seminar
1992

SAMPLE PURIFICATION

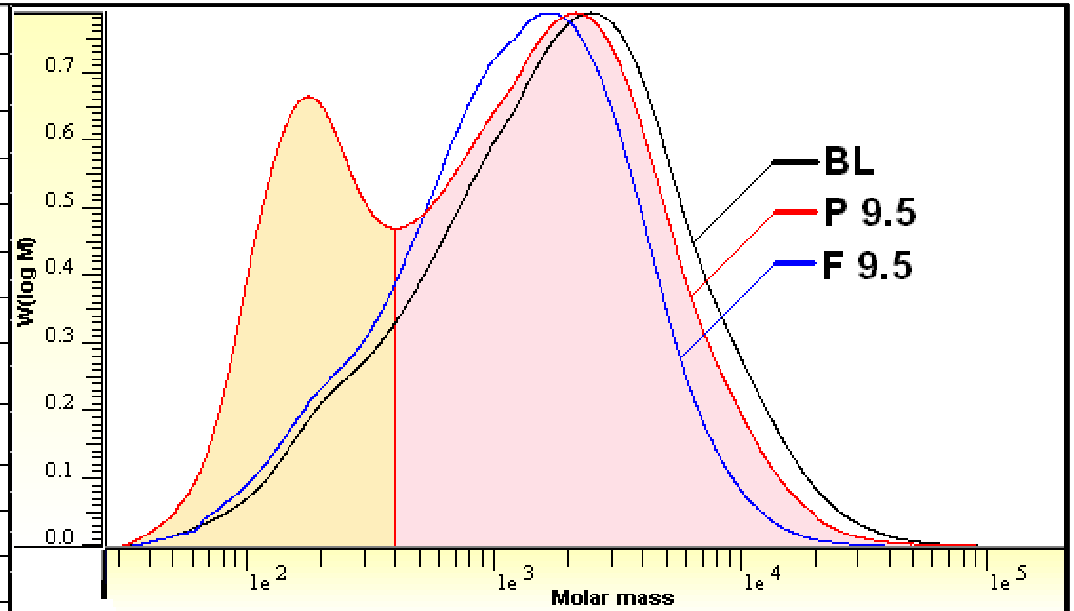
Preliminary Research Results





GPC

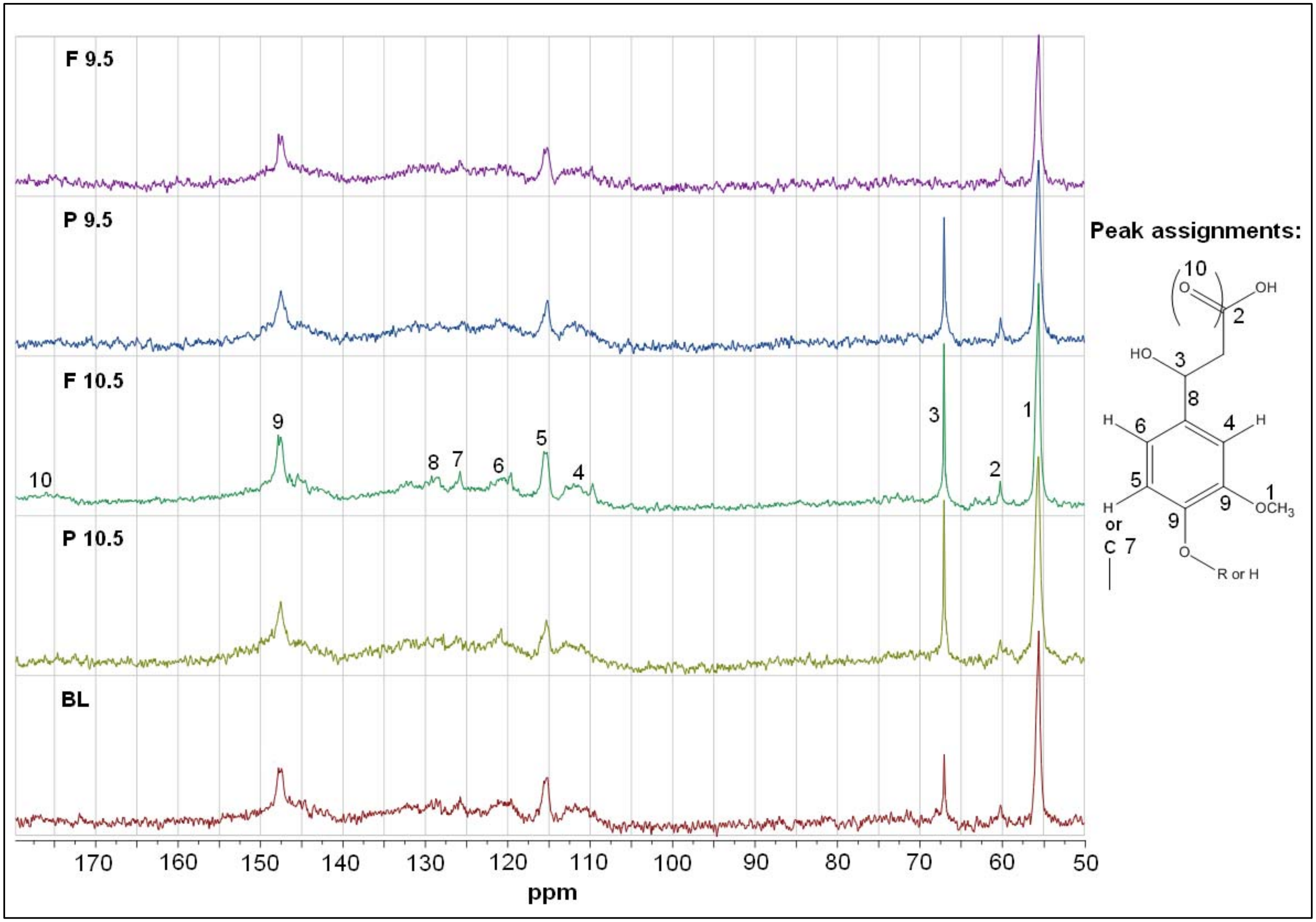
	Samples analyzed by us				
	Sample	M_w	M_n	PD	DP*
Polymer	BL	3602	812	4.44	13.6
	P 10.5	2940	1695	1.73	11.1
	F 10.5	2718	795	3.42	10.3
	P 9.5	2979	1796	1.66	11.3
	F 9.5	2102	736	2.86	8.0
Mono	P 10.5	151	136	1.11	
	P 9.5	158	141	1.12	
Polymer	**Moosavifar et al.** no data on pH				
	BL	5500			20.8
	F	3600			13.6
	Wallmo et al. at pH 9.5				
	BL	5100	1160	4.40	19.3



* using 264 g mol^{-1} as the hypothetical average weight of acetylated monomers

Henrik Wallmo, *PhD Thesis*, Chalmers Univesity of Technology, 1999
Ali Moosavifar et al, *Nordic Pulp Paper Res. J*, 2006, **21**: 180-87

^{13}C-NMR



F 9.5
P 9.5
F 10.5
P 10.5
BL
10
9
8
7
6
5
4
3
2
1
170
160
150
140
130
120
110
100
90
80
70
60
50
ppm
Peak assignments:
10
O
OH
2
HO
3
8
H
6
4
H
5
H
or
C 7
9
9
1
OCH3
O
R or H

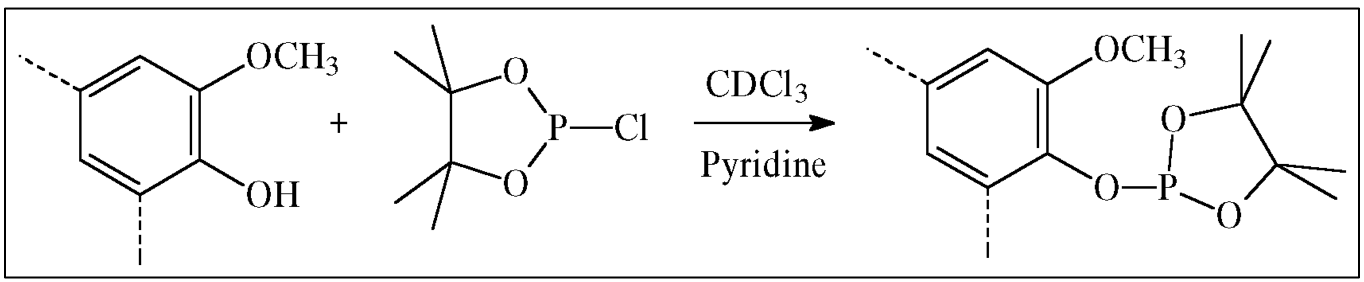
^{1}H-NMR

Sample name	Hydrogen content of selected groups (in mol/mol% relative to all H contraining funct groups)						
	Carboxylic acid	Formyl	Phenolic	Aromatic, Vinyl	Aliphatic	Methoxyl	Aliphatic
	13.50-10.50 ppm	10.10-9.35 ppm	9.35-8.00 ppm	8.00-6.00 ppm	6.00-4.05 ppm	4.05-3.45 ppm	2.25-0.00 ppm
	-C(O)OH	-C(O)H	HC-OH	CH=CH CH_2=CH	CH-O C-CH_2-O	-OCH_3	C-CH_2-C C-CH_3
BL	1.3	1.5	6.7	20.2	8.4	45.8	14.4
P 10.5	0.8	1.0	3.7	19.7	8.2	49.2	16.0
F 10.5	1.2	1.7	5.7	19.6	6.8	44.6	16.9
P 9.5	1.1	0.9	4.2	18.7	5.9	52.4	16.7
F 9.5	1.7	1.6	6.2	19.8	7.9	41.2	17.4

F samples contain significantly higher amounts of –OH groups of all examined types causing possibly their better solubility.

^{31}P-NMR

Sample name	Total –OH content (mmol g^{-1})	Hydroxyl content of selected groups (mmol g^{-1})			
		Aliphatic hydroxyl	Phenolic in G	Phenolic @ G position	Carboxylic hydroxyl
	149.0-133.8 ppm	149.0-145.6 ppm	144.4-140.4 ppm	140.4-137.6 ppm	136.0-133.8 ppm
BL	6.37	1.49	1.73	2.46	0.69
P 10.5	3.18	0.91	0.85	1.03	0.39
F 10.5	5.76	1.22	1.57	2.2	0.78
P 9.5	4.3	1.11	1.14	1.47	0.59
F 9.5	6.74	1.27	1.8	2.55	1.11



Derivatization of phenolic structures with 2–chloro–4,4,5,5–tetramethyl–1,3,2–dioxaphospholane (TMDP).

PYROLYSIS

- O/C and H/C molar ratios of purified LignoBoost precipitate lignin and of its pyrolysis oil show promising results

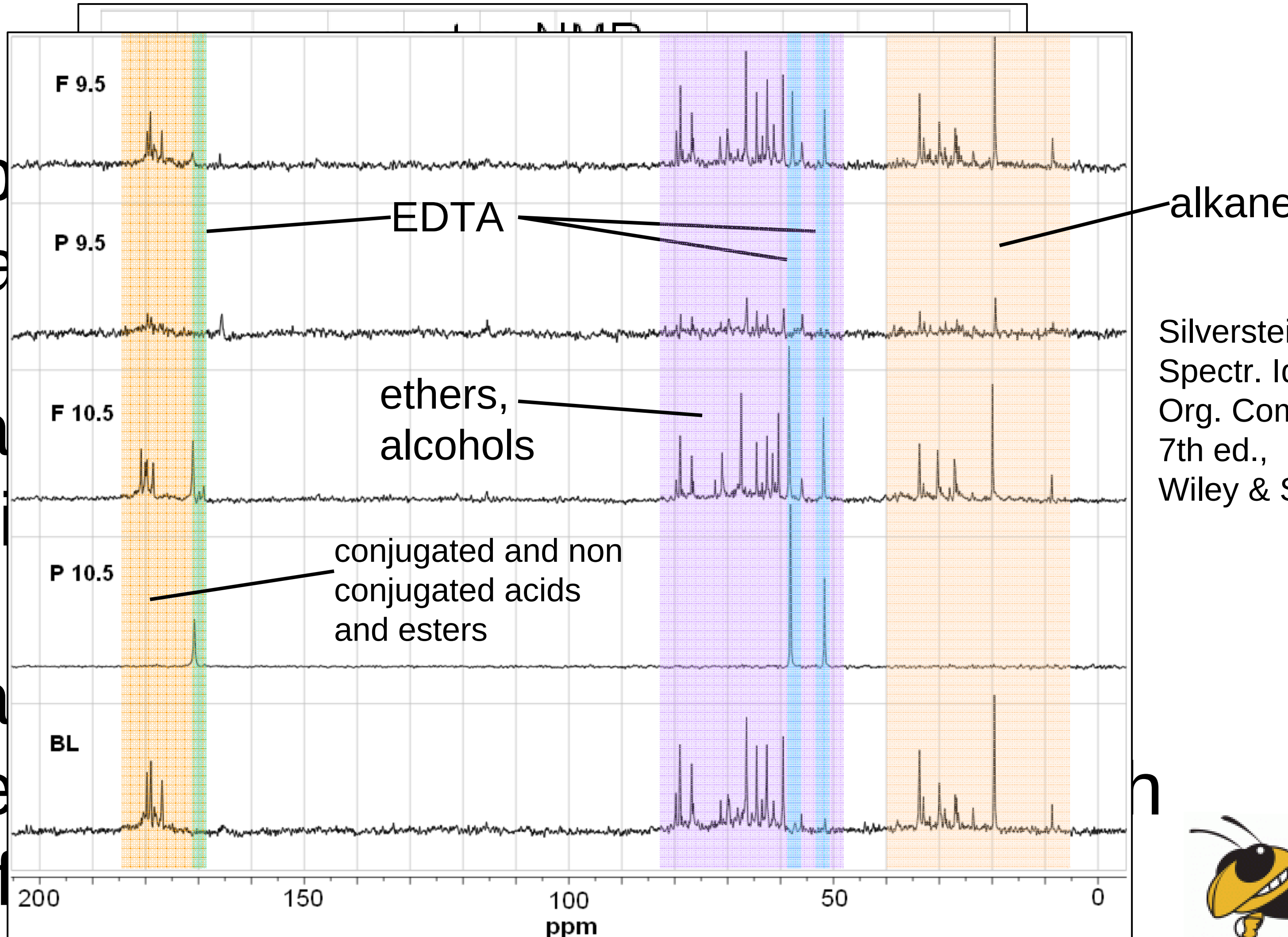
Pyrolysis [wt%]			
sample	**oil**	**char**	**gas**
BL crude	33.16	64.14	2.71
P 9.5 crude	31.53	67.55	0.92
P 9.5 purified	**42.98**	42.25	14.78

	Gasoline	**P 9.5 (pur) lignin**	**P 9.5 (pur) pyrolysis oil**
O/C molar ratio	0	0.34	**0.26**
H/C molar ratio	1-2	1.12	**1.34**

FURTHER ANALYSIS

EXPERIMENTAL

- Rep
  sma
- Ana
  chai
- Ana
  whe   n
  Kraf



Silverstein et al,
Spectr. Ident.
Org. Comp.,
7th ed.,
Wiley & Sons

Fredrik Ohman et al, *Nordic Pulp Paper Res J*, 2007, **22**:188-193
Raimo Alen et al, *Cellulose Chemistry and Technology*, 1985, **19**: 537-541

POSSIBLE UTILIZATION

- Pyrolysis showed promising results meaning that further analysis can be fruitful
- Complete analysis and comparison of the outcome of different lignin degrading enzymes and converting microorganisms are ongoing

Thanks for listening!

Questions?